DECLARATION

This is to declare that

a) the thesis has been composed by myself; and
b) the work described herein is my own.

Duncan James Mackay

The following series of Postgraduate lectures were attended during the period of the work-

The bioinorganic chemistry of Xenobiotics (Dr. Rowley)
Elementary electronics
Mass spectroscopy
Zeolites (Dr. Lowe)
High Pressure Liquid Chromatography (Prof. Knox)
Introduction to computer programming

In addition a two day training course on the operation of a Scanning Electron Microscope was attended, a couple of Chemical Society symposiums on aspects of colloidal science were attended, and tutoring to first year students was carried out.
ACKNOWLEDGEMENTS

I wish to thank Dr. W.D. Cooper for his assistance and support throughout the work. My thanks also go to Tioxide International for supplying the rutile pigment and the Haake viscometer. I would also like to thank Carol for typing the majority of the text and Blanche for drawing the figures. Lastly, I wish to thank the reproduction department at Warren Spring Laboratory for running off the necessary copies of the thesis.
DEDICATION

I would like to dedicate this work to my Father, Mother, sister, Blanche, Glen, Sam, and Annie.
THE BEHAVIOUR OF RUTILE IN
AQUEOUS AMINOALCOHOL SOLUTION

Duncan James Mackay

Part A

Submitted for the Degree of Doctor of Philosophy
of
The University of Edinburgh

Supervisor
Dr. W.D. Cooper

October 1985
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CHAPTER 1

INTRODUCTION
1. INTRODUCTION

The colloidal state was recognised last century by Graham but only relatively recently has significant progress been made in the characterisation and understanding of colloidal systems. The development of techniques in other areas of physics and chemistry has enabled such progress in colloid science to be made.

Colloid science is concerned with the behaviour of finely divided matter. Colloidal matter possesses dimensions in the range 1-1000 nm, although it is not necessary for all to be so, eg thin films and fibrous particles also exhibit typical colloidal behaviour. The properties of colloidal systems are governed by the fact that a significant proportion of molecules lie within or are associated with interfacial regions. Such molecules are in a different energy state to those present in the bulk phases. An essential facet of the colloidal state is the large surface area to volume ratio of the particles or phases concerned. The bulk properties of these systems are, consequently, largely determined by the surface chemistry of the interfacial regions.

Colloidal systems can be broadly classified as

* colloidal dispersions, eg emulsions, aerosols, sols, foams;
* solutions of macromolecular substances; or as
* association colloids, ie solutions of surface active materials which form micellar structures.

The colloidal dispersions are thermodynamically unstable and consequently are subject to a driving force to minimise the interfacial area.

Disperse colloids can be produced in two ways - either by degradation of a bulk phase or by aggregation of molecular species. The production of a finely divided powder such as rutile pigment involves both techniques. Precipitation of the crystals from the reaction mixture represents the latter technique, whereas subsequent milling of the pigment to give a finer product is the degradation technique. Because of the tendency of finely divided particles to aggregate, as the result of
the attractive forces between particles and the influence of the mechanical forces involved, an equilibrium particle size distribution is reached after prolonged milling. However, more finely divided particles can be obtained by milling in the presence of a surface active material. The latter modifies the surface free energies of the interfacial regions such that dispersion of the particles is more favourable.

The ability of a colloidal dispersion to resist aggregation is generally referred to as its stability. The stability is governed by the relative strengths of the various interparticle forces which exist. An understanding of these forces is dependent upon a sound knowledge of intermolecular forces. The major developments in our understanding have derived from the realisation that, unlike the forces between ions, atoms, or molecules, which fall off rapidly with separation, the forces between colloidal particles can be of a significantly longer range. These interparticle forces include

* Born forces (repulsive)
* van der Waals forces (attractive)
* electrostatic forces (generally repulsive)
* steric forces (attractive or repulsive)
* solvation forces (repulsive or attractive).

The Born interaction, although short range, is an omnipresent force and prevents interpenetration of electron clouds. The van der Waals interaction is also an omnipresent force. The stability of a colloidal system is consequently dominated by the repulsive interactions resulting from either the adsorption of ionic species or macromolecules at the particle-liquid interface.

The interparticle interactions dominate the behaviour of colloidal systems so that modification of, in particular, the repulsive interactions enables the bulk properties to be altered to meet a desired specification. Advances in the understanding of the stability of colloidal systems have been of great importance to numerous industries. The paint, dyestuffs, printing, pharmaceutical, photographic, food, polymer, chemical and agricultural industries exploit the physical properties of colloidal systems but also encounter problems associated
with the preparation and stability of the same systems. Such industrial applications include: enhancing the rate of settling of finely dispersed solids, maintaining a uniformly dispersed system, improving the filterability of a slurry, achieving and maintaining desired flow properties of high solids content slurries, the selective separation of mineral ores, and the preparation and dispersion of finely divided pigments. The interactions between the dispersed phases govern the behaviour of these systems and so modification of these interactions through the adsorption of additives at the interfacial regions can be made in order to achieve a desired effect on the bulk properties.

**Basis of the Thesis**

During the manufacture of several grades of rutile pigment an organic additive is often used to assist in the final milling and dispersing stages. The organic species is usually present at up to 1% by weight and such compounds include polyhydroxy species, complex amines, silicone oils, and simple aminoalcohols. The organic additive is believed to have one or more of the following functions:

i) to act as an aid in the milling process - the adsorbed species reduces the energy requirements of the comminution process;

ii) to improve the wettability of the pigment particles - the adsorbed organic minimises the energy required to replace the solid/gas interfaces with solid/liquid interfaces; and

iii) to modify the stability with respect to aggregation of the dispersed pigment particles.

Despite a voluminous patent literature on the bulk effects of various organic additive recipes, little published information on their interfacial behaviour exists. It is necessary to assess whether

a) the additive reduces the viscosity of the milled slurry sufficiently;
b) the additive has a positive benefit on the wetting and dispersion of the pigment particles;

c) the additive modifies the interaction between the particle surface and dispersion medium, and consequently that between dispersed particles.

The numerous patents often claim that the presence of such organics gives pigments an increased speed of wetting and improved dispersion stability. However, since the organic is normally added to the pigment prior to the final milling, and consequently before the pigment is dispersed in aqueous or non-aqueous media, it is possible that the major effect of the additive is in permitting the formation of a less tightly agglomerated powder.

Some work has been carried out to study the effects of silicone oils on the dispersion of rutile\(^1\) and of polyhydroxy compounds on the dispersion of alumina coated rutile\(^2\). It was concluded that the silicone polymers did not improve the ease of wetting but improved the stability with respect to aggregation. On the other hand, the polyhydroxy species were considered not to affect the stability of the dispersion.

Parfitt and Wharton\(^3\) studied the dispersion of rutile in aqueous surfactant solutions and concluded that, although adsorption is of great importance, there was no direct relationship between the dispersibility and the degree of adsorption, and that the dispersibility was not a function of the magnitude of the zeta potential. However, good agreement between the value of the contact angle and the surfactant concentration below which dispersion was poor was found. At low surfactant concentrations the ease of dispersion was controlled by the high value of the contact angle, whereas at higher concentrations poorer dispersibility could be ascribed to instability with respect to coagulation.

No systematic study of the effect of aminoalcohols on the milling and dispersibility of rutile pigment has been performed. Of particular interest is the use of

1-aminopropan-2-ol (MIPA)
2-amino, 2-methylpropan-1-ol (AMP).
Both these low molecular weight organic species are reported to give beneficial effects to two stages in the preparation of rutile pigment -

i) Sandmilling

the aqueous sandmilling of concentrated rutile dispersions, 50-60% w/w, at alkaline pH values is facilitated by the addition of up to 0.5% w/w, on rutile, of aminoalcohol.

ii) Dispersion

the dispersibility of rutile in aqueous media at solids content of 65-75% w/w is improved by the addition of up to 1.5% w/w, on rutile, of aminoalcohol.

The aminoalcohol apparently modifies the rheology of concentrated rutile dispersions, and alters the wetting or stability of the particles.

If it is assumed that the specific area of the rutile (Type I) is $7 \text{ m}^2 \text{ g}^{-1}$ and that the monolayer coverage is equivalent to $0.4 \text{ nm}^2$ per adsorbed aminoalcohol molecule then the surface coverage of adsorbate is about $30 \mu\text{mol g}^{-1}$. The upper concentrations of aminoalcohol given above would therefore be equivilent to about double and six times the monolayer coverage.

The explanation of how such small organic molecules are able to influence the colloidal behaviour of rutile dispersions is not known. Significant charge stabilisation is unlikely with such molecules in the high pH range encountered. The $pK_a$ values of MIPA and AMP are close to 9.5 and so even at this pH only 50% of the molecules are present as the positively charged conjugate acid. Specific adsorption of this ionic species would lower the double layer potential, however specific adsorption of the neutral species within the Stern layer could modify the double layer capacitance and hence the interparticle repulsion.

The low molecular weight (<90 amu) precludes the possibility of steric stabilisation.
However, the possible existence of structured zones, comprised of solute and dispersion medium, at the particle surface may play a role in improving both the dispersibility and milling of the aqueous pigment slurries. As a consequence of the presence of two functional groups, namely hydroxyl and amino, which are highly polar and capable of participating in hydrogen bonding the formation of such ordered zones is favoured. In addition, the large electrical field strength associated with the rutile crystal surface encourages solvent structuring.

The paucity of experimental data prevents discussion of the influence of aminoalcohols on the properties of rutile dispersions. The present work was carried out to investigate how the behaviour of aqueous rutile dispersions is modified by the presence of aminoalcohols, in particular MIPA.

Experiments were carried out to study -

* the adsorption of MIPA onto rutile
* the effect on the electrokinetic behaviour of dispersed rutile
* the changes in the particle-particle interactions of dilute rutile dispersions
* the effect of MIPA on the efficiency of dispersion of rutile pigment in aqueous solution
* the dynamic viscosity of aqueous MIPA solutions
* the effect of MIPA on the force required to achieve coagulation of dispersed rutile particles
* the rheological behaviour of high solids content rutile dispersions in the presence of small additions of MIPA.

These studies were performed as a function of MIPA concentration, pH, ionic strength, and type of backing electrolyte.

In addition, general observations on the behaviour of rutile in the presence of MIPA were made.

It was necessary to utilise such a wide variety of techniques to investigate the rutile-aminoalcohol system because of the anticipated subtle mode of influence of the organic.
CHAPTER 2

TITANIUM DIOXIDE
2. TITANIUM DIOXIDE

Titanium dioxide is an important pigment because of its high refractive index, chemical inertness, whiteness, and low toxicity. There are three crystal forms, namely tetragonal rutile, tetragonal anatase, and orthorhombic brookite. Only anatase and rutile are produced commercially, the latter possessing the more compact structure. Rutile is also the most thermodynamically stable form. Titanium dioxide is manufactured by one of two methods, the classical sulphate process or the more contemporary chloride process. The rutile used for the present work was produced by the former method.

2.1 Physical Properties

Most manufacturers of titanium dioxide offer a range of pigments varying in surface character and therefore dispersibility. The so-called type I pigments are free from surface coatings of other oxides. Table 2.1 gives some of the physical properties of such a rutile pigment. The optimum primary particle size for the uniform scattering of white light is $0.2 \times 10^{-6}$ m so that larger particles preferentially scatter the longer wavelengths of light and smaller particles preferentially scatter the shorter wavelengths. The pigment normally consists of irregular, though roughly spherical particles of uniform size with diameters in the range 100-400 nm. Pigments give the maximum scattering of light with wavelength equal to twice the particle diameter if the particles are uniformly dispersed. In addition, with the same light the pigment will give the best brightness and hiding power.

<table>
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<th>Physical Properties</th>
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<tr>
<td>Density/kg m$^{-3}$</td>
<td>4200</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.76</td>
</tr>
<tr>
<td>Specific Surface Area/m$^2$ g$^{-1}$</td>
<td>6-8</td>
</tr>
<tr>
<td>Primary Particle Size/m</td>
<td>$(0.1-0.4) \times 10^{-6}$</td>
</tr>
<tr>
<td>Dispersant Demand</td>
<td>High</td>
</tr>
</tbody>
</table>

The efficiency of light scattering is a function of the difference in refractive indices of the pigment and its dispersion medium. The
exceptionally high index for rutile makes the pigment virtually unmatched as a white pigment.

2.2 The Rutile Surface

The interaction between the pigment and a surrounding liquid is governed by the chemistry of the interfacial region, and in particular by the surface of the particle. The rutile surface contains terminal and bridged hydroxyl groups, the former possessing a basic nature and the latter an acidic nature; labile Ti-O-Ti groups; water molecules chemisorbed at Lewis acid sites; water molecules physically adsorbed to surface hydroxyl groups; and chemisorbed anions introduced by the manufacturing process e.g. chloride. The surface also contains potential electron donor and acceptor lattice sites, and may possess adsorbed oxidising agents such as hydroxyl radicals.

Anhydrous rutile readily adsorbs water. The resultant hydrated surface is amphoteric in nature due to the formation of the hydroxylic species mentioned above. The nature and surface location of these adsorbed species have been extensively studied by techniques such as infra-red spectroscopy, heat of immersion, temperature programmed desorption, and chemical reaction. The conclusions have been reviewed by several workers\(^5,6\).

The majority of the strongly bound hydroxyl groups result from the dissociative chemisorption of water and consist of approximately equal numbers of basic and acidic types\(^7\). The dissociative adsorption process is believed to involve the following sequence\(^8,9\):

(i) initial adsorption of a water molecule at a five-coordinate titanium (IV) site;

(ii) ionisation of the molecule in the strong crystal surface field to give the terminal hydroxyl group;

(iii) migration of the displaced proton to a neighbouring Ti-O-Ti site leading to the formation of the bridged hydroxyl group from the lattice oxide anion.
Physically adsorbed water may be bound by hydrogen bond formation with terminal hydroxyls, by weak or non-dissociative adsorption on surface cations, and by condensation within particle micropores.

The thermal stability of the various hydroxylic species is affected by the presence of adjacent lattice defects or adsorbed ions. The condensed, weakly bound water can be removed at temperatures up to 150°C, as can dissociated water on the (100) and (101) crystal planes. Hydrogen bonded water can be retained so tightly that desorption only occurs on elimination of the associated surface hydroxyl groups. Heating above 200°C results in the loss of the strongly, bound dissociated water from the (110) crystal plane. The remaining terminal hydroxyl groups are too widely separated to permit their diffusion and mutual condensation to occur at a significant rate.

The terminal hydroxyl groups are ionic in character, are weakly basic \( \text{p} K_a \sim 12 \), and are capable of exchange with other anions.

The bridged hydroxyl groups are partially covalent and are weakly acidic \( \text{p} K_a \sim 3 \).

Adsorption of compounds containing the amino group occurs at the rutile surface. The Bronsted acidity of the bridged hydroxyls permits protonation of adsorbed primary amines. Some amines are not protonated but instead adsorb by coordination with surface titanium ions. Adsorption of amines can also occur through hydrogen bond formation.

2.3 Electrochemistry of Rutile

As a result of the amphoteric nature of the rutile surface the dispersed pigment is able to buffer the pH of aqueous media at values close to 7. The different types of hydroxyl group result in the potential determining ions being hydrogen and hydroxide. The ionic nature of the surface gives rise to an electrical diffuse double layer when rutile is dispersed in aqueous solution. A description of the oxide-aqueous solution interface is given in Appendix C.
2.4 Photochemical Activity of Rutile

The surface of titanium dioxide is capable of oxidising or reducing a variety of adsorbed compounds when exposed to light with wavelengths in the range 300-400 nm. Absorption of such light by the crystal lattice produces excited species in which electrons are promoted from the valence band to the conduction band within the lattice electronic structure. Electron-hole pairs, or excitons, are formed and these are able to migrate through the lattice. The excitons are unstable and will decay, transferring thermal energy to the crystal lattice in the process, unless they are trapped by some other process. Irradiation of aqueous rutile dispersions leads to the production of hydroxyl and hydroperoxyl radicals on the particle surface.

The photogenerated oxy-species act as oxidising agents so that adsorbed organic compounds may be oxidised. The precise mechanisms by which the surface oxidants are formed and the photocatalysed reactions occur remain the subject of debate.

The photoactivity of rutile pigments is generally an undesirable property so that steps are taken to minimise the effect, namely surface modification.

2.5 Surface Modification

The surface of rutile is often treated to improve the dispersibility of the pigment and to minimise the photoactivity. Organic compounds are often adsorbed to assist the dispersibility, whereas other oxides, such as silica or alumina, are used as surface modifiers to effect the latter requirement.

The adsorption of an organic electrolyte, such as an aminoalcohol, on a pigment is likely to follow a complex isotherm because of the interactions between the ions and the electrical double layer. The isotherms often resemble the classical Langmuir isotherm, the plateau of the curve corresponding to neutralisation of the surface charge. The precise form of the isotherm is determined by the electrochemistry of the surface-solution interface, in particular, whether the pigment particles
possess a constant surface potential or surface charge. The organic species will chemisorb to the titanium dioxide surface via the hydroxyl groups or Lewis acid sites. The possibility of hydrogen bond formation will increase the adsorption.

Amines are generally strongly adsorbed on oxides due to the formation of protonated adducts with Bronsted acid sites, coordinated species with Lewis acid sites, and hydrogen bonded adducts with hydroxyl groups. The presence of other adsorbed species, e.g., water, other ions, often affects the adsorption of amines. Aminoalcohols can adsorb via both polar functional groups, although the amino group is more basic and is consequently the more likely to interact directly with the surface.

### 2.6 Adsorption From Solution

The adsorption of a species (molecule or ion) from solution on the surface of a solid can be considered to involve the following sequence:

- (a) removal of the species from bulk solution;
- (b) displacement of solvent from the surface; and
- (c) attachment of the species to the surface.

As the result of the thermal motion there are frequent collisions between the solution species and particle surfaces. On such contact one of the following events can take place:

(i) the species is held to the solid surface by physical forces or chemical interaction;

(ii) the species is repelled from the surface by chemical forces such as electrostatic repulsion;

(iii) the species can only make temporary contact with the surface because of the action of thermal agitation.

For adsorption to take place there must be a net release of energy during the process, i.e., the binding energy released as the adsorbate adsorbs at the surface must exceed the sum of the energies required to
overcome electrostatic repulsion and to remove the solvent molecules from the surface. The total free energy of adsorption is composed of various factors:

- a coulombic free energy term which is a function of the diffuse layer potential. The free energy term is negative when the adsorbing species is opposite in sign to that of the surface;

- a solvation free energy term which takes account of the energy changes in the solvation shell of a species on adsorption. This term is close to zero for titanium dioxide because its dielectric constant is of the same order as that of water;

- a hydrophobic interaction free energy term which represents the energy changes associated with interactions between non-polar species;

- a London dispersion or Van der Waals free energy term;

- a chemical interaction free energy term which takes into account the energy changes due to specific chemical bonding.

This approach can be useful in the interpretation of data for adsorption of an organic at a solid surface.

The adsorption of small organics, such as the aminoalcohols, can be considered to be dominated by the contributions of the chemical interaction and electrical free energy terms.

The adsorptivity is described by an isotherm which relates the mass of solute adsorbed per unit mass of adsorbent to the bulk solution concentration of solute after adsorption. The Langmuir and Freundlich isotherms are the most widely used. For systems exhibiting the former adsorption behaviour the relevant parameters fit the expression

\[ \frac{C}{M} = a + \frac{C}{b} \]  

(2.1)
where $C$ is the equilibrium adsorbate concentration;

$M$ is the mass of adsorbate adsorbed per unit mass of adsorbent;

$a$, $b$ are constants for a given system.

For systems showing Freundlich adsorption behaviour the relevant equation is

$$M = b C^a$$

As explained in Chapter 3 the Stern model of the electrical double layer makes use of the Langmuir isotherm to describe the equilibrium between ions within the Outer Helmholtz Plane and those in the diffuse layer.

The adsorption of solute which behave as Bronsted bases on oxide surfaces is more complex. A variation in solution pH not only alters the number of available surface sites but also alters the degree of dissociation of the solute. The extent of adsorption, for a given concentration of solute, is consequently governed by the relative concentrations of active surface sites and the solute counter-ion, as dictated by the pH.

Rendall and Smith$^{10}$ developed a model based on the Grahame description of the double layer to explain the existence of a pH of maximum adsorption. Allowance was made to take into account adsorption of both the ionised and neutral solute molecule.

Muller et al$^{11}$ carried out a more rigorous treatment which allowed for heterogeneity of the solid surface. The isotherm equation was shown to simplify to limiting cases which are well-known in the literature. The approach takes account of the effect of pH on solute dissociation, the influence of pH on the surface charge, and the heterogeneity of the surface. However, application of the isotherm expression requires data for the surface charge variation with both pH and ionic strength, and adsorption data for the molecular solute.
CHAPTER 3

ELECTROCHEMISTRY OF THE SOLID-ELECTROLYTE SOLUTION INTERFACE
3. THE ELECTROCHEMISTRY OF THE SOLID-ELECTROLYTE SOLUTION INTERFACE

3.1 Introduction

When a solid surface is brought into contact with an aqueous solution the surface acquires a net electrical charge. As a consequence of the need for electroneutrality this surface charge is balanced by a region of opposite charge within the solution close to the solid surface. This combination of an essentially localised surface charge and a diffuse layer of charge in solution is known as the electrical diffuse double layer. The properties of this double layer influence the adsorption by a solid surface of chemical species from bulk solution, and also strongly influence the interaction between colloidal particles dispersed in an aqueous solution$^{12-16}$.

Studies on the mercury/water interface$^{17,18}$ have led workers to the modern theories of ion adsorption at the solid-aqueous electrolyte interface. Alteration of the surface charge density on a mercury drop by external circuitry can give information about the change in double layer capacitance as a function of solution conditions. The surface is renewable if contaminated. However, the principles developed for the mercury-aqueous electrolyte need to be modified when extended to the more practical colloids since the dispersed phase is often a solid insulator rather than a liquid metal.

Other workers have studied the silver iodide-aqueous electrolyte interface which is a more appropriate model system. With this system the components of the dispersed phase are also to be found in the dispersion medium thereby completely determining the total double layer potential by the composition of the phases.

The general principles governing adsorption of both cations and anions have been shown to be the same for both the model interfaces.

Many colloidal systems met in practice are inorganic oxides dispersed in aqueous electrolyte solution and thus the detailed interfacial electrochemistry of such dispersions has received much attention. For these oxides both the hydroxyl ion and the hydronium ion
are the species which determine the double layer potential. Attempts to relate the properties of the oxide-water interface to those of the well established silver halide-water interface have revealed large differences in the magnitude of interfacial electrochemical parameters. There have been arguments that the thermodynamic treatment of the silver iodide-water interface cannot be extended to the oxide-water interface.

The aim of this chapter is to review the electrochemistry of the solid-solution interface.

3.2 Surface Charge Formation

The most common mechanisms by which an interface can acquire a charge can be summarised as follows.

- a) charge transfer across the interface;
- b) isomorphic substitution;
- c) preferential adsorption of ions;
- d) surface group dissociation;
- e) adsorption and orientation of dipolar molecules;
- f) unequal dissolution of oppositely charged ions of which the solid phase may be composed.

Case a) is typically found with the mercury-aqueous solution interface.

Isomorphic substitution is a typical surface charge acquisition mechanism for clay minerals in which replacement of a cation by one of a lower valency renders the surface negative (e.g. replacement of Si$^{4+}$ by Al$^{3+}$). Characteristically the surface charge of such systems remains constant and independent of solution pH and composition.

The preferential adsorption of ions occurs to an appreciable extent only if the adsorbing species has a high affinity for the surface, because the adsorption must proceed against an increasing opposing potential difference generated by the adsorption process. The affinity of monovalent cations for surfaces is normally insufficient to produce a
substantial potential difference whereas anions and multivalent cations can produce potentials of a few tens of millivolts. However considerable potential differences can be achieved in two situations -

(i) the adsorbing ion is surface active, for example soaps, polyelectrolytes, small charged organic molecules;

(ii) the adsorbing ion is potential determining i.e. it is one of the constituent ions of the solid phase.

Case d) is the common mechanism for oxide and biological systems. Surface units such as carboxyl, amino, and hydroxyl groups possess dissociation equilibria involving transfer of H\(^+\) and OH\(^-\) ions to and from the solution. Such equilibrium reactions depend upon the pH and ionic strength of the solution.

For colloidal systems in which H\(^+\) and OH\(^-\) ions are potential determining (e.g. titanium dioxide) there exists a certain pH at which the surface contains equal numbers of positive and negative charges and so bears no net charge; below this pH the surface is positively charged and above this pH it is negatively charged. This point of zero charge (p.z.c.) is dependent upon the crystal habit of the solid, its age and history. Also of extreme importance is the presence of specifically adsorbed ions (i.e. ions held to the surface by forces other than or in addition to coulombic forces). Specifically adsorbed cations tend to make the surface more negative and hence the p.z.c. is lowered. Similarly specifically adsorbed anions raise the point of zero charge. Such changes in the p.z.c. of oxides are only likely to be of importance for anion and polyvalent ion adsorption because monovalent cations tend to be only weakly adsorbed. In the absence of specific adsorption the surface charge is independent of ionic strength at the p.z.c. Where specific adsorption by ions or surface active species occurs it is a matter of convenience whether the surface charge is taken to be the charge on the surface proper plus that contributed by the adsorbed species.

Case e) is a consequence of the fact that molecular forces act quite asymmetrically on surface molecules. Dipolar molecules will thus exhibit a preferential orientation. For example, water at the air-water
interface is oriented with the oxygen atoms pointing away from the water. Such a layer of oriented dipolar molecules acts as the analogue of a plane parallel capacitor and generates a potential difference; the magnitude of which depends upon the dipole density, the dipole moment, and the angle of orientation of the dipole to the surface. The presence of such a dipolar layer can influence the interaction between particles in a colloidal dispersion.

Once a surface charge has been formed the electrical double layer will form and expressions must be found to show how the potential and charge density vary with distance from the surface.

3.3 Interfacial Potentials

The derivation of expressions describing the potential difference across interfacial regions has been reviewed by several authors$^{18,23}$. The Nernst equation is derivable from equilibrium thermodynamic considerations and relates the surface potential to the chemical activities of the potential determining ions.

$$
\phi_0 = \frac{RT}{z_i F} \ln \left( \frac{a_i}{a_0} \right)
$$

where $\phi_0$ is the surface potential, $R$ the universal gas constant, $T$ is the temperature, $F$ the Faraday constant, $z_i$ is the valency of the ionic species $i$, $a_i$ is the chemical activity of species $i$, and $a_0$ is the standard chemical activity.

Several assumptions are made in the derivation of this equation. For example, it is assumed that the surface activity of the potential determining ion is independent of the surface potential.

For the silver iodide-water interface, in which both silver ions and iodide ions act as primary potential determining species, the Nernst equation is found to be accurately obeyed$^{21}$. However, its use for describing the oxide-water interface has been criticised$^{20,21,24}$. 

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The appropriate equation takes the form

\[ \psi_0 = 2.303 kT (\text{pH}_z - \text{pH})/e \]  

(3.2)

where \( \psi_0 \) is the surface potential, \( k \) the Boltzmann constant, \( T \) the temperature in Kelvin, \( e \) the protonic charge, and \( \text{pH}_z \) the value of the negative logarithm of the hydrogen ion concentration at the point of zero charge. This expression is not satisfactory in describing the surface potential of oxides since the number of hydrogen ions at the surface at the point of zero charge is low. This fact means that an important assumption in the derivation of the Nernst equation is no longer applicable, namely that the surface activity of hydrogen ions remains constant when the bulk activity alters. Levine and Smith\(^{21}\) have presented a modified form of the Nernst equation allowing for the role of the surface hydrogen ions. The additional term in the expression has the effect of lowering the expected surface potential which is in keeping with experimental observations.

3.4 The Electrical Diffuse Double Layer

Electroneutrality requires that the solution surrounding a colloidal particle carrying a net charge must itself carry a charge of the same magnitude but opposite sign. The charges in solution are mobile and this has important consequences for the potential and charge distribution relative to the particle surface. The requirement to lower the coulombic energy results in the attraction of counterions and the repulsion of co-ions. However, thermal motion maximises the entropy and both ion types tend towards an homogeneous distribution. When the electrostatic forces are balanced by the thermal mixing, thereby giving the minimum free energy, the situation is similar to that for electrolyte solutions as described in the Debye-Hückel theory. In colloidal systems, however, the potentials tend to be much higher and the particles are larger thereby producing the need for a more complex theoretical treatment.

The separation of charge that occurs at an interface between two phases is called an electrical double layer since it consists of two regions of opposite charge, in the ideal case. The simplest model of
such a system is normally attributed to Helmholtz in which both regions of charge are rigidly fixed in parallel planes to form a molecular condenser. Although the model can be used to derive some of the electrokinetic relationships, it has long been known to give a poor representation of the real situation. Whilst the charge on a metal or semiconductor surface may be assumed to be located in a plane, the same does not hold true for the charge in a liquid phase. The model for the diffuse electrical double layer is described in the next section.

3.4.1 The Gouy-Chapman Double Layer (Fig. 3.5)

The classical picture of the diffuse double layer was independently developed by Gouy\textsuperscript{25} and Chapman\textsuperscript{26}. The approach being similar to that of the Debye-Hückel theory developed a decade later. Both theories express the combined result of electrostatic interaction and Brownian movement in terms of a Boltzmann distribution for all ion types. The ion distribution can be expressed as

\[ n_i = n_{i0} \exp \left( -\frac{z_i e \psi}{kT} \right) \]  

(3.3)

where \( n_i \) is the number of ions of type \( i \) per unit volume at a distance \( x \) from the particle surface, \( e \) is the protonic charge, \( z_i \) is the valency of ion type \( i \), \( k \) is the Boltzmann constant and \( \psi \) is the potential at distance \( x \). Hence both \( n_i \) and \( \psi \) are functions of the distance from the surface, with \( n_{i0} \) being the value of \( n_i \) in the bulk solution where \( \psi \) is zero. The equation is consistent with the fact that counterions are attracted and co-ions repelled from the surface. The change in ion concentration as a function of distance can be seen in figure 3.1.

The relationship between the charge density of the double layer and the electrical potential at a distance \( x \) from the surface is given by the Poisson equation

\[ \frac{d^2 \psi}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_o} \]  

(3.4)
FIGURE 3.1 The variation in the concentration of counterions and co-ions as a function of distance from a charged surface.
where \( p \) is the space charge density, \( \varepsilon_r \) is the relative dielectric constant of the solution, and \( \varepsilon_0 \) is the permittivity of a vacuum.

The space charge density is the result of unequal concentrations of counterions and co-ions and is thus a function of distance from the surface

\[
\rho = \sum_{i} z_i n_i e_i
\]  \hspace{1cm} (3.5)

Combination of equations (3.3)-(3.5) yields the Poisson-Boltzmann expression

\[
d^2\psi/dx^2 = -\frac{e}{\varepsilon_r \varepsilon_0} \sum_{i} z_i n_i \exp (-z_i e\psi/kT)
\]  \hspace{1cm} (3.6)

This equation forms the basis of the Gouy-Chapman theory. The solution of this equation has been reviewed by several authors. In colloidal systems the values of the electrostatic potentials over much of the double layer are such that \( z_i e \psi \gg kT \) thus requiring the solution of the complete, non-linear form of the Poisson-Boltzmann equation (P.B. equation).

For a symmetrical electrolyte the P.B. equation gives

\[
d^2\psi/dx^2 = \frac{2z_i n_i \exp e}{\varepsilon_r \varepsilon_0} \frac{z_i e \psi}{\sinh \left( \frac{z_i e \psi}{kT} \right)}
\]  \hspace{1cm} (3.7)

which on solving gives the following expression for the dependence of potential on distance from the particle surface

\[
\psi = \frac{2kT}{z_i e} \ln \left[ \frac{1 + \gamma \exp (-\kappa x)}{1 - \gamma \exp (-\kappa x)} \right]
\]  \hspace{1cm} (3.8)

in which
This factor $\kappa$ (Kappa) has dimensions of reciprocal length and the parameter $1/\kappa$ is an important quantity commonly known as the double layer thickness or characteristic Debye-Hückel length. The effect of ionic strength and valency upon the double layer thickness at $25^\circ C$ in water can be seen from the values in table 3.1.

**TABLE 3.1.**

Characteristic Debye length at $25^\circ C$ for various electrolyte solutions

<table>
<thead>
<tr>
<th>1:1 ELECTROLYTE</th>
<th>2:2 ELECTROLYTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration/mol dm$^{-3}$</td>
<td>Concentration/mol dm$^{-3}$</td>
</tr>
<tr>
<td>10$^{-5}$</td>
<td>10$^{-5}$</td>
</tr>
<tr>
<td>10$^{-3}$</td>
<td>10$^{-3}$</td>
</tr>
<tr>
<td>10$^{-1}$</td>
<td>10$^{-1}$</td>
</tr>
</tbody>
</table>

The factor $\gamma$ in equation (3.8) is given by the following expression:

$$
\gamma = \frac{(\exp(z_i e \psi_o / 2kT) - 1)}{(\exp(z_i e \psi_o / 2kT) + 1)}
$$

in which $\psi_o$ represents the surface potential. The assumption of a symmetrical electrolyte is normally valid even in asymmetric cases since in colloidal systems the behaviour is largely determined by the valency of the counterion and the valency of the co-ion can be ignored$^{15,22}$. At this point it is worthwhile to note that for low potentials ($\psi_o < 25/z_i$ mV) equation (3.7) can be simplified to

$$
d^2\psi/dx^2 = \kappa^2\psi
$$

This simplification is essentially the linear approximation used in the Debye-Hückel theory.
3.4.1.1 Poisson-Boltzmann equation for flat plates

A double integration of equation (3.7) is carried out in order to give the potential-distance relation. The first integration is performed using the boundary conditions \( \psi = 0 \) and \( d\psi/dx = 0 \) at \( x = \infty \). The further condition is introduced for the second integration \( \psi = \psi_0 \) at \( x = 0 \). The result is often quoted as \( 29 \).

\[
\tanh \left( z e \phi /4kT \right) = \tanh \left( z e \phi_0 /4kT \right) \exp (-\kappa x) \quad (3.12)
\]

and is the general solution of the P.B. equation for flat plates. Plots of this function for various values of \( \psi_0 \) show an approximately exponential fall of electrostatic potential to about 1\% of its value at the surface in a distance of the order 4-5 \( \kappa \).

For small potentials, that is for \( z e \psi_0 /4kT \ll 1 \), equation (3.12) reduces to the simple expression

\[
\psi = \psi_0 \exp (-\kappa x) \quad (3.13)
\]

This equation clearly shows the reason that \( 1/\kappa \) is often taken to be the double layer thickness. An increase in \( \kappa \) makes the double layer thinner (compresses the double layer) and makes the potential fall off more rapidly with distance not only in equation (3.13) but also for the complete expression (3.12).

An important assumption in the derivation of equation (3.12) is that the electrical double layer is fully developed and hence there is no interference between the double layers of individual particles. However when double layer overlap occurs as is the case for colliding particles the boundary conditions for solving equation (3.7) have to be modified \( 15 \).

The relationship between the surface charge density, \( \sigma_0 \), and the surface potential, \( \psi_0 \), can be given as

\[
\sigma_0 = (8n_\infty \varepsilon_r \varepsilon_0 kT)^{1/2} \sinh \left( z e \psi_0 /2kT \right) \quad (3.14)
\]

This is the charge contained in a cylinder of unit cross-sectional
area extending from the surface to infinity.

For small values of surface potential the equation simplifies for

$$\sigma_o = \varepsilon_r \varepsilon_o \psi_o \kappa$$

which is the equation of a plane condenser with plate separation $1/\kappa$.

The differential capacitance of the diffuse layer follows from integration of equation (3.14) with respect to the surface potential

$$d \sigma_o / d \psi_o = \kappa \varepsilon_r \varepsilon_o \cosh \left( \frac{z e \psi_o}{2kT} \right)$$

It can be seen that at constant surface potential the surface charge increases with an increase in $\kappa$ (or with increasing electrolyte ionic strength). The applicability of the above equations to the solid-liquid interface is accepted by workers; the flat plate approximation is found to be valid for many colloidal systems.

The surface potential at the surface of a silver iodide particle depends upon the concentration of silver and iodide ions in solution. Addition of inert electrolyte produces a rise in $\kappa$ and a corresponding increase in surface charge density as a result of the adsorption of sufficient potential determining ions to keep $\psi_o$ constant. As a contrast, the charge density at an ionogenic surface (i.e. one whose charge is determined by the dissociation of surface groups) remains approximately constant on addition of inert electrolyte and hence by equation (3.15) the surface potential decreases.

Figure 3.2 shows the variation of surface potential with surface charge density as predicted by the Gouy-Chapman model. The situation is that of a 0.01 mol dm$^{-3}$ aqueous solution of a symmetrical, univalent indifferent electrolyte.

Figure 3.3 depicts how the decay of potential with distance depends upon the electrolyte concentration for a surface of constant charge density.
FIGURE 3.2 The surface potential as a function of the surface charge density according to the Gouy-Chapman model of the double layer. The electrolyte is uni-univalent at a concentration of 0.01M.
FIGURE 3.3 The decay of potential from a charged surface. The surface charge density has been taken to be 0.0158 Cm$^{-2}$, the temperature to be 20°C, and the electrolyte as a 1:1 type.
3.4.1.2 Poisson-Boltzmann equation for spheres

The complete P.B. equation cannot be solved analytically for the case of spherical symmetry. The linearised equation familiar to the Debye-Hückel theory of strong electrolytes can be used for the description of colloidal systems with low surface potentials. Applying the boundary conditions $\psi = \psi_0$ at $r = a$ (where $a$ is the radius, measured from the particle centre, at the inner boundary of the diffuse layer, and $r$ is the distance from the particle centre) and $\psi = d\psi/dr = 0$ at $r = \infty$ leads to

$$\psi(r) = \psi_0 (a/r) \exp (-\kappa (r - a)) \quad (3.17)$$

For high values of the factor $\kappa a$ the double layers around spherical particles can be treated as if of flat plate geometry.

The equation relating surface charge density to the surface potential can be given as

$$\sigma_o = \varepsilon_r \varepsilon_o \psi_0 (1 + \kappa a)/a \quad (3.18)$$

For large $\kappa a$ this expression reduces to the corresponding equation for flat plates.

In cases where the surface potential is too large to permit use of the linearised expression numerical solutions of equation (3.6) must replace analytical methods.

Gronwall et al\textsuperscript{30} and Müller\textsuperscript{31} obtained more exact solutions by retaining more terms in the expansion of the exponential. Extensive numerical data for a wide range of $\kappa a$ values and also including asymmetrical electrolytes have been tabulated by Loeb et al\textsuperscript{32} and Hoskin\textsuperscript{33}. Stigter\textsuperscript{3b} has formulated interpolation equations for the tabulated data of Loeb et al. Other workers have derived approximate analytical formulae to suit different situations\textsuperscript{35-38}.

For finite concentrations of dispersed particles the effect of double layer overlap must be taken into account. Mille and Vanderkooi
have carried out numerical calculations taking double layer interaction into account\textsuperscript{39}.

These refinements are necessary to enable exact calculations testing the theory to be carried out. The use of the more elementary form (equation (3.17)) is adequate in situations where the particles need to be treated as spheres.

From the determination of the approximate solutions an accurate expression for the surface charge density has been proposed\textsuperscript{32,38}

\[ \sigma = \frac{2 n_\infty z e}{\kappa} \left( \frac{z e \psi_0}{2 \sinh \left( \frac{z e \psi_0}{2kT} \right)} + \frac{z e \psi_0}{4 \tanh \left( \frac{z e \psi_0}{4kT} \right) \kappa a} \right) \] (3.19)

which reduces to equation (3.14) for large values of $\kappa a$ and low values of $\psi_0$.

The graphs in figure 3.4 show the variation of potential as a function of distance from the surface for flat plates and spheres. The curves show that for spherical symmetry the potential falls off more rapidly than for flat plates and that the decay is more pronounced the smaller the radius of the particle. The graphs also show that bivalent ions are significantly more effective in compressing the double layer.

3.4.2 Modifications to the Gouy-Chapman Theory

The classical treatment of Gouy and Chapman required the use of several simplifying assumptions

a) the particle surface is flat, of infinite extent, and of uniform charge density,
b) the ions in the diffuse region are point charges distributed according to the Boltzmann type distribution,
c) the dispersion medium only influences the double layer through the dielectric constant,
d) the dielectric constant of the medium is independent of distance from the particle surface.
FIGURE 3.4  The double layer potential as a function of distance from the particle surface. Upper curves refer to $\psi_0=154$ mV, lower curves to $\psi_0=51$ mV.
These assumptions have been the subject of much debate with various corrections to the P.B. equation being suggested. Several reviews have been written on the subject notably by Haydon\textsuperscript{28} and by Bell and Levine\textsuperscript{40-41}. The corrections take into account such factors as ion size, dielectric constant variation, ion polarisation, electrostriction of ionic atmospheres, ion pair formation, use of local activity coefficients, compressibility of the dispersion medium, screened image forces, and self-atmosphere image effects in which the work done against its own ionic atmosphere in bringing an ion from bulk solution to its position in the double layer is considered.

From extensive theoretical studies Levine and Bell have concluded that many of the effects are mutually compensating and that for flat plates the uncorrected Poisson-Boltzmann gives rise to little error for 1:1 electrolytes at concentrations below 0.1 mol dm\textsuperscript{-3} and surface potentials not exceeding 75 mV.

The neglect of ionic dimensions by the Gouy-Chapman model leads to unsatisfactory quantitative agreement between theory and experiment. A simple calculation indicates that treating the ions as point charges has the impossible consequence that a surface concentration of ions as high as 200 mol dm\textsuperscript{-3} could exist. The finite size of the ions, whether solvated or not, limits their distance of closest approach to a surface and hence their maximum concentration. In addition the high electric field strength near a charged surface (\(\sim 10^7\) V m\textsuperscript{-1}) is likely to produce ordering of the solvent dipolar molecules, especially for water. The effect of this will be to incorporate a distance dependent solvent dielectric permittivity into the equations describing the electrical properties of the double layer thereby invalidating the assumption that the solvent is a structureless dielectric of constant permittivity.

Experimentally, the shortcomings of the classic Gouy-Chapman model become obvious when measured values of the electrical capacitance of an interface are compared with the theoretical values. The system most extensively studied in this respect is the mercury-aqueous electrolyte interface\textsuperscript{42} with which measured interfacial capacitances rarely attain the values predicted by the Gouy-Chapman theory\textsuperscript{17}.
FIGURE 3.5 The Gouy-Chapman picture of the electrical double layer
In current theories of the double layer such shortcomings are alleviated, although not eliminated, by dividing the space charge in the electrolyte solution into two distinct regions —

(i) the compact or inner region adjacent to the surface in which the charge and potential distributions are largely determined by the geometrical restrictions of ionic and molecular size, and the short range interactions (e.g. chemical) between ions, the surface, and neighbouring dipoles; and

(ii) the diffuse region located at a distance from the surface where the Poisson-Boltzmann equation may be expected to give a reasonable description of the potential distribution.

Such an approach has been shown to significantly improve the theoretical description of the mercury-solution interface, at least for simple ions.

3.4.3 The Compact Double Layer - Stern's Model

In 1924, Stern introduced a more elaborate theory in which a finite ion size correction in the region close to a charged surface was introduced and the possibility of a specific interaction between adsorbed ions and the surface was considered. This work forms the basis of modern electrical double layer theory.

Stern's model of the double layer is a combination of the molecular condenser model of Perrin and the Gouy-Chapman layer model. The model is pictured in figure 3.6, in which the double layer charges and potentials are defined such that \( \sigma_o \) and \( \phi_o \), \( \sigma_s \) and \( \phi_s \), and \( \sigma_d \) and \( \phi_d \) are the charge densities and potentials of the surface, the Stern layer, and the diffuse layer, respectively. The diffuse region of the double layer starts at a distance \( \delta \) from the surface and for distances \( x \), such that \( x > \delta \), specific interaction forces are assumed to be negligible. The distance of closest approach to the surface is given by \( x = \delta \) so that the region \( 0 < x < \delta \) is free of charge. The ions located at the distance \( x = \delta \) are considered to be relatively immobile and constitute what is known as the Stern layer.
FIGURE 3.6 The Stern picture of the electrical double layer
The charge and potential distribution in the diffuse layer, i.e. $x > \delta$, is given by the Gouy-Chapman model. The charge density within the Stern layer is described by a Langmuir adsorption isotherm, modified by the incorporation of a Boltzmann factor. The expression given by Stern for the charge density is shown in equation 3.20

$$\sigma_s = \frac{z^+ e N_s}{1 + \frac{N_A}{n^+ M} \exp \left( \frac{z^+ e \phi_s + \Theta^+}{kT} \right)} + \frac{z^- e N_s}{1 + \frac{N_A}{n^- M} \exp \left( \frac{z^- e \phi_s + \Theta^-}{kT} \right)}$$

(3.20)

where $N_s$ is the number of available adsorption sites in the Stern layer, $N_A$ is Avogadro's number, $M$ is the solvent molecular weight, $n^+$ is the bulk concentration of cations (in units of ions m$^{-3}$), $n^-$ is that for the anions, and $\Theta^+$ and $\Theta^-$ represent the free energies associated with specific adsorption. These free energies represent the sum of all the non-coulombic contributions to adsorption, such as specific bond formation, lateral interaction between adsorbed species, and changes in the degree of solvation of the ions.

Parsons$^{18}$ has expressed some misgivings about this separation into electrical and chemical contributions but it is common practice in surface chemistry.

Normally, the adsorption of one ionic species predominates so that equation (3.20) can be simplified

$$\sigma_s = \frac{z e N_s}{1 + \frac{N_A}{n_\infty M} \exp \left( \frac{z e \phi_s + \Theta}{kT} \right)}$$

(3.21)

The requirement of electroneutrality gives

$$\sigma_o = -(\sigma_s + \sigma_d)$$

(3.22)
i.e. the surface charge is compensated by the sum of the Stern layer and diffuse layer charges. The differential electrical capacity of the Stern layer can be given as

\[ C_s = \frac{\sigma_0}{\left(\psi_o - \psi_s\right)} = \frac{\varepsilon_s \varepsilon_o}{\delta} \quad (3.23) \]

where \( \varepsilon_s \) is the dielectric constant of the Stern layer. This equation is derived by treating the Stern layer as a molecular condenser of thickness \( \delta \) and permittivity \( \varepsilon_s \varepsilon_o \).

The expression for the diffuse layer charge is given by equation (3.14) with the sign reversed and \( \psi_o \) replaced by \( \psi_s \). Using the assumption that \( \psi_s = \psi_d \), equations (3.14), (3.21), (3.22) and (3.23) can be combined to give a relation between the surface potential and the diffuse layer potential for a flat double layer:

\[ \phi_o = \phi_d + \frac{\delta}{\varepsilon_s \varepsilon_o} \left[ \left(8\varepsilon_r \varepsilon_o n_\infty \kappa T \right)^{1/2} \sinh \left( \frac{z e \phi_d}{2 \kappa T} \right) - A \right] \quad (3.24) \]

in which

\[ A = \frac{z e N_s}{1 + \frac{N_A}{n_\infty} \exp \left( \frac{z e \phi_d + \Theta}{\kappa T} \right)} \]

Similarly for the case of a spherical double layer at low \( \phi_d \) values, where the linear Poisson-Boltzmann approximation is valid, equations (3.18), (3.21), (3.22) and (3.23) can be combined to give:

\[ \phi_o = \phi_d + \frac{\delta}{\varepsilon_s \varepsilon_o} \left[ \frac{\varepsilon_r \varepsilon_o}{(a + \delta)} \phi_d \left( 1 + \kappa (a + \delta) \right) - A \right] \quad (3.25) \]

in which \( a \) is the particle radius.
In effect the Gouy-Chapman model is applied to a particle of radius a plus the Stern layer thickness. The presence of this Stern layer of specifically adsorbed ions has important consequences for the potential distribution in the electrolyte solution. Figure 3.6 shows that across the molecular condenser the potential decays linearly from \( \psi_0 \) to \( \psi_d \) at the boundary between the Stern and Gouy layers. Beyond the distance \( \delta \) from the surface the character of the Gouy-Chapman layer is as laid down originally, e.g. with regard to the compressing effect of \( \kappa \).

The total capacitance of the double layer, \( C \), in the presence of a molecular condenser results from the combination of the individual capacitances of the Stern and Gouy layers. If there is no specific adsorption of ions then the system is treated as two capacitors in series and hence:

\[
(C)^{-1} = (C_s)^{-1} + (C_d)^{-1}
\]  

(3.26)

from which it is clear that the value of \( C \) is dominated by the smaller of its contributing factors. The capacitance of the diffuse layer is an increasing function of electrolyte concentration and of \( \psi_d \), as given by equation (3.16), and hence the overall capacitance of the double layer will be governed by that of the diffuse layer at low values of \( \psi_d \) and electrolyte concentration. At higher values of these latter two parameters the Stern layer capacitance will govern the overall capacitance. The capacitance of the Stern layer as given by

\[
C_s = \varepsilon_s \varepsilon_0 / \delta
\]  

(3.27)

does not depend upon the electrolyte concentration except insofar as the permittivity is affected.

The classical Stern model has been reviewed by many authors\(^{15,17-18,46}\). The inclusion of the molecular condenser, which allows for finite ionic size, improves the agreement between experimental values and predicted values of the double layer capacitance for the mercury-solution\(^{17}\) and silver iodide-solution\(^{47}\) interfaces. The
inclusion of the factor for specific adsorption enables a theoretical explanation of the reversal of sign of a measured zeta potential in the presence of surface active ions to be postulated. When specific adsorption occurs, counter-ion adsorption generally predominates over co-ion adsorption and the typical potential distribution would be that depicted in figure 3.6. However, it is possible for reversal of charge sign to take place within the Stern layer i.e. for $\psi_0$ and $\psi_S$ to have opposite signs (figure 3.7(a)). This situation is most likely to occur with polyvalent or surface-active counter-ions which exhibit large free energies of adsorption. On the other hand adsorption of surface active co-ions could create a situation, as shown in figure 3.7(b), in which the Stern potential has the same sign as the surface potential but is greater in magnitude.

The model is able to explain such phenomena but further modifications have been found necessary.

3.4.4 Grahame's Refinement of the Stern Model

Grahame\textsuperscript{17} distinguished between the Stern plane, also referred to as the outer Helmholtz plane (OHP), to indicate the distance of closest approach of fully solvated ions and the inner Helmholtz plane (IHP), situated at the distance of closest approach of specifically adsorbed ions (desolvated on the side closest to the charged surface). This modification was introduced originally because it had been found that the double layer capacity at positive potentials was greater than at negative potentials, indicating that the distance of closest approach for anions was lower than that for cations (see equation (3.23)). However, such a distinction between the two planes is necessary since even though the specifically adsorbed ions are of the same size (or same ion) as the ions defining the position of the OHP they are desolvated in the direction of the surface thereby permitting closer approach to the surface than the OHP. A schematic representation of the Grahame model is given in figure 3.8. The dielectric constant between the surface and the OHP, $\varepsilon_S$, is assumed to be constant in this model. The new parameters introduced by Grahame are the dielectric constant of the solid, $\sigma_I$ and $\Phi_I$ the charge density and mean potential of the IHP, and the distances $\beta$ and $\gamma$,
FIGURE 3.7(a) Reversal of the double layer charge due to adsorption of counter-ions

FIGURE 3.7(b) Superequivalent adsorption of surface active co-ions leading to an increase in the magnitude of the double layer charge
IHP 0 H

\[ \frac{c}{c} = \frac{a}{K(x+y)} \]

\[ K = \frac{S}{(x+y)} \]

**FIGURE 3.8** Grahame's refined model of the electrical double layer (example is for adsorption of co-ions within the IHP)

\[
\begin{align*}
(\psi_0 - \psi_I) &= \beta \sigma_o / K(\beta + \gamma) \\
(\psi_I - \psi_d) &= \gamma (\sigma_o + \sigma_I) / K(\beta + \gamma) \\
K &= \varepsilon_S \varepsilon_o / (\beta + \gamma)
\end{align*}
\]
where $\beta$ is the distance between surface and the IHP and $\gamma$ is the distance between the IHP and OHP. Thus $\beta + \gamma = \delta$, with $\delta$ representing the distance at which the diffuse layer commences.

A capacitance can be assigned to the region between the surface and IHP, and the region between the IHP and OHP. These are defined by the following expressions:

$$C_\beta = \frac{d\sigma}{d(\psi_o - \psi_i)} \quad (3.28)$$

$$C_\gamma = \frac{d\sigma}{d(\psi_i - \psi_s)} \quad (3.29)$$

In more complicated cases (e.g., adsorbed surfactant molecules in addition to specifically adsorbed ions) extra regions can be defined but a simplified expression for one overall Stern capacitance is often used:

$$(C)^{-1} = (C_s)^{-1} + \left(1 + \frac{\sigma}{\phi_o}\right)(C_d)^{-1} \quad (3.30)$$

At this point it is worth explaining the significance of the double layer capacitance. Capacitance is a measure of the screening of a surface charge; the better the screening the more charges can be present on the surface at a given surface potential. Screening is improved by the presence of counterions, preferably specifically adsorbed. On the other hand it is inhibited by organic adsorbates which can lower $\varepsilon_s$ and/or increase the value of $\delta$ thereby lowering $C_s$, as given by equation (3.27). In general, the capacitance of the double layer increases with specific adsorption and decreases in the presence of organic species. The extent of change in the capacitance depends both on the amount of adsorption and mode of adsorption.

### 3.4.5 The Electrical Double Layer as Viewed by Stern and Grahame

The double layer is divided into three main regions —

(i) the surface layer, with a charge $\sigma_0$. If there is strong specific adsorption of an ionic species then it is customary to consider
such charges as part of the surface charge; with weak specific adsorption (e.g. physical bonding) the charge may be considered as part of the surface charge or as part of the double layer charge;

(ii) the Stern layer or molecular condenser, defined as that part of the solution phase close enough to the surface to experience specific interactions with that surface. This layer can be subdivided into two regions representing two different degrees of interaction between solvated ions and the surface;

(iii) a diffuse layer in which ions only experience the forces of electrostatic attraction or repulsion and thermal agitation.

The distinction between (ii) and (iii) is not clearly defined but since the range of specific interaction is short the Stern layer is seldom more than a few molecular layers thick. For covalent bond, ligand exchange, or hydrogen bond formation contact between the ion and surface is essential, hence the definition of the inner Helmholtz plane. Lower specific interaction can exist if the counterion remains solvated but shares one or two solvent molecules with the surface, these ions locate the outer Helmholtz plane.

Ions adsorbed in the Stern layer are subject to electrostatic and specific interactions which may oppose each other. If the latter occurs and the specific adsorption outweighs the electrostatic effect then the ions adsorb against the electric field thereby producing a situation known as superequivalent adsorption. The potential at the Stern plane is now of greater magnitude than the surface.

Even when there is no specific adsorption of ions (e.g. silver iodide in a solution of potassium nitrate) the Stern layer still exists because of the finite size of the counterions.

Both Stern and Grahame treat the diffuse region of the double layer as ideal in that ion size effects are neglected. Strictly speaking, this assumption implies that any deviations from ideal behaviour in the
diffuse layer are assigned to the Stern layer.

The diffuse layer plays a leading role in the stability of electrocratic colloids since it is the diffuse layer overlap which is experienced initially as particles come together. The role played by the Stern layers is more subtle because the sign and magnitude of the diffuse layer charge depends upon the properties of the Stern region.

The procedure of Stern and Grahame amounts to treating the electrical double layer as successive layers of molecular capacitors characterised by sharp changes in permittivity between neighbouring layers.

At large electrolyte concentrations and high surface potential the value of the capacitance of the Stern layer, \( C_S \), can be measured. For the silver iodide-aqueous electrolyte interface capacitance values of ca. 0.1-0.2 F m\(^{-2}\) have been measured. Taking the Stern layer thickness to be 5 \( \times \) 10\(^{-10}\) m gives a dielectric constant of ca. 7 which indicates considerable ordering of the water molecules close to the surface. Similarly, measurements of the mercury-aqueous electrolyte interface suggest a value of \( C_S \) in the range 0.16-0.3 F m\(^{-2}\) depending on the potential applied to the mercury surface. Using the Grahame model gives a value for \( \beta \) of ca. 1.5 \( \times \) 10\(^{-10}\) m, \( \delta \) is ca. 6 \( \times \) 10\(^{-10}\) m, and a value for \( \varepsilon_S \) of ca. 20.

The integral capacity per unit area of the Stern layer is given by

\[
K_S = \frac{\sigma_o}{\varepsilon} \frac{\varepsilon_S \varepsilon_o}{(\phi_o - \phi_d)} \delta
\]  

(3.31)

Using Grahame's assumption that the permittivity of the Stern layer is constant leads to the following expressions

\[
K_I = \frac{\sigma_o}{\varepsilon} \frac{\varepsilon_S \varepsilon_o}{(\phi_o - \phi_I)} \beta
\]  

(3.32)
\[ K_0 = \frac{-\sigma_d}{\varepsilon_s \varepsilon_o} = \frac{\varepsilon_s \varepsilon_o}{(\phi_I - \phi_d)} \gamma \] (3.33)

for the integral capacities of the IHP and the region between the IHP and OHP respectively.

The above treatment is only an approximation to the real situation in that the permittivity within the Stern layer varies with distance from the surface. More elaborate analyses have been devised in order to incorporate a continuously variable dielectric permittivity into the double layer model thereby producing a smoother variation of potential in the Stern layer.

3.4.6 The Dielectric Permittivity of the Inner Region of the Double Layer

The potential drop across the inner layer of the double layer is often 0.1-1 V, and as this occurs across a distance of less than \( 1 \times 10^{-9} \) m the electric field strengths are high (\( \sim 10^8 - 10^9 \) V m\(^{-1}\)). It is to be expected that such large fields would produce considerable orientation of dipolar solvent molecules with a consequent decrease in the permittivity. The expectation is borne out by theoretical calculations\(^8\), by direct experiment at lower field strengths\(^9\), and by the measured inner layer capacitance of the mercury-aqueous electrolyte interface\(^{17}\).

The elementary models of the inner layer assume a value for the permittivity of between 10 \( \varepsilon_0 \) and 50 \( \varepsilon_0 \). The more elaborate models of Grahame\(^{17}\) and Bockris et al\(^{50}\) introduce two zones in the Stern layer each with a different permittivity. The zone between the charged surface and IHP is normally the thinner thereby exhibiting the greater field strength and is assigned a low permittivity. For water, the limiting value of 6 \( \varepsilon_0 \), corresponding to zero orientation polarisation, is often used. The zone between the IHP and OHP is assumed to have a lower level of dipole orientation corresponding to a permittivity of 20-40 \( \varepsilon_0 \).

3.4.7 The Discreteness of Charge Effect

Both the Gouy-Chapman and Stern-Grahame treatments of the double
layer assume a uniformly charged surface i.e. the charge is smeared out. However, the surface charges are to be found at discrete sites. This has the consequence that the electrostatic work of adsorption is no longer directly related to the IHP potential. When an ion is adsorbed into the IHP it causes a rearrangement of existing surface charges and in doing so imposes a self-atmosphere potential $\Phi_B$ on itself. The main consequence of allowing for this discreteness of charge, in the double layer theory, is that under certain conditions the theory now predicts a maximum in the OHP potential as the surface potential magnitude is increased. Experimentally it is observed that for some sols (in particular silver halides) both the zeta potential and critical coagulation concentration pass through a maximum$^{52}$ as the surface potential is increased.

The importance of the discreteness of charge effect lies in its ability to explain phenomena which are not explicable using the simple version of the Gouy-Chapman-Stern-Grahame theory$^{52}$.

The picture of the double layer is therefore amended to take into account the fact that the double layer consists of the overlapping ionic atmospheres of each individual surface charge, and the potential in any plane parallel to the surface therefore fluctuates from location to location according to the degree of overlap between the ionic atmospheres.

### 3.4.8 Thickness of the Stern Layer

The values taken for the distance parameters $\beta$ and $\gamma$ (the surface to IHP separation and IHP to OHP distance, respectively) are very important in any analysis of the behaviour of ions within the Stern layer. Macdonald and Barlow have reviewed the various values used by workers$^{51}$.

Of the two distances, $\beta$ is the less ambiguous and equating its value with either the radius of a partially solvated ion or the crystallographic radius of the ion is normal practice. Therefore the values of $(2-3) \times 10^{-10}$ m often quoted should not be far out. It is conceivable that the value of $\beta$ may vary with the electrical conditions and molecular/ionic concentrations between the surface and IHP as a result of compression of the hydration shells of adsorbed ions. But such an effect
is only likely to be of importance at high electric field strengths. The constancy of the integral capacity of the inner region, with change in the charge, for a number of systems\textsuperscript{53-55} is in keeping with this assumption. However, it should be noted that for the case of ionised monolayers a model has been set up which allows for a variation in $\beta$ with surface charge.

The distance, $\gamma$, is much more difficult to define. The definition of $\gamma$ is often chosen to simplify the mathematics in the calculation of the discrete-ion potential. The most common concept for the distance is the limit of approach of fully hydrated diffuse layer ions to the surface, but the assumption that the OHP coincides with the plane of permittivity discontinuity has been criticised\textsuperscript{52}.

Buff and Stillinger\textsuperscript{56} distinguish between the two planes in their general theory. There is the possibility that the OHP represents a smearing out of local fluctuations as a result of interaction between ionic hydration layers.

Measurements of the capacity of the Stern layer can only give the ratio between the permittivity and the thickness thereby making interpretation difficult.

3.4.9 The Diffuse Layer

The major assumptions in the use of the Poisson-Boltzmann equation for the description of the diffuse region of the electrical double layer have been reviewed by Haydon\textsuperscript{28}. The validity of these approximations tends to be good at low values of potential and electrolyte concentration.

Improvements which can be applied to the treatment of the diffuse layer are -

(i) the allowance for the finite volume of ions;

(ii) the modification of the solution permittivity to allow for the influence of the double layer electric field;
(iii) to take account of the effect of ionic polarisation in the double layer field; and

(iv) the incorporation of the self-atmosphere effect.

The image-self-atmosphere and cavity effects for the ions in the diffuse layer\textsuperscript{57-58} are the counter-parts of the discrete-ion effect in the Stern layer. It has been found that these effects constitute the major corrections to the PB equation, at least for electrolyte concentrations <0.1 M\textsuperscript{59}.

When all of the major corrections are considered the overall correction to the equation is small. For 1:1 electrolytes, at modest concentrations, (<10\textsuperscript{-2} M) the correction to the simple theory is less than 2\% for \(\psi_d\) <100 mV.

However, the statistical mechanical basis of the PB equation and of the Gouy-Chapman-Stern-Grahame model of the double layer has been questioned. The complete PB equation, as given by equation (3.6), does not satisfy the physical requirement that the electric fields of the individual charges be linearly superposable.

In spite of the associated doubt of the validity of the equation, as a result of this violation, it has been suggested that better agreement with experiment is achieved by using the complete PB equation instead of the linear form of the equation. The error involved in using the latter approximation (i.e. assuming \(z e \psi_0/kT \ll 1\)) can be large for many colloidal systems\textsuperscript{60}.

It is also probably safe to assume that for dilute electrolyte solutions the more exact statistical mechanics treatments\textsuperscript{61} do not significantly improve upon the Poisson-Boltzmann equation.

The success of the modified Gouy-Chapman theory in its quantitative description of the diffuse double layer for the case of 1:1 aqueous electrolytes at moderate concentrations (less than 0.1 M) and surface charge densities of less than 30 \(\mu\text{C} \text{cm}^{-2}\) is due to the cancellation of errors. However, it has been shown that such success no longer prevails
under conditions of stronger ionic interactions, such as those in charge asymmetric systems. Bhuiyan et al. modified the Poisson-Boltzmann treatment to allow for finite ion size effects and fluctuations in the electric field strength. Their study indicated that the Gouy-Chapman theory tends to overestimate the extent to which other counterions screen the surface charge from a given counterion. Thus it predicts an electrical double layer which is too thick and potential drop which is too high. This shortcoming of the classical theory becomes more pronounced at higher electrolyte concentrations and with increase in the surface charge density. However, for 1:1 electrolytes and 2:1 electrolytes in which the counterion is univalent the theory is satisfactory within the conditions stated earlier. But in cases where the counterion is divalent this model breaks down even at low electrolyte concentrations and surface charge densities.

3.5 The Importance of the Zeta Potential

Electrokinetic measurements are frequently used to study the electrical double layer properties of colloidal systems. Such studies rely upon the phenomenon that occurs as one charged phase moves with respect to an adjoining phase. The interaction between the mechanical and electrical forces which occurs as liquid flows through the pores of a packed bed or as charged particles move through a surrounding liquid can be used to gain information of the electrical potential in the interfacial region. There are four major electrokinetic effects -

(i) electro-osmosis, in which a liquid moves with respect to a solid under the influence of an external electric field;

(ii) electrophoresis, in which charged particles move through a liquid in the presence of an external electric field;

(iii) streaming potential, in which a liquid is made to flow past a solid surface and the resultant electric potential is measured; and

(iv) sedimentation potential, in which the electrical potential generated by the gravity settling of particles is measured.
The results of such electrokinetic measurements are normally interpreted in terms of the electrokinetic or zeta potential, $\zeta$. This represents the potential within the diffuse double layer, surrounding a charged surface, at what is known as the slipping plane i.e. the plane separating the mobile and stationary phases. It is an imaginary plane located near to the surface and within which the fluid is assumed to remain stationary with respect to the surface. The location of the slipping plane is, in general, not known but cannot be located closer to the surface than the OHP. In fact if the surface is able to immobilise a considerable quantity of dispersion medium the zeta potential will represent the potential at a plane located within the diffuse layer. There has been considerable debate regarding the position of the slipping plane, although it is commonly assumed to coincide with the OHP. In addition there have been questions concerning the validity of treating the slipping plane as infinitesimally thin; possibly a slipping zone is more correct.

Despite such reservations the determination of the zeta potential yields useful information. When the OHP potential is zero then so also is the zeta potential and, in the absence of specific adsorption, a zero surface potential necessitates a zero zeta potential. The identity of the zeta potential and OHP potential probably exists for small surface potentials but at higher values the viscosity of the dispersion medium is increased due to the increased electric field strength causing the shear plane to shift further from the surface and hence the zeta potential magnitude is expected to be lower than that of the OHP. This effect also occurs as the electrolyte concentration is raised. However, since both potentials exist within the diffuse layer they must possess the same sign and exhibit the same behaviour with respect to inert electrolyte - or potential-determining ion concentration. Thus comparison of zeta potentials obtained in inert electrolyte with those from other electrolytes can yield information on ionic adsorption within the OHP of the electrical double layer.

A further analysis of the relevance of the zeta potential to discussions about the electrical double layer and stability of electrocratic dispersions will be given in the experimental section on electrophoresis. The literature contains a large amount of data on
various surfaces, including oxides, which can be best rationalized on the assumption that the zeta potential and OHP potential are equal. Therefore the properties of a colloidal dispersion which are governed by the behaviour of the electrical double layer are often analysed in terms of the electrokinetic potential.

It must be realised that a single electrokinetic measurement is not sufficient to characterise the solid-liquid interface. Figure 3.9 shows the electrical double layer potential variation with distance for three interfaces. All three cases yield the same zeta potential and yet the structure of the double layer is vastly different in each case.64

Case (1) - a high positive surface potential with a low to moderate adsorption of anionic solute within the Stern layer and with a high concentration of inert electrolyte giving a thin diffuse layer.

Case (2) - a lower positive surface potential with little specific adsorption and a low inert electrolyte concentration giving an extended diffuse layer.

Case (3) - a negative but low surface potential with strong adsorption of counterions leading to charge reversal within the IHP and moderate extension of the diffuse layer.

All three cases are not hypothetical but closely approximate to the following real systems -

Case (1) - ferric oxide at pH 4.0 in the presence of $10^{-4}$ mol dm$^{-3}$ potassium sulphate and $10^{-2}$ mol dm$^{-3}$ potassium chloride.

Case (2) - ferric oxide at pH 7.0 in the presence of $10^{-4}$ mol dm$^{-3}$ potassium chloride.

Case (3) - ferric oxide at pH 8.5 in the presence of $10^{-3}$ mol dm$^{-3}$ potassium chloride and $10^{-4}$ mol dm$^{-3}$ quaternary ammonium salt.

An understanding of the electrical double layer can only be obtained through a systematic series of zeta potential measurements as the
FIGURE 3.9 Examples of three double layer potential distributions giving rise to the same zeta potential.
concentration of each ion is varied.

3.6 Simple Inorganic Ions and the Solid-Liquid Interface

The ionic species which exert a fundamental control on the surface charge density and potential of a dispersed solid are known as the potential determining ions. The ions controlling the extension of the diffuse part of the double layer but which are not involved with any specific interactions with the surface are known as inert or indifferent electrolyte ions. A further type is the specifically adsorbed ion which resides within the Stern layer and participates in specific interactions with the surface groups.

The absence or presence and the relative amounts of these ionic species determine the nature of the electrical double layer.

3.6.1 Potential-Determining Ions and Indifferent Ions

The differential adsorption of ions from an electrolyte solution onto a solid surface or the differential dissolution of one type of ion from the solid surface crystal lattice are common processes by which an electrical double layer is formed. At thermodynamic equilibrium the electrochemical potentials of the active ions are the same in the solid phase and bulk aqueous electrolyte solution. The surface potential of the silver halide-aqueous electrolyte systems is governed by the bulk solution activities of the silver cation and halide anion, which are therefore the potential-determining species. The Gibbs adsorption isotherm can be used to relate the surface charge density to the surface excesses (in moles per unit area) of the potential-determining ions (p.d.i.) in the following way:

\[ \sigma_0 = \sum z_i F \Gamma_i \]  

(3.34)

where \( i \) is the \( i \)th p.d.i., and \( \Gamma_i \) represents the surface excess of the \( i \)th species.
For colloidal dispersions such as the silver halides and barium sulphate the p.d.i. are the ions that actually generate the surface charge. However, there are many systems in which surface charge is generated by the degree of ionisation of surface groups.

Colloidal latex particles often possess acidic carboxyl groups on the surface which produce a surface charge according to the equation

\[
K_a = \frac{v_- H^+}{V_0}
\]

where \( K_a \) is the dissociation constant for the surface groups and \( v_-, v_o \) are the numbers of negative, neutral groups per unit area, respectively, at a given interfacial concentration, \( H^+ \), of protons.

The Boltzmann expression can be used to show the dependency of the surface potential (taken to be the plane of the carboxylate groups) upon the bulk hydrogen ion concentration. The resulting equation

\[
K_a = \frac{v_-}{v_o} \left[ H^+ \right] \exp \left( \frac{-e \phi_0}{kT} \right)
\]

shows that pH is the measure of the potential determining ion concentration.

The simple inorganic oxides (e.g. silica, alumina, rutile) and biosurfaces develop surface charges due to the ionisation of zwitterionic surface sites. The surface hydroxyl groups of oxides possess amphoteric behaviour and hence the potential-determining species for such surfaces are the hydrogen and hydroxyl ions. The surface charge density can be given as

\[
\sigma_o = e (v_+ - v_-)
\]
in which $e$ is the proton charge and $v_+, v_-$ are the numbers of positive and negative sites per unit area.

For colloidal dispersions of the silver halides and oxides there must be a certain bulk concentration of potential-determining ion for which the surface charge density is zero. This condition is known as the point of zero charge (p.z.c.) and can be determined by direct measurement of the surface charge as a function of p.d.i. concentration. There is a second, often quoted, point which is related to the electrokinetic properties of the dispersion and is known as the isoelectric point (i.e.p.). The p.d.i. concentration is such that the zeta potential is zero. These two points may or may not be coincident depending on the absence or presence of specific adsorption at the solid-liquid interface.

3.6.2 The Point of Zero Charge

The determination of the p.z.c. is not easily carried out but the usual technique is outlined below. It is assumed that if the solid is prepared at its p.z.c., and then subjected to dialysis and drying, when placed in a solution of the appropriate p.d.i. concentration necessary to give the p.z.c., will cause no change in that concentration, irrespective of the concentration of other ions, providing there is no specific adsorption of said ions. Thus an oxide, for example rutile, prepared in this fashion will cause no change in solution pH once dispersed. The method involves adding a known mass of solid to a known volume and concentration of an indifferent electrolyte. The initial pH is noted and the sample is titrated with a standard solution of a strong base and the volume required to achieve a given pH noted. Sufficient time must be allowed after each aliquot of alkali to establish equilibrium.

A curve of solution pH against volume of alkali is plotted and compared with that from a reference titration (as above without the dispersed solid). The additional alkali required to reach the same equilibrium solution pH corresponds to the quantity of hydroxide ions taken up by the solid surface in order to establish that pH value. The net increase in negative surface charge per unit area can easily be determined, assuming the only process involving the hydroxide ion is that of acid-base equilibrium. The comparable data for the acid titration of
the dispersed solid are determined and a plot of relative surface charge density against pH can be constructed. If the procedure is repeated at different indifferent electrolyte concentrations a series of isotherms is found which possess a common point. This is the p.z.c. because only at this pH is the surface charge density independent of the supporting (indifferent) electrolyte. Figure 3.10 shows the type of result obtained for an oxide such as rutile. Because the surface potential is fixed by the bulk solution pH the surface charge density increases with an increase in supporting electrolyte concentration, as predicted by equation (3.15).

The technique is only as accurate as the determination of the surface area of the dispersed solid. Aside from the problems associated with irregular particle shape and Ostwald ripening there is the difficulty in interpretation of the experimental results. Direct measurement of particle size, even for regular shapes, can give lower surface areas because of the effect of surface roughness. In fact any of the techniques utilising a dry sample is likely to give a value for the area which for all its accuracy bears little relation to the effective surface area in solution. A recent review has discussed the merits of the various surface area determination techniques.

The point of zero charge is an important characteristic of a solid, although the values quoted for a given material are function of its source, method of preparation, pretreatment, and presence of surface impurities. Typical values for some solids are given in table 3.2

<table>
<thead>
<tr>
<th>Material</th>
<th>Point of Zero Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile (TiO₂)</td>
<td>pH 6.0</td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>pH 2-3.7</td>
</tr>
<tr>
<td>Magnesia (MgO)</td>
<td>pH 12</td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>pH 9.5</td>
</tr>
<tr>
<td>Corundum (Al₂O₃)</td>
<td>pH 9.0</td>
</tr>
<tr>
<td>Silver Iodide</td>
<td>pAg 5.6</td>
</tr>
<tr>
<td>Silver Chloride</td>
<td>pAg 4</td>
</tr>
</tbody>
</table>

TABLE 3.2.

Point of zero charge for some ionic solids
FIGURE 3.10 Surface charge density as a function of pH for an oxide.
(numbers refer to electrolyte molarity)
The point of zero charge has been correlated with surface thermodynamic properties such as the heat of neutralisation\(^67\) and the heat of immersion\(^68\). The value of the latter was found to increase as the p.z.c. of the oxide increased; thus quartz has a typical value heat of immersion of \(-0.3\ J\ m^{-2}\) whereas rutile has a value of \(-0.5\ J\ m^{-2}\). The same thermodynamic property has been linked to the electrostatic field strength generated at the oxide surface\(^68-69\). The latter parameter is significantly influenced by the charge distribution on the solid surface and hence also is the point of zero charge\(^70\). It is the field strength associated with the solid surface of oxides which determines the degree of interaction with the dispersing medium and its solute species. Thus it is logical that the greater the field the more extensive the interaction between the oxide surface and aqueous solution. The equilibrium constants for the dissociation reactions involving hydrogen and hydroxyl ions are related to the value of the p.z.c. Since these constants are a function of the surface field strength then so are the points of zero charge.

3.6.3 The Isoelectric Point

The point at which the zeta potential is zero is known as the isoelectric point (i.e.p.). Measuring the electrokinetic potential as a function of pH for a dispersion of TiO\(_2\) in aqueous KNO\(_3\) solution would indicate the following

(i) KNO\(_3\) is an indifferent electrolyte for TiO\(_2\);

(ii) the i.e.p. is equal to the p.z.c. for this dispersion;

(iii) H\(^+\) and OH\(^-\) are potential-determining ions.

Figure 3.11 gives typical data for the system\(^71\).

It should be noted that the most steeply sloping curve is the one of lowest indifferent electrolyte concentration which is the opposite to that found in figure 3.10.
FIGURE 3.11 The variation of the zeta potential as a function pH in aqueous KNO₃ solution for TiO₂
The measured value for the i.e.p. of a solid may be in error due to the presence of trace impurities in the dispersion medium, (the effect on the measured p.z.c. is minimised by the use of a larger solids content and hence higher surface area over which to spread the impurity). An impurity which is often present is soluble silicate, formed by prolonged storage of electrolyte solutions in glassware, and the problem will be more severe in alkaline solution. Furlong et al.\textsuperscript{72} have carried out a study of the problem and have shown that the i.e.p. of TiO\textsubscript{2} can shift by 0.2 pH units even at a pH value of 6 over a period of 2 months. The shift is to a lower value which indicates the presence of silica in the system. The effect is even more pronounced for alumina when stored in glass vessels.

Contamination problems can be minimised by observing the following precautions -

1) storing samples either dry or as high solids content slurries in aged, hard glass (at neutral or acidic pH) or in aged polythene bottles;

ii) using aliquots of the dispersion as wash liquor for all surfaces with which the sample comes into contact thereby removing any easily adsorbed impurities; and

iii) preparing low solids content dispersions for microelectrophoresis by centrifuging a more concentrated dispersion and redispersing a fraction of the solid in the supernatant.

The influence of the indifferent electrolyte concentration is to affect the zeta potential at p.d.i. concentrations other than that at the i.e.p. A simple Gouy-Chapman model of the electrical double layer would predict a decrease in $\zeta$ with increase in the electrolyte concentration, if the position of the shear plane was assumed to be at a fixed distance from the surface.

The other important effect of the concentration of indifferent electrolyte is that it has a strong influence upon the surface charge density for a surface at constant surface potential. As kappa
(reciprocal of double layer thickness) increases the rate of decay of potential near the surface rises. Since

\[ \sigma_0 = -4\pi \varepsilon_0 \varepsilon_r \left( \frac{d\phi}{dx} \right)_{x=0} \]  

(3.38)

the increasing indifferent electrolyte concentration forces more p.d.i. to adsorb at the surface in order to maintain the \( \phi_0 \) value.

3.6.4 Specifically Adsorbed Ions

An ion which is adsorbed at a surface by forces other than by the electrical potential is regarded as being specifically adsorbed. The additional forces may be chemical in type (e.g. covalent or ionic bonding with the surface species) or physical (e.g. van der Waals forces between the ion and the surface or between clusters of adsorbed ions). For the former forces to be involved it is obvious that the adsorption must take place within the IHP, as can occur at the mercury-solution interface\(^{17}\). Specific adsorption may also be present with ions adsorbed at the OHP, although they retain their solvation sheaths\(^{73}\).

Specifically adsorbed ions can be recognised by their ability to reverse the sign of the zeta potential, whereas the indifferent ions can only reduce the latter to an asymptotic value of zero. A useful distinction between the various types of ion has been made by Fuerstenau\(^{66}\). Figure 3.12 indicates that a physically adsorbed ion, i.e. at the OHP, does not affect the point of zero charge (equal to isoelectric point) but can modify the magnitude and/or reverse the sign of the zeta potential. Its effects are only apparent when the particle surface charge is of the opposite sign. On the other hand, a chemisorbed ion shifts the p.z.c. and i.e.p., and remains adsorbed even when the surface charge is the same sign.

As the concentration of specifically adsorbed counterions increases not only does the zeta potential change sign but the surface charge density also increases as indicated by equation (3.38). An increase in the surface charge at a fixed potential-determining ion concentration is equivalent to a shift in the p.z.c., as indicated in table 3.3.
FIGURE 3.12 The zeta potential of an oxide at various pH values in the presence of different types of electrolyte: 1 indifferent electrolyte; 2 physically adsorbed cation; 3 physically adsorbed anion; 4 chemically adsorbed anion
TABLE 3.3.
The effect of specific ion adsorption on the point of zero charge and the point of zeta potential reversal for an oxide

<table>
<thead>
<tr>
<th>CATION ADSORPTION</th>
<th>moves to lower pH</th>
<th>moves to higher pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANION ADSORPTION</td>
<td>moves to higher pH</td>
<td>moves to lower pH</td>
</tr>
</tbody>
</table>

Specific adsorption of cations suppress surface dissociation reactions which give rise to positive surface sites and promote those giving negative sites thereby effectively increasing the negative charge of the surface. The p.z.c. therefore shifts to a higher concentration of the positively charged potential-determining ion. The specific adsorption of anions has the opposite effect.

The p.d.i. concentration at which the zeta potential changes sign (p.z.r.) is also a function of the existence of specific adsorption of anions or cations. Specific adsorption of anions tends to make the zeta potential more negative. The term i.e.p. is best reserved for the point at which the zeta potential is zero as the result of adjustment of the p.d.i. concentration\(^6\). Figure 3.13 shows the electrical potential-distance profiles at the p.z.r. and p.z.c. in the presence of anionic specific adsorption. Since \(\sigma_0 = 0\), by definition, at the p.z.c. then \(\psi_0 = \psi_d = \zeta\).

In general it is found that the greater the ionic size the greater the extent of specific adsorption, therefore anions show a greater tendency towards specific adsorption at a solid-solution interface. However, the larger cations e.g. \(\text{Cs}^+\), quaternary ammonium ions, etc do exhibit relatively strong specific adsorption\(^7\). Ions possessing a strong primary hydration sheath tend to show minimal specific adsorption effects, however a decrease in the strength of the ion-solvent molecules interaction increases the tendency towards specific adsorption.

It is important to realise that even in the absence of the specific adsorption of ions the electrical double layer must still be regarded as possessing a Stern layer because of the finite size of the counterions.
FIGURE 3.13 The potential profile for the Stern model of the double layer at A the p.z.r.; and at B the p.z.c. in the presence of specifically adsorbed counterions
3.6.5 Summary

The electrical properties of the solid-solution interface depend to a large extent upon the concentration, type, and location of the ions present. The relative concentrations of the potential-determining ions govern the surface charge and thereby the surface potential of the solid surface. The ionic strength of the indifferent electrolyte counterions determine the properties of the diffuse region of the double layer and thereby the degree of electrostatic interaction experienced on the mutual approach of dispersed particles each possessing an electrical double layer. Ions which undergo specific adsorption within the Stern layer have a pronounced effect upon both the potential-distance profile and the electrical capacitance of the double layer. In particular, the specific adsorption of counterions can often lead to charge reversal so that the diffuse layer charge possesses the same sign as the surface charge. In addition an ion which behaves as an indifferent species at low surface potentials can at higher potentials be specifically adsorbed.

3.7 The Gouy-Chapman-Stern-Grahame (GCSG) Model of the Interface

The Gouy-Chapman-Stern-Grahame model of the electrical double layer, as depicted in figure 3.8, is often used as the basis for the description of both the charge and potential distributions within the solid-solution interfacial region of numerous colloidal dispersions. For the silver halide-aqueous electrolyte interface the surface potential is assumed to be a function of the p.d.i. concentration, as given by the Nernst equation. However, for the more commonly met interfaces, such as oxides and polymer lattices, a more complex relationship between \( \phi_0 \) and p.d.i. concentration is required. The assumptions concerning the nature of the compact and diffuse layers are essentially the same in all the models used to describe the given solid-solution interface, although to reduce the number of parameters the IHP and OHP are often assumed to be coincident, thereby giving the Stern plane. For this simplified picture \( \phi_I = \phi_d = \phi_s \), and \( \sigma_I = \sigma_s \).

The basic equations for the GCSG model can be given as
as a result of the concept of electroneutrality. The integral capacity of the compact region per unit area is given as

\[ (K_S)^{-1} = (K_I)^{-1} + (K_0)^{-1} \]  \hspace{1cm} (3.40)

Using the assumption that the dielectric permittivity of the compact layer is uniform then

\[ K_S = \frac{\varepsilon_S \varepsilon_0}{\delta} \]  \hspace{1cm} (3.31)

so that

\[ \phi_0 - \phi_I = \frac{\sigma_o \beta}{K_S \gamma} \]  \hspace{1cm} (3.41)

and

\[ \phi_I - \phi_d = \frac{(\sigma_o + \sigma_I)(\gamma - \beta)}{K_S \gamma} \]  \hspace{1cm} (3.42)

(c.f. equations in Section 3.4.5). Combination of these last two equations yields

\[ \phi_0 - \phi_d = \frac{\sigma_o}{K_S} + \frac{\sigma_I(\gamma - \beta)}{K_S \gamma} \]  \hspace{1cm} (3.43)

The GCSG model therefore indicates that at the p.z.c. \( \phi_o = \phi_I \), since \( \sigma_o = 0 \) (equation (3.41)). Figure 3.14 shows the potential distribution at the p.z.c. and p.z.r. for the GCSG picture of the double layer. In the absence of specific adsorption, i.e. \( \sigma_I = 0 \), the following equality is found \( \phi_o = \phi_I = \phi_d = 0 \) at the p.z.c. At the p.z.r. by definition \( \phi_d = \xi = 0 \) and so from equation (3.14) (the surface values replaced by the Stern plane values) \( \sigma_d = 0 \); so from the electroneutrality expression we have \( \sigma_o = -\sigma_I \) and hence equation
FIGURE 3.14 The potential profile for the GCSG model of the electrical double layer: A at the p.z.r.; and B at the p.z.c. for the case of the specific adsorption of an anion.
(3.42) gives $\phi_I = \phi_d = 0$, as shown in figure 3.14(A). Equation (3.41) therefore gives the following:

$$\psi_o = \sigma_a e / K_s \gamma$$

(3.44)

The equations just mentioned do not adequately define the double layer in that there are insufficient equations to determine all the unknown parameters. Two further equations are necessary - a) one giving the surface potential in terms of the concentration of potential-determining ions; and b) one linking $\psi_I$ and $\sigma_I$ (or $\psi_S$ and $\sigma_S$).

The latter equation can be developed from the Stern model of the double layer:

$$\sigma_I = z e N_s C \exp \left[-\left(\frac{z e}{kT}\phi_I + \theta_+\right)\right]$$

(3.45)

where the symbols have the same meaning as in equation (3.20) and $C$ is the mole fraction of electrolyte in the bulk solution.

The specific chemical adsorption potential, $\theta_+$, is essentially independent of the surface charge, at least for simple inorganic ions at the mercury-solution interface, if $\phi_I$ is replaced by the micropotential, $\psi_I$. For systems possessing a high diffuse layer capacitance the expression for $\psi_I$ can be written as

$$\psi_I = \psi_I - \frac{\sigma_I K_s}{K_1 K_0}$$

(3.46)

where the latter term = $\psi_B$, the self-atmosphere potential. Smith has pointed out that this substitution for $\phi_I$ is only strictly valid when both the surface and diffuse layer can be regarded as conductors. For the more usual situation in which the permittivity of the surface is similar to that of the compact region of the double layer the corresponding equation is

52
If $K_1 = K_0$ then it follows that $K_1 = K_0 = 2K_s$ and thus for the mercury-solution interface $\phi_\beta$ is given by $-\sigma_1/4K_s$, whereas for the more commonly met colloidal systems $\phi_\beta$ is given by $-\sigma_1/2K_s$. Therefore it would be expected that the self-atmosphere potential effect, section 3.4.7, is more important in the latter systems.

The final equation required to complete the GCSG model of the double layer is the relation between the concentration of potential-determining ions and the surface potential.

For the silver halide-solution interface the Nernst equation is often assumed to apply i.e.

$$\phi_o = \frac{kT}{ze} \ln \left( \frac{[\text{Ag}]}{[\text{Ag}]_{p.z.c.}} \right)$$

(3.48)

A similar equation is expected to hold for any system in which the p.d.i. are themselves constituents of the solid's crystal lattice. However, for other colloidal systems a more elaborate expression for the surface potential must be set up and, as will be shown in the subsequent sections, linking the potential with the surface charge density often proves to be difficult.

For the polymeric lattices, the most successful models describing the acquisition of the surface charge postulate that one or more dissociation reactions occur at specific sites on the solid-liquid interface.

The oxide surfaces are described by more elaborate models involving both surface site dissociation and site binding reactions (i.e. the chemical binding of electrolyte ions to the surface charge groups). Such models are successful in reconciling the experimental data on the magnitudes of surface charges and electrokinetic potentials, but do so at the expense of losing the distinction between potential-determining
ions, indifferent ions, and specifically adsorbed ions.

In contrast to the situation for the silver halide type interfaces the site dissociation models focus attention on the surface charge, and the surface potential is subsequently calculated as a dependent variable using relatively simple Boltzmann equations to link the surface and bulk ion concentrations.

3.8 Site Dissociation Models - An Overview

The earliest investigations of the electrical double layer paid little attention to the mechanism by which the surface charge was generated and in fact supposed that \( \sigma_0 \) was a consequence of the surface potential. However, the surface site dissociation (ionisation) models pay heed to the mechanisms of surface charge acquisition by permitting the surface group densities and ionisation equilibrium constants to directly influence the electrical parameters of the solid-solution interface. The formulation of relationships between \( \sigma_0 \) and \( \phi_0 \) for use with the Gouy-Chapman-Stern-Grahame models of the double layer was carried out by various workers including Hunter and Wright\textsuperscript{76}, Levine and Smith\textsuperscript{78}, and Yates et al\textsuperscript{81}. Subsequently a series of papers by Healy et al\textsuperscript{77,79,80} gave useful methods for describing the behaviour of oxides in aqueous solutions of indifferent electrolytes. Development of surface charge occurs via protolytic ionisation reactions with a diffuse layer of counterions providing electrical neutrality. No compact layer is taken to be present. Solutions to the sets of equations appropriate for such assumptions have been obtained for dilute dispersions in which interparticle separations are sufficiently large so that interactions are negligible\textsuperscript{77}. Similarly solutions have been obtained for systems for which equilibrium interactions between particles approaching each other as the result of Brownian motion need to be considered\textsuperscript{79–80}. In these models the effect of the supporting electrolyte on \( \sigma_0 \) is exerted only through the concentration dependence of \( \sigma_d \). The simple diffuse layer models for ionisable particles assume that only hydrogen ions specifically interact with the surface groups while all other ionic solutes accumulate in the diffuse layer. However, many solutes do interact with the surface via specific chemical interactions; supporting evidence for this comes from the phenomenon of superequivalent adsorption and the shifts in the p.z.c.
or i.e.p. and the charge reversal observed in the presence of the given ion or solute. The classical double layer treatments take such specific adsorption into account by introducing either a specific adsorption potential or free energy term. However, specific adsorption can also be allowed for by introducing an adsorption reaction characterised by an equilibrium or binding constant. Yates et al\(^{81}\) found it necessary to allow for weak adsorption of the indifferent electrolyte ions and hence introduced an ion binding equilibrium constant to an otherwise simple diffuse layer treatment of the ionisable surface-solution interface. The picture of the electrical double layer becomes that of Stern and Grahame in which the supporting electrolyte ions adsorb at surface sites via complexation.

It is clear from the literature\(^{65}\) that the GCSG models of the diffuse and compact layers of charge are sufficiently good for certain applications regardless of the identity of the solid surface giving rise to the double layer. But it is equally clear that the Nernst equation is inadequate to relate the surface potential to the hydrogen ion activity. On the other hand the surface ionisation models give reasonable accuracy when used for the same correlation in the study of proteins. Several workers have subsequently applied such ionisation models and their offshoots to oxide dispersions. An excellent review of such models has recently been published by Healy and White\(^{75}\).

Yates et al\(^{81}\) suggested that the counterions were able to form weak ion pair complexes with the charged surface groups thereby providing a mechanism for the electrolyte to influence the acquisition of surface charge by ionisation processes. All surface sites involved in protonic exchange need to be taken into account when defining \(\sigma_0\); thus for rutile in aqueous potassium nitrate solution the ionisation and electrolyte binding reactions can be written as

\[
\begin{align*}
\text{TiOH} & = \text{TiO}^- + \text{H}^+ \\
\text{TiOH}^+ & = \text{TiOH} + \text{H}^+ \\
\text{K}^+ + \text{TiO}^- & = \text{TiO}^- \text{K}^+ \\
\text{NO}_3^- + \text{TiOH}^+ & = \text{TiOH}^+ \text{NO}_3^-
\end{align*}
\]
The surface charge, \( \sigma_0 \), can then be related to the surface densities of the various groups:

\[
\sigma_0 = e N_A \left( \Gamma_{\text{TiOH}^+} + \Gamma_{\text{TiOH}^+\text{NO}_3^-} - \Gamma_{\text{TiO}^-} - \Gamma_{\text{TiO-K}^+} \right)
\]  

\((3.49)\)

The Stern layer charge, \( \sigma_s \), can be quoted as:

\[
\sigma_s = e N_A \left( \Gamma_{\text{K}^+} - \Gamma_{\text{NO}_3^-} \right)
\]  

\((3.50)\)

assuming that the concentration of hydrogen and hydroxyl ions is small relative to the electrolyte concentration.

With this binding modification, the surface ionisation model and the GCSG double layer equations adequately describe both the pH and ionic strength dependence of \( \sigma_0 \) for oxides\(^{81}\).

A further refinement of the treatment was introduced by Davies et al\(^{82}\) who allowed for the variation of the various ionisation and electrolyte binding equilibrium constants with \( \phi_0 \). The quantitative modelling of the pH and ionic strength dependence of \( \phi_0 \) and zeta potential was successful for both polymer lattices and oxides.

The site dissociation/site binding models treat the surface potential as a necessary consequence of chemically produced surface charges. Thus the value of \( \sigma_0 \), and hence \( \phi_0 \), is limited by the maximum ionisation of the surface sites. Mathematically the models consist of a set of simultaneous equations which can be solved either numerically or graphically. If the complete GCSG model for the structure of the electrical double layer is assumed then the appropriate equations consist of:

1. a set describing the thermodynamic, electrostatic, and stoichiometric constraints on the surface, compact and diffuse layer charges, namely:

   a) an equilibrium constant expression for each possible surface functional group ionisation reaction, including parameters accounting for the influence of \( \phi_0 \);
b) an equilibrium constant expression for each possible complexation reaction between electrolyte ions and the ionised surface sites again including factors allowing for the influence of $\psi_0$;

c) an expression giving the limitation on the maximum attainable surface charge;

d) an equation defining $\sigma_0$ in terms of the ionised and complexed ionised surface sites, e.g. equation (3.49);

e) an equation defining the compact layer charge, $\sigma_s$, in terms of the complexed ionised surface sites; and

f) an expression giving the electroneutrality constraint.

(2) A set expressing the constraints imposed by the particular electrical double layer model invoked i.e. the particular equations relating $\sigma_0$, $\sigma_s$, and $\sigma_d$ to $\psi_0$, $\psi_I$, and $\psi_d$.

The development and use of such a model requires a knowledge of the types of surface functional groups involved, the total surface density of each type, the specific surface area of the solid, and the dissociation and electrolyte complexation equilibrium constants for each type of surface site.

Since the models must be able to account for both the chemical and electrical behaviour of the practical system experimental data on the properties of the particle surface, and the pH and ionic strength dependence of surface charge as well as a measure of the electrical effect of the solid on the solution are required. The properties of the colloidal dispersion that are independent of the particular model chosen to describe the interface can be determined using various methods.65 Measuring the composition of the particle surface, the solid solubility, the surface area of the particle, the particle size distribution, the type, and densities of the surface functional groups satisfactorily defines the solid surface. Additional information concerning the
adsorption densities of supporting electrolyte ions and the electrokinetic mobilities, as a function of pH and ionic strength, is desirable. However, the equilibrium constants for both the ionisation and complexation reactions are dependent upon the particular electrical double layer structure assumed. Estimates of these constants from experimental data can be obtained through approximations and extrapolations.

The application of such site dissociation models to oxides, in particular titanium dioxide, is described in Appendix C.
CHAPTER 4

INTERACTION BETWEEN DISPERSED PARTICLES
4. THE INTERACTION BETWEEN DISPERSED PARTICLES

Most solids dispersed in a liquid constitute what is known as a thermodynamically unstable system. This is due to the large solid-liquid interfacial area which promotes aggregation of the particles. The larger the area the greater the instability. A colloidal dispersion of one phase in a second phase can be stabilised by introducing a potential energy barrier to aggregation or by reducing the interfacial tension to zero. The latter explains the stability of microemulsions involving oil, water, and surfactants. It is the adsorption of the latter at the oil-water interface which causes a near zero interfacial tension.

However, most dispersions can only be stabilised against aggregation through the presence of a potential energy barrier. The colliding particles must possess sufficient thermal energy to surmount this barrier in order to aggregate. The situation is analogous to that associated with the kinetics of reacting chemical species. The barriers arise from the interactions between particles. The main types of interparticle forces can be listed as:

1. Electrostatic: arising from the overlap of electrical double layers. Normally repulsive, but can be attractive eg interaction of oppositely charged particles.

2. Van der Waals: originating in molecular dispersive interactions. Attractive forces (although repulsive types have been reported for certain systems).

3. Steric: arising from the geometry and conformation of adsorbed macromolecules. These forces can be attractive or repulsive depending upon the degree of particle surface coverage by the macromolecule and upon the liquid medium properties.

4. Solvation: associated with the structured layers of ions and molecules near a surface eg the hydration forces found by Pashley and workers.
It is the combination of these interactions which determines the net potential energy of the system and hence the bulk rheological properties and the colloidal stability.

4.1 The Attractive Interaction ($V_A$)

The attractive forces between macroscopic particles arise from the electromagnetic and electrostatic interactions between the individual atoms/molecules. There are various types of interatomic/intermolecular attractive forces. Table 4.1 lists some of these forces.

**TABLE 4.1 - Intermolecular Attractive Forces**

<table>
<thead>
<tr>
<th>Type</th>
<th>Distance Dependence</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-Ion</td>
<td>$1/r^2$</td>
<td></td>
</tr>
<tr>
<td>Ion-Dipole</td>
<td>$1/r^3$</td>
<td></td>
</tr>
<tr>
<td>Dipole-Dipole</td>
<td>$1/r^7$</td>
<td>Keesom Effect</td>
</tr>
<tr>
<td>Ion-Induced Dipole</td>
<td>$1/r^5$</td>
<td></td>
</tr>
<tr>
<td>Dipole-Induced Dipole</td>
<td>$1/r^7$</td>
<td>Debye Effect</td>
</tr>
<tr>
<td>Induced Dipole-Induced Dipole</td>
<td>$1/r^7$</td>
<td>London Effect</td>
</tr>
</tbody>
</table>

It was van der Waals who first introduced the concept of attractive interactions between neutral molecules. The phenomenon is the result of the combination of three different effects\textsuperscript{15}. The interaction between dipole moments is known as the Keesom effect and that between a dipole and an induced dipole as the Debye effect. The third effect is the attraction which exists between any two apolar molecules and is the result of induced dipole - induced dipole interaction. London\textsuperscript{84} discovered this attractive force which is, in all cases except for extremely polar molecules like water or ammonia, stronger than the other two effects. The three components of the van der Waals attraction all give rise to an attractive energy varying inversely as the sixth power of the interatomic distance. However, a fundamental difference between the Keesom and Debye forces on the one hand and the London force on the other appears when the summation of the attractive interactions between
conglomerations of atoms are considered in calculating the interaction between particles composed of many atoms. The electric field strength acting on an atom is the vectorial sum of the individual fields generated by each of the other atoms; so that the total energy of interaction due to the Keesom and Debye effects is less than the sum of the components. The particle-particle interaction is thus effectively zero.

However, the induced dipole-induced dipole interaction between two atoms is, to a first approximation, independent of the interaction with other atoms.

There are two methods of calculating the attractive force between solid particles. The first, the microscopic approach, assumes that the interactions between individual atoms are additive so that for particle-particle interaction the total London energy of attraction may be found by summation overall pairs of atoms. The variation of the attractive force with separation becomes more significant with an inverse square dependency.

Hamaker\textsuperscript{85} derived an expression for the total attractive potential energy, $V_A$, between two spherical particles

$$V_A = -\frac{A_m}{6} \left( \frac{2a_1 a_2}{H (2a_1 + 2a_2 + H)} + \frac{2a_1 a_2}{(2a_1 + H)(2a_2 + H)} \right) + \ln \left( \frac{(2a_1 + 2a_2 + H) H}{(2a_1 + H)(2a_2 + H)} \right) \tag{4.1}$$

where $A_m$ is the Hamaker constant;

$a_1, a_2$ are the particle radii;

$H$ is the distance between particle surfaces.
The decay of the attractive energy is relatively slow and explains the long range character of the so-called London-van der Waals dispersion forces.

The Hamaker constant depends upon the nature of particles and the dispersion medium separating them. The evaluation of $A_m$ is a major problem because its value is related to the electronic properties of the constituent atoms eg the polarisibility. However, estimations can be made based on spectroscopic data or the surface free energies of the phases. The methods of evaluating $A_m$ have been reviewed by Gregory$^{86}$. Values of the constant typically lie in the range $10^{-19}$ - $10^{-21}$ J, the lower its value the lower the attraction.

The attraction between two particles is modified by immersion in a liquid medium. The effective Hamaker constant for a dispersion can be calculated from the following expression:

$$A_m = (A_2^{0.5} - A_1^{0.5})^2$$ \hspace{1cm} (4.2)

where subscripts 1 and 2 refer to the Hamaker constants of the dispersion medium and particles, respectively. The interparticle attraction is weakest when the particles and dispersion medium are chemically similar. Because the values of $A_1$ and $A_2$ are often similar in magnitude it is not possible to know $A_m$ for a particular colloidal system to much better than an order of magnitude. For aqueous dispersions of titanium dioxide a value of about $8 \times 10^{-20}$ J is typical.

The second approach, the macroscopic approach, for the calculation of the attractive force makes use of the optical properties of the interacting materials, particles and dispersion medium, to derive the expression for the potential energy. However, the appropriate optical data is only available for a limited number of materials. Consequently the Hamaker approach is the most used method for calculating $V_A$ as a function of interparticle separation. Krupp has discussed and compared the two approaches$^{87}$.
Two refinements to the Hamaker treatment should be mentioned. Firstly, transmission of the attractive force through the dispersion medium produces a decrease in the force as the result of the influence of the dielectric permittivity of the medium. Secondly, a finite time is required for the London force to reach a distant atom. This retardation of the attractive force is important for distances greater than the characteristic wavelength of the intrinsic electronic oscillations of the atoms (approx $10^{-7}$ m). A reduction in $V_A$ is consequently apparent.

Schenkel and Kitchener have derived a useful formula to calculate the retarded attractive energy for interacting spherical particles with radii larger than the distance of separation between surfaces, $H$

for $H < 15$ nm

$$V_A = -\frac{A_m a_1 a_2}{6H (a_1 + a_2)} \left(\frac{\lambda}{\lambda + 11.12 H}\right)$$ (4.3)

for $H > 15$ nm

$$V_A = -\frac{2 A_m a_1 a_2}{(a_1 + a_2)} \left(\frac{2.45 \lambda}{120 \pi H^2} - \frac{2.17 \lambda^2}{720 \pi^2 H^3} + \frac{0.59 \lambda^3}{3360 \pi^3 H^4}\right)$$ (4.4)

where $\lambda$ is the characteristic electronic frequency.

For spherical particles of radius <100 nm the Hamaker expression (equation 4.1), with the value of $A_m$ corrected for transmission effects, is satisfactory. For larger particles retardation effects need to be considered and consequently equations 4.3 and 4.4 are more satisfactory.

The attractive forces between particles suspended in a gas or liquid phase have been measured as a function of interparticle separation. Good agreement between theory and experiment has been found.

The shape of the $V_A$-distance curve is such that an infinitely deep potential energy well exists at small (<0.1 nm) separations. However, a second universal force becomes dominant at such separations. This
second universal force becomes dominant at such separations. This so-called Born repulsion is the result of the overlapping of approaching electron clouds and leads to a rapidly rising repulsive potential. The interaction energy-distance curve therefore exhibits a finite, though deep, potential energy well into which colliding particles will fall.

Thus the form of the potential energy-distance curve between two particles dictates that once the particles approach each other, as the result of either thermal motion or shear induced motion, aggregation shall occur. To hinder this tendency a potential energy barrier can be introduced into the total interaction energy-distance curve; the particles must consequently possess sufficient kinetic energy to overcome the imposed activation energy.

4.2 Electrostatic Repulsion \( (V_R) \)

As the electrical double layers of two approaching particles overlap a repulsive force is generated which increases as the particles come closer together. Various expressions have been proposed to describe the repulsive potential energy, \( V_R \). The following equations apply to spherical particles with small surface potentials. For dispersions in which \( \kappa a \gg 1 \) (large particles in aqueous solution with moderate supporting electrolyte concentration) the following can be used:

\[
V_R = \frac{4 \pi \varepsilon_0 \varepsilon_r a \phi_0^2}{2} \ln \left( 1 + \exp \left( -\kappa H \right) \right)
\]

where \( a \) is the radius of the particle;
and \( H \) is the interparticle separation along the line joining the particle centres.

For the case where \( \kappa a \ll 1 \) (small particles in non-aqueous solution or in aqueous solution with low electrolyte concentration) the following is applicable:
\[
V_R = \frac{4 \pi \varepsilon_0 \varepsilon_r a^2 \psi_o^2}{(H + 2a)} \beta \exp \left(-\kappa H\right) \tag{4.6}
\]

The factor \(\beta\) allows for the loss of spherical symmetry in the double layers as they overlap.\(^{15}\)

Both these equations are sufficiently accurate up to surface potentials of about 50 mV. For intermediate values of \(\kappa a\) and higher potentials the mathematics is complex but methods are available for determining \(V_R\). Hogg et al.\(^{90}\) derived an expression for the electrostatic interaction between two spherical particles based on Derjaguin's method

\[
V_R = \frac{4 \pi \varepsilon_0 \varepsilon_r a_1 a_2 (\psi_1^2 + \psi_2^2)}{4 (a_1 + a_2)} \left[ \frac{2 \psi_1 \psi_2}{(\psi_1^2 + \psi_2^2)} \right] \frac{P + N}{1 + \exp \left(-\kappa H\right)} \tag{4.7}
\]

in which

\[
P = \ln \left(\frac{1 + \exp \left(-\kappa H\right)}{1 - \exp \left(-\kappa H\right)}\right)
\]

and

\[
N = \ln \left(1 - \exp \left(-2 \kappa H\right)\right)
\]

where \(\varepsilon_0\) is the permittivity of a vacuum;
\(\varepsilon_r\) is the dielectric constant of the dispersion medium;
\(a_1, a_2\) are the radii of the interacting particles;
\(\psi_1, \psi_2\) are the surface potentials of the particles;
\(\kappa\) is the Debye-Hückel reciprocal length.

This expression is applicable for \(\kappa a > 5\) and surface potentials less than about 50 mV.

The range of \(V_R\) and its magnitude at any interparticle separation can be altered by varying the ionic composition of the dispersing medium. The dependency of \(V_R\) upon \(\kappa\), the inverse of the diffuse layer thickness, enables the influence of the indifferent electrolyte to be assessed. The larger the ionic concentration, the larger \(\kappa\) and hence the value of \(V_R\) falls off more rapidly with interparticle separation. The valency of the
counterion also influences the ionic strength, and the higher the valency, the faster the decay of $V_R$. For example, for a univalent, symmetrical electrolyte (such as an alkali metal halide) at 25°C the following is true -

<table>
<thead>
<tr>
<th>Electrolyte Concentration/mol dm⁻³</th>
<th>10⁻⁵</th>
<th>10⁻³</th>
<th>10⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interparticle separation at which $V_R$ becomes important/approx $\frac{4}{K}$</td>
<td>400 nm</td>
<td>40 nm</td>
<td>4 nm</td>
</tr>
</tbody>
</table>

The surface potential, $\psi_0$, is the other major controlling factor on which the electrostatic repulsion depends. Thus the bulk concentration of potential determining ions also has a significant effect upon the $V_R$ versus distance function. For oxides, and surfaces whose surface potential and surface charge is determined by the concentration of hydrogen ions, the pH of the solution has an important influence upon the repulsive force experienced by approaching particles.

As the double layers of two approaching particles overlap the surface charge density must decrease with decreasing separation at a constant surface potential. This result assumes that the change in surface charge takes place with a characteristic time faster than the time of the Brownian encounter so that thermodynamic equilibrium is maintained. The evaluation of the expression for $V_R$ under this condition gives the constant potential interaction, eg equation (4.7).

If, on the other hand, the redistribution of surface charge is slow, then the interaction is taken to occur at constant surface charge and the potential increases to infinity as the interparticle separation decreases. Frens derived an expression for the general situation of interacting spherical particles under conditions of constant surface charge\(^9\)

$$V_R^\sigma = V_R^\psi - \frac{4 \pi \varepsilon_0 \varepsilon_r a_1 a_2 (\psi_1^2 + \psi_2^2)}{2 (a_1 + a_2)} \left[ \ln (1 - \exp (-2 K H)) \right]$$ (4.8)
where $V_R^\sigma$ is the repulsive potential energy under conditions of constant surface charge;

$V_R^\psi$ is the repulsive potential energy under conditions of constant surface potential.

The evaluation of the repulsive interaction under conditions of constant charge leads to higher values than for constant potential.

Several workers have carried out more complex mathematical treatments to evaluate $V_R$ as a function of interparticle separation. Honig and Mul presented tables and limiting equations for interaction at constant charge and constant potential based on Derjaguin's method of analysis\textsuperscript{92}. Glendinning and Russel give an exact solution to the linearised Poisson-Boltzmann equation for the repulsive interaction between two spheres\textsuperscript{93}. The results of the treatment are applicable for $0.1 \leq \kappa a \leq 20$ over the full range of separation. The analysis indicated that, whereas use of the Derjaguin approximation ($1/k < a$) was satisfactory for interaction at constant potential, at small separations Derjaguin's approximation for interaction at constant charge was in error. Barouch et al\textsuperscript{94,95} also solved the Poisson-Boltzmann equation to evaluate $V_R$ for interaction at constant surface potential. It was shown that when the surface potentials of two interacting spheres were of the same sign but different magnitude the electrostatic repulsive energy decreased because a portion of the surfaces could be attractive despite the rest of the surfaces being repulsive. The results of the analysis were compared with those calculated using the model of Hogg et al, i.e equation 4.7. At large separations ($\kappa H > 10$) the repulsive energies were in good agreement, however for particles that differ in size and in the magnitude of the surface potentials the Hogg et al model gives larger energies, the discrepancy increasing as the separation decreases. But for dispersions containing only one type of particle, in which the radii of interacting particles can be taken to be equal, equation 4.7 is sufficiently accurate.

A model, introduced by Ninham and Parsegian\textsuperscript{96}, describes the intermediate situation in which both the surface potential and surface
charge density change during the approach of particles. This regulation theory is applicable to a surface possessing ionisable groups.

By assuming that the surface potential remains constant during double layer overlap it follows that the surface charge decreases as the interparticle separation decreases until $\sigma_0 = 0$ at $H = 0$. Similarly, by assuming constant surface charge interaction the surface potential increases on decreasing separation. However, with particles whose surfaces possess ionisable functional groups adjustment of their surface charges on approach of two particles is possible such that the total free energy of the system is minimised at each separation. In minimising the free energy both the surface charge and surface potential change ie regulate. The ability of the surfaces to react to a decrease in the separation is a function of the dissociation constants of the surface groups, the point of zero charge of the surface, and the ionic strength of the dispersion medium.

Healy et al have further developed the regulation approach.\textsuperscript{97}

The calculations of $V_R$ based on the regulation theory typically give values which lie between those given by assuming constant charge and constant potential interaction. The three approaches generally give agreement for separations greater than 10 nm.

Silver halide dispersions exhibit essentially perfect regulation and consequently interaction at constant surface potential is a reasonable assumption. However, interaction of inorganic oxide particles (eg rutile) is better described by assuming that regulation takes place. Because of the values of the dissociation constants of the functional groups on the rutile surface the interaction of two rutile particles more closely conforms to the constant potential case, although at small separations (less than about 5 nm) the interaction tends towards the constant charge type.

For cases in which there is specific adsorption of ions at the solid-liquid interface the equations for $V_R$ can still be used if $\phi_0$ is replaced by the outer Helmholtz plane potential and the distance term, $H$, is replaced by $(H - 2 \delta)$ in which $\delta$ is the Stern layer thickness.
However, the nature of the Stern layer does influence the interaction between particles. The properties of the diffuse layer are only affected by the valency and concentration of the electrolytes whereas the Stern layer is also influenced by the specific type of ion.

In situations where there is no specific adsorption of ions and the determination of the surface charge density (and hence $\phi_o$) is difficult then the measured zeta potential can be used in place of $\phi_o$ in the expressions for $V_R$.

The strength of the repulsive interaction is a function of the electrical double layer properties, so that changes in the potential determining ion concentration or bulk ionic strength have a pronounced effect on the form of the $V_R$ - separation relationship.

4.3 The Total Interaction Between Electrostatically Stabilised Particles (DLVO theory)

The total energy of interaction between the colloidal particles is found by the summation of the repulsion and attractive curves. The general character of the curve is shown in Fig. 4.1 where the potential energy of interaction is plotted against the interparticle separation. The properties of the two contributing curves determine the shape. The repulsive interaction, $V_R$, exhibits an exponential decay with a range of the order of the double layer thickness. It does remain finite for all interparticle separations. The attractive interaction, $V_A$, depends on some inverse power of the separation and so it predominates both at small distances and large distances. At intermediate values the repulsive force may predominate but the numerical values of the two opposing forces determine whether this is the case. At very small separations the Born repulsion force prevails. The particular form of the total energy distance curve depends upon the properties of both the particles and the dispersing medium but some general features can be described.

The potential energy barrier $V_{\text{max}}$ must be surmounted before the particles can make lasting contact in the primary minimum energy well. If $V_{\text{max}}$ is $\gg kT$ (the thermal energy of the particles) in an unsheared
FIG. 41 POTENTIAL ENERGIES BETWEEN PARTICLES SHOWING ENERGY BARRIER, PRIMARY MINIMUM, AND SECONDARY MINIMUM.
system, no lasting contacts between the particles will occur and the suspension is said to be stable.

Aggregation of particles in the primary minimum is usually termed coagulation.

If $V_A$ predominates over $V_R$ at all distances so that there is no maximum in the total potential curve, irreversible coagulation occurs; this usually happens in the presence of high electrolyte concentrations in which $V_R$ very rapidly falls with distance from the particle surface.

For a given solid dispersed in a given liquid the attractive interaction between the particles is effectively fixed. However, the repulsion force can be varied by altering the structure of the electrical double layers. Thus changes in the ionic strength (which is a function of ion concentration and valency) and surface potential will produce changes in the total interaction energy, $V_T$. Figure 4.2 shows how increasing the electrolyte concentration and hence increasing $\kappa$ affects both the height of the energy barrier and its location. Figure 4.3 shows how the interaction curves vary with the surface potential. It is thus possible to calculate an interaction curve for a system given the electrolyte composition, particle size, $A_m$, and a value for the double layer potential responsible for the repulsion eg the zeta potential.

There is a secondary minimum energy well, $V_{sec}$ at a greater distance of separation where particles can come together with a liquid layer between them. This happens when $|V_{sec}| > kT$. Since $V_R$ and $V_A$ are roughly proportional to particle radius, $a$, $V_{sec}$ becomes increasingly important as particle size increases, especially for plate-like particles. This effect also increases with increasing electrolyte concentration since due to the higher ionic concentration in the liquid, the neutralising effect of the co-ions in the electrical double layer can take place over a shorter distance. This reduces the distance over which $V_R$ operates. As $V_A$ is unaffected, this also reduces $V_{max}$ which assists in bringing the particles together. Systems in which aggregation in the secondary minimum occurs are said to be reversible ie they can be fairly readily redispersed by moderate shear forces. This type of reversible
**FIG. 4.2** INFLUENCE OF $K$ UPON THE TOTAL ENERGY OF INTERACTION BETWEEN TWO EQUAL SPHERES.

$a = 10^{-5}$ cm  \hspace{1em}  $A_m = 10^{-19}$ J  \hspace{1em}  $\varphi_0 = 26$ mV

**FIG. 4.3** INFLUENCE OF SURFACE POTENTIAL ON THE TOTAL ENERGY OF INTERACTION BETWEEN TWO EQUAL SPHERES

$a = 10^{-5}$ cm  \hspace{1em}  $A_m = 10^{-19}$ J  \hspace{1em}  $K = 10^6$ cm$^{-1}$

\[ V_T \]

\[ K \rightarrow 0 \]

\[ K = 10^5 \text{ cm}^{-1} \]

\[ K = 10^6 \text{ cm}^{-1} \]

\[ K = 3 \times 10^5 \text{ cm}^{-1} \]

\[ K = 10^7 \]

\[ \varphi_0 = 32 \text{ mV} \]

\[ \varphi_0 = 26 \text{ mV} \]

\[ \varphi_0 = 19 \text{ mV} \]

\[ \varphi_0 = 13 \text{ mV} \]
aggregation is thought to explain thixotropy, i.e., sol to gel transformation. On standing, some systems may change from secondary minimum to primary minimum aggregation. There may be several reasons for this, the first is that the particles have a distribution of surface properties and thus some will be more likely to pass over the appropriate energy barrier into the primary minimum. In addition, changes at the surface of the particles may occur due to chemical or physico-chemical reactions occurring during storage; these may change the nature of the surface charges. Aggregation occurring in the secondary minimum is usually termed flocculation in order to distinguish it from coagulation described earlier, since both the circumstances under which it occurs and the reagents used to encourage it to happen are rather different.

It should be realised that the configuration of curves shown in Fig. 4.1 gives a generalised picture of the situation existing and not all systems will display all the features shown. Frequently the energy maximum and minima will have different values.

The total interaction energy–distance curve can exhibit a time dependency in that the electrical double layer can age leading to changes in the $V_R$ term$^{98}$. If the overlapping double layers interact under constant surface charge conditions then ionic redistribution can occur within each double layer in order to reattain thermodynamic equilibrium i.e., interaction at constant surface potential. This aging process results in a deepening of the primary minimum and a reduction in the magnitude of $V_{max}$.

The foregoing, which is based on the DLVO theory developed by Deryaguin and Landau$^{99}$ and Verwey and Overbeek$^{15}$, satisfactorily explains the behaviour of what are termed charge stabilised systems.

In non-aqueous media, charge stabilisation is not important unless the solvent has the ability to solvate ions. The medium molecules must therefore possess a certain degree of polarity. Liquids such as ethanol and acetone would permit charge-charge interactions between dispersed particles. Because of the low dielectric constant of such liquids the concentration of dissolved ions will be small and hence a thick electrical double layer is formed around the particles. If the solids
content is such that the interparticle distance is less than the double layer thickness then the analysis of the stability becomes one of a multi-body interaction. In addition the low dielectric constant favours the formation of ion pairs which interact with the particle surfaces in a manner different from that of the constituent ions. The properties of the double layer are likely to differ from those in an aqueous medium.

For small additions of non-aqueous liquids to aqueous dispersions the behaviour with respect to stability is influenced by both changes in the point of zero charge of the particle and in the structure of the Stern layer.

The $V_R$ term dominates the total interaction energy-distance relationship for such non-aqueous systems. Therefore variations in the electrical double layer are important since changes in the surface potential or ionic composition of the bulk solution alter the magnitude of the $V_R$ term and hence the degree of repulsion between approaching particles.

4.4 Solvation Forces

Recent theoretical and experimental work have indicated that the continuum theories of particle interactions are not always applicable at small separations for aqueous systems. At interparticle separations of less than about 3 nm structural or hydration forces which can be attractive or repulsive, oscillatory or monotonic exist. These forces arise due to particle surface induced solvent structuring and liquid induced surface structuring. Consequently DLVO theory is only valid at surface separations down to about 3 nm in such systems. The energy barrier which determines the stability of colloidal dispersions generally occurs close to the particle separation at which these short range forces exist.

It is the view of Pashley\textsuperscript{100} that exponentially repulsive hydration forces between surfaces exist only if a hydrated ionic species in the dispersion medium is specifically adsorbed at the inner or outer Helmholtz plane. The strength of the hydration force can be roughly correlated with the hydration energy of the ion. Although the experimental measurements of these hydration forces have been made using mica surfaces the main conclusions of the studies can probably be applied to other surfaces, thus\textsuperscript{101}
negatively charged surfaces in water or dilute electrolyte solution mainly possess adsorbed hydroxyl and hydrogen ions. These ions do not give rise to hydration forces and therefore DLVO theory adequately describes the interaction between particles.

at intermediate electrolyte concentrations (for a 1:1 electrolyte values of about $10^{-3}$ mol dm$^{-3}$) the cations begin to compete for surface adsorption sites with the hydrogen ions. However, on close approach of two surfaces the cations, together with their solvation shells, are displaced by hydrogen cations. Deviations from DLVO theory occur at separations below 3 nm, in particular the kinetic energy barrier to coagulation in the primary minimum becomes weaker and the primary minimum moves out slightly and also becomes less deep.

at high electrolyte concentrations, specific for each cation (for KNO$_3$ approx $10^{-3}$ mol dm$^{-3}$), the adsorbed cations remain bound as the two surfaces approach. A strong repulsive force at small separations is present due to the presence of the partially solvated cations. At sufficiently high electrolyte concentrations this solvation force is the only repulsive force between the surfaces, and together with the van der Waals attractive force gives rise to an energy minimum analogous to the secondary minimum of conventional DLVO theory.

decreasing the pH replaces bound electrolyte cations by hydrogen cations with a consequent disappearance of the solvation forces.

If a bulk electrolyte solution contains solvated ions which can specifically adsorb at a colloidal particle surface then coagulation into a deep primary minimum can be prevented, although coagulation into a secondary minimum at slightly greater separations would still be possible. The magnitude of the solvation force depends upon the nature of the cation, i.e. is it a structure-making or structure-breaking species, and the nature of the particle surface. The stronger the solvation energy of the cation the greater the solvation repulsive force but the higher the electrolyte concentration at which the force is first detected. For potassium ions the force, although weaker than for lithium, sodium and
divalent cations, becomes apparent at a bulk electrolyte concentration of about $10^{-4}$ mol dm$^{-3}$.

Although the direct measurements of the solvation force have involved mica surfaces for which cation exchange is important for the formation of a surface charge, the main conclusions of the studies are probably applicable to inorganic oxides, such as rutile, for which specific adsorption of cations also influences the surface charge.

4.5 Solvent Structuring at Interfaces

The existence of solvent structuring near surfaces and the effect on particle interactions has been of great interest. Recent theoretical treatments of the role of solvent structuring have predicted that strong repulsive and attractive forces at small surface separations can exist as the result of pronounced solvent layering over several molecular diameters from the surface$^{102}$. The oscillatory force follows the form of the solvent density profile. The van der Waals force at such separations (approx 4 solvent molecular diameters) is consequently modified.

Numerous studies have been carried out to measure the extent of the ordering of water molecules from a variety of surfaces. Some workers have reported the existence of long range ordering of water but it would appear that the ordering of water molecules is restricted to distances of less than about 5 nm from a surface. However, the associated repulsive force as two such surfaces approach is significant, is exponential in form, and possesses a decay length of the order of the diameter of a water molecule. This solvent structure repulsive force can be removed if another species can adsorb more strongly than the solvent at the surface. The reader is referred to the literature for further details of water structuring near surfaces$^{103-108}$.

4.6 Kinetics of Particle Aggregation

As stated earlier most colloidal dispersions are thermodynamically unstable and therefore tend to reduce their interfacial surface area to a minimum. However, the presence of an electrical barrier to coagulation
or a steric barrier to flocculation will slow down the aggregation process.

The formation of a colloidal dispersion, either by the fragmentation of larger particles or by the precipitation of dissolved material, gives rise to a system of particles each located within the potential energy fields of all the others. The nature of the interaction energy - separation curve for two interacting particles both possessing an electrical double layer has already been described. As a result of the thermal motion the particles approach each other thereby experiencing greater mutual attraction or repulsion. The Brownian motion induced collisions may thus lead to coagulation if the kinetic energy is sufficiently large to surmount the potential energy maximum. Depending upon the depth of the potential energy minimum, into which particles have aggregated, further collisions involving the flocs or coagula can lead to break-up and redispersion of the primary particles. The relative rates at which the particles enter and leave the energy minima govern the coagula or floc size distribution and therefore the flow properties of the dispersion. The kinetics of the coagulation process can be treated as a two-body rate reaction and that of flocculation as a dynamic equilibrium reaction.

4.6.1 Basic Aggregation Kinetics

It was von Smoluchowski who laid the foundation for the theory of the irreversible coagulation of particles\textsuperscript{109}. If there is a negligible repulsive interaction then particles approaching as the result of diffusion experience the strong van der Waals attractive force which draws them together within the deep primary minimum. This so-called rapid coagulation can be achieved in a dispersion of charged particles by adding sufficient electrolyte to make $V_R$ negligible. The aggregation rate therefore depends upon the frequency of the collisions. The rate can be expressed as:

$$-dn_1/dt = k_0 n_1^2$$

(4.9)

where $n_1$ is the number of primary particles per unit volume; and
$k_0$ is the second order rate constant (for aqueous systems at 25°C the value of $k_0$ is $6.16 \times 10^{-18}$ m$^3$ s$^{-1}$). A simple expression giving the rate constant for diffusion controlled coagulation can be quoted as

$$k_0 = 4k_BT/3\eta$$

(4.10)

where $k_B$ is the Boltzmann constant and $\eta$ is the liquid viscosity, at the temperature $T$.

Smoluchowski assumed that the attractive interaction could be represented by a deep potential well with a vertical wall, whereas the van der Waals interaction is in fact long range. The enhanced collision frequency, however, only increases the value of $k_0$ by a few percent. There are, however, other corrections which are significant including the influence of the hydrodynamic interaction as particles approach (on close approach work has to be done to displace the intervening liquid with resultant lowering of the diffusion coefficient of a particle), and the influence of polydispersibility and anisotropy of the particles\textsuperscript{110,111}.

To allow for the possibility of collisions between primary particles and coagula the treatment can be extended to give the following expression for the total number of particles (primary plus coagula)

$$\sum_{k=1}^{\infty} n_k = \frac{n_0}{1+(t/T_{1/2})}\quad(4.11)$$

in which $n_0$ is the initial number of particles; $n_k$ is the number of coagula consisting of $k$ primary particles;

and $T_{1/2}$ is the time of coagulation. The factor $T_{1/2}$ gives the time required in order to reduce the total number of particles and coagula to halve the initial number

$$T_{1/2} = 1/(4\pi DRn_0)$$

(4.12)

where $D$ is the diffusion coefficient of primary particles;

and $R$ is the distance between the centres of the particles when coagulated in the primary minimum.
A general expression can be written which gives the number of coagula comprising \( k \) primary particles, \( n_k \), as a function of time

\[
\frac{n_0 (t/T)^{k-1}}{(1+(t/T)^k)^{k+1}}
\]

Figure 4.4 shows how the various particle sizes change in number during the course of rapid coagulation.

In the presence of a potential energy barrier the rate of coagulation is decreased because only a fraction of the interparticle collisions lead to permanent particle contact. Smoluchowski introduced a parameter \( \alpha \) into equations (4.11) and (4.12) to allow for the fraction of collisions successful in giving coagulation. However, this approach is limited in that there is no theory linking \( \alpha \) to the parameters influencing the magnitude of the energy barrier.

The treatment due to Fuchs\(^{112}\), originally developed for the coagulation of smokes, is commonly used to describe the rate of slow coagulation, although it only applies to the initial stages of coagulation where primary particle collisions with other primary particles are the norm. The rate equation for the process can be written as

\[
\frac{-dn_1}{dt} = kn_1^2
\]  

(4.14)

for the primary particles. Similarly, the rate of disappearance of all particles, can be written:

\[
\frac{-d(\Sigma n_k)}{dt} = k'(\Sigma n_k)^2
\]  

(4.15)

An integral form of the equations enables experimental determination of the rate constant to be made. A plot of reciprocal particle number against time should be linear with slope \( k \) (or \( k' \)). It is usual to take the initial slope of the plot since the slope decreases with time of coagulation due to the changes in the height of the potential energy barrier associated with a particle size increase.
FIG. 4.4 VARIATION OF THE PARTICLE NUMBER $n_k$ AS A FUNCTION OF TIME DURING RAPID COAGULATION.
A factor, $W$, is commonly used to describe the colloidal stability of a dispersion. In the presence of the energy barrier only a fraction, $1/W$, of the interparticle encounters lead to permanent contact. This stability ratio, $W$, is equal to the ratio of the rate constants for slow and rapid coagulation:

$$W = \frac{k_0}{k} \quad (4.16)$$

Fuchs\textsuperscript{112} derived a theoretical relationship between the stability ratio and the total potential energy of interaction, $V_T$, between particles. McGown and Parfitt modified the final expression to take account of the long range attractive interaction, $V_A$, and thus\textsuperscript{113}

$$W = \frac{\int_0^{\infty} \exp \left( \frac{V_T}{k_B T} \right) \frac{dS}{S^2}}{\int_0^{\infty} \exp \left( \frac{V_A}{k_B T} \right) \frac{dS}{S^2}} \quad (4.17)$$

where

$$S = \frac{2 (a_1 + a_2 + H)}{(a_1 + a_2)}$$

The graphical, or numerical integration, of this function for given values of the parameters comprising $V_T$ enables comparison between the theoretical and experimental values of $W$ to be made. An approximate form of equation (4.17) can be used

$$W = \left( \frac{1}{2 \kappa a} \right) \exp \left( \frac{V_{\text{MAX}}}{k_B T} \right) \quad (4.18)$$

where $\kappa$ is the reciprocal double layer thickness; $V_{\text{MAX}}$ is the potential energy maximum.
The use of the stability ratio enables a link to be made between the energetics of interparticle interaction and the rate of aggregation.

4.6.2 The Effect of a Distribution of Particle Sizes and Surface Potentials on the Stability

The coagulation of an initially polydisperse suspension (range of particle sizes) proceeds at a different rate, partly because the smaller particles appear to decrease in number more quickly than the larger particles. This so-called Weigner effect can be qualitatively explained since the disappearance of the small particles is more noticeable than that of the larger particles. It can also be shown that the probability of collision between particles of different size is greater than that between equal sized particles.\(^{110}\) The rate of coagulation is therefore faster for the more polydispersed system.

Cooper\(^{114}\) calculated the stability ratio for dispersions possessing a distribution (in fact a Gaussian type) of particle sizes or surface potentials. It was shown that such dispersions were less stable than the corresponding monodisperse system. The difference in stability increased as the deviation about the mean surface potential, or particle size, increased. Prieve and Lin\(^{115}\) carried out a more detailed analysis and not only confirmed Cooper's results but discovered that a distribution in either the surface charge or potential substantially reduces the sensitivity of the stability ratio to changes in the ionic strength, and that for a given standard deviation about the mean a variation in the Stern potential had a more profound effect on stability than the same variation in particle size. A standard deviation in the Stern potential of 10% of the mean was shown to reduce the value of \(W\) by orders of magnitude, at low ionic strengths.

Lee has shown theoretically that the initial particle size distribution has a pronounced effect upon the coagulation rate.\(^{116}\) The greater the geometric standard deviation based on the particle radius (assuming a lognormal size distribution) the faster the rate as is shown by equation (4.19)
\[
\frac{2k_B T_0 \tau}{(n/n_0) = (1 + \frac{1}{3n_0} (1 + \exp (\ln \sigma_0)^2))}
\]

where \( \sigma_0 \) is the initial geometric standard deviation; and \( \eta_0 \) is the liquid viscosity.

As the result of coagulation, the particle size distribution is constantly changing and tends towards an equilibrium value. Lee has found that the same state is reached irrespective of the initial size distribution. The asymptotic value of the standard deviation, \( \sigma_\infty \), was found to be 1.32. However, the time required to reach this limiting value increases with the value of \( \sigma_0 \), the initial geometric standard deviation, and

\[
t_\infty = \frac{+10 (\exp (9n^2 \sigma_0) - 2) - 1}{2k_B T_0 (1 + \exp (\ln \sigma_0))}
\]

where the sign convention refers to the cases \( \sigma_0 < \sigma_\infty \) and \( \sigma_0 > \sigma_\infty \), respectively.

For highly anisotropic particles the coagulation rates are likely to be larger than for the corresponding case of spheres due to the increased collision diameter and diffusion constant.

Thus far only irreversible aggregation into the primary minimum has been considered, which if allowed to progress to the ultimate would coalesce all particles into one large coagulum. However, if the potential minimum is not too deep then there exists the possibility of coagula break-up, which occurs in opposition to the aggregation process. A dynamic situation of reversible aggregation can then be considered to exist. Such reversible coalescence between particles possessing electrical double layers is, however, more likely to be associated with interaction at the separation corresponding to the secondary potential energy minimum.
4.6.3 Kinetics of Reversible Aggregation in Charge Stabilised Systems

For dispersions of fairly large particles (typically >1 µm diameter) a shallow secondary minimum exists at an interparticle separation of 10-30 nm. Provided that a sufficiently high energy barrier exists at shorter separations, then such weak attraction is expected to give reversible aggregation. Various workers have studied this effect\textsuperscript{117-119}. The process is considered to be a dynamic equilibrium between primary particles and aggregates of various sizes.\textsuperscript{117,118} The net rate of disappearance of primary particles can be written in terms of the rate equations for the various aggregate formation and break up stages\textsuperscript{117}. In the absence of shearing forces particles approach each other as the result of Brownian motion and may aggregate if a third body (e.g., solvent molecule or another aggregate) is present to remove the excess energy present during collision. Thus the reversible dimerisation process can be written:

\[ M + M + S \rightarrow D + S' \]

or

\[ M + M + P \rightarrow D + P' \]

where \( M \) represents a primary particle, and \( S \) and \( S' \) represent the solvent molecules in their normal and excited states, respectively; \( P \) and \( P' \) similarly represent the states of an aggregate, and \( D \) represents the doublet.

The doublets dissociate when they have gained sufficient energy from Brownian collision with solvent molecules or other particles to break the weak linking bond. The value of the equilibrium constant for the aggregation is found to increase as the initial particle concentration is increased because the formation of aggregates possessing more than one interparticle link per primary particle is more likely at higher solids content. The relationship between the equilibrium constant and \( V_T \) for linear aggregate formation as a result of Brownian induced encounters can be given as

\[
K = 2 \pi \int_R^\infty r^2 \left( \exp(-V_T/k_BT) - 1 \right) \, dr \quad (4.21)
\]
where \( r \) is the distance between particle centres and \( R \) is the distance of closest approach.

Hogg and Yang\textsuperscript{120} considered reversible aggregation into a secondary minimum and derived a simple expression for the associated stability ratio, \( W_s \),

\[
W_s = \left[1 - \exp \left( \frac{V_{\text{MIN}}}{kT} \right) \right]^{-1} \tag{4.22}
\]

where \( V_{\text{MIN}} \) is the depth of the secondary minimum.

Calculations indicated that the kinetics of secondary minimum aggregation were less sensitive to the ionic strength than were those for primary minimum aggregation. For a secondary minimum depth of 10 kT the value of \( W_s \) is unity.

Mamur\textsuperscript{121} developed a model which allowed the calculation of a stability ratio for combined primary and secondary minimum aggregation. The model predicts that the overall stability ratio is sensitive to the existence of a secondary minimum eg for a depth of -0.75 kT the overall stability ratio does not exceed a value of 25 despite the height of the energy barrier to primary aggregation being as large as 20 kT. A secondary minimum depth of -3 kT is predicted to limit \( W \) to values of less than 2.

Prieve and Ruckenstein\textsuperscript{122} presented an analysis which indicated that aggregation in the secondary minimum is initially rapid but that after a relaxation time, which increases with the depth of the secondary minimum, the total rate of aggregation in the primary and secondary minima slows to the steady state value predicted by Fuch's theory.

A recent approach by Bentz and Nir takes account of the distribution of aggregate sizes and allows for aggregate breakup\textsuperscript{123}. The model emphasises the dynamic nature of the aggregation process and the distinction between the rate of aggregation and the extent of aggregation.

Reversible aggregation into the primary minimum can occur if there exists an effective "stand-off" distance at ca 1 nm separation. This
repulsive barrier, possibly associated with a structured solvent layer, gives rise to a shallow primary minimum and a reduced energy barrier, which are conditions leading to reversible aggregation. Polystyrene latex particles dispersed in aqueous electrolyte solution have been shown to exhibit reversible aggregation into a shallow primary minimum\textsuperscript{117}. However, ageing of the electrical double layers produces changes in the repulsive interaction with a consequent deepening of the primary minimum and lowering of the primary barrier, $V_{\text{MAX}}$. The aggregation therefore becomes irreversible.

The repeptisation of coagulated particles can be achieved by dilution of the electrolyte solution or by the addition of sufficient potential determining ions to increase the surface potential. A low Hamaker constant and high Stern layer potential are favourable to redispersion. In addition, the presence of a finite distance of closest approach between particles as the result of the presence of a structured solvent layer reduces both the depth of the primary minimum and the height of the energy barrier thereby enhancing the repeptisation. Realistic values of $A_m$ and $\phi_0$ when used in conjunction with structured layers of ca 0.5 nm thickness show that theory can predict repeptisation.

The total potential energy of interaction – distance curve corresponding to the coagulating conditions is replaced by the curve corresponding to the repeptisation conditions, but redispersion will only take place if the latter energy profile is such that little activation energy is required to surmount the energy maximum, $V_{\text{MAX}}$, and if the process does not require a net increase in the potential energy of the system. The choice of conditions pertaining to both the coagulating and repeptising processes is therefore important\textsuperscript{125}. As mentioned previously, the electrical double layers age and so the ease of repeptisation is time dependent.

Because of the finite time required for ion adsorption and desorption to take place rate effects become significant. Consequently both particle aggregation and repeptisation should be viewed as dynamic phenomena\textsuperscript{124}.

83
The size, shape, density, strength, and internal properties of the aggregates influence the bulk behaviour of a colloidal dispersion, including the flow behaviour. The size and shape of the flow units affect the rheological properties of a dispersion in the manners described in Chapter 6. The strength of the aggregates is dependent upon the depth of the appropriate potential energy minimum, which is itself a function of the various attractive and repulsive interactions between the particles. Under conditions where reversible aggregation can occur it is the strength of the aggregates relative to the energy of collisions that is important in determining the flow unit size distribution.

The internal properties of flocs have been studied by Cornell et al. Direct microscopic examination of aqueous polystyrene latex dispersions which had aggregated into a shallow secondary potential energy minimum highlighted the following:

(i) the primary particles within the flocs were able to migrate to different positions within the floc;

(ii) particle doublets within flocs were observed to rotate independently of the other particles;

(iii) particle doublets within flocs were observed to break-up with the two primary particles moving to new positions within the floc; and

(iv) the floc shape was able to change from linear chains to clusters as a result of bending motion.

The reversible flocculation therefore gave rise to aggregates within which the primary particles were mobile.

The role of the floc density in influencing the bulk rheological behaviour has been considered by Firth and Hunter. The floc density or degree of branching within a floc can be described by a factor $C_{FP}$, which is the ratio of the volume fraction of flocs, $C_f$, to the volume fraction of suspended particles, $c$. Thus the more open the floc structure the larger the $C_{FP}$ value. The various floc structures
considered can be thought of as consisting of cubical unit cells the
sides of which contain the line of centres of the primary particles. For
each unit cell the ratio of the number of particles, \( N_p \), to the number
of interparticle bonds, \( N_B \), can be calculated. This ratio can be
related to \( C_{FP} \) by the empirical relationship

\[
\frac{N_p}{N_B} = \frac{(C_{FP} - 1)}{(C_{FP} + 0.7)}
\]

(4.23)

The number of particles per floc can be given by:

\[
N_p = \frac{a^3}{C_{FP} r^3}
\]

(4.24)

where \( a \) is the floc radius, and \( r \) is the primary particle radius.

Combining the two equations gives an expression for the number of
bonds per floc;

\[
N_B = \frac{(a/r)^3(C_{FP} + 0.7)/(C_{FP}(C_{FP} - 1))}{(C_{FP} + 0.7)/(C_{FP}(C_{FP} - 1))}
\]

(4.25)

The value of \( C_{FP} \) can be evaluated directly from experiment and the
elastic floc model of Hunter et al allows one to predict how its value
depends upon such parameters as the particle concentration and radius,
the interaction energy between the particles, and the maximum shear rate
to which the dispersion has been subjected. Equation (4.26) gives the
derived relationship:

\[
C_{FP} = 1.5 + \frac{V_T}{(5B\eta_0 Y_C)}
\]

(4.26)

where \( V_T \) is the total potential energy of interaction as given by the
equations described earlier;
\( B \) is a factor related to the packing structure of the system;
\( \eta_0 \) is the liquid viscosity; and
\( Y_C \) is the maximum shear rate to which the dispersion has been
subjected.
The Bingham yield stress associated with pseudoplastic flow behaviour can be related to the value of \( C_{PP} \) and hence to the total interaction energy between the particles.

Although the effect of particle shape on the viscosity of a dispersion has been extensively studied the factors influencing the shape of the aggregates, resulting from the coagulation/flocculation of primary particles have been little studied. For systems of particles possessing electrical double layers analysis of the electrostatic force field around a linear aggregate shows that the repulsion is weaker at the ends\(^{127}\). This idea has been used recently in a theoretical approach to aggregate structure.

Sonntag et al have proposed a model for the formation of linear aggregates of spherical particles under slow coagulation conditions\(^{129}\).

The probabilities of particle collision with the end of a chain and with the chain sides were calculated and compared. From these values the onset of branching was estimated.

Experiments have shown that chain-like aggregate structures tend to be formed under conditions of slow aggregation which has been predicted by the theory of Thomas and McCorkle\(^{127}\).

Thus, although an aggregate possessing many inter-particle contacts is thermodynamically favoured, the kinetics of the aggregation process favours the more extended chain-like structures.

The model of Sonntag et al assumes that only linear aggregates are formed. As the aggregate grows the probability of a particle approaching the chain side increases because of the larger collision area, whereas the probability of collision at the chain ends remains constant.

There is therefore a critical chain length, \( L_c \), at which the probabilities become equal. At this time the aggregate structures begin to branch. The value \( L_c \) is a function of the particle size, the diffuse layer potential, electrolyte concentration, and Hamaker constant. It increases with an increase in the repulsive interaction between the
particles, increases with an increase in particle size, and decreases with a rise in the Hamaker constant. However, the predictions of the model are dependent upon the approximation used to evaluate the interaction potential between an approaching particle and the side of the chain, ie use of constant surface potential or constant surface charge.

The model can be extended to the situation of reversible aggregation, in which the depth of the primary minimum, in the total interaction energy-distance curve, is sufficiently small to permit aggregate breakup by the thermally induced interparticle collisions. It is assumed that the probability of aggregate breakup into two small units is independent of the size of the aggregate, and it is also assumed that the same is true for the growth of the aggregate. The simultaneous growth and destruction leads to a dynamic state of equilibrium between formation and breakup, which will occur at a definite total aggregate concentration. Linear growth of the aggregate chains can no longer occur but further aggregation is possible via branching. The stationary total aggregate concentration is found to be a function of the ratio between the aggregate formation and aggregate breakup coefficients. The latter are functions of the depth of the potential energy minimum.

This model is only applicable to dispersions undergoing slow aggregation (ie large W values), in which anisotropic or oriented aggregation will be favoured. The influence of the rotation of the aggregate is ignored whereas it would be expected that the primary particle-aggregate collision probabilities would be a function of the rotational energies. Neglect of this contribution can only be justified in cases where the time for collision is smaller than the time for rotation.

As stated earlier the strength of an aggregate depends upon the number and strength of the interparticle bonds. For particles interacting via electrical double layers it is the depth of the potential energy minimum into which the particles have aggregated which governs the binding strength between particles.

In the presence of a shear field a critical size of aggregate exists, above which the hydrodynamic forces rupture and break-up the
aggregate. The rupture occurs when the applied shear stress exceeds the yield stress associated with the weakest interparticle link.

4.8 Summary

The subsequent behaviour of a freshly made colloidal dispersion is governed by the total potential energy - distance curve for the interaction between the particles. The rate at which particles collide is a function of the strength of the long range attraction forces, the thermal energy of the particles, the effective collision volume of the particles, and the applied velocity gradients. The rate of particle aggregation depends on, in addition to the rate of collision, the height of the energy barrier in the VT curve, if present, and the depth of the potential minimum into which the particles aggregate.
CHAPTER 5

DISPERSION OF POWDERS IN LIQUIDS
5. DISPERSION OF POWDERS IN LIQUIDS

Many of the powders used in practice as pigments or fillers contain particles of colloidal dimension and hence have large surface areas. Thus the process of dispersing a dry powder in a liquid to a large extent depends upon the interaction between the particle surface and the liquid.

In the dry state the powder normally consists of aggregates of the primary particles and clusters of aggregates and/or primary particles known as agglomerates. Aggregates consist of particles joined at crystal faces and thus possess a surface area significantly less than the sum of the individual components. On the other hand agglomerates have a more open structure with small areas of contact between the components. The state of the powder is a function of many factors and so a knowledge of the manufacturing and storage conditions is desirable if the phenomenon of interparticle bond breakage is to be fully understood.

The intimate incorporation of a powder, such as rutile pigment, into a liquid is normally considered to consist of three main stages:

* wetting of the particle surface;

* milling and mixing to break up the clusters of particles and disperse them throughout the liquid;

* reduction in particle number as the result of both ortho- and peri-kinetic coagulation.

In practice these stages overlap, although it is often the case that one is found to dominate. The term "dispersibility" is used to describe the efficiency of the first two stages and is defined as the ease with which the primary particles in a powder are distributed within a continuous liquid medium such that each particle is completely wetted by the liquid and no longer makes permanent contact with other particles. It is in fact rare for all particles in a dispersion to exist as primary particles but it is not easy to ascertain whether the particle clusters arise from poor dispersibility or from the coagulation of well dispersed particles.
The dispersion of a dry powder in a liquid medium requires the input of energy. In practice the latter comes from two sources:

* the chemical nature of the components;
* the mechanical energy of milling/mixing.

The former chemical energy can be optimised through the use of surfactants and surface treatment of the powder. The mechanical energy, on the other hand, is a function of both the properties (particularly viscosity) of the millbase and the geometry/type of the mill.

Before discussing the three stages of the dispersion process in more detail the nature of the interparticle forces present in the powder that must be overcome to achieve dispersion will be described.

5.1 Powder agglomeration

The forces holding particles together as a powder may be of several types:

a) van der Waals forces;

b) surface tension forces;

c) mechanical forces due to interlocking of irregular shaped particles;

d) forces arising from the plastic welding caused by the coalescence of particles under high compressive loads;

e) electrostatic forces; and

f) solid bridge forces as the result of crystallisation at contact points.

All of these forces are sensitive to changes in the environment and the history of the powder, hence the relative importance of each in a given system will be a complex function of a variety of factors which may
be difficult to define. Such a wide variety of mechanisms by which particles are held together as a powder makes it difficult to quantify the process of dispersion. However, the deagglomeration during the early stages of the dispersion process can be approximated by considering the relative magnitudes of the van der Waals forces and that of gravity\textsuperscript{130}.

A measure of the cohesiveness of a powder can be made by determining the tensile strength. This involves determining the force required to fracture a sample of the powder\textsuperscript{131}. Experience has shown that powders of high tensile strength are those which tend to be more difficult to disperse, particularly in a poorly wetting liquid. A high tensile strength and consequently a significant cohesiveness tends to make the deagglomeration of a pigment less easy. Type I rutile (as used in this study) possesses a higher tensile strength than other rutile pigments\textsuperscript{130}.

Numerous workers have attempted to model the flow behaviour of powders in terms of the interparticle forces and tensile strength. Such approaches may be of use in quantifying the dispersion process\textsuperscript{132}. It is to be hoped that workers will combine the models which already exist to describe the flow of fine powders in hoppers and pipelines with those describing the efficiency of mixing/grinding in mills so that a better understanding of the overall dispersion process can be reached.

As a result of the numerous forces a powder consists of a collection of particles which possess varying degrees of complexity. The latter will itself depend upon the method of production of the powder e.g. dry grinding a solid will give rise to fractured particles of irregular shape whereas production by precipitation produces several distinct types of particle. Pigments such as rutile formed from the Sulphate Process will typically contain the following types of particle:

a) primary particles

The primary particles form as the result of the mutual growth and fusion of several crystals. These particles are generally plate- or needle-like in shape. It is believed that a significant amount of immobilised liquid medium can be trapped at the particle surface. The existence of both adsorbed layers and entrapped liquid in surface
irregularities account for this immobile liquid. Experiments have shown that 0.1 μm particles can possess adsorbed layers 0.01 μm thick.

b) agglomerates

These are clusters of primary particles in which interparticle contact is restricted to the edges or corners of the primary particles. The structure is therefore rather loose and open i.e. the voidage is large.

c) aggregates

These are clusters of primary particles in which the interparticle contact occurs at the crystal faces. These clusters possess a tighter, stronger structure than the agglomerates. Some aggregates are not broken down by the dispersion process and are therefore believed to account for the primary flow units responsible for the rheological properties. A significant volume of dispersion medium can be immobilised within the void spaces of the aggregates. The type and strength of the bonds between the primary particles varies with the production method. Powders produced by precipitation followed by filtration and drying can give individual primary particles held together by residual traces of soluble salts - such aggregates are known as cemented aggregates. Calcination of the powder forms sintered aggregates which possess stronger chemical bonds between the individual primary particles.

d) flocculates

These consist of loosely bound clusters of particles i.e. aggregates, agglomerates, and primary particles. They tend to possess a rather weak structure, although the surface chemistry of the system governs the bonding strength. The flocculates are rather sensitive to shear rate and therefore represent a significant contribution to the flow properties of the system.

Titanium dioxide powder is normally comprised of 3 volumes of air to each volume of pigment. Only small numbers of aggregates exist so that the pigment largely contains primary particles bound together as agglomerates and flocculates. The dispersion of rutile therefore involves replacing the relatively large volume of air with liquid and breaking down the clusters of primary particles.
5.2 Wetting the particle surfaces

Wetting refers to the displacement of gas or other contaminants which are adsorbed at the particle surfaces with simultaneous adsorption of the dispersion medium at the surfaces. It is necessary for the liquid to not only wet the external surfaces but also it must displace the gas from the internal surfaces within particle clusters.

Beginning with the pigment being added to the surface of the dispersion medium. Penetration of the medium into the pigment mass causes detachment of the smaller particle clusters as they are engulfed by the advancing interface. The larger agglomerates will also tend to be engulfed but will not detach from the bulk pigment until the bulk density of the agglomerate exceeds that of the medium. Penetration of the latter into the void spaces of the agglomerate, albeit relatively slowly, increases the bulk density towards that of the medium. The following phenomena can now happen to the isolated agglomerate:

* continued penetration of medium with expulsion of air as bubbles and detachment of the outermost particles;

* continued penetration of medium leading to the build up of internal gas pressure with consequent disruption of the agglomerate and separation into smaller clusters.

Further penetration of the medium can result in deagglomeration of the fragments. The situation prior to mixing or milling would be that the pigment is submerged in the medium, most of the air having been displaced, and the particles largely wetted by the liquid. The extent of wetting is not only dependent upon the surface chemistry of the system but it is also a function of the dimensions of the interstices in the particle clusters, the nature of the mechanical process used to bring together the components of the system, and the strengths of the clusters (the innermost interstices of the more strongly bound clusters containing air-pigment interfaces).

The replacement of the solid-gas interface with the solid-liquid interface can be conveniently split into three distinct phases. The
...energetics of each can be described in terms of the Young-Dupre equation, and the work involved related to both the liquid surface tension and contact angle. The three phases are designated as adhesional wetting, spreading wetting, and immersional wetting. For the case of a cube of unit dimension one can derive the following expressions for the phases:

a) adhesional wetting (W_a)

As 1 cm² of the solid surface(s) is brought into contact with an equal area of the liquid surface (L) a unit surface area of each disappears to form a unit area of the solid-liquid interface. The work involved can be given as

\[ W_a = \gamma_{SL} - (\gamma_{SV} + \gamma_{LV}) \]  

(5.1)

in which the terms refer to the interfacial tensions at the solid-liquid, solid-vapour, and liquid-vapour interfaces respectively; the vapour being that due to the individual phases.

b) spreading wetting (W_s)

As liquid spreads over a unit area of solid surface equivalent areas of liquid surface and solid-liquid interface are formed. The decrease in free energy (or work) involved for a unit area of surface can be written as

\[ W_s = \gamma_{SL} + \gamma_{LV} - \gamma_{SV} \]  

(5.2)

c) immersional wetting (W_i)

The complete immersion of a unit area of solid surface in a liquid involves the exchange of a solid-vapour interface for the solid-liquid interface with no change in the liquid-vapour interface. The work can be given as

\[ W_i = \gamma_{SL} - \gamma_{SV} \]  

(5.3)

The three types of wetting differ in that there is a decrease in the area of the liquid-vapour interface in the first, an increase in the interface in the second, and no change in the third.
Although values for $\gamma_{SV}$ and $\gamma_{SL}$ are not readily measurable the Dupre equation, which applies for systems at equilibrium, can be used to relate these two interfacial tensions from a knowledge of $\gamma_{LV}$ and the contact angle ($\theta$) between the three phases

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$  \hspace{1cm} (5.4)

(It should be noted that the term on the left hand side of this equation refers to the solid-solid vapour interfacial tension under equilibrium conditions. For a solid surface in contact with another vapour e.g. water the wetting process must take account of an additional energy term, which can be relatively large\[135].)

Therefore for the case of a solid cube of unit dimension the energy changes can be written as

$$W_a = - \gamma_{LV} (1 + \cos \theta)$$  \hspace{1cm} (5.5)

$$W_s = - \gamma_{LV} (\cos \theta - 1)$$  \hspace{1cm} (5.6)

$$W_i = - 4 \gamma_{LV} \cos \theta$$  \hspace{1cm} (5.7)

These relations indicate under what conditions, if any a particular stage in the wetting process is spontaneous, i.e. $W < 0$. If $W$ is positive then work must be expended on the system for the process to take place. Thus

i) adhesional wetting is spontaneous when $\theta < 180^\circ$, and hence is invariably spontaneous.

ii) spreading wetting is spontaneous only when $\theta = 0^\circ$, and consequently work must be done to achieve spreading at all other values.

iii) immersional wetting is spontaneous when $\theta < 90^\circ$.

The total work for the overall wetting process, $W_{TOT}$, is given by the sum of those for the separate stages

$$W_{TOT} = W_a + W_s + W_i = - 6 \gamma_{LV} \cos \theta$$  \hspace{1cm} (5.8)
The requirement that $\theta = 0^\circ$ for spontaneous spreading wetting explains why certain powders require an energy input in order to achieve complete submergence within the liquid medium. The addition of surface active agents ensure that $\theta$ is reduced to a value close to zero so that less energy need be expended in achieving complete wetting. Rearrangement of equation (5.4) shows that if $\theta < 90^\circ$ then a decrease in $\gamma_{LV}$ and/or $\gamma_{SL}$ obtained by the addition of a surfactant, will lower $\theta$ and thereby improve the wetting.

Experimental measurements of contact angles tend to be limited to flat surfaces since for powders such measurements are very difficult due to factors such as surface roughness, hysteresis, variable pore sizes, and impurities.

Once the cluster external surfaces have been wetted the liquid needs to penetrate the interstices. This phenomenon is less easy to define. For the simple case of a cylindrical tube of uniform cross-section (radius $R$) a pressure, $P$, must be exceeded in order to force liquid into the pore

$$P = -2 \gamma_{LV} \cos \theta/R$$

(5.9)

Clearly penetration is only spontaneous when $\theta < 90^\circ$. If $\theta$ is not zero then combination of equations (5.4) and (5.9) shows that the factor $\gamma_{SL}$ needs to be made as small as is possible in order to improve the extent of penetration. However, if the contact angle is zero then

$$P = -2 \frac{\gamma_{LV}}{R}$$

(5.10)

so that in this case the value of $\gamma_{LV}$ should be large.

Changes in $\gamma_{LV}$ are accompanied by changes in $\theta$ so that, assuming the only variable interfacial tension to be $\gamma_{LV}$, the value of $P$ will reach a constant value determined by the value of the factor $(\gamma_{SV} - \gamma_{SL})$. It is therefore desirable to maximise the value of the latter while keeping $\gamma_{LV}$ as small as possible.
However, the clusters of particles are filled with air and penetration of liquid into the interstitial regions will produce an increase in the internal air pressure. Unless this excess pressure can escape then complete wetting of the particles would be impossible. The importance of the structure of the particle cluster to the wetting behaviour has been investigated\textsuperscript{136}.

The rate of penetration of the liquid into the interstices is an important factor since it will decide whether the particle clusters are incorporated into the liquid with all surfaces wetted or just the external surfaces. It is therefore desirable to obtain as large a rate as possible. For horizontal pores the rate of entry of liquid can be given as\textsuperscript{137}

\[
dL/dt = R \gamma_{LV} \cos \theta / 4 \eta L \quad (5.11)
\]

where \( L \) is the distance of penetration at time \( t \), and \( \eta \) is the liquid viscosity. Clearly a high surface tension, low contact angle, low viscosity, and large pore radius are desirable for rapid penetration.

Zisman\textsuperscript{138} has carried out work into the relationships between the surface energies of solids, the nature of the liquid, and the appropriate contact angles.

Once the powder has been partially wetted the next stage is to both mix and break down the remaining agglomerates by mechanical forces.

5.3 Mechanical breakdown of clusters

The milling action disrupts the particle clusters, the energy required depending on both the magnitude of the aggregative forces and the degree of wetting. The more intense the milling the fewer clusters, in particular the more tightly held together aggregates, remaining in the dispersion. Agitation or mixing during the process tends to speed up the whole process.

It is generally accepted that the deagglomeration is brought about by impact and/or shearing forces. Disruption by shearing relies on
viscous drag forces within the system, whereas the comminution process operates best in conditions of minimal viscosity. The two mechanisms therefore operate best within well-defined viscosity limits. There is a wide range of milling equipment and Table 5.1 indicates one classification in terms of milling action. The hybrid mills employ both impact and shearing mechanisms in achieving the powder dispersion.

Table 5.1 - Dispersion equipment

<table>
<thead>
<tr>
<th>OPTIMUM VISCOSITY</th>
<th>TYPE OF MILL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IMPACT</td>
</tr>
<tr>
<td>Very high</td>
<td>3-roll mill</td>
</tr>
<tr>
<td>High</td>
<td>High speed stone mill; Colloid mill</td>
</tr>
<tr>
<td>Moderate</td>
<td>Shot mill</td>
</tr>
<tr>
<td>Low</td>
<td>Roll mill Attritor disc impeller</td>
</tr>
<tr>
<td>Very low</td>
<td>Micronisers; Impingement mills</td>
</tr>
</tbody>
</table>

Patton\textsuperscript{139} gives a comprehensive discussion of the commonly used dispersion equipment.

Once the powder has been wetted and broken down to primary particles and the smallest groups of primary particles possible under the operating conditions it is essential to prevent the separated particles from aggregating in order to maintain the quality of dispersion. The stability, with respect to a decrease in particle number with time, of the colloidal dispersion must be such that the degradation of the properties of the system as a result of coagulation or flocculation is minimised.

5.4 Colloidal stability of dispersed particles

As a consequence of the energetic requirement that the interfacial area should be minimised dispersed particles which collide because of Brownian motion form coagula. The frequency of these encounters is
determined by the concentration and physical properties of the particles, the viscosity of the medium, and the temperature. However, the rate of particle aggregation can be reduced by introducing an energy barrier over which the colliding particles must pass in order to remain in close contact. Electrostatic or steric (or a combination of both) forces are the major source of this kinetic barrier to aggregation.

This interaction of particles each enclosed within an electrical double layer can be described adequately by the classical DLVO theory. On the other hand particles possessing adsorbed polymers on the surface interact in a manner which can be described by the HVO model. Thus in order to maintain the wetted and milled particles in the dispersed state it must be ensured that there exists an effective barrier to aggregation.

5.5 Additives

The addition of surface active agents is important in that

* the degree of particle wetting can be improved;
* the rate of the dispersion process can be increased;
* the work input required can be lowered; and
* the stability of the dispersion can be improved.

The surface active agents can modify

* the interfacial tensions
* the contact angle
* the change in energy associated with the formation of new solid-liquid interface
* the magnitude and type of interparticle interactions
* the viscosity of the medium.

Thus the additives, which can range from simple inorganics to low and high molecular weight organic molecules, can influence the wetting stage, the milling stage, and the subsequent aggregation stage.

For oxides the dispersion efficiency has been shown to be related to changes in the interfacial tensions and is independent of the liquid
polarity. The efficiency of dispersion is consequently largely determined by the degree of lowering of surface energies as the result of adsorption.

The process of dispersion may also be affected by the presence of adsorbed vapours, the effect being dependent upon the surface coverage. The existence of these mono- and multi-layer coatings can lead to the formation of clusters of particles held together by thin intermediate films of the condensed vapour (e.g. water) which require the consumption of energy in the mill in order to achieve dispersion. However, at appropriate surface coverages such adsorbed vapours can improve the ease of particle dispersion.

The movement of material within a mill depends primarily on the rheological properties of the slurry. Therefore modification of the flow properties of the latter by the addition of surface active agents is a useful method through which to improve the efficiency of the milling. The efficiency is also dependent upon the factors which influence the formation and propagation of structural defects, in particular cracks, within particles. Rehbinder and co-workers conducted a systematic study of the effect of liquids, with and without additives, on the fracture of solids. It was concluded that the adsorption of surface active species at structural defects, already in existence or formed during the milling stage, on the surfaces of particles minimised the increase in energy associated with the formation of new interfaces and thereby improved the dispersion efficiency. Since their work various workers have investigated the effect of additives on the milling process.

Unfortunately the elucidation of the mechanisms by which the additives enhance the dispersion of powders in liquids is made difficult because the majority of experimental studies failed to properly control such factors as pH and ionic strength.

The majority of the studies on the effect of additives on the milling process interpreted the data in terms of two main mechanisms, namely the "Rehbinder effect" and that formulated by Westwood et al.
Rehbinder effect

This is the reduction of the surface free energy of solids as the consequence of the adsorption of surface active agents. The energy consumption necessary to create new solid-liquid interfaces will therefore be reduced. However, the actual fraction of the total milling energy input needed to create new surfaces is only ca. 1% so that the relevance of the "Rehbinder effect" could be no more than academic. The influence of the additives on other important properties of the system, such as crack initiation, plastic deformation, crack propagation, wetting, and coagulation, are not considered in this mechanism. In addition to the influence on the surface free energies the influence on the parameters associated with the strength of solids e.g. crack initiation, crack length, etc, need to be considered.

Westwood et al\textsuperscript{144} mechanism

Studies on the effect of additives on the hardness of both crystalline and amorphous solids led Westwood et al to suggest that adsorption caused mobility of near surface structural faults. Changes in the electronic states of the atoms at these defects, as a consequence of chemical interaction with the adsorbed molecules, influence specific interactions between the dislocations and point defects.

Other mechanisms

Chemisorption and formation of high energy complexes between the additive and surface defect has been considered to play a role in the milling process\textsuperscript{145}.

Other workers have considered the role of the additives in affecting the flow properties of the system within the mill\textsuperscript{146}.

The milling of a partially wetted powder to produce well wetted and dispersed particles is comprised of several processes each of which can be influenced by the presence of chemical additives. Further carefully controlled work needs to be performed in order to elucidate the various mechanisms and their mutual interaction.
5.6 Assessment of dispersion

Numerous experimental methods are available by which to assess the quality of dispersion of a solid in a liquid. The methods are often empirical and qualitative, and generally make use of a relevant physical property of the final product. Thus for paints the optical properties of the final dispersion are frequently used as measures of the quality of dispersion. More fundamental properties such as the sedimentation and rheological behaviour, and the particle size distribution can give more useful information on the degree of dispersion. The literature on such methods is extensive.133,139,147-151.

5.7 Rheology of Dispersions

The rheological characteristics of a pigment dispersion undergo major changes as the dry powder is completely dispersed in the medium. Various successive stages in the incorporation of a relatively large volume of pigment can be envisaged:

a) agglomerated dry pigment with a volume of internal voids which may exceed the volume of liquid. The apparent consistency of the system is high;

b) wetted and partially dispersed pigment but with a large number of clumps of particles within which the majority of the available liquid is immobilised. The system consistency is lower than for a) but is still high;

c) progressive breakdown of pigment clumps with release of trapped liquid and consequent further reduction in the viscosity;

d) pigment dispersed as primary particles but tending to aggregate rapidly on reduction or elimination of a shearing stress. Flow properties of system is characterised by shear thinning behaviour;

e) pigment particles adsorbing material from the dispersion medium so that the effective volume of the pigment phase is increased and
that of the medium is decreased. The flow behaviour is more Newtonian but the system is slightly more viscous than d).

Once all air has been displaced the rheological behaviour of a pigment dispersion normally falls between two extremes - highly dilatant and highly shear thinning. The rheological aspects of concentrated dispersions are considered in the following chapter.
CHAPTER 6

RHEOLOGY OF COLLOIDAL DISPERSIONS
6. THE RHEOLOGY OF COLLOIDAL DISPERSIONS

Rheology is the science of the deformation and flow of matter. Its study has contributed a great deal towards the understanding of the nature of colloidal systems. Rheology is also a subject of prime technological importance - many industries assess the suitability of their products in terms of their flow behaviour. The paint industry uses the rheological properties of its products both to assess the degree of dispersion of the pigments and to achieve the desired product characteristics, such as prevention of phase separation. At an earlier stage the pigment manufacturer often wishes to optimise the process operation involving the wet milling of the pigment e.g. titanium dioxide. This optimisation can be achieved by the selective use of a grinding aid which aids the ease of wetting of the solid phase by the liquid vehicle and which lowers the viscosity of the mill base. One such grinding aid is monoisopropanolamine (MIPA) which is the low molecular weight organic species studied in the present experimental work. The study of the rheological behaviour of aqueous titanium dioxide in the presence of MIPA will be described later, but a review of some of the relevant aspects of rheological behaviour will be presented.

There are two general approaches to the study of flow behaviour, the first being to set up mathematical expressions which describe rheological phenomena without reference to the causes, i.e. carrying out a curve-fitting exercise, and the second being to correlate the observed flow properties with the detailed structure of the material in question.

Numerous papers have been published on suspension rheology and range in emphasis over a broad spectrum from the study of a single well-defined flow field to the study of three-phase mixtures of ill-defined particles exhibiting the properties of both fluids and powders. A number of excellent reviews are available\textsuperscript{152-162}. Each tends to focus on certain aspects of the wide range of rheological behaviour which will now be described in more detail.

6.1 Introduction

The rheological properties of a dispersion or suspension depend upon
the relative importance of the main agencies contributing to the flow behaviour. These agencies can be summarised as:

a) the hydrodynamic interaction between the suspending liquid and the particles;

b) the specific interaction between the liquid and particles;

c) the interparticle attraction forces which promote the formation of flocs/coagula or structure within the dispersion thereby modifying the hydrodynamic interactions;

d) the shorter range interparticle repulsive forces which inhibit or prevent floc/coagula formation;

e) particle-particle contact which introduces steric effects and thereby frictional or granular behaviour.

The interplay between the various factors which influence the relative importance of the five main agencies has been summarised by Cheng\textsuperscript{163} in figure 6.1. These factors include particle size and shape, the mechanical properties of the particles, the liquid viscosity, the interaction between particles, and the physico-chemical interactions between the solid and liquid. The double-headed arrows are intended to convey the important idea that the factors influence the details of the interactions and are subsequently themselves affected by the consequences of the interactions.

Figure 6.2 shows how the rheological behaviour depends on the type of interaction i.e. hydrodynamic, frictional, or interparticle attraction. The increasing effect of interparticle attraction is plotted along the x-axis, and the effect of hydrodynamic interaction and of particle-particle contact i.e. frictional interaction are combined on the y-axis. The combined effect may be measured in terms of particle concentration. At low to medium concentration the importance of hydrodynamic interactions increases; from medium to high concentration interparticle frictional contact becomes increasingly important; and at very high concentration the frictional effect predominates over the
FIGURE 6.1 Interaction of factors affecting suspension viscosity
FIG. 6.2  RELATION BETWEEN DIFFERENT TYPES OF RHEOLOGICAL BEHAVIOUR AND THE THREE CATEGORIES OF INTERACTIONS
hydrodynamic effect. The various types of flow behaviour are displayed within the plot.

In a system for which there is negligible interparticle interaction the hydrodynamic effect predominates at low to medium particle concentration. If the liquid exhibits Newtonian behaviour, i.e. the viscosity is independent of the shear stress, then the dispersion will be Newtonian. Figure 6.3 shows that the viscosity initially increases linearly with concentration but as the latter continues to rise the relationship becomes non-linear and at sufficiently high particle concentration non-Newtonian behaviour is obtained. (It should be noted that a plot such as figure 6.3 is an equilibrium curve consisting of points taken at a given shear rate from a series of flow curves.) The transition from Newtonian to non-Newtonian behaviour is ill-defined since it is complicated by the fact that in addition to being dependent upon the particle concentration the transition also depends upon the shear rate. It is generally found that the shear rate at which the non-Newtonian behaviour begins decreases as the concentration is raised. The onset of non-Newtonian behaviour has been inferred by Cheng from the available literature\textsuperscript{163}. The deduced qualitative behaviour is shown in figure 6.4. Despite the difficulty in interpreting some of the experimental results, it appears that for many systems as the shear rate increases the dispersion first changes from possessing Newtonian properties to exhibiting shear-thinning or pseudoplastic behaviour, and then shows shear-thickening or dilatant behaviour. The relative proportions of pseudoplasticity and dilatancy depends upon the particle concentration.

Many equations have been devised for describing the non-Newtonian flow behaviour. Some of the more common expressions are:

\textbf{Ostwald-de Waele Power Law}

\[
\tau = K \dot{\gamma}^n
\]  

(6.1)

where \(\tau\) is the shear stress, \(\dot{\gamma}\) is the shear rate, \(K\) is the power law consistency coefficient, and \(n\) is a dimensionless exponent such that for \(n < 1\) pseudoplastic behaviour is predicted and for \(n > 1\) dilatancy is predicted.
FIG. 6.3 RELATIVE VISCOSITY AS A FUNCTION OF SOLID CONCENTRATION

FIG. 6.4 CHANGES IN THE SHAPE OF THE RHEOGRAM AT INCREASING PARTICLE CONCENTRATION (CONCENTRATION INCREASES 1 TO 6)
Bingham Plastic

\[ \tau = \tau_y + \eta_{PL} \dot{\gamma} \]  
(6.2)

where \( \tau_y \) is the yield stress and \( \eta_{PL} \) is the plastic viscosity.

Herschel-Bulkley

\[ \tau = \tau_y + K \dot{\gamma}^n \]  
(6.3)

Casson

\[ \tau^{0.5} = \tau_y^{0.5} + k \dot{\gamma}^{0.5} \]  
(6.4)

Oka Unified Law\textsuperscript{164}

\[ \frac{d \tau}{(\tau + a)^m} = k \frac{d \dot{\gamma}}{(\dot{\gamma} + b)^m} \]  
(6.5)

in which \( a, b, k, \) and \( m \) are material parameters. Integration of the differential equation for the boundary condition \( \tau = 0 \) when \( \dot{\gamma} = 0 \) gives rise to a family of pseudoplastic flow curves. Applying the boundary condition \( \tau = \tau_y \) when \( \dot{\gamma} = 0 \) gives a family of viscoplastic flow curves. The Oka expression gives, as special cases, the previous four expressions given the suitable choice of values for the material parameters.

The non-Newtonian behaviour of systems is often caused by the nature of the interparticle interactions and such behaviour is discussed in later sections. The effects on the flow properties due to variations in the physical parameters of the solid phase will be considered.

6.2 The Effect of Physical Parameters on Rheological Behaviour

There are four main physical parameters which have been extensively studied, namely particle concentration, particle size, particle size distribution, and particle shape. The effect of the variation of each on the viscosity of a dispersion will be considered separately.
6.2.1 Effect of Particle Concentration

When solid particles are added to a pure liquid and the mixture caused to flow, the presence of the particles distorts the streamlines such that they curve around the particles instead of remaining parallel as they would in a uniform shear field. This distortion produces a rise in the viscosity since more energy is required to maintain the flow. For dilute dispersions of non-interacting particles this is the only effect giving rise to the viscosity increase, but as the particle concentration increases the streamline distortion around one particle influences the degree of distortion around neighbouring particles. The particles are now interacting in that there is a mutual influence on the hydrodynamic forces existing in the interparticle liquid. Additionally, there exists the possibility of temporary doublets or triplets forming between particles with the resultant immobilisation of the intervening liquid. This occluded liquid is no longer available for the dispersion of particles and hence the effective particle concentration has increased.

At higher concentrations it becomes necessary to consider the flow of the liquid film existing between particle surfaces as either the particles move relative to each other in the shear field or the film is compressed as particles approach each other. At sufficiently high concentrations the viscosity may increase as the result of changes in the packing of the particles during flow.

The hydrodynamic effects mentioned can be summarised in order of increasing importance as the particle concentration is raised:

a) streamline distortion by individual particles;

b) mutual interference of streamline distortion;

c) formation of temporary aggregates with consequent immobilisation of some liquid;

d) flow, either shear or extensional, of a film of liquid separating particle surfaces;
change in the packing structure of particles as the result of flow.

Most of the viscosity-determining factors have been incorporated to varying extents into the theoretical models of various workers. It is very likely that all of the factors play a part in determining viscosity at a given particle concentration. However, as a result of the complexity associated with developing a theory to take account of all these factors the majority of the theoretical studies only consider one or two of the factors. It is therefore not surprising that the predictions of these various expressions do not agree with one another. Moreover, all of these equations fail to take account of the effects of particle size, shape, and size distribution. In spite of these shortcomings the various viscosity/particle concentration relations are useful.

At finite concentrations, a dispersion exhibiting Newtonian behaviour can be described by a relative viscosity function

\[ \eta_r = \frac{\eta}{\eta_0} = F(c) \tag{6.6} \]

where \( \eta \) is the dispersion viscosity, \( \eta_0 \) is the pure liquid viscosity, \( \eta_r \) is the relative viscosity and \( c \) is the volume fraction \( c = n \cdot v \), in which \( n \) is the number of particles per unit volume and \( v \) is the volume of a particle).

The function behaves in accordance with the curve in figure 6.3. As the particle concentration tends to zero the slope of the curve tends to a limiting value known as the intrinsic viscosity, \( k_1 \), while at high concentrations the behaviour is governed by the existence of a packing fraction \( c_m \), beyond which the particles form a semi-rigid structure leading to either stoppage of flow or dilatant behaviour. This packing fraction is a function of the type of packing, the particle shape and the particle size distribution.

For dilute dispersions, i.e. \( c < 0.05 \), Einstein\textsuperscript{165} derived the following expression

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\[
\eta_r = \frac{1 + c/2}{(1 - c)^2}
\] (6.7)

For sufficiently low concentrations, i.e. \( c < 0.02 \), the equation can be simplified to give

\[
\eta_r = 1 + k_1 c
\] (6.8)

As the result of experimental difficulties in obtaining the conditions required for the derivation of the equation numerous values for \( k_1 \) have been suggested. Ward and Whitmore\(^{166}\) found values in the range 1.9 to 4.0 depending on the particle size distribution. A value of 2.5 is often used. Kurgaev found that the Einstein equation can be applied at higher concentrations (0.15 < \( c < 0.18 \)) if a value for \( k_1 \) within the range 4.5-4.75 is used. It has been shown theoretically\(^{167}\) that for \( c < 0.4 \) a value for \( k_1 \) of 4.5 is useful.

The work of Einstein has been extended by other workers, e.g. Guth and Simha\(^{168}\), Batchelor\(^{169}\), Hinch and Leal\(^{170}\), and Oliver and Ward\(^{171}\). The usefulness of these investigations lies not so much in the practical sense but more in the insight they give into the mechanisms affecting the viscosity. Jeffrey and Acrivos\(^{160}\) give a useful review of the many investigations.

For concentrated dispersions numerous formulae have been derived to describe the relationship between the relative viscosity and solids volume fraction.

Rutgers has given a comprehensive review of the work in this area\(^{152-159}\). Many of the formulae express the relationship between \( \eta_r \) and \( c \) through a polynomial of unknown order:

\[
\eta_r = 1 + k_1 c + k_2 c^2 + k_3 c^3 + \ldots \ldots
\] (6.9)

The use of a polynomial is often justified by the fact that the \( k_i \) coefficients represent the particle interactions between \( i \) particles. As the concentration is increased higher order polynomials are necessary to predict the value of \( \eta_r \). For non-spherical particles the coefficients depend upon the particle size and shape.
When particle crowding becomes the dominant factor then equation (6.9) can be modified to take account of this effect. Division of the polynomial by the factor $(1 - c/c_m)$ now satisfies the condition that $\eta_r \rightarrow \infty$ as $c \rightarrow c_m$. Expansion of this expression for the case $c/c_m < 1$ allows an estimate of the intrinsic viscosity to be made.

$$\eta_r = 1 + (k_1 + \frac{1}{c_m})c + (k_2 + \frac{1}{c_m})c^2 + \ldots$$ (6.10)

Mooney proposed the relationship

$$\eta_r = \exp \left[ \frac{2.5 c}{(1 - \frac{c}{c_m})} \right]$$ (6.11)

He introduced a crowding factor $k \,(= 1/c_m)$ which for a monodisperse dispersion of spheres has a value in the range 1.39 to 1.91.

The comparison of the predicted values for $\eta_r$ using the various equations indicates that for solids volume fractions $< 0.3$ they are similar but deviate enormously for higher concentrations.

It is generally recognised that there is no single relationship that can give the viscosity as a function of the volume fraction of the particles alone. Particle shape and size distribution are two of the most important additional factors that need to be considered. Therefore the successful empirical expressions will contain adjustable parameters which need to be determined by experiment. So until these parameters can be predicted such formulae are limited to correlating experimental data. Cheng has stated that since there is such a proliferation of viscosity-concentration equations one gets the impression that given any experimental data there exists an equation to fit them, and vice versa. Cheng believes that one of the most useful expressions is of the form:

$$\eta_r = \frac{1 + k_1 c + k_2 c^2 + k_3 c^3 + \ldots}{(1 - (\frac{c}{c_m})^{1/3})}$$ (6.12)
6.2.2 Effect of Particle Size

Numerous attempts have been carried out to establish qualitatively how particle size affects viscosity. However, these studies often produced conflicting experimental observations, probably as the result of extraneous effects due to particle shape and polydispersity. Other effects which can contribute to anomalies in the results of such investigations include particle swelling due to liquid adsorption, and the presence of an adsorbed layer on the particles. The presence of the latter, either solvent or surface active agent, perturbs the streamlines during flow and thereby raises the viscosity. This adsorbed layer can be considered to either increase the effective particle size or to increase the effective volume fraction of particles. This phenomenon must be taken into account when considering dispersions of sub-micron particles.

However, it can be concluded that the absolute size of the particles has no effect on the dispersion viscosity provided they are well-dispersed and are only influenced by hydrodynamic forces. In practice, however, the effect of the variation in particle size can be observed in rheological data. The wall-effect associated with the practical use of a viscometer is one potential source of error. The ratio of the particle size to the relevant viscometer dimension should be very small so that no spurious conclusions arising from the existence of the particle-wall interaction during a measurement can arise. There are several reasons, associated with the microscopic properties of a dispersion, which give rise to the viscosity dependence on the particle size. These are

* the presence of adsorbed surface layers
* the existence of Brownian motion
* the increasing importance of colloidal forces as the particle size is reduced.

6.2.3 Effect of Particle Size Distribution

Compared with the effort devoted to studying the effects of particle concentration and size on dispersion rheology, relatively little work has examined the effect of particle size distribution. However, a qualitative understanding of its influence on viscosity has been gained
and numerous mathematical equations and empirical correlations which summarise the experimental data more or less satisfactorily have been devised. But there is still the need for a quantitative treatment which will permit prediction of the rheological properties of a given system. The most important result from theory is that for a given total particle volume concentration the viscosity can be minimised through the suitable choice of the size distribution and conversely that it is possible to maximise the solids content without exceeding the maximum acceptable viscosity by the use of an optimum particle size distribution. These predictions have been confirmed by some of the limited experimental work.

6.2.4 Effect of Particle Shape

The influence particle shape has on the rheological properties of a dispersion is the least researched area. Little quantitative data exists for industrially important systems in which the particles exhibit a marked degree of anisometry. The basic studies have tended to concentrate on the flow behaviour of single particles possessing at least one plane or axis of symmetry.

In spite of the numerous sophisticated methods available for the characterisation of particle shape there has been little attempt at relating the viscosity behaviour of dispersions of irregularly shaped particles to the detailed geometry of the particles. But it is clear that at a given solids volume fraction anisometric particles give a higher viscosity than spherical particles of the same mean size. The magnitude of the viscosity increase rises as the anisometry of the irregular particle becomes more pronounced. In addition there is evidence that the effect of particle size distribution on viscosity is less important in concentrated, irregular shaped particle dispersions.

6.3 The Effect of Colloidal Forces on Rheological Behaviour

This section contains a discussion of the way in which the degree of aggregation of a dispersion affects the rheological properties. Dispersions of colloidal particles can be unstable with respect to aggregation and so the colloidal forces will contribute towards the flow behaviour. In addition dispersions or suspensions can sediment thereby
behaving as a two phase system with non-homogeneous bulk properties or they can exhibit ageing effects. Both these factors complicate the description of the rheological behaviour and so in discussing the latter it will be assumed that the dispersion behaves as a homogeneous material which does not age.

As discussed earlier the flow properties depend on the particle properties and on the interparticle interaction forces. Figures 6.1 and 6.2 conveniently summarise the complex relationships between the various influencing factors and the flow behaviour. The rheological properties of dispersed and flocculated systems are different and reflect the role that the interfacial properties play in determining the flow characteristics. Under conditions where there is negligible attraction between particles (e.g. the particles are large or there is a net repulsive force between particles) the rheology is determined by the hydrodynamic and frictional interactions. However, because of the presence of a deformable interfacial layer, either an electrical double layer or a steric layer, many colloidal dispersions cannot be treated as a system of rigid particles dispersed in liquid. The flow units (particle plus layer) are deformable both by the shear field and by interparticle collisions leading to viscous energy losses not considered in classical treatments.

As the interparticle attraction increases the viscosity of a dispersion increases as a result of the formation of aggregates, flocs or coagula. The effective size and shape of the flow units vary and thereby influence the rheological behaviour. The occluded dispersion medium produces an increase in the effective particle concentration. Under conditions in which the interparticle attraction results in the formation of an extended structure throughout the dispersion shear-thinning behaviour will be observed because the structure and flocs are shear sensitive and therefore undergo breakups in the presence of a shear field. When the interparticle attraction is small, the flocs are weak and easily broken up but with an increasing attractive interaction the flocs are more able to sustain a finite shear stress without breakup. This introduces a yield stress to the system which now exhibits viscoplastic flow behaviour.
It is the colloidal interaction forces which governs the flow properties of many dispersions. The rheological behaviour of dispersions can vary widely, as illustrated by the following three model systems.

Aqueous polystyrene lattices at volume fraction as high as 0.50 exhibit moderate shear-thinning behaviour at high ionic strengths or low surface charge densities\(^1\). Reduction in the ionic strength dramatically increases the viscosity at low shear rates with the formation of an apparent yield stress. It is believed that the increase in the interparticle electrostatic repulsion leads to the formation of an ordered, crystalline-type structure which possesses elasticity.

Non-aqueous polyvinyl chloride dispersions exhibit different behaviour\(^1\). Under good solvency conditions, for which the dispersion should be stable, slight shear-thinning behaviour is observed. However, with poor solvency the highly flocculated dispersions exhibit higher viscosities and an apparent yield stress.

Similar effects have been noted for non-aqueous dispersions of carbon blacks\(^1\). The changes in rheological behaviour with increasing solid volume fraction are significant. Increasing the value enhances the shear-thinning behaviour with the appearance of an apparent yield stress. There exists a significant effect due to the solids concentration as is shown by the fact that at low shear rates the viscosity, at a volume fraction of 0.047, is two orders of magnitude higher than at a volume fraction of 0.011. The small size of the particles (~13 nm) and the absence of any stabilisation apparently favours the formation of extensive network structures.

These examples highlight the sensitivity of the flow properties of a colloidal dispersion to both the nature and strength of the interparticle forces.

6.3.1 Dispersed Systems

The rheology of monodispered colloidal dispersions has been reviewed by Krieger\(^1\). Such systems are frequently non-Newtonian and may exhibit time dependency e.g. thixotropy. The flow behaviour is a function of the
relative values of the average interparticle separation and the range of
the repulsive forces.

6.3.1.1 Dilute dispersions

The equations described in section 6.2.1 apply to rigid non-interacting particles. However, in the case of interacting particles the interfacial layers surrounding the particles can affect the viscosity by three mechanisms. Firstly, the effective volume concentration of solids is given by the volume of the particles plus the interfacial layers, electrical double layers or steric layers of polymer molecules. Secondly, the layer is distorted by the shear stress which results in energy dissipation within the layer which is in addition to the bulk dissipation. Thirdly, interparticle collision leads to overlap of the interfacial layers, thereby causing distortion and energy dissipation. These mechanisms affect the value of \( k_1 \).

The presence of a surface charge on the particles gives rise to an additional contribution to the suspension viscosity due to increased energy dissipation within the electrical double layers and suspending medium.

There are three distinct effects which are classified as the primary, secondary, and tertiary electroviscous effects, although the order does not refer to their interrelation or relative importance.

The primary effect results from the increase in the viscous drag forces on the particles as their electrical double layers are distorted by the shear field. The effect can exist down to particle concentrations approaching infinite dilution. The simple Einstein equation is modified by incorporating parameters associated with the electrical double layer\(^{175,178-180}\).

The secondary electroviscous effect results from the overlap and subsequent repulsion of the electrical double layers. The repulsive forces prevent the close approach of the particles leading to finite particle separation (hence large effective particle size). This gives perturbation of the shear field. Experimentally the magnitude of this
effect can be estimated by comparing the slope of the experimental curve of relative viscosity \( (\eta/\eta_0) \) as a function of solid content with the theoretical value calculated solely from the hydrodynamic interactions.

The secondary effect is not restricted to collisions between two particles but is also applicable to higher order interactions and is important throughout the full range of volume fractions. It appears as a correction to \( k_2 \) (equation 6.9)\textsuperscript{181-182}.

The secondary electroviscous effect can alter the viscosity of a monodisperse latex by an order of magnitude\textsuperscript{157} and hence is more readily measured experimentally than the primary effect.

The tertiary electroviscous effect arises from changes in the size and shape of polyelectrolytes brought about by changes in the electrical properties of the system. By altering the ionic strength and/or pH of aqueous dispersions of polyelectrolytes the electrostatic interaction between different portions of the macromolecule changes with consequent modifications in the size and shape of the molecule. Under conditions of high electrostatic repulsion the molecules adopt extended configurations e.g. rigid or kinked cylinders, whereas at high ionic strength, where electrostatic repulsion is minimal, a compact, globular shape is favoured. The changes in conformation and hence size and shape modify the values of \( k_1 \) and \( k_2 \) in equation (6.9).

6.3.1.2 Concentrated dispersions

At volume fractions greater than about 0.1 the suspension viscosity is increased due to the formation of temporary doublets, triplets, and higher order multiplets which enhance the rate of energy dissipation. (The mean free path of a particle within the suspension decreases as the concentration rises.) Figure 6.3 shows the change in relative viscosity of a suspension of rigid particles as a function of volume fraction of solids. The relative viscosity is found to increase more rapidly with solids content than predicted by the Einstein equation. The slope of the curve attains the limiting value of 2.5 only for very dilute suspensions and, further, the viscosity is found to increase to infinity above a certain volume fraction \( (c_m) \) - the packing fraction. At this
concentration the particles become locked into a rigid structure and flow ceases. Thus in concentrated systems, $\eta/\eta_0$ depends in a complex way on $c$, i.e. $\eta = \eta_0 F(c)$. The form of $F(c)$ has been the subject of many theoretical and experimental studies. The equations given in section 6.2.1 apply to non-interacting rigid spheres.

For a monodisperse system of spherical particles possessing a net repulsive interaction the following expression has been derived\(^{183}\)

$$\eta = \eta_0 \exp \frac{2.5}{1 - 1.65c}$$ \hspace{1cm} (6.13)

The particles are assumed to pack such that there is the largest interparticle separation possible. However, if there can exist a net attractive interparticle force, then random packing of the particles would be expected (in this case $c_m = 0.64$) giving

$$\eta = \eta_0 \exp \frac{2.5}{1 - 1.56c}$$ \hspace{1cm} (6.14)

Without going into details, as with dilute suspensions, the additional volume of the interfacial layer affects the effective particle volume concentration. The layers are deformed by the shear field with resultant changes in the effective particle shape and mechanical properties. The coefficients $k_1$, i.e. $[\eta]$, $k_2$ and $k_3$ are thereby altered. The crowding factor can be interpreted as being equal to the reciprocal of the close-packing volume concentration, $c_m$, at which the viscosity becomes infinite. This is closely related to, if it not exactly equals, the sedimentation volume and is clearly dependent on the thickness of the interfacial layer.

Recently, Gillespie\(^{184}\) has given an expression taking account of aggregate shape, packing density, and the number of primary particles per aggregate. The expression due to Einstein, equation (6.7), was extended so that the effects of particle size distribution, shape, and existence of particle aggregation due to colloidal forces could be allowed for. An expression for the relative viscosity as a function of the effective solids volume fraction, $c_{EFF}$, of the dispersion was given
\[
\eta_r = \frac{1 + c_{\text{EFF}}/2}{(1 - c_{\text{EFF}})^2}
\]  
(6.15)

and \(c_{\text{EFF}}\) is related to the true solids volume fraction by the equation

\[
c_{\text{EFF}} = p c + s p^2 c^2
\]  
(6.16)

The so-called "Einstein hydrodynamic factor", \(p\), is a function of the number of primary particles in a floc, the shape of the floc, and the type of packing. The particle interaction parameter, \(s\), is a function of the shape and size distribution of the particles. It has a value of 0.9 for a system of monodispersed spheres, but increases in value as the axial ratio of the flow units increases and decreases in value as the size distribution of the flow units increases. Equation (6.15) can therefore take account of size and shape changes brought about by flocculation.

### 6.3.2 Non-Newtonian Behaviour

At volume fractions greater than about 0.25 it is common for dispersions to exhibit non-Newtonian flow behaviour. The qualitative change in the latter as a function of volume fraction is shown in figure 6.4. At lower concentrations the viscosity is nearly independent of shear rate but as the concentration is increased a shear-thinning zone develops which separates two Newtonian regions i.e. the zero shear and the upper shear region. The zone extends to lower shear rates with increasing concentration. A plastic region can be found at higher particle volume fractions in which the shear stress becomes independent of shear rate thereby giving a yield stress. At higher particle concentrations still shear-thinning and dilatant behaviour is observed. A shear-thinning region at low shear rates is sometimes followed by either a shear-thickening region or a discontinuity in the flow behaviour.

Viscoplastic behaviour results from the formation of a structure within the system\textsuperscript{159}. An increase in the particle concentration increases the number of interparticle interactions. Numerous models have
been developed which attempt to predict the flow behaviour from the solids volume fraction and the particle interactions\textsuperscript{185-187}.

Dispersions possessing a high solids volume fraction (curves 5, 6, figure 6.4) exhibit dilatant and shear-thickening flow behaviour beyond a certain shear rate. Volume dilatancy describes the behaviour of a system in which the particle packing volume increases on shearing. If the solids content is sufficiently high, shearing produces an increase in the volume of the dispersion as air is entrapped, thereby giving the system a dry appearance, and if the shearing continues sample fracture occurs.

The mechanism of shear-thickening appears to be related to the electrical properties of a dispersion, i.e. the zeta potential of the particles, the dielectric constant of the liquid, and the ionic strength. For such behaviour to be observed the particles must experience a significant repulsive interaction as they encounter each other. Hoffman has developed a model to explain both shear-thickening and dilatant flow behaviour\textsuperscript{188,189}.

6.3.3 Flocculated Dispersions

The particles of a suspension will aggregate to form flocs if the repulsive interactions cannot overcome the attractive forces. The equations used for calculating the viscosity of a dispersion of rigid particles can again be used if the overall floc volume, including the occluded liquid, is substituted for $c$. Allowances should be made for the overall shape and mechanical properties of a floc and the viscous dissipation within the floc. But the special feature of the rheology of flocculated systems is the breakdown of the flocs under shear and the recovery of structure at rest. These structural changes are rate processes and the system can exhibit thixotropic behaviour. When such a system is subjected to prolonged shear, a quasi-equilibrium state is set up where the rate of break-up is in dynamic balance with the recovery rate. This gives an equilibrium floc size or structure which depends on the shear rate. The viscosity due to the equilibrium structure gives the most common type of non-Newtonian behaviour, namely shear-thinning or pseudoplasticity, in which the viscosity decreases with increase in shear rate.

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Under certain situations, the flocs can form into a structure that extends right through a suspension and can sustain a significant stress, the yield stress, $\tau_y$, without giving continuous deformation or flow. But on exceeding the yield stress, the viscosity decreases with shear rate. Such behaviour is known as viscoplasticity.

The equilibrium floc structure at high shear rates often takes on certain properties such that the shear stress–shear rate relationship becomes asymptotic to a Bingham plastic flow curve above a shear rate $\dot{\gamma}_o$ (figure 6.5). The extrapolated yield stress, $\tau_B$, is related to the floc structure and floc properties.

Most of the equations derived to describe the flow properties are based on the assumption that the shear-thinning is the result of the breakdown of a three-dimensional network structure of aggregated particles or flow units. The equations tend to be empirical and applicable under a fixed set of conditions. That structures do form has been confirmed experimentally\textsuperscript{190-192}. Several workers have equated the apparent yield stress, $\tau_B$, and the critical shear rate, $\dot{\gamma}_o$, with the interaction forces between the flow units\textsuperscript{193-199}.

A comparison of some of these theories has been made by Chaffey\textsuperscript{200}.

The rheological behaviour can be explained in terms of the interparticle interactions such as the van der Waals attractive force and the repulsive force due to electrical double layer overlap. The theories describing the pseudoplastic behaviour can be roughly classified as either phenomenological or structural. The former involve the derivation of equations from a mathematical model and contain parameters whose values are found through comparison with experimental data. However, these parameters often cannot be interpreted in terms of the microscopic properties of the dispersion. The parameters arising from the structural theories, on the other hand, give a detailed picture of the system on the microscopic level. The viscosity equations increase in complexity as the model used to describe the colloidal dispersion becomes more detailed\textsuperscript{201-202}.  

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FIG. 6.5 FLOW CURVE FOR A COAGULATED DISPERSION
However, these models neglect specific changes in the shape of flocs other than those due to simple changes of size. Mason et al\textsuperscript{203} have observed the rearrangement of chain-like flocs to a more spherical shape in the presence of a shear. The chain structure favoured on an interaction energy basis is forced into a form which is hydrodynamically favoured. In addition Mewis et al\textsuperscript{204} have shown that the structures present in a suspension subject to shear differ from those present at rest, a phenomenon they have termed as structural hysteresis. The importance of the internal structure of the flow units has been considered by Michaels and Bolger\textsuperscript{205}. In studying the rheological behaviour of aqueous, flocculated, kaolin suspensions they concluded that even at high shear rates the strength of the interactive forces between flow units was the most important factor influencing the shear stress-shear rate relationship. They consequently developed a structural model for the description of such a system.

The Michaels and Bolger Model

According to the model an aggregated dispersions subject to only Brownian movement can be taken to be composed of rigid flocs which cluster into large but comparatively weak aggregates. When such a system is subjected to shear the aggregates fragment into smaller units, the smallest being a floc. At low shear rates the aggregates were assumed to deform and break up as the shear rate was increased. However, no single flocs were taken to exist in this low shear rate region. The aggregates were assumed to form network structures within this low shear rate range, although the strength of the network was taken to be a function of the shear rate. At high shear rates the aggregates were assumed to be broken down completely into the individual flocs. No structural network present. The flocs interact as strongly as ever, but the hydrodynamic forces separate the floc clusters as quickly as they can form. As a result many temporary floc doublets, triplets, etc form due to the floc-floc collisions, but no gross aggregation can take place.

The complete equilibrium flow curve equation for the low shear rate range can be given as:
\[
\tau = \tau_N + \frac{5 A_m c^2_F C^2_A F}{16\pi a_0 d_F (C_{AF}-1)d_A} + \eta_o \dot{\gamma} \left(1 + 2.5 \frac{C_{AF}}{c_F}\right) \quad (6.17)
\]

and at high shear rates:

\[
\tau = \frac{A_m c^2_F}{2\pi^2 a_0 d^2_F} + \eta_o \dot{\gamma} \left(1 + 2.5 c_F\right) \quad (6.18)
\]

since \(\tau_N = 0\) as \(\dot{\gamma} \to \infty\).

where \(\tau_N\) is the yield strength of the flocculated structure

- \(A_m\) is the Hamaker constant
- \(c_F\) is the floc volume fraction

\[
C_{AF} = \frac{c_A}{c_F}
\]

where \(c_A\) is the aggregate volume fraction

- \(a_0\) is the minimum separation between two flocs in close contact
- \(d_F\) is the average floc diameter
- \(d_A\) is the average aggregate diameter
- \(\dot{\gamma}\) is the shear rate
- \(\tau\) is the shear stress

The features of the shear stress-shear rate curve (figure 6.5) can now be related to the model predictions. From equation (6.18) the slope of the linear portion, \(\eta_{PL}\), should be

\[
\eta_{PL} = \eta_o \left(1 + 2.5 c_F\right) \quad (6.19)
\]

By comparing experimental data with the prediction Michaels and Bolger were able to conclude that the flow units present at high shear rates were flocs and not individual primary particles. Using equation (6.18) in the limit \(\dot{\gamma} \to 0\) gives for the Bingham yield stress, \(\tau_B\)
Comparison with experimental data gives reasonable values for $a_0$ and $d_F$. However, estimated values of the Hamaker constant were found to be at least an order of magnitude too high, no doubt due to the neglect of interparticle forces other than the van der Waals attractive forces. It was found that the ratio $A_m/d_F^2$ was approximately the same for the five kaolin slurries studied and this was taken as evidence for the assertion of Reich and Vold\textsuperscript{206} that the equilibrium floc size, at a given shear rate, increases as the interparticle attractive forces increase. However, it should be noted that given a system of particles and liquid the Hamaker constant is fixed, thus for all the kaolin slurries studied $A_m$ should be the same. The authors also did not consider the existence of either repulsive interactions between the particles nor of additional attractive forces.

The model was extended by Hunter and Nicol\textsuperscript{196} who made allowance for the existence of repulsive interactions between particles. The yield strength, $\tau_B$, was then found to vary with the square of the zeta potential. For system possessing a secondary minimum in the total interaction energy-distance curve it was further predicted that $\tau_B$ would be given by

$$\tau_B = \frac{A_m c^2_F}{2\pi^2 a_0 d_F^2} \frac{1}{(K_a)^2} \kappa^2$$

(6.20)

where $\kappa$ is the reciprocal double layer thickness, and $a_s$ is the interparticle separation at which the secondary minimum is located. The predicted dependences of $\tau_B$ on the square of the zeta potential and $(\kappa a_s)^{-2} (1 - (\kappa a_s)^{-1}) \kappa^2$ were found for aqueous suspensions of kaolin, although the primary particle volume fraction was <0.05. However, difficulties were experienced in assessing the results for the suspensions exhibiting retarded flocculation, in particular the data indicated that the strength of the interfloc bonds was higher than predicted from DLVO theory. This discrepancy is most likely due to the rather simplistic expressions assumed for $V_A$ and $V_R$ in the analysis.
of the authors. The fact that the clay particles were anisotropic and the suspension polydisperse further complicate matters since the model was derived assuming spherical particles.

The analysis for those dispersions undergoing slow aggregation has been extended by Friend and Hunter\textsuperscript{207} who used more detailed expressions for the electrostatic interaction term. The flow curves for aqueous suspensions of monodispersed polystyrene and poly (methylmethacrylate) lattices (c < 0.07) were measured and the predictions of the model tested. The value of $\tau_B$ was found to be a maximum at the isoelectric point for both types of latex, and the predicted linearity between $\tau_B$ and $\zeta^2$ was found.

Firth and Hunter\textsuperscript{208} observed that the energy dissipation process not only involves the separation of the particles but also the stretching of the interparticle bonds. This "elastic floc" model provides the basis for the most successful theory of pseudoplastic flow behaviour. The structure and strength of the flocs are related to the rheological properties.

The Elastic Floc Model\textsuperscript{209}

The basic flow unit is considered to be an elastic floc which can undergo extension and compression during shear flow and mutual collisions. The model develops equations relating the characteristic flow parameters $\tau_B$, $\eta_{PL}$, and $\dot{\gamma}_o$ (figure 6.5) to the properties of the flow units. The floc structure has been considered in some detail in the previous chapter. A schematic picture of the structures present in an aggregated suspension is given in figure 6.6. Experimental observations\textsuperscript{210} on the value of $\zeta$ at $\dot{\gamma} < \dot{\gamma}_c$ showed no measurable dependence on $\dot{\gamma}$ and hence the flocs formed at $\dot{\gamma}_c$ must at $\dot{\gamma} < \dot{\gamma}_c$ be grouped in a close packed structure in order to maintain the $\zeta$ value. The units formed at $\dot{\gamma}_c$ were called flocculi and for $\dot{\gamma} < \dot{\gamma}_c$ several flocculi were assumed to group together to form a close packed structure called a floc. At still lower rates of shear, $\dot{\gamma} < \dot{\gamma}_o$ aggregates of these flocs were taken to form. Thus it is not common for the flow units to be primary particles.
FIG. 6.6 STRUCTURE IN AN AGGREGATED SYSTEM ACCORDING TO THE ELASTIC FLOC MODEL
Armed with this picture the various energy dissipation processes within the flow units were considered. The viscosity of a system increases as the quantity of external energy which can be dissipated within the system increases. The largest contributions to the energy dissipation are:

a) viscous energy dissipation due to the presence of particles in the system, and

b) the energy dissipation during rupture of the flocs.

The energy, supplied by the shearing field, required to rupture a floc doublet is composed of two types, namely, the energy required to break the bonds between the flocs, and the energy required to stretch the bonds between particles within a floc (as the force must be transmitted from the shear field to the floc-floc interface). The latter energy requirement is the more significant since, although the energy necessary to break a bond is greater than that to stretch the bond, there are many more bonds to be stretched. This bond stretching energy is composed of:

a) The energy required to overcome the interparticle forces keeping the particles in an energy minimum. This elastic energy can be related to the distance of closest approach between two particles, the distance at which the attractive forces between them is a maximum, the number of particle links between colliding flocs per unit area, and the maximum attraction force between the particles. The latter depends upon the parameters associated with the classical DLVO theory. The Hamaker constant, the dielectric constant of the liquid medium, the ionic strength, concentration of potential determining ions, and the surface potential of the particles will influence the maximum attraction force.

b) The energy required to overcome the viscous drag resulting from the displacement of particles within a floc during stretching.

c) The energy involved in floc shape and/or volume change during stretching, which is accompanied by some internal movement of liquid within the floc.
The energy dissipation due to the rupture of a floc was considered to be negligible at modest shear rates (\( \dot{\gamma} < 2000 \text{ s}^{-1} \)) and so only the rupture of floc doublets need be considered. The contribution to the energy dissipation by the internal movement of liquid within the flocs is normally taken to be the dominant factor. So that this term and the viscous drag factor determine the viscosity of the system.

Recently, it has been suggested that the third energy dissipation term (i.e. \( c_3 \)) should be included in the second. Experiments on calcium hydroxide showed that the rheological properties could be predicted by the elastic floc model without the need to introduce a term taking account of fluid movement within the flocs.

The model allows the 3 flow curve parameters (figure 6.5) to be related to the structure of the flow units, as given by \( \text{CFP} \), (section 4.7), and the strength of the interparticle bonds as given by the application of DLVO theory.

\[
\text{CFP} = 1.5 + \frac{1}{5b \eta_o \gamma_c r \frac{1}{d^2}} [\frac{A_m}{12 d^2} - B(\kappa, d, \zeta^2)] 
\]

(6.22)

where \( b \) is a factor depending on the packing structure of the flocculi; \( r \) is the primary particle radius, and \( d \) is the interparticle distance at which the primary minimum has the steepest wall i.e. the force of interaction is at a maximum.

The prediction that \( \text{CFP} \) is a linear function of the square of the zeta potential has been confirmed experimentally.

The plastic viscosity can be related to the floc volume fraction, \( c_F \), by using the Einstein equation, or for higher volume fractions the Mooney equation

\[
\eta_{PL} = \eta_o \exp \left[ \frac{2.5 c_F}{1 - k' c_F} \right] 
\]

(6.23)
where $c_F = C_{FP} c$.

The critical shear rate, $\dot{\gamma}_o$, can also be linked to the interaction energy between the particles thus:

$$\dot{\gamma}_o = \frac{N_F r A_m}{5 \eta_o 12 d^2} \left[ \frac{1}{\chi} - B(\kappa, \zeta^2) \right]$$

(6.24)

where $N_F$ is the number of links formed between two flocs on collision.

The dependence of $\dot{\gamma}_o$ on $\zeta^2$ has been demonstrated experimentally. The importance of $\dot{\gamma}_o$ is that it represents the point at which the shear field exerts sufficient force to just prevent the formation of floc aggregates. It should be noted that for particles with radius $>2 \mu m$ hydrodynamic forces become comparable with the colloidal interaction forces and thus for systems of such particles the flow units at high shear rates would be expected to be the primary particles.

The Bingham yield stress can be quoted as

$$\tau_B = \beta \lambda \eta_o \dot{\gamma} r_F^2 \delta c^2 C_{FP}/r^3$$

(6.25)

where $\beta$ is a constant allowing for the hydrodynamic shielding of a doublet of spheres by the neighbouring spheres; $\lambda$ is the so-called orthokinetic capture efficiency; $r_F$ is the floc radius; and $\delta$ is the distance moved by a primary particle relative to its neighbours within a floc, as the result of the distortion caused by the shear field.

The equation only considers the energy dissipation due to the movement of liquid into and out of the spaces between the primary particles within the flocs and ignores the contribution due to the stretching of the interparticle bonds. $\tau_B$ is independent of the shear rate so long as $\delta$ does not depend upon it; in fact $\delta$ is expected to be governed by the magnitude of the maximum slope of the potential energy minimum well into which the flocs have aggregated. The validity of equation (6.25) has been checked experimentally with the expected
linearity between $\tau_B$ and $c^2$, and $\tau_B$ and $\zeta^2$ (since $C_{FP} \propto \zeta^2$) found. In addition the derived values for $\delta$ (a few Å) satisfy the assumption that distortion of the floc by the hydrodynamic forces is minimal.

The elastic floc model has been criticised\textsuperscript{215}

6.4 Summary

The rheological properties of dilute suspensions of interacting particles, dispersed or aggregated, can be reasonably successfully described by theory, but for concentrated suspensions the theories are not fully developed. The concepts and theories in classical colloidal chemistry have provided the means by which the most successful models, describing the flow behaviour of interacting particles, have been developed. Further application of the ideas of colloid chemistry to the rheological behaviour of dispersions will provide a greater understanding of the latter.
CHAPTER 7

EXPERIMENTAL METHODS AND MATERIALS
7. EXPERIMENTAL METHODS AND MATERIALS

This chapter defines the materials used in the studies and describes the experimental techniques adopted.

7.1 Materials

A summary of the main features of the various materials used is given in the following sections.

7.1.1 Distilled Water

Two purities of distilled water were used. Single distilled water was derived from tap water using a commercially available all-Pyrex still. This water was used to rinse glassware such as beakers, test-tubes, volumetric flasks, and pipettes. It was also used as the feedstock for a Pyrex double still. The resulting triply distilled water was used as the working solvent for all reagent solutions and rutile dispersions. The specific conductivity of this water was less than $1.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. Both types of distilled water were collected in 25 dm$^3$ borosilicate glass aspirators and were allowed to equilibrate with the carbon dioxide of the atmosphere. The pH of the water was therefore about 5.7.

7.1.2 Electrolyte Solutions

The electrolyte solutions were prepared using Analar grade salts and triply distilled water. The salts were dried at 150°C before use - this being essential for the deliquescent lithium chloride.

7.1.3 Acid Solutions

Concentrated nitric acid was diluted to give an approximately 1 mol dm$^{-3}$ solution which was used to adjust the pH of the rutile dispersions.

Hydrochloric acid was used in the quantitative analysis of the aminoalcohol solutions. From BDH standard volumetric reagent grade
hydrochloric acid suitable dilutions were made in order to obtain working standard solutions.

7.1.4 Alkali Solutions

Potassium hydroxide solution was used to adjust the pH of the rutile dispersions. Analar grade pellets were dissolved in triply distilled water as required and the fresh solution used for pH adjustment.

Sodium hydroxide solutions were used in the quantitative analysis of the aminoalcohol solutions. A 50% w/w solution was prepared using BP-grade pellets and triple distilled water from which carbon dioxide had been removed by boiling and purging with nitrogen. The viscous solution was allowed to stand in a plastic bottle so that precipitated sodium carbonate could settle. After a period of about 4 weeks the solution was filtered through a sintered glass Buchner funnel. An appropriate volume of the solution was removed and diluted with carbon dioxide free triple distilled water to give a working stock sodium hydroxide solution of about 0.4 mol dm$^{-3}$. The stock solution was stored in a borosilicate aspirator which was occasionally purged with nitrogen. A breather tube incorporating a sodalime trap was fitted to prevent entry of carbon dioxide during removal of stock solution. Repeated standardisation of the stock sodium hydroxide solution indicated that there was no loss of titratable base content over the period of use.

7.1.5 Aminoalcohols

The monoisopropylamine (MIPA) and the aminomethylpropanol (AMP) were obtained as pure compounds from Koch-Light. Table 7.1 shows some of the physical properties of these compounds. The value for the melting point of AMP results in handling problems such that it is difficult to make up aqueous solutions of known concentration without resorting to quantitative analysis. Being a viscous liquid at room temperature MIPA is easier to handle and hence the majority of the work was carried out using this aminoalcohol.
As the result of the slight volatility of the MIPA it was found that the most effective method of quantitatively making up a solution of the aminoalcohol involved transferring the pure MIPA, using a dropper, to a weighing bottle containing approximately 20 cm$^3$ of triple distilled water. The bottle was sealed with a ground glass stopper, the final weighing recorded, and the contents quantitatively transferred to a volumetric flask. The solution was then made up to the mark, again with triple distilled water. Solutions were generally made up when required, although analysis showed that there was no change in the MIPA content of a solution stored for 30 days in a standard volumetric flask.

The chemical structure of the organic molecules is shown in Fig. 7.1. The presence of the amino group confers basicity upon the molecules, the functional group being able to act as both a Bronsted base and Lewis base. The acid-base reactions with water can be represented as

\[
\text{-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{-NH}_3^+ + \text{OH}^- \quad (A)
\]

\[
\text{-NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{-NH}_2 + \text{H}_3\text{O}^+ \quad (B)
\]

The ionisation constant for reaction (B), i.e. the dissociation of the conjugate acid, is equivalent to a $pK_a$ value, at 25°C, of 9.68 for AMP and 9.45 for MIPA.
FIGURE 7.1 The chemical structures of MIPA and AMP
Thus at a pH of 9.45 half the MIPA molecules exist as the protonated amino group.

The hydroxyl functional group confers additional polarity to the molecules so that both organics are extremely soluble in water.

As a result of the basicity of aqueous solutions of aminoalcohols they act as buffers to pH changes. Even a solution of MIPA at low concentration (~5 x 10^{-3} mol dm^{-3}) can act as an effective buffer to the pH change brought about by absorption of atmospheric carbon dioxide.

7.1.6 Rutile Pigment

The titanium dioxide was supplied by Tioxide International. The pigment was in the rutile crystalline form and was of the Type I class of titanium dioxide. The supplied pigment was a milled calciner product subjected to a series of acid/base slurry washings. The initial wash was carried out at a solids concentration of 200 g dm^{-3} in 1 mol dm^{-3} sodium hydroxide at a temperature of 80°C. The pigment subsequently underwent several reslurry washings using distilled water before being reslurried at 200 g dm^{-3} in 0.1 mol dm^{-3} sulphuric acid at a temperature of 80°C. Several reslurry washings in distilled water followed before the filter cake was dried at 100°C. The pigment was crushed and dry milled in a fluid energy mill.

The pigment was analysed for impurities before and after the washing process. The results are shown in Table 7.2. The alumina and silica contents were less than 100 ppm in keeping with the Type I classification of the rutile. The zinc oxide content remained rather high after washing. The solubility of this impurity was checked by slurring the rutile at 200 g dm^{-3} in both 0.1 mol dm^{-3} nitric acid and 0.1 mol dm^{-3} MIPA. (The latter possessing a pH of about 10). Each slurry was stirred for 50 hours at room temperature and then filtered. The filtrates were analysed for zinc. The acid leached out the equivalent of 93 mg dm^{-3} of zinc oxide whereas the MIPA solution leached out less than 5 mg dm^{-3}. If all the zinc had been leached from the slurred rutile then the concentration would have been 280 mg dm^{-3} of zinc oxide. Since the majority of the experimental work was carried out under alkaline conditions the
leaching of zinc ions into the bulk solution was not considered to be a major problem.

TABLE 7.2. - Analysis of Rutile Sample CLDD 1281

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Before Wash</th>
<th>After Wash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% w/w</td>
<td>% w/w</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>(&lt;0.01)</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>(0.04)</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.31</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>(0.11)</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.23</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>(0.09)</td>
<td></td>
</tr>
<tr>
<td>S₅O₃</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(0.03)</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>2100 ppm</td>
<td>50 ppm</td>
</tr>
<tr>
<td></td>
<td>(40)</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>74 ppm</td>
<td>310 ppm</td>
</tr>
<tr>
<td></td>
<td>(600)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>30 ppm</td>
<td>30 ppm</td>
</tr>
</tbody>
</table>

The sodium content of the pigment increased as the result of washing. This was probably due to the addition of sodium hydroxide to the final wash as an aid to the rate of filtration. Leaching of these sodium ions would represent a significant contribution to the ionic strength of concentrated dispersions eg complete leaching would produce a contribution of 0.01 mol dm⁻³ to the ionic strength of a 50% w/w slurry.

In order to reduce the possible contamination of the dispersion medium, through the dissolution of ionic species from the rutile particles, the pigment was subjected to Soxhlet extraction with triple distilled water. Approximately 40 g of rutile was transferred to a Soxhlet thimble and about 500 cm³ triple distilled water used as the
extracting fluid. The process was continued for 15 days with the water being replaced with fresh triple distilled water from time to time. The first couple of 500 cm\(^3\) batches of wash water were cloudy due to the presence of suspended rutile particles and impurities. The remaining batches during the 15 day extraction were clear. At the end of the washing process the complete Soxhlet condenser and thimble were dried in an oven at 105°C. The thimble was extracted, the rutile pigment removed, and ground using a marble mortar and pestle. The powder was stored in a clear glass storage bottle. A mass yield of >97% was achieved.

The efficiency of the extraction was checked by measuring both the pH and conductivity of the distilled water as a function of the wash time. Equal volumes of wash liquid were used and after known extraction times the water was removed for the measurements and replaced with a fresh batch. The results of this study are presented in Table 7.3. The dissolution of ionic impurities from the rutile becomes increasingly less

\[
\begin{array}{c|cc}
\text{Cumulative Wash Time /hour} & \text{500 cm}^3 \text{ Batches of Wash Water} \\
& \text{pH} & \text{Specific Conductivity /ohm}^{-1} \text{ cm}^{-1} \\
21 & 8.1 & 7.62 \times 10^{-5} \\
43 & 7.70 & 1.17 \times 10^{-5} \\
65 & 7.05 & 4.97 \times 10^{-6} \\
87 & 6.70 & 3.48 \times 10^{-6} \\
157 & 6.25 & 4.22 \times 10^{-6} \\
227 & 6.11 & 2.81 \times 10^{-6} \\
345 & 6.18 & 3.33 \times 10^{-6} \\
\end{array}
\]

TABLE 7.3. - The Variation in pH and Specific Conductivity of the Pigment Wash Water
significant as the time of washing increases. After 13 days of extraction the final wash water gave a negative test with silver nitrate solution indicating the absence of chloride ions. It can be concluded that a 14 day Soxhlet extraction is sufficient to remove the vast majority of soluble ionic impurities held at or near to the rutile particle surface. A further study consisted of dispersing 0.98 g of washed rutile in 30 cm\(^3\) distilled water, maintaining the state of dispersion by end over end rotation for 26 days, centrifuging a sample, and measuring the conductivity of the supernatant. The latter was 5.20 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1} \) whereas a blank distilled water sample subjected to 26 days contact with a similar glass flask gave a value of 2.58 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}.

For the purposes of the majority of the experiments the washed rutile, stored in a glass storage bottle, was used. However, for the rheological measurements at high solids content it was impractical to use the washed pigment and so the unwashed rutile, as received, was used. As the result of the need for relatively large quantities of pigment a second batch of unwashed pigment (CLDD 1484) was used for a number of the rheological measurements. A similar leaching process as carried out on the CLDD 1281 batch was performed with the exceptions that nitric acid was used for the low pH leach and the order of leaching was reversed i.e. the final wash was with the acid. Analysis of the pigment gave the figures enclosed in brackets in Table 7.2. The important differences between the two leached pigments are that batch CLDD 1484 possesses

(i) a higher silica content; and
(ii) a higher sodium salt content.

Boiling 70 g of this pigment in 1dm\(^3\) distilled water for 15 mins gave about 0.2% soluble salts.

7.2 Experimental Techniques

This section describes the experimental methods used to study the behaviour of rutile in aqueous aminoalcohol solution. The experimental techniques covered the following topics -

- the quantitative analysis of aminoalcohol solutions;
• the measurement of the electrophoretic mobility of rutile particles;
• the measurement of the stability with respect to coagulation of rutile particles;
• the measurement of the degree of aminoalcohol adsorption by rutile particles;
• the measurement of the relative ease of dispersion of rutile particles in aqueous solution;
• the measurement of the relative ease of pigment redispersion as a function of the sedimentation force;
• the measurement of the viscosity of aqueous aminoalcohol solutions;
• the measurement of the rheological flow curves of concentrated dispersions of rutile;

7.2.1 Quantitative Analysis of Aminoalcohol Solutions

7.2.1.1 Introduction.

In order to be able to perform studies on the adsorption of aminoalcohols, in particular MIPA, by rutile a method for measuring the concentration of the organic species in aqueous solution is required. The analytical method should possess the following attributes -

(a) accuracy;
(b) reproducibility; and
(c) specificity.

Measurement of the adsorption isotherm necessitates accurate determination of the solution concentration of absorbate. The analytical method would need to be precise enough to differentiate between a $2.0 \times 10^{-2}$ and a $1.9 \times 10^{-2}$ mol dm$^{-3}$ solution. For an adsorption solution of 10 cm$^3$ such a decrease in concentration would be equivalent to a reduction in the adsorbate of $10^{-5}$ moles. If it is assumed that 0.2 g
adsorbent produces this concentration change and that a 5% precision in
the quantity of adsorbate adsorbed per unit weight of adsorbent is
required, then a precision of 0.18% in the solution concentrations of
adsorbate is necessary. The relationship between the precision of the
analytical method and that of the quantity of adsorbate adsorbed can
readily be derived, thus

\[ R^2 = \frac{P^2 \left( 1 + \frac{c^2}{c_0^2} \right)}{c^2 \left( 1 - \frac{c}{c_0} \right)} \]  

(7.1)

where \( P \) = fractional error in the analytical method;
\( R \) = fractional error in the quantity of adsorbate;
\( c_0, c \) = initial and equilibrium concentration of adsorbate in bulk
solution, respectively.

Figure 7.2 shows how the percentage error in the analytical method
depends on the adsorbate concentration ratio \( c/c_0 \) for various desired
percentage errors in the quantity of adsorbate removed from bulk
solution.

By selecting an analytical technique for the measurement of the
adsorbate solution concentration with a precision of better than 1% it is
possible to achieve values for the quantity of adsorbate adsorbed with a
precision better than about 10%, for solutions representing adsorbate
concentration ratios less than about 0.9.

There are several methods by which the concentration of an
aminoalcohol in aqueous solution could be determined. Spectrophotometric
analysis involves detection of one or both functional groups. However,
the precision is not sufficiently good. An analytical method which
involves stoichiometric reaction of one of the functional groups is the
preferred choice. Two such methods were used, both involving reaction of
the amino group. The first was derived from the ninhydrin analytical
Numbers refer to % error in quantity adsorbate.

FIGURE 7.2 Dependence of the accuracy of the analytical method on the concentration ratio as a function of the required precision in the quantity of adsorbate.
procedure used in the analysis of amino acid solutions and the second was the potentiometric titration of the protonated amino group. Both methods were relatively quick to perform, although neither was specific to an aminoalcohol.

A third technique involving the use of a Rayleigh interferometer was investigated but the precision was found to be significantly poorer than was acceptable.

The two selected analytical methods had to be closely studied to ensure that in each the correct procedure to obtain reliable results was followed.

7.2.1.2 Colourimetric Analysis

The ninhydrin colourimetric analysis for amino acids is a standard technique used by biochemists. The chemical reaction between the ninhydrin and the amino group results in the formation of a complex which strongly absorbs light at a wavelength of 570 nm. A spectrophotometer is used to measure the degree of light absorbance and hence the concentration of amino groups present in the original sample. Most classes of compound possessing an amino group will react to give a coloured complex, however the extinction coefficient at 570 nm will be different. Thus a calibration line is required for a given compound.

The method was first developed by Stein and Moore\textsuperscript{216} and was subsequently modified by several workers. The experimental procedure adopted in this study was based on that due to Rosen\textsuperscript{217}.

The following reagent solutions were prepared:

(1) Sodium cyanide solution \((9.51 \times 10^{-3}\) mol dm\(^{-3}\)).

(2) Acetate buffer solution: 360 g sodium acetate trihydrate and 67 cm\(^3\) glacial acetic acid were made up to 1 dm\(^{3}\) with triple distilled water. This buffer solution had a pH of 5.3 which ensured that the ninhydrin reaction mixture remained at the optimum pH.
(3) Acetate buffer - cyanide solution: the sodium cyanide solution was diluted 50-fold using the acetate buffer solution.

(4) Ninhydrin solution: ninhydrin was dissolved in distilled water and decolourised with activated carbon. The deep yellow solution was filtered hot. The filtrate was cooled and the crystallised ninhydrin filtered, washed with cold distilled water, dried, and stored in a darkened glass bottle. The purified crystals had a slight green tinge, were odourless, and gave a light yellow solution in water which turned dark yellow on boiling. A 3% (by weight) solution of ninhydrin in Analar methyl cellosolve (methoxy ethanol) was made up and the pale green solution transferred to a stoppered conical flask. The latter was covered with silver foil and stored in the dark. The purity of the methyl cellosolve was checked to ensure that no peroxides were present. Addition of a few drops to a 10% aqueous potassium iodide solution gave a clear solution thereby indicating the absence of peroxides.

(5) Diluent: a 1:1 (by volume) solution of distilled water and isopropanol was made up for use as the quenching and diluting reagent.

The general procedure involved boiling aliquots of the acetate-cyanide solution and ninhydrin solution together with the sample for a short time. Diluent was then added and on cooling the absorbance at 570 nm measured.

Studies on the effect of the boiling time and the time elapsed since addition of the diluent on the absorbance reading indicated that care had to be taken to ensure that all the samples, including the blanks, were given the same boiling time. Figure 7.3 shows how the absorbance of a blank sample varied with the boiling time and time since dilution. Figure 7.4 shows how the absorbance readings for standard amino acid samples varied as a function of boiling time. All the optical density readings were taken with respect to a blank boiled for 15 mins. The two graphs indicate that samples and blanks need to be boiled for the same period of time in order to obtain meaningful results. If a sample is subjected to a longer reaction time than the blank then too high an absorbance value would be measured, similarly a shorter reaction time
FIGURE 7.3
The absorbance of a blank sample as a function of the boiling time and time elapsed since dilution.

- X 35-55 mins. since dilution
- • 80-100 mins. since dilution
- □ 120-145 mins. since dilution

Absorbance vs. Boiling Time (mins.)

Values:
- X 0.22
- • 0.20
- □ 0.18
- • 0.16
- • 0.14
- • 0.12
- • 0.10
- • 0.08
- • 0.06
- • 0.04
- • 0.02
- • 0.00
The absorbance values of two amino acid solutions as a function of boiling time.
would give too low a value. The variation in absorbance shown in Fig. 7.4, for a given concentration of amino acid, can consequently be explained since all the readings were taken relative to a blank boiled for 15 mins.

The variation in absorbance of a 0.132 m mol dm$^{-3}$ solution of MIPA was determined as a function of reaction time. Each reading was taken with respect to a blank boiled for the appropriate time. The values indicated that the reaction between ninhydrin and MIPA was complete within 10 mins and that up to about 40 mins the absorbance was effectively constant.

On the basis of the above studies the following procedure was used for the quantitative analysis of aminoalcohol solutions by the ninhydrin reaction:

0.5 cm$^3$ each of the ninhydrin and acetate-cyanide solutions were pipetted into standard pyrex ground glass neck test tubes and 1 cm$^3$ of sample (containing between 0.02 and 0.4 micromoles of amino group) or distilled water added to each. A Hirsch filter funnel rubber sealing ring was pushed onto each test tube and a glass ball placed in the neck of each tube. The latter prevented the build up of gas pressure and minimised loss of liquid as the contents of the test tube was heated to 100°C. To ensure that each reaction mixture was heated for the same time each test tube was immersed in the boiling water bath at a staggered time interval of 45 s. The water bath possessed a lid with several location ports for introducing the test tubes. The size of a port was variable through the addition or removal of concentric rings of variable diameter. The Hirsch sealing rings allowed the test tubes to be immersed without touching the bottom of the bath and minimised the gaps through which steam could escape. After a reaction time of 15 mins a test tube was removed, 5 cm$^3$ of diluent added with the stream directed at the centre of the reaction mixture so as to entrain as much air as possible (oxidation of the mixture prevents additional formation of the coloured complex), the tube stoppered, and vigorously shaken. The solution was allowed to cool to room temperature and the absorbance at 570 nm with respect to a blank measured using an SP 600 spectrophotometer and 1 cm glass cells.
All samples on removal from the water bath were deep red but on dilution and cooling the colour changed to purple for the aminoalcohol samples or a pale yellow for the blank. The coloured complex was stable for several hours with no more than a 2% reduction in the absorbance at 570 nm after 3 hours. If the blank gave a reading against the diluent greater than about 0.12 the ninhydrin solution was discarded and a fresh solution made up. Two blanks were used for each analysis, the one giving the lowest reading with respect to the diluent and/or the more stable reading with respect to time was selected as reference against which the absorbance of the test samples was measured.

The procedure was checked by measuring the absorbance as a function of the sample concentration for β-alanine solutions. Figure 7.5 shows the calibration lines for two volumes of added diluent. The Beer-Lambert relationship is followed for both. The extinction coefficient for the purple complex can be calculated to be 2240 m² mol⁻¹ which compares with the literature value of 2160 m² mol⁻¹. The ratio of the two sample dilutions is 1.71 which compares with the ratio of the calibration line slopes of 1.77.

The calibration line for MIPA solutions was measured using two sets of standard solutions. Figure 7.6 shows the two sets of data. Linear regression gives the slopes and intercepts to be:

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>SLOPE</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1.761 ±0.034</td>
<td>-(0.030 ±0.010)</td>
</tr>
<tr>
<td>•</td>
<td>1.726 ±0.010</td>
<td>-(0.003 ±0.003)</td>
</tr>
</tbody>
</table>

The extinction coefficient of the coloured complex can be calculated to be 1220 m² mol⁻¹. This indicates that the colour yield for the ninhydrin reaction with MIPA is only 54% of that for the primary amino acids. The method is therefore less sensitive for MIPA than it is for the simple amino acids. In addition on occasions it was noted that the calibration line had a different slope, varying by up to ±10%. This was found to be the result of slight variations in the absorbance of the blanks. Consequently whenever an analysis was carried out four standard MIPA solutions were also included. The correlation coefficient for the resulting calibration line was always better than 0.9.
FIGURE 7.5 Calibration line for β-alanine

Absorbance

[Alanine]/mM

X 5cm$^3$ diluent
O 10cm$^3$ diluent
FIGURE 7.6 Calibration line for MIPA
The ninhydrin method was able to analyse down to MIPA concentrations of $0.02 \times 10^{-3}$ mol dm$^{-3}$ with a precision of about 2%.

7.2.1.3 Potentiometric Titration

The Bronsted basicity of the amino group permits quantitative analysis for aminoalcohols by an acid-base neutralisation reaction. Accuracy is obtained by performing a potentiometric titration in which the rate of change of pH with the titrant volume is measured. Several variants of the titration method were investigated.

The following procedure was used for each titration - the appropriate volume of sample was pipetted into a 50 cm$^3$ glass beaker and triple distilled water added to make the volume up to about 40 cm$^3$. A small magnetic stirrer was added, the beaker mounted on a magnetic stirrer motor, a Radiometer combination glass electrode immersed such that the liquid junction porous hole was submerged, and the tip of a 5 cm$^3$ burette located just below the solution surface. A stream of nitrogen gas was gently bubbled through the solution via a Pasteur pipette. The titration was performed, care being taken to add small aliquots of titrant when close to the neutralisation point. The burette could be read to ±0.001 cm$^3$ and the pH measured to ±0.01 units.

The variants of the titration method investigated included:

(a) direct titration against standard acid;
(b) addition of excess alkali and backtitration against standard acid;
(c) addition of excess acid and backtitration against standard alkali;
(d) performing the titrations in electrolyte solution;
(e) performing the titrations in the presence of formaldehyde.

Details of the studies carried out are given in Appendix A. A standard potentiometric technique for the quantitative analysis of MIPA samples, involving the use of formaldehyde solution, was developed.

Analar formaldehyde solution was neutralised to a pH value of about 6.5 by the addition of potassium hydroxide. Excess hydrochloric acid was added to the MIPA sample and the mixture titrated against standard sodium hydroxide. As the strong acid equivalence point was reached the alkali
was added in aliquots of less than 0.02 cm$^3$ and the rate of nitrogen bubbling was increased. Once a pH reading of between 6 and 7.5 had been attained the volume of alkali added was recorded and 5 cm$^3$ of the neutralised formaldehyde solution added. The pH immediately fell to a value of about 4.6. On reaching a steady reading the additions of the alkali were continued. After each aliquot the pH would gradually decrease with time but this did not influence the final answer. Between pH values of 6 and 9.5 the additions of alkali were kept small (less than 0.03 cm$^3$). The MIPA equivalence point was well defined and reproducible. Figure 7.7 shows the form of a typical titration curve. The MIPA end point was determined directly from the graph. The total concentration of MIPA, present in solution as the free base or conjugate acid, could readily be calculated. The concentration of MIPA existing in the neutral form, ie with the free amino group, in a sample of partially neutralised MIPA could also be determined from the same titration. The difference between the number of moles hydrochloric acid added and the number of moles titrated by the alkali was equal to the number of moles of MIPA present as the neutral species.

The sodium hydroxide titrant was always standardised against hydrochloric acid at the beginning and end of any day during which quantitative MIPA analysis was carried out. Alkali concentrations between 0.1 and 0.4 mol dm$^{-3}$ were found to be the most useful. The stock sodium hydroxide solution was diluted, where required, using carbon dioxide free triple distilled water. Once the burette was filled with the alkali a soda-lime trap was fitted to prevent the absorption of atmospheric carbon dioxide.

Hydrochloric acid concentrations in the range 0.08-0.2 mol dm$^{-3}$ were used.

The titration was found to give an accuracy and precision of better than 1%. Duplicate titrations were performed in the majority of cases.

A suitable technique for the quantitative analysis of AMP samples was investigated in a similar fashion. Direct titration against strong acid gave a sharp, well defined end-point, however, the standard method devised for MIPA samples did not give a satisfactory end-point. Although
The form of the potentiometric titration curve for MPA

FIGURE 7.7

pH

Volume Alkali

HCHO Addition

Aminoalcohol End-point
the range of pH values associated with the equivalence point was sufficiently large the corresponding range of titrant volume was considered to be excessive. Sufficiently well defined end-points were found if the AMP sample was titrated against strong acid in the presence of excess alkali and a few drops of neutral formaldehyde solution. An accuracy of about 1.2% was possible using this titration method.

The analysis of triethanolamine (TEA) samples was found to be most accurate if titration against strong alkali in the presence of excess acid, with no added formaldehyde, was performed. Once again the standard method devised for MIPA gave an unsatisfactory end-point.

Propylamine and ammonia solutions were analysed using the method developed for MIPA samples, again with an accuracy and reproducibility better than 1%.

7.2.1.4 Summary

Both the ninhydrin colourimetric method and the potentiometric titration method were used for the quantitative analysis of aqueous aminoalcohol samples. The former was used for concentrations less than 2 x 10^{-3} mol dm^{-3}, the lower limit being about 0.02 x 10^{-3} mol dm^{-3}.

7.2.2 Electrophoresis

Electrophoresis is one of four related phenomena which involve inducing relative motion between a charged colloidal particle and its electrical double layer. The differential movement produces a plane of shear, the electrical potential of which is measured by these four electrokinetic techniques. As discussed in Chapter 3 the plane of shear is normally assumed to coincide with the Stern plane and so the measured potential, i.e. the zeta potential, can be equated with the Stern potential \( \Phi_d \). Electrophoresis can therefore provide information on the properties of the electrical double layer as a function of dispersion medium composition.

The technique involves applying a dc electrical field to a dilute dispersion and measuring the electrophoretic mobility. Conversion to the
equivalent zeta potential involves the use of either equations or tabulated functions which are derived from theoretical analyses of the hydrodynamic and electrical behaviour of the system. Several expressions relating the mobility to the zeta potential have been derived, each finding application under different conditions. As a rough guide, for aqueous dispersions with $\kappa a$ values $>10$ the following simple relationship can be used (mobility in units of $\mu$m s$^{-1}$ per V cm$^{-1}$)

\[ \zeta = 12.85 \mu_{EP} \text{ mV (25°C)} \]

Various electrophoresis techniques exist including microelectrophoresis, moving boundary methods, and the newer laser Doppler electrophoresis. The former method, which involves following the motion of individual particles using a microscope, is the most common. It possesses the following advantages -

(i) the particles are observed in their normal dispersion environment;

(ii) the high magnification leads to short observation times and so the particle environment has little chance to change within the timescale of an observation;

(iii) very dilute dispersions can be studied so that coagulation can be kept at a low rate;

(iv) a wider range of ionic strengths can be studied as the result of the minimal particle interactions;

(v) time effects can be observed by noting the behaviour of a single particle over a suitable period of time; and

(vi) in a polydisperse sol only those particles within a desired size range can be observed.

However, the laser Doppler methods have the advantage that particles of radius down to a few nanometers can be studied.
Stationary Levels. Microelectrophoresis is performed using a glass cell within which resides the dilute dispersion. On the application of the electric field a well defined set of flow conditions is set up. The dispersion medium experiences electro-osmotic flow as the result of the surface charge on the glass walls. The counter-ions, within the double layer associated with the glass surface, migrate towards the electrode of the same polarity as the surface charge (or strictly speaking same sign as the Stern layer charge). This motion is transferred to all the liquid layers by frictional forces so that a state is rapidly reached in which the entire liquid content of the cell moves with a uniform velocity. Since the cell is closed by the electrodes at either end there exists a return flow of liquid. Figure 7.8 shows the situation for a cylindrical microelectrophoresis cell. Unlike the electro-osmotic flow, \( V_{EO} \), which is uniform across the cell, the reverse flow has a maximum value down the central axis of the cell with a monotonic decrease to zero on moving towards the walls. By applying Poiseuille's law the location of the two positions within the cell at which there is no net liquid velocity can be determined. For a cell of circular cross-section there are two stationary levels located at 0.146 of the internal cell diameter from each wall. Therefore only at these two positions can the electrophoretic velocity of the dispersed particles be measured directly. The overall profile of dispersed particle velocity through the cell is parabolic. However, the rate of change of velocity with cell depth tends to be large in the region of the stationary levels so that, both inaccuracies in focussing and too large a depth of focus can lead to a significant error in the measured electrophoretic velocity. However, it is not necessary to restrict observations to the stationary levels in a cell. Measurements of particle velocities can be made at any level within the cell and an equation used to permit calculation of \( V_{EP} \), the electrophoretic velocity. The equation can be derived from the condition of zero overall fluid transport within the cell. Equation 7.2 applies to cells of circular cross-section, such as was used in this work.

\[
V = V_{EP} + V_{EO} \left(2 \left(\frac{r}{a}\right)^2 - 1\right)
\] (7.2)

where \( V \) is the observed particle velocity,
\( a \) is the inner radius of the cell, and
\( r \) is the distance from the centre of the cell.
FIGURE 7.8 The flow conditions within a closed cylindrical electrophoresis cell in the presence of a d.c. electric field
By plotting $V$ against $(r/a)^2$ a straight line should be obtained, the equation for which enables both $V_{EP}$ and $V_{EO}$ to be calculated.

**Microelectrophoresis Cell.** The commonly met microelectrophoresis cells are either of rectangular or circular cross-section and they may be thick - or thin-walled. Each type has its advantages and therefore areas of application. For aqueous dispersions the cylindrical cell is the preferred choice. The advantages of this cell include -

(i) the small cross-sectional area (typically 0.03 cm$^2$) gives rise to small electric currents so that problems due to polarisation can be avoided;

(ii) the volume of dispersion required to fill the cell is small;

(iii) the cell can be illuminated from a direction perpendicular to that of observation which permits easier detection of very small particles;

(iv) more effective control of the temperature is possible leading to the minimisation of troublesome convection currents.

However, cylindrical cells possess poorer optical properties since considerable distortion of the image of a dispersed particle can occur unless special precautions are taken. In addition, each level in the cell is a cylindrical plane within the tube and is consequently not flat in the field of view of the microscope. The geometry of the cell is such that observation is made via a planoconcave cylindrical lens (the outer surface is ground flat) and hence focussing on dispersed particles at a given level is complicated. The image is distorted as the result of refraction. It can be shown that the optical correction to the measured depth in the cell is negligible in cases where both the cell and microscope objective lens are immersed in water.

The cylindrical cell may be thick-walled, as with the Mattson cell$^{218}$, or thin-walled as with the van Gils cell$^{219}$. The latter has the added advantage that no optical correction need be applied to the measured depth within the cell.
A van Gils microelectrophoresis cell supported within a metal frame, both for added strength and to give a steady location in the electrophoresis instrument, was used in the present study. The fine capillary tube was attached by wider diameter tube to a reservoir at each end. The reservoirs had ground glass necks so that the electrodes could be inserted to give a firm fit. The dimensions of the capillary section of the cell were measured with the aid of the microelectrophoresis apparatus, a Rank Bros MK3 version. Micrometer scale readings for the location of the outer and inner tube walls, top and bottom of the cell, were recorded several times. The backlash in the micrometer was taken into account by approaching the wall from both directions and averaging the measurements. The van Gils cell had the following dimensions:

- upper wall thickness: 89 ±4 μm
- lower wall thickness: 74 ±5 μm
- capillary diameter: 1839 ±5 μm

The effective cell length was determined by measuring the cell constant for a series of standard potassium chloride solutions at 25°C. The conductivity of the electrolyte solutions, in the range 0.001 mol dm⁻³ to 0.100 mol dm⁻³, contained in the cell was measured using a standard conductivity meter connected across the platinum electrodes. The mean cell constant (effective length/cross-sectional area) was found to be (3.29 ±0.07) x 10² cm⁻¹. The effective cell length was therefore (8.78 ±0.19) cm, which compared with a ruler length of 8.2 cm. A second van Gils cell was also used and its characteristic dimensions were:

- capillary diameter: 946 μm
- effective cell length: (7.46 ±0.09) cm
- geometric capillary length: 7.3 cm

The cells were kept meticulously clean to minimise contamination of the internal walls of the capillary. When necessary the cell would be filled with a 16% V/V solution of the general purpose glass cleaning detergent RBS-25 and left for no more than 30 mins. The cell would then be rinsed out with copious amounts of single distilled water and then stored filled with triple distilled water. Between electrophoresis experiments on the same day the old dispersion was poured away and, after
rinsing with copious quantities of distilled water, the cell was refilled with triple distilled water until required for a subsequent test.

**Microelectrophoresis Apparatus.** A commercial unit (Rank Bros MK3) was used for the measurement of electrophoretic mobilities. The optical components were checked for calibration where necessary. The important parameters were -

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>depth of focus</td>
<td>20 μm</td>
</tr>
<tr>
<td>magnification</td>
<td>X 340</td>
</tr>
<tr>
<td>eyepiece graticule side</td>
<td>29 ±1 μm</td>
</tr>
</tbody>
</table>

The magnification was estimated from the combination of the marked magnifications of the eyepiece and objective, and the observation that the size of the graticule squares was a function of whether the objective was submerged under water or in air. The calibration of the eyepiece graticule square dimensions was accomplished by immersing a standard scale, etched on a glass slide, in the water bath of the microelectrophoresis apparatus.

The reading on the water bath thermostat dial was checked against the measured temperature and found to be slightly in error. Therefore for all experiments the water bath temperature was directly measured.

The voltage output of the supply unit was checked for accuracy and reproducibility. A dilute solution of potassium chloride was added to the electrophoresis cell and the platinum foil electrodes inserted. A digital voltmeter was set up across the electrode terminals and its reading compared with that of the Rank power supply for various dial settings. The results showed that -

- the actual voltage was, typically, more than 30% higher than the nominal setting;
- the actual voltages were not reproducible;
- the actual voltage was not symmetrical with respect to electrode polarity reversal.
On blacking the platinum foils (see later) and repeating the test these shortcomings were eliminated. The power supply dial reading now coincided with the voltmeter reading to within 1%, for both electrode polarities. At a setting of zero the voltmeter also read zero so that the power supply was deemed to be acceptable.

Electrodes. Platinum foil bonded to a piece of silver wire passing through a glass holder was used as an electrode. The holder included a ground glass cone which enabled an air tight fit to be obtained when in position in the electrophoresis cell reservoirs. The platinum foil was arranged as an open ended cylinder with diameter of about 3 mm. The external section of the silver wire was attached to a standard copper insulated wire, the other end of which terminated in a hook connector.

In order to function in an acceptable manner the electrodes had to possess the following properties -

- equal particle speeds on reversal of the electrode polarity;
- a linear relationship between particle speed, at a given position in the cell, and applied voltage.

If the observed behaviour did not produce either or both of these criteria then the electrodes were cleaned or coated with platinum black to minimise polarisation effects by an increase in the effective area. It was however, often sufficient to merely clean both electrodes by immersing in boiling 2 mol dm$^{-3}$ sulphuric acid followed by hot distilled water. However, if a check on particle speed, at a fixed cell level, as a function of the applied voltage failed to give a linear plot with a correlation coefficient greater than 0.98 and an intercept of (0,0), (within error), then the platinum foils were coated with a layer of platinum black.

Fresh platinum was deposited on each electrode surface by using the latter as the cathode in the electrolysis of chloroplatinic acid solution. The electrode was immersed in the latter and using a copper anode a suitable current from an accumulator (54 A hr), adjustable using a variable resistor (setting usually at 25 Ω), was passed through the
solution. On removal the platinum foil was coated black by the presence of the deposited platinum. The foil was first cleaned in hot sulphuric acid and then distilled water before being stored, immersed in triple distilled water.

**Experimental Procedure.** The measurement of the particle electrophoretic mobility for a dilute dispersion was carried out in the following standard way -

(1) **Preparation of the Dispersion.** The pH of about 40 cm³ of dispersion medium was measured and adjusted where necessary. A sample was then transferred to a small sample bottle and a microspatula used to add a small quantity of the rutile powder. The latter was subsequently dispersed in the solution by ultrasonic irradiation. Sufficient volume of this dispersion was mixed into the remainder of the dispersion medium so that a faintly white sol was obtained. The pH was remeasured, an aliquot transferred to a clean stoppered sample bottle, and the sol subjected to a further period of ultrasonic irradiation. The sol was then ready for use. For a dispersion within the pH range 6-8 nitrogen was bubbled through the sample during the pH measurement.

(2) **Preparation of the Microelectrophoresis Apparatus.** The van Gils cell was rinsed with several portions of the dispersion before being mounted into the water bath of the microelectrophoresis apparatus. The cell was then filled with the sol until the latter overflowed from both reservoirs. The electrodes were inserted carefully, so as to avoid trapping air bubbles, and the cables connected to the voltage supply terminals. The optical components were then assembled, care being taken to avoid trapping an air bubble on the lens of the submerged objective. The locations of both inner walls of the capillary section of the cell were measured several times so that both the radius, a, and the value of r for each level within the cell to be studied could be calculated. The actual micrometer scale readings corresponding to the values of the factor \((r/a)^2\) (0.1 to 1 in steps of 0.1) were then evaluated. During this time the contents of the van Gils cell were able to reach thermal equilibrium. All measurements were carried out at 25°C.
(3) Measuring the Mobilities. A convention for describing the motion of the particles under the action of the electric field had to be defined. The system was arranged such that the centre of the capillary tube was in view through the binocular microscope. The observed section ran from the top to the bottom of the field of vision and so application of the electric field caused the particles to move up or down. There was no optical reversal of motion in the two planes containing the long axis of the capillary and so upwards motion corresponded with migration towards the electrode at the back of the water bath. This top electrode was always connected such that it was positive when the voltage supply polarity switch was up.

The odd values of the factor \((r/a)^2\) were taken in the upper half of the cell and the even values in the lower. Particle velocities were measured beginning at the upper inner wall progressing towards the centre and then at the lower inner wall progressing towards the centre. At each of the 10 levels at least 10 particle transit times across a chosen number of microscope graticule squares were measured, the electrode polarity being reversed between successive timings. The direction of movement was also noted. Once all the levels had been studied a few repeat timings at one of the levels were taken in order to check for ageing effects.

(4) Analysis of the Particle Timings. At each cell level the average reciprocal time (and standard deviation) was calculated for both the electrode polarities. If the two were within experimental error then all the timings were combined to give an overall average reciprocal time for that level. The corresponding value of the factor \((r/a)^2\) was calculated for each cell level from a knowledge of the cell diameter and the measured micrometer scale readings. The appropriate particle velocities, for each level, were calculated by multiplying the average reciprocal time by the number of graticule squares over which the timing was taken. Convention was chosen such that motion towards the positive electrode gave a positive velocity. A plot of particle velocity against \((r/a)^2\) was made for both the upper five cell levels and the lower five. Under ideal conditions both would be straight lines possessing the same slope and intercept ie all the points would lie on the same line. Linear regression analysis was applied to both lines and to the line involving
all the \((r/a)^2\) values. Graphical plots of the data points were also made. Only if the slopes and intercepts of the lines, for the upper and lower cell levels, were within error and if the combined line had a correlation coefficient greater than 0.98 was the data taken as being good enough to calculate the electrophoretic and electro-osmotic mobilities.

(5) **Calculation of Particle Mobility.** The electrophoretic mobility of the particles was calculated by dividing the velocity, determined from the graph, by the electric field strength applied.

(6) **Sources of Error.** There are numerous potential sources of error associated with the determination of particle electrophoretic velocities. These include:

- micrometer backlash;

- depth of focus of the microscope. The finite value means that particles in levels above and below the required level can be observed. Typically this gives rise to an error of about 3% in a single particle velocity measurement;

- Brownian motion of the particles is superimposed on the observed particle movement under the action of the electric field. The magnitude of the error will depend both upon the particle size and the distance over which the particle is timed. Typically the error in a single velocity measurement would be about 2%;

- poor behaviour of the electrodes. Polarisation of the electrodes with consequent poor performance can occur and would be shown up as non-agreement of timings with respect to polarity reversal;

- asymmetric flow conditions within the cell. The existence of convection currents or small leaks can introduce significant additional velocity components. However, asymmetric flow induced by the existence of different electro-osmotic potentials at the upper and lower walls is the more common condition. Non-equal potentials displace the stationary levels from their normal
positions within the cell thereby giving rise to an inability to
determine the electrophoretic mobility of a particle. Such an
effect manifests itself by giving two distinct lines when the
observed particle velocity is plotted against \((r/a)^2\) for the
upper and lower levels. Attention to cell cleanliness minimises
such effects;

- timing errors due to human error;

- since the same particle is preferably not timed several times at
a given level there will, of necessity, be a range of particle
speeds reflecting a range of mobilities and, hence zeta
potentials.

The above errors are taken into account by the use of linear regres-
sion analysis. Converting the resultant electrophoretic velocity into
the corresponding mobility introduces a further set of errors due to -

- the measured effective cell length;
- the dimension of the microscope graticule;
- uncertainty in the applied voltage.

In practice only the first of these is of any significance. The
electrophoretic mobilities tabulated in the results tables are quoted
with the errors determined from the regression analysis and the measured
error in the cell length.

7.2.3 Particle Counting

Direct particle counting as a function of time was used to measure
the stability of a dilute dispersion with respect to coagulation. The
kinetic theory of coagulation due to Smoluchowski shows that the plot of
reciprocal particle number concentration against time should be linear,
at least up to the half-life of the dispersion. The Smoluchowski rate
expression gives, on integration,

\[
\frac{1}{N} = \frac{1}{N_0} + k_r t \tag{7.3}
\]
where $N$ is the number of primary particles in unit volume of dispersion at time $t$;

$N_0$ is the initial number of primary particles, and

$k_r$ is the second order rate constant.

The rate of change of particle number with respect to time is a function of the particle number at any given time and the rate constant. Thus determination of $k_r$, from the slope of the $1/N$ versus $t$ plot, gives a measure of the stability of the dispersion.

The dispersion was prepared by dispersing rutile powder in about 40 cm$^3$ of aqueous solution. An initial count to obtain the average particle number was carried out each time to ensure that neither too little nor too much rutile was present - a particle number density of between $2 \times 10^{14}$ and $6 \times 10^{14}$ m$^{-3}$ was satisfactory for counting purposes. Once a satisfactory particle number had been obtained the dispersion was subjected to a further dose of ultrasonic irradiation before being transferred to a thermostatted water bath. Pyrex conical flasks (50 cm$^3$) with ground glass stoppers were the preferred choice of container and were held in place, partially immersed in the water bath, by clips. Several dispersions could be set up simultaneously in this manner. Time zero was taken to be when the dispersion was removed from the ultrasonic water tank. At known times samples of the dispersion were removed using a fine-tipped dropper and transferred to the counting cell. The number of particles within the boundaries of four graticule squares were counted a minimum of four times for each sample.

The correct choice of counting vessel was important. Four different types were considered -

(a) a bacteria counting chamber;
(b) a small path length spectrophotometric cell;
(c) a standard spectrophotometric cell;
(d) a microelectrophoresis cell.

The latter two permit observation of the dispersion without the need to remove samples, thereby not disturbing the particles. However, type (c) is difficult to maintain at a constant temperature and hence convection currents hinder the counting process. The microelectrophoresis cell
restricts measurements to a single dispersion. But the small path length cell and the counting chamber have neither of these drawbacks. The latter has a total depth less than the optical depth of focus and hence all particles within the chamber can be observed. The former can typically hold a sample of dispersion with a depth, in the direction of observation, greater than that associated with the depth of focus but sufficiently small that internal flow of the liquid is negligible. Initial particle counts were carried out to assess the relative merits of these two types.

A Vickers binocular microscope, (possessing various filters to minimise heat transfer from the halogen light source and to give different coloured backgrounds for the observations), with a dark field condenser was exclusively used for the particle counting. A background colour of either emerald green or light blue was chosen since each permitted good resolution of the particles with minimum eyestrain. The working dimensions for the counting were:

- graticule square length: 41.5 μm
- depth of focus: 19.8 ±1.1 μm
- dispersion volume in count: $1.36 \times 10^{-13}$ m³

After numerous comparisons between the counting cell and the bacteria counting chamber it was concluded that, although the particles were less clearly resolved in the former, the counting cell was the superior type. Two important disadvantages of the bacteria chambers were discovered:

- poor distribution of particles leading to regions of high particle numbers and regions of low numbers was often found;

- flow of surplus dispersion from outwith the boundaries of the chamber could significantly affect the particle count. Despite applying a large thumb pressure to the glass cover slip, which covered the counting chamber, dispersion medium from the surrounding areas could often be observed to flow into the counting chamber between the cover slip and plastic sealing ring of the bacteria counting glass slide.
Therefore oblong glass cells of wall thickness 880 μm and internal thicknesses of between 800 and 2000 μm were used to carry out the particle counting. Between actual particle counts the cells were cleaned with distilled water to minimise errors due to the presence of extraneous particles. When necessary the cells were cleaned with a dilute solution of RBS-25. In use the cells were simple to use and the only particle motion observed was that of Brownian motion or sedimentation. It was noted that particle resolution became slightly enhanced as the total number of dispersed particles decreased.

7.2.4 Adsorption Isotherms

The specific surface area of the washed rutile was determined by carrying out a multi-point BET isotherm using nitrogen gas.

Investigations into the nature of the interaction between the rutile surface and aqueous MIPA solutions were carried out by measuring the adsorption isotherm, at 25°C, for a variety of solution conditions. Variables studied included MIPA concentration, time of adsorption, pH, and ionic strength. The following procedure was adopted for the measurement of an isotherm.

A quantity of rutile was accurately weighed into a standard Quickfit ground-glass neck test-tube. Up to 8 such tubes were made up for each isotherm. To each tube 10 cm³ of the appropriate solution was added and the tube tightly stoppered. The pigment was dispersed in the solution by subjecting each tube to ultrasonic irradiation for a minimum of 30 mins. During this time each tube was regularly removed, inverted several times, and replaced in the ultrasonic bath. Once dispersion was complete each tube was removed, the tightness of the ground glass stopper checked, and paraffin wax tape used to seal the stopper and test-tube neck. The tubes were clipped into position on the rotating section of an end-over-end (EOE) apparatus which was submerged in a large thermostat water tank. The contents of each test-tube were maintained in a dispersed state through the gentle mixing caused by the two tube inversions per revolution. The rotational speed of the EOE was typically about 35 rpm. At the end of the selected adsorption time the tubes were removed and the pigment separated from the dispersion medium by centrifugal
sedimentation. A two stage separation was found to be necessary in order to obtain satisfactory clarity of the dispersion medium. The dispersions were subjected to an acceleration of approx 70,000 g in a 10 x 10 cm$^3$ angle rotor for about 40 mins. The supernatant of each sedimented dispersion was carefully removed using a Pasteur pipette. Each of these solutions were subsequently subjected to an acceleration of approx 100,000 g in a 3 x 3 cm$^3$ swing-out rotor for about 30 mins. In this manner at least 6 cm$^3$ of the adsorption isotherm solution was available for quantitative analysis. An MSE ultracentrifuge type Superspeed 50 was used.

Duplicate analysis for MIPA concentration was performed on all the isotherm solutions and the corresponding before adsorption solutions.

Graphs of the quantity of MIPA adsorbed per unit weight of rutile against the post-adsorption solution MIPA concentration were plotted.

Although the best method of measuring adsorption isotherms involves optimising the weight of adsorbent for each initial concentration of adsorbate so as to obtain an acceptable quantity of adsorbed species, such a procedure is time-consuming and would necessitate repetition for adsorbate solutions which, in spite of being of the same concentration, differ in a property such as pH or ionic strength. The isotherms reported in this work were performed using roughly 0.2 g pigment in 10 cm$^3$ of adsorbate solution (giving a total rutile surface area of about 1.4 m$^2$). The error analysis developed in section 7.2.1.1 indicates that, given the 1% accuracy of the analytical method, percentage errors of less than 20% in the quantity of solute adsorbed for fractional changes in the bulk solute concentration of greater than 7%.

7.2.5 Dispersibility of Rutile Pigment

The paint industry, of necessity, has a deep interest in the degree of dispersion of a pigment in a given dispersion medium. Numerous empirical and semi-empirical techniques exist for assessing the degree of dispersion of concentrated sols. However, it was considered to be of more use to study the degree of dispersion in dilute sols using the method adopted by Parfitt and Wharton.
The ease with which rutile pigment was dispersed to give primary particles in aqueous solution was studied as a function of solution composition. Roughly 10 mg of rutile was weighed out accurately into a clean Quickfit test tube and 10 cm$^3$ of solution added carefully by allowing it to flow down the walls. The ground glass stopper was fitted tightly, the neck wrapped with Parafilm, and the tube attached to an EOE apparatus submerged in a 25°C water bath. Dispersion of the rutile was therefore achieved through gentle tube inversion - a rotational speed of 15 rpm (equivalent to one inversion every 2 s) was chosen. After a known time had elapsed the tube was removed and a sample of the dispersion taken for particle counting. If necessary the aliquot of dispersion was diluted by a known amount with triple distilled water prior to the particle count. In this manner the number density of primary particles dispersed per unit weight of rutile powder could be determined as a function both of the number of inversions and of the dispersion medium composition. Numerous such experiments were performed in order to assess the effect of the following factors on the ease of dispersion - MIPA concentration, pH, ionic strength, type of electrolyte, number of inversions, and combinations of all these.

7.2.6 Centrifugation and the Force of Coagulation

A novel technique for studying the coagulation behaviour of aqueous hydrophobic dispersions without the need for the addition of electrolyte has been developed by Melville, Willis and Smith$^{222}$. The method involves measuring the force required to achieve coagulation by subjecting the sol to various centrifugal accelerations and assessing the ease of subsequent redispersion of the sedimented pigment.

A similar procedure was developed to assess the dependence of the force, necessary for aggregation of the rutile, upon the composition of the aqueous dispersion medium. Approximately 3 mg of rutile pigment was dispersed in about 30 cm$^3$ of aqueous solution and the particle number determined by direct microscopic counting. A sample was transferred to a clean polypropylene centrifuge tube and the top securely sealed. Using a 3 x 20 cm$^3$ swing-out rotor (radius 13.08 cm) the sample was centrifuged in an MSE Superspeed 50 ultra-centrifuge at a known speed for a set time. The centrifuge tube was then removed, firmly stoppered, and mechanically
rotated EOE at 15 rpm for 15 minutes (at 25°C). At the end of this redispersion stage a sample of the dispersion was removed, diluted in distilled water, if necessary, and the number of primary particles per unit volume counted. The fraction of original particles redispersed as a function both of the sedimenting force and solution composition could then be determined. The variables studied included MIPA concentration, pH, ionic strength, electrolyte type, and, obviously, centrifugal force.

Any polypropylene centrifuge tube which became scored or etched on its inner walls was replaced because of the potential inhibition of rutile particle redispersion by entrapment.

7.2.7 Dynamic Viscosity of Aminoalcohol Solutions

The presence of two polar functional group capable of participation in hydrogen bonding suggests that the aminoalcohol molecule could interfere with the microscopic structure of water, i.e. act as a structure maker or structure breaker. Therefore the viscosity of water as a function of MIPA concentration, pH, ionic strength, and electrolyte type was investigated.

The relative viscosities of the aqueous solutions were measured, at 25°C, using an Ubellohde capillary viscometer. Triple distilled water, filtered through a sintered glass buchner funnel, was used as the reference. All solutions were similarly filtered to avoid introducing dirt particles into the viscometer. The latter was rinsed, first with distilled water, then with Analar acetone, and finally dried in a stream of nitrogen immediately prior to about 40 cm³ of solution being transferred to its reservoir. At least two measurements were made of the time taken by the solution to pass the two viscometer markings. The relative viscosity of the solution was calculated as the ratio of its flow time to that of distilled water, assuming the densities of the solution and distilled water were equal. The latter was a reasonable assumption for the solutions studied.

The viscosities of MIPA solutions as a function of concentration, pH, ionic strength, and electrolyte type were measured.
7.2.8 Rheological Behaviour of Rutile Slurries

The study of the flow properties of high solids content aqueous slurries can give important information concerning the state of dispersion of the slurry, the nature of the particle interactions, and the effect of additives. By measuring the shear stress - shear rate relationship of aqueous rutile slurries as a function of the MIPA content of the dispersion medium it was hoped that through such studies a deeper insight into the cause-and-effect properties of MIPA could be reached.

7.2.8.1 Viscometer. A rotating coaxial type viscometer was used to carry out all the measurements. A Haake model "Rotovisco" rotating viscometer with the MV and SV range of bobs and cups was exclusively used. The system was used with a dual measuring head and thermostatted water jacket. A range of ten bob speeds, 3-486 rpm, could be used and the dual measuring head extended the useful torque range of a given bob and cup combination.

7.2.8.2 Calibration of the Viscometer. The five bob and cup combinations were calibrated using standard oils whose flow behaviour was Newtonian and whose viscosity was known at 25°C. This procedure was necessary since parameters which are a function of the bob and cup are required to convert the instrument readings into actual shear stress and shear rate values.

7.2.8.3 Preparation of the Viscometer. The Haake Rotovisco was allowed to warm up for a minimum of 15 mins before measurements were taken. It was necessary to reset the zero scale reading when a different bob was fitted to the measuring head. The scale was set to zero, using the appropriate adjusting screw, with the bob rotating (setting 3) in air. This was repeated for both ranges of the measuring head. The corresponding cup was filled to the appropriate level with the slurry sample and then fitted to the measuring head, within the water jacket. The measurements of the equilibrium flow behaviour of the sample were then recorded.

7.2.8.4 Preparation of the Slurry. The high solids content rutile slurries were made up in a 500 cm³ plastic storage bottle. The unwashed
rutile powder (CLDD 1281) was used because of the difficulty in producing the washed pigment in sufficient quantities. For each slurry a known weight of pigment and aqueous solution were mixed together in stages. A palate knife was used to achieve the initial mixing and then a 12 bladed crown, disc-type mixing rotor, attached to a Black and Decker drill, was used to obtain final dispersion and mixing. The drill was set to a nominal speed of 2400 rpm and the contents of the plastic bottle subjected to the action of the high speed impeller for a period of about 60 mins. The position of the rotor within the slurry was regularly varied during the mixing and deagglomeration process in order to prevent the formation of "dead zones".

Although the optimum geometric factors for this type of milling were adhered to as closely as possible it was not always practical to do so. If the initial slurry was too viscous, as indicated by the observation that the slurry could not fill the hole left by the impeller on its removal, then additional distilled water was added until the slurry became sufficiently fluid for efficient mixing. After mixing a sample of the slurry was transferred to the appropriate viscometer cup and the remainder covered to minimise loss of water. The effect of the addition of small volumes of MIPA solutions, of various compositions, was assessed by incorporating these aliquots into a known weight of slurry. The "new" slurry was hand mixed using a palate knife before being subjected to the more thorough mixing and dispersion of the high speed impeller. A sample of this slurry was then studied in the viscometer. This process of sequentially adding aliquots of MIPA solutions was repeated until the slurry behaved as a low viscosity Newtonian fluid.

The solids content of a slurry was measured on initial preparation and after all the MIPA additions had been made. A known weight of slurry was dried at 105°C, reweighed and the solids content calculated.

A few drops of slurry were, on occasions, diluted in distilled water and a sample observed under the microscope to check for the presence of agglomerates. This was carried out as a rapid, qualitative assessment of the degree of dispersion of the slurry, but being aware of the possible influence of the dilution process.
7.2.9 pH Measurements

All pH measurements were made using a Radiometer meter and combination glass electrode. The pH meter possessed the facilities of a temperature control and a control for adjusting the Nernst slope to follow the electrode response. A dual range switch enabled the pH range 4-10 to be expanded. The pH could be read to ±0.01 units.

The combination electrode was kept immersed in a solution of buffer at pH 4 when not required. Fast response of the electrode was ensured by this procedure. The height of the saturated potassium chloride solution in the electrode was maintained at a level above that of the storage solution (and sample solution when carrying out a measurement) in order to provide a hydrostatic pressure for the flow of the electrolyte solution through the liquid junction porous plug into the storage or sample solution.

Calibration of the combination electrode was regularly carried out (each day on which pH measurements were to be made) using standard buffer solutions with pH values of 4.01 and 9.18, at 25°C.

Both standards were primary buffers and were prepared from buffer tablets and distilled water. Any tablet which was chipped or had excessive extraneous powder attached was discarded. The buffer tablet was dissolved in about 40 cm³ of hot distilled water, the solution transferred to a 100 cm³ volumetric flask, and more distilled water added to the mark. Both pH buffer solutions were prepared in this manner. The buffer solutions were made up fresh each week when pH measurements were being made regularly. The combination electrode was calibrated by ensuring the correct pH was indicated for both the buffer solutions. Adjustments of the temperature and slope controls were made where necessary in order to obtain the calibration. The response of the electrode was noted by observing the time taken for the reading to reach within 98% of the buffer pH on transferring from one standard solution to the other, after washing. Invariably the response was rapid, taking less than 10 s.
pH measurements of buffer standards and sample solutions were performed with the solution being stirred by a magnetic stirrer. The electrode was rinsed with copious amounts of distilled water on transfer from one solution to another. Excess water was removed by blotting a tissue against the tip of the glass bulb.

The largest sources of error in pH measurements are those due to the reference electrode liquid junction and the operator, namely poor rinsing, poor maintenance of the electrode, and poor calibration. However, it is believed that, by following the procedures discussed above, errors no greater than ±0.05 units were incurred.

7.2.10 Preparation of Glassware

Before use all glassware was rinsed with copious quantities of distilled water and where appropriate stored, filled with distilled water. When necessary glassware (and the polypropylene centrifuge tubes) was soaked in a dilute solution of RBS-25 surfactant for several hours and then in distilled water before final rinsing with more distilled water. All pipettes, burettes, volumetric flasks, etc were religiously rinsed first with single distilled water and then triple distilled water before use.
CHAPTER 8

RESULTS AND INITIAL DISCUSSION
8. EXPERIMENTAL RESULTS AND INITIAL DISCUSSION

This chapter gives the results of the experiments performed using the methods described in the previous chapter. Tabulated data are presented in Appendix B. Initial discussion on the interpretation of the data, the possible sources of error, and improvements in the methods are also included.

Since aminoalcohols are relatively strong bases a change in concentration gives rise to corresponding changes in both solution pH and ionic strength. Similarly partial neutralisation of an aminoalcohol solution increases the ionic strength. Given a series of aqueous solutions of different MIPA concentration is a range of ionic strength and pH values as determined by the amino functional group dissociation. If the same series of MIPA solutions are titrated by strong acid to the same degree of neutralisation then the pH values will be the same whereas the ionic strengths will differ. Addition of the same number of moles of strong acid to each MIPA solution, on the other hand, gives rise to a series of solutions of the same ionic strength but different pH. It becomes clear, therefore, that performing experiments designed to study the effect of either MIPA concentration or pH or ionic strength under conditions where the other two variables are fixed is not easy. Working in a narrow pH range or MIPA concentration range can minimise the problem. However, if a fixed MIPA concentration solution is to be used, in a complete study of the effect of pH, the only way to ensure constant ionic strength and hence constant double layer thickness is to work with a total ionic strength equivalent to the MIPA concentration. Inert electrolyte being used to complement the MIPA conjugate acid concentration where necessary. Such a method effectively limits experiments to MIPA concentrations less than 0.01 mol dm⁻³ if the diffuse layer thickness is not to be negligible and, in addition, it is unlikely that simple inorganic ions will have the same influence as the conjugate acid form of MIPA on the properties of the electrical double layer surrounding a rutile particle. In order to study the effect of MIPA concentration such problems can only be avoided by working at a constant pH which is at least as alkaline as the natural pH of the highest MIPA concentration. Under these conditions the ionic strength is constant being determined by the hydroxyl ion content.
For the purposes of the present work the pH and ionic strength contributions from MIPA were evaluated using one of the following methods.

MIPA Solution pH

a) Measured, where possible, using a Radiometer electrode and pH meter standardised at two pH values, namely 4.01 and 9.18. The measurements were carried out at ca. 15°C whereas the majority of the experiments were performed at 25°C. The variation of the MIPA dissociation constant with temperature, figure 8.1, allows a correction factor to be applied

\[ \text{pH} (25°C) = \text{pH} (15°C) - 0.15 \]  

(8.1)

b) Calculated using the dissociation constant for MIPA solutions at equilibrium pH or using the Henderson-Hasselbach equation for partially neutralised MIPA solutions. Equation (8.2) was used for the former calculations

\[ \text{pH} = 14 + \log_{10} \left( \frac{K_b c}{2} \right) \]  

(8.2)

where \( c \) is the MIPA concentration in mol dm\(^{-3}\), and \( K_b \) is the dissociation constant. At 25°C \( K_b = 2.818 \times 10^{-5} \) mol dm\(^{-3}\). It was possible to use this simplified form of the full quadratic expression because of the relatively small degree of dissociation.

The standard Henderson-Hasselbach expression for buffers, equation (8.3), was used for the partially neutralised MIPA solutions

\[ \text{pH} = pK_a + \log_{10} \left( \frac{c - c^+}{c^+} \right) \]  

(8.3)

where \( c^+ \) is the concentration of MIPA present as the conjugate acid.

MIPA Solution Ionic Strength

a) Under equilibrium MIPA solution conditions the ionic strength contribution from MIPA was calculated using equation (8.4)
FIGURE 8.1 The variation of the $pK_a$ value with temp. for MIPA and AMP.
For solutions of pH higher than the equilibrium value the ionic strength was calculated from the concentration of hydroxyl ions.

c) For MIPA solutions partially neutralised by strong acid the ionic strength contribution from MIPA was taken to be equal to that of the added acid, if the volume and concentration of the latter were known, or was calculated from equation (8.3). The contribution from the normal dissociation of the MIPA solution, equation (8.4), was also included.

The results of the above calculations being added to the contribution, if any, from inorganic electrolytes.

The experimental work on the electrophoretic mobility of rutile particles, the stability of dilute aqueous dispersions of rutile, the loss of MIPA from solution in rutile dispersions, the dispersibility of rutile, the rheological behaviour of concentrated rutile dispersions, the centrifugal force required to prevent the redispersion of dilute rutile dispersions, and the dynamic viscosity behaviour of aqueous MIPA solutions were carried out as a function of pH, ionic strength, and MIPA concentration.

8.1 Electrophoresis Studies

The tabulated results of the various experiments are given in tables B.1.1-B.1.7 in appendix B.

All the recorded experiments were found to satisfy the necessary criteria for electrophoresis, namely

* symmetrical parabolic particle velocity-cell depth profile
* rectilinear particle movement
* reproducibility of particle speeds with respect to electrode polarity reversal
* linear dependence of particle velocity, at a given level, on the applied potential field.

Rectilinear movement was the norm, although the measurements at the last couple of cell levels for dispersions at high ionic strength were made more awkward by the increased tendency to monitor the larger particles which were slowly settling down the cell. The percentage error based on the standard deviation of the mean of the reciprocal time for all the measurements at a given level was found to be <5%. When such reproducibility was not obtained the electrodes were coated with platinum black to increase the effective surface area. Subsequently the linearity of particle velocity with applied electric field was checked and found to be good.

Figure 8.1.1 illustrates a typical graph found for the variation of particle velocity, \( V \), with location in the cell, \( (r/a)^2 \). Linearity was found not only for the levels within each half of the van Gils cell but also for all levels. The first criterion for electrophoresis was therefore satisfied. The correlation coefficient for the best straight line passing near all the data points was usually found to be greater than 0.98. Experiments giving a value less than this were discounted.

The errors associated with the tabulated values for the electrophoretic mobility and electro-osmotic mobility are based on the sum of errors obtained from the linear regression analysis of the \( V \) against \( (r/a)^2 \) plot and the errors in the effective cell length and microscope eyepiece graticule dimensions. The fractional errors in the electrophoretic mobilities are larger than those for the electro-osmotic mobilities because the electrophoretic velocities are calculated from the sum of the electro-osmotic velocity and the intercept of the line. For conditions such that the electrophoretic velocity is negative the two values are of opposite sign so that the calculation gives the difference between two numbers of similar magnitude thereby giving rise to a larger error.

Figure 8.1.2 shows the variation of electrophoretic mobility for both unwashed and washed rutile as a function of solution pH. Potassium nitrate was used as the backing electrolyte. For ionic strengths less
Figure 8.11 Typical plot of $V$ against $\left(\frac{r}{a}\right)^2$.

Axes:
- Vertical: $V/\text{grat}^2/\text{s}^2$
- Horizontal: $\left(\frac{r}{a}\right)^2$

Legend:
- $X$ Lower levels
- $\circ$ Upper levels
FIGURE 8.1.2 Electrophoretic mobility of rutile
than $1.2 \times 10^{-3}$ mol dm$^{-3}$ the isoelectric points for the two samples were found to be

\[
\text{unwashed pH} \sim 3.8 \quad \text{washed pH} \sim 5.6
\]

These values are within the reported range of values found by various workers\textsuperscript{223}. The rise in i.e.p. on washing indicates the removal of surface specifically adsorbed anions e.g. chloride, sulphate\textsuperscript{224-225}. The electrophoretic behaviour is similar to that found by Furlong and Parfitt\textsuperscript{225} for their rutile sample A. The measured i.e.p. for the washed rutile (CLDD 1281) also compares well with the value quoted by Cornell et al\textsuperscript{226} for a rutile free from surface impurities.

Figure 8.1.3 shows how the electro-osmotic mobility associated with the van Gils cell wall varied as a function of solution pH and ionic strength. The values appear to be in reasonable agreement with literature values. It was found that the higher MIPA concentration samples tended to give a lower electro-osmotic mobility indicating adsorption of the organic at the cell walls. In fact rutile dispersed in 0.5 mol dm$^{-3}$ MIPA solution gave a value for the electro-osmotic mobility of $\sim 3 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ whereas at that pH (= 11.6) a value much higher would be expected. Despite thorough washing the results for the experiments immediately following, EP31-EP34, suggested the presence of MIPA at the cell walls. Future experiments were performed in another cell and the MIPA concentration of the dispersions was kept below 0.01 mol dm$^{-3}$ for the vast majority of the experiments.

Figure 8.1.4 shows the effect of MIPA concentration at a given dispersion pH. The results at pH 11.1, i.e. EP85-EP88, indicate that for MIPA concentrations up to ca. 0.010 mol dm$^{-3}$, at this pH, there is a slight increase in the magnitude of the electrophoretic mobility. The data at pH 10.6, EP81-EP84, tend to confirm this view, although the increase is small namely $0.4 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$. The electro-osmotic mobilities follow the pH and ionic strength variations, as would be anticipated. The results for pH 11.3, EP40-EP46, although giving acceptable electro-osmotic mobilities, give rather low electrophoretic mobilities. However, the general conclusion that for low MIPA concentrations there is little difference in electrophoretic mobility appears to be correct.
FIGURE 8.1.3 Electro-osmotic mobilities
FIGURE 8.4 Electroosmotic mobility as a function of MIPA concentration

\[ \mu_{EP} \times 10^8 / \text{m}^2 \text{V}^{-1} \text{s}^{-1} \]

- \( \times \) EP 40-46
- \( \Delta \) EP 81-84
- ○ EP 85-88
- pH 11-1
- \( \bullet \) IS 2-4 x 10^{-3} M
- \( \bullet \) IS 7 x 10^{-3} M
- \( \bullet \) IS 1 x 10^{-3} M
- \( \bullet \) IS 2 x 10^{-3} M
- \( \bullet \) IS 5 x 10^{-3} M
Figure 8.1.5 shows the dependence of the electrophoretic mobility on pH for rutile dispersed in 4x10⁻³ mol dm⁻³ MIPA solution. Although the ionic strength was also a variable (<4.2x10⁻³ mol dm⁻³) two important observations can be made:

i) the i.e.p. is shifted to a higher value, pH ~7;

ii) there is a maximum in the electrophoretic mobility at pH ~10.6.

The shift in the isoelectric point suggests that a cationic species has specifically adsorbed within the rutile particle's Stern layer. The species would appear to be the conjugate acid form of MIPA.

The maximum in the mobility would appear to be a real effect since, although the variation in mobility is approximately followed by the change in ionic strength, the change in ionic strength within the pH range of maximum variation of the mobility (10.2-11.1) is minimal. In addition even at similar ionic strengths the mobilities are not the same, e.g. EP63 and EP80. The series of experiments should be repeated at the same total ionic strength (using a 1:1 electrolyte).

Figure 8.1.6 shows how the electrophoretic mobility of rutile dispersed in 4x10⁻³ mol dm⁻³ MIPA solution varies with ionic strength for various 1:1 electrolytes. The results for KNO₃ at pH 11.3 clearly show the effect of an increase in the value of kappa on the measured mobility. Comparison of the mobility values for KNO₃ and LiCl as electrolytes indicates that rutile dispersed in 4x10⁻³ mol dm⁻³ MIPA possesses a higher zeta potential with the latter as backing electrolyte. The corresponding electro-osmotic mobilities being within experimental error. The other two electrolytes, KCl and NaF, also give a higher zeta potential; the effect being greatest with the NaF. Both LiCl and KCl have been shown to be indifferent electrolytes towards anatase²²⁷ so that the observed phenomenon must be associated with changes in the electrical double layer brought about by differences in the interaction between the MIPA molecules and the inorganic ions.

Table B.1.7 shows how the electrophoretic mobility of rutile subjected to several days contact with a MIPA solution varies as a
FIGURE 8.1.5 $\mu_{EP}$ as a function of pH for a constant MIPA concentration
FIGURE 8.1.6 \( \mu_{EP} \) as a function of ionic strength

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
<th>[MIPA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO_3</td>
<td>11.3</td>
<td>4 mM</td>
</tr>
<tr>
<td>KNO_3</td>
<td>10.5</td>
<td>4 mM</td>
</tr>
<tr>
<td>LiCl</td>
<td>10.5</td>
<td>4 mM</td>
</tr>
<tr>
<td>KCl</td>
<td>10.5</td>
<td>4 mM</td>
</tr>
<tr>
<td>NaF</td>
<td>10.4</td>
<td>4 mM</td>
</tr>
<tr>
<td>LiCl</td>
<td>11.3</td>
<td>4 mM</td>
</tr>
</tbody>
</table>
function of the equilibrium concentration and quantity of amino loss during the period of contact. The mobility shows a tendency to decrease in magnitude as the amino loss associated with the rutile increases or as the MIPA content increases. The electro-osmotic mobility also decreases as these two factors increase.

For some dispersions it was noted that for cell levels close to the level at which no net particle migration occurs there was a distribution of particle velocities. This was indicative of the heterogeneous nature of the surface groups of the rutile particles. However, given a sufficient particle number it was possible to monitor a typical particle for each timing. If there were insufficient numbers within the field of view in such a situation, then a wider range of particle velocities were recorded with a consequent increase in the uncertainty of the migration velocity for that value of r/a.

Occasionally the timings at a given level were repeated at the completion of the experiment to check for ageing effects. Only sols possessing conditions leading to particle instability with respect to coagulation showed any change in particle migration velocity outwith random error.

Since the electrophoresis experiments were performed under conditions such that $10 < \kappa a < 50$ then it would be expected that the retardation and relaxation effects associated with the double layer would be significant\(^{228}\). Consequently the conversion of electrophoretic mobilities to zeta potentials needs to make use of either the tabulated results of Wiersema et al\(^{229}\) or the analytical results of O'Brien and White\(^{230}\).

### 8.2 Coagulation Rate Studies

The tabulated results of the various particle counting experiments are given in tables B.2.1–B.2.11. The values of the rate constant, $k$, were determined from the following expression

$$k = 1.364 \times 10^{-13} \times m/60 \quad (m^3 \text{ s}^{-1})$$
where \( m \) is the slope of the initial portion of the \( 1/N \) against \( t \) plot, with \( t \) in units of mins. Similarly the value of \( N_0 \) is found from the expression

\[
N_0 = c/1.364 \times 10^{-13} \quad (\text{m}^{-3})
\]

where \( c \) is the intercept of the best straight line passing through the same initial data points.

The quoted error for each rate constant was calculated from the standard error associated with the slope of the line as determined by linear regression analysis.

Using most of the measured rate constants for rutile dispersed in high ionic strength solution, table B.2.1, an experimental value for the rapid rate constant, \( k_0 \), was calculated

\[
k_0 \text{ (exptl.)} = (6.08 \pm 0.37) \times 10^{-18} \, \text{m}^3 \, \text{s}^{-1}
\]

which compares with the theoretical value of

\[
k_0 \text{ (theory)} = 6.16 \times 10^{-18} \, \text{m}^3 \, \text{s}^{-1}
\]

Following the recommendation of Marmur\(^{231}\) the stability ratio, \( W \), was calculated using this experimental \( k_0 \) value; thus

\[
W = 6.08 \times 10^{-18}/k
\]

At a pH = 5.7 the critical coagulation concentration for the washed rutile was ca. 0.01 mol dm\(^{-3}\). Figure 8.2.1 shows how the stability ratio varied with the solution ionic strength, comprised of the potential determining ions and potassium nitrate. The rutile is more stable, under equal ionic strengths, at a pH of 9.7 but the value of \( W \) remained below ca. 20 for all the dispersions.

Figure 8.2.2 shows the variation of \( W \) with ionic strength (KNO\(_3\)) at pH 11.1 which indicates that the critical coagulation concentration is approximately 0.025 M 1:1 electrolyte. The inclusion of the barium
FIGURE 8.2.1 $W$ as a function of ionic strength for rutile in potassium nitrate solution (pH=5.8)
FIGURE 8.2.2 W as a function of ionic strength in potassium nitrate solution (pH = 11.1)
nitrate sample shows the influence of the counterion valency, although the effect is not as marked as predicted by the Schulze-Hardy rule.

There is no obvious functional dependence of the stability ratio on the MIPA concentration of the dispersion - each dispersion being split into two samples, with the particle count being alternated between the samples - as is shown in table B.2.3. The value of W ranges from 7.5 up to 22, but there is no discernible dependence on pH or ionic strength.

The variation of W with ionic strength for a dispersion of fixed MIPA concentration is shown in figure 8.2.3 for both 0.1 M and 0.001 M MIPA. There is the expected decrease in the stability ratio with an increase in the ionic strength, although the results for the weaker MIPA dispersion are somewhat scattered. Generally, however, at a given ionic strength rutile dispersed in electrolyte solution at the same pH is slightly more stable than in the presence of MIPA. It was noted that the measured stability of rutile dispersed in a MIPA solution was generally higher if a fresh stock MIPA solution was used as the source. If the stock solution was left to age for more than ca. 8 days the MIPA dispersions made up using aliquots of the stock were sometimes found to have a W value up to 3 times lower. However, this was not always the case. The stock solutions of MIPA were usually ca. 0.1 mol dm\(^{-3}\) and were made up fresh for a given series of experiments, although it was found to be useful to keep the solution for up to ca. 20 days for use in other experiments. Analytical measurements showed that there was no detectable loss of titratable amino groups from either a 0.1 mol dm\(^{-3}\) MIPA solution left for 8 weeks in a volumetric flask at room temperature or from a 0.1 mol dm\(^{-3}\) MIPA solution subjected to EOE at 25°C for 26 days in a Quickfit test-tube. As a result of the alkalinity of the solution, pH ~11.1, it is possible that dissolution of silicate species from the glass surfaces of the volumetric flask could result in detectable changes in the interaction between rutile particles due to adsorption of the complex species within the Stern layer. However, it is likely that borosilicate glass flasks were used for most of the MIPA solutions.

Under conditions of constant pH, 11.3, and ionic strength, 2x10\(^{-3}\) mol dm\(^{-3}\), there appears to be a slight increase in stability with an increase in the MIPA concentration (figure 8.2.4).
FIGURE 8.2.3 W as a function of ionic strength (KNO₃) for 0.1M MIPA, 0.001M MIPA

- 1mM MIPA, pH 10.2
- KNO₃, pH 11.2
- 0.1M MIPA, pH 11.2

ΔBa(NO₃)₂
FIGURE 8.2.4 $W$ as a function of MIPA concentration at constant pH(11.3) and ionic strength

FIGURE 8.2.5 $W$ as a function of pH at constant ionic strength for 0.0102M MIPA
Figure 8.2.5 shows the variation of $W$ with pH at constant ionic strength for a 0.0102 mol dm$^{-3}$ MIPA dispersion. Once again there is scatter in the limited data but the increased stability at pH 7.4 may be associated with differences between the counterions K$^+$ and MIPA$^+$ (PC166). The pairs of particle counts PC147 and 148, PC149 and 150, and PC151 and 152 show how the stability of a rutile dispersion depends upon the nature of the counterion at different pH values. An increase in the ionic strength and decrease in the pH from 10.3 to 9.4 reduces the stability of rutile dispersed in KNO$_3$ but increases the stability of rutile dispersed in 0.02 mol dm$^{-3}$ MIPA for which the counterion is the conjugate acid form of MIPA.

The limited results in table B.2.9 suggest that the stability of rutile dispersed in MIPA solution increases with an increase in temperature.

The stability constants for rutile particles equilibrated with MIPA solutions and redispersed in a solution of equivalent pH and MIPA concentration to the final equilibrium solution are given in tables B.2.10 and B.2.11. The $W$ values are, in general, within the range 2–9, although once again there does not appear to be any trend. Notable exceptions to the general behaviour were PC83, 84, and 90 on the one hand, and PC91–93 on the other hand. The former dispersions were found to have $W$ values of ca. 60, whereas the corresponding dispersions for [MIPA] ~0.05 M (PC86–88) were less stable $W < 10$. The dispersions with a $W$ of 60 were observed to possess a distinct red colouration when held up to the daylight. The samples PC91–93 had a stability ratio close to unity, the rutile particles being those of adsorption isotherm 19. The presence of 0.019 mol dm$^{-3}$ MIPA$^+$ clearly lowers the stability of such rutile particles, although an increase in stability of normal rutile was found as the [MIPA$^+$] increased (PC147, 149, 151).

The importance of ageing phenomena in affecting the stability of rutile showed up for samples PC95–106.

The rutile for these particle counts was taken from the appropriate test-tube used for adsorption isotherm 20. The rutile had been in contact with the appropriate MIPA solution for a further 8 days after
completion of the adsorption isotherm before being used for PC95-98 and for a further 20 days before being used for PC99-103. The latter gave consistently lower W values. However, the observed behaviour could also be related to the amount of amino loss associated with the particular rutile particles.

Particle counts for rutile dispersed in aqueous AMP solution gave similar results to that for MIPA

<table>
<thead>
<tr>
<th>[AMP]/mol dm⁻³</th>
<th>pH</th>
<th>Electrolyte</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>~11.2</td>
<td>-</td>
<td>6.25</td>
</tr>
<tr>
<td>0.10</td>
<td>~11.2</td>
<td>0.12 mM Ba(NO₃)₂</td>
<td>2.84</td>
</tr>
</tbody>
</table>

It should be pointed out that for the vast majority of the particle counts it was possible to use at least 4 data points from the start of the experiment and obtain an acceptable straight line, generally up to t = 14 min. But as is apparent from the recorded results for W there is a general lack of a clear set of conclusions. In saying that, it is also apparent that MIPA does not give rise to either a dramatic increase or decrease in the measured stability ratio. However, the ease of redispersion of a rutile sediment, which is not of the voluminous type associated with flocculated systems, does suggest that the particles may be aggregating into either a secondary minimum potential energy well²³₂-²³³ or a shallow primary minimum potential energy well²³⁴. The particles attaining sufficient energy to redispersed from simple agitation.

Several of the particle counts were carried out for up to 70 hours (PC144-166). Between counts the conical flask containing the dispersion was left stoppered in the thermostated water bath. All the resulting 1/N against t plots gave the type of behaviour shown in figure 8.2.6. The particle number reached a plateau value after a time of typically 30 mins - the actual value depending on the slope (and hence stability ratio) of the initial linear portion. The lower the stability the shorter the time before the appearance of the plateau. The particle number concentration at the plateau being within the range 2.2-2.7x10⁻¹⁴ m⁻³; the smaller values being associated, in general, with the less stable dispersions.
The levelling off of the particle number suggests the existence of a process by which the primary particle number can increase i.e. a redispersion mechanism occurring in opposition to the normal coagulation process\textsuperscript{233}. After a further period of several hours the particle number decreased once again; this effect was in part due to neutralisation of the high pH dispersions by carbon dioxide absorption and in part by exchange of potential determining ions with the rutile surface (drop in pH towards the i.e.p.). As the result of the buffering capacity of MIPA solutions the decrease in number was less dramatic for the rutile dispersed in MIPA solution.

\section{8.3 Loss of MIPA from Solution in the Presence of Rutile}

The results of the numerous adsorption isotherms (AI) carried out are given in tables B.3.1-B.3.34 in appendix B. The isotherms up to number AI25 were performed such that the dispersions were open to the light. As the result of the discovery that the washed rutile was able to catalyse the photo-oxidation of MIPA it was necessary to carry out the remaining isotherms, AI26-AI34, under conditions in which the dispersions were kept in the dark. Despite the measured decrease in the MIPA concentration being due to a combination of adsorption and oxidation for the isotherms determined in the presence of light the results can still give information on what factors influence the adsorption of MIPA at the rutile interface - adsorption must take place before the photo-oxidative reaction. The graphs and discussion of the trends are presented in appendix B. The remaining isotherms (performed in the dark) are discussed in this chapter. The graphs are presented in terms of the quantity of amino loss as a function of final MIPA concentrations.

The errors associated with the determination of the isotherms include:

a) the quality of the initial dispersion and the subsequent ability to maintain that initial quality while undergoing EOE agitation. Clearly inefficient initial dispersion lowers the effective particle surface area that is available for interaction with the solution. Each rutile-MIPA solution sample was subjected to ultrasonic irradiation for at least 30 mins with frequent adjustment of the position of the test-tube within the
ultrasonic bath in order to ensure that adequate deagglomeration was taking place, as indicated by the appearance of waves on the dispersion surface. The tubes were also occasionally removed and inverted several times in order to assist the dispersion process. The only samples which were difficult to disperse were those at high ionic strength (>0.03 mol dm$^{-3}$) and/or low pH (<7). These initially contained rutile pigment which merely settled rapidly to give a gritty sediment, but on careful ultrasonic irradiation it was possible to obtain a good dispersion. However, coagulation in such samples rapidly degraded the quality of dispersion to produce rutile coagula which settled to form a rather voluminous sediment. The relatively gentle agitation afforded by the EOE apparatus clearly prevented settling and maintained the rutile in a suspended state but coagulation could still take place both in the time between removing the test-tube from the ultrasonic bath and installing on the EOE apparatus (~60 s), and during the timescale of the isotherm.

b) the adsorption of MIPA would result in a change in both the bulk solution pH and ionic strength as the consequence of the disturbance of the equilibrium reaction involving dissociation of the amino group.

c) the quantitative analysis of the MIPA concentration introduced errors as discussed in Section 7.2.1. Under the conditions of the experiments (0.25 g rutile in 10 cm$^3$ of solution) a 0.0002 mol dm$^{-3}$ decrease in MIPA concentration was equivalent to an amino loss of 8 μmol g$^{-1}$ for samples analysed by the potentiometric titration method, whereas an error of ca. 5 μmol g$^{-1}$ was typical for analysis by the ninhydrin method. In practice the absolute error for the titration technique was ca. ±20 μmol g$^{-1}$.

d) a further source of error was found to be associated with the time for which each dispersion was illuminated by either daylight or fluorescent tubes. It was discovered that the loss of MIPA from solution, in the presence of rutile, was a function of the time for which the sample was illuminated and that oxidation of some of the MIPA had taken place. Thus the measured decrease in MIPA concentration could not be solely ascribed to adsorption. Changes in the bulk solution properties, i.e. pH, ionic strength, MIPA concentration, would therefore be expected to not only affect the degree of adsorption of MIPA but also
the amount of rutile-light induced oxidation. However, it would be expected that, at least for low bulk MIPA concentrations, changes in the latter would reflect changes in the former because the MIPA needs to be adsorbed before the rutile catalysed decomposition can take place.

**Effect of Light on the Amino Loss**

As the result of carrying out the isotherms AI1-AI25 and observations noted on the change in dispersion quality with time and the smell of such rutile dispersions it was decided to look at the effect of light on the amount of amino loss.

Table B.3.19 shows how ordinary daylight has a significant effect upon the measured amino loss from various MIPA solutions. The samples protected from light were covered with silver foil. The differences between the covered and open samples are very marked. The amino loss from the open to light dispersion can be up to 20 times greater than from the corresponding covered sample.

The effect of the intensity and colour of the light striking the dispersion was studied, albeit rather crudely, by covering the test-tubes with different colours of theatrical lighting gel. The results of the investigation are given in table B.3.24. Both the intensity and wavelength of the light influence the extent of amino loss, with the yellow colour being almost as good as using silver foil.

This photocatalytic reaction between MIPA and rutile was completely unexpected. Although, the photooxidative properties of rutile are well known\(^{223}\) it was not anticipated that rutile dispersed in MIPA solution within a Pyrex test-tube immersed under ca. 6 inches of water within a large thermostat bath into which light can enter only through the top and glass front panel could significantly, if at all, initiate the photooxidation of MIPA. The water tank itself was located several yards away from the window. Any light falling on the dispersions was either daylight or light from standard fluorescent tubes both of which would need to pass through layers of glass and a depth of water. On average the tubes would be in natural darkness for at least 12 hours out of each 24 hours. Most of the work carried out to study the photocatalytic
properties of rutile use high intensity ultraviolet radiation sources. In addition, oxygen is required for the process to take place. Frank and Bard found that anatase was able to completely oxidise aqueous solutions of cyanide within 2 days if placed in sunlight. However, oxygen gas was continuously bubbled through the sample. Their study also indicated that the position of the dispersion within the beam of light, for those systems illuminated by lamp, was critical.

It is apparent that the present work has highlighted an interesting phenomenon.

Table B.3.28 and figure 8.3.1 (Al 25) show the effect of the fraction of the time of equilibration in the presence of light. The amino loss increases rapidly up to a fraction of ca. 0.7. The elbow at ca. 0.16 may be a real effect but more experimental work would be required to confirm the effect.

The photocatalytic effect of rutile was also found when dispersed in aqueous triethanolamine solution (TEA). A 0.0905 mol dm\(^{-3}\) solution when subjected to 21 days equilibration with rutile gave amino losses of 276 and 12 \(\mu\)mol g\(^{-1}\) in the presence and absence of light, respectively.

The remaining isotherms were carried out with the test-tubes covered by silver foil.

**Adsorption in the Absence of Light**

The effect of a variable time of equilibration was investigated for 0.1 mol dm\(^{-3}\) MIPA (Al 26). The results are given in table B.3.29 and figure 8.3.2. The amino loss reaches a plateau value of ca. 38 \(\mu\)mol g\(^{-1}\) in under 24 hours.

Al 28 (table B.3.31 and figure 8.3.3) shows how the adsorption of MIPA varies with concentration (<5x10\(^{-3}\) mol dm\(^{-3}\)) at a constant pH 11.0. There is a steady increase in adsorption from 0 to 14 \(\mu\)mol g\(^{-1}\) over the concentration range studied. The plateau region at 5 \(\mu\)mol g\(^{-1}\) needs to
FIGURE 8.3.1  AI 25
be confirmed by further work since the errors involved can account for its existence.

The influence of variable pH at a constant MIPA concentration and ionic strength has been studied for 8x10^{-3} mol dm^{-3} MIPA (AI 30). Table B.3.33 and figure 8.3.4 show that both high and low pH values do not favour adsorption, whereas there is maximum in adsorption at values close to that of the pK_a value.

AI 27 was performed to study the effect of ionic strength on the adsorption. The results (table B.3.30 and figure 8.3.5) are for lithium chloride as the backing electrolyte. The nature of the isotherm is similar to that for AI 24 in that at low ionic strengths the amount of amino loss fluctuates. At higher ionic strength the amino loss decreases. The validity of the isotherm in the low ionic strength range needs to be investigated further.

Similar studies on the effect of ionic strength were carried out using 5x10^{-3} mol dm^{-3} MIPA. Both LiCl (AI 31) and KNO_3 (AI 29) were used as backing electrolytes. Figure 8.3.6 shows the dramatic effect that KNO_3 has on the adsorption of MIPA. The presence of 2.3x10^{-3} mol dm^{-3} electrolyte is sufficient to lower the quantity of MIPA adsorbed by a factor of three. The effect of LiCl is even more pronounced. The increase in ionic strength can modify the adsorption of MIPA as the result of a decrease in the diffuse layer thickness or the increased competition between electrolyte ions and MIPA molecules for locations within the Stern layer i.e. Li^+ or K^+, and MIPA compete for sites within the OHP.

**Specific Surface Area of the Rutile Pigment**

The BET isotherm produced the following data:

<table>
<thead>
<tr>
<th>P/P_0</th>
<th>0.049</th>
<th>0.0981</th>
<th>0.1961</th>
<th>0.2942</th>
</tr>
</thead>
<tbody>
<tr>
<td>[w(P_0/P-1)]^{-1}/g^{-1}</td>
<td>13.194</td>
<td>24.979</td>
<td>48.375</td>
<td>70.969</td>
</tr>
</tbody>
</table>

The graph was linear with the following parameters
FIGURE 8.3.5  AI 27 (no light)
slope = 235.791 ±1.598 g\(^{-1}\)
intercept = 1.806 ±0.296 g\(^{-1}\)

Applying the BET equation leads to

weight of adsorbate in monolayer = \((4.209 ±0.029) \times 10^{-3}\) g

value of the BET constant = 131.6 ±21.6

specific surface area = 7.26 ±0.05 m\(^{2}\) g\(^{-1}\)

[It was assumed that the cross-sectional area of the nitrogen molecule when present in a monolayer was 0.162 nm\(^{2}\)].

8.4 The Dispersibility of Rutile

The degree of dispersion of rutile was initially assessed by measuring the optical density of a diluted dispersion. A calibration line for rutile concentration against optical density (at 400 nm) was measured using a 1 cm cell in a Unicam SP 600 spectrophotometer and the linearity was good. The Lambert-Beer law was found to hold up to a rutile concentration of ca. 40 \(\mu\)mol cm\(^{-3}\) with an extinction coefficient of 1800 m\(^{2}\) mol\(^{-1}\). However, it was decided to use direct particle counting as the quantitative technique for assessing the degree of dispersion. Particle counting need not be carried out at a fixed temperature and the existence of larger agglomerates, which may be slow to settle as the result of a relatively low bulk density, can be allowed for in the analysis. The optical density measurements can be influenced both by temperature and by suspended particle size.

An initial study using the optical density method to measure the dispersed rutile concentration was carried out to investigate the effect of MIPA content. A 10 cm\(^{3}\) aliquot of MIPA solution was added to ca. 5 mg rutile, subjected to ultrasonic irradiation for 30 mins, rotated end over end at 15 rpm for 2 hours, left to stand for 3 days, rotated end over end at 15 rpm for a further 2 hours, left to stand for 20 hours (25°C) and a sample of dispersion taken for analysis. The results are given in table 8.4.1.
Table 8.4.1. Dispersed rutile concentration as a function of MIPA content

<table>
<thead>
<tr>
<th>[MIPA]/mol dm(^{-3})</th>
<th>g MIPA per g rutile</th>
<th>[TiO(_2)]/μg cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>1.57</td>
<td>371</td>
</tr>
<tr>
<td>0.10</td>
<td>14.2</td>
<td>449</td>
</tr>
<tr>
<td>0.50</td>
<td>78.3</td>
<td>422</td>
</tr>
<tr>
<td>1.00</td>
<td>157</td>
<td>410</td>
</tr>
</tbody>
</table>

The data suggests that, as with other dispersants, there is an optimum concentration of MIPA. It should be noted that the procedure adopted for this study meant that the three stages of wetting, dispersion, and subsequent coagulation of the particles were involved so that interpretation of the data should take this into account. Poor wetting of the particles will show up as poor dispersibility but, under the conditions of the above study, good wetting with subsequent coagulation will also show up as poor dispersibility.

The majority of the dispersibility studies were assessed by direct particle counting. The results of these experiments are recorded in tables B.4.2-B.4.32. The EOE apparatus rotated at 15 rpm thereby giving 30 tube inversions per minute. The table headings have the following meaning:

- NUM: number of primary rutile particles dispersed from 1 g of rutile
- R: weight MIPA per unit weight rutile
- NI: number of tube inversions.

The various experiments studied the effects of the [MIPA], pH, ionic strength, electrolyte type, and time of dispersion on the value of NUM.

The errors associated with the technique include:

a) dispersion of the dry rutile on addition of the dispersing solution and before being subjected to the EOE agitation. This effect was
minimised by transferring the solution to the inclined test-tube via a bulb pipette positioned such that the solution spread out and ran down the test-tube walls;

b) slight variations in the sizes of the test-tubes would vary the force experienced by the rutile particles on tube inversion - the magnitude of this effect being unknown;

c) the dilution of the extracted sample of dispersion for particle counting could introduce an error in the subsequent number of particles counted;

d) the actual particle counting introduced an error associated with counting a representative sample. However, the particle number within 4 of the graticule squares was determined at least 5 times which gave an error, based on the standard deviation on the mean, of <7%.

The dispersibility of rutile in distilled water of different pH is shown in figure 8.4.1 and table B.4.6. Little rutile is dispersed at pH values less than 10, the dispersibility improving rapidly up to pH 12. At very high pH, >12.5, the dispersed particle number falls off, possibly due to the ionic strength effect. The poorly dispersed samples contained large agglomerates which were observed to settle rapidly, both in the test-tube and counting cell. It was found for all samples that if the dispersed particle number was <4x10^{11} then such agglomerates would be present.

Figure 8.4.2 and table B.4.7 shows the effect of a change in the KNO_{3} concentration, at various pH values, on the dispersibility of rutile. The variation with respect to pH follows the trend found earlier. At each pH an increase in the electrolyte concentration decreased the number of dispersed rutile particles. Since little time elapsed between removing a tube from the EOE and carrying out the particle count, <60 s, it is not likely that, especially for ionic strengths less than 12x10^{-3} mol dm^{-3}, the increased rate of coagulation would significantly lower the dispersed particle number. (It should be noted that in the work of Parfitt et al^{220} the samples were allowed to

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FIGURE 8.4.1 NUM as a function of pH (dist. water)
FIGURE 8.4.2 The dispersibility of rutile as a function of KNO₃ concentration for different solution pH values
stand for 18 hours before the dispersed particle concentration was measured.) It would therefore appear that the wetting and deagglomeration stages of the dispersion process are affected by the electrical properties of the double layer.

A similar study on the effect of ionic strength on the dispersibility in dilute MIPA solutions is shown in figure 8.4.3 (table B.4.8). For a given MIPA concentration the dispersed particle number falls with an increase in the KNO₃ concentration. The number of particles dispersed at a given [KNO₃] being larger the higher the [MIPA], although since each solution was allowed to reach the pH determined by the MIPA dissociation there is also a pH effect. In fact the results for the 1x10⁻³ mol dm⁻³ MIPA, pH ~10.3, are similar to those for the pH 10.2 electrolyte solution. But in general, the MIPA solutions dispersed more rutile particles under the same conditions of ionic strength and pH.

Table B.4.9 and figure 8.4.4 show the effect of a change in pH, at constant ionic strength, as the result of changes in the MIPA concentration. The dispersed particle number was plotted against the fraction of MIPA present as the conjugate acid and clearly shows that there is little change until the fraction approaches 0.9 at which point the dispersed particle number becomes insignificant.

Figure 8.4.5 shows the results of two studies on the effect of pH on the dispersing power of a given MIPA concentration. Table B.4.10 gives the data for 0.02 mol dm⁻³ MIPA in which the ionic strength was also a variable, being equal to the [MIPA⁺]. Table B.4.11 gives the data for 0.01 mol dm⁻³ MIPA in which the ionic strength was held constant. The change in pH has a lesser influence on the dispersed particle number when the ionic strength is held constant, at least for pH values in the range 9.7-10.7. Below pH ~9.5 the drop in number is significant. Over the same pH range the zeta potential of rutile in the presence of MIPA (figure 8.1.5) falls rapidly.

The influence of different electrolytes on the dispersing power of MIPA was initially studied for the conditions shown in table B.4.12. The major conclusion being that the valency of the counterion is important. The results for barium nitrate, table B.4.13, confirm this view.
FIGURE 8.4.3 The dispersibility of rutile as a function of MIPA concentration and KNO$_3$ concentration.
FIGURE 8.4.4 The dispersibility of rutile as a function of the fraction of MIPA neutralised
FIGURE 8.4.5 The dispersibility of rutile as a function of pH in the presence of MIPA
An extensive study on the dispersing power of 0.02 mol dm\(^{-3}\) MIPA as a function of ionic strength and pH was carried out, table B.4.15 and figure 8.4.6. The results confirm the conclusion that for pH values >9.5 the variation of dispersed particle number with ionic strength is largely independent of the pH. If the same data is plotted against the KNO\(_3\) concentration the results are more scattered with the lower pH samples giving, in general, a lower value of particle number.

An equivalent study for 5\times10^{-3} mol dm\(^{-3}\) MIPA was also performed, table B.4.16 and figure 8.4.7. A similar set of conclusions can be made from these results.

The dispersing power of a MIPA solution as a function of concentration, at a pH of 11.4, was investigated, table B.4.17 and figure 8.4.8. A definite improvement in the dispersing power was found, with an increase in particle number of 150% over the MIPA concentration range studied. Data for AMP and triethanolamine (TEA) are also shown.

The dispersing power of dilute MIPA solutions (<1\times10^{-3} mol dm\(^{-3}\)) under equilibrium pH conditions as a function of KNO\(_3\) concentration was studied, table B.4.19 and figure 8.4.9. The data indicates that a decrease in [MIPA] for a given [KNO\(_3\)] reduces the dispersing power. The effect of increasing electrolyte concentration is as pronounced as previously observed.

The importance of water in the dispersion process was examined by making a 0.019 mol dm\(^{-3}\) MIPA solution up using various relative volumes of water and Analar acetone (table B.4.21). The data confirm the view that water must be present in sufficient quantity to allow MIPA to act as a dispersant. Since MIPA is soluble in acetone it can approach the rutile particle surfaces. However, some stage within either the wetting phases or deagglomeration phase is clearly hindered by the absence of water. The observation that at least 50% v/v water is necessary in order to noticeably improve the dispersing power of MIPA suggests that water and acetone molecules compete for position near to the rutile particle surfaces.

The significance of the amino and hydroxyl functional groups in determining the dispersing power was investigated by using combinations
FIGURE 8.4.6 The dispersibility of rutile in the presence of 0.0202M MIPA as a function of ionic strength and pH
FIGURE 8.4.7 The dispersibility of rutile in the presence of 0.005M MIPA as a function of ionic strength and pH
FIGURE 8.4.8 The dispersibility of rutile as a function of MIPA concentration at pH=11.4
FIGURE 8.4.9 The dispersibility of rutile in low MIPA concentration solutions as a function of KNO₃ concentration.
of isopropanol and 1-aminopropane. The results are shown in table B.4.22 and figure 8.4.10. The dispersed particle number is plotted against the aminopropane mole fraction for two experiments, each for different periods of EOE agitation. When there is no amine present there is negligible dispersion of the rutile. For both sets of data there is a definite minimum in the dispersing power within the amine mole fraction range 0.16-0.64. Since no attempt was made to measure the pH of the solutions it is possible that the inability of the 0.26 mol dm\(^{-3}\) isopropanol solution to disperse the rutile was merely due to the low pH (ca. 6). Despite the simultaneous rise in solution pH as the amine fraction increases there is still a decrease in dispersing power after the initial significant rise. Over the amine concentration range studied it would be expected that the solution pH varied between 11.4 and 12.0 (calculated assuming a pK\(_b\) value of 3.47).

The rate of the dispersion process is an important factor. The previous studies were carried out for a constant number of tube inversions, 2700, but the trends observed could depend upon the time of dispersion since different dispersing solutions may reach their optimum dispersing power after different periods of agitation (for the present work an increase in the value of NI is directly proportional to the time of dispersion).

**Time of Dispersion Studies**

Numerous experiments were carried out to assess the effect of the number of tube inversions, NI, on the number of rutile particles dispersed. Tables B.4.25-B.4.32 give the data.

Figure 8.4.11 shows the variation of NUM with the logarithm of NI for several solutions. Clearly there is a significant difference between the MIPA solution and distilled water at the same pH. Within 30 s the number of dispersed particles is ca. 50% of the peak value in the case of the MIPA solution, whereas 15 mins is the time interval before the particle number becomes significant for the distilled water. Increasing the ionic strength of the latter increases the time before the particle number becomes significant.
FIGURE 8.4.10 The dispersibility of rutile in aqueous mixtures of 1-aminopropane and isopropanol
FIGURE 8.4.11 The effect of different times of dispersion on the number of particles dispersed
Tables B.4.27-B.4.31 give the data for studies carried out to assess the effect of \( \text{MIPA} \) concentration, electrolyte concentration and electrolyte type on the rate of appearance of dispersed rutile particles. The electrolytes investigated included \( \text{KNO}_3 \), \( \text{KCL} \), \( \text{NaF} \), \( \text{LiCL} \), and \( \text{NaNO}_3 \). Increasing the electrolyte concentration to \( \text{MIPA} \) concentration ratio increased the time interval before a significant particle number was observed. However, for electrolyte concentrations greater than 0.025 mol dm\(^{-3}\) both \( \text{KNO}_3 \) and \( \text{LiCL} \) gave a reduction in particle number as the time of dispersion increased. This was possibly a coagulation effect. On the other hand \( \text{NaF} \) showed no such effect — in fact this electrolyte had the least inhibiting effect on the dispersing ability of \( \text{MIPA} \).

It was also observed that if the rutile powder was moistened with distilled water before the addition of the dispersion medium a significantly lower number of particles were dispersed.

### 8.5 Dynamic Viscosity of Aqueous Solutions

The results of the experiments carried out to investigate the dynamic viscosity of \( \text{MIPA} \) solutions are given in tables B.5.1-B.5.7 and the results for 1-aminopropane are given in tables B.5.8-B.5.10. The relative viscosity values, \( \eta_r \), were converted to the actual viscosity by multiplying by the viscosity of distilled water (at 25°C \( \eta = 0.8904 \text{ cp} \)). The actual timings recorded for the flow of a solution through the viscometer were reproducible to better than 0.04%, although the majority of results were better than 0.015%.

Table B.5.1 shows how the viscosity varied with the \( \text{MIPA} \) concentration. Figure 8.5.1 indicates that the solution viscosity rises with increasing concentration. The presence of both the hydroxyl and amino functional groups enable the \( \text{MIPA} \) molecule to form structured regions within aqueous solution as the result of extensive hydrogen bonding with both the water molecules and other \( \text{MIPA} \) molecules. Included in the graph are values for 1-aminopropane solutions. Up to a concentration of ca. 0.5 mol dm\(^{-3}\) the solution viscosity is the same as for \( \text{MIPA} \), but for higher concentrations the viscosity of the amine is slightly greater. Because of the similarity between the curves the contribution of the hydroxyl group to the viscosity of \( \text{MIPA} \) solutions appears to be minimal.
FIGURE 8.5.1 Dynamic viscosity as a function of MIPA concentration (25°C)
Figure 8.5.2 shows how the reduced viscosity varies with MIPA concentration. For most solute solutions such a plot gives a monotonic rise in \((\eta SP/c)\) with \(c\) which on extrapolation to infinite dilution gives the intrinsic viscosity of the system. However, there is a definite minimum in the plot at a concentration of ca. 0.8 g per 100 cm\(^3\). Such behaviour is typical of aqueous solutions of polyelectrolytes for which the minimum is the result of conformational changes in the polymer molecule. The reason for the existence of such a curve for MIPA solutions is unknown. (A further study, table B.5.3, indicated that the value used for the flow time of distilled water can have a significant effect upon the values of reduced viscosity.)

A study of the effect of pH on the solution viscosity of 0.5 mol dm\(^{-3}\) MIPA at a constant ionic strength of 1.5 mol dm\(^{-3}\) indicated (figure 8.5.3) that the viscosity fell as the pH was lowered from 11.8 to 4.0 but increased significantly at very low pH. Protonation of the amino group prevents the formation of hydrogen bonds between the nitrogen atom and other polar atoms thereby lowering the viscosity. It should be noted that over the range of KNO\(_3\) concentrations used (table B.5.4) the viscosity of a solution of KNO\(_3\) is ca. 0.98-0.99 cp. The viscosity of the MIPA-KNO\(_3\) mixture is significantly less than this indicating that the presence of the MIPA molecules interferes with the electrolyte-water interaction.

The effect of ionic strength, using KNO\(_3\) as the backing electrolyte, on the viscosity of a 0.5 mol dm\(^{-3}\) MIPA solution is shown in figure 8.5.4. Data for three pH values are included, the [MIPA\(^+\)] being added to [KNO\(_3\)] to give the ionic strength. The results show that an increase in the [KNO\(_3\)] produces a decrease in the viscosity for all 3 pH values, the viscosity falling below that of the equivalent KNO\(_3\) solution. The fact that the viscosities for the solutions at pH 9.6 and 1.6 are approximately the same over the range of ionic strength examined could be fortuitous (cf. minimum in viscosity as a function of pH). The lower viscosities for these two pH values could be interpreted as indicating that the MIPA\(^+\)-KNO\(_3\) combination is more structure breaking than KNO\(_3\) alone.

Figures 8.5.5 and 8.5.6 give the results for the variation of the viscosity of a 0.5 mol dm\(^{-3}\) MIPA solution, at equilibrium pH, with
FIGURE 8.5.2 Reduced viscosity as a function of MIPA concentration
FIGURE 8.5.3 Dynamic viscosity as a function of pH (conc. MIPA=0.5M, IS=1.5M)
FIGURE 8.5.4 Dynamic viscosity as a function of ionic strength for 0.5M MIPA
FIGURE 8.5.5 Dynamic viscosity as a function of LiCl concentration for 0.5M MIPA
\((\text{NH}_4)_2\text{SO}_4\) Solution

**FIGURE 8.5.6** Dynamic viscosity as a function of \((\text{NH}_4)_2\text{SO}_4\) concentration for 0.5M MIPA
electrolyte concentration for LiCl and (NH$_4$)$_2$SO$_4$, respectively. Both these curves show an increasing viscosity with increasing electrolyte concentration in contrast to the case for KNO$_3$. Included in both figures are values for the viscosity of the actual electrolytes. The viscosity of the MIPA-LiCl solution is greater than that of the appropriate LiCl solution, although the two viscosities approach each other at ca. 2 mol dm$^{-3}$. The viscosity of the ammonium sulphate solution is equal to or greater than that for the mixture with MIPA.

It would appear that MIPA combines with simple inorganic ions, in aqueous solution, in such a way that the normal interaction between the ions and water molecules is disrupted. The results for LiCl and (NH$_4$)$_2$SO$_4$ would suggest that, assuming additivity, the MIPA makes little or no positive contribution to the viscosity of the solution. This being unlikely, indicates that the degree of solvation of the electrolyte ions is upset by the presence of MIPA molecules.

The dynamic viscosity of aqueous 1-aminopropane solutions was studied. Table B.5.8 shows how the viscosity varied with the amine concentration; the data is plotted in figure 8.5.1. The reduced viscosity shows a similar variation with concentration as does MIPA (figure 8.5.2). The minimum in its value occurring at a value of $c$ of between 0.5 and 1.3 g per 100 cm$^3$.

Figure 8.5.7 gives the variation of viscosity for a 0.59 mol dm$^{-3}$ amine solution with [KNO$_3$]. The curve is of the same shape as found for MIPA. The pH effect is seen in figure 8.5.8 where the viscosity-ionic strength curves are plotted for an equilibrium pH amine solution and for an acidic solution. Again the similarity with respect to MIPA solutions is apparent.

The dynamic viscosity of aqueous MIPA solutions appears to be dominated by the amino functional group.

8.6 Rheology of Concentrated Rutile Slurries

The Haake bobs and cups were calibrated using two standard Newtonian oils (table B.6.1), chosen to possess viscosities within the range
FIGURE 8.5.7 Dynamic viscosity as a function of KNO₃ concentration for 0.59M propylamine
FIGURE 8.5.8 Dynamic viscosity as a function of ionic strength for 0.597M propylamine.
expected for the rutile slurries. The bob and cup parameters, K and A, were not within error for a given system (e.g. MW I or SV II) for the two oils. This was not unexpected since various factors, such as end effects, modify the response of a given bob and cup. For the more viscous slurries the system parameters determined using the higher viscosity oil were used to convert the Haake viscometer readings to shear stress and shear rate values.

Table B.6.2 contains details of the slurries studied. From slurry S onwards the rutile sample CLDD 1484 was used. Each slurry was used to produce up to eight other slurries through the addition of small volumes of MIPA and/or electrolyte. It was observed that on adding an aliquot of MIPA the slurry became significantly more fluid when gently stirred with a palate knife, but on milling the slurry would thicken. Increasing the ionic strength of the added MIPA solution reduced the thinning effect.

The results for the various slurries studied are tabulated immediately following table B.6.2. The initial milling of the slurry was carried out for typically 60 mins while milling of the slurries produced from the mother slurry were milled for 15 mins. The rheological measurements were carried out by following the sequence -

a) increasing the shear rate from minimum to maximum measuring the recorded torque once it had attained its maximum value before proceeding to the next shear rate;

b) decreasing the shear rate from maximum to minimum and recording the steady torque value;

c) increasing the shear rate to the maximum once more.

The latter two sets of measurements were generally in good agreement. The shear stress value at a given shear rate was generally taken as the mean of these two sets.

Increasing the MIPA content of the slurries not only had a major effect on the viscosity of the slurry but also led to the appearance of
time dependent flow behaviour at the higher shear rates studied, namely
the viscosity increased. Assessment of the type of particle present by
diluting a sample of slurry in distilled water and observing under a
microscope indicated that increasing the MIPA content led to the
production of more primary particles.

A typical set of flow curves is shown in figure 8.6.1 (slurry L).
The curves can be recognised as representing pseudoplastic flow
behaviour. The increasing shear rate tends to break down the weaker flow
units, such as agglomerates and floccules, with a consequent decrease in
the viscosity. Increasing the MIPA content, in this case from 0.0192 to
0.0379% w/w, reduces the pseudoplastic characteristics, and in fact the
slurry viscosity becomes less dependent upon the shear rate. A similar
series of curves was found for all the slurries, although clearly the
degree of pseudoplastic behaviour was also a function of the electrolyte
content.

The effect of a variation in the solids content of the slurry was
studied both in the absence and presence of MIPA. The results indicate
that the slurry viscosity rises exponentially with solids content (θ), at
a given shear rate (figure 8.6.2). In the absence of MIPA the viscosity
(at γ = 24.5 s\(^{-1}\)) appears to approach infinity at a θ value of ca. 49%.
However, in the presence of 0.02% w/w MIPA the limit appears at ca. 55%.
The presence of such a small quantity of MIPA (equivalent to ca. 2.5
µmol g\(^{-1}\) if all adsorbed by the rutile) exerts a dramatic effect on the
viscosity of the slurry. At a solids content of 45% w/w the presence of
such an amount reduces the viscosity from 27 to 6.5 poise at a shear rate
of 24.5 s\(^{-1}\). The MIPA improves the dispersibility of the rutile.

Figure 8.6.3 shows how the viscosity, at a given shear rate, varies
with the MIPA content for a constant slurry solids content. The presence
of ca. 0.04% w/w MIPA appears to be sufficient to reduce the viscosity of
a 51% solids slurry to less than 2 poise for shear rates in the range
2-570 s\(^{-1}\).

The presence of backing electrolytes reduces the ability of MIPA to
lower the viscosity of slurries, an increase in the inert electrolyte
content increases the quantity of MIPA required to achieve a desired
FIGURE 8.6.1 Typical series of flow curves (slurry L)

Increasing MIPA content

\( \tau / \text{dyne cm}^2 \) vs. \( \gamma / \text{s}^{-1} \)
% MIPA (w/w)

- 0
- 0.0191
+ 0.0198
△ 0.0232

FIGURE 8.6.2 Viscosity (at γ = 24.5 s\(^{-1}\)) variation with the solids content
FIGURE 8.6.3 Viscosity at selected shear rates as a function of MIPA content.
viscosity. A rise in electrolyte content increases the viscosity of the slurry as the result of increased aggregation of the rutile. Additions as small as 0.2 μmol g⁻¹ KNO₃ can significantly increase the viscosity, slurry CC. Raising the MIPA content with respect to the electrolyte lowers the viscosity, although the viscosity at low shear rates may remain excessively high, eg slurry P.

The electrolyte type appears to be important in that lithium chloride, in equivalent amounts (in terms of moles), does not inhibit the viscosity lowering ability of MIPA as much as potassium nitrate - compare slurries FF and GG.

The results indicate that the longer a slurry, of a given MIPA content, was milled the lower its viscosity.

8.7 Centrifugation and the Force of Coagulation

Numerous experiments to measure the effect of the centrifugal force on the fraction of rutile which can redisperse were performed - the results are given in tables B.7.1-B.7.21. The table headings have the following meaning:

\[ t_c \] - time of centrifugation
\[ \omega \] - rotor speed (radians s⁻¹)
\[ C_0 \] - initial particle number, m⁻³
\[ C \] - redispersed particle number, m⁻³
\[ F \] - fraction redispersed ( = C/C_0).

The first couple of experiments were performed using an angle rotor but the rutile sedimented on the walls of the centrifuge tube rather than the base; so that the subsequent redispersion of the rutile occurred from more than one location. The experiments from table B.7.6 onwards were therefore carried out using a swing-out rotor for which the rutile formed a sediment at the base of the tube.

The effect of a change in the initial dispersed particle number on the value of F, table B.7.5, gave no clear trend. Therefore the value of \( C_0 \) for all samples was kept constant at a value of ca. \( 10^{15} \) m⁻³. In
addition the polypropylene centrifuge tubes were numbered to aid identification of bogus tubes. It was noticed that surface scratches encouraged rutile particles to sediment at these sections of the plastic tubes and so any suspect tube was discarded. However, given undamaged tubes there was no difference in the value of F for 3 polypropylene tubes picked at random, table B.7.7.

It was observed that an increase in the solution ionic strength increased the size of the rutile sediment formed on centrifugation, in fact the rutile tended to smear across the base of the tubes. Increasing the relative concentration of MIPA to the ionic strength reduced the extent of smearing. The higher the rotor speed the more spread out the sediment. It was also noted that during the redispersion stage some of the higher ionic strength samples reformed a sediment on the tube walls.

It was estimated that the error in the value of F due to the particle counting was ±10%.

Table B.7.6 and figure 8.7.1 show the effect of ω and KNO₃ concentration on the value of F for a 5x10⁻³ mol dm⁻³ MIPA solution. The data indicates that an increase in the electrolyte content lowers the force required to prevent redispersion of the rutile. The equivalent experiments for 0.02 mol dm⁻³ MIPA were performed, table B.7.8 and figure 8.7.2. The effect is more marked for this MIPA concentration. Even an ionic strength of 3x10⁻³ mol dm⁻³ was sufficient to significantly lower the force required to irreversibly coagulate the particles. In the presence of only the MIPA even a centrifugal force of 5.2x10⁴ g was insufficient to prevent redispersion of the rutile (g-force = 1.308x10⁻²xω²).

Table B.7.9 and figure 8.7.3 show the effect of the centrifugal force on the fraction of rutile redispersed in high pH distilled water. Although the rutile is more easily redispersed than for the MIPA samples containing >4x10⁻³ mol dm⁻³ electrolyte, the difference between the high pH water and 0.02 mol dm⁻³ MIPA sample is significant. The presence of the aminoalcohol apparently increases the steepness of the kinetic energy barrier to coagulation.
The fraction of rutile redispersed as a function of centrifugal force for 0.005M KIPA solutions of varying KNO₃ concentration.
The fraction of particles redispersed as a function of \( \omega \) for 0.02M MF4 solutions of varying KNO₃ concentrations.

- [KNO₃]/mol dm\(^{-3}\):
  - X: 0
  - O: 0.0037
  - •: 0.0052
  - △: 0.0074
  - +: 0.0149
Figure 8.7.3. The fraction of tritium radiolysed as a function of $\omega$ for distilled water as a function of pH.
The effect of a variation in [MIPA], at a given pH, on the value of F for various centrifugal forces was investigated, tables B.7.10-B.7.13. Figures 8.7.4 and 8.7.5 show results for MIPA concentrations up to 0.01 mol dm$^{-3}$ at a pH ca. 11. The effect of [MIPA] becomes more pronounced at higher centrifugal forces, the greater the concentration the larger the F value. MIPA concentrations above ca. 4x10$^{-3}$ mol dm$^{-3}$ show a definite difference from high pH distilled water. Comparison of the results shown in figure 8.7.6 with those of the previous two figures highlights the pronounced role that simple electrolytes, even at relatively low concentrations, play in determining the force of interaction between dispersed particles. The results in table B.7.14 and shown in figure 8.7.7 confirm the roles that [MIPA] and [KNO$_3$] play in determining the variation of F with $\omega$. The filled symbols represent the higher ionic strength dispersion.

The effect of solution pH at a constant total ionic strength was studied, table B.7.15 and B.7.16. Figure 8.7.8(a) gives the variation of F with $\omega$. For each pH an increase in the centrifugal force reduces the fraction of rutile redispersed, although the variation is dependent on the pH. Figure 8.7.8(b) replots the data to give F as a function of pH. The results show that on decreasing the pH from 10.7 to 9.6 the value of F increases, for a given centrifugal force. An increase in the latter reducing the magnitude of the effect.

Table B.7.17 and figure 8.7.9 show how F depends upon the [MIPA] at a fixed pH and centrifugal force. Over the range 2x10$^{-5}$ to 4x10$^{-3}$ mol dm$^{-3}$ MIPA there is little change in the fraction of rutile redispersed. Figure 8.7.10 gives the results of a similar study carried out at a pH 11.4. The data in table B.7.18 shows that high pH distilled water gives rise to less easily coagulated rutile particles than low pH water.

Solutions of AMP, TEA, and aminopropane at similar concentrations were studied, table B.7.19. The limited results indicate that both AMP and the amine are as effective as MIPA in preventing irreversible coagulation of rutile. The triethanolamine appears to be less effective.
FIGURE 8.7.4: The fraction rutile dispersed as a function of ω for different MPA concentrations (PH ca. 11).
Figure 8.7.5 The fraction of rutile redispersing as a function of ω for low MIPA concentrations
FIGURE 8.7.6

The fraction of rutile redisersed as a function of \( \omega \) for different MIPA concentrations (pH11, IS=0.005M).

\( \text{[MIPA]} / \text{mol dm}^{-3} \)
- \( \times \) \( 2 \times 10^{-5} \)
- \( \circ \) \( 1 \times 10^{-4} \)
- \( \bullet \) \( 5 \times 10^{-4} \)
- \( \triangle \) \( 8 \times 10^{-4} \)
- \( + \) \( 2 \times 10^{-3} \)
- \( \nabla \) \( 5 \times 10^{-3} \)
FIGURE 8.7.7
The variation of the fraction of rutile dispersed with ω, conc. MIPA, conc. KNO₃.

<table>
<thead>
<tr>
<th>[MIPA]/mol dm³</th>
<th>2 × 10⁻⁵</th>
<th>2 × 10⁻⁴</th>
<th>6 × 10⁻⁴</th>
<th>6 × 10⁻⁴</th>
<th>0.020</th>
<th>0.020</th>
<th>0.050</th>
<th>0.150</th>
<th>0.250</th>
</tr>
</thead>
<tbody>
<tr>
<td>[KNO₃]/mol dm³</td>
<td>2 × 10⁻⁴</td>
<td>2 × 10⁻³</td>
<td>2 × 10⁻³</td>
<td>2 × 10⁻³</td>
<td>2 × 10⁻⁴</td>
<td>2 × 10⁻³</td>
<td>5 × 10⁻³</td>
<td>5 × 10⁻³</td>
<td>5 × 10⁻³</td>
</tr>
<tr>
<td>pH</td>
<td>10.95</td>
<td>10.96</td>
<td>10.95</td>
<td>10.95</td>
<td>11.02</td>
<td>11.03</td>
<td>11.58</td>
<td>11.58</td>
<td>11.59</td>
</tr>
</tbody>
</table>
FIGURE 8.7.8(b) \( F \) as a function of \( \text{pH} \) for different \( \omega \) values
FIGURE 8.7.9 The fraction of rutile redispersed as a function of MIPA concentration (pH=10.95)
A function of MPA concentration (pH=11.3) as a function of HCl concentration.

The extraction of urate redispersal as a function of pH.

Figure 8.7.10 The extraction of urate redispersal as a function of pH.

pH 11.77

\[ 0 = 1257 \]
The fraction of rutile redispersed as a function of the additive for different \( \omega \) (rad s\(^{-1}\)).

<table>
<thead>
<tr>
<th>Additive</th>
<th>( \text{C}_{\text{mol dm}^{-3}} )</th>
<th>( \text{F} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMP</td>
<td>0.0108</td>
<td>0.96</td>
</tr>
<tr>
<td>T.E.A.</td>
<td>0.0105</td>
<td>0.80</td>
</tr>
<tr>
<td>Amino-propane</td>
<td>0.0104</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Graph showing data points for AMP, T.E.A., and amino-propane with \( \omega \) values from 0 to 2600 rad s\(^{-1}\).
8.8 Other Experimental Studies

Various additional investigations were performed including surface tension measurements, heat capacity of aqueous solutions, sedimentation rates, repeptisation, observations of the general behaviour of rutile in the presence of MIPA.

8.8.1 Surface Tension of Aqueous MIPA Solutions

The ease of dispersion of rutile in such solutions indicates a lowering of the surface free energy at the solid-liquid interface. Although this parameter is difficult to measure it was considered of potential use to measure the liquid–air interfacial tension of aqueous solutions as a function of MIPA concentration. The drop weight method was used with measurements performed in a constant temperature room (25°C).

The dependence of the liquid-air interfacial tension on the MIPA concentration is shown in table 8.8.1.

Table 8.8.1. The variation of the surface tension of water with the MIPA concentration (25°C)

<table>
<thead>
<tr>
<th>[MIPA]/mol dm⁻³</th>
<th>γ/ N m⁻¹</th>
<th>[MIPA]</th>
<th>γ/ N m⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0722</td>
<td>0.050</td>
<td>0.0716</td>
</tr>
<tr>
<td>0.002</td>
<td>0.0717</td>
<td>0.075</td>
<td>0.0710</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0714</td>
<td>0.100</td>
<td>0.0710</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0715</td>
<td>0.125</td>
<td>0.0708</td>
</tr>
</tbody>
</table>

Over the range studied MIPA has little effect on the surface tension.
8.8.2 Thermal Heat Capacity of Aqueous MIPA Solutions

The possible change in the hydrogen bonding properties of water as a consequence of the presence of MIPA molecules was studied both by dynamic viscosity measurements and by determining the thermal heat capacity of aqueous solutions. The latter measurements were made by the technique of Differential Thermal Analysis (DTA). The method involved measuring the difference in the heat energy input as a function of temperature between a sample of solution and a reference (usually air) - the difference being proportional to the specific heat capacity and mass of the sample. To obtain a value for the specific heat capacity it was therefore necessary to measure the heat energy input difference as a function of sample mass.

A Du Pont DTA instrument was used and samples were sealed, using a high pressure die press, into aluminium pods. The sample and reference pods were placed in position on the instrument and the temperature was raised at a rate of 10°C per minute. The difference in the heat energy inputs was taken from the recorded chartpaper at a temperature of 60°C. The sample pod was reweighed and compared with the starting weight in order to check for loss by evaporation.

Figure 8.8.1 shows the results of the differential thermal analysis experiments on distilled water and MIPA solution. The slope of the line for a given solution is proportional to its specific heat capacity. Within the limits of the experimental error there appears to be no influence of such MIPA concentrations on the heat capacity of water. However, closer control of such experimental factors as positioning of the aluminium pods on the detector regions of the DTA apparatus needs to be achieved and the study repeated to double check.

8.8.3 General Observations

a) The ability of MIPA solutions to disperse rutile pigment was noted to be dependent on ionic strength and pH. A qualitative study was carried out in which ca 20 mg rutile was mixed with 0.1 mol dm⁻³ MIPA solutions of various pH values and ionic strengths. The presence of a surface foam on shaking and the quality of dispersion were noted. The
FIGURE 8.8.1 The variation in heat input of samples of distilled water and MIPA as a function of sample mass.
samples were rotated at 15 rpm for 10 days and allowed to stand before a final observation was carried out. Table 8.8.2 contains details on the existence of a surface foam and a good dispersion. Table 8.8.3 gives details concerning the formation of a sediment.

**TABLE 8.8.2** Qualitative study on the ability of MIPA to affect interfaces.

<table>
<thead>
<tr>
<th>Tube</th>
<th>Ionic Strength (\text{mol dm}^{-3})</th>
<th>pH</th>
<th>Dispersion</th>
<th>Foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(10^{-3})</td>
<td>11.18</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
<td>0.008</td>
<td>10.30</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>0.051</td>
<td>9.5</td>
<td>+/-</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>0.102</td>
<td>2.51</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.101</td>
<td>11.21</td>
<td>+/-</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>0.107</td>
<td>10.25</td>
<td>+/-</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>0.150</td>
<td>9.46</td>
<td>-</td>
<td>+/-</td>
</tr>
<tr>
<td>8</td>
<td>0.200</td>
<td>7.43</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE 8.8.3** The influence of MIPA upon the formation of a sediment (Samples as for table 8.8.2)

<table>
<thead>
<tr>
<th>Tube</th>
<th>After 10 days of rotation</th>
<th>After further 1 (\frac{1}{4}) hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no sediment</td>
<td>sediment + dispersion</td>
</tr>
<tr>
<td>2</td>
<td>no sediment</td>
<td>sediment + dispersion</td>
</tr>
<tr>
<td>3</td>
<td>little sediment</td>
<td>redispersion easy</td>
</tr>
<tr>
<td>4</td>
<td>rutile adheres to stopper</td>
<td>non-redispersible</td>
</tr>
<tr>
<td>5</td>
<td>sediment</td>
<td>non-redispersible</td>
</tr>
<tr>
<td>6</td>
<td>sediment</td>
<td>non-redispersible</td>
</tr>
<tr>
<td>7</td>
<td>sediment</td>
<td>non-redispersible</td>
</tr>
<tr>
<td>8</td>
<td>sediment</td>
<td>non-redispersible</td>
</tr>
</tbody>
</table>
The results indicate that neutralisation of the MIPA prevents foaming and this is not an ionic strength effect. High ionic strength prevents the formation of a good dispersion, although given sufficient agitation an acceptable dispersion may form. A coarse dispersion possessing a large sediment volume is normally formed with a high ionic strength dispersion medium – the sediment does not redisperse. A good, milky in appearance dispersion forms a small sediment volume which is readily redispersed if MIPA is present in solution.

b) A well dispersed rutile dispersion is milk-like in appearance and will flow over and coat the walls of its glass container. A poorly dispersed one will rapidly drain from the container walls and may form plugs of pigment.

c) After centrifugal sedimentation of rutile dispersions it is found that a high ionic strength leads to the formation of a widely spread-out sediment whereas an initially well dispersed sol gives a more localised sediment.

d) The addition of MIPA to a coarse sediment of rutile causes the spontaneous formation of a milky dispersion.

e) Dispersion of rutile in about 10 cm$^3$ of a 0.1 mol dm$^{-3}$ MIPA solution produces a temperature rise of about 0.2°C.

f) The addition of rutile pigment to an aqueous MIPA solution produces a cracking sound as the agglomerates enter the solution and are observed to disperse.

g) Rutile powder which is carefully added to a MIPA solution leaves a trail of finely dispersed particles as the large agglomerates of pigment fall through the solution. The limiting ionic strength, above which the trailing was negligible for a range of electrolyte solutions was estimated.
<table>
<thead>
<tr>
<th>MIPA concentration /mol dm(^{-3})</th>
<th>KNO(_3) limiting concentration /mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.007</td>
</tr>
<tr>
<td>0.02</td>
<td>0.016</td>
</tr>
<tr>
<td>0.04</td>
<td>0.021</td>
</tr>
<tr>
<td>0.08</td>
<td>0.027</td>
</tr>
<tr>
<td>0.10</td>
<td>0.025</td>
</tr>
<tr>
<td>0.20</td>
<td>0.026</td>
</tr>
</tbody>
</table>

For a 0.1 mol dm\(^{-3}\) AMP solution the limiting concentration of barium nitrate is approximately 0.0004 mol dm\(^{-3}\).

8.8.4 Photo-oxidation Reaction

The fact that rutile was able to photocatalyse a reaction involving MIPA when exposed to natural light initiated a series of tests to detect and identify the reaction products. Various columns were used in order to try to separate the components by gas-liquid chromatography. However, no suitable packing was found. Ultraviolet spectroscopy proved to be of more use. The following aqueous solutions gave these features

- MIPA - band <230 nm
- acetone - broad peak ca. 265 nm
- MIPA + acetone - band <230 nm + peak 265 nm
- MIPA after contact with rutile - band <230 nm + peak 280 nm

The strength of the peak at 280 nm in the MIPA solution after equilibration with rutile in the presence of light increases as the measured amino loss of the solution increases. The peak is due to a carbonyl group but is not due to acetone. The structure of the MIPA molecule and the nature of the odour associated with the reaction product suggests that the photo-oxidation gives acetaldehyde and methylamine.
CHAPTER 9

DISCUSSION
9. DISCUSSION

The experimental data has indicated that the properties of aqueous dispersions of rutile are modified, in some cases only subtly, by the presence of MIPA (and other similar organic compounds eg AMP, TEA, and propylamine).

Monoisopropanolamine is adsorbed at the rutile-aqueous solution interface, although the amount of adsorption within the Stern layer is a function of pH and bulk electrolyte concentration. In the presence of even diffuse light the dispersed rutile catalyses the photo-oxidation of the organic species. Since diffusion into and adsorption within the Stern layer is probably the rate determining step in the reaction the effect of ionic strength on the total decrease in the aminoalcohol concentration reflects the effect on the amount of adsorption, namely the backing electrolyte competes successfully with the organic species for sites at the interface.

The electrical potential at the shear plane is relatively unaffected by the presence of MIPA. The isoelectric point shifts to a slightly higher pH which is indicative of the specific adsorption of a cationic species, namely the conjugate acid form of MIPA. A subtle effect is apparent within the pH range 10-11, a maximum in the zeta potential is observed in the presence of $4 \times 10^{-3}$ mol dm$^{-3}$ MIPA solution.

The stability of a dilute aqueous rutile dispersion against particle aggregation is low ($w < 20$). The presence of MIPA has negligible effect on the measured stability ratio. However, the decrease in primary particle number with time suggests that the particle aggregation is reversible with the effect more pronounced if the dispersion medium contains MIPA, at alkaline pH.

The ease of dispersion of rutile powder in aqueous solution is greatly enhanced if MIPA is present. In MIPA solutions at the equilibrium pH (ie ~11) the dispersion is effectively instantaneous. Under similar conditions of pH and ionic strength but with no MIPA energy needs to be applied, eg agitation, before the rutile is dispersed. An increase in the dispersion medium ionic strength reduces the ability of
MIPA to disperse rutile. The surface tension of water is not significantly affected by the presence of MIPA even at concentrations of 0.1 mol dm\(^{-3}\).

The force required to cause aggregation, into the primary minimum, of dispersed rutile particles is significantly increased by the presence of MIPA. Increasing the ionic strength decreases the force required.

The dynamic viscosity of aqueous MIPA solutions indicates that the organic molecule is a strong structure making species. The variation of the solution viscosity as a function of ionic strength indicates that MIPA molecules and electrolyte ions, in particular cations, interact with each other and the solvent.

The rheological behaviour of concentrated aqueous rutile slurries (c<50% w/w) is pseudoplastic. The presence of relatively small amounts of MIPA (about 0.03% w/w) produces a significant lowering of the slurry viscosity at a given shear rate, and enables a higher solids concentration slurry to be produced which can still flow.

It appears that MIPA assists in the dispersion of rutile and reduces the viscosity of concentrated rutile slurries by introducing an additional repulsive interaction at small particle separations. The structure making properties of the organic molecule suggest the existence of a solvation interaction due to MIPA molecules adsorbed within the Stern layer.

**9.1 The Interaction Between MIPA and Water**

The behaviour of solutes in water is generally explained by the structural changes in the solvent upon the introduction of the solute. In solutions of electrolytes with large ions, such as K\(^+\), Cl\(^-\) and NO\(_3\)^-, the ions tend to decrease the extent of intermolecular hydrogen bonding of the water in the vicinity of the ions - these are electrostrictive structure breakers. However, in solutions of electrolytes with small ions, such as Li\(^+\) and F\(^-\), the ions tend to promote water structure in their vicinity - these are electrostrictive structure makers. Organic solutes possess nonpolar groups which also promote water structures as
the result of the hydrophobic interaction. Aminoalcohols, such as MIPA, although possessing a hydrocarbon backbone are highly polar solutes because of the hydroxyl and amino functional groups. Consequently the solubility in water is effectively infinite and hence the organic solute is fully hydrated.

The viscosity B coefficient of a solute gives a measure of the degree and type of interaction between the solute and solvent. The viscosity of aqueous solute solutions can be expressed by the Jones-Dole equation:

$$\eta_r = 1 + A/c + Bc$$  \hspace{1cm} (9.1)

where $\eta_r$ is the relative viscosity
A is the constant relating to ion-ion interaction
B is the viscosity B coefficient
c is the solute concentration.

By plotting the term $(\eta_r-1)/c$ against $c$ a straight line can be drawn with the slope giving B and the intercept A. The resulting plots for aqueous solutions of MIPA and propylamine (at the equilibrium solution pH) are shown in Figure 9.1. The B coefficients are given in Table 9.1 along with the values for various electrolyte ions and organic solutes (at 25°C).

<table>
<thead>
<tr>
<th>Organic</th>
<th>$B$/dm$^3$ mol$^{-1}$</th>
<th>Ion</th>
<th>$B$/dm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIPA</td>
<td>0.321 ±0.007</td>
<td>Li$^+$</td>
<td>0.1495</td>
</tr>
<tr>
<td>Propylamine</td>
<td>0.315 ±0.018</td>
<td>Na$^+$</td>
<td>0.0863</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H$^+$</td>
<td>0.069</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.875</td>
<td>K$^+$</td>
<td>-0.0070</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg$^{2+}$</td>
<td>0.3852</td>
</tr>
<tr>
<td>Arginine</td>
<td>0.36</td>
<td>Cl$^-$</td>
<td>-0.0070</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO$_3^-$</td>
<td>-0.0460</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OH$^-$</td>
<td>0.109</td>
</tr>
</tbody>
</table>

203
Figure 9.1  Jones-Dole plot.

- X MIPA
- ○ Propylamine
The viscosity $B$ coefficient is specific for the solute and temperature. The $B$ coefficient of a given electrolyte is an additive property of the constituent ions. The $B$ coefficients can be strongly correlated with the entropy of solvation of the solute or ion$^{238}$. Negative values are associated with species which exert a structure breaking effect on water eg $K^+$, $NO_3^-$. Positive values are associated with species which exert a structure making effect, ie are strongly hydrated, eg $Li^+$, $F^-$, $Mg^{2+}$.

Clearly, MIPA influences the water structure as for the latter type of solute. Since the $B$ coefficient for propylamine is, within error, the same as for MIPA it is likely that the hydroxyl functional group of the aminoalcohol plays a minor role in the interaction with water. It does, however, reduce the volatility of the organic.

An extension of the Einstein equation describing the viscosity-particle concentration relationship (see section 6.2.1) to solutions of strongly hydrated solutes can be carried out to give the following

$$
\eta_r = \exp \left( \frac{2.5 V c}{1 - QV c} \right) \tag{9.2}
$$

where $V$ is the effective rigid molar volume of the solute

$Q$ is an arbitrary constant.

Expanding the exponential term gives for small $c$

$$
\eta_r - 1 = 2.5 V c \tag{9.3}
$$

Comparison with the Jones-Dole equation shows that $B \approx 2.5 V$ (for MIPA the value of the Jones-Dole coefficient $A$ is $-0.0134 \pm 0.0043 \text{ dm}^{3/2} \text{ mol}^{-1/2}$ and so for small $c$ the second term in equation 9.1 can be neglected).

Thus for MIPA the value of $V$ is $0.128 \text{ dm}^3 \text{ mol}^{-1}$. The rigid molar volume represents the molar volume of solute plus any water of hydration which is held too firmly to participate in the viscous shearing process. The molar volume of MIPA in solution is $0.0780 \text{ dm}^3 \text{ mol}^{-1}$. The $V$ value
therefore indicates that the MIPA molecule behaves as if there were 
\[
\frac{(0.128 - 0.0780)}{0.018} = 2.8
\]
molecules of water bound to it.

The A coefficient in the Jones-Dole equation takes account of the 
ionic interaction contribution to the viscosity. Its effectively 
negligible value indicates that the conjugate acid form of MIPA (or 
propylamine) does not contribute to the solution viscosity, under the 
given conditions of pH.

The variation in solution viscosity with pH, at constant ionic 
strength and MIPA concentration, (as shown in figure 8.5.3) can be 
explained if the changes in the type and concentration of constituent 
ions is considered. At high pH, greater than about 11, the ions present 
are MIPA⁺ and OH⁻. As the solution pH is lowered by the addition of 
nitric acid the OH⁻ ions are replaced by NO₃⁻ ions and the concentration 
of MIPA⁺ increases at the expense of the concentration of the neutral 
species. Below a pH of about 7 the electrolyte composition includes H⁺ 
ions in addition to an increased NO₃⁻ content. The reduction in 
viscosity down to a pH of about 4 is due to the replacement of structure 
making hydroxyl ions by structure breaking nitrate ions and the loss of 
the structure making neutral MIPA molecule. At lower pH values the 
addition of hydrogen ions which are structure making species causes the 
viscosity to rise.

At a given pH and MIPA concentration the solution viscosity 
decreases as the KNO₃ concentration is increased, figure 8.5.4. The 
viscosity rapidly falls to values below that of the corresponding 
concentration of KNO₃. At high ionic strength the solution viscosity 
tends towards the viscosity of pure water. The difference between the 
highest pH solution and the other two solutions (figure 8.5.4) is 
possibly due to differences between MIPA⁺ and K⁺ in their interaction 
with water. The presence of the KNO₃ clearly has an adverse effect on 
the structure making properties of the MIPA molecule. Since KNO₃ is a 
structure breaker and MIPA a structure maker there will be a tendency for 
the solutes to repel each other\textsuperscript{239}. The net result will be a neutralisation 
of the structure making influence of MIPA and a resultant rise in 
the structure breaking effect. Solutions of strongly structure breaking 
electrolytes, such as NH₄I, also exhibit a decreasing viscosity with
increasing concentration and at certain concentrations the viscosity is lower than for pure water.

If a structure making electrolyte such as LiCl (B = 0.143 dm$^3$ mol$^{-1}$) or (NH$_4$)$_2$SO$_4$ (B = 0.201 dm$^3$ mol$^{-1}$) is used as backing electrolyte the viscosity of a MIPA solution increases as the ionic strength is increased, in contrast to the case with KNO$_3$ (figures 8.5.5 and 8.5.6). The increase in viscosity is not simply due to the additive contributions of the relevant B coefficients. With LiCl the viscosity of the MIPA solution is slightly greater than for the electrolyte alone whereas for the (NH$_4$)$_2$SO$_4$ system the viscosity of the MIPA solution falls below that of the electrolyte alone. For both systems the increase in viscosity is the result of the increase in the concentration of the structure making electrolyte. In the case of the sulphate electrolyte there appears to be competition between MIPA molecules and sulphate ions for water molecules with the consequence that the mixed solution possesses a lower viscosity.

Aqueous propylamine solutions show similar variations in viscosity with increasing KNO$_3$ concentration and pH as do MIPA solutions.

**9.2 Nature of the Electrical Double Layer**

The electrophoresis and adsorption isotherm data can provide information on the properties of the electrical double layer associated with the rutile-solution interface. Unfortunately as the result of the photo-catalytic effect of the rutile and the oxidation of the MIPA the directly useful adsorption isotherm data is limited.

**9.2.1 Zeta Potentials**

Taking a particle radius of $0.1 \times 10^{-6}$ m for the rutile leads to $\kappa a$ values between 5 and 30 for the dispersions studied. In this region the effects of electrophoretic relaxation and retardation are pronounced. Consequently the classical approaches of Smoluchowski, Huckel, and Henry cannot be applied. The numerical computations due to O'Brien and White$^{230}$ take these effects into account and consequently are the best available mobility to zeta potential conversions. The computations
appropriate to the case of a 1:1 electrolyte with limiting conductivity for each ion equal to 75 ohm$^{-1}$ cm$^2$ mol$^{-1}$ were used in the present study to convert the mobility values.

Figure 9.2 shows the variation of zeta potential with pH for electrolyte solution and 4 x $10^{-3}$ mol dm$^{-3}$ MIPA solution. The magnitudes of the zeta potential in KNO$_3$ solution are in reasonable agreement with values given by other workers, e.g. Wiese and Healy$^{240}$, Webb et al$^{241}$ and Yates (see figure C.7 in appendix C). The presence of the 4 x $10^{-3}$ mol dm$^{-3}$ MIPA shifts the isoelectric point to a slightly higher pH indicating specific adsorption of the conjugate acid form of MIPA. At pH values below the iep the magnitude of the zeta potential is lower than for KNO$_3$, however this is probably due to the higher ionic strength associated with the MIPA solution (neutralisation of the organic base giving 4 x $10^{-3}$ mol dm$^{-3}$ ionic strength). At high pH the MIPA is largely present in solution as the free base. For pH values above 10 the zeta potential is significantly more negative in the presence of MIPA. Although partly due to a slightly lower ionic strength in the pH range 10.1-10.6 the effect is apparent at pH above 11 for which there is little difference in ionic strength. Adsorption of neutral MIPA molecules within the Stern layer would displace specifically adsorbed cations thereby increasing the potential drop within the diffuse layer and hence increasing the measured zeta potential.

The electrophoretic mobilities for the dispersions containing 4 x $10^{-3}$ mol dm$^{-3}$ MIPA in the pH range 10-11 were of such a value that no corresponding zeta potential could be obtained from the O'Brien and White method. For $\kappa a$ values greater than about 4 the mobility passes through a maximum as the zeta potential is increased. The dimensionless mobility values of these dispersions were in the range 3.2-4.1 ($\kappa a$ in the range 6-10). The experimental error in the electrophoretic mobilities was no greater than 10% which is insufficient to give acceptable dimensionless mobilities. Extrapolation of the conversion curves would suggest that the zeta potentials of these dispersions do not exceed -130 mV. The approach used by O'Brien and White makes various assumptions including the uniformity of the solution viscosity and dielectric constant throughout the dispersion medium. The structure making properties of MIPA and its adsorption within the Stern layer could lead to an increase and
Figure 9.2 Variation of zeta potential with pH

- ○ 1mM KNO$_3$
- × 4mM MIPA
decrease in the Stern layer viscosity and dielectric constant, respectively.

The effect of ionic strength and electrolyte type on the zeta potential of rutile dispersed in $4 \times 10^{-3}$ mol dm$^{-3}$ MIPA is shown in figure 9.3. The decreasing magnitude of the zeta potential with increasing KNO$_3$ concentration is readily explained in terms of the decrease in both the diffuse layer thickness and the potential drop. The data for the other electrolytes suggest that there is some specific type of interaction between the electrolyte ions and the MIPA molecules. The effect may be related to the positive interaction that exists between solute species which are both structure makers. The MIPA molecule is a structure maker as are Li$^+$ and Na$^+$. The fluoride ion is also a structure maker.

Although experiments were performed, under conditions of constant pH and ionic strength, to study the effect of MIPA concentration on the zeta potential no clear trend was found in the variation of the electrophoretic mobility (figure 8.1.4). It was noted that the value of the electro-osmotic mobility was markedly lower in solutions with greater than about 0.01 mol dm$^{-3}$ MIPA. Adsorption of the organic at the electrophoresis cell walls was therefore a problem.

9.2.2 Adsorption of MIPA

The study of the interaction between MIPA and the rutile-solution interface was made more complex by the oxidation of the MIPA brought about by the photocatalytic properties of the rutile surface. Consequently the measured changes in the bulk MIPA concentration were not solely the result of adsorption (figure 8.3.1). However, the trends in the isotherms can be useful for the qualitative description of the effect of solution variables on the extent of MIPA adsorption (see appendix B). These adsorption isotherms, carried out in the presence of diffuse light, indicate that the ionic strength of the solution has a significant effect on the MIPA loss even at values for which the quality of dispersion is good.

The limited data corresponding to isotherms carried out with the dispersions covered provides information on the actual adsorption of MIPA.
[MIPA] = 4 mM

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td>11.3</td>
</tr>
<tr>
<td>KNO₃</td>
<td>10.5</td>
</tr>
<tr>
<td>LiCl</td>
<td>10.5</td>
</tr>
<tr>
<td>KCl</td>
<td>10.5</td>
</tr>
<tr>
<td>NaF</td>
<td>10.4</td>
</tr>
<tr>
<td>LiCl</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Figure 9.3 Dependence of zeta potential on electrolyte
at the rutile surface. The isotherm showing the dependence of the quantity of adsorption on the bulk MIPA concentration, at fixed pH (11.0), is given in figure 8.3.3. The shape of the curve is not of the Langmuir type which is typical for the adsorption of small solutes or ions. Analysis of this data in terms of the Stern adsorption isotherm is consequently not practical.

The dependence of the adsorption on solution pH for constant MIPA concentration (8 \times 10^{-3} \text{ mol dm}^{-3}) and constant ionic strength (9 \times 10^{-3} \text{ mol dm}^{-3}) is shown in figure 8.3.4. The shape of the isotherm suggests the existence of a maximum in the quantity of adsorption at a solution pH of about 9.2. If the adsorption ratio, S (defined as the ratio of the amount adsorbed to the amount remaining in solution) is plotted as a function of pH, as suggested by Rendall and Smith\textsuperscript{10}, the curve shown in figure 9.4 is produced. At low pH values the MIPA is mainly present as the cationic form (eg at pH 7 \text{ MIPA}^+/\text{MIPA} = 280) so that increased adsorption due to electrostatic attraction to the negatively charged rutile surface would be expected. However, the zeta potential is falling rapidly to less negative values over the pH range 9-7. The increasing concentration of positively charged adsorbate is offset by the reduced electrostatic attraction. At high pH the MIPA is mainly present as the neutral molecule for which adsorption at the rutile surface is by non-electrostatic forces. The adsorption exhibits a maximum at a pH which is approximately the same as the pK\textsubscript{a} value for MIPA.

The data shown in figure 8.3.2 indicates that adsorption of MIPA at the rutile-solution interface reaches equilibrium within an hour. If the maximum adsorption of neutral MIPA molecules is taken to be 40 \text{ \mu mol g}^{-1} and the specific surface area of the rutile particles is 7.26 \text{ m}^{2} \text{ g}^{-1} (as measured from a BET isotherm using nitrogen) then the number of MIPA molecules adsorbed within the Stern layer is equal to \(40 \times 10^{-6} \times 6.023 \times 10^{23}/7.26 = 3.32 \times 10^{18} \text{ m}^{-2}\). The area per adsorbed molecule is therefore 0.3 nm\(^2\), which is in reasonable agreement with the area occupied by a molecule such as SDS under conditions where repulsion between the charged head groups is low (0.33 nm\(^2\))\textsuperscript{242}. The adsorption density for the neutral MIPA is in close agreement with the literature surface site densities associated with rutile, eg a value of 5 \times 10^{18} per m\(^2\) is often used in calculations based on the site dissociation models of the oxide-solution.
Figure 9.4 Effect of pH on the adsorption of MIPA
interface (see appendix C) and a value for the surface hydroxyl group density of $7-8 \times 10^{18} \text{ m}^{-2}$ has been reported\textsuperscript{243}. 


9.3 The Interaction Between Rutile Particles

The nature of the particle-particle interaction in a dispersion effectively controls the bulk properties. The stability with respect to particle aggregation of a dispersion is closely linked with the form of the potential energy-particle separation curve, as discussed in chapter 4. For the purposes of this study DLVO theory was used to estimate the total potential energy of interaction between dispersed particles using equations 4.1 and 4.3, 4.4 for $V_A$ assuming non-retarded and retarded attractive interaction, respectively, and equations 4.7 and 4.8 for $V_R$ under conditions of constant potential and constant charge, respectively.

Although the rutile particles are unlikely to interact under conditions of perfect regulation, i.e. constant surface potential, the gains made with respect to improved accuracy by calculating $V_R$ according to regulation theory are largely offset by the greater complexity and larger number of physical parameters associated with the theory. The general arguments discussed below will remain valid if the $V_R$ contribution to the total energy of interaction is determined by using the equations given in chapter 4. Because of the magnitude of the difference in the $pK$ values of the surface hydroxyl groups the charge regulation at the rutile-solution interface will be more closely akin to interaction under conditions of constant potential.
9.3.1 The $V_T$ - Distance Curve

Figure 9.5 shows the theoretical total energy of interaction-particle separation curve for an aqueous rutile dispersion. The appropriate values of the physical parameters were chosen to be -

- Particle radius = $0.1 \times 10^{-6}$ m
- Hamaker constant = $8 \times 10^{-20}$ J
- Surface potential = 50 mV
- Ionic strength = 0.005 mol dm$^{-3}$
- Reciprocal double layer thickness = $2.32 \times 10^{8}$ m$^{-1}$
- Dielectric constant of dispersion medium = 78.5
- Temp = 25°C.

The two curves represent the cases for interaction under conditions of constant surface potential with non-retarded or retarded attraction. A deep primary minimum exists at separations below about 1 nm, a large energy barrier to aggregation in the primary minimum has its maximum at a separation of about 2.7 nm, and at larger separations a relatively shallow (approx - 1.5 kT) secondary minimum is evident. For the particle radius selected, which is the radius of the primary rutile particles, the differences between the curves for a non-retarded and retarded attractive interaction are relatively small - at separations greater than about 1.5 nm the net potential energy is more repulsive for the latter form of attraction.

If constant surface charge density is assumed the potential energy curve at separations less than about 10 nm is significantly more repulsive, eg the height of the energy barrier becomes 288 kT (67 kT for constant potential) and moves to a smaller separation, 0.7 nm as opposed to 2.7 nm. The depth and location of the secondary minimum are not affected.

Table 9.3 shows the effect of an increase in any one of the physical parameters on the magnitude of the energy maximum, secondary minimum, and their respective locations.

As discussed in chapter 4 the existence of the Stern layer (or outer Helmholtz plane) can be taken into account by incorporating its thickness, $\delta$, into the expression for $V_R$ (replace H by $H-2\delta$). Figure 9.6 shows the effect on the potential energy of interaction profile at small
Figure 9.5 The energy profile according to DLVO theory
Figure 9.6  The effect of a Stern layer on the energy profile

closest approach

1 2 3 4

Stern Layer /nm
1 0.25
2 0.50
3 0.80
4 1.00

H/nm
Table 9.3  Effect of parameters on the main factors of the total potential energy profile

<table>
<thead>
<tr>
<th>Effect of increase in</th>
<th>$V_{\text{MAX}}$</th>
<th>$H_{\text{MAX}}$</th>
<th>$V_{\text{MIN}}$</th>
<th>$H_{\text{MIN}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamaker constant</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>Particle radius</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>Surface potential</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
</tr>
</tbody>
</table>

separations (interaction at constant potential and retarded attraction was assumed). The physical parameters are the same as for figure 9.5. The effect of introducing a Stern layer around each particle, which is taken to introduce a distance of closest approach equal to $2\delta$ (where $\delta$ is the Stern layer thickness), is to reduce the depth of the primary minimum and increase the height of the energy barrier. The collision energy of the particles must therefore be greater if aggregation into the primary minimum is to occur and, conversely, less energy is required to cause redispersion of primary particles which have aggregated into the primary minimum. If the adsorption of a solute at the rutile-solution interface results in an increase in the Stern layer thickness then a shift in the total energy of interaction profile would be expected, namely curve 1→4 (assuming the outer Helmholtz potential remains the same).

An increase in the Stern layer thickness also reduces the depth of the secondary minimum and increases the particle separation at which the minimum occurs. Table 9.4 shows how these parameters vary with the Stern layer thickness.

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Table 9.4 Variation of the location and depth of the secondary minimum with Stern layer thickness

<table>
<thead>
<tr>
<th>Stern layer thickness/nm</th>
<th>Depth of minimum/kT</th>
<th>Location of minimum/nm</th>
<th>$A_m = 8 \times 10^{-20} \text{J}$</th>
<th>$a = 0.1 \times 10^{-6} \text{m}$</th>
<th>$\psi = 50 \text{mV}$</th>
<th>$\kappa = 2.32 \times 10^8 \text{m}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>-0.92</td>
<td>29</td>
<td>8 x 10^{-20}</td>
<td>0.1 x 10^{-6}</td>
<td>50 mV</td>
<td>2.32 x 10^8 m^{-1}</td>
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<tr>
<td>0.50</td>
<td>-0.88</td>
<td>30</td>
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<td>0.80</td>
<td>-0.84</td>
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</tr>
<tr>
<td>1.00</td>
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<td>32</td>
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</table>

Adsorption of neutral MIPA molecules at the rutile surface would be expected to produce a Stern layer which would differ in thickness and potential drop to the case with no MIPA. The increase in the layer thickness on adsorption could be understood in terms of the structure making properties of the organic species.

9.3.2 The Stability Ratio, $W$, For a Rutile Dispersion

Experimentally it was found that the stability ratio for the rutile dispersions was less than about 30 and that the presence of MIPA had no significant effect on the stability ratio. However, it was observed that the primary particle number reached a steady state value under conditions of low ionic strength. In the presence of MIPA this steady state condition is maintained for a significantly longer time probably as the result of the pH buffering capacity which reduces the rate of ageing of the electrical double layers due to surface potential - charge changes. Redispersion of the flocculated particles was more readily achieved if MIPA was present in solution.

Although MIPA does not produce a marked change in the stability ratio it does significantly affect the force required to achieve irreversible aggregation of rutile particles. The results of the aggregation force studies reflect differences in the particle interaction at small separations, whereas the particle counts probably reflect differences in the interaction at larger separations.

Calculation of the theoretical stability ratio (calculated using equation 4.17) corresponding to the conditions of the potential energy profile shown in figure 9.5 gives a value of $7.4 \times 10^{26}$ which is clearly much greater than the experimental values of <30. Figure 9.7 shows how...
Figure 9.7  Theoretical stability ratio as a function of Stern potential

\[ A_m = 8 \times 10^{-20} \text{J} \]
\[ a = 0.1 \times 10^{-6} \text{m} \]
\[ \kappa = 1.80 \times 10^{8} \text{ m}^{-1} \]
the theoretical stability ratio varies with the potential at the Stern plane. For values greater than about 28 mV the ratio increases rapidly. In order to obtain a W value which is of the same order of magnitude as experimental values an unrealistically large Hamaker constant (approx $3 \times 10^{-19}$ J) has to be assumed, given the double layer properties, such as ionic strength and $\phi$, which are taken from the experimental conditions.

The large discrepancy between the experimental stability ratios, both in the absence and presence of MIPA, and the theoretical stability ratios could be due to one, or more, of the following possibilities -

i) a distribution in the particle size of the aggregating particles;

ii) a distribution in the double layer properties, in particular the Stern plane potential;

iii) aggregation is into a secondary minimum rather than a primary minimum;

iv) dissolution of multi-valent species from the rutile particles with a consequent significant effect on the properties of the double layer, eg diffuse layer thickness.

9.3.2.1 Particle Size Distribution

As discussed in section 4.6.2, the effect of a distribution in the particle size is to reduce the stability ratio of the distribution. However, a large distribution in the particle sizes of the dispersed rutile would be necessary to give calculated stability ratios which are within a few orders of magnitude, let alone the same as the experimental values. The primary particle size of the Type I rutile pigment is manufactured within a relatively small radius range typically 0.08-0.13 micron, and since the particle counting method allows one to only count particles within a relatively small size range, a wide range in the sizes of the interacting rutile particles in an unlikely explanation. The energy of interaction profile is relatively insensitive to small changes in the particle size. Table 9.5 indicates how the theoretical W value depends on the particle size for constant potential and retarded
attractive interaction. Table 9.6 shows how the theoretical stability ratio varies if the interacting particles are of different sizes. The stability ratio remains several orders of magnitude larger than the experimental value even for the interaction between the smallest rutile particle size likely to be present and a particle twice the average size of 0.1 μm.

<table>
<thead>
<tr>
<th>Table 9.5</th>
<th>Variation of the stability ratio with particle radius (identical particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A = 8 \times 10^{-20}$ J, $\phi = 50$ mV, $\kappa = 2.32 \times 10^8$ m$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Particle radius/μm</td>
<td>0.05</td>
</tr>
<tr>
<td>log $W$</td>
<td>12.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 9.6</th>
<th>Variation of the stability ratio with particle radius for non-identical sized particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A = 8 \times 10^{-20}$ J, $\phi = 50$ mV, $\kappa = 2.32 \times 10^8$ m$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Radius/μm</td>
<td>particle 1</td>
</tr>
<tr>
<td></td>
<td>particle 2</td>
</tr>
<tr>
<td>log $W$</td>
<td>17.3</td>
</tr>
</tbody>
</table>

9.3.2.2 Dissolution of Multi-Valent Ions

The desorption of ions such as titanium IV or aluminium III from the rutile particle surface would lead to extensive changes in the electrical double layer and consequently in the energy of interaction profile. However, experiments on the supernatant of a 1% w/w rutile dispersion (mixed for about 2 1/2 hours) indicated that the solution conductivity was less than that of a 10$^{-4}$ mol dm$^{-3}$ KNO$_3$ solution. In addition the rutile had been subjected to several days of Soxhlet washing, see section 7.1.6. The presence of multi-valent ions in the dispersion medium is therefore unlikely.

9.3.2.3 Stern Potential Distribution

A distribution in the potential at the Stern plane will lead to a
distribution in the double layer repulsive interaction as two particles approach. Because of this distribution the overall stability, taking into account all combinations of Stern potential, is significantly lower than that appropriate to the mean potential. The values of the potential which are less than the mean have the greatest influence on the stability ratio. A distribution in the Stern potential of dispersed particles will be the normal situation. Variations in the surface charge densities and the structure of the inner region of the double layers would give rise to a range of Stern potentials. Therefore a range of repulsive interaction profiles are produced as particles approach one another, i.e. the situation is akin to a heteroflocculation.

The approach of Cooper, discussed in section 4.6.2, has been used to investigate the effect of a distribution in the Stern, or diffuse, layer potential. The form of the distribution was assumed to be normal (Gaussian) with a standard deviation of \( \sigma \). The overall stability ratio, \( W_T \), was calculated from equation 9.6

\[
\frac{1}{W_T} = \sum P_{ij}/W_{ij}
\]  

(9.6)

where \( P_{ij} \) is the probability of collision between particles of types \( i \) and \( j \)

\( W_{ij} \) is the stability ratio for the interaction between particles of types \( i \) and \( j \)

The summation was carried out for all combinations of types \( i \) and \( j \).

The probability of the occurrence of particles with a Stern potential \( x_i \) was given by

\[
P_i = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(x_i - \bar{x})^2}{2\sigma^2} \right)
\]  

(9.7)

where \( \sigma \) is the standard deviation about the mean

\( \bar{x} \) is the mean value

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The probability of collision between particles $i$ and $j$ was taken to be the product of the individual probabilities

$$P_{ij} = P_i P_j \quad (9.8)$$

The stability ratio for each combination of particle types covering the range of potentials $\bar{x} \pm 3\sigma$ was calculated using equation 4.17 and the various terms in equation 9.6 summed to obtain the overall stability ratio. Table 9.7 gives values for $W_T$ and $W$, the value appropriate to the case where only particles possessing the mean potential interact, for a range of distributions as characterised by the standard deviation. The interaction between particles was taken to occur under constant potential and non-retarded attractive interactions.

**Table 9.7** The overall stability ratio of a dispersion possessing a distribution of Stern potentials

<table>
<thead>
<tr>
<th>Ionic Strength /mol dm$^{-3}$</th>
<th>Kappa $\times 10^{-8}$/m$^{-1}$</th>
<th>$\sigma$</th>
<th>$W_T$</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>2.32</td>
<td>2</td>
<td>$2.05 \times 10^{12}$</td>
<td>$2.78 \times 10^{16}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>$1.11 \times 10^{7}$</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>$2.25 \times 10^{4}$</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>$2.78 \times 10^{3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>$1.20 \times 10^{3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>891</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.01</td>
<td>3.29</td>
<td>2</td>
<td>$3.00 \times 10^{5}$</td>
<td>$2.56 \times 10^{8}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>$1.10 \times 10^{3}$</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>321</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>242</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>248</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>284</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Clearly the effect of even a modest distribution of Stern potentials is to reduce the stability of the dispersion by several orders of magnitude. The slight increase in stability for the higher ionic strength at larger \( \sigma \) values probably reflects the increasing importance of the potential values greater than the mean.

The total energy of interaction profile for the case of two particles possessing different Stern potentials exhibits changes from the profile for particles which both possess the mean potential. Figure 9.8 shows the profiles for particles possessing the same mean potential but different values. The conditions represent interaction at constant potential and with retarded attraction. Physical parameters for the curves are

\[
A_m = 8 \times 10^{-20} \text{ J} \quad a = 0.1 \times 10^{-6} \text{ m} \quad \kappa = 2.32 \times 10^7 \text{ m}^{-1}
\]

An increase in the difference in potentials about the mean value influences the height of the energy maximum. The depth of the secondary minimum is not significantly changed.

A distribution in the Stern plane potential of the rutile particles would therefore at least partly explain the discrepancy between DLVO theory and experiment. The experimental zeta potentials had an error of between 10 and 20\% which can, in part, be ascribed to a measure of the distribution of Stern plane potentials (clearly some of the experimental error would be associated with other random errors). In addition it was observed during some of the electrophoresis experiments that, especially at cell levels for which the flow of the dispersion medium was of similar magnitude but in the opposite direction to the particle velocity, a few rutile particles migrated at a noticeably slower rate and a few in the opposite direction to the majority of the particles.

A further consideration to this distribution of potentials at the Stern plane is that the surface potential is not uniformly spread over the particle surface but in fact arises from the discrete surface charges. Consequently as two particles approach to small separations rather than experiencing a mean potential the discrete nature of the surface potential is experienced. It then becomes possible that the
Figure 9.8
The energy profile for particles possessing different potentials

Stern Potentials

<table>
<thead>
<tr>
<th>Potentia</th>
<th>/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
</tr>
</tbody>
</table>

H/nm
interacting particles realign on close approach so that the minimum repulsion occurs, i.e., areas corresponding to low surface potentials align to minimise the repulsion. The measured zeta potential is only an average (and probably a weighted average) of the potential responsible for the repulsive interaction and thus does not provide a true picture of the situation.

9.3.2.4 Secondary Minimum Aggregation

It is possible that the rutile particles are able to aggregate into a secondary minimum in the total energy of interaction profile. The calculated stability ratios refer to aggregation into the primary minimum. If aggregation into both minimums can take place then the overall stability ratio of the dispersion, $W_T$, can be approximated by

$$\frac{1}{W_T} = \frac{1}{W_p} + \frac{1}{W_s}$$

(9.9)

where $W_p$ is the stability ratio corresponding to primary minimum aggregation;

$W_s$ is the stability ratio corresponding to secondary minimum aggregation.

As discussed in section 4.6.3 Hogg and Yang\(^{120}\), and Marmur\(^{121}\) have shown that the stability of a dispersion could be controlled by the magnitude of the depth of the secondary minimum. Figure 9.9 shows the dependence of $W_s$ on the depth of the minimum according to Hogg and Yang. Marmur showed that for depths greater in magnitude than 0.75 kT the overall stability ratio, $W_T$, would not exceed about 25 despite an increase in the energy barrier to primary aggregation.

Table 9.8 gives a comparison between experimental stability ratio values and theoretical stability ratios. The zeta potential corresponding to the ionic strength (taken from figure 9.3 for potassium nitrate and $4 \times 10^{-3}$ mol dm\(^{-3}\) MIPA solution) was used in the determination of the total energy of interaction profile. Constant potential and retarded attraction were assumed, and the physical parameters were chosen as
Figure 9.9 Secondary minimum stability ratio as function of minimum depth
\[ A_m = 8 \times 10^{-20} \text{ J} \quad a = 0.1 \times 10^{-6} \text{ m} \]

**Table 9.8 Comparison of experimental stability ratios with secondary minimum stability ratios**

<table>
<thead>
<tr>
<th>Stern Potential</th>
<th>Ionic Strength</th>
<th>( W_{\text{EXP}} )</th>
<th>( V_{\text{MIN}} )</th>
<th>( W_s \text{ 1)} )</th>
<th>( W_s \text{ 2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>/mV</td>
<td>/mol dm(^{-3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.003</td>
<td>4.3</td>
<td>-0.43</td>
<td>2.9</td>
<td>&gt;40</td>
</tr>
<tr>
<td>55</td>
<td>0.004</td>
<td>4.1</td>
<td>-0.68</td>
<td>2.0</td>
<td>~30</td>
</tr>
<tr>
<td>50</td>
<td>0.005</td>
<td>3.7</td>
<td>-0.96</td>
<td>1.6</td>
<td>13</td>
</tr>
<tr>
<td>47</td>
<td>0.006</td>
<td>3.3</td>
<td>-1.28</td>
<td>1.4</td>
<td>6.8</td>
</tr>
</tbody>
</table>

1) Calculated using the Hogg and Yang approach
2) Calculated using the Marmur approach.

The agreement with experimental stability ratios can be considered to be satisfactory, in that the correct order of magnitude can be obtained, although for secondary minimum depths of less than about 0.75 kT in magnitude the approach of Marmur gives significantly higher stability ratios. However, no account was taken by Marmur of the possibility of a distribution in the Stern plane potentials, and hence in the height of the energy barrier to aggregation in the primary minimum, which would significantly increase the contribution of \( W \) to \( W_{\text{T}} \) (equation 9.9).

The following observations on the behaviour of the rutile dispersions, both in the absence and presence of MIPA, suggest that aggregation into a secondary minimum is a possibility -

* the primary particle rate of disappearance as a function of time reaches a steady state under conditions of relatively low ionic strength. Such an effect can be interpreted in terms of reversible aggregation;

* gentle agitation of the dispersion would result in the redispersion of the primary particles, the ease of redispersion being better if MIPA was present. (The effect was time dependent in that if the
aggregated dispersion was left too long redispersion by agitation was not possible - the time being significantly longer if MIPA was present.)

9.3.2.5 Summary

The experimental stability ratio for the aqueous rutile dispersions, both in the presence and absence of MIPA, can be explained using classical DLVO theory if a distribution in the Stern plane potential is taken to exist and if aggregation into a secondary minimum takes place in addition to primary minimum aggregation.

The similarity in $W$ values for dispersions with and without MIPA suggests that the organic species only significantly influences the particle-particle interaction at small separations.

9.3.3 The Force Required to Cause Irreversible Aggregation

The results of the centrifuge studies given in section 8.7 indicate that the force required to prevent redispersion by gentle end-over-end inversion of the aggregated and sedimented rutile particles was significantly higher in the presence of MIPA. At high pH (about 11) the effect only became significant for MIPA concentrations greater than about 0.01 mol dm$^{-3}$ (figures 8.7.9 and 8.7.10). At this MIPA concentration the adsorption of the organic at the rutile interface probably represents the equivalent of saturation of the surface sites, see section 9.2.2

The effect of an increase in the solution ionic strength on the force required was marked (see figure 8.7.2). An increase in the ionic strength also has an effect on the amount of MIPA adsorbed within the Stern layer (figure 8.3.6). The concentration of the MIPA relative to the electrolyte concentration appears to be an additional factor influencing the force necessary, see figure 8.7.7. The effect on pH on the fraction of the particles redispersed, under conditions of constant MIPA concentration and ionic strength, indicated that at pH values close to the $pK_a$ value for MIPA the centrifugal force required to obtain a given fraction was higher, figures 8.7.8(a) and 8.7.8(b). The adsorption isotherm also indicates a maximum in the quantity of MIPA adsorption at pH values close to 9.5, figure 9.4.
The MIPA modifies the particle interaction such that the force required to achieve irreversible aggregation in the primary minimum increases. The total energy of interaction profile is therefore altered by the adsorption of the MIPA. Two possible, although not necessarily mutually exclusive, reasons can be envisaged -

a) the slope of the $V_T$ curve leading to the energy barrier is increased in magnitude; or

b) the depth of the primary minimum is reduced to a value such that the energy barrier to redispersion is sufficiently small to allow agitation to break up the aggregates.

An increase in the slope of the energy profile on the approach to the energy maximum would require a change in either the attractive or repulsive interaction. A change in the attractive interaction due to adsorption of MIPA is not a realistic possibility for such a low molecular weight species. However, a decrease in the Hamaker constant from $8 \times 10^{-20}$ J to $1 \times 10^{-20}$ J leads to an increase in the maximum slope, which approaching particles experience, by a factor of 2.2. Such a change would also however, significantly affect the stability of the dispersion and that is not observed. An increase in the double layer repulsion due to adsorption of MIPA would also increase the maximum slope in the energy of interaction profile as two particles approach. For example, an increase in the Stern plane potential from 70 mV to 90 mV, at an ionic strength of 0.002 mol dm$^{-3}$, increases the maximum slope by a factor of 1.9. A decrease in the double layer thickness, at constant Stern potential, also increases the maximum repulsive force experienced by approaching particles, but the presence of MIPA in solution (at the alkaline pH values considered) does not contribute to the dispersion medium ionic strength. A significant change in the double layer repulsive interaction would be required to explain the difference between the dispersions with and without MIPA but this change would affect the observed stability of the dispersion and such a difference in the stability ratios of dispersions with and without MIPA is not observed.

The second proposed possible explanation for the increased force necessary to irreversibly aggregate the particles in the presence of MIPA
requires the existence of an additional repulsive interaction at small particle separations. Such an addition to the energy of interaction could be the result of either

* an increased thickness of the Stern layer; or

* the creation of a solvation type force of repulsion possessing a short range of action.

The fact that the changes in the magnitude of the centrifugal force necessary to achieve a given fraction of redispersible particles closely follow the changes in the amount of MIPA adsorbed (with respect to pH and ionic strength variations) strongly suggests that changes within the Stern layer of a rutile particle are responsible for the effect.

As shown in figure 9.6 the effect of taking the Stern layer as a distance of closest approach to a particle is to significantly reduce the depth of the primary minimum. A Stern layer thickness of 1 nm would be sufficient to reduce the energy barrier to redispersion to a few kT. Thus if the adsorption of MIPA produced an increase in the Stern layer thickness value of about 1 nm then classical DLVO theory is able to explain the observed centrifuge effect. The fact that the presence, of MIPA within the dispersion medium produces a slight increase in the magnitude of the zeta potential tends to support the view of an increase in the Stern layer thickness. However, the total energy of interaction profile would also be altered in that the height of the energy barrier would be increased and the depth of the secondary minimum decreased. Consequently the stability of the dispersion would be greater - no change observed in practice.

The strong structure making properties of the MIPA molecule could allow the type of short range solvation force discovered by Pashley\textsuperscript{100} and others to be present. The adsorption of MIPA within the Stern layer would occur such that partial dehydration of the molecule takes place. The close approach of two particles prevents desorption of the MIPA molecule and since the removal of the remaining hydration atmosphere requires a significant amount of energy (MIPA is a structure making molecule in water) a net repulsive force is experienced.
The total energy of interaction profile was determined by taking into account the short range repulsive hydration force. The overall potential energy of interaction was given as the sum of the three constituent parts

\[ V_T = V_A + V_R + V_S \]  

(9.10)

where \( V_A \) is the attractive interaction
\( V_R \) is the double layer interaction
\( V_S \) is the solvation interaction.

The expression for \( V_S \) was based on the form of the short range force measured for mica surfaces\(^{100} \)

\[ V_S = V_0 \exp\left(-\frac{H}{d}\right) \]  

(9.11)

where \( V_0 \) is the value of the interaction at zero particle separation
\( d \) is the decay length of the solvation force.

Figures 9.10 and 9.11 show the total energy profile for the following conditions - constant potential, retarded attraction

\[ A_m = 8 \times 10^{-20} \text{ J} \quad \alpha = 0.1 \times 10^{-6} \text{ m} \quad \phi = 50 \text{ mV} \]
\[ \text{Ionic strength} = 0.005 \text{ mol dm}^{-3} \quad \kappa = 2.32 \times 10^8 \text{ m}^{-1} \]

Figure 9.10 assumes a decay length of 0.2 nm for the solvation force and shows the effect of a variation in the value \( V_0 \) (equation 9.11) on the form of the energy curve. The same is true of figure 9.11 except that the decay length is taken to be 0.3 nm. The energy profiles are only modified by the solvation interaction at particle separations less than that at which the energy barrier is located. By suitable selection of the two parameters, \( V_0 \) and \( d \), it is possible to obtain an energy profile in which there exists a relatively shallow minimum at particle separations less than the energy barrier. An additional deeper minimum may also exist at smaller separations (curve 1 in figure 9.11).

The decay length of the solvation force will be a function of the nature of the particle surface and also the nature of the adsorbed species. Values of 0.2 and 0.3 nm are of the same magnitude as has been
Figure 9.10 Effect of solvation energy on interaction profile (decay length = 0.2 nm)

\[
\frac{V_s}{kT} \text{ (at surface)}
\]

1. 5000
2. 10000
3. 15000
Figure 9.11 Effect of solvation energy on interaction profile

Decay Length 0.3 nm
$\psi_0/kT$ (at surface)

1  1000
2  1500
3  2000
measured for the solvation forces for various cations on mica surfaces eg values of 0.3 nm and 0.17 nm have been quoted for lithium and potassium ions, respectively\textsuperscript{100}. 

The correct magnitude of the pre-exponential factor is less easy to assess without actual measurements of the solvation force. 

The ready redispersion of rutile particles which have been subjected to high centrifugal forces can therefore be understood in terms of the energy profiles shown in figures 9.10 and 9.11. The particles aggregate into the relatively shallow minimum to the left of the energy barrier, which is characteristic of DLVO theory, but are unable to overcome the steep barrier to aggregation into the deeper minimum that may, or may not, exist at smaller separations. The energy barrier to redispersion is sufficiently small that the particles can redisperse as the result of agitation. As the ionic strength is increased the amount of MIPA adsorbed decreases so both $V_R$ and $V_S$ become less important with the result that irreversible aggregation of the rutile particles can occur. 

In the absence of MIPA the solvation force is not present and the energy profile has either the form shown in figure 9.5 or 9.6. The energy minimum at separations less than the energy barrier is sufficiently deep to prevent redispersion. 

The fact that there is not a sudden decrease to zero, in the fraction of particles redispersed, at some critical centrifugal force probably indicates that there is a distribution of total energy of interaction profiles. 

The maximum slope of the energy profile, which is experienced by approaching particles, can be readily calculated. For the conditions appropriate to the profiles in figures 9.10 and 9.11 the force is about $3.7 \times 10^{-11}$ J m\(^{-1}\). Assuming the primary particle radius is $0.1 \times 10^{-6}$ m the weight of a rutile particle is $1.76 \times 10^{-17}$ kg. Applying Newton's Second Law gives the following expression for the centrifugal force, $F_C$, experienced by a particle
\[ F_c = 2.30 \times 10^{-18} \omega^2 \quad (9.12) \]

where \( \omega \) is the rotational speed.

For a rotational speed of 2000 rad s\(^{-1} \) the value of \( F_c \) is 9.2 \( \times \) 10\(^{-12} \) J m\(^{-1} \) which is of similar magnitude to the maximum force predicted by the DLVO theory. The latter therefore appears to be validated at such particle separations.

### 9.4 Dispersion of Rutile

The description of the dispersion process has been given in chapter 5. The wetting stage becomes spontaneous if the contact angle is zero. The dispersibility studies were carried out such that spreading wetting would take place inspite of a contact angle \( \theta > 0^\circ \). The contact angle of the rutile-water-air combination is zero and it is unlikely that adsorption of a molecule such as MIPA would be able to produce a significant rise in the angle, especially as the molecule is highly polar and hence hydrophilic.

Rearrangement of equation 5.4 gives

\[ \cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (9.13) \]

from which it can be seen that for \( \theta < 90^\circ \) a decrease in both \( \gamma_{LV} \) and \( \gamma_{SL} \) will lower the contact angle. Surfactants generally accomplish this and consequently improve wetting of the powder. However, over the range of concentrations studied MIPA has a negligible effect on the \( \gamma_{LV} \) term (table 8.8.1). Adsorption of MIPA may lower the \( \gamma_{SL} \) term but since the contact angle is close to zero to begin with this effect is likely to be small.

If the contact angle is taken to be zero then a high value for \( \gamma_{LV} \) favours penetration of the liquid phase into the pores of the powder agglomerates, equation 5.10. The rate of penetration is also favoured, equation 5.11.
It does not appear that MIPA has a significant effect on the wetting of the rutile particles, however by adsorbing at the solid surface the organic species may lower the surface free energy and hence the energy required to increase the solid-liquid interfacial area.

Most of the dispersion studies reported in the literature were carried out such that separation of the effects associated with the wetting stage and the flocculation behaviour was not feasible. Because the wetting stage of the rutile in aqueous solution, with and without MIPA, is favoured under the conditions of the present studies the effects observed are most likely to be related to the pigment disruption and prevention of aggregation stages.

9.4.1 The Effect of pH

The dispersibility of rutile in distilled water as a function of pH (figure 8.4.1) can be explained as the result of the development of an increasing potential at the Stern layer as the pH is increased. At high pH the ionic strength becomes significant so that the diffuse layer potential decreases as reflected by the reduction in the dispersibility. At acidic pH values effectively zero primary particles are formed in spite of a relatively large (about 20 mV) zeta potential. The development of the electrical double layer around each particle is insufficient to disperse the primary particles. However, with similar magnitudes of the zeta potential but of negative sign there is measurable dispersion of primary particles. This could be due to the influence of the short range repulsive solvation forces which probably exist as hydrated and partially hydrated cations adsorb within the Stern layer - this additional repulsive interaction does not exist under acidic pH conditions.

Under conditions of constant ionic strength and MIPA concentration the variation in the dispersibility of rutile with pH follows a similar trend. The number of dispersed primary particles increases as the zeta potential increases in magnitude. At low pH there is effectively no formation of primary particles. The actual number of primary particles formed is significantly higher than for the equivalent pH distilled water, given the same time of dispersion. Since MIPA has relatively little effect on the magnitude of the zeta potential the marked increase
in the dispersibility could be the result of an increased repulsive solvation interaction since MIPA is a strongly hydrated species. The results presented in figure 8.4.4 indicate that as long as about 40% of the total MIPA exists in solution as the neutral molecule the dispersion of rutile is good.

9.4.2 Effect of MIPA Concentration

Figure 8.4.8 shows how the dispersibility depends on the concentration of MIPA under conditions of fixed pH and ionic strength. The number of primary particles formed gradually increases up to a MIPA concentration of about 0.004 mol dm\(^{-3}\) after which there is a more rapid increase in the number. The transition occurs at a MIPA to rutile weight ratio of about 0.3. At MIPA concentrations above 0.1 mol dm\(^{-3}\) there is relatively little change in the particle number. The transition may be related to the point at which the adsorption of MIPA is at the saturation value and subsequent increases in the MIPA concentration merely serves to modify the amount of energy required to disperse the primary particles. (The MIPA to rutile weight ratio of 0.3 corresponds to a starting MIPA concentration of 0.1 mol dm\(^{-3}\) for the adsorption isotherm studies.)

9.4.3 Effect of Ionic Strength

The ionic strength of the dispersion medium has an important effect on the dispersibility of rutile. Figure 8.4.2 shows the decrease in primary particle number as a function of KNO\(_3\) concentration for distilled water at various pH values. The drop in number is due to the reduction in zeta potential and stability of the dispersed particles (figure 8.2.2). A similar trend is found for MIPA solutions (figures 8.4.3 and 8.4.9) although the slope of the curve is slightly steeper. Again, the decrease can be related to a change in the zeta potential (EP66-EP69) and stability (figure 8.2.3). A backing KNO\(_3\) concentration of between 0.02 and 0.03 mol dm\(^{-3}\) is sufficient to prevent the existence of primary particles of rutile - a higher electrolyte concentration being required the higher the MIPA concentration. The same electrolyte concentration results in a dispersion stability ratio of about 1. The sharper decrease in dispersed particle number with ionic strength for MIPA solutions and the similarity to the trend observed in the absence of MIPA suggests that
MIPA does not influence the stability of the dispersed particles to aggregation (as borne out by the W values).

The type of backing electrolyte also affects the dispersibility of rutile in the presence of MIPA. A divalent cation such as Ba$^{2+}$ even at an ionic strength of about $4 \times 10^{-4}$ mol dm$^{-3}$ totally prevents dispersion (table B.4.13). On the other hand LiCl at equivalent concentrations to KNO$_3$ allows a slightly greater number of primary particles to be formed (table B.4.14) at the lower ionic strength values. If the dispersion medium contains potassium sulphate, at a given ionic strength, the dispersed particle number is significantly higher than for the KNO$_3$ system, table B.4.12.

9.4.4 Rate of Dispersion

By studying the rate at which the rutile is dispersed as primary particles it becomes possible to assess the factors which influence the amount of energy required to disrupt the powder agglomerates. The results shown in figure 8.4.11 indicate that the rate of dispersion of rutile is significantly faster in the presence of MIPA. The rate is reduced as the ionic strength is increased, both in the presence and absence of MIPA. There is also a marked delay before a measureable number of primary particles is formed both in the absence of MIPA and as the ionic strength of a MIPA solution is increased.

Since the rutile is dispersed within a much shorter timescale and consequently uses less energy if MIPA is present the organic molecule must be lowering the free energy associated with the formation of the new rutile-solution interfaces. The development of a short range repulsive solvation force as MIPA adsorbs within the Stern layer could provide the necessary energy to break up the primary particle clusters. In addition, the presence of the organic species at the rutile-solution interface may lower the surface free energy as the result of the Rehbinder effect (see section 5.5).

The observation that rutile powder on contact with an aqueous solution of MIPA emits a detectable cracking noise as the pigment explodes into smaller fragments indicates that the displacement of air
from within the pigment clusters gives sufficient energy to disperse the particles. On increasing the ionic strength this effect diminishes. This supports the view that MIPA significantly reduces the energy required to form primary particles. The presence of electrolyte counteracts the effect, probably as the result of competition for sites within the Stern layer.

9.4.5 Dispersibility in Other Media

If acetone is added to the water the number of primary rutile particles formed, at a given MIPA concentration, drops sharply as the mole fraction of water is reduced, (table B.4.21). It is clear that water must be present in large quantities if MIPA is to be able to exert its dispersibility properties. There will be competition between the acetone, water and MIPA molecules for sites at the rutile-solution interface, and the structure making properties of MIPA with water will be nullified.

The dispersibility of rutile in mixtures of propylamine and isopropanol in water indicates that the propylamine is essential for dispersion of rutile. It is therefore likely that the hydroxyl group of the aminoalcohol plays little part in the dispersion process.

9.4.6 Conclusion

MIPA improves the dispersibility of rutile in aqueous solution by lowering the energy required to disrupt the pigment clusters. Adsorption of the strongly hydrated MIPA molecule at the rutile surface gives rise to the existence of a short range repulsive solvation force.

9.5 The Rheological Behaviour of Rutile Slurries

The flow behaviour of aqueous rutile dispersions at high solids content is significantly modified by the presence of MIPA. Analysis of rheological data is subject to numerous difficulties arising from -

* measurement errors associated with the shear stress - shear rate data (eg end effects, wall slippage)
To avoid the problems in linking some characteristic of the dispersion, which may not be readily measured, to some parameter in an equilibrium flow curve equation derived from some model of the process, it was considered that analysis of the equilibrium shear stress – shear rate data of a given slurry would be best achieved in terms of the Ostwald-de Waele power law (equation 6.1).

9.5.1 Effect of Solids Volume Fraction

The effect of a variation of the rutile concentration on the rheological characteristics of the dispersion was studied (slurries X, Y, Z, AA and BB). Figure 8.6.2 shows the dependence of the viscosity on the solids content at a shear rate of 24.5 s⁻¹. The data for rutile in the absence of MIPA can be fitted to a polynomial expression of the form discussed in section 6.2.1. Similarly the data appropriate to each MIPA content can be fitted. The data was fitted to an equation of the type

$$\eta_r = A + Bc + Cc^2 + Dc^3$$

(9.14)

where $\eta_r$ is the relative viscosity

$c$ is the solids volume concentration

Table 9.9 gives values for the coefficients for the slurries; included are the coefficients if a simple quadratic expression is used. The fitting of the data was carried out such that the curve included the point $c = 0$ $\eta_r = 1$ (the viscosity of water was taken to be $0.89 \times 10^{-2}$ poise).

The literature expressions for the dependence of viscosity on the solids content (see section 6.2) indicate that the polynomial coefficients should be in the ranges

$$A = 1 \quad B = 2-4 \quad C = 7-14 \quad D = 16-50$$
Table 9.9 Coefficients for equation 9.14

<table>
<thead>
<tr>
<th>Slurry (% w/w on rutile)</th>
<th>Coefficient A</th>
<th>Coefficient B</th>
<th>Coefficient C</th>
<th>Coefficient D</th>
</tr>
</thead>
<tbody>
<tr>
<td>X + Y</td>
<td>-1.25</td>
<td>1.73x10^5</td>
<td>-4.34x10^6</td>
<td>2.82x10^7</td>
</tr>
<tr>
<td></td>
<td>66.5</td>
<td>-9.67x10^4</td>
<td>1.20x10^6</td>
<td>-</td>
</tr>
<tr>
<td>Z</td>
<td>0.0191</td>
<td>1.03</td>
<td>4.96x10^5</td>
<td>-9.51x10^6</td>
</tr>
<tr>
<td></td>
<td>7.55</td>
<td>-1.38x10^5</td>
<td>1.33x10^6</td>
<td>-</td>
</tr>
<tr>
<td>AA</td>
<td>0.0198</td>
<td>0.99</td>
<td>-1.11x10^5</td>
<td>1.45x10^6</td>
</tr>
<tr>
<td></td>
<td>0.57</td>
<td>-6.96x10^4</td>
<td>7.10x10^5</td>
<td>-</td>
</tr>
<tr>
<td>BB</td>
<td>0.0232</td>
<td>1.03</td>
<td>3.11x10^5</td>
<td>-5.94x10^6</td>
</tr>
<tr>
<td></td>
<td>3.09</td>
<td>-9.79x10^4</td>
<td>9.34x10^5</td>
<td>-</td>
</tr>
</tbody>
</table>

(The correlation coefficients were all greater than 0.93.)

Clearly the rutile dispersions behave in a non-Newtonian manner at solids volume fractions of greater than about 0.05. Although the polynomial type equation is expected to apply up to volume fractions of 0.4 it does so only if the dispersions behave in a Newtonian manner.

Goodwin et al\textsuperscript{245} developed a model to describe the viscosity, at low shear rates, of concentrated polystyrene latex dispersions. An equation giving the dispersion viscosity in terms of the contribution from hydrodynamic interactions and electrostatic interactions was derived.

\[
\eta = \frac{h}{(2a+H)^3} \exp (E) + \eta_0 \left( 1 - \frac{c}{c_m} \right)^{-2.5} c_m
\]  

(9.15)
where \( \eta_0 \) is the viscosity of the dispersion medium
\( c_m \) is the close packing volume fraction
\( a \) is the particle radius
\( H \) is the mean separation of nearest neighbouring particles
\[ c_m^{1/3} = 2a \left( \frac{c_m}{c} + 2a \right) \]
\( E \) is the interaction energy between particles (in units of kT)

The value of \( E \) is calculated assuming the particles can be described by face-centred cubic symmetry, thus

\[ E = 4 \left( V_1 + V_2 \right) - 11 V \]  
(9.16)

where \( V \) is the DLVO interaction energy at particle separation \( H \)
\( V_1, V_2 \) are the DLVO interaction energies for particle separations \( H_1 \) and \( H_2 \), respectively

with \( H_1 = 0.866H - 0.2679a \)
\[ H_2 = 1.118H + 0.2361a \]

The predicted curves by the model are shown in figure 9.12, in which equations 4.1 and 4.7 were used to calculate the DLVO interaction (using a constant charge equation for \( V_R \) has no significant effect since for the separations at which the constant charge repulsive energy is greater than that for constant potential the solids content of the dispersion would be \( >0.4 \)). The experimental data for slurry BB (at a shear rate of \( 1 \text{s}^{-1} \)) are included. By allowing for the interaction between particles the agreement between experiment and theory is improved. Agreement between the theory and experiment is further improved if equation 9.17 is used to evaluate the double layer repulsion

\[ V_R = 2 \pi \varepsilon_r \varepsilon_0 a \phi^2 \ln \left( 1 + \exp \left( -K\varepsilon \right) \right) \]  
(9.17)

By selecting values for the Stern potential of 90 mV, the particle radius of \( 0.1 \times 10^{-6} \text{m} \), the Hamaker constant of \( 8 \times 10^{-20} \text{J} \), and the ionic strength of \( 1 \times 10^{-3} \text{mol dm}^{-3} \) the predicted relative viscosity
against solids volume fraction curve rapidly increases for c values above 0.22. (The above equation for Vₐ is valid for large ka values).

The agreement of the Goodwin et al equation with the rutile slurry is good considering that DLVO theory is not expected to be applicable to dispersions in which multi-particle interaction is the norm. At a solids volume fraction of 0.1 the average interparticle separation (assuming a particle size of 0.1 x 10⁻⁶ m) is about 1.7 x 10⁻⁷ m.

The theoretical curve in figure 9.12 assume a maximum packing density of 0.64 for the particles, however it is possible that the particles pack in a more open structure and, if so, the predicted curves would shift towards lower volume fractions.

Although the approach of Goodwin et al was developed to explain the variation with solids content of the zero shear rate viscosity of a dispersion for which the viscosity is due to structure formation as the result of repulsive interactions between the particles the general approach will be valid for those slurries in which structure formation is due to net attractive particle interaction. The effect of MIPA is to shift the nᵣ-c curve to higher c values thereby indicating a reduced attraction between particles.

Table 9.10 gives the values of the parameters resulting from the interpretation of the shear stress - shear rate in terms of equation 6.1. Plots of log τ against log γ were made for slurries, X, Y, Z, AA and BB for each of the solids concentrations. The slopes had an error of no greater than 10% and the viscosity at a shear rate of unity had an error no greater than 8%. The values of the slope show that all the slurries were pseudoplastic in rheological behaviour. An increase in the MIPA content generally reduced the pseudoplastic behaviour, although only slightly. At a given solids concentration the presence of as little as 2 x 10⁻⁴ g MIPA per g rutile is sufficient to reduce the viscosity (at γ = 1 s⁻¹) by a factor of 4.

With this amount of MIPA the flow behaviour of a 10% v/v rutile slurry is almost Newtonian.
Figure 9.12 Relative viscosity – solids content relationship
Table 9.10 Analysis of flow curves using equation 6.1

<table>
<thead>
<tr>
<th>Slurry</th>
<th>c (v/v)</th>
<th>slope</th>
<th>intercept (η at γ = 1 s⁻¹)/poise</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.116</td>
<td>0.315</td>
<td>468</td>
</tr>
<tr>
<td></td>
<td>0.102</td>
<td>0.330</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>0.0895</td>
<td>0.267</td>
<td>83.2</td>
</tr>
<tr>
<td></td>
<td>0.0757</td>
<td>0.288</td>
<td>24.0</td>
</tr>
<tr>
<td>Y</td>
<td>0.111</td>
<td>0.316</td>
<td>288</td>
</tr>
<tr>
<td></td>
<td>0.103</td>
<td>0.337</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>0.101</td>
<td>0.342</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>0.0967</td>
<td>0.353</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>0.0931</td>
<td>0.278</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>0.0840</td>
<td>0.325</td>
<td>41.7</td>
</tr>
<tr>
<td>Z</td>
<td>0.128</td>
<td>0.331</td>
<td>324</td>
</tr>
<tr>
<td></td>
<td>0.119</td>
<td>0.398</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>0.115</td>
<td>0.340</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>0.113</td>
<td>0.354</td>
<td>67.6</td>
</tr>
<tr>
<td></td>
<td>0.105</td>
<td>0.415</td>
<td>38.0</td>
</tr>
<tr>
<td>AA</td>
<td>0.120</td>
<td>0.318</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>0.119</td>
<td>0.339</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>0.117</td>
<td>0.337</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>0.112</td>
<td>0.362</td>
<td>58.9</td>
</tr>
<tr>
<td></td>
<td>0.108</td>
<td>0.426</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>0.106</td>
<td>0.386</td>
<td>41.7</td>
</tr>
<tr>
<td></td>
<td>0.0990</td>
<td>0.849</td>
<td>0.36</td>
</tr>
<tr>
<td>BB</td>
<td>0.129</td>
<td>0.383</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>0.125</td>
<td>0.392</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>0.123</td>
<td>0.416</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>0.119</td>
<td>0.381</td>
<td>89.1</td>
</tr>
<tr>
<td></td>
<td>0.116</td>
<td>0.402</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>0.113</td>
<td>0.410</td>
<td>47.9</td>
</tr>
<tr>
<td></td>
<td>0.109</td>
<td>0.414</td>
<td>38.9</td>
</tr>
</tbody>
</table>

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9.5.2 The Effect of an Increasing MIPA Concentration

The various shear stress - shear rate flow curves for the dispersions derived from slurry G (c = 0.123 v/v) by the addition of aliquots of MIPA solution have been analysed in terms of the power law equation (eq 6.1), the Cross equation and the Casson equation. The experimental data fits all three expressions i.e.

\[
\log \tau = \log K + n \log \gamma \quad \text{power law (log } \tau \text{ versus log } \gamma) \\
\eta = \eta_0 + \frac{c}{\gamma^{0.67}} \quad \text{Cross equation (} \eta \text{ versus } \gamma^{0.67}) \\
\tau^{0.5} = k_0 + k_1 \gamma^{0.5} \quad \text{Casson equation (} \tau^{1/2} \text{ versus } \gamma^{1/2})
\]

The appropriate plots give straight lines with correlation coefficients >0.96 and errors in the slopes and intercepts of less than 15%. Tables 9.11 and 9.12 contain the appropriate parameters. The last column in table 9.11 contains the values of the Cross parameter \( \alpha \) which represents the ratio of the rate constants for floc breakup and formation. These values of \( \alpha \) were calculated by dividing the viscosity value in the third column by the slope, \( C \), of the Cross equation. If the value of \( \alpha \) is interpreted as defined by the Cross model then it would appear that for these rutile dispersions the rate constant for floc breakage by Brownian motion is equal to the rate constant for floc breakage by viscous shearing and, in fact, that at high MIPA content the rate constant for Brownian motion induced floc breakage becomes more dominant.

The intercept of the Cross equation gives the slurry viscosity at an infinite rate of shear. The values indicate that if sufficient MIPA is present the limiting viscosity of the slurry can attain a value only 5 times that of pure water.
Table 9.11 Interpretation of the flow curve in terms of the power law and Cross equation for slurry G

<table>
<thead>
<tr>
<th>MIPA Content (% w/w)</th>
<th>Equation 6.1</th>
<th>Cross Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>slope</td>
<td>η at γ = 1 (poise)</td>
</tr>
<tr>
<td>0.0160</td>
<td>0.352</td>
<td>282</td>
</tr>
<tr>
<td>0.0181</td>
<td>0.371</td>
<td>240</td>
</tr>
<tr>
<td>0.0203</td>
<td>0.384</td>
<td>200</td>
</tr>
<tr>
<td>0.0226</td>
<td>0.360</td>
<td>170</td>
</tr>
<tr>
<td>0.0252</td>
<td>0.377</td>
<td>148</td>
</tr>
<tr>
<td>0.0285</td>
<td>0.469</td>
<td>69</td>
</tr>
<tr>
<td>0.0420</td>
<td>0.506</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 9.12 Interpretation of the equilibrium flow curve in terms of the Casson equation for slurry G

<table>
<thead>
<tr>
<th>MIPA Content (% w/w)</th>
<th>k_o</th>
<th>k_1</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0160</td>
<td>19.8</td>
<td>1.66</td>
<td>63.2</td>
<td>73.7</td>
</tr>
<tr>
<td>0.0181</td>
<td>18.4</td>
<td>1.70</td>
<td>63.7</td>
<td>67.4</td>
</tr>
<tr>
<td>0.0203</td>
<td>17.1</td>
<td>1.61</td>
<td>62.6</td>
<td>65.1</td>
</tr>
<tr>
<td>0.0226</td>
<td>15.5</td>
<td>1.35</td>
<td>58.8</td>
<td>66.8</td>
</tr>
<tr>
<td>0.0252</td>
<td>14.4</td>
<td>1.35</td>
<td>58.8</td>
<td>62.0</td>
</tr>
<tr>
<td>0.0285</td>
<td>12.6</td>
<td>1.05</td>
<td>53.4</td>
<td>64.5</td>
</tr>
<tr>
<td>0.0420</td>
<td>2.3</td>
<td>0.30</td>
<td>26.3</td>
<td>26.3</td>
</tr>
</tbody>
</table>
The values in the third column of table 9.11 show the strong effect that MIPA has on the flocculated structure of the dispersion which exists at very low shear rates. The values of the Casson parameter $k_0$ (table 9.12) confirm the fact that MIPA reduces the attractive interaction between particles which are forced into close contact by the high particle concentration.

Observation of the state of dispersion of a slurry, by diluting a sample and observing under a microscope, indicated that as the MIPA content was raised the better the degree of dispersion.

[It should be pointed out that the actual values of the parameters associated with a particular equation, in particular the Casson factors $\alpha$ and $\beta$, need not be strictly interpreted in terms of the original derivation since the models, of necessity, were derived using assumptions which need not be correct for any given system].

The rheological behaviour of the aqueous rutile dispersions in the solids concentration (v/v) range 0.07-0.13 was pseudoplastic ie shear thinning. The dispersions were highly flocculated at low shear rates. The addition of small amounts of MIPA (typically <0.02% w/w on rutile) significantly lowered the viscosity of the dispersion with the flow behaviour becoming more Newtonian at higher MIPA contents (say about 0.04% w/w). The organic species reduced the attractive interaction between the particles so that a more dispersed system was formed. If electrolyte was added in similar quantities to the MIPA the viscosity lowering effect due to the MIPA was nullified eg slurry R. Similarly, using 50% neutralised MIPA had a much less marked lowering influence on the viscosity eg slurry H. MIPA is therefore most effective when present in solution as the neutral molecule and when the ionic strength is low.

The quantities of MIPA which were found to be effective in lowering the viscosity represent concentrations of either, approx 2.5 $\mu$mol g\(^{-1}\) rutile or $2 \times 10^{-3}$ mol dm\(^{-3}\) in solution. The amount is significantly less than that required for total saturation of the Stern layer. The dispersibility studies indicated that this level of MIPA content was sufficient to enhance the ease of dispersion of the rutile. These same studies also showed the negative influences of a reduction in pH or
increase in the ionic strength. The force of aggregation studies indicated that for MIPA concentrations above about 0.01 mol dm$^{-3}$ the presence of the additional short range repulsive force becomes apparent. The MIPA concentration at which this force is observed may be a function of the particle concentration so that at higher solids content, as for the slurries used for the rheological studies, the existence of the solvation force becomes observable at lower bulk MIPA concentrations.

9.6 Summary

MIPA molecules are strongly solvated in aqueous solution but a decrease in solution pH or increase in the ionic strength, particularly if the electrolyte is a structure breaking type, reduces the structure making ability. The aminoalcohol adsorbs with the Stern layer at the rutile-aqueous solution interface and modifies the particle-particle interaction at small separations. The strength of the binding of the organic molecule to the rutile surface and to the partial solvation shell gives rise to a short range solvation force which significantly reduces the depth of the primary minimum. The ease of dispersion of rutile pigment in aqueous solution is vastly improved if MIPA is present, probably as the result of the formation of the additional short range repulsive force. Similarly, the viscosity of concentrated aqueous rutile slurries is greatly reduced by the presence of neutral MIPA molecules - the degree of aggregation is reduced thereby reducing the viscous energy losses due to the presence of flocs.

Adsorption of the MIPA has relatively little effect on the zeta potential and stability of the rutile particles.
CHAPTER 10

RECOMMENDATIONS FOR FUTURE WORK
10. RECOMMENDATIONS FOR FUTURE WORK

The experimental work described in this thesis represents the first detailed study of the modifications to the colloidal properties of aqueous rutile dispersions brought about through the presence of an aminoalcohol. The work covered a relatively wide range of techniques and looked at a variety of colloidal properties eg stability, dispersion, viscosity. Consequently a number of additional studies which would be required to completely understand the role played by an aminoalcohol, such as MIPA, in modifying the behaviour of aqueous rutile dispersions have been identified. These studies would serve to further develop understanding in the following general areas

* the interaction between the organic molecule and water;

* the modification to the properties of the diffuse electrical double layer as the result of adsorption of the organic molecule;

* the modification of the interaction between rutile particles in the presence of the organic;

* the changes in the dispersion process brought about by the presence of the organic species;

* the nature of the interaction between the organic molecule and electrolyte ions.

10.1 Interaction with Water

The dynamic solution viscosity studies should be extended to include measurements of the viscosity of aqueous solutions as a function of MIPA concentration under conditions of constant pH and ionic strength - a range of pH (and ionic strength) values should be looked at in order to assess the relative effects of the neutral and cationic MIPA molecule. The viscosity B (and A) coefficient can therefore be determined for different solution conditions and hence the degree of structure making assessed. The variation of the viscosity with temperature would also provide information on the type and extent of interaction between the organic and water.
Density measurements as a function of MIPA concentration would permit determination of the partial molar volume at infinite dilution of MIPA. Coupled with the viscosity B coefficient an estimate of the degree of ion-solvent interaction could be made.

Although measurements of the heat capacity of MIPA solutions failed to show a detectable difference from that of distilled water it would be expected that by performing studies involving measurements on a bulk property which is dependent upon the hydrogen bonding characteristic of the water molecules the effect of an aminoalcohol on the structure could be investigated.

10.2 Modifications to the Electrical Double Layer

The adsorption of MIPA by the rutile surface should be further investigated, in the absence of light. At fixed ionic strength and pH, the variation in the amount adsorbed as a function of the MIPA concentration should be studied so that the surface coverage can be better estimated for a given bulk MIPA concentration. To further investigate the relative importances of the neutral and cationic organic solute in adsorption at the rutile-solution interface it would be necessary to measure isotherms under conditions of constant ionic strength and total MIPA concentration as a function of pH for various MIPA concentrations. The variation in the degree of dissociation of the organic base and in the magnitude of the rutile surface charge should allow the relative strengths of adsorption of the two species to be estimated. The two forms of MIPA will interact with water in different ways as a consequence of changes in the degree of solvation of the solute and so the results of such adsorption isotherms should be linked to changes in the viscosity of water under similar conditions of MIPA ionisation. Since the effect of electrolyte concentration has been shown to be an important variable in influencing the behaviour of rutile dispersions in the presence of MIPA the dependence of the amount of MIPA adsorbed on the bulk electrolyte concentration should be studied – competition for adsorption sites within the Stern layer may be an important factor.
The zeta potential of the rutile should be measured over a wide range of MIPA concentration with conditions of pH and ionic strength carefully controlled. In addition, electrophoresis studies, at constant ionic strength, as a function of pH, both in the absence and presence of MIPA, should be carried out to further elucidate the differences in the zeta potential at high pH. The particular type of backing electrolyte is apparently of importance in determining the magnitude of the zeta potential so that further studies of this effect should be performed. The results of all these electrophoresis investigations should be linked to the corresponding adsorption isotherms which ought to reflect changes in the nature of the Stern layer.

Surface charge density measurements on the rutile particles would significantly improve the knowledge of the double layer structure, however since MIPA is a base the interpretation of the titration data could be difficult.

10.3 Modification of the Interaction Between Particles

The conclusions concerning the stability of the rutile particles in the absence and presence of MIPA should be checked by measuring another property of the dispersion, apart from the decrease in particle number, which changes with time eg sediment height/volume.

The centrifugation work, which provided information on the nature of the interaction energy profile at small separations, should be extended to more concentrated dispersions and the structure of the resulting sediments examined using a microscope - the nature of the particle packing can provide information on the interaction between neighbouring particles.

The behaviour of other oxides, eg silica or alumina, in the presence of aqueous MIPA solutions should be studied (at least one type of fine silica was found to be not readily dispersed in 0.1 mol dm$^{-3}$ MIPA solution).

The nature of the rutile sediment formed as the result of particle aggregation and gravity settling could be investigated by examination
under an electron microscope. Although scanning electron microscopy was used in the present study to look at the rutile dispersions, a satisfactory method of sample preparation was not found (freeze drying and sputter coating, and natural evaporation were tried). Such studies may provide relevant data on the interparticle separation within the aggregates.

10.4 Modifications to the Dispersion Process

The effect of aminoalcohols on the process of incorporating the dry pigment into aqueous solution as dispersed primary particles could be further investigated by measuring the particle size distribution as a function of the same variables studied in the present study. In addition it would be useful to directly measure the contact angle of the rutile-aqueous solution-air interface and assess the effect of MIPA. It would be preferable to carry out such measurements on the pigment powder rather than on a pressed tablet and so conventional techniques, such as the sessile drop method, would not be feasible. Although there are difficulties associated with measuring the contact angle of a powder useful data could probably be obtained, eg by using the rate of capillary penetration method.

Further useful information on the dispersion process could be obtained by measuring the heat of immersion of the rutile powder as a function of the dispersion medium composition.

10.5 Summary

By performing the types of studies suggested the role played by organic species such as MIPA in influencing the behaviour of rutile particles in aqueous solution should be further elucidated. Once the understanding is considered to be satisfactory it will be necessary to examine the behaviour of commercial rutile pigments which possess surface impurities or coatings.
REFERENCES


4. Tioxide International Ltd BTP:164 (Part one).


60. Ref. 15, page 23.
64. Ref. 46, chpt. 6.


110. Muller, H. Kolloid Zh., (1926), 38, 1.


112. Fuchs, N.Z. Physik, (1934), 89, 736.


121. Marmur, A. J. Colloid Interface Sci., (1979), 72, 41.


128. Firth, B.A. and Hunter, R.J. J. Colloid Interface Sci., (1976), 57, 266.


137. Washburn, E.D. Physical Rev. (1921), 17, 374.


155. Eirich, F.R. (Ed.) "Rheology, theory, and Application", Vols. 1-5, Academic, N.Y.


186. van de Ven, T.G.M. and Hunter, R.J. J. Colloid Interface Sci., (1979), 68, 135.


210. Firth, B.A. and Hunter, R.J. J. Colloid Interface Sci., (1976), 57, 266.


    (1948), 16, 1.