HETEROFLOCCULATION OF RUTILE
DISPERSIONS IN AQUEOUS ELECTROLYTES

by

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A Thesis submitted for the
Degree of Doctor of Philosophy

University of Edinburgh

September, 1975
To my parents
I declare that the work described in this thesis has not been submitted for any other degree and is the original work of the author except where acknowledgement is made by reference. The work was carried out in the Chemistry Department of the University of Edinburgh between October 1972 and September 1975 under the supervision of Dr. W.D. Cooper.

Postgraduate courses attended include: Environmental Chemistry (2 terms lectures); Computing (1 week Fortran programming course and 1 week introduction to Edinburgh Multi Access System); High Speed Liquid Chromatography (5 lectures - Prof. J.H. Knox and Dr. J.N. Done); Chemical Aspects of Oil Products Research (5 lectures - Staff of Shell Research Ltd.); E.S.C.A. and Photoelectron Spectroscopy (5 lectures - Dr. D.A. Whan and Dr. S. Cradock); Thermal Analysis (5 lectures - Dr. B.M. Lowe).
Acknowledgements

The author is indebted to her supervisor, Dr. W.D. Cooper, for his constant encouragement and interest throughout the work.

She thanks Tioxide International Ltd. for the award of a research grant, and Professor G.D. Parfitt for his continued interest in the project.

The assistance of the technical staff of the Chemistry Department is appreciated, and the author is grateful to Mrs. J. Gorrie for undertaking the typing.
Abstract

Previous studies of colloidal stability and heteroflocculation have been reviewed, and the relevant theories of electrostatic interactions discussed. Colloidal dispersions of coated and pure rutile samples and carbon blacks in aqueous electrolytes have been described. Choice of system was determined by the surface properties, particle size and Hamaker constant of the samples. Systems were chosen so that size should be the same for both samples, and similarly for the Hamaker constant, as far as possible.

Coated rutile samples were studied with a view to heteroflocculation of the two samples. The stability behaviour of pure rutile was studied to eliminate effects of dissolution of ions from any surface coating. Adsorption of surfactant onto pure rutile was carried out to give information on the surface charge distribution.

Carbon blacks were used as a test of the experimental techniques employed, and in heteroflocculation experiments with rutile.

The coated rutile samples were found to be unsuitable for heteroflocculation experiments since dissolution of ions from the coatings occurred. These dissolved species subsequently adsorbed onto particles and the electrophoresis cell walls. This contamination was detected by microelectrophoresis where the value of the potential at the cell wall was obtained, as a matter of course, for every electrophoresis experiment and compared with literature values.

Dispersions of pure rutile were found to be much less stable than predicted by theory. An uneven distribution of surface charge, resulting in discrete areas of high and low potential, was postulated. Instability was presumed to result from low potential interactions between neighbouring particles.
Abstract (contd.)

Adsorption of surfactant was found to indicate at least two different types of surface site. Adsorption of a cationic surfactant was found to considerably increase the stability of the rutile, whereas an anionic surfactant had little effect on stability.

A study of several carbon blacks showed that, where there were known to be different types of surface groups, the stability was less than predicted from theory.

The experimental stability of Graphon agreed with predictions of theory, and it was used in heteroflocculation experiments with rutile. Heteroflocculation was found to occur in the mixed systems, and the stability ratio for the mixed interaction was explained in terms of an extended form of the Hogg, Healy and Fuerstenau equation.
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1. INTRODUCTION

1.1 General Introduction

Lyophobic colloids have a high surface free energy, and because colloidal particles are very small, of the order of 10-1000 nm, the surface area to volume ratio is very large. This situation is thermodynamically unstable and any process which reduces this ratio, as does flocculation, is favoured.

Most colloidal particles in solution possess surface electric charge. Repulsion between particles as a result of their charge tends to reduce the rate of coagulation. When particle number reduces rapidly with time the colloidal dispersion is said to be unstable, and is stable when the decrease in number is very slow.

As a result of electromagnetic interactions between atoms and molecules in neighbouring colloidal particles, the particles experience a force of attraction for one another.

Theories concerning the repulsive and attractive forces on colloidal particles and their effect on stability were separately developed by Derjaguin and Landau and Verwey and Overbeek. Since the approaches by these authors were very similar the theory was subsequently known as the DLVO theory. They stated that the total potential energy of interaction between two colloidal particles was the sum of the potential energy of repulsion, $V_R$, and the potential energy of attraction, $V_A$.

$$V_T = V_R + V_A$$

This theory was originally envisaged only for monodisperse single component sols. It was later extended by Derjaguin for
application in the instance of heterocoagulation, that is the coagulation of colloidal particles dissimilar in terms of size or surface potential or both. Hamaker's expression for the attraction between dissimilar particles was used. Simpler expressions for use in determining stability in heterocoagulating systems were obtained by Hogg, Healy and Fuerstenau who employed the linear Debye-Huckel approximation and restricted their analysis to systems in which the solid materials were of the same chemical type.

1.2 Choice of system

DLVO theory has formed the basis of extensive experimental and theoretical studies. These have shown that, despite a qualitative success, there are shortcomings, due to assumptions and simplifications in the theory, which shows it to be of limited value quantitatively for many practical systems.

The great majority of studies of behaviour of colloids have involved dispersions containing only one colloid component. In some cases attempts have been made to check DLVO theory using well defined model systems such as polystyrene latices and AgI sols.

However, many naturally occurring dispersions or colloidal systems of practical industrial importance consist of a mixture of colloidal particles, which possess different surface properties, size or chemical composition. In addition, information regarding the geometry of the particles or the exact nature of the distribution of charge around a colloidal particle may be incomplete.

It has been the aim of the research reported here to study the stability behaviour of a colloid of practical significance, namely rutile (titanium dioxide), in the light of DLVO theory. The stability
behaviour of this colloid is of prime importance in its industrial applications as a pigment.

Advantages resulting from the choice of rutile in the study of a more practical system were:-

a) Oxides are particularly suitable for study in aqueous solutions. Since hydrogen ions are potential-determining, surface potential can easily be altered by varying pH.

b) By use of samples of rutile of the same particle size and having approximately spherical shape, the only variable was surface potential.

c) Studies of heteroflocculation were not complicated by dissimilar chemical types of colloid.

1.3 Previous Work

1.3.1. Early stability theories

The concept of colloidal stability has long been appreciated. As early as 1857 Faraday gave a detailed description of the properties of gold sols. Around the beginning of this century Hardy studied the properties of denatured egg-albumin and found that a mass of flocs resulted when the albumin was uncharged. Burton also realised that the electrical charge of particles, reflected in their electrophoretic velocity, is an important factor in preventing flocculation. By comparing the influence of aluminium salts on the electrophoresis and on the stability of a gold sol, he showed that the greater the electrophoretic velocity the greater was the stability. Powis found that there was a critical particle potential, as calculated from the electrophoretic velocity, below which particles were found to coagulate. These early interpretations
of the relationship between charge and stability have since been shown to be over simplified. However, the general idea that the stability of hydrophobic sols is governed by the particle charge remains.

The phenomenon of electrophoresis, the movement of colloidal particles due to their potential (zeta potential) towards one electrode when an electric field is applied to the dispersion, was first observed by Quincke. Helmholtz presented a theory of electrokinetic phenomena and emphasised that the electrophoretic velocity is proportional to the zeta potential, and not to the charge of the colloidal particle.

Early attempts to explain colloid stability were largely based on the surface charge on the particles. Freundlich at first believed in the idea of a coagulation mechanism based on the neutralisation of charge by the adsorption of an equivalent amount of counterion. Later, however, as a result of experimental observations, he rejected this idea.

Ostwald, in 1938, obviously was not satisfied with the then current ideas on colloid stability: "I believe that a colloid chemist, if asked today to explain the coagulation of a lyophobic hydrosol by electrolytes, will make a rather unhappy face."

He chose to ignore the colloidal particles in a dispersion and focussed his attention on the electrolyte medium, proposing an "activity-coefficient theory of coagulation." The interionic forces were assumed to play an important role in coagulation, and activity coefficient, being a measure of these forces, acted as a criterion of stability. This theory was obviously inadequate in that it completely disregards the properties of the particles, and
in the fact that activity coefficient is not an ideal parameter for characterisation of the electrolyte medium.

1.3.2. DLVO theory

Gouy\textsuperscript{20} and Chapman\textsuperscript{21} developed the concept of an electrical double layer surrounding a colloidal particle in mathematical terms. Hamaker\textsuperscript{4} evaluated the attraction between particles in terms of the London-van der Waals force, which depended on the nature of the colloid material, the medium, and the distance of separation. Several authors\textsuperscript{22-24} studied stability in terms of a repulsive force arising due to interaction of electrical double layers around the particles, and an attractive force. Finally, Derjaguin and Landau\textsuperscript{1} and Verwey and Overbeek\textsuperscript{2} produced a more comprehensive approach to colloid stability resulting from the sum of repulsive and attractive forces. Since the advent of DLVO theory much work has been done to test the theory. Early work consisted mainly of investigations into the stability of single colloid component dispersions, and some work was done on idealised systems.

Polymer latices have been called "model colloids" because of their well defined spherical shape and the high degree of monodispersity. In addition, by careful control of polymerisation conditions a range of sizes can readily be prepared. For these reasons latices have proved attractive for stability studies in the light of DLVO theory.

Watillon and Joseph-Petit\textsuperscript{25} studied the interactions between charged spherical polystyrene latex particles in aqueous electrolyte. They found that the zeta potentials experimentally measured were a reasonable approximation to the potential governing the electrostatic repulsion.
A colloidal suspension of spherical particles of crosslinked polystyrene was used by Schenkel and Kitchener specifically to test the DLVO theory. The theory was found to give a satisfactory interpretation of the properties of the suspension in a 1-1 electrolyte.

The stability of monodisperse polystyrene latices of various sizes was studied by Ottewill and Shaw. They plotted log stability versus log electrolyte concentration for the experimental results and obtained the corresponding slopes $\frac{d \log W_{\text{expt}}}{d \log C_e}$. Theory predicted an increase in slope with increase in particle size. This was not observed experimentally.

Bibeau and Matijevic examined the stability and electrophoretic mobility of a polyvinyl chloride sol at various concentrations of sodium and magnesium salts as a function of the surface concentration of an anionic surfactant, sodium dodecyl sulphate. In this study, the actual surface concentration of the potential determining species was measured and the stability of the sol interpreted in terms of the DLVO theory of coagulation using these values of surface charge. At moderate to large surface coverage the zeta potentials were found to be less than the potential expected from the true surfactant concentration, and, over a wide range of surface charge densities and electrolyte concentration, the net charge at the shear plane was nearly constant. It was suggested that the location of the shear plane was determined by a critical charge density.

Romo studied the stability of rutile suspensions in non-aqueous media. The experimental stabilities found for n-butyl alcohol and n-butyramine as dispersion media could be interpreted in terms of DLVO theory as being due to electrostatic repulsion. It was found, however, that for melamine and linseed oil thinned with xylene as medium, the
stability could not be explained in terms of DLVO theory and was probably due to entropic repulsion of the interacting adsorbed polymeric molecules.

Matijevic and coworkers have studied the stability of many systems in which there is no straightforward correlation between measured zeta potential and colloidal stability. The reversal of charge of lyophobic colloids by hydrolysed metal ions was studied. In a study using aluminium nitrate it was found that, depending on the concentration and pH of the medium, then either flocculation or stabilization by charge reversal of the negatively charged colloid would occur. This took place only if sufficient hydrolysed species were present. Similar experiments were carried out using ferric nitrate and aluminium sulphate.

A study of the stability of colloidal silica in the presence of various concentrations of simple aqueous electrolytes as a function of pH was conducted by Matijevic et al. Electrophoretic mobilities were reported as a function of pH and concentration, but no correlation was found between critical coagulation concentration and mobility. Titration curves were given for the exchange of calcium ion for silanolic hydrogen on the particle surface, and ion exchange proposed as the primary reason for the destabilization of the sols. The initial stability of the silica sols was due to the surface being highly hydrated, resulting in behaviour more typical of a lyophilic colloid. A similar effect was found for the case of chromium hydroxide sols. The particle mobility was found to be still rather high at the critical coagulation concentration, indicating that the particle charge was not the essential criterion in the stability of these sols. It was suggested that the particles were strongly hydrated and
this was primarily responsible for their stability.

The stability of graphitised carbon blacks has also been explained on the basis of DLVO theory. Parfitt and Pictor used Sterling MTG, consisting of approximately spherical particles of radius 125 nm and Graphon, consisting of aggregates of 100 nm radius constructed from primary particles of radius 12.5 nm. In the case of Graphon in high concentration of aqueous electrolyte where the electrical double layer is thin, the radius effective in stability calculations was 12.5 nm and agreement was found between experimentally measured zeta potential and stability. For the Sterling MTG, despite high zeta potentials, the systems were unstable. However, this was accounted for by the presence of a secondary minimum in the potential energy diagrams.

The effect of particle size on the stability of monodisperse selenium sols at fixed pH in aqueous electrolyte has been given some attention more recently. The results were interpreted in terms of DLVO theory. It was found that the coagulation of small particles into the primary minimum could be described by using the simple model of a critical barrier height. For large particles, good agreement was obtained with experiment on the basis of secondary minimum flocculation.

Wiese and Healy were encouraged to consider the effect of particle size on colloid stability theoretically since experimental work had shown that particle size increase did not always result in stability increase as predicted by DLVO theory. Instead of relying on the kinetic approach to stability as employed in the DLVO theory, that is the presence of an energy barrier greater than the kinetic energy of the particles, they considered the possibility
of secondary minimum flocculation in addition to flocculation into the primary minimum. They constructed coagulation diagrams which showed that both the height of the energy barrier to flocculation into the primary minimum and the depth of the secondary minimum were important. They applied this approach to experimental results on the flocculation of a series of polystyrene latex particles, which had previously seemed to violate the DLVO theory. Reasonable agreement was obtained on consideration of secondary minimum coagulation for the larger particles.

1.3.3. Heteroflocculation

Many studies have been concerned with the flocculation of identical particles. Until comparatively recently, little had been done to investigate heteroflocculation, that is flocculation of dissimilar particles. The extension of the DLVO theory to heteroflocculation by Derjaguin and subsequently the treatment of Devereux and de Bruyn proved very tedious mathematically. The simplification of these equations enabled comparisons to be made between experimentally measured stabilities in mixed systems and those predicted by this modified form of DLVO theory. Hetero-interactions are of considerable importance in practical systems, for example in water filtration, deposition of dirt particles on fibres, froth flotation of minerals, selective flocculation of minerals from mixtures of mineral slimes, and so on.

As in the case of homoflocculation, latices have been used in the study of heteroflocculation because of their "model colloid" characteristics. Kitahara and Ushiyama examined mixed systems containing two different latices and compared the results with
those predicted by DLVO theory extended to consider heteroflocculating particles. They used the magnitude of the energy barrier, $V_{\text{max}}$, as a measure of stability, which Overbeek suggested was a valid criterion. They found that the combination of latex particles which yielded the smallest $V_{\text{max}}$ from theory-based calculations agreed with the preferred type of coagulation obtained from the experimental stability results. In this case the latex particles differed in terms of their surface potentials, as reflected in the measured zeta potentials.

The extended DLVO theory is also useful in cases of heteroflocculation between particles of different size. The behaviour of mixed systems of graphitized carbon blacks in aqueous sodium dodecyl sulphate, where the carbon blacks had identical surface characteristics and only differed in particle size, was examined. The experimental stability ratios for the mixed systems were in reasonable agreement with values predicted by theory.

Princen and de Vena-Peplinski attempted to show that coagulation between oppositely charged particles could be described entirely from consideration of particle size alone, without taking account of the report that mutual flocculation (flocculation between oppositely charged colloidal particles) was greatest when the total charge on the two colloids was equal and opposite in sign. This was later questioned by Kruyt and Troelstra, who suggested that colloidal particle size could well influence maximum flocculation rate. In the study of the mutual flocculation of zinc oxide and titanium dioxide, the authors found that the most extensive flocculation obtained was independent of pH (and, therefore, of zeta potential) and could be accurately predicted from the ratios of particle sizes and densities for the case where there was minimum interaction.
between the two colloid components.

There have been several studies of mixed oxide systems. Pugh and Kitchener \(^{46}\) considered the possibilities of selective flocculation theoretically since it appeared that a process to remove impurity minerals from kaolin slurries \(^{47}\) could be an experimental example. They performed calculations on the basis of the extended DLVO theory, considering a range of values of size, surface potential, double layer thickness and Hamaker constant to evaluate the feasibility of selective flocculation. They concluded that a wide range of flocculation rates, reflected in stability ratios, was possible and, in suitable cases, separation of one colloid from a mixture ought to be possible provided the surface potentials of the various colloids were sufficiently different. This theory was tested using a quartz and rutile mixture. \(^{48}\) A study was made of the stability regions for the separate suspensions and then for a suspension containing equal quantities of each solid material as a percentage weight. The suspensions were considered stable if there was no reduction of the weight percent solids in suspension after thirty minutes. It was predicted from the flocculation results for quartz and rutile separately that selective flocculation would occur around pH 5.6. This was found experimentally, and additional confirmation was obtained from the chemical analysis carried out at this pH. The supernatant liquid analysis gave % silica as 98 and the sediment analysis gave % titania as 93. Similar experiments conducted on quartz-hematite mixtures gave very similar results, in this case the region of selective flocculation being pH 7-7.5 where the quartz was stable and had a surface potential of -60mV and hematite was unstable with a surface potential of around -30mV. In addition, from flocculation results obtained using NaCl electrolyte, values of the Hamaker constant were
estimated for hematite, quartz and rutile. These values were compared with previous theoretical and experimental results.

Heteroflocculation in mixed oxide colloidal dispersion has been studied by Healy et al. They examined the flocculation in mixed systems of colloidal tin oxide and alumina, and of titania and alumina. The zeta potential, isoelectric point and stability of the individual oxide dispersions were measured. The heteroflocculation behaviour of the mixed oxide systems was predicted from the behaviour of the separate oxides, but their experimental results could not be explained in such terms. It was realised that dissolution of one oxide species affected the isoelectric point of the other oxide species present. Where dissolution did occur it was necessary to measure the rate of change of isoelectric point of the other oxide present. In the case of tin oxide dispersed in supernatant liquid from an alumina suspension equilibrated for 24 hours, and similarly, of alumina dispersed in supernatant liquid from a tin oxide suspension, each oxide was shown to have an isoelectric point around pH 7.5. In the absence of soluble adsorbing metal ion species, tin oxide showed an isoelectric point at pH 4.5, and alumina at pH 9.1. Thus, in the absence of soluble metal ion species, rapid mutual flocculation would be expected to occur in the pH range 4.5 to 9.1. However, the mixed tin oxide-alumina system consists of particles either of tin oxide with aluminium species adsorbed or alumina with tin species adsorbed, all of which possess an isoelectric point of around pH 7.5 and therefore undergo rapid coagulation in the pH region 7-8. Experiments on the mixed titania-alumina system also indicated a shift in isoelectric point as a result of adsorption of soluble species. In this case the presence of soluble aluminium
species caused a shift in value from pH 5.9 to 8.9, that is to the isolectric point of alumina, and not to some intermediate pH. It was found that, after mixing the two oxides, the coagulation - pH range was strongly time dependent. After 15 seconds, although soluble aluminium species shifted the isolectric point of titania by about 0.5 pH unit the graph of log W (stability ratio) versus pH did show the form of heteroflocculation predicted from the separate isolectric points. However, after 24 hours equilibration all particles behaved as alumina and underwent rapid coagulation only in the region of pH 9.

Heteroflocculation in mixed oxide dispersions was also studied by Harding, who measured sedimentation volume and viscosity in alumina-silica and alumina-titania systems. The sedimentation results were equilibrium values, obtained over periods of 24 hours or longer. Over the whole pH range examined, mutual flocculation of alumina with silica occurred, the isolectric points being pH 9.0 and pH 2.2 respectively. From experiments concerning the flocculation of alumina with titania, where the ratios of solid employed were 9:1 and 1:9, it was found that in the former case the mixed system behaved like alumina alone, and in the latter case like titania alone. This was explained by the formation of a layer of alumina particles around each titania particle or vice versa. There was no mention of actual dissolution of aluminium species, as in the experiments of Healy et al. The experimental data were consistent with the predictions of DLVO theory, and mutual flocculation of oppositely charged species was no more extensive than rapid flocculation of a single colloidal species.
In many practical situations, such as deposition of dirt particles onto textiles, an understanding of the interactions between an approximate sphere and a plane surface is necessary. Marshall and Kitchener used a rotating disc technique to study the deposition of carbon blacks from dilute detergent suspensions onto smooth planar solids of glass, polystyrene and other materials. Although qualitative agreement with theory was found, in that deposition was reduced by increased zeta potentials of like sign or decreased salt concentration, the results could not be explained quantitatively by the DLVO theory. It was postulated that the surfaces made contact at projections from the "smooth" surface of around 5 nm. In a further study by Hull and Kitchener, in which they deposited polystyrene latex particles onto smooth plastic films, calculations for attraction and repulsion of spherical particles approaching such projections were performed. This hypothesis proved inadequate since, although it reduced the calculated value of stability ratio, this value was still much larger than that obtained by experiment. It was found that when the particles and plastic film were oppositely charged, the rate of deposition was as predicted from the Levich theory of diffusion of controlled transport to a rotating disc. When both particles and planar surface were negatively charged, DLVO theory modified for sphere-plate interactions could not account for the kinetics. The anomalous deposition indicated that this model for sphere-plate interaction was not ideal and that deposition was occurring onto areas of preferred geometry or surface potential, or both.

A similar study by Clint et al of deposition of negatively charged polystyrene latex particles, onto a smooth polystyrene surface cast onto a glass disc, as a function of electrolyte concentration found that the
results were consistent with the predictions of theory. The stability ratio for deposition was found to be very sensitive to the potential on the planar surface, which was much smaller than that on the latex particles. In these experiments, however, the potentials generally were relatively low and not a great deal of stability would be expected.

Heteroflocculation need not be confined to interactions between particles differing in size, potential or chemical type. It is also important for flocculation of particles identical in these respects but where there is a local variation in the electrical properties of the surfaces. Such a case is that of flocculation of clay particles in aqueous solutions. It is well known that kaolinite and montmorillonite, common constituents of clays, are plate-like and unusual in possessing two crystallographically different surfaces. Since the charges on the face and edge of these plates are of opposite sign, a cardhouse structure is built up resulting from edge to face flocculation. Schofield and Samson examined the flocculation of kaolinite. They showed that part of the crystal structure, presumed to be the face, adsorbed sodium and was therefore initially negatively charged, while other parts of the surface, presumably the edges, adsorbed chloride and were therefore initially positively charged. Flegmann et al studied the rheological properties of several kaolinite suspensions as a function of pH. They found that a maximum in the yield stress versus pH curve corresponded approximately with the pH at which the charge on the edge of the kaolinite particles was zero. They explained this result by suggesting that edge to edge flocculation was occurring to produce chainlike flocs. The experimental work also included measurement of the zeta potentials on the crystal face and edge of the kaolinites. The zeta potential of the crystal face was obtained at the point where all positive charges on the edge surface had been neutralised by adsorption of hexadecyl sulphate
ions and the value for the edge surface obtained similarly by neutralis-
ation of the negative charge on the face by adsorption of cetyltrimethyl-
ammonium ions. The relationship between rheological properties and
flocculation of clay suspensions was analysed, and indicated that the
rheological properties could be interpreted qualitatively in terms
of the potential energy curves obtained from the zeta potential data
with the aid of heteroflocculation theory. In his study of mutual
flocculation in clay suspensions, van Olphen pointed out another
unusual feature of these systems, namely the different electrochemical
behaviour of the flat face surface and the edge surface. As a result
of isomorphous lattice substitutions (of aluminium for silicon, or
magnesium for aluminium), the plate-like crystal has an interior net
negative charge, which is compensated by positive counter-ions which
are adsorbed onto the face surfaces. Consequently, these surfaces
carry a negative electrical double layer, the charge of which is
fixed by the interior lattice substitutions. The lattice is disrupted
at the edges of the plates and a broken bond exposed. At this surface
an electrical double layer is created by the adsorption of potential
determining ions, and this double layer is of the constant potential type.
Thus an edge to face interaction involves a mixed constant surface
potential-constant surface charge interaction.

Bierman pointed out that for particles with different potentials
a constant potential model implies that at very small distances of
separation the surface charge densities tend towards infinity. It
also indicates that as the distance of separation decreases, the
potential energy of interaction can change from repulsion to attraction
as the sign of surface charge density of the particle with lower
potential changes. Just as the constant potential model becomes
physically unrealistic as separation tends to zero, so too does the constant charge model which implies that the potential of the particles tend to plus or minus infinity. In most practical systems there is a tendency towards one or other of the extremes of constant charge or constant potential.

Frens, Engel and Overbeek\textsuperscript{58} have demonstrated that the equilibrium with respect to the potential determining ions at the silver iodide/aqueous electrolyte interface is established very slowly, suggesting that, in the rapid Brownian collision between two silver iodide particles, such an equilibrium may not hold. This led Frens\textsuperscript{59} to propose that the usual assumption that surface potentials on approaching particles remain constant should be replaced by the idea of constancy of surface charge density on interacting particles. He compared the two cases of constant charge and constant potential for parallel flat plates and for two spherical particles, using the original numerical tables of Verwey and Overbeek\textsuperscript{2} for the exact interaction energy and the solution of the Poisson-Boltzmann equation in terms of elliptic integrals. Weise and Healy\textsuperscript{37} used the method of Frens in the calculation of the interaction at constant surface charge. For the general situation of interacting dissimilar double layers around spherical particles they stated the potential energy of repulsion to be that for the constant potential case modified by the size, potential at infinite particle separation and distance of separation of the particles, and the dielectric constant of the dispersion medium.

Jones and Levine\textsuperscript{60} compared the conditions of constant surface potential and constant surface charge for two parallel plates in binary, Z-Z valency type electrolyte, using a simple approximate method of determining the double layer interaction, namely an extension of the linear superposition approximation. This gave the double layer
interaction to be the same for both the constant charge and constant potential models.

Computations by Honig and Mul\textsuperscript{61} resulted in a series of tables of the repulsive energy due to the interaction of diffuse double layers. Calculations were performed for flat plates and spheres at constant charge and constant potential. They presented limiting equations for four cases, namely small particle separations, large separations, moderate potentials and moderate charge densities.

As previously mentioned, there are practical systems such as clay dispersions where the interaction is a mixture of constant charge and constant potential. Kar, Chander and Mika\textsuperscript{62} have considered this mixed case and compared it with the constant potential and constant charge models. They derived expressions for the potential energy of repulsion dependent on distance of separation, the dispersion medium dielectric constant and properties of the particles, in terms of potential for one particle and charge for the other particle.

Until comparatively recently most studies of interactions between colloidal particles were concerned with ascertaining the effect of the total potential energy of interaction, that is the effect of repulsive and attractive forces together. Although mathematical expressions are available for calculation of the potential energy of attraction, $V_A$, and the potential energy of repulsion, $V_R$, neither had been tested by experiment. Much work in this area has been done by Tabor. Together with Winterton\textsuperscript{63,64} he measured the force of attraction between two molecularly smooth mica surfaces directly. The mica sheets were silvered on the back surfaces and then glued onto hemispherical glass formers. These were then arranged to be mutually
perpendicular, and under these conditions \( F_A \), the attractive force, is equivalent to that between a sphere and a flat plate.

One of the hemicylindrical surfaces was rigidly supported and the other attached to a light cantilever beam. During the measurements one surface was moved slowly towards the other, and at a critical distance of separation the surfaces flicked together. Since this distance depended directly on the stiffness of the cantilever, a direct measurement of the attractive force was obtained. The distance of separation was measured by multiple beam interferometry, which has been described in some detail. Using this technique it became possible to measure the attractive force with a distance of only 5 nm separating the two surfaces. Later this work was extended so that the force could be measured down to a separation of 1.4 nm and the accuracy was increased. The measured force was found to agree with the unretarded force equation at distances of less than 10 nm and with the retarded equation at distances greater than 20 nm. This was a much shorter distance than had been previously considered as
requiring an approach incorporating retardation.

Visser\textsuperscript{66} also measured the force of adhesion between carbon blacks and a cellophane film in aqueous solution. Two concentric cylinders were employed, the inner one coated with the cellophane film and aqueous medium between the two. Carbon black particles were first deposited onto the film, then their percentage removal measured as a function of pH as the film was rapidly rotated in the medium. The force required to remove particles was related to the force of adhesion and a maximum in adhesion was found at pH 3.3, which coincided with the isoelectric point of the carbon black as shown by electrophoretic mobility measurements. The interaction of carbon black with cellophane was treated as a sphere-plate interaction and the force determined from experiment was found to agree reasonably with that according to Hamaker's equation for the van der Waals force of adhesion between a sphere and flat plate.

Tabor\textsuperscript{67,68} also conducted a study into direct measurement of repulsive forces, in conjunction with Roberts. They measured the repulsive force exerted by the diffuse electrical double layers on two solid surfaces as a function of their distance of separation in aqueous media. One surface was an optically flat glass surface. The other was an optically smooth hemispherical rubber surface with very low elastic modulus which was pressed onto the glass through an aqueous solution. The rubber was easily deformed over dust particles or local protrusions and provided a parallel flat interface over the greater part of the contact area. The distance between the surfaces was measured by use of interference fringes at separations of more than 100nm and by measuring reflected light intensity at separations of less than this. By loading the rubber hemisphere, they measured the pressure
exerted by the rubber as a function of the distance of separation between sphere and plate. With $10 \text{ mol m}^{-3}$ sodium dodecyl sulphate solution as the liquid medium, a pressure of approximately $4.5 \times 10^{4} \text{ N m}^{-2}$ was found for a liquid film thickness of $14 \pm 2 \text{ nm}$. An increase of the surfactant concentration to $100 \text{ mol m}^{-3}$ resulted in a decrease of film thickness to $11 \pm 1 \text{ nm}$. This was explained by indicating that when the ion concentration was increased the "centre of gravity" of the charge moved closer to the surface.

From the results of experimental work performed in systems where heteroflocculation occurs it has been shown that DLVO theory is generally valid, at least qualitatively, and in many cases semi-quantitatively. Because of this, and from direct experimental measurements made of attractive and repulsive forces, some reliance can be placed on the expressions commonly used in evaluating potential energies of attraction and repulsion. For practical systems, however, many cases show the need for individual modifications or extensions of the fundamental theory. This does not mean that the theory is unsound, but that each particular system has to be understood before interpreting results in terms of the theory of heteroflocculation. In the work reported in this thesis, the heteroflocculation behaviour of colloidal rutile has been studied. It has been shown that the experimental results can only be considered in terms of DLVO theory after a detailed study of the surface properties of the rutile particles.
2. THEORETICAL

The total energy of interaction between colloidal particles is obtained from summation of the potential energies of repulsion and attraction.

2.1 Potential energy of repulsion

Colloidal particles dispersed in a polar medium (e.g. aqueous electrolyte) are generally electrically charged. There are several mechanisms by which this charge may be acquired.

a) Ionisation. Dissociation of any ionic groups present in the particle surface (e.g. - COOH) may occur.

b) Ion adsorption. The particles may adsorb unequal amounts of the different types of ion present in the medium.

c) Dissolution. With particles of ionic solids, dissolution of each type of ion may occur to a different extent (e.g. instance of silver halides, where the silver ions are potential-determining).

d) Dipolar molecule adsorption and/or orientation. Such dipoles at the particle surface will not directly contribute to the net charge on the particle, but they may have an important effect on the electrical double layer. The dipoles may be the result of the deformation of polarizable molecules in the electric field at the interface.

Since a dispersion of colloidal particles in aqueous electrolyte is overall electrically neutral, any charge on the particles requires a compensating charge of opposite sign in the electrolyte medium.

An initial model of charge distribution at the colloid/dispersion medium interface was suggested by Helmholtz. This showed immobile charges in solution at the colloidal particle surface exactly balancing the charge in the solid at the surface as shown in Fig. 2.1.1.
Fig 21.1 Electrical double layer (Helmholtz)

Particle surface

+ - + - + - electrolyte
+ - - - + medium
+ + - + -
+ - - - -
+ + - + -
+ - - + +
+ - + + +

↔ space charge region

Fig 21.2 Electrical double layer (Gouy-Chapman)
Because two layers of charge were involved this was called the electrical double layer.

However, the Helmholtz model neglected the effect of thermal motion of the ions in solution, this motion causing the outer layer of charge to become much more diffuse. The ionic atmosphere round colloidal particles was studied by Gouy and Chapman, and that surrounding ions in electrolytes studied by Debye and Hückel. The former authors developed a theory of the electrical double layer on this basis. Fig. 2.1.2 shows a schematic representation of the Gouy-Chapman double layer.

In the theory several simplifying approximations were made

a) The charge on the particle surface is assumed to be uniformly smeared out.

b) The ions in the double layer are assumed to have no size, i.e. are point charges.

c) The effect of the electrolyte medium is uniform and brought about by the bulk dielectric constant and bulk viscosity.

The coulombic interaction between the charges present in the double layer is described by the Poisson equation,

\[ \nabla^2 \psi = -\frac{\rho}{\varepsilon} \]  \hspace{1cm} (2.1.1)

where \( \nabla^2 \) is the Laplace operator \( (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) \), \( \psi \) the potential, \( \rho \) the charge density at \( (x,y,z) \).

\( \varepsilon \) is the permittivity rationalised S.I. units. This corresponds to \( \varepsilon = \varepsilon_r \varepsilon_\infty \) where \( \varepsilon_r \) is the dielectric constant of the material (i.e. the ratio of its permittivity to the permittivity of a vacuum, a dimensionless quantity) and \( \varepsilon_\infty \) is the permittivity of a vacuum, equal to \( 8.854 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-1} \text{ s}^2 \text{ A}^{-2} \).
The distribution of ions in the solution, resulting from their thermal motion, is governed by the Boltzmann equation,

\[ n_+ = n \exp(-z_+ e\psi/kT) \] (2.1.2)
\[ n_- = n \exp(-z_- e\psi/kT) \] (2.1.3)

where \( n \) is the bulk ion concentration, and \( n_+ \) and \( n_- \) the concentrations of positive and negative ions at a point where the potential is \( \psi \).

The space charge density is given by the summation of ionic charges per unit volume,

\[ \rho = \sum_i z_i n_i \] (2.1.4)

Combination of equations (2.1.1-4) yields

\[ \nabla^2 \psi = -\frac{1}{\epsilon} \left\{ z_- n_\exp(-z_- e\psi/kT) + z_+ n_\exp(-z_+ e\psi/kT) \right\} \] (2.1.5)

For a symmetrical electrolyte where \( z_+ = -z_- = z \), equation (2.1.5) becomes

\[ \nabla^2 \psi = -\frac{1}{\epsilon} \{ -z_\exp(ze\psi/kT) + z_\exp(-ze\psi/kT) \} \]

\[ = \frac{2z\epsilon}{\epsilon} \sinh(ze\psi/kT) \] (2.1.6)

In solving the above equation analytically the important parameters are

(i) the value of the potential, \( \psi \), because this governs the possibility of expanding the exponentials retaining only a few terms.

(ii) the radius of curvature of the surface because this determines the form of \( \nabla^2 \psi \).

For the case of a flat double layer, the potential need only be evaluated in a direction normal to the surface, and equation (2.1.7) becomes

\[ \frac{\partial^2 \psi}{\partial x^2} = \frac{2z\epsilon}{\epsilon} \sinh(ze\psi/kT) \] (2.1.8)
When \((ze\psi/kT)\) is small, the exponential terms can be expanded and higher orders ignored. Then

\[
\frac{\partial^2\psi}{\partial x^2} = \frac{2ne^2z}{ckT} = \kappa^2 \psi
\]

(2.1.9)

where

\[
\kappa = \left(\frac{2ne^2z}{ckT}\right)^{1/2}
\]

(2.1.10)

One solution of equation (2.1.9) is

\[
\psi = \psi_o \exp(-\kappa x)
\]

(2.1.11)

This illustrates that the rate of decay of potential in the double layer with distance is controlled by \(\kappa\).

From equation (2.1.11), when the potential drops to \(\psi_o/e\), the distance from the surface is \(1/\kappa\). This distance is defined to be the double layer thickness, though it will not extend to the distance at which the concentrations of positive and negative ions are the same. This definition is used for all electrical double layers, although the simplification made in deriving equation (2.1.9) will not always be applicable. Fig. 2.1.3 illustrates \(\psi\) as a function of \(x\) for high and low \(\kappa\).

For curved surfaces the Gouy-Chapman theory for a flat plate can only be used for the case where the double layer is thin compared with a large particle radius, i.e. \(\kappa a \gg 1\) where \(a\) is the particle radius.

To apply the theory to the double layer round a spherical particle, the electric potential is a function of \(r\), the distance from the centre of the particle. Using spherical co-ordinates, the Poisson-Boltzmann equation now becomes

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = -\frac{1}{\epsilon} \sum_i z_i e n_i \exp(-z_i e\psi/kT)
\]

(2.1.12)
Fig 2.13 $\psi$ as a function of distance $x$ for thin (high $\kappa$) and thick (low $\kappa$) double layer.

Fig 2.14 $\psi$ as a function of distance $x$ according to Stern.
For the case of small particles,

$$\psi = \psi_o \left(\frac{a}{r}\right) \exp\left(\kappa (a-r)\right)$$  \hfill (2.1.13)

where $\psi$ is the potential at distance $r$ from the particle centre and $a$ the particle radius.

Among parameters affecting the rate of decay of potential with distance are the valency and concentration of electrolyte ions.

a) Influence of valency

This affects the potential distribution in two ways, altering the surface potential and the double layer thickness.

If $ze\psi_o/kT$ is a constant, $M$, then $\psi_o = MkT/ze$ and $\psi_o \propto 1/z$.

If $M = 8$, then $\psi_o = 205\text{mV}$ for $z = 1$

$$\psi_o = 102.5\text{mV} \text{ for } z = 2, \text{ at } 25^\circ\text{C}.$$  

The effect of valency on double layer thickness is evident from equation (2.1.10), $\kappa \propto z$. For bivalent ions the exponential tail decreases twice as rapidly with distance as for monovalent ions.

b) Influence of electrolyte concentration.

Since $\kappa \propto n^1$, altering ion concentration alters the double layer thickness. Table 2.1 illustrates the effect of varying ion concentration on double layer thickness.

<table>
<thead>
<tr>
<th>Concentration/mol dm$^{-3}$</th>
<th>KCl</th>
<th>$\frac{1}{\kappa/a}$ (for $z=1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-5}$</td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>
The Gouy-Chapman theory does not give a completely adequate description of the potential at any point in an electrical double layer. It has several defects, the most serious being to neglect the finite dimensions of the ions. This is particularly important at higher electrolyte concentration and can be demonstrated in the following example. If one considers a large double layer potential of 300mV in a 1-1 electrolyte of concentration 1 mol m\(^{-3}\), then according to equation (2.1.2), the concentration of counterions close to a positively charged surface is

\[
    n_\text{c} = n \exp\left(\frac{z\varepsilon}{kT}\right) = e^{12} = 16 \times 10^4 \text{ mol m}^{-3}
\]

Obviously, in view of the finite dimensions of the ions, this concentration is physically ridiculous.

To overcome this difficulty, Stern modified the double layer model to account for the finite ion size, and Fig. 2.1.4 gives a schematic representation of the Stern model of the electrical double layer. In this model, ions adsorbed onto the charged surface form one layer of thickness \(\delta\), where \(\delta\) is a few Angstroms. In this layer the potential decays linearly as in a classical plate condenser. Beyond the adsorbed layer the ions are mobile and this region corresponds to the diffuse layer of Gouy-Chapman theory. The interface at distance \(\delta\), termed the Stern plane, was taken as the site of the centres of any ions specifically adsorbed onto the solid surface. This model of the inner region of the double layer was later modified by Grahame. He suggested that the Stern plane indicated the closest distance of approach of hydrated ions in solution, and could be termed the "outer Helmholtz plane", and that an "inner Helmholtz plane" indicated the centres of any specifically adsorbed ions, usually desolvated in the direction of the surface. This is illustrated in Fig. 2.1.5, for the
Fig 2.1.5 Electrical double layer (Grahame)

specifically
adsorbed ions
completely solvated ions
the mercury/solution interface. It should also be noted that, in aqueous solutions, simple inorganic cations are more strongly solvated than anions and possess a larger solvated radius. Because of this, specific adsorption of anions is more favourable than adsorption of cations. In addition, counter-ion adsorption usually predominates over co-ion adsorption. Specific adsorption of ions can have a dramatic effect on the potential at the Stern plane. For example, if surface active counter-ions are specifically adsorbed then a reversal of sign of charge can occur in the Stern layer. Similarly, adsorption of co-ions can increase the potential at the Stern plane.

Interaction of two dissimilar double layers

Consider two parallel plates separated by distance 2d in aqueous electrolyte. The simplified Poisson-Boltzmann expression is

$$\frac{\partial^2 \psi}{\partial x^2} = \kappa^2 \psi \quad (2.1.9)$$

for small surface potential. Solving equation (2.1.9) gives

$$\psi = A_1 \cosh(\kappa x) + A_2 \sinh(\kappa x) \quad (2.1.14)$$

which is an alternative form of equation (2.1.11).

If $\psi = \psi_{01}$ at $x = 0$ and $\psi = \psi_{02}$ at $x = 2d$, then

$$\psi = \psi_{01} \cosh(\kappa x) + \left( \frac{\psi_{02} - \psi_{01} \cosh(2kd)}{\sinh(2kd)} \right) \sinh(\kappa x) \quad (2.1.15)$$

is the equation for the electric potential between the plates.

Fig. 2.1.6 represents the electric potential between the surfaces of two charged particles.
Fig 2.1.6 $\psi$ as a function of distance of separation between two charged surfaces

Fig 2.1.7 Geometry of interaction between spherical particles, radii $a_1$ and $a_2$
The free energy of the electrical double layer is given by
\[ G = - \int_{0}^{\psi_0} \sigma d\psi_0 \tag{2.1.16} \]
where \( \psi_0 \) is the surface potential and \( \sigma \) the surface charge density. Since
\[ \sigma = \varepsilon K \psi_0 \tag{2.1.17} \]
for small values of \( \psi_0 \), then
\[ G = - \frac{1}{2} \sigma \psi_0 \tag{2.1.18} \]
Hence in evaluating free energy, either surface charge density or surface potential may be held constant. It is common practice to assume surface potential to be constant.

Therefore, for a system of two dissimilar double layers, as shown in Fig. 2.1.6, the free energy can be written
\[ G = \frac{1}{2} (\sigma_1 \psi_1 + \sigma_2 \psi_2) \tag{2.1.19} \]
with
\[ \sigma_1 = - \varepsilon \left( \frac{d\psi}{dx} \right)_{x=0} \tag{2.1.20} \]
and
\[ \sigma_2 = + \varepsilon \left( \frac{d\psi}{dx} \right)_{x=2d} \tag{2.1.21} \]
By combination of equations (2.1.15), (2.1.20) and (2.1.21), \( \sigma_1 \) and \( \sigma_2 \) can be expressed as follows:
\[ \sigma_1 = -\varepsilon K (\psi_{01} \cosech(2Kd) - \psi_{02} \coth(2Kd)) \tag{2.1.22} \]
\[ \sigma_2 = \varepsilon K (\psi_{02} \coth(2Kd) - \psi_{01} \cosech(2Kd)) \tag{2.1.23} \]
After substitution of \( \sigma_1 \) and \( \sigma_2 \) for electrical double layers separated by distance 2d, equation (2.19) becomes
\[ G_{2d} = \frac{-\varepsilon K}{2} (2\psi_{01} \psi_{02} \cosech(2Kd) - (\psi_{01}^2 + \psi_{02}^2) \coth(2Kd)) \tag{2.1.24} \]
At large separations, \( d \to \infty \) and

\[
G_\infty = -\frac{\varepsilon k}{2} \left( \psi_{01}^2 + \psi_{02}^2 \right)
\]

(2.1.25)

Electrostatic potential energy, \( V_{el} \), is given by

\[
V_{el} = G_{2d} - G_\infty
= \frac{\varepsilon k}{2} \left\{ (\psi_{01}^2 + \psi_{02}^2) \left( 1 - \coth(2kd) \right) + 2\psi_0 \psi_2 \cosech(2kd) \right\}
\]

(2.1.26)

Equation (2.1.26) expresses the potential energy of interaction between two dissimilar infinite flat plates in terms of their surface potentials and interplate separation.

Derjaguin\(^72\) extended this to consider the electrostatic interaction between dissimilar spherical double layers, assuming that the double layer thickness was small compared with particle size.

The spheres were considered as being composed of infinitesimally thin slices each assumed to be a flat plate. Thus the overall interaction was made up of an infinite number of flat plate interactions, and the potential energy given by an integral

\[
V_R = \int_0^\infty 2\pi h V_{el} \, dh
\]

(2.1.27)

where \( h \) is the radius of the ring as shown in Fig. 2.1.7. From geometrical considerations and employing differentiation

\[
dH = \left\{ \frac{1}{(a_1^2 - h^2)^{1/2}} + \frac{1}{(a_2^2 - h^2)^{1/2}} \right\} \, dh
\]

(2.1.28)

When \( h \ll a_1 \) and \( h \ll a_2 \),

\[
\text{then } dh = \frac{a_1 a_2}{a_1 + a_2} \, dH
\]

(2.1.29)

and equation (2.1.27) becomes
H = 2d in the flat plate case and equation (2.1.30) can be evaluated analytically,

$$V_R = \frac{2\pi a_1 a_2}{a_1^2 + a_2^2} \int_{H_0}^{\infty} v_{e1}(H) dH$$  \hspace{1cm} (2.1.30)$$

$$V_R = \frac{\varepsilon \pi a_1 a_2 (\psi_0^2 + \psi_0^2)}{(a_1^2 + a_2^2)} \frac{2\psi_0 \psi_0}{\psi_0^2 + \psi_0^2} \ln \left( \frac{1 + \exp(-\kappa H_0)}{1 - \exp(-\kappa H_0)} \right) + \ln(1 - \exp(-2\kappa H_0)) \right)$$

$$V_R = \frac{2\varepsilon a_0}{(a_1^2 + a_2^2)} \ln \left( 1 + \exp(-\kappa H_0) \right)$$  \hspace{1cm} (2.1.32)$$

In the case of identical spherical particles equation (2.1.31) reduces to

$$V_R = 2\pi a_0^2 \ln \left( 1 + \exp(-\kappa H_0) \right)$$

The relationship (2.1.31) only holds exactly for $\psi_0^1$ and/or $\psi_0^2$ less than 25mV and double layer thickness small compared with particle size, i.e. $\kappa a \gg 1$. However, the equations is a good approximation up to $\psi_0^1$, $\psi_0^2$ of 50-60mV.

Verwey and Overbeek have shown that Derjaguin's method gives a good approximation for the interaction provided $\kappa a > 10$, an error of about 10% for $\kappa a = 5$, and 30% for $\kappa a = 2$.

In the experiments performed during this work on rutile, the colloidal particles had a radius of ~100 nm and were dispersed in KCl electrolyte of concentration 1 mol $\cdot$ m$^{-3}$. In these circumstances, $\kappa a = 10$, and equation (2.1.31) can be used with confidence for potentials up to around 50mV. For the case of 100 nm radius particles in non-aqueous media where $\kappa$ may be very small, then equation (2.1.31) will be highly inaccurate.

The equations derived for the electrostatic potential energy are based on the Gouy-Chapman theory. Verwey and Overbeek have shown that use of this theory to evaluate $V_R$ is adequate since the
differences between it and the Stern theory are only significant at very short distances of separation. Since $V_A$, the potential energy of attraction, would predominate at short distances in any case, the modification would be negligible.

**Constant charge v. constant potential**

The double layer interaction has been evaluated on the basis of the surface potential on the particles remaining constant during the interaction. There is no mathematical reason why this should be so, as can be seen from equation (2.1.18) and, in some cases, chemical reasons why it should not be so. Bierman showed that the constant potential model became physically unrealistic as interparticle separation decreased.

For the constant potential model to hold, the particle surface would have to allow rapid exchange of ions to maintain constant $\psi_o$. Frens showed that a constant charge class is possibly more common than usually assumed since many surfaces cannot sustain a high exchange current. Fig. 2.1.8 shows the shape of $V_R$ curves on the basis of a constant surface potential model and for a constant surface charge model. The equation derived for constant surface charge given by Wiese and Healy is

\[ V_R = V_R - \frac{2\pi \varepsilon a_1 a_2 (\psi^2 + \psi_0^2)}{a_1 + a_2} \ln(1 - \exp(-2\varepsilon a_0)) \]  

(2.1.33)

calculated by the method of Frens, using the Derjaguin approximation.

Bell and Peterson have given a comprehensive account of the electrical double layer interaction forces between dissimilar spheres
Fig 2.1.8 $V_R$ v. $H_o$ for (i) constant potential model, (ii) constant charge model.

Fig 2.1.9 $\psi$ as a function of distance ($x$) between two dissimilar charged particles.
on the basis of constant surface charge and constant surface potential models. For calculations at small separations they used the Derjaguin approximation, and at larger separations used the linear superposition approximation of Bell et al.\textsuperscript{74} The authors presented the results graphically and pointed out that at short distances of separation the constant charge model always gave repulsion whereas, except for identical particles, the constant potential model gave an attractive force.

If the constant potential model holds, then for the interaction between particles of unequal potential, the surface charge density \( \alpha \frac{d\psi}{dx} \) of one particle will change sign at closer distances. This is illustrated in Fig. 2.1.9. Thus it is possible to obtain an attractive electrostatic double layer interaction at shorter distances of interparticle separation. Both the constant potential and constant charge models can be criticised, the former since surface charge density tends to infinity at short distances of interparticle separation and the latter since the surface potential tends to infinity as interparticle separation decreases. In a real system, there will be a tendency towards one or other of the extremes. In some cases, such as edge to face flocculation in clays, the potential energy of interaction between dissimilar electrical double layers results from constant potential behaviour at the edges and constant charge on the faces. Kar et al\textsuperscript{62} derived an equation to describe the potential energy of repulsion in such a system:-
\[ V_{\psi} = \frac{\pi a_1 a_2}{(a_1 + a_2)} \left\{ \left( \frac{2\sigma_2 \psi}{\kappa} \right) \left( \frac{\pi}{2} - \frac{1}{\tan^{-1}(\sinh(kH))} \right) - \left( \sigma_2^2 / \epsilon \kappa - \epsilon \psi \right) \ln \left( 1 + \exp(-2kH) \right) \right\} \] 

(2.1.34)

where particle 1 is held at constant surface potential and particle 2 at constant surface charge.

The magnitude of the potential energy of interaction between electrical double layers shows the repulsion between colloidal particles, but to estimate the stability of a given system it is necessary to combine potential energy of repulsion with potential energy of attraction.

2.2 Potential energy of attraction

All atoms and molecules experience attractive van der Waals forces. Consequently, the attractive potential energy between colloidal particles arises from these forces between molecules in the interacting particles. There are three different types of interaction:

a) between a dipole and an induced dipole – Debye potential energy,

\[ V_{\text{Debye}} = -\frac{1}{2} \alpha F^2 \] 

(2.2.1)

where \( \alpha \) is the polarizability of the atom or molecule and \( F \) is the field strength.

b) dipole-dipole interaction – Keesom potential energy,

\[ V_{\text{Keesom}} = \int E \exp(-E/kT) d\psi d\theta / \int \exp(-E/kT) d\psi d\theta \] 

(2.2.2)

where \( E \) is the energy of interaction and \( \psi \) and \( \theta \) are angular terms.

c) potential energy arising from London dispersion forces.

At any time an atom will have a small dipole moment since the electron distribution will not be symmetrical. This dipole moment will induce neighbouring dipoles.
London = \(-\frac{3a^2\hbar v}{4r^6}\) \hspace{1cm} (2.2.3)

where \(\hbar\) is Planck's constant, \(v\) is a characteristic frequency for the material and \(r\) the separation between atoms or molecules.

All these energies are dependent on the inverse of the sixth power of the separation distance and are consequently of very short range. Only in the case of London-van der Waals forces are the resultant energies additive for colloidal particles which are composed of large numbers of molecules. The resultant London dispersion energy is significant compared with the thermal energy and operates over distances of the order of several double layer thicknesses.

There are two basic methods of estimating the attractive potential energy between solid particles:-

i) the microscopic approach of Hamaker,\(^4\) which is based on the summation of interactions between the atoms of two separate particles.

ii) the macroscopic approach of Lifshitz,\(^75,76\) which treats the interacting phases and medium as being continuous.

The microscopic approach

Hamaker obtained the total energy of attraction for macroscopic bodies by integrating the interaction terms over all pairs of atoms or molecules. His expression for the potential energy of the van der Waals attraction \(V_A\), consisted of a geometrical factor multiplied by an interaction parameter. For the case of attraction between two dissimilar spherical particles in a vacuum he gave,

\[
V_A = -\frac{A}{6} \left( \frac{2a_1a_2}{(2(a_1+a_2)+H)H} + \frac{2a_1a_2}{(2a_1+H)(2a_2+H)} + \ln \frac{(2(a_1+a_2)+H)H}{(2a_1+H)(2a_2+H)} \right)
\] \hspace{1cm} (2.2.4)
where \( a_1 \) and \( a_2 \) are the particle radii, \( H \) the interparticle separation and \( A \) termed the Hamaker constant. For two bodies of the same material 1, this constant \( A_{11} \) is given by

\[
A_{11} = \pi \frac{q_1^2 B_{11}}{2}
\]

(2.2.5)

where \( q_1 \) is the number of atoms (or molecules) per unit volume.

\( B_{11} \) is the London constant in the equation for attraction between two atoms of type 1,

\[
V_{11} = -3h \nu_1 a_1^2/4r^6 = -B_{11}/r^2
\]

(2.2.6)

where \( h \) is Planck's constant, \( \nu_1 \) the characteristic frequency of the atom (taken as a single frequency occurring in the ultraviolet), \( a_1 \) the polarizability and \( r \) the distance between the two atoms.

The Hamaker constant for the interaction between bodies of different materials is given by

\[
A_{12} = \pi \frac{q_1 q_2 B_{12}}{2}
\]

(2.2.7)

where \( B_{12} \) is given by \( B_{11} B_{22} \).

When a medium separates the interacting particles the attractive force is reduced by competing particle-medium and medium-medium interactions. Hamaker showed that the total constant \( A_T \) for such a system could be expressed

\[
A_T = A_{12} + A_{33} - A_{13} - A_{23}
\]

(2.2.7)

where subscripts 1, 2 refer to particles and 3 to the medium.

Assuming a geometric mean relationship

\[
A_{12} = (A_{11} A_{22})^{1/2}
\]

(2.2.9)

and equation (2.2.8) can be written

\[
A_T = (A_{11}^{1/2} - A_{33}^{1/2})(A_{22}^{1/2} - A_{33}^{1/2})
\]

(2.2.10)

It has, however, been shown by Bargeman and Van Voorst Vader \(^{77}\) that this assumption is incorrect because it does not account for the screening effects of the medium.
To account for transmission of the London force through the medium, Verwey and Overbeek\(^7^8\) have suggested that the right hand side of equation (2.2.10) be divided by the square of the refractive index.

However, subsequent work of Ninham and Parsegian\(^7^9,^8^0\) indicated that the insertion of a material, such as a liquid, between the interacting particles, could not be dealt with merely by the insertion of an arbitrary "dielectric constant" at a single frequency. They showed that, to account for the presence of a medium, it was necessary to consider contributions from all interaction frequencies.

At large distances of separation the finite time required for propagation of the dispersion forces causes a phase difference between the oscillating electrons of interacting molecules, thus retarding the force. Casimir and Polder\(^8^1\) found that at very large separations the dependence of the London equation on the inverse sixth power of distance changed to the inverse seventh power, and provided a complicated solution to the retarded force. Schenkel and Kitchener\(^2^6\) derived useful approximate formulae for spherical particles at distances of separation much smaller than the particle radius.

For \(\mathcal{H} \ll a\), they approximated the energy of attraction to

\[
V_A = -\frac{Aa}{12\mathcal{H}} \quad (2.2.11)
\]

and where \(\mathcal{H} \gg \lambda/6\) (\(\lambda\) being the wavelength of the intrinsic electronic oscillations of the atoms)

\[
V_A(\text{partially retarded}) = \frac{Aa}{\pi} \left(\frac{2.45\lambda}{120\mathcal{H}^2} - \frac{\lambda^2}{1045\mathcal{H}^3} + \frac{\lambda^3}{5.62 \times 10^4 \mathcal{H}^4}\right) \quad (2.2.12)
\]

At distances of separation greater than \(2\lambda\), the London force is practically fully retarded, and

\[
V_A(\text{fully retarded}) = 2.45Aa \frac{\lambda}{120\pi\mathcal{H}^2} \quad (2.2.13)
\]
The macroscopic approach

Lifshitz and coworkers \textsuperscript{75,76} developed a theory for the interaction between solid bodies based on their bulk material properties. In the macroscopic approach contributions from all interaction frequencies are considered and considerably more data is required for computation of an interaction constant than for the Hamaker approach which requires only one frequency.

Ninham and Parsegian \textsuperscript{82} criticised the Hamaker approach as being intrinsically unsound for condensed systems, although valid for dilute gases. They favoured the Lifshitz approach in that it considers all interactions and treats the effect of intervening medium realistically.

Criticisms of approach to forces of attraction included;

a) much of the van der Waals force in a highly polar medium such as water comes from polarization at infrared and microwave frequencies rather than the ultraviolet (as assumed by Hamaker).

b) it is incorrect to consider the van der Waals force between liquid layers as being the sum of individual interactions between unit segments of the constituent materials.

c) the van der Waals force contains a temperature-dependent component due to the low-frequency contribution.

d) dielectric data are well enough known through the range of frequencies to draw these conclusions and to make quantitative numerical estimates with little ambiguity.

Useful articles on calculation and merits of approach to Hamaker constants have been written by Grégor\textsuperscript{83} and Visser\textsuperscript{84}.

For materials for which potential energies of attraction have been calculated by both the microscopic and macroscopic approach, there has been little difference between results obtained using either
Fig 2.3.1 Potential energy of repulsion ($V_R$), attraction ($V_A$), and total potential energy ($V_T$), as a function of interparticle separation ($H_o$).
approach, in most cases. However, the Lifshitz approach is generally favoured, in theory if not in practice, as being more fundamentally sound. Before it can be used more extensively, the necessary experimental data on relative permittivity as a function of frequency must be obtained.

2.3 Total potential energy

The total potential energy of interaction between colloidal particles is obtained by summation of the energies of attraction and repulsion. These are both functions of interparticle separation, the former decreasing as an inverse power of the square of the distance of separation, the latter showing exponential behaviour with distance. Van der Waals attraction increases as interparticle distance decreases until the point where Born repulsion, due to the overlapping of electron clouds, predominates at atomic distances. This, however, is of no importance since at a few Angstroms separation particles remain flocculated in the primary minimum. At intermediate and large distances of separation the form of total potential energy as a function of distance depends largely on the \( V_R \) term.

Fig. 2.3.1. illustrates a typical plot of potential energy as a function of distance for colloidal particles in dilute aqueous electrolyte. The important features with regard to flocculation are the depth of primary minimum, the height of the energy barrier \( E \), and the depth of the secondary minimum. Generally, if \( E \) is large compared with the thermal energy of the colloidal particles then this will act as a barrier to flocculation and the suspension will be stable. If the electrolyte concentration is increased or surface potential reduced so that the energy barrier \( E \) is lowered, then particles may flocculate into the
Fig 2.3.2 $V_T$ v. $H$ for $\alpha$=(i)100nm, (ii)300nm, (iii)500nm

$A = 8 \times 10^{-20} \text{J}$
$K = 0.1 \text{nm}^{-1}$
$\varepsilon = 78.3$
$\psi = \psi_\perp = 30 \text{mV}$
Fig 2.3.3 $V_T$ v. $H$ for $K =$ (i) 1 nm$^4$, (ii) 0.1 nm$^4$, (iii) 0.01 nm$^4$.

- $A = 8 \times 10^{-20}$ J
- $a = 100$ nm
- $\varepsilon = 78.3$
- $\psi_1 = \psi_2 = 30$ mV
Fig 2.3.4a $V_T$ v. $H$ for $\psi_1 = \psi_2 = (i) 20mV, (ii) 30mV, (iii) 40mV, (iv) 50mV

$A = 8 \times 10^{-20} J$

$\alpha = 100 \text{nm}$

$\Sigma = 78.3$

$K = 0.1 \text{nm}^{-1}$
Fig 2.3.4b $V_T$ v. $H$ for (i) $\psi_1 = \psi_2 = 20$ mV, (ii) $\psi_1 = \psi_2 = 50$ mV, (iii) $\psi_1 = 20$ mV, $\psi_2 = 50$ mV

$A = 8 \times 10^{-29}$ J
$
\alpha = 100 \text{ nm}$
$
\varepsilon = 78.3$
$
K = 0.1 \text{ nm}^{-1}$
primary minimum. Once flocculated into the primary minimum the particles are not readily redispersed. However, if the secondary minimum is sufficiently deep, and the height of E proves a barrier to flocculation into the primary minimum, then the resultant secondary minimum flocs consist of loose aggregates of particles which are easily redispersed by shaking. Since both the attractive and repulsive potential energies are approximately proportional to particle radius, the secondary minimum becomes increasingly significant with increase in particle size. This is illustrated in Fig. 2.3.2.

Variation of the parameters in the potential energy equations can have a marked effect on the resultant potential energy curves. For any specified system the potential energy of attraction is usually defined, and any variation of \( V_T \) is occasioned by changes in \( V_R \). Fig. 2.3.3 shows the effect of varying double layer thickness, \( 1/\kappa \), a measure of electrolyte concentration, on \( V_T \) as a function of interparticle separation. Fig. 2.3.4a illustrates that \( V_T \) increases as particle potential increases, and Fig. 2.3.4b shows the way in which the lower surface potential dominates in the interaction between particles possessing different surface potentials.

In some systems adsorption of certain long chain polymeric molecules can give the particles stability at electrolyte concentrations where flocculation would normally occur. If the polymer chains extend some distance into the medium then interaction between these chains as particles approach one another is accompanied by a decrease in entropy. Since this interaction involves a positive free energy change, there is an energy barrier to particle aggregation. This effect is termed steric stabilisation, \( V_S \), an additional term in the equation for
Fig 2.3.5 The effect of the steric stabilization term, $V_S$, on the potential energy curve: 

$V_T = V_A + V_R$;  
$V_T = V_R + V_A + V_S$
obtaining total potential energy:

\[ V_T = V_R + V_A + V_S \]

The influence of this term on the form of the total potential energy plot is shown in Fig. 2.3.5.

These energy relationships indicate whether or not a dispersion may be expected to be stable, but give no indication of the rate of flocculation. To obtain this information, a study of the kinetics of flocculation is required.

2.4. Kinetics of flocculation

Rapid flocculation

In the absence of any forces between them, colloidal particles will flocculate at the rate determined by their Brownian motion alone. Smoluchowski \(^85\) assumed that every encounter between particles led to a permanent bond being formed (Fig. 2.4.1), and that rapid flocculation resulted from collisions due to Brownian motion. He considered flocculation as a diffusion problem and used the first equation of Fick to obtain the number of particles, \( J \), diffusing towards a central fixed particle:

\[ J = D \cdot 4\pi r^2 \frac{\partial N}{\partial r} \quad (2.4.1) \]

where \( D \) is the diffusion constant of the particles, \( r \) the distance from the centre of the fixed particle and \( N \) the number of particles in unit volume. The diffusion constant, \( D \), for Brownian motion is given by

\[ D = \frac{kT}{6\pi \eta a} \quad (2.4.2) \]

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, \( \eta \) the viscosity of the medium and \( a \) the particle radius.
Fig 2.4.1 Interaction energy v. interparticle separation in the absence of any forces (Smoluchowski)
By considering the central particle also to be subject to Brownian motion, Smoluchowski obtained the following equation for the rate of disappearance of primary particles:

\[- \frac{dN}{dt} = 8\pi DRN^2\]  \hspace{1cm} (2.4.3)

where \(N\) is the number of primary particles present at time \(t\) and \(R\) the minimum separation of the particles, that is the inter-centre distance. Equation (2.4.2) only describes the flocculation process at the very beginning, and was therefore extended to give the rate of disappearance of particles of all types, so that

\[- \frac{dN}{dt} = 4\pi DRN^2\]  \hspace{1cm} (2.4.4)

where \(N\) is now the number of particles of all types. Equation (2.4.3) shows that flocculation proceeds as a second order reaction. The reaction rate constant for rapid flocculation \(k_0\), can be evaluated from known quantities where

\[k_0 = 4\pi DR\]  \hspace{1cm} (2.4.5)

By substituting \(R = 2a\), \(D = kT/6\pi \eta a\), the rapid rate constant is given by

\[k_0 = 4kT/3\eta\]  \hspace{1cm} (2.4.6)

Deviations from this rate constant may occur if the particles are non-spherical and if the sample is polydisperse. Both of these cases lead to higher \(k_0\) values than predicted by equation (2.4.6), but the effect is only significant if there is marked deviation from the idealised case. Müller showed that the assumption made by Smoluchowski that collisions between particles of any size ratio are equally probable is a bad approximation when the sol is strongly polydisperse. He showed deviations from the predicted rate to be important for \(a_1/a_2 > 10\).
Smoluchowski's theory of rapid flocculation assumes that there is no attraction between particles until they come into contact, and takes no account of the long range van der Waals attractive forces. McGown and Parfitt\cite{87} modified equation (2.4.4) to allow for the increase in the rapid rate of flocculation arising from these attractive forces, to give

$$\frac{dN}{dt} = \frac{4\pi DN^2}{\int_{2a}^{\infty} \left( \exp\left( \frac{V_A}{kT} / R^2 \right) / R^2 \right) dR}$$

(2.4.7)

Another modification to the calculation of rates of flocculation was made by Spielman\cite{88} who criticised the assumption of additivity of single particle Brownian diffusion coefficients. Smoluchowski assumed that the particles diffused independently of one another, but it is known that the viscous motion of two neighbouring particles is quite different from that for a single particle.\cite{89,90} Thus the equations of Smoluchowski are only valid for particles widely separated, and become questionable at closer distances, where colloidal particle interaction is most important. Spielman calculated the effect of viscous interactions on the rate of flocculation and found that, for rapid flocculation, the rate was reduced to 60-70% of that predicted by Smoluchowski.

**Slow flocculation**

The theory for slow flocculation proposed by Smoluchowski was a simple extension of his theory of rapid flocculation. He assumed that in the case of rapid flocculation every encounter between particles led to permanent adhesion whereas this was only true for a fraction, $\alpha$, of encounters for slow flocculation. This approach, however, showed no connection between $\alpha$ and parameters such as particle potential, electrolyte concentration and so on.
A more successful approach was that of Fuchs who treated the slow flocculation of particles as a problem of diffusion in a field of force, and obtained the following expression for the reduction of particle number with time:

\[
-\frac{dN}{dt} = \frac{4\pi N^2}{\int_2^\infty \frac{\exp(V_T/kT)}{R^2} dR}
\]

(2.4.8)

2.5 Stability

The stability of a dispersion is expressed in terms of a ratio, \(W\), of the rapid rate of flocculation to the reduced (or slow) rate. Thus, \(W\) can be written

\[
W = \frac{\int_2^\infty \frac{\exp(V_T/kT)}{2a^2} dR}{\int_2^\infty \frac{\exp(V_A/kT)}{2a^2} dR}
\]

(2.5.1)

Where \(s = R/a\) and \(R = 2a + H\), \(H\) being the minimum distance of separation between particle surfaces, then equation (2.5.1) becomes

\[
W = \frac{\int_2^\infty \frac{\exp(V_T/kT)}{s^2} ds}{\int_2^\infty \frac{\exp(V_A/kT)}{s^2} ds}
\]

(2.5.2)

Neglecting the correction of McGown and Parfitt to the rapid rate, the stability ratio becomes

\[
W = 2\int_2^\infty \frac{\exp(V_T/kT)}{s^2} ds
\]

(2.5.3)

To apply this expression to practical cases, evaluation of the integral is usually performed graphically or numerically. The forms of the quantities \(V_T\) and \(\frac{\exp(V_T/kT)}{s^2}\) are shown in Fig.2.5.1. A useful approximation given by Overbeek to obtain stability ratios in terms of the potential energy maximum, \(V_{\text{max}}\), is

\[
W = 2\int_2^\infty \frac{\exp(V_T/kT)}{s^2} ds = \frac{1}{2k} \exp(V_{\text{max}}/kT)
\]

(2.5.4)
Fig 2.5.1 Potential energy of interaction, $V$, and $(\exp(V_T/kT)/s^2)$ plotted as a function of $s$
In circumstances where heteroflocculation takes place there are three possible interactions which may occur between the particles. Particles of type 1 may interact with one another, similarly for type 2, and type 1 may interact with type 2. For each case a separate stability ratio may be defined, \( W_{11}, W_{22}, \) and \( W_{12} \), and a probability of occurrence will be associated with each interaction.

Thus

\[
P_{11} = n^2 \quad (2.5.5)
\]
\[
P_{22} = (1-n)^2 \quad (2.5.6)
\]
\[
P_{12} = 2n(1-n) \quad (2.5.7)
\]

where \( n \) is the fraction of particles of type 1 present in the system.

An overall stability ratio, corresponding to that measured experimentally can be given in terms of the stability ratios for the different interactions and depends on the frequency of encounters being determined only by relative particle numbers:

\[
\frac{1}{W_T} = \frac{n^2}{W_{11}} + \frac{(1-n)^2}{W_{22}} + \frac{2n(1-n)}{W_{12}} \quad (2.5.8)
\]

This equation enables estimation of \( W_{12} \), the stability ratio for the hetero-interaction.
3. EXPERIMENTAL

3.1. Materials

3.1.1 Rutile samples

All rutile samples used were supplied by Tioxide International Ltd. Samples used in the initial stability work were

A) M/187/300/7, an alumina coated rutile
B) M/187/302/6, a silica coated rutile
C) CL/D 636, a pure rutile.

The analyses of these samples are shown below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>M/187/300/7</td>
<td>3.65</td>
<td>2.23</td>
<td>1.17</td>
<td>0.33</td>
<td>14.9</td>
</tr>
<tr>
<td>M/187/302/6</td>
<td>0.40</td>
<td>1.63</td>
<td>0.07</td>
<td>-</td>
<td>14.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Cl</th>
<th>Fe</th>
<th>Sn</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL/D 636</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.29</td>
<td>&lt;3</td>
<td>32</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Samples (A) and (B) were used as received, but (C) contained chloride ion impurity which was removed by a cycle of washing the solid in a Soxhlet extractor, then heating to 250°C. This procedure was repeated until the wash water no longer showed any reaction with silver nitrate solution.

Two pure rutile samples used in the later work were

D) CLDD/887A, which had been heated to 400°C in air for 15 hours.
E) CLDD/887B, which had been heated to 750°C in air for 4 hours.

Sample (E) was used in all the surfactant adsorption experiments. The surface areas of (D) and (E) from nitrogen (σ = 1.62 x 10⁻⁹ m² molecule⁻¹) B.E.T. adsorption isotherms were 14.8 m² g⁻¹ and 4.53 m² g⁻¹ respectively.
Plate 1

Electron micrograph of rutile (D)
Plate 2

Electron micrograph of rutile (E)
The analyses follow:

<table>
<thead>
<tr>
<th>Element</th>
<th>CLDD/887A</th>
<th>CLDD/887B</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO ppm</td>
<td>&lt;20</td>
<td>49</td>
</tr>
<tr>
<td>ZnO ppm</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Fe ppm</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>Sn ppm</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$ ppm</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Pb ppm</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>K$_2$O ppm</td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td>Nb$_2$O$_5$ ppm</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Sb$_2$O$_3$ ppm</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Al$_2$O$_3$ %</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>SiO$_2$ %</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb$_2$O$_5$ %</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>SO$_3$ %</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Cl %</td>
<td>0.066</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The major analytical difference between (D) and (E) is in the chloride ion content. The higher calcination temperature for (E) not only causes reduction in surface area but also removes chloride ion impurity. Samples (D) and (E) were used both in the untreated state and after the washing/heat cycle referred to earlier for removal of chloride. Plates 1 and 2 are electron micrographs of samples (D) and (E) showing that the particles of (D) are cigar-shaped while those of (E) heated to a higher temperature approximate to spheres.

Measurements of particle size were made from Plate 2 and from a separate micrograph of sample (E), assuming the particles to approximate to spheres. Histograms of the size distributions are shown.
Fig 3.2.1 Frequency v. particle diameter
Fig 3.2.2  %Frequency v. diameter/nm
separately in (Fig. 3.2.1) and combined in Fig. 3.2.2, and illustrate an approximately Gaussian distribution of size around a peak value of ca. 210 nm diameter. The average of all the size data was 106.5 ± 24.4 nm radius. This value was used in determination of zeta potentials and in potential energy calculations.

The radius obtained from the micrographs assumes the particles to be smooth and accurately spherical. However, in reality there will be irregularities in the particle surface and deviations from spherical shape. This is evident from the value of radius corresponding to an equivalent sphere as determined from the surface area of sample (E), the radius being 155.5 nm. Therefore, as expected, the true surface area of the rutile particles is somewhat greater than that calculated using the radius obtained from the micrographs.

3.1.2 Carbon blacks

Carbon blacks have often been used in surface chemistry studies since they possess a relatively inert non-polar surface which can be well characterized. In the present work, they were used as a test of the experimental techniques of electrophoresis and particle counting, and in heteroflocculation experiments with rutile. The following samples (supplied by the Cabot Corporation) were used:

a) Graphon, which consists of small aggregates of primary particles, overall radius approximately 100 nm.

b) Black Pearls A.

c) Vulcan 6 (untreated).

Samples (b) and (c) were analysed in terms of surface acid groups.
Acid groups meq. g\(^{-1}\) | Surface area m\(^2\) g\(^{-1}\)
--- | ---
Black Pearls A | Strong: 0.4 | Weak: 0.98 | 284
Vulcan 6 | 0.028 | 0.47 | 110

The carbon blacks were used as received.

3.1.3. Electrolytes

Most colloidal dispersions were prepared using aqueous solutions of KCl, but KNO\(_3\) and NaCl were also used. The electrolyte solutions were made up using AnalaR reagents in water which had been de-ionised by passing through an ion-exchange column (Permutit "Deminrolit") and subsequently twice distilled in all-Pyrex apparatus. The conductivity of the water so-obtained was less than 10\(^{-6}\) mho.

3.1.4. Surfactants

An anionic and a cationic surfactant were used. The sodium dodecyl sulphate (SDS) was supplied by Geigy Ltd. A graph of surface tension versus log of concentration showed no minimum, and the critical micelle concentration (c.m.c.) (8 mol m\(^{-3}\) in 1 mol m\(^{-3}\) KCl) agreed with literature values\(^92\) with the effect of KCl being similar to NaCl and of little consequence at such low concentration.

The cationic surfactant cetyltrimethylammonium bromide (CTAB) was supplied by B.D.H. Chemicals Ltd. There was no minimum in a surface tension versus log concentration plot and the c.m.c. found from the plot was 1.2 mol m\(^{-3}\) CTAB in 1 mol m\(^{-3}\) KCl. The value of c.m.c. found from conductivity measurements was 1.6 mol m\(^{-3}\). No data for CTAB in 1 mol m\(^{-3}\) KCl was available in the literature. Neither surfactant was purified further before use.
3.1.5 Glassware

All glassware was cleaned using ultrasonic irradiation (Dawe Soniclean 500W Generator, 40 kHz) and rinsed with copious amounts of distilled water as described in (3.1.3). This was found to be more efficient than any chemical means. Occasionally surfactant (either SDS or CTAB) was used to assist in removing deposited particles.

3.2 Electrophoresis

3.2.1 Theory

There are four electrokinetic phenomena, electrophoresis, electro-osmosis, streaming potential and sedimentation potential, but electrophoresis is the most suitable of these for obtaining zeta potentials of colloidal particles in dilute dispersions. The electrokinetic or zeta potential (\(\zeta\)) is the potential at the surface of shear which arises as a result of the relative movement between the charged particle surface and the electrolyte medium under the influence of an applied electric field.

The slipping plane, at the surface of shear, is assumed to be very close to the Stern plane (Fig. 3.2.3). Consequently the magnitude of \(\zeta\) is close to that of the Stern potential, \(\Psi_0\). Since repulsion results from the interaction of the outer part of electrical double layers then the corresponding interaction potential is \(\Psi_0\), and \(\zeta\) is the nearest measurable quantity.

When electrophoresis takes place, simultaneous electro-osmosis of the dispersion medium occurs. In the enclosed environment of an electrophoresis cell whose inner walls are charged, the application of an electric field causes electro-osmotic movement of the liquid
Fig 3.2.3 Location of Stern plane and surface of shear, with corresponding potentials.
adjacent to the walls and a compensating liquid flow in the opposing
direction down the centre of the cell.

\[
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\]

Flow pattern of liquid in an enclosed cell

There are two levels, an upper and a lower one, in the cell at
which these opposing liquid flows just balance. These are termed
stationary levels and only at these locations is the true electrophoretic
velocity directly observed.

In a cell where the flow is through a cylindrical capillary, then
Poiseuille's equation for the relationship between the electro-osmotic
velocity, \(V_{EO}\), and the reverse flow velocity, \(V_L\) is

\[
V_L = V_{EO} - c(b^2 - x^2)
\]  

(3.2.1)

where \(V_L\) is the liquid velocity at a distance \(x\) from the capillary
centre, \(b\) is the capillary radius and \(c\) is a constant.

Since the total liquid transport must be zero,

\[
\int_0^b V_L(2\pi x)dx = 0
\]  

(3.2.2)

Solving equations (3.2.1) and (3.2.2) yields

\[
c = 2V_{EO}/b^2
\]  

(3.2.3)

Therefore,

\[
V_L = V_{EO}(2(x/b)^2 - 1)
\]  

(3.2.4)
Stationary levels are located where there is no net liquid flow, i.e. $V = 0$. Then $(x/b)^2 = 0.5$ and $x = 0.707b$ (3.2.5) and the electrophoretic velocity can be measured directly at these positions.

Several equations have been proposed for obtaining zeta potential values from electrophoretic velocity data.

The Smoluchowski equation

By considering electrophoresis to be the reverse of electro-osmosis, Smoluchowski derived an equation for relating the electrophoretic mobility, $\mu_E$ (electrophoretic velocity/potential gradient) to the zeta potential:

$$\mu_E = \frac{\varepsilon \zeta}{\eta}$$ (3.2.6)

where $\mu_E$ is expressed in units of $m^2 V^{-1} s^{-1}$.

Restrictions to the applicability of this equation are that:

i) double layer thickness be small compared with the particle radius, i.e. $\kappa a >> 1$.

ii) the particle be non-conducting

iii) permittivity and viscosity are constant throughout the diffuse double layer and the bulk liquid.

Equation (3.2.6) was used rather indiscriminately for some time, in spite of the listed restrictions, until an alternative, apparently different equation was proposed.
The Hückel equation

In 1924 Hückel's newly gained knowledge in the theory of the conductance of strong electrolytes led him to propose an equation for electrophoretic mobility:

$$\mu_E = \frac{\zeta}{1.5\eta}$$  \hspace{1cm} (3.2.7)

This equation incorporated the electrophoretic retardation caused by the action of the electric field on the double layer.

The apparent discrepancy between the equations of Smoluchowski and Hückel was resolved by Henry:

The Henry equation

Henry showed that the deformation of the electric field by the presence of the non-conducting particle was implicitly accounted for by Smoluchowski, whereas Hückel had supposed that the field in the double layer and bulk liquid is uninfluenced by the particle's presence.

Henry then went on to derive a general expression for the electrophoretic mobility of non-conducting spheres:

$$\mu_E = \left(\frac{\zeta}{1.5\eta}\right)f(\kappa a)$$  \hspace{1cm} (3.2.8)

where $f(\kappa a)$ is a function in terms of powers of $\kappa a$, and varies between 1.0 (Hückel equation) and 1.5 (Smoluchowski equation).

Henry's mathematical treatment resembled that of Hückel, but now took account fully of the deformation of the electric field by the presence of the colloidal particle. The resulting electrophoretic retardation arises from the movement of the counterions in the opposite direction to that of the particle under the influence of an applied field. Another effect caused by the opposing movements of counterions and particles in an electric field is the deformation of the otherwise
Fig 3.2.4 Forces exerted on a particle during electrophoresis. $\bigcirc$ represents the particle and $\bigcirc$ the ionic atmosphere.
symmetric double layer round the charged particle. The double layer tends to restore its symmetry by charge transport and diffusion but this takes a finite time, the time of relaxation. This relaxation effect is not considered in the Henry treatment.

The forces acting on a particle during electrophoresis are shown in Fig. 3.2.4.

The force exerted by the d.c. field, \( X \), on the charge of the sphere \( Q \), is given by

\[
k_1 = QX \quad (3.2.9)
\]

The Stokes friction retards the motion of the particle,

\[
k_2 = -6\pi\eta a^2 E \quad (3.2.10)
\]

where \( \eta \) is the viscosity of the medium and \( a \) the particle radius.

Forces \( k_3 \) and \( k_4 \) are also retarding forces, in this case resulting from the ionic atmosphere.

The first of these represents the retardation effect and the second represents the relaxation effect. Overbeek and Booth both derived equations for spherical particles allowing for retardation and relaxation, expressing electrophoretic mobility as a power series. Overbeek gives the following expression for electrophoretic mobility (for symmetrical electrolytes)

\[
\mu_E = (\xi X/1.5\eta) \left\{ F_1(ka) - z^2(\xi/\kT)^2 F_3(ka) - \right. \\
\left. \frac{(\rho_+ + \rho_-)}{2e} \left( \frac{\xi}{1.5\eta e} \right)(\xi/\kT)^2 F_4(ka) \right\} 
\]  

(3.2.14)

where \( Z \) is the valency of ions in the electrolyte, and \( \rho \) a frictional coefficient. Overbeek gives a table of values of the functions \( F_{1-4}(ka) \)
for various values of $\kappa a$. Both he and Booth found that mathematical difficulties forced them to develop these equations for a restricted number of terms only, and they were valid for $(Ze\zeta/kT) < 1$, as the relaxation effect was overestimated at higher potentials.

These approaches were superseded by that of Wiersema, Loeb and Overbeek who, using the assumptions made earlier by Overbeek, were able to solve the relevant differential equations numerically with the aid of a computer. The assumptions made by Overbeek were

i) Only a single particle is considered, and interactions between colloidal particles are neglected.

ii) The particle, and its adhering adjacent layer, is treated as a rigid sphere.

iii) The permittivity of the sphere is uniform throughout.

iv) The sphere is non-conducting.

v) The charge of the sphere is uniformly distributed over the surface.

vi) Gouy-Chapman theory describes the mobile part of the electrical double layer.

vii) The permittivity and viscosity of the liquid surrounding the sphere are constant throughout the mobile part of the double layer.

viii) Only one type of positive and negative ion is considered present in the double layer.

ix) The Brownian motion of the particles is neglected.

Wiersema et al. found that, for moderately low values, their numerical results were in quantitative agreement with the approximations of Overbeek and Booth, and this provided a check on their computations. Figs. 3.2.5 and 3.2.6 show some results of their computations, giving the relationship between electrophoretic mobility and zeta potential as a function of $\kappa a$. 
Fig 3.2.5 Electrophoretic mobility and zeta potential for colloidal particles in a 1-1 electrolyte solution. $e\zeta/kT=1,2,3$ and 4
Fig 3.2.6 Electrophoretic mobility and zeta potential for spherical colloidal particles in electrolyte solutions containing polyvalent ions:—counter-ion valency labelled first.

\[ \frac{e\zeta}{kT} = 2 \]
If permittivity and viscosity were not constant in the double layer as assumed, for example if the field strength close to the surface of shear was sufficiently high to significantly decrease $\varepsilon$ or increase $\eta$ by dipole orientation, then this would obviously complicate calculations of zeta potentials. This problem was examined by Lyklema and Overbeek who concluded that the effect of field strength on $\varepsilon$ is insignificant but that any effect on $\eta$ might be important.

A significant positive viscoelectric effect would result in movement of the effective shear plane away from the particle surface. If the surface potential remained constant, $\zeta$ might be expected to be lower. However, relocation of the surface of shear could well alter the relationship between $\psi_o$, $\psi_0$, and $\zeta$. More recently Stigter and Hunter have suggested that the viscoelectric effect has been overestimated by Lyklema and Overbeek, and is unimportant for most practical situations.

3.2.2. Technique

There are two methods associated with electrophoresis, namely the moving boundary method and microelectrophoresis where the movement of the particles is studied using an ultramicroscope. For dilute suspensions of particles visible through the ultramicroscope the technique of microelectrophoresis is generally preferred since it has the following advantages:

i) The particles are observed in their normal environment.

ii) Since very dilute dispersion can be studied, measurements of electrophoretic mobility can be made even at high electrolyte concentrations and for very low zeta potentials, with little problem of flocculation.
iii) Observation times are short due to the high magnification of the ultramicroscope system.

iv) In a polydisperse sol particles of different sizes can be observed individually.

Microelectrophoresis is not suited to the study of concentrated dispersions.

Before conducting microelectrophoresis experiments a choice of suitable electrophoresis cell must be made. The cell commonly consists of a single channel whose shape is of rectangular or cylindrical cross-section, the latter being either thin or thick-walled. There are advantages and disadvantages with each type of cell.

Advantages of the cylindrical cell are:

a) Ease of thermostatting, especially with thin-walled cells, virtually eliminating convection currents.
b) Only a small volume of dispersion is required.
c) Platinum black electrodes may be used in place of the reversible electrodes required for the flat cell, since the small cylindrical cross-sectional area leads to only small electric currents for a given field strength.

Disadvantages of the cylindrical cell:

a) An optical correction must be made for refraction at the cell walls. However, this is only important for thick-walled cells. If the wall is very thin (e.g. $2 \times 10^{-5}$ m) then any optical correction is negligible.
b) Particles must only be timed moving across the centre of the field of view.
c) Any settling of particles on the lower cell wall alters its surface potential and causes distortion of the liquid flow pattern in the cell. This effect is minimised by using dilute dispersions.
Plate 3

Micro-electrophoresis cell
Since aqueous dispersion media were employed in this work, a thin-walled cylindrical electrophoresis cell was used and the dispersions studied sufficiently dilute to prevent distortion of flow by sedimenting particles.

The cell was constructed in Pyrex from a fine cylindrical machine-drawn capillary (examined by microscope to ensure uniformity of diameter and wall thickness) and two electrode compartments (Plate 3). This cell is of the van Gils\textsuperscript{102} type and the internal diameter and wall thickness were 1410 \textmu m and 215 \textmu m respectively. The effective cell length, found by conductivity measurements of KCl solutions in the electrophoresis cell and in a cell of known cell constant, was 8.77 \times 10^{-2} \text{ m}. Cylindrical foil platinum blacked electrodes were inserted into the cell via ground glass joints.

The cell was mounted in a water-filled Perspex tank fitted to a horizontal microscope stage, and the water in the tank maintained at 25.0 ± 0.1{}^\circ \text{C} by circulation through an external thermostat unit (Haake Constant Temperature Circulator FK). An applied DC potential of 50.0 ± 0.1V was supplied by a voltage stabilised power supply, and the precise reversibility of the potential was monitored using a high impedance digital electrometer connected across the electrophoresis cell.

Dispersions were prepared by adding less than 1 mg of solid to 5-10 ml of electrolyte in a small sample bottle and subjecting it to two minutes of ultrasonic irradiation. The clean electrophoresis cell was rinsed with a little of the dispersion before filling. After allowing 5-10 mins. for equilibration of the dispersion, the particles
in the cell were observed under dark ground illumination conditions at an overall magnification of 200X, using a Vickers Photoplan microscope.

Particle velocity was measured at eleven levels through the electrophoresis cell, corresponding to equal intervals between adjacent values of \((x/b)^2\). At each level the time taken for particles to travel across a number of eye piece graticule lines (previously measured using a calibrated stage micrometer) under the applied electric field was measured using a stopwatch reading to 0.1 sec. Timings were generally 5-10 secs, this being the optimum for minimising Brownian motion error and operator timing error. The average value of \(1/t\) for eight readings at each level was plotted against \((x/b)^2\), the potential gradient being reversed after each particle timing. The slope and intercept of the plot of \(1/t\) against \((x/b)^2\) were obtained from least squares analysis of the data, and the linearity of the plot indicated true parabolic flow in the cell. As shown in equation (3.2.5) the electrophoretic velocity was obtained from the value when \((x/b)^2 = 0.5\), and the electro-osmotic velocity from the slope of the graph. The value of the latter velocity is unobtainable from conventional electrophoresis experiments where particle velocity is measured only at the stationary levels. The corresponding electrophoretic and electro-osmotic mobilities (velocity under unit potential gradient) were calculated knowing the magnitude of the applied potential and the effective inter-electrode distance. Subsequently, equation (3.2.8) was used to evaluate \(\zeta\).
3.3 Particle counting

3.3.1 Theory

The rate at which particles aggregate is given by

$$\frac{dN}{dt} = k^1 N^2$$  \hspace{1cm} (3.3.1)

where $N$ is the number of particles per unit volume of sol at time $t$ and $k^1$ the second order rate constant. Integration of (3.3.1) yields

$$\frac{1}{N} = \frac{1}{N_0} + k^1 t$$  \hspace{1cm} (3.3.2)

where $N_0$ is the particle number at $t = 0$. Hence a plot of $1/N$ v. $t$ is linear with a gradient equal to the rate constant for flocculation. Both the rate constant for rapid flocculation ($k_o$), and rate constants for slow flocculation may be obtained from plots of $1/N$ v. time, and the value of $k_o$ checked with that predicted by equation (2.4.6), modified by Spielman.

Experimental stability ratios were obtained from the ratio of rapid to reduced rate constant, i.e.

$$W = \frac{k_o}{k^1}$$  \hspace{1cm} (3.3.3)

3.3.2 Technique

Dispersions were prepared in the same way as for electrophoresis with the particle concentration being of the order of $10^8$ particles per ml. A disposable syringe was used to fill a 2 mm spectrophotometer cell (with the dispersion) after both syringe and cell had been quickly rinsed with dispersion. As soon as the cell was filled, a stop clock was started. The cell was laid flat on the microscope stage and the focussing adjusted so that the particles viewed were halfway through
the cell, far from either wall. Particles were counted in a number of
gratings squares, the area of which was calculated from the side
length, and the depth of dispersion viewed was determined by measure-
ment of the depth of focus. For any given time usually around fifteen
counts were taken, and the average of these values plotted.

3.4 Surfactant adsorption

3.4.1. Adsorption from solution

Approximately 0.5 g solid was accurately weighed into an 11 ml
Pyrex test tube. 10 ml of surfactant solution was pipetted into the
tube, which was then stoppered and given two minutes ultrasonic irradiation.
After sealing the stopper in with Parafilm the tube was clamped to a disc
rotating end over end in a thermostatted (25±0.2°C) water tank, and left
for 1 week to allow ample time for adsorption equilibrium to be reached.
The concentrated dispersion was then ultracentrifuged at 40,000 rev min⁻¹
for at least 1 hour and the clear supernatant surfactant solution then
removed for concentration determination.

3.4.2. Determination of surfactant concentration

Standard solutions of cetyltrimethylammonium bromide (CTAB)
and sodium dodecyl sulphate (SDS) were prepared. The method of Barr,
Oliver and Stubbings,¹⁰⁴ using bromophenol blue as indicator, was used
to determine the concentration of SDS before and after adsorption.
The volumes used were smaller and it was found that use of a bottle
recommended for the titrations created difficulties in determining the
end point. Consequently, a long Pyrex test tube was used instead and
the smaller diameter facilitated end point determination.
In the case of finding the concentration of CTAB before and after adsorption, excess standard SDS solution was added, and the concentration of CTAB evaluated by back titration. This was necessary since the appearance of blue colouration in the chloroform was easier to detect than its disappearance.
4. RESULTS AND DISCUSSION

Before studying heteroflocculation of mixed colloidal systems it is essential to examine the behaviour of the individual systems separately and to ensure that each colloid in the mixed system retains its own distinctive surface properties. Should the surface of one colloid be affected by contamination due to the presence of another colloid in the dispersion then the surface properties and stability behaviour of the colloids initially will differ from that after mixing. Consequently, heteroflocculation occurring between the two colloids will not represent the interaction between particles of the initial separate dispersions, but between particles with altered surface properties.

In the present work two rutile samples, one with an alumina coating (A) and the other with a silica coating (B), were chosen for study of heteroflocculation between particles possessing different surface potentials. The choice of particles composed of the same basic rutile eliminated any difference in size or Hamaker constant between the two samples, and they only differed in their dependence of zeta potential on pH. However, the surface coatings were found to be unstable in solution, so that ionised species dissolved in the dispersion medium and, in a mixed system, re-adsorbed onto particles of the other sample present. Thus heteroflocculation between the initial separate dispersions of the two samples could not be observed.

To eliminate any problems of contamination arising from dissolution of surface coating, pure rutile samples were subsequently studied. These were found to be much less stable than theory predicted and several reasons for this behaviour were proposed.
To check that the experimental techniques employed in the rutile studies were valid, carbon blacks, whose behaviour has often been examined and found to agree with theoretical predictions, were also studied. It was possible to explain the zeta potentials and stability behaviour in terms of surface groups.

Since the Hamaker constants for rutile and carbon blacks in water do not differ by a large amount, and the particle sizes of rutile and Graphon were very similar, heteroflocculation experiments with rutile and Graphon were performed where the essential difference between the samples was their potential. The results for Graphon with sample (A) confirmed the effect of dissolution of aluminium species from the coating. This was not a problem in the case of Graphon with (E) which showed that heteroflocculation did occur.

Since heteroflocculation studies can only usefully be performed on systems where the surface properties of the particles have been examined, this was a primary consideration for each experimental system under review. Problems of contamination were brought to light in the work with coated rutile samples (A) and (B).

4.1 Coated rutile samples (A) and (B)

4.1.1 Electrophoresis

Electrophoresis results for each sample as a function of pH in 1 mol m\(^{-3}\) KNO\(_3\) are illustrated in Fig. 4.1.1. Also shown are results for pure rutile (C) and pure alumina, both in 1 mol m\(^{-3}\) KCl, (which can be directly compared with 1 mol m\(^{-3}\) KNO\(_3\) since both are indifferent electrolytes), together with data of Pugh\(^{105}\) for pure silica. Although the results for silica were obtained without backing electrolyte, in the region of low pH the ionic strength should be similar to that for
Fig 4.1.1 Zeta potential v. pH for O A, □ B, △ C, ◊ Al₂O₃, □ SiO₂ (Pugh)
Fig 4.1.2 Typical plot of velocity v. $(x/b)^2$.
all the other samples. The behaviour of the silica-coated sample (B) bears a strong resemblance to that of pure silica. However, the alumina-coated sample (A), which might be expected to behave similarly to pure alumina, shows no resemblance to either pure alumina or pure rutile, but exhibits features more like those of sample (B). This suggested that the surface of particles of (A) was at least partially covered by silica species. It is postulated that the silica coating of (B) was not stable in solution and that silica species from solution adsorbed onto the electrophoresis cell walls. When sample (A) was subsequently introduced into the cell some of these silica species desorbed from the cell walls and were adsorbed onto the surface of particles of (A). Since the dependence of the zeta potential of glass as a function of pH and of electrolyte concentration is known, then any contamination of the glass by, for example, silica, may be detected by a change in the zeta potential arising from electro-osmosis at the cell wall. This information may be obtained by a detailed analysis of the particle electrophoresis results.

As described in section 3.2.2, instead of measuring particle velocity at the stationary levels only, measurements were made as a function of distance through the cell. Fig. 4.1.2 shows a typical plot of velocity vs. \((x/b)^2\), the abscissa being an indication of distance through the cell, and the data for the upper (□) and lower (O) parts of the cell lying on the same line. Several authors have measured particle velocities at the stationary levels only. Less frequently measurements have been taken only at one stationary level. Occasionally checks are made to confirm the parabolic distribution of the observed particle mobility as a function of depth through the electrophoresis cell. Measurement
Fig 4.1.3 \((1/t)\) v. \((x/b)^2\) for A in 0.1mol m\(^{-3}\) KCl, showing distorted liquid flow
Fig 4.1.4 Velocity v. distance through cell showing distorted liquid flow
of the particle velocity profile through the cell has particular advantages when the electrophoretic mobility is low. For all particle mobilities, the method has advantages in that it enables easy confirmation of true electrophoresis and in addition allows calculation of the electro-osmotic velocity at the cell wall, the latter being particularly useful in detecting contamination.

The requirements for true electrophoresis, as given by van der Minne and Hermanie, stipulate that (a) particle mobility should be independent of the sign of electrode polarity and (b) the distribution of mobilities through the cell should be symmetrical about the axis of the capillary. Fig. 4.1.3 illustrates results for sample (A) in 0.1 mol m$^{-3}$ KCl at pH 4.9 and, by its non-linear form indicates a distorted parabola (Fig. 4.1.4) showing that criterion (b) has not been satisfied. The data for the upper (D) and lower (O) parts of the cell give lines of different slope implying that the upper and lower wall potentials are not the same. The calculated wall potential values are -114 and -130 mV respectively, the former result showing better agreement with values quoted in the literature. Wijga determined the zeta potential of glass as a function of KNO$_3$ concentration, and found it to be approximately -118 mV for a pH around 5.5. From the data of Benes and Paulenova for the dependence of the zeta potential of glass on pH, Fig. 4.1.5, the value of $\zeta$ at pH 4.9 is -104 mV. The deviation of the cell wall potentials from literature values indicates contamination of the walls, more pronounced in the case of the lower wall. Extensive deposition onto the bottom surface of the capillary was observed and this was undoubtedly the explanation for the difference in zeta potential between the lower and upper cell walls. As the parabolic liquid flow pattern through the cell had become distorted, no reliable prediction of the particle electrophoretic mobility could be made.
Experimental points $x, \bar{x}$: data from Table 4.1.1

Fig 4.1.5 ζ-potential v. pH for glass (Benes and Paulenova)
Fig 4.1.6  $(1/t)_v.(x/b)^2$ for sample A in 1mol m$^3$KCl
Removal of deposited particles was achieved by repeated bursts of ultrasonic irradiation and washing with distilled water. Reliable results were then obtained for sample (A) in 1 mol m\(^{-3}\) KCl at pH 6.65, and the results are shown in Fig. 4.1.6 and Table 4.1.1. Also included are data for sample (A) obtained from an electrophoresis experiment using a cell which had previously contained sample (B). Particles adhering to the cell walls had been removed, so that the walls appeared clean when viewed through the microscope, but there had been insufficient washing to completely remove adsorbed contaminant deposited by sample (B). Both sets of data apparently satisfy the criteria for true electrophoresis, giving linear plots of 1/t against \((x/b)^2\), and these give different values for the zeta potentials for electrophoresis and electro-osmosis respectively.

<table>
<thead>
<tr>
<th>Table 4.1.1. Zeta potential of (A) and Pyrex glass in contact with 1 mol m(^{-3}) KCl at pH 6.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (A)</td>
</tr>
<tr>
<td>Cell wall contaminated</td>
</tr>
<tr>
<td>Cell wall uncontaminated</td>
</tr>
</tbody>
</table>

The experimental zeta potential obtained for the uncontaminated cell wall compares favourably with the literature values but the value for the contaminated cell is considerably lower. The corresponding zeta potential for particles of sample (A) is also lower. Thus some of the contaminating silica species present in the system which, by adsorption, will tend to make particles of (A) less negatively charged, have adsorbed onto both the cell walls and particles affecting their
Fig 4.1.7 Zeta potential v. pH for A in
○ 0.1 mol m⁻³ KCl, □ 1 mol m⁻³ KCl
Fig 4.1.8 Zeta potential v. pH for □ A, ○ C, and △ Al₂O₃, all in 1mol m⁻³ KCl
zeta potentials. Since it is possible, from the literature to predict the potential at the glass surface arising from electro-osmosis at a particular solution pH, comparison of experimental zeta potentials for glass with literature values can provide a clear indication of possible contamination of the glass surface.

It was evident that sample (B) was unsuitable for use in systems containing another colloid since the behaviour of the latter could be affected by contamination of the particle surface. Consequently no further experiments were carried out with the silica-coated sample. In addition, special care was taken with cell cleaning and a check always made on the zeta potential of the glass cell wall.

Electrophoresis experiments using sample (A) were repeated, as a function of pH in 0.1 mol m$^{-3}$ KCl, and the isoelectric point was found to be at pH 5.5 (Fig. 4.1.7), considerably higher than the previous value of pH 2.65 (Fig. 4.1.1). Also shown are results for (A) in 1 mol m$^{-3}$ KCl. The isoelectric point agrees with that for 0.1 mol m$^{-3}$ KCl within experimental error. To check that these curves of $\zeta$ v. pH for (A) were a true representation of the behaviour of alumina-coated rutile, the graph for (A) in 1 mol m$^{-3}$ KCl was compared with those for pure rutile (C) and pure alumina, both in the same electrolyte. The three curves are shown in Fig. 4.1.8, where it can be seen that, for the most part, the curve for the alumina-coated rutile lies between those of the pure samples. The fact that it is closer to the curve for the pure rutile suggests that the surface is not completely covered by aluminium species but that there is a large proportion of pure rutile exposed. This fact is relevant in the interpretation of stability measurements made on this sample.
4.1.2. Stability measurements

Particle counting experiments, as previously described, were performed on dispersions of \( \text{(A)} \) in 100 mol m\(^{-3} \) KCl and 100 mol m\(^{-3} \) KNO\(_3\), and rapid rate constants calculated. The results are shown in Table 4.1.2.

<table>
<thead>
<tr>
<th>(A) in KCl (10^{18} x k_o/m^3 s^{-1} )</th>
<th>(A) in KNO(_3) (10^{18} x k_o/m^3 s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.19 ± 0.37</td>
<td>2.54 ± 1.06</td>
</tr>
<tr>
<td>6.73 ± 0.34</td>
<td>3.10 ± 0.91</td>
</tr>
<tr>
<td></td>
<td>4.38 ± 1.57</td>
</tr>
<tr>
<td></td>
<td>4.89 ± 1.88</td>
</tr>
<tr>
<td>Mean of all six values</td>
<td>4.14 ± 0.63</td>
</tr>
</tbody>
</table>

The mean value was used in stability ratio calculations. The value predicted by equation (2.4.6) at 25°C is \( 5.49 \times 10^{-18} m^3 s^{-1} \), but this does not take into consideration either the viscous interactions discussed by Spielman which will tend to reduce the flocculation rate constants, or the effect of the potential energy of attraction between particles which will increase the rate constants. For conditions where flocculation occurs at the rapid rate, the retardation factor is approximately 0.63. The effect of attraction between the colloid particles is to increase the rate by a factor

\[
\frac{1}{2 \int_0^\infty (\exp(V_A/kT))ds/s^2}
\]

(section 2.5)
Fig 4.1.9 Typical plot of $1/N$ v. $t$
Picton\textsuperscript{114} has computed this factor for several values of Hamaker constant, and for $A = 8 \times 10^{-20}$ J, gives the factor to be 1.2.

Therefore the net effect of these two factors is to reduce $k_0$ predicted by theory to $4.15 \times 10^{-18}$ m$^3$ s$^{-1}$. Thus the experimental value of $k_0$ may be considered reliable.

Rate constants were obtained by particle counting for (A) dispersed in 1 mol m$^{-3}$ KCl. A typical plot of $1/N$ against time is shown in Fig. 4.1.9. Stability ratios were calculated for several pH values, mainly chosen at zeta potential values where some stability was predicted by theory. The results are given in Table 4.1.3. Also shown are the stability ratio values calculated using equation 2.5.2 in computer programme STABIL (Appendix 1), with the full expressions (2.1.31) and (2.2.4) for $V_R$ and $V_A$. These calculated values of log $W$ are shown as a function of potential in Fig. 4.1.10.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\zeta$/mV</th>
<th>$W_{\text{exptl.}}$</th>
<th>log $W_{\text{calc.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>+26</td>
<td>1.4</td>
<td>4.4</td>
</tr>
<tr>
<td>6.4</td>
<td>-29</td>
<td>1.7</td>
<td>7.4</td>
</tr>
<tr>
<td>6.4</td>
<td>-29</td>
<td>1.3</td>
<td>7.4</td>
</tr>
<tr>
<td>6.5</td>
<td>-31</td>
<td>$\approx 1$</td>
<td>9.4</td>
</tr>
<tr>
<td>6.58</td>
<td>-33</td>
<td>2.1</td>
<td>11.7</td>
</tr>
<tr>
<td>6.8</td>
<td>-37</td>
<td>$\approx 1$</td>
<td>&gt;15</td>
</tr>
<tr>
<td>8.55</td>
<td>-53</td>
<td>1.4</td>
<td>&gt;15</td>
</tr>
<tr>
<td>8.55</td>
<td>-53</td>
<td>1.5</td>
<td>&gt;15</td>
</tr>
</tbody>
</table>

In each case the experimental stability ratio is much lower than that predicted by theory, even at high values of $\zeta$. As there is no
Fig 4.1.10 LogW v. ψ for rutile particles, radius 100nm
secondary minimum of any depth in the curves of $v_T$ v. $H$ for these experimental conditions, secondary minimum flocculation can be rejected as an explanation for the instability. A possible solution was desorption of aluminium species from the surface of the particles.

A dispersion of (A) in 1 mol m$^{-3}$ KCl was ultracentrifuged to remove all particles and some of the clear supernatant was tested for the presence of aluminium ions with Alizarin-S Reagent which produces, as a positive response, a red precipitate or colouration in ammoniacal solution. Sensitivity is quoted as 0.7 μg Al. A definite red colouration was found on testing the supernatant indicating the presence of aluminium in solution. The aluminium may have been present as Al$^{3+}$, and as trivalent counter-ions are much more effective in countering the charge on particles than the monovalent K$^+$ ions, the double layer is compressed. As the double layer thickness reduces, so too does the repulsive potential energy between particles, and the resultant stability. There was no certainty, however, that the aluminium ions were present as Al$^{3+}$. According to Matijevic, Mathai, Ottewill and Kerker, 110 who obtained critical coagulation concentrations of aluminium salt solutions for negatively charged silver halide sols, in the pH range 4-7 a tetravalent hydrolysis product was indicated. Coagulation and electrophoresis measurements showed that the hydrolysed aluminium species reversed the charge of the originally negative silver halide sols, whereas the simple hydrated Al$^{3+}$ did not. The complex ion proposed was Al$_8$(OH)$_4$$^{4+}$.$^{20}$ This ion need only be present in small concentration, smaller than for Al$^{3+}$, to cause flocculation of the rutile particles.

The effect of reducing double layer thickness by introducing Al$^{3+}$ ions is illustrated in Table 4.1.4.
Table 4.1.4. Double layer thickness and theoretical stability ratio for several concentration values of $\text{Al}^{3+}$ in a dispersion of (A) in 1 mol $\text{m}^{-3}$ KCl

<table>
<thead>
<tr>
<th>$\text{Al}^{3+}/\text{mol m}^{-3}$</th>
<th>$\kappa/\text{nm}$</th>
<th>$\zeta/\text{mV}$</th>
<th>log $W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>3.2</td>
<td>40</td>
<td>3.5</td>
</tr>
<tr>
<td>1</td>
<td>3.2</td>
<td>50</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Thus an aluminium ion concentration between 1 mol $\text{m}^{-3}$ and 5 mol $\text{m}^{-3}$ is sufficient to cause instability even with a surface potential of 50 mV. If the aluminium species are tetravalent then the concentration required is correspondingly lower.

4.2 Pure rutile samples (D) and (E)

The coated rutile samples were found to be unsuitable for heteroflocculation studies since their surface properties changed on mixing the two colloids. Ion dissolution and surface changes on mixing colloids were not expected to occur with pure rutile samples.
Fig 4.2.1 Zeta potential v. pH for D in 1 mol m⁻³ KCl; ○ unwashed, □ washed sample
Fig 4.2.2 Zeta potential v. pH for E in 1 mol m$^{-3}$ KCl; ○ unwashed, □ washed sample.
4.2.1. Electrophoresis

Fig. 4.2.1 shows $\zeta$ as a function of pH (O) for sample (D). Also shown are experimental points (□) obtained from electrophoresis data on a batch of the sample which had been subjected to the washing/heat cycle for removal of chloride ion impurity. Fig. 4.2.2 gives the zeta potential behaviour of sample (E) with pH, both before (O) and after (□) the washing/heat treatment. For both unwashed samples, the isoelectric point was found at the same pH, 5.3, as expected if the chloride ion impurity of (D) was essentially contained within each particle.

The analytical data for samples (D) and (E) (section 3.1.1) show that the chloride ion content of sample (E) was low, and much less than that of (D). Thus it was expected that the Soxhlet/heat treatment of (D) would remove chloride ion impurity and alter the relationship between $\zeta$ and pH. This was found to be so. The fact that the $\zeta$ v. pH behaviour did not resemble that of (E), with its very low concentration of chloride ion impurity, indicates that the higher calcination temperature employed not only eliminates chloride ion impurity but also alters the character of the surface, by causing sintering. This is supported by the surface area data given as 14.8 $\text{m}^2\text{g}^{-1}$ for (D) and 4.53 $\text{m}^2\text{g}^{-1}$ for (E). Because of the low chloride ion content of (E), little or no variation of the behaviour of $\zeta$ with pH was expected, or found experimentally, after the washing/heat treatment.

4.2.2. Stability

The untreated sample (D) which contained considerable chloride ion impurity was unsuitable for stability studies since, even after repeated washing and drying, it still only showed a maximum zeta potential of little
more than 30 mV. However, sample (E) untreated, for which zeta potentials in the range +45 to -50 mV were readily attained, was satisfactory for stability studies. By careful choice of pH, stability measurements could be made with the particles having a zeta potential of 40-50 mV, at which they would be expected to have marked stability. Since the radius of particles of (E) is slightly larger than 100 nm the log W v. η curve for this sample would be shifted to slightly higher log W values for the same pH, compared with Fig. 4.1.10. Table 4.2.1 gives values of experimental and predicted stability ratio (W_{exptl} and W_{calc}) at three pH values where stability was expected. In evaluation of W_{calc}, the Hamaker constant of rutile was taken as 8 x 10^{-20} J, obtained by Fowkes.115

<table>
<thead>
<tr>
<th>pH</th>
<th>ζ/mV</th>
<th>W_{exptl}</th>
<th>log W_{calc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
<td>+22</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>7.7</td>
<td>-51</td>
<td>21.7</td>
<td>&gt;30</td>
</tr>
<tr>
<td>8.0</td>
<td>-52</td>
<td>43.8</td>
<td>&gt;30</td>
</tr>
</tbody>
</table>

These experimental results are similar to, but somewhat larger than, those obtained for the alumina-coated sample. In this case, however, there was no coating on the particles which could dissolve in the same way as the aluminium species from sample (A). An alternative possibility was the dissolution of Ti^{4+} species. The supernatant liquid of a dispersion of (E) in 1 mol m^{-3} KCl was tested for the presence of Ti(IV). Hydrogen peroxide was added to a quantity of dispersion medium which had been acidified with dilute sulphuric acid. A positive response to this test
is the appearance of a yellow colour, the intensity dependant on the
ccentration of Ti(IV) present. There was no detectable colouration
of the medium and it was concluded that there was no dissolution of
Ti(IV) species into the dispersion medium.

A number of alternative explanations for the lack of stability of
rutile dispersions were considered:-

1) The zeta potential values may have been distributed about a mean value,
that is a potential distribution existed in the particle population. If
this were so, then the resultant stability ratio for all combinations of
potentials would be less than the value for the mean potential.

2) A particle size distribution may have been the cause of the instability,
since the total stability ratio for a spread of sizes about a mean value
is less than that for the mean size.

3) There may have been a spread of potential values on each individual
particle surface, resulting from discrete areas of charge differing in
magnitude from one another. This would mean that, although the experi-
mentally measured zeta potential was the mean of high and low potential
values on the particle surface, when two particles approached one another
they would orient themselves so that the low potential values were effective
in determining the potential energy of repulsion. Thus in a dispersion
containing only one colloid sample there would be a number of different
interaction potentials possible and the particles could undergo hetero-
flocculation. However, the lowest potentials would be most favourable
energetically for inter-particle interaction, and therefore the resultant
stability ratio would be less than that predicted from the mean zeta
potential.
Although many authors studying the flocculation of colloidal dispersions assume the particle population to be uniform in size and surface potential, for most practical systems this is highly improbable. The effects of a distribution in (a) particle potential and (b) particle size, on stability were therefore studied.

The effect of a potential distribution

A computer programme (POLYPSI) was written to evaluate the resultant stability ratio on the basis of interactions between particles possessing several different potentials. The treatment used was identical with that of Cooper,\(^\text{116}\) who considered the effect of a spread in potential and a spread in size separately. In the calculations involved here particle size was fixed, and consequently \(V_A\) terms as a function of interparticle separation, \(H\), were the same for each combination of potentials. The mean potential (\(\psi\)) and the associated standard deviation (\(\sigma\)) were read into the programme together with an interval integer, which specified the number of intervals into which the assumed Gaussian potential distribution was divided. The probabilities of all combinations of two potentials in the histogram were calculated. \(V_R\) was calculated as a function of \(H\) for all combinations of pairs of potentials, and, combined with the \(V_A\) contribution as a function of \(H\), resulted in a series of \(W\) values. Combinations of these stability ratios with their probabilities of occurrence gave a final stability ratio, \(W_T\). Table 4.2.2 gives the variation of this \(W_T\) value with \(\psi\) and \(\sigma\). Also shown is the calculated stability ratio using the mean potential only (\(W_M\)).
Comparison of the stability ratio values with and without a spread of potential values immediately shows that if there is a wide spread in values the resultant stability ratio is considerably reduced. The values of potential below the mean value have more effect on resultant stability ratio than do values above the mean. There are two reasons for this, the first illustrated in Fig. 2.3.3 (b), which shows that the potential energy curve for interaction between particles with high and low potential does not lie intermediate between the individual curves but closer to that for the low potential. Also the distribution of stability ratios for different interaction potentials is not symmetrical about the value of stability ratio for interaction between two particles, each possessing the mean surface potential. Fig. 4.1.10 shows this since the plot of log W v. \( \psi \) is a curve rather than a straight line.

Since calculations showed that a spread of potential markedly reduces stability, the possibility of a spread of potential values about a mean value was investigated by electrophoresis. The apparatus used was as
described in section 3.2.2, and the mean zeta potential obtained as previously described. In addition, several single particles were timed at each stationary level. Each particle was timed moving to the left and right, four times in each direction. The deviation from the mean time for each particle was compared with that for several particles. If there was a large deviation then it was obvious that the particles were travelling at different speeds and possessed different surface potentials. The deviations from mean potential are shown in Table 4.2.3, \( \Delta \zeta \) representing deviation from the mean at the upper and lower stationary levels respectively.

![Table 4.2.3](image)

From comparison of results from Table 4.2.3 with those in Table 4.2.2 it can be seen that the spread in potentials obtained experimentally for (E) was small and of little significance for reducing stability ratio. Although a value of 5 mV for \( \sigma \) reduced the stability ratio for a mean potential of 40 mV by a factor of \( 10^{10} \) the final stability ratio was still many orders of magnitude greater than the experimental values.
The effect of a size distribution

Although polydispersity of potential, which was found experimentally to be rather small, could not account for the lack of stability, polydispersity in terms of particle size might tend to reduce the stability ratio. A similar computer programme (POLYRAD) to that used for polydispersity of potential was employed to calculate the effect of a spread in particle size in the sample. The mean particle radius and standard deviation used were those obtained from sizing the particles on the electron micrographs of rutile (E) (section 3.1.1). Results of the calculations are given in Table 4.2.4 for $W_T$, total stability for all combinations of size, and $W_M$ for the mean size only.

<table>
<thead>
<tr>
<th>$\psi$/mV</th>
<th>$W_T$</th>
<th>$W_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.9</td>
<td>3.5</td>
</tr>
<tr>
<td>30</td>
<td>$4.6 \times 10^6$</td>
<td>$6.0 \times 10^8$</td>
</tr>
<tr>
<td>35</td>
<td>$2.8 \times 10^{10}$</td>
<td>$3.7 \times 10^{15}$</td>
</tr>
</tbody>
</table>

The calculations show that polydispersity of size reduces the predicted stability ratio, but the effect is less than that of a spread in potential and resultant stability ratios still much larger than the experimental values.

Heterogeneity of surface charge

Neither polydispersity of size nor potential could fully account for the low experimental stability ratios compared with the values predicted by theory. It was evident that the experimentally measured
zeta potential bore no simple relation to the potential determining stability. Since the particles would have to be unreasonably large for a plot of $V_T$ v. $H$ to exhibit a secondary minimum, and then only a shallow trough, flocculation must occur into a primary minimum.

It was postulated that the particles had a heterogeneous surface in terms of charge distribution. This implied that each particle surface was composed of discrete areas of high and low charge. In electrophoresis experiments the particles exhibited a net smeared out charge, but for particle-particle interactions, although high-high, high-low, and low-low charge interactions were all possible, the lower charge areas gave rise to the lack of stability.

It would be expected that the particles would "see" the discrete areas of charge at distances up to say $2\kappa^{-1}$ or $3\kappa^{-1}$ ($\kappa^{-1}$ = double layer thickness), and beyond this the charge on the particles would appear to be more uniformly smeared out, with the experimentally measured zeta potential determining stability. Thus when interaction between neighbouring particles of sample (E) led to flocculation, this was not homoflocculation, but a form of heteroflocculation within a single sample of colloidal particles since the interaction potentials were unlikely to be identical.

To determine experimentally whether the rutile particles had uniformly distributed surface charge, or in fact high and low charge regions, a cationic and an anionic surfactant were separately adsorbed onto the particle surface and the behaviour of zeta potential and stability then studied. It was expected that with adsorbed surfactant the surface charge heterogeneity would be altered and that this might be detected in the relationship between zeta potential and stability.
Fig 4.2.3 Adsorption of SDS onto rutile E (at fixed pH)
Fig 4.2.4 Adsorption of CTAB onto rutile E (at fixed pH)
4.2.3. Adsorption of surfactant

Adsorption of sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB), both prepared in 1 mol m\(^{-3}\) KCl, was carried out as previously described (section 3.4.1). Surfactant concentrations were determined before and after adsorption by the method of Barr, Oliver and Stubbings (3.4.2). Adsorption of each surfactant was performed under two sets of conditions:

1) pH was kept constant and surfactant concentration varied,
2) surfactant concentration was constant and pH varied.

The adsorption isotherms for the first category are shown in Figs. 4.2.3 and 4.2.4 for SDS and CTAB adsorption respectively. The isotherm for SDS adsorption shows a steep rise beyond an equilibrium concentration of 6 mol m\(^{-3}\). Similar results were obtained by Day, Greenwood and Parfitt\(^{117}\) for adsorption of SDS onto Graphon. They explained their results by invoking a change in orientation of the adsorbed dodecyl sulphate anion (DS\(^{-}\)). They observed a point of inflection at a surfactant concentration of about half the cmc in isotherms for adsorption from aqueous solution and, assuming the DS\(^{-}\) to be lying parallel to the surface, evaluated the surface area occupied per DS\(^{-}\) ion. For each DS\(^{-}\) lying flat they found the surface area occupied to be 0.80 nm\(^2\), and doing the same calculation at higher surfactant concentration where the DS\(^{-}\) was considered to be adsorbed perpendicular to the surface, found the area occupied to be 0.28 nm\(^2\) per ion. Assuming the change in adsorption behaviour in Fig. 4.2.3 to occur at an equilibrium SDS concentration of 6 mol m\(^{-3}\), the area occupied by DS\(^{-}\) lying flat on the rutile surface was found to be 0.80 nm\(^2\) per adsorbed DS\(^{-}\) ion (in good agreement with results for Graphon\(^{117}\)). The plateau region of the adsorption isotherm was
Fig 4.2.5 Adsorption of ○ SDS and □ CTAB at several initial pH values
reached at around the c.m.c., but complete monolayer coverage, using a value of 0.28 nm$^2$ per DS$^-$, was not achieved.

Fig. 4.2.4 shows the more usual form of isotherm with no evidence of change of orientation in adsorption of cetyltrimethylammonium cation (CTA$^+$). Again the adsorption reached a maximum value at surfactant concentrations around the c.m.c., and assuming the CTA$^+$ to be adsorbed with the cetyl chain perpendicular to the particle surface with each CTA$^+$ ion occupying an area of 0.35 nm$^2$ then the maximum adsorption corresponded to less than monolayer coverage.

The solution pH for the adsorption illustrated in Figs. 4.2.3 and 4.2.4 was about 5.5, that is close to the isoelectric point of the rutile sample. At this point not all the sites on the rutile particles are uncharged, but there is a numerical balance between positively and negatively charged sites. Moving away from the isoelectric point to higher or lower pH results in more negatively or positively charged sites respectively being available. Therefore, at pH values below the isoelectric point SDS adsorption should be more strongly favoured, and above the isoelectric point adsorption of CTAB preferred.

Adsorption of 2 mol m$^{-3}$ SDS was studied at four pH values below pH 5.5, and adsorption of 1 mol m$^{-3}$ CTAB at four values above pH 5.5. The results are shown in Fig. 4.2.5.

If the surface charge was evenly distributed over the particle surface at all pH values it might be expected that adsorption of a cationic surfactant would mirror that of an anionic surfactant. The adsorption isotherms for CTAB and SDS shown in Fig. 4.2.5 are completely different. The shapes of the isotherms might be expected to be similar. The fact
Fig 4.2.6 Zeta potential of E after DS\(^{-}\) adsorption
Fig 4.2.7 Zeta potential of E after CTA\(^+\) adsorption
Fig 4.2.8 Zeta potential v. initial pH for E after adsorption of
○ DS\textsuperscript{−}, and □ CTA\textsuperscript{+}
that they are not is indicative of there being different types of adsorption site on the rutile particles, so that a positive site is not simply a doubly protonated negative site.

4.2.4. Electrophoresis after surfactant adsorption

Because the adsorbed surfactant concentration on rutile reaches a plateau at lower equilibrium surfactant concentration for CTAB than for SDS, the maximum zeta potential for the particles is also attained at lower surfactant concentration. This is very evident in comparison of Fig. 4.2.6 with Fig. 4.2.7. The former shows variation of zeta potential for sample (E), after surfactant adsorption, as a function of equilibrium SDS concentration, and the latter giving the same information for CTAB adsorption. In both cases the maximum zeta potential is reached at an equilibrium surfactant concentration a little lower than that for the plateau region of the adsorption isotherms.

When surfactant was adsorbed at different pH values it was impossible to predict the variation of zeta potential since adsorption occurred to differing extents on surfaces possessing different initial zeta potentials. Zeta potential as a function of initial pH is given for SDS and CTAB in Fig. 4.2.8, showing no systematic variation with pH.

4.2.5. Stability after surfactant adsorption

The stability behaviour of rutile (E) was studied after adsorption of surfactant at fixed pH and for various initial pH values. Results obtained for fixed pH are shown in Table 4.2.4. From the adsorption data and surface area of the particles the fraction of surface covered (ΔC) by adsorbed surfactant was evaluated.
<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\zeta$/mV</th>
<th>$W_{\text{expt}}$</th>
<th>$\Delta c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>-29.0</td>
<td>3.4</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>-35.1</td>
<td>4.4</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>-45.1</td>
<td>5.4</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>-53.3</td>
<td>5.2</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>-60.4</td>
<td>2.6</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>-73.6</td>
<td>3.2</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>-73.9</td>
<td>73.6</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>-76.9</td>
<td>3.1</td>
<td>0.69</td>
</tr>
<tr>
<td>CTAB</td>
<td>63.2</td>
<td>289</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>77.7</td>
<td>&gt;10,000</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>80.9</td>
<td>760</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>65.8</td>
<td>986</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>81.0</td>
<td>&gt;10,000</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>84.2</td>
<td>&gt;10,000</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>73.3</td>
<td>362</td>
<td>0.60</td>
</tr>
</tbody>
</table>

pH = 5.5

The results for (E) with DS$^-$/ adsorbed show little stability with the exception of the value at a surface coverage of 0.74. It appears that at low surface coverages there was not sufficient reduction in the heterogeneity of surface potential to give a stability ratio more representative of the mean zeta potential. At the higher surface coverage
of 0.74 the particles attained a measure of stability but still orders of magnitude too low. However, there were competing effects, one being increase in surface coverage by surfactant which ought to reduce heterogeneity of surface potential and therefore increase stability. The other effect was variation in ionic strength, the equilibrium SDS concentration increasing from 0.35 mol m\(^{-3}\) to 9.74 mol m\(^{-3}\) corresponding to zeta potential increasing from -29.0 to -76.9 mV. The effect of increasing ionic strength was to compress the electrical double and consequently reduce repulsion between particles. However, the increase in zeta potential more than allowed for this effect and the stability predicted was still greater than the experimental values. It may be that the adsorption sites for DS\(^-\) adsorption were located such that adsorption did not in fact significantly reduce heterogeneity of potential. For example, adsorption may have occurred preferentially onto areas of high charge density, with sufficient on low charge sites only to, at most, change the sign of charge.

Rutile particles with CTA\(^+\) adsorbed showed considerably greater stability than either pure rutile particles with no adsorbed surfactant, or particles with DS\(^-\) adsorbed. It seemed that adsorption of CTA\(^+\) ions occurred in such a way as to reduce surface heterogeneity and make an experimental zeta potential more meaningful in determining stability. Calculations of surface potentials on rutile after CTA\(^+\) adsorption were made assuming a simplified model of the surface in which only two types of surface site (A and B) were considered to be present. It was assumed that the potential at surface sites where adsorption had occurred was \(\psi_A\) with \(a\) as the fraction of the surface having this potential, and the remainder of the surface, fraction \((1-a)\) had a surface potential \(\psi_B\).
Then

$$\psi_{\text{average}} = a\psi_A + (1-a)\psi_B \quad (4.2.1)$$

Simultaneous equations were written for pairs of results given in Table 4.2.5.

Table 4.2.5. Adsorption data relating surface coverage, and zeta potentials from Fig. 4.2.7 for CTAB

<table>
<thead>
<tr>
<th>Equilibrium CTAB /mol m(^{-3})</th>
<th>(\Delta c)</th>
<th>(\zeta/\text{mV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>0.3735</td>
<td>0.35</td>
</tr>
<tr>
<td>2)</td>
<td>0.3925</td>
<td>0.36</td>
</tr>
<tr>
<td>3)</td>
<td>1.9150</td>
<td>0.38</td>
</tr>
<tr>
<td>4)</td>
<td>3.2565</td>
<td>0.47</td>
</tr>
<tr>
<td>5)</td>
<td>3.2700</td>
<td>0.51</td>
</tr>
<tr>
<td>6)</td>
<td>7.1225</td>
<td>0.57</td>
</tr>
</tbody>
</table>

An example is given as follows:—

1) \(0.35\ \psi_A + 0.65\ \psi_B = 71.7\)

2) \(0.36\ \psi_A + 0.64\ \psi_B = 72\)

\[\therefore \quad \psi_A = +91.2 \text{ mV}, \quad \psi_B = +61.2 \text{ mV.}\]

This procedure was repeated for the other two pairs of results ((3) + (4) and (5) + (6)). The values obtained for \(\psi_A\) were +84.3 mV and +116.9 mV respectively and for \(\psi_B\) were +67.7 mV and 33.5 mV respectively.

The mean values of \(\psi_A\) and \(\psi_B\) were then obtained and found to be +97.5 mV and +54.1 mV. This meant that, on the basis of a two site only model, the lowest potential was more than 50 mV, which is more than sufficient to ensure stability.
Taking the mean values of $\psi_A$ and $\psi_B$ and assuming a mean surface coverage of 0.44 then at the zero point of charge, where the product of number and potential of the A sites would have to be equivalent to that of the B sites, the potential $\psi_A$ would be -68.9 mV. Thus, if only sites A and B were present with potentials of -68.9 mV and +54.1 mV respectively ($\psi_B$ remains unchanged since there was no surfactant adsorption onto B type sites) then it is very likely that, in dispersion of rutile (E) with no surfactant, at pH values around 8 where stability measurements were made (Table 4.2.1) the potential at B sites would change from +54.1 mV to some negative value which would be less than the $\psi_A$ value so that the net zeta potential would be that found experimentally (in the case of pH 8, $\zeta = -52$ mV). Thus, depending on the actual distribution of the different sites, there could be a considerable difference in value of potential at different surface sites. In the present instance, if there were equal numbers of sites A and B, then $\psi_B$ would be -35.1 mV. However, if the fraction of A sites was greater than 0.5, then $\psi_B$ could be sufficiently low so that interaction between type B sites on different particles could result in instability. This model based on the idea of only two different surface sites is probably a simplified picture of the true surface structure. However, it is a useful guide to obtain a semi-quantitative representation of the uneven charge distribution. In reality there may be more types of surface site present but is is impossible to calculate potentials for more than two types on the basis of the present data.

The effect of areas of high and low potential on stability will depend on the distances of separation at which any particular value of potential is relevant to the potential energy calculations.
potential energy has been computed, using the lowest value of surface potential from zero separation up to a specified limit, from which point the potential corresponding to uniformly distributed surface charge has been employed. Several different distance limits have been considered for the point of change over from low potential to average potential. The results are illustrated in Table 4.2.6.

Table 4.2.6. Stability ratios for inter-particle interactions where $\psi = 20$ mV up to distance $H$, and $\psi = 50$ mV thereafter.

<table>
<thead>
<tr>
<th>$H$/nm</th>
<th>$\log W_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&gt;36</td>
</tr>
<tr>
<td>10</td>
<td>28.8</td>
</tr>
<tr>
<td>20</td>
<td>10.4</td>
</tr>
<tr>
<td>30</td>
<td>2.6</td>
</tr>
<tr>
<td>40</td>
<td>0.6</td>
</tr>
<tr>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.6</td>
</tr>
</tbody>
</table>

These results are only an indication of the effect of different potentials being effective at different distances, indicating that the low potential areas would have to determine stability (or lack of it) in interparticle interactions at distances of separation of up to $3k^{-1} - 4k^{-1}$. In reality, of course, there would not be a sharp change over point between a low potential of interaction and the higher, even charge distribution value, but a gradual transition.
The interaction between neighbouring particles, at distances of separation where particles can distinguish between areas of high and low surface potential, will be most energetically favourable between sites with the lowest value of surface potential. Richmond\textsuperscript{118} considered charge lattices where the charge was not uniformly smeared out over the surface but distributed in discrete amounts in a periodic manner. He obtained the interaction energy curves, for like charges, for instances where a) two charge lattices interlaced one another, b) the lattices were directly superimposed, and c) the charge was uniformly distributed over each surface. The potential energy maximum for case (a) was found to be considerably below the value for case (c) and, therefore configuration (a) was preferred. Conversely, when the lattices were directly superimposed, the potential energy maximum was far greater than for (c), and therefore case (b) was the most unfavourable energetically. The author pointed out that there are many experimental systems, including biological systems and latex particles, which do not have surface charge uniformly distributed. It is, therefore, quite reasonable to suppose that, (in view of the experimental results,) rutile sample (E) (and probably other rutile samples) falls into this category.

In obtaining experimental stability ratios for rutile particles there were several experimental points which made accurate determination of very slow rate constants impossible. The particles were counted in the centre of a 2 mm spectrophotometer cell filled with dispersion. There was a possibility of some heteroflocculation at the cell walls and counting was done at the cell centre to minimise this effect. However, sedimentation will have some importance over a long time scale. Also as the change in particle number with time becomes less the scatter in
values of 1/N becomes more important. Consequently, when \( W_{\text{expt}} \) reaches
a value of several hundred then it is unlikely that there can be any
true distinction made between a value of say 300 and 500. All values
of \( W_{\text{expt}} \) for (E) with adsorbed CTA\(^+\) showed the dispersions to be stable.
Certainly the experimental values were still apparently lower than those
of theory, but a value of \( 10^{30} \) or so could not be measured experimentally.
There was increased stability with adsorbed CTAB even at only 0.35 surface
coverage. The CTA\(^+\) ions were adsorbed at different sites from the DS\(^-\) ions and possibly reduced the surface heterogeneity by adsorbing onto the
most highly charged areas to an extent to reverse the sign of charge and to
a lesser extent on areas of low surface charge, so that the resultant
positive charge on both types of area became closer in magnitude.

A possibility which required investigation was that the adsorbed
CTA\(^+\) ions on rutile might not be causing stability by reducing the heteroge-
neity of surface charge but by sterically stabilising the particles.
If this were so, then addition of electrolyte to the system ought to have
little effect on stability, since the barrier to flocculation is a physical
one rather than an electrical one. A quantity of electrolyte was added to
a dispersion of (E) in CTAB/1 mol m\(^{-3}\) KCl which had shown considerable
stability. It was then found to flocculate at the rapid rate.
Therefore, steric stabilization could be discounted as the cause of the
increased rutile stability.

The stability measurements were made at around pH 5.5, close to the
isoelectric point of the rutile sample. It would be expected that any
heterogeneity of surface charge and related distribution of surface sites
would be dependent on pH and would be least significant at the isoelectric
point. Adsorption and stability measurements were made at several
different values of initial pH, with the expectation that at pH values far from the isoelectric point the distribution of surface charge would be even more heterogeneous. Stability results are given in Table 4.2.7.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Initial pH</th>
<th>ζ/mV</th>
<th>W expt</th>
<th>Δc</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>2.95</td>
<td>-47.2</td>
<td>15.0</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>-56.4</td>
<td>8.5</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>4.40</td>
<td>-54.7</td>
<td>11.4</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>5.20</td>
<td>-56.4</td>
<td>14.5</td>
<td>0.09</td>
</tr>
<tr>
<td>CTAB</td>
<td>6.40</td>
<td>71.0</td>
<td>&gt;10,000</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>7.65</td>
<td>65.3</td>
<td>465</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>8.60</td>
<td>60.7</td>
<td>118</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>9.30</td>
<td>74.5</td>
<td>69</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The data for SDS were again unexpected in that all values of stability ratio were within experimental error of one another. Comparing these results with those for SDS in Table 4.2.4, in this instance the stability ratios obtained were a little higher for lower zeta potential. Fractional surface coverages were similar. It is, however, interesting to note in Table 4.2.7 that for only 0.09 coverage, the value of zeta potential and stability ratio were no lower than for any higher surface coverage. As pH was reduced heterogeneity of surface charge probably increased. It is possible that this increase in
heterogeneity was just counteracted by increasing the fraction of surface covered by adsorbed surfactant, so that the situation of distribution of surface sites was the same for each initial pH value.

The results for the stability ratio as a function of initial pH for CTAB adsorption show a marked decrease in stability with increase in pH. Since the fractional surface coverage increased with increasing pH, increased stability would be expected for the similar zeta potential values obtained experimentally. It appears that the increase in uneven distribution of surface charge was not countered by increased adsorption. Since different sites were involved for SDS and CTAB adsorption it was to be expected that their behaviour would be different in this respect. The results for CTA\(^+\) adsorption may be compared with those in Table 4.2.4 where for similar surface coverage and zeta potential the experimental stability ratios were much greater. The explanation for this can possibly be made in terms of the distribution of charge on the particle surface.

Among others, Jones and Hockey\(^{119}\) have investigated the surface structure of rutile using infra-red spectroscopic techniques. Their studies showed two types of hydroxyl species present on the outgassed oxide. They suggested that the (110) crystal face adsorbed water dissociatively to give equal quantities of the two types of hydroxyl species. One type was supposed to be a terminal hydroxyl, readily removed on raising the outgassing temperature, whereas the other was considered to be bridged between Ti ions which were five co-ordinate with respect to lattice oxygens. Obviously the existence of different types of site such as these would help to explain any heterogeneity of surface charge and adsorption to different extents on different sites.
Fig 4.3.1 Zeta potential v. pH for ○ Graphon, □ Black Pearls A, △ Vulcan 6, all in 1 mol m$^{-3}$ KCl.
4.3. Carbon blacks

Carbon blacks have been extensively used in studies of colloid stability, in polar and non-polar media, with and without adsorbed surfactant. In this work several carbon blacks were employed as a test of the techniques used for the rutile samples and with a view to subsequent heteroflocculation with rutile.

4.3.1. Electrophoresis

The curves of zeta potential as a function of pH are shown in Fig. 4.3.1. Graphon, Black Pearls A and Vulcan 6 were each separately dispersed in 1 mol m$^{-3}$ KCl. Constant ionic strength was not maintained with varying pH, but, with the exception of dispersions at pH 3, addition of acid or alkali did not cause significant deviation from the initial dispersion medium ionic strength.

The zeta potential values for Black Pearls A show two distinct regions compatible with the analytical data for strong and weak acid groups (section 3.1.2). Vulcan 6 also shows two distinct regions but the behaviour at low pH differs considerably from that of Black Pearls A. The latter had a much higher concentration of strong acid groups on the surface. There were no analytical data available for Graphon, but if the electrophoresis results are interpreted in the same way as for the other two carbon blacks, then it appears that there were few strong acid groups on the surface and the concentration of weak acid groups was also fairly low.

All zeta potentials were calculated from mobilities assuming a particle radius of 100 nm. This value was obtained as a peak in the size distribution for small aggregates of Graphon particles obtained by
Electron microscopy showed that aqueous dispersions of Graphon are broken down by ultrasonic irradiation to aggregates of primary particles. Because of their large surface area, Black Pearls A and Vulcan 6 have much smaller values for equivalent sphere radius. It is probable that these samples also exist as aggregates. However, the actual radius of an aggregate is unknown. In the ultramicroscope Black Pearls A particles appear to be smaller than either Graphon or Vulcan 6 which are of comparable size. However, this is a poor indication of size since only the scattered light from the particles is actually viewed. A reduction in particle radius does not greatly affect the magnitude of the zeta potential, but is more important in the interpretation of experimental stability ratios.

4.3.2. Stability

The rate constants for slow flocculation were obtained from direct counts of particle concentration as a function of time for each carbon black dispersion. Stability ratios were evaluated from this data using a rapid rate constant of $5.48 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$ as given by Smoluchowski. Measurement of the rate constant for rapid flocculation for Graphon gave a mean value of $(4.75 \pm 0.96) \text{ m}^3 \text{ s}^{-1}$. Since this value was within experimental error of that of Smoluchowski, the latter was used for all three carbon blacks. Stability ratio values are given in Table 4.3.1 together with zeta potentials and $\Delta \zeta$ values, $\Delta \zeta$ being the difference between the standard deviation of $\zeta$ for particles observed throughout the depth of the cell and the average for single particle timings at the stationary levels.

The values of $\Delta \zeta$ are in all cases very small showing that the samples are essentially monodisperse in terms of potential, and any experimental
stability ratios lower than those predicted by theory cannot be explained in terms of a spread in potential in any sample.

Table 4.3.1. Experimental stability ratios and zeta potentials for carbon blacks in 1 mol m\(^{-3}\) KCl

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>(\zeta)/mV</th>
<th>(\Delta\zeta)/mV</th>
<th>(W_{\text{expt}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphon</td>
<td>3.02</td>
<td>+46.5</td>
<td>+0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.20</td>
<td>+25</td>
<td></td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>+25</td>
<td></td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>-23.2</td>
<td>+0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.43</td>
<td>-23.2</td>
<td>+0.0</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>-25</td>
<td></td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>6.58</td>
<td>-24.3</td>
<td>+0.0</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>6.80</td>
<td>-27.4</td>
<td>+3.0</td>
<td>130</td>
</tr>
<tr>
<td>Black Pearls A</td>
<td>3.2</td>
<td>-5.4</td>
<td>+0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>-25.5</td>
<td>+1.0</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>-32.9</td>
<td>+0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.86</td>
<td>-46.2</td>
<td>+1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.77</td>
<td>-58.9</td>
<td>+3.0</td>
<td>490</td>
</tr>
<tr>
<td>Vulcan 6</td>
<td>3.34</td>
<td>+41.4</td>
<td>+1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.65</td>
<td>+35.7</td>
<td>+0.0</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>8.80</td>
<td>-43.8</td>
<td>+0.0</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>9.37</td>
<td>-43.8</td>
<td>+0.0</td>
<td></td>
</tr>
</tbody>
</table>
Fig 4.3.2 $\log W$ v. $\psi$, — theoretical values, ○, □, △ represent experimental values for Graphon, Black Pearls A, and Vulcan 6 respectively.
By consideration of the errors involved in obtaining rate constants, the experimental stability ratios for Graphon were in reasonable agreement with theoretical values. This is illustrated in Fig. 4.3.2. The curve for $\log W$ against $\xi$ was calculated from theory taking particle radius as $100$ nm and a Hamaker constant of $5 \times 10^{-20}$ J. This is the value estimated by Fowkes \textsuperscript{115} for graphite in water from interfacial tension data, and agrees with the data of Parfitt and Picton \textsuperscript{35} in their study of the stability of dispersions of graphitized carbon blacks in aqueous SDS.

The experimental stability ratios for Black Pearls A and Vulcan 6, also plotted in Fig. 4.3.2, were orders of magnitude lower than the theoretical values for 100 nm radius particles. Comparison with results for 25, 50 and 75 nm radius particles showed that agreement was better the smaller the radius. However, it is unlikely that the radius of aggregate of particles was less than 50 nm. Therefore the stability ratios could not be explained simply of terms of size and potential. It is more probable that the stability was governed by types of surface sites, not unlike the behaviour of the pure rutile samples studied (section 4.3.2). In the case of both Black Pearls A and Vulcan 6 a mixture of charged surface groups was present. Thus, the distribution of surface charge may have been uneven, so that the potential effective in stability measurements could be considerably less than the mean zeta potential obtained from electrophoresis experiments.

Since its stability behaviour was closest to that predicted by theory, Graphon was chosen for hetero-flocculation experiments with rutile.
4.4. Heteroflocculation of Graphon with rutile

4.4.1. Graphon and rutile sample (A)

It has been shown that dissolution of aluminium species from the rutile surface occurred and that the effect of the resulting multivalent ions in the dispersion medium was to reduce stability by compression of the electrical double layer. Consequently, a study of the mixed Graphon/coated rutile system was expected to show apparent "super-heteroflocculation", due to the effect of aluminium ions on the stability of Graphon in the mixed environment but not on dispersions of Graphon alone.

Since the mean values of rapid rate constant for Graphon and rutile, \((4.75 \pm 0.96) \times 10^{-18} \text{m}^3\text{s}^{-1}\) and \((4.14 \pm 0.63) \times 10^{-18} \text{m}^3\text{s}^{-1}\) respectively, were within experimental error of one another, the mean of all values for each sample was taken for the rapid rate constant, namely \((4.34 \pm 0.50) \times 10^{-18} \text{m}^3\text{s}^{-1}\).

Stability ratios were obtained for Graphon and (A) separately in 1 mol m\(^{-3}\) KCl, pH \(\approx 6.5\), and subsequently for the mixed system for several values of \(n\), where \(n\) is the fraction of particles of (A) in the mixed dispersion. Stability ratios \(W_{AA}\), \(W_{BB}\) and \(W_T\) were obtained experimentally for sample (A), Graphon and mixed dispersion respectively, and \(W_{AB}\) was obtained from the Hogg, Healy and Fuerstenau equation 5

\[
\frac{1}{W_T} = \frac{n^2}{W_{AA}} + \frac{2n(1-n)}{W_{AB}} + \frac{(1-n)^2}{W_{BB}}
\]  

(2.5.8)

Two sets of stability ratio data were obtained at pH \(\approx 6.5\). The zeta potentials of (A) and Graphon at this pH were -30 mV and -20 mV respectively. The corresponding stability ratio for (A) was
always $W = 1$, but, for Graphon, values of $W = 84.5$ and $W = 131.5$ were obtained. The reason for the two different values of $W$ for Graphon was probably that the zeta potential was not exactly $-20$ mV in each case. Table 4.4.1 shows the resultant stability ratios for mixed dispersions of (A) and Graphon, together with the stability ratios for the mixed interaction, $W_{AB}$, calculated from equation (2.5.8).

<table>
<thead>
<tr>
<th>$n_A$ (fraction of (A))</th>
<th>$W_T$</th>
<th>$W_{AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.9</td>
<td>0.98</td>
</tr>
<tr>
<td>0.2</td>
<td>3.2</td>
<td>1.21</td>
</tr>
<tr>
<td>0.3</td>
<td>1.0</td>
<td>0.47</td>
</tr>
<tr>
<td>0.4</td>
<td>1.0</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Mean $W_{AB} = 0.81 \pm 0.35$

Since the stability ratio for a single system is the ratio of the rapid rate of flocculation to the reduced rate of flocculation, a value of $W$ which is less than 1 implies that the true rapid rate constant for the system has not been used. In the mixed Graphon/rutile (A) system $W_{AB}$ was found to be less than 1. The reason for this lay in the values for $W_{AA}$ and $W_{BB}$ which were used in equation (2.5.8) for calculation of $W_{AB}$. It would be expected that, in view of the evidence presented (4.1) concerning dissolution of aluminium species from the surface of
particles of (A), these species would also affect the stability of Graphon in the mixed systems. Therefore, $W_{BB}$ should be lower in the presence of (A) than in the Graphon dispersion alone. The effect of aluminium species on the stability of Graphon was examined. A dispersion of (A) in $1 \text{ mol m}^{-3}$ was centrifuged and Graphon dispersed in some of the removed supernatant liquor. Stability measurements for this dispersion, obtained at pH $\approx 6.5$, showed the Graphon to be unstable in the presence of the aluminium ions in the dispersion medium.

If $W_{AB}$ is set to 1.0, then $W_{BB}$ can be calculated from equation (2.5.8) for each value of $n$. (Table 4.4.2).

<table>
<thead>
<tr>
<th>$n_A$ (fraction of (A))</th>
<th>$W_T$</th>
<th>$W_{BB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.9</td>
<td>57.9</td>
</tr>
<tr>
<td>0.2</td>
<td>3.2</td>
<td>-13.6 (80*)</td>
</tr>
<tr>
<td>0.3</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.4</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$W_{AA} = 1.0$  
*if $W_{AB} = 1.21$

$W_{AB} = 1.0$

It is evident that the stability ratio for Graphon is lower in the presence of aluminium ions from the rutile (A) particles.

Using the mean stability ratios for the A-A, B-B interactions, and $W_{AB} = 1.0$ for the A-B interaction, $W_T$ was calculated as a function of $n$
Fig 4.4.1 $1/W_T$ v. $n$ for $W_{AA} = 1.0$, $W_{BB} = 84.5$, $W_{AB} = 1.0$; --- heteroflocculation, ---- no heteroflocculation.

○ experimental data for A/Graphon system
using equation (2.5.8). When \( \frac{W_{AB}}{WT} \) is very large no heteroflocculation occurs and equation (2.5.8) reduces to

\[
\frac{1}{WT} = \frac{n^2}{W_{AA}} + \frac{(1-n)^2}{W_{BB}}
\]  

(4.4.1)

Figure (4.4.1) shows \( \frac{1}{WT} \), evaluated using equations (2.5.8) and (4.4.1), plotted as a function of \( n \), together with the experimental values of \( \frac{1}{WT} \).

Table 4.4.3 gives results similar to those in Table 4.4.1 for further heteroflocculation experiments with the Graphon/(A) mixed system. The final column, \( W_{BB} \), gives similar data to those shown in Table 4.4.2 where \( \frac{W_{AB}}{W} \) is set to 1.0 and the stability ratio for Graphon in the presence of aluminium ions calculated. Again it is found to be lower than in a dispersion containing Graphon alone.

<table>
<thead>
<tr>
<th>n (fraction of A)</th>
<th>( \frac{W}{T} )</th>
<th>( W_{AB} )</th>
<th>( W_{BB} ) (if ( W_{AB} = 1.0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>1.4</td>
<td>0.54</td>
<td>1.93</td>
</tr>
<tr>
<td>0.59</td>
<td>1.0</td>
<td>0.74</td>
<td>1.0</td>
</tr>
<tr>
<td>0.64</td>
<td>1.0</td>
<td>0.78</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Mean \( W_{AB} = 0.69 \pm 0.13 \)

\( W_{AA} = 1.0 \)

\( W_{BB} = 131.5 \)
Fig 4.4.2 $1/W_T$ v. $n$ for $W_{AA} = 1.0, W_{BB} = 13.5, W_{AB} = 1.0$, with and without hetero-flocculation. ○ experimental data for A/Graphon system
Fig. 4.4.2 gives $1/W_T$ as a function of $n$, for the instance where heteroflocculation with $W_{AB} = 1.0$ was considered (equation 2.5.8), and where there was no heteroflocculation (equation 4.4.1). The experimental values of $1/W_T$ are also shown.

Figs. 4.4.1 and 4.4.2 apparently indicate that heteroflocculation occurred in the mixed system, but the presence of (A) markedly affected the stability of Graphon, and the instability of the mixed systems was primarily due to aluminium species rather than heteroflocculation.

The heteroflocculation behaviour of rutile/Graphon mixed systems could, however, be studied when pure uncoated rutile was used.

4.4.2. Graphon and rutile (E)

The stability behaviour of mixed systems of rutile (E) and Graphon in 1 mol m$^{-3}$ KCl was studied in the same way as described in (4.4.1). The resultant stability ratios for mixed dispersions of (E) and Graphon, and the values of $W_{AB}$ calculated from equation (2.5.8), are given in Table 4.4.4.

<table>
<thead>
<tr>
<th>$n_A$ (fraction of E)</th>
<th>$W_T$</th>
<th>$W_{AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>13.2</td>
<td>5.7</td>
</tr>
<tr>
<td>0.20</td>
<td>6.8</td>
<td>2.8</td>
</tr>
<tr>
<td>0.50</td>
<td>7.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.67</td>
<td>12.9</td>
<td>6.8</td>
</tr>
<tr>
<td>0.86</td>
<td>12.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>

$W_{AA} = 19.4$  
Mean $W_{AB} = 4.7 \pm 1.6$

$W_{BB} = 81.7$
Fig 4.4.3 $1/W_T$ v. $n$ for $W_{AA} = 19.4$, $W_{BB} = 81.7$, $W_{AB} = 4.7$, with— and--- without heteroflocculation. ○ experimental data for E/Graphon system.
In this case, since both individual dispersions had some measure of stability, the hetero-interaction was more pronounced in its effect on $W_T$. Graphs of $1/W_T$ against $n$ were drawn using equations (2.5.8) and (4.4.1) and the results are shown in Fig. 4.4.3. The curves representing the cases where heteroflocculation is taken into account and where none occurs are widely separated and the experimental points indicate heteroflocculation had occurred.

In the present instance the explanation of the low stability ratios for the mixed systems could not be found in terms of ion dissolution or similar effect on double layer thickness. The stability results are best explained in terms of a hetero-interaction between the rutile and Graphon particles.

As previously explained in section (4.2.2) the pure rutile particles themselves undergo heteroflocculation with one another, between regions of different potential, since their surfaces are presumed to consist of discrete areas of high and low charge density. Consequently, addition of Graphon to such a system introduces another type of particle with which the rutile may heteroflocculate. Therefore, although the simple Hogg, Healy and Fuerstenau equation is used to evaluate stability ratios for mixed interactions between two components, in fact it would possibly be more accurate to consider a much larger number of interaction terms to allow for several different rutile-rutile and rutile-Graphon interactions. Since this would prove very complex and impossible to solve numerically due to lack of information about the surface sites, the best compromise which can be achieved is to use the experimentally obtained stability ratio for rutile in the equation of Hogg et al. This at least accounts for the different rutile-rutile interactions, but will not completely allow
for all rutile-Graphon interactions. This is the most probable reason for $W_{AB}$ being lower than the value which would be obtained from theory if the interaction potentials used were those which gave the experimentally obtained stability ratios for rutile and Graphon. In the case of rutile, the potential inserted for this purpose would be considerably less than the experimentally measured zeta potential. However, for the mixed rutile/Graphon interactions there would be several values of potential required for rutile, corresponding to different surface sites. It can be seen that heteroflocculation between rutile and Graphon does occur but a quantitative assessment is prohibited due to lack of information regarding the areas and distribution of surface charge on the rutile surface.

4.5. Conclusions.

1) Before heteroflocculation can be studied, the surface characteristics of the separate systems must be examined and found to remain unchanged in the mixed system. In the work with coated rutile samples, (B) was found to contaminate (A), affecting its surface properties.

2) The presence of contaminating species was confirmed by a detailed analysis of electrophoresis results obtained from mobility data at several levels through the electrophoresis cell. This extended treatment of electrophoresis data was used for all zeta potential determinations.

3) Dispersions of pure rutile (E) were found to be much less stable than predicted by theory. The experimental zeta potential gave no indication of surface charge distribution, usually assumed to be uniformly smeared out over the surface. The potential required to give the experimentally measured stability was much lower than the zeta potential, and
it was postulated that the charge on the particles was unevenly distributed over the surface, resulting in discrete areas of high and low potential. Except at separations of several double layer thicknesses ($\kappa^{-1} > 3$), where the charge would appear to be smeared out, although all combinations of high and low potential interactions occurred, instability resulted from low-low potential interactions.

4) Adsorption of anionic and cationic surfactant indicated the presence of at least two types of surface site. Adsorption of anionic surfactant had no significant effect on the stability of rutile, suggesting that it had little effect on the surface heterogeneity. However, the cationic surfactant adsorption resulted in a considerable increase in stability, which was related to a decrease in heterogeneity of surface charge. Steric stabilization was eliminated as a reason for the influence of the cationic surfactant on stability.

5) A study of several carbon blacks showed that where there were known to be different types of surface group the stability was less than that predicted by theory. The relative amounts of the surface groups were known, but not their surface distribution. The instability may have been due to uneven distribution of surface charge.

6) Graphon was found to exhibit the stability expected from predictions of theory, and was used in examination of mixed systems of Graphon and pure rutile (E). Heteroflocculation was found to occur in the mixed systems, with the possibility of several rutile-Graphon interactions.
Future work

Of the work presented in this thesis, the major area which requires further investigation is the stability behaviour of rutile. By studying the stability under different conditions, a more detailed understanding of the rutile surface may be obtained. Although adsorption of cationic surfactant onto pure rutile resulted in increased rutile stability which could be interpreted in terms of a reduction in the heterogeneity of surface charge, the similar work with an anionic surfactant showed little effect on stability. This implies adsorption of surfactant selectively mainly onto areas of high charge density, so that there is little overall change in the relative magnitudes of the surface charge densities in different areas. This should give some indication of the proportion of surface covered by a particular type of surface site, with corresponding charge density.

Further information about the rutile surface would be obtained by the following experiments:

a) adsorption of a series of cationic surfactants with increasing size of head group. It has been assumed (and this seems the most probable orientation) that adsorption of CTA⁺ onto rutile occurs with the charged head group towards the particle surface, and the tail projecting vertically into the dispersion medium. Adsorption data for cationic surfactants with smaller and larger head groups, combined with stability data, could help to give a picture of the size and extent of the negatively charged surface sites on rutile.

b) Similar studies with a series of anionic surfactants should give useful information regarding size and extent of positively charged sites.
c) The adsorption of anionic surfactant onto rutile with pre-adsorbed cationic surfactant, and similar adsorption of cationic surfactant onto a surface with pre-adsorbed anionic surfactant, ought to give useful information regarding the nature of the surface sites. For example, if CTA\(^+\) were pre-adsorbed, with the head group towards the particle surface, then the surface would become more hydrophobic and adsorption of DS\(^-\) would not be a charge interaction unless there were sites available which were specific to DS\(^-\) and not to CTA\(^+\). Consequently, adsorption of the second surfactant might occur in two ways, either charged head group towards the surface, or the tail hydrophobic part towards the chains of the CTA\(^+\) ions and DS\(^-\) charged head groups pointing outwards into the dispersion medium. The results of adsorption could be interpreted from the corresponding zeta potentials and stabilities.
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APPENDIX 1

COMPUTER PROGRAMMES

1) STABIL: evaluates $V_A$, $V_R$ and $V_T$ as a function of $H$, and gives resultant stability ratio, $W$.

2) POLYPSI: effect of a potential distribution on $W$.

3) POLYRAD: effect of a size distribution on $W$.

4) AVIT: evaluates average $l/t$ value and standard deviation using any number of values of $t$.

5) LMSQ: least squares analysis.

6) AVGEZ: calculates zeta potentials of particles and cell wall from velocities for electrophoresis and electro-osmosis in graticules per second.

4), 5) and 6) are used for calculating electrophoresis results.
CALCULATION OF P.E. CURVES AND STABILITY RATIO FOR COLLOIDAL 2 DISPERSIONS USING CONSTANT CHARGE AND CONSTANT POTENTIAL 3 MODELS

INTEGER I,J,K

DOUBLE PRECISION E1,L1,L2,A1,A2,A21,KX,KY,KZ,K,S1,S2

1,EB,K1,P33,P34,P31,PS2,EC,APM,E,G,SUM,SUM1,VR1,AA,AB,AC,VA,VR,E3,

9VR(5),VS(5),VU(5),HA(5),W,WW,E2,RD,AE,AF,STEP,STEP1,VRPS,VRSIG

READ,APM,E
10 READ,A2

IF(A2.GT.9999.)GOTO 29

READ,A21,KX

I=0
J=0
H=0

APM=-APM/6.

A1=A2/A21

WRITE(6,200)A1,A2

C=0.25*(I1+A2)

200 FORMAT(' ',"PTCLE RAD 1= 'E9.2,'M,PTCLE RAD 2= 'E9.2,'M')

WRITE(6,203)APM,E,KX

203 FORMAT(' ',"A= 'E7.1,'J= 'F4.1,'KA= 'E9.1")

READ,M

GOTO (1,2,3,4,5)

1 WRITE(6,300)

300 FORMAT('0','CONSTANT POTENTIAL ON A1 AND A2')

GOTO 5

2 WRITE(6,301)

301 FORMAT('0','CONSTANT CHARGE ON A1 AND A2')

GOTO 5

3 WRITE(6,302)

302 FORMAT('0','CONSTANT POTENTIAL ON A1 AND CHARGE ON A2')

GOTO 5

4 WRITE(6,303)

303 FORMAT('0','CONSTANT CHARGE ON A1 AND POTENTIAL ON A2')

GOTO 5

5 GOTO (128,128,130,131,132)

128 READ,PS1,PS2

WRITE(6,600)PS1,PS2

600 FORMAT('0','PS1= 'E15.3,'PS2= 'E15.3)

GOTO 132

130 READ,PS1,S2

WRITE(6,601)PS1,S2

601 FORMAT('0','PS1= 'E15.3,'S2= 'E15.3)

GOTO 132

131 READ,PS2,S1

WRITE(6,602)PS2,S1

602 FORMAT('0','PS2= 'E15.3,'S1= 'E15.3)

132 K=4.114E-21

EE=E*1.112D-10

EC=1.602D-19

SUM=1./6.

SUM1=1./6.

WRITE(6,201)

201 FORMAT('0','VA VR VT H VA VR VT H')

GOTO 501

501 IF(I-K)11,12,12

11 H=I+G/500.
XX = G / 500.
IF (H.GT.37. / KA) GOTO 400
GOTO 150
12 H = H + G / 25.
IF (H.GT.37. / KA) GOTO 400
150 A = DEXP (2. * KA * H)
GOTO 401
400 A = DEXP (74.)
401 B = 1. / A
C = 1. / (A - B)
X = 82. / (7. * EE * KA)
Y = A + B
Z = A - B
GOTO (116, 116, 117, 118), H
116 PS1 = PS1 / (1. D3)
PS2 = PS2 / (1. D3)
GOTO 503
119 PS1 = X * (2. * S2 / Z + S1 * Y / Z)
PS2 = X * (2. * S1 / Z + S2 * Y / Z)
GOTO 503
117 PS2 = (Z * S2 * X / 2. * PS1) / Y
PS1 = PS1 / (1. D3)
PS2 = PS2 / (1. D3)
GOTO 503
118 PS1 = (Z * S1 * X / 2. * PS2) / Y
PS1 = PS1 / (1. D3)
PS2 = PS2 / (1. D3)
503 PS3 = PS1 * PS1 + PS2 * PS2
PS4 = 2. * PS1 * PS2
AA = 2. * A1 * A2
AC = AA + AA + AB
VA = AF * (AA / AB + AA / AC + DLOG (AE / AC))
IF (H.GT.150. / KA) 14, 15, 15
14 E1 = 1. / DEXP (KA * H)
GOTO 16
15 E1 = 1. * E - 65
16 L1 = DLOG (1. + E1)
L2 = DLOG (1. - E1)
VRPS = VR1 * ((PS4 / PS3) * (L1 - L2) + L1 + L2)
GOTO (504, 505, 504, 504), X
505 VRSIG = VRPS - 2. * VR1 * DLOG (1. - E)
VR = VRSIG / KT
GOTO 506
504 VR = VRPS / KT
506 VA = VA / KT
VT = VA + VR
777 IF (ABS (VT) - 90.) 17, 18, 18
17 E2 = EXP (VT)
GOTO 19
18 E2 = 1. * E - 25
19 IF (DABS (VA) - 9.0D1) 20, 21, 21
20 E3 = DEXP (VA)
GOTO 22
21 E3 = 1. * E - 25
22 IF (H - G) 23, 24, 24
23 AD = G / 500.
GOTO 25
24 AD = G / 25.
25 AE = A1 + A2 + H
AF = AD * (A1 + A2) / (2. * AE * AE)
CALCULATION OF STABILITY RATIO
STEP = AF * E2
STEP1 = AF * E3
SUM = SUM + STEP
\[ \text{SU1}=\text{SUM1}+\text{STEP1} \]
\[ \text{IF}(\text{I}-5)30,31,31 \]
\[ \text{IF}(\text{I}-500.0-10)32,26,26 \]
\[ \text{IF}(\text{DA}BS(\text{V}1)-1000.)33,34,34 \]
\[ \text{IF}(\text{V}1.\text{GT}.0.0)\text{GOTO}50 \]
\[ \text{VR}=-1000. \]
\[ \text{GOTO}33 \]
\[ \text{VR}=1000. \]
\[ \text{IF}(\text{DA}BS(\text{VA})-1.0D3)35,36,36 \]
\[ \text{VA}=-1000. \]
\[ \text{IF}(\text{DA}BS(\text{VT})-1000.)37,38,38 \]
\[ \text{VT}=1000. \]
\[ \text{J}=\text{J}+1 \]
\[ \text{H}=\text{H}+1.0 \]
\[ \text{IF}(\text{H}.\text{EQ}.XX)\text{GOTO}700 \]
\[ \text{GOTO}701 \]
\[ \text{CONTINUE} \]
\[ \text{VP}(\text{J})=\text{VA} \]
\[ \text{VS}(\text{J})=\text{VR} \]
\[ \text{VU}(\text{J})=\text{VT} \]
\[ \text{HA}(\text{J})=\text{H} \]
\[ \text{IF}(\text{J}-4)39,40,40 \]
\[ \text{WRITE}(6,202)(\text{VP( JA)}, \text{VS( JA)}, \text{VU( JA)}, \text{HA( JA)}, \text{JA}=1, J) \]
\[ \text{FORMAT(' '}, 4(3F8.1,F6.1)) \]
\[ \text{J}=0 \]
\[ \text{GOTO}39 \]
\[ \text{I}=0 \]
\[ \text{H}=\text{H}+1.0 \]
\[ \text{IF}(\text{H}.\text{EQ}.XX)\text{GOTO}700 \]
\[ \text{GOTO}701 \]
\[ \text{CONTINUE} \]
\[ \text{VA}=-1000. \]
\[ \text{GOTO}33 \]
\[ \text{J}=0 \]
\[ \text{H}=\text{H}+1.0 \]
\[ \text{PS1}=\text{PS1}+1.0D3 \]
\[ \text{PS2}=\text{PS2}+1.0D3 \]
\[ \text{IF}(\text{H}.-(\text{A1+A2}))501,28,28 \]
\[ \text{W}=\text{SUM1}/\text{SUM1} \]
\[ \text{AFH}=-\text{AFH}+6. \]
\[ \text{WW}=\text{DLOG10}(\text{W}) \]
\[ \text{WRITE}(6,204)W,WW \]
\[ \text{FORMAT(' '}, 'W=' ,E17.9,'WW=' ,E15.3) \]
\[ \text{GOTO}10 \]
\[ \text{CONTINUE} \]
\[ \text{STOP} \]
\[ \text{END} \]
THIS PROGRAM CALCULATES THE RESULTANT STABILITY RATIO FROM A SPREAD IN PARTICLE POTENTIALS

REAL PSA, PS(20), P(20), S, SUM, PA(20, 20), X

PSA IS MEAN POTENTIAL, S IS STANDARD DEVIATION

J IS EVEN NUMBER OF INTERVALS INTO WHICH HISTOGRAM IS DIVIDED

17 READ, J, S, PSA
IF (J .LT. 0) GOTO 18
SUM = 0.
CALL HIST (PSA, S, J, PS, P)
WRITE (6, 99)
99 FORMAT (' ', 2X, 'PROB', 4X, 'POTNL', 4X, 'MV', 5X, 'I')
DO 10 I = 1, J
10 WRITE (6, 100) P(I), PS(I), I
WRITE (6, 101) SUM + P(I)
100 CONTINUE
CALL PROB (P, J, PA)
L = 0
L = L + 1
IF (L .GT. 1) GOTO 5
WRITE (6, 200) L
WRITE (6, 201) SUM
200 FORMAT (' ', 3X, 'RUN NUMBER=', 12)
WRITE (6, 202) SUM
201 FORMAT (' ', 3X, 'SUM PROB=', F6.4)
CALL STADRA (PS, J, W)
L = 0
L = L + 1
IF (L .GT. 1) GOTO 6
WRITE (6, 800) W
800 FORMAT (' ', 3X, 'W(I, J)', 3X, 'I', 3X, 'J')
DO 70 I = 1, J
WRITE (6, 900) W(I, L), I, L
70 CONTINUE
X = 0.
DO 90 I = 1, J
DO 90 L = 1, J
X = X + PA(I, L) / W(I, L)
90 CONTINUE
X = 1. / X
WRITE (6, 1100) X
1100 FORMAT ('0', 2X, 'WT=', E10.3)
GOTO 17
18 CONTINUE
STOP
END

SUBROUTINE HIST (PSA, S, J, PS, P)
POTENTIAL DISTRIBUTION HISTOGRAM

REAL PSA, PSB, PSC, PS(J), P(J), S
INTEGER I
PSC = 3 * S / J
I = 0
2 I = I + 1
IF (I .GT. 0.5 * J) GOTO 3
PS(I) = PSA + PSC * (I + I - J - 1)
PSB = PS(I)
P(I) = 2. * PSC * 0.398916 * EXP(-I * P5I3 - PSA) * 2 / (2 * S * S) / S
GOTO 4
3 PS(I) = PSA + PSC - PS(I - 1 + 1)
P(I) = P(I - 1 + 1)
GOTO 4
4 IF (I .LT. J) GOTO 2
RETURN
END

SUBROUTINE PROB(P, J, PA)
CALCULATES COLLISION PROBABILITY BETWEEN PARTICLES
REAL P(20), PA(20, 20), P1
INTEGER I, K, L, M
P1 = 0
30 DO 1 = 1, 3
K = I, J
CPA(I, N) = P(I) * P(K)
P1 = P1 + PA(I, K)
30 CONTINUE
L = J - 1
40 DO 1 = 1, L
K = M, J
PA(N, I) = PA(K, I)
P1 = P1 + PA(K, I)
40 CONTINUE
50 DO 50 I = 1, J
K = I, J
PA(I, K) = PA(I, K) / P1
50 CONTINUE
RETURN
END

SUBROUTINE STARPA (PS, J, I)
REAL PS(20), P(20, 20), A, EPS, APN, K, KT, G, SUN(20, 20), SUM1, H, K1, L1, L2,
2AD, AE, AF, STEP(20, 20), STEP1, UR(20, 20), UT(20, 20), VA, E2(20, 20), E3
DOUBLE PRECISION A21, SA, SB, EP
INTEGER I, K1, J, L, M
A = 1.0E-7
EPS = 78.3 * 1.112E-10
APM = 8.0E-20
K = 1.47E8
KT = 1.114E-21
WRITE (6, 1000) A, EPS, APN, K, KT
1000 FORMAT (' ', 'RADIUS= ', 'E7.1', 'M. EPS= ', 'E10.3', 'APM= ', 'E8.1', 'J. K= ',
3E7.1, 'K-1. KT= ', 'E10.3', 'J')
C = EPS * A / 8.
APM = - APM / 6.
H = 0.0
G = 0.5 * A
60 DO 62 I = 1, J
K = I, J
SUN(I, K1) = 1. / 6.
62 CONTINUE
SUM1 = 1. / 6.
16 IF (H .GE. G) GOTO 7
H = H + G / 500.
GOTO 6
7 H = H + G / 25.
8 E1 = EXP(-K * H)
L1 = ALOG (1 + E1)
L2 = ALOG (1 - E1)
A1 = 2. * A * A
A3 = A2 + 2. * A1
VA = ARP * (A1 / A2 + A1 / A3 + ALOG (A2 / A3))
VA = VA / KT
IF (ABS (VA) * GE 90.) GOTO 12
E3 = EXP (VA)
GOTO 13
12 E3 = 1. * E - 25
13 IF (H * GE G) GOTO 14
AD = G / 500.
GOTO 15
14 AD = G / 25.
15 AE = A + A + H
SA = H / A
SB = 1. * D0 + 1. * D0 + SA
EP = 0.101
A21 = 1. * D0
AF = Dspieli (SB, A21, EP) * AD * (A + A) / (2. * AE * AE)
D060 I = 1, J
D060 K1 = I, J
PS1 = PS(1)
PS2 = PS(K1)
PS1 = PS1 / 1. * E3
PS2 = PS2 / 1. * E3
PS3 = (PS1 + PS2) * 2
PS4 = PS3 - (4. * PS1 * PS2)
UR (I, K1) = C * (L1 * S3 * L1 + PS4 * L2)
UT (I, K1) = VA + (UR (I, K1) / KT)
IF (ABS (UT (I, K1)) * GE 90.) GOTO 9
E2 (I, K1) = EXP (UT (I, K1))
GOTO 11
9 E2(I, K1) = 1. * E - 25
11 CONTINUE
CALCULATION OF STABILITY RATIO
STEP (I, K1) = AF * E2 (I, K1)
STEP1 = AF * E3
SUM (I, K1) = SUM (I, K1) + STEP (I, K1)
60 CONTINUE
SUM1 = SUM1 + STEP1
IF (H * LT (A + A)) GOTO 16
D061 I = 1, J
D061 K1 = I, J
W (I, K1) = SUM (I, K1) / SUM1
61 CONTINUE
L = J - 1
D090 I = 1, L
H = I + 1
D090 K1 = H, J
W (K1, I) = W (I, K1)
90 CONTINUE
RETURN
END
REAL FUNCTION Dspieli*8 (S, A21, EPS)
The double precision function Dspieli calculates the ratio of the relative diffusion coefficients at infinite and finite separations for two dissimilar spheres
S = R / A1 WHERE R = CENTRE TO CENTRE DISTANCE
I.E. Dspieli = D12(INFINITY) / D12(S) = L.A. SPIELMAN,
J. COLL. INT. SCI., 33, P562, (1970)
EPS IS A CONVERGENCE PARAMETER
DOUBLE PRECISION S, A21, EPS, AD, BD, A, B, AMB, APB, KS1, KS2, LS1, LS2, N2, H,
JN, ET2, AN, CN, DN, AND RAND, CHD, RND, MLA, SAM, SAB, MAA, CARB, FAMP, FMA
IF (S.LT.(5.DO+A21)) GOTO 70
DSQIEL=1.DO
RETURN
70 IF(S-(1.1L0+A21))40,50,50
40 DSQIEL=1.DO/((1.DO+1.DO/A21)*(S-1.DO-A21))
GOTO 60
50 AD=(S*S-A21*A21+1.DO)/(2.DO*S)
BD=AD+DSQRT(AD*AD-1.DO)
B=BD+DSQRT(BD*BD-1.DO)
A=DLOG(AD)
B=BD-DSQRT(AD-1.DO)
BS1=I)LOG(A)
BS2=B
70

THE FOLLOWING LOOP CALCULATES THE TERMS OF THE SERIES FOR KS1,KS2, LS1 AND LS2

N=0
10 N1=N1+1
N=DFACT(N1)
M=N1*N1
N2=DFACT(M)
K9=(N+1.DO)/( (N2-1.DO)*(N2+1.DO)*(N2*3.DO)*RT2 )
X1=(N-0.5DO)*AMB
Y1=(N-0.5DO)*APB
X2=X1+AMB
Y2=Y1+APB
X3=X2+AMB
Y3=Y2+APB
S1AMB=DSINH(X1)
S1APB=DSINH(Y1)
C1APB=DLOG(Y1)
S2AMB=DSINH(X2)
S2APB=DSINH(Y2)
C2APB=DLOG(Y2)
S3AMB=DSINH(X3)
S3APB=DSINH(Y3)
C3APB=DLOG(Y3)
E1AMB=DEXP(-X2)
DLTA=4.DO*S2AMB*SAMB**2
KNUD=KN/DLTA

A=-((N+3.DO)*(N+2.DO)*(2.DO*(N2+1.DO)*SAMB)**2)*SDAMB-(N2+1.DO)**2*EAMB*SAMB+
2.DO*(N2+1.DO)*SAMB*C2APB-2.DO*(N2+1.DO)*SAMB*C1APB-
2.(N2+1.DO)*(N2+1.DO)*SAMB*C1APB

B=-((N+3.DO)*(N2+1.DO)*(2.DO*(N2+1.DO)*SAMB**2)*SDAMB-(N2+1.DO)**2*EAMB*SAMB+
2.DO*(N2+1.DO)*SAMB*C2APB-2.DO*(N2+1.DO)*SAMB*C1APB

C=-((N2+1.DO)*(N2+3.DO)*(2.DO*(N2+1.DO)*SAMB**2)*SDAMB-(N2+1.DO)**2*EAMB*SAMB+
2.DO*(N2+1.DO)*SAMB*C2APB-2.DO*(N2+1.DO)*SAMB*C1APB

D=-((N2+1.DO)*(N2+3.DO)*(2.DO*(N2+1.DO)*SAMB**2)*SDAMB-(N2+1.DO)**2*EAMB*SAMB+
2.DO*(N2+1.DO)*SAMB*C2APB-2.DO*(N2+1.DO)*SAMB*C1APB
KNUD = (N2+3.DO) * (-4.DO*E1AMB*S2AMB - (N2+1.DO) **2*EAMB*SAMB +
1 2.DO*(N2-1.DO)*S2AMB*C2APB-2.DO*(N2+1.DO)*S3AMB*C1APB +
2 (N2-1.DO) * (N2+1.DO) * SAMB*CAPB) * KNUD

CND = -(N2-1.DO) * (2.DO*(N2+1.DO)*S1AMB*S3APB -
1 2.DO*(N2+3.DO)*S2AMB*S2APB - (N2+1.DO) * (N2+3.DO) * SAMB*SAPB)*
2 KNUD

DND = (N2-1.DO) * (-4.DO*E1AMB*S2AMB + (N2+1.DO) **2*EBMA*SAMB +
1 2.DO*(N2+1.DO)*S1AMB*C3APB - 2.DO*(N2+3.DO)*S2AMB*C2APB -
2 (N2+1.DO) * (N2+3.DO) * SAMB*CAPB) * KNUD

X1 = (N2+1.DO) * (-AN+And-BN+BND-CN+CN-DN+DND)
X2 = (N2+1.DO) * (-AN-AND+Bh+BN-CD-CN-CN+DN+DND)
Y1 = (N2+1.DO) * (+AN+AND+Bn+BND-CN+CN-CN+DN+DND)
Y2 = (N2+1.DO) * (+AN-AND-Bn+BND-CN-CN-CN+DN+DND)

KS1 = KS1+X1
KS2 = KS2+X2
LS1 = LS1+Y1
LS2 = LS2+Y2

F = (KS1*KS2-LS1*LS2) / (KS1+KS2-LS1-LS2)

IF (N1.GT.1) GOTO 30

20 FH = F
GOTO 10

30 IF (DABS (((F-Fh)/Fh).GT.EPS) GOTO 20
SA = DSINH(A)
DSPIEL = RT2*(1.DO+1.DO/A21) * SA/F/6.DO

60 CONTINUE
RETURN

END
THIS PROGRAM CALCULATES THE RESULTANT STABILITY RATIO FROM A SPREAD IN PARTICLE SIZE

INTEGER I,J,K,KA,L
REAL XA,S,X(20),P(20),PA(20,20),% (20,20),A,B
J MUST BE EVEN
READ J,S,XA
108 FORMAT(I2,2E10.2)
CALL HIST(XA,S,J,X,P)
L=0
L=L+1
K=0
IF(L.GT.1)GOTO 111
WRITE(6,109) L
109 FORMAT('RUN NUMBER ',I2)
WRITE(6,110) XA,S,J
WRITE(6,113) 'AV RAD ',E10.2,' STD DEV ',E10.2,' INTERVALS ')
WRITE(6,112) XA,S,J
112 FORMAT('X(I) P(I) I X(I) P(I) I X(I) P(I) I')
DO 124 1=1,3
X(I)=X(I)*1.E8
IF(K.GT.4)GOTO 116
K=K+1
116 GOTO(101,114,115),K
101 WRITE(6,102) X(I),P(I),I
102 FORMAT(F7.1,F7.4,I3)
114 WRITE(6,117) X(I),P(I),I
117 FORMAT('+',34X,F7.1,F7.4,4I3)
126 CONTINUE
X(I)=X(I)*1.E-8
124 CONTINUE
K=0
CALL PROB(P,J,PA)
L=0
L=L+1
IF(L.GT.1)GOTO 107
WRITE(6,110)
110 FORMAT('X(I) X(K) PA(I,K) I K X(I) X(K) PA(I,K) I K')
DO 125 1=1,3
DO 125 K=1,J
X(I)=X(I)*1.E8
IF(I-K) 105,106,105
105 X(K)=X(I)
106 IF(K.AN.EQ.4)GOTO 119
K=1
119 GOTO(103,120,121),K
103 WRITE(6,104) X(I),X(K),PA(I,K),I,K
104 FORMAT(2F7.1,F8.4,2I5)
120 WRITE(6,122) X(I),X(K),PA(I,K),I,K
122 FORMAT('+',34X,2F7.1,F8.4,2I5)
GOTO 127
**SUBROUTINE HIST(XA,S,J,X,P)**

SIZE DISTRIBUTION HISTOGRAM

REAL XA,XB,XC,X(20),P(20),S
INTEGER I
XC=3.*S/J
I=0

200 I=I+1
IF(I-0.5*J) 201,201,202

201 X(I)=XA+XC*(I+I-J-1)
XB=X(I)
P(I)=2.*XC*0.39916*EXP(-((XB-XA)**2)/(2*S*S))/S
GOTO203

202 X(I)=XA+XA-X(J-I+1)
P(I)=P(J-I+1)
GOTO203

203 IF(I-J)200,204,204

204 RETURN

END

**SUBROUTINE PROB(P,J,PA)**

CALCULATES COLLISION PROBABILITY BETWEEN PARTICLES

REAL P(20),PA(20,20),P1

**SUBROUTINE STABLA(X,J,W)**

CONTINUE

L=0
L=L+1
IF(L.GT.1) GOTO 150
WRITE(6,159)
159 FORHAT('STABILITY RATIOS ')
WRITE(6,160)
160 FORMAT(' ',10X,'W(I,J) I J W(I,J) I J
1 W(I,J) I J')
K=0

150 DO 130 I=1,J
DO 130 L=1,J
K=K+1
IF(K.NE.5) GOTO 1141
N1

141 GOTO(142,143,144),K

142 WRITE(6,140) W(I,L),I,L
140 FORMAT(' ',F18.1,13,14)
GOTO145

143 WRITE(6,146) W(I,L),I,L
146 FORMAT(' **',25X,F18.1,13,14)
GOTO145

144 WRITE(6,147) W(I,L),I,L
147 FORMAT(' **',50X,F18.1,13,14)

145 CONTINUE

130 CONTINUE

A=A+P(I,L)/W(I,L)

128 CONTINUE

A=1./A

WRITE(6,133) A
133 FORMAT('0.',F20.3)
STOP

END

**SUBROUTINE HIST(XA,S,J,X,P)**

SIZE DISTRIBUTION HISTOGRAM

REAL XA,XB,XC,X(20),P(20),S
INTEGER I
XC=3.*S/J
I=0

200 I=I+1
IF(I-0.5*J) 201,201,202

201 X(I)=XA+XC*(I+I-J-1)
XB=X(I)
P(I)=2.*XC*0.39916*EXP(-((XB-XA)**2)/(2*S*S))/S
GOTO203

202 X(I)=XA+XA-X(J-I+1)
P(I)=P(J-I+1)
GOTO203

203 IF(I-J)200,204,204

204 RETURN

END

**SUBROUTINE PROB(P,J,PA)**

CALCULATES COLLISION PROBABILITY BETWEEN PARTICLES

REAL P(20),PA(20,20),P1
INTEGER I, K, L, M
P = 0
DO 300 I = 1, J
DO 300 K = 1, J
PA(I, K) = P(I) * P(K)
P = P + PA(I, K)
300 CONTINUE
L = J - 1
DO 301 I = 1, L
M = I + 1
DO 301 K = M, J
PA(K, I) = PA(I, K)
P = P + PA(K, I)
301 CONTINUE
D = 0.112D - 10
WRITE (6, 411) PS, D, AP, K, KT, EPS
WRITE (6, 411) PS, D, AP, K, KT, EPS
PS = PS / 1.63
D = D / PS
D = PS / 6.
DO 400 I = 1, J
DO 400 K = 1, J
AR1 = X(I)
AR2 = X(K1)
A1 = AR1 * AR2
A2 = AR1 + AR2
A3 = A1 / A2
SUM = 1. / 6.
SUN = 1. / 6.
G = 0.25 * A2
H = 1. * 10
MI = 1
N = 0
408 IF(H - G) 401, 402, 402
401 H = H + G / 500.
GOTO 403
402 H = H + G / 25.
403 A1 = A2 * A2 + H
A2 = A1 + A2 + H
A3 = A1 + A2
A4 = A1 + A2
A5 = A1 / A2
A7 = (A2 + H) ** 2
IF(H - (150 / K)) 420, 419, 419
420 E1 = EXP(-K * H)
GOTO 421
419 E1 = 1. * E-65
421 L1 = ALOG((1 + E1)
L2 = ALOG(A6)
\[ VA = -B_2 \cdot (2 \cdot A_1 \cdot A_H + L_2) \]
\[ VT = VA + VR \]
\[ VT = VT / KT \]
\[ VR = VT - VA \]
\[ IF (ABS(VT) - 100.) \]

423 \[ E_2 = EXP(VT) \]
\[ GOTO 428 \]

424 \[ E_2 = 1. \cdot E^{-25} \]

428 \[ CON T INUE \]
\[ IF (ABS(VT) - 100.) \]

425 \[ E_3 = EXP(VA) \]
\[ GOTO 429 \]

426 \[ E_3 = 1. \cdot E^{-25} \]

429 \[ CON T INUE \]
\[ N = N + 1 \]
\[ IF (N - 2) \]

417 \[ IF (H - G) \]

405 \[ AA = G / 500. \]
\[ GOTO 407 \]

406 \[ AA = G / 25. \]

407 \[ A_21 = A_2 / A_1 \]
\[ S = H / A_1 \]
\[ SS = 1. \cdot D0 + A_21 + S \]
\[ XD = 1 \]

\[ A_H = A_2 \cdot AA \cdot XD / (A_H^7 + A_H^7) \]
\[ STEP = A_H \cdot E^{2} \]

427 \[ STEP_1 = A_H \cdot E^{2} \]
\[ SUN = SUN + STEP \]
\[ SUN_1 = SUN_1 + STEP_1 \]
\[ IF (H - (A_2 + A_2)) \]

404 \[ WA = SUN / SUN_1 \]
\[ W(I, K_1) = WA \]

400 \[ CON T INUE \]
\[ L = J - 1 \]
\[ DO 409 \]
\[ I = 1, L \]
\[ H = I + 1 \]
\[ DO 409 \]
\[ K_1 = H, J \]
\[ W(K_1, I) = W(I, K_1) \]

409 \[ CON T INUE \]
\[ RETURN \]
\[ END \]
C  CALCULATION OF AV 1/T AND STD. DEVIATION
D  IMENSION F(20)
D  IMENSION SUM(20)
D  IMENSION T(20)
D  IMENSION VE1(20)
I  INTEGER X,Y,Z,IR,IS,J,JA,XX,D
R  EAL T,SUM,F,V,SUMS,SUM1,A,VE
C  OMMON X,IR,IS,Z,A,XX
R  EAD,D
D  I S NO. OF SETS OF DATA
D  O 60 IJ=1,D
R  EAD,X,Z
X I S NO. OF READINGS OF TIME, Z I S NO. OF LEVELS READ
X X=X/2
J A=0
R  EAD,IR
R  I S NO. OF LEVELS READ FROM LOWER TO CENTRE
I S=Z-IR
S I S NO. OF LEVELS FROM CENTRE TO UPPER WALL
R  EAD(5,19)A
19 F  ORMAT(F6.1)
W  RITE (6,400)A
400 F  ORMAT('! ','A= ',F6.1)
A I S MEAN CROSS-SECTIONAL RADIUS
R  EAD, (F(I),I=1,Z)
W  RITE (6,600) (F(I),I=1,Z)
600 F  ORMAT('! ','9F7.1')
W  RITE (6,100)
100 F  ORMAT(6X,'AVP',6X,'SDP',6X,'AVN',6X,'SDN',7X,'AV',7X,'SD')
D  O10 I=1,Z
R  EAD,B
R  EAD,(T(K),K=1,X)
C  A  L L AVTIME(B,T,SUMP,SDP,SUMH,SDN,SYMS,SD)
W  RITE (6,200) SUMP,SDP,SUMH,SDN,SYMS,SD
200 F  ORMAT(4X,6(F6.3,3X))
J A=JA+1
V E1(JA)=SUMS
10 C  ONTINUE
60 C  ONTINUE
S T O P
E N D
S U B R O U T I N E AVTIME(B,T,SUMP,SDP,SUMH,SDN,SYMS,SD)
I  NTEGER X,Z,IR,IS,XX
I  NTEGER X,IR,IS,Z,A,XX
R  EAL T(20)
S UHP=0
S UMN=0
S QP=0
S QN=0
D  O10 J=1,XX
T(J)=B/T(J)
S UMP=SUMP+T(J)
S QP=SQP+T(J)*T(J)
10 C  ONTINUE
D O20 K=1,XX
J=K+XX
T(J)=B/T(J)
S UHN=SUMH+T(J)
S QN=SQN+T(J)*T(J)
20 C  ONTINUE
SUMP = SUMP / XX
SUMN = SUMN / XX
SUHS = (SUMP + SUMN) / 2
SDP = SQRT (((SQR / XX) - SUMP * SUMP)
SDN = SQRT (((SQR / XX) - SUMN * SUMN)
SD = SQRT (((SQR + SQR) / X) - SUHS * SUHS)
RETURN
END
LEAST SQUARES ANALYSIS OF POINTS SATISFYING EQUATION $Y = A + B \times X$

REAL $X(30), Y(30), A, B, SX, SY, SX2, SXY, SY2, STD, AER, BER, AER2, BER2$

INTEGER $I, N$

$N$ IS THE NUMBER OF $X,Y$ PAIRS

READ, $N$

READ, $(X(I), I = 1, N)$

READ, $(Y(I), I = 1, N)$

$SX = 0$

$SY = 0$

$SX2 = 0$

$SXY = 0$

$SY2 = 0$

DO 10 $I = 1, N$

$SX = SX + X(I)$

$SY = SY + Y(I)$

$SX2 = SX2 + (X(I))^2$

$SXY = SXY + (X(I)) \times (Y(I))$

$SY2 = SY2 + (Y(I))^2$

10 CONTINUE

$D = (\frac{(SX \times SY - N \times SXY)}{(SX^2 - N \times SX2)})$

$A = (\frac{Y - B \times SX}{N})$

$STD = \sqrt{\frac{SY2 - SY \times SY/N}{N - 2}}$

$AER = 3 \times 10^{-6} \times (\frac{SX - STD}{A})$

$BER = 3 \times 10^{-6} \times (\frac{SY - STD}{B})$

WRITE (6, 100)

100 FORMAT ('0', 2X, 'BEST SLOPE', 5X, 'ERROR', 8X, 'BEST INTERCEPT', 4X, 2' ERROR')

WRITE (6, 200) $B, BER, A, AER$

200 FORMAT ('0', 3X, E10.4, 2X, E10.4, 6X, E10.4, 4X, E10.4)

$BK = B \times 5.52E-16$

$BERK = BER \times 5.52E-16$

WRITE (6, 500) $BK, BERK$

500 FORMAT ('0', 'BK = ', 4X, 12.3, 5X, 'BERK =', 4X, 12.3)

STOP

END
CALCULATION OF ZETA POTENTIALS OF PARTICLES AND ELECTROPHORESIS CELL WALL

REAL VE,L,PI,N,FKA,V,EPS,ZP,ZW,VEE
INTEGER I,D
D IS THE NO. OF SETS OF DATA
VE IS IN GRATS/S, L IN M, V IN VOLS
EPS IS DIELECTRIC CONST, W IS VISCOSITY, ZP IS PARTICLE POTNL,
ZW IS WALL POTNL

READ,D
PI=3.142
READ,L,N,FKA,V,EPS
DO 10 I=1,D
READ,VE,VEE
VE=VE*47.E-6
VEE=VEE*47.E-6

EPS=EPS*1.112E-10
ZP=VE*L*6.*PI*N/(FKA*V*EPS)
ZW=4.*PI*N*VEE*L/(EPS*V)
ZP=ZP*1.E3
ZW=ZW*1.E3

VE=VE/47.E-6
VEE=VEE/47.E-6
EPS=EPS/1.112E-10
WRITE(6,100) VE,VEE,ZP,ZW
100 FORMAT('0',VE='F7.4',GRAVS/S,'2X',VEE='F7.4',GRAVS/S,'2X,'PARTICLE POTNL=','F6.1','MV.')
10 CONTINUE
STOP
END

RCC 370/158 **** **** EDCE 1458 END JOB 215 DURNO, CHEM
RCC 370/158 **** **** EDCE 1458 END JOB 215 DURNO, CHEM
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Previous studies of colloidal stability and heteroflocculation have been reviewed, and the relevant theories of electrostatic interactions discussed. Colloidal dispersions of coated and pure rutile samples and carbon blacks in aqueous electrolytes have been described. Choice of system was determined by the surface properties, particle size and Hamaker constant of the samples. Systems were chosen so that size should be the same for both samples, and similarly for the Hamaker constant, as far as possible.

Coated rutile samples were studied with a view to heteroflocculation of the two samples. The stability behaviour of pure rutile was studied to eliminate effects of dissolution of ions from any surface coating. Adsorption of surfactant onto pure rutile was carried out to give information on the surface charge distribution.

Carbon blacks were used as a test of the experimental techniques employed, and in heteroflocculation experiments with rutile.

The coated rutile samples were found to be unsuitable for heteroflocculation experiments since dissolution of ions from the coatings occurred. These dissolved species subsequently adsorbed onto particles and the electrophoresis cell walls. This contamination was detected by microelectrophoresis where the value of the potential at the cell wall was obtained, as a matter of course, for every electrophoresis experiment and compared with literature values.

Dispersions of pure rutile were found to be much less stable than predicted by theory. An uneven distribution of surface charge, resulting in discrete areas of high and low potential, was postulated. Instability was presumed to result from low potential interactions between neighbouring particles.
Adsorption of surfactant was found to indicate at least two different types of surface site. Adsorption of a cationic surfactant was found to considerably increase the stability of the rutile, whereas an anionic surfactant had little effect on stability.

A study of several carbon blacks showed that, where there were known to be different types of surface groups, the stability was less than predicted from theory.

The experimental stability of Graphon agreed with predictions of theory, and it was used in heteroflocculation experiments with rutile. Heteroflocculation was found to occur in the mixed systems, and the stability ratio for the mixed interaction was explained in terms of an extended form of the Hogg, Healy and Fuerstenau equation.