Dye Binding Studies on Alumina coated surfaces

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The University of Edinburgh, 2004
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Abstract

This project deals with the design, synthesis and evaluation of ink jet dyes to bind to inorganic oxide surfaces particularly that of aluminium oxide. Alumina is applied as a coating on ink jet paper for use in the high added value markets. Chapter 1 provides an overview on the ink jet printing industry but focusing mainly on printing on paper, ink development, papers required for printing, dyes and adsorption isotherms.

'Simple' azo dyes are considered in chapter 2 and binding of these dyes to aluminium trihydroxide [Al(OH)₃] is examined. Synthetic routes to novel phosphonic acid azo dyes were developed. Isotherm studies demonstrated that phosphonic acid dyes bind much more strongly to Al(OH)₃ when compared against sulfonic, carboxylic, boronic, arsonic and phosphinic acid analogues. Dyes with different acidic functional groups were applied to different papers via ink jet method and the prints were analysed for their light, ozone and humidity fastness properties. It was found that on changing the functional group of the dye, the humidity fastness was greatly affected. Other ink jet properties such as ozone and light fastness were more dependent on factors such as paper type and the percentage of inorganic oxide coated on the paper.

In chapter 3, more complex phosphonic acid azo dyes were designed and synthesised to analyse both binding properties and ink jet properties.

In chapter 4, adsorption isotherms are reported on dyes in the presence of cyclodextrin to examine the effect of cyclodextrin on binding strength and surface coverage of the dyes. ROESY NMR studies were undertaken to provide conclusive evidence of the inclusion complex, dye-cyclodextrin and UV/Vis and NMR studies were performed to determine the strength of these complexes. Analysis of the isotherm results indicate that the ternary complex, cyclodextrin-dye-Al(OH)₃ is formed on the surface and is thought to be thermodynamically more stable than dye-
surface or cyclodextrin-surface interactions. Ink jet tests results on dyes with cyclodextrin showed improved the light fastness properties.
Preface and Declaration

Since graduating from the University of Edinburgh in 2000 with BSc(Hon) degree in Chemistry, the author has been engaged in full time researcher under the supervision of Professor P. A. Tasker and Dr H. McNab at the university of Edinburgh and Dr P. Wight at Avecia (Blackely, Manchester).

No part of the work referred to in this thesis has been submitted in support of an application for another degree or qualification from this or any other university or other institute of learning.
I would like to thank, first and foremost my supervisor, Prof. Peter Tasker, for his enthusiasm and support over the last few years, and for his encouragement, especially towards the end. In addition, I would like to thank Dr Paul Wight and Ms Patricia Dunwoody at Avecia for their support and for not getting cross at the constant barrage of questions. I also wish to thank the EPSRC and Avecia for funding this project.

I thank Dr Hamish McNab for being the organic chemistry guru and helping me with my numerous synthetic problems. I would also like to say a big thank you to Dr Philip Camp for all his help with solution modelling and for being so patient every time I send the wrong file.

I thank Dr J. Bella, Mr J. R. A. Millar, Mr W. Kerr and Mr. E. Perez for their help with NMR spectroscopy. I am grateful to Mr Alan Taylor (esp for pushing me to the front of the queue whenever I needed a mass spec) for all the mass spectrometry he has carried out for me, and to Tim Calder for C/H/N analysis.

On a more personal note, I would like to thank Jenny and Rachel for their support and friendship and for the many drunken nights at 'scrubway'.

I wish to say thanks to Dr David K. Henderson for all his help in my project and for re-reading my chapters many times.

Finally, I would like to thank my family (esp my aunt and my grandmother) and Joysheel for their constant encouragement and belief in me.
Abbreviations

δ  chemical shift (NMR)
Å  Angstrom
Al(O)(OH)$_3$  aluminium oxy/hroxide
Al$_2$O$_3$  aluminium oxide
Alk  alkyl
approx.  approximately
Ar  aryl
at. %  atomic percentage
ATH  aluminium trihydroxide
br  broad
c.a.  circa (approximately)
CAD  computer aided design
ccp  cubic close packed
CD$_3$COCH$_3$  deuterated acetone
CDCl$_3$  deuterated chloroform
CDS  chemical database service
cf  compare (compared with)
CHN  carbon, hydrogen, nitrogen (elemental analysis)
cm  centimetre
cm$^{-1}$  wavenumber
conc.  concentration
cont.  continued
CRT  cathode ray tube
CSD  Cambridge Structural Database
d  doublet
D$_2$O  deuterated water
d$_6$  deuterated
DCU  data collection unit (LPR)
dd  doublet of doublets
DDM  data dumpa module (LPR)
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tbody>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>eg.</td>
<td>for example</td>
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<tr>
<td>EI MS</td>
<td>electron impact mass spectrometry</td>
</tr>
<tr>
<td>ES</td>
<td>electrospray</td>
</tr>
<tr>
<td>et al.</td>
<td><em>et al.</em> (and others)</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>FABMS</td>
<td>fast atom bombardment mass spectrometry</td>
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<tr>
<td>g</td>
<td>grams</td>
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<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close packed</td>
</tr>
<tr>
<td>HF</td>
<td>humidity fastness</td>
</tr>
<tr>
<td>HTS</td>
<td>high throughput screen</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
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<tr>
<td>K</td>
<td>equilibrium constant</td>
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<tr>
<td>L</td>
<td>ligand</td>
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<tr>
<td>LCD</td>
<td>liquid crystal display</td>
</tr>
<tr>
<td>LF</td>
<td>light fastness</td>
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<tr>
<td>m</td>
<td><em>meta</em></td>
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<tr>
<td>M</td>
<td>metal</td>
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<tr>
<td>m</td>
<td>metre</td>
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<tr>
<td>M</td>
<td>molar, mol dm(^{-3})</td>
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<tr>
<td>m</td>
<td>multiplet</td>
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<tr>
<td>m.p.</td>
<td>melting point</td>
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<tr>
<td>m/z</td>
<td>molecular ion (MS)</td>
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<tr>
<td>md</td>
<td>medium</td>
</tr>
<tr>
<td>MeCN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
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<tr>
<td>mg</td>
<td>milligram</td>
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<tr>
<td>MHz</td>
<td>mega hertz</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
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<tr>
<td>ml</td>
<td>millilitre</td>
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<tr>
<td>mmol</td>
<td>millimolar</td>
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<tr>
<td>MS</td>
<td>mass spectrometry</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>o</td>
<td>ortho</td>
</tr>
<tr>
<td>°C</td>
<td>degree Centigrade</td>
</tr>
<tr>
<td>OD</td>
<td>optical density</td>
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<tr>
<td>OF</td>
<td>ozone fastness</td>
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<tr>
<td>OH</td>
<td>hydroxide anion</td>
</tr>
<tr>
<td>p</td>
<td>para</td>
</tr>
<tr>
<td>pet. ether</td>
<td>petroleum ether</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>pK&lt;sub&gt;a&lt;/sub&gt;</td>
<td>-log&lt;sub&gt;10&lt;/sub&gt;K&lt;sub&gt;a&lt;/sub&gt;</td>
</tr>
<tr>
<td>PVA</td>
<td>polyvinyl alcohol</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>ROD</td>
<td>relative optical density</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>st</td>
<td>strong</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
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<tr>
<td>UV/vis</td>
<td>ultraviolet/visible (emission spectroscopy)</td>
</tr>
<tr>
<td>v</td>
<td>wavenumber</td>
</tr>
<tr>
<td>vs.</td>
<td>versus</td>
</tr>
<tr>
<td>vst</td>
<td>very strong</td>
</tr>
<tr>
<td>WF</td>
<td>water/wet fastness</td>
</tr>
<tr>
<td>wk</td>
<td>weak</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>Z</td>
<td>number of asymmetric units per cell</td>
</tr>
</tbody>
</table>
\( \alpha \text{-CD} \)  \quad \text{alpha cyclodextrin}

\( \varepsilon \)  \quad \text{extinction coefficient}

\( \lambda \)  \quad \text{wavelength}
CHAPTER 1

Introduction and Aims
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1. Introduction

This thesis will address how the uptake of water-soluble dyes on metal oxide-coated paper depends on the types and disposition of anionic pendant groups in the dye system. Initially adsorption isotherms will be determined using well-characterised aluminium trihydroxide (Alcan’s ATH). The dyes will be further tested for their ink jet properties to determine the effect of different anionic functional groups on ink jet properties of the dyes.

Tasker et al. have suggested recently that the binding of surface ligands can be greatly enhanced by “multisite attachment” via a combination of conventional metal-donor interactions and other forms of secondary binding between the ligand and surface hydroxide groups or water molecules.

The significance of “multisite attachment” in enhancing the binding of dyes to aluminium oxides will be established by comparing the uptakes of model compounds containing water-solubilising functional groups (X= CO₂H, SO₂H and PO₃H₂), which are thought to bind to aluminium oxides used in paper treatments. Previous work carried out at Edinburgh showed that phosphonic acids had a high affinity for alumina. Consequently the binding of phosphonic acid containing dyes was selected for study in this project. Incorporation of suitable chromophores to allow their uptake to be monitored drew on expertise of Avecia’s, ink jet dye business at Blackley, in Manchester. The results from binding studies are used to guide the design of dyes that bind more strongly to coated media.

1.1 Overview of ink jet printing

Today’s market is such that it continuously demands advancement in the performance of printing and recording devices. As computer systems continually increase the rate at which data are accumulated, manipulated and processed and with colour cathode ray tubes (CRTs), the standard output device, further enhancing the
capability of these new computers, demand for colour hard copies has become a necessity. As a consequence, electrostatic, thermal, laser and ink jet printers have been developed. In this study, we are primarily concerned with what is universally thought to be the most versatile type and producing the most exciting colours, ink jet printers.

1.1.1 History of ink jet printing

Although ink jet printing is considered relatively modern, the concept and mechanism by which a liquid stream breaks up into droplets (Rayleigh instability) was first described mathematically by Lord Rayleigh in 1878. He was the first to note that highly charged droplets disintegrate once the repulsive force between the like elementary charges on the surface exceed the forces from surface tension (figure 1.1).

In 1951, Elmquist of Siemens developed the first practical ink jet device which used the Rayleigh instability principle. This led to the production of the Mingograph, which was the first commercial ink jet chart recorder for analog voltage signals. In early 1960s, Sweet of Stanford University showed that when a pressure wave pattern was applied to a nozzle/orifice, the ink jet stream can be broken into little droplets. An electric charge can then be used on the droplets, with the charged droplets flying into a gutter and the uncharged droplets used in forming the image. This printing process was called continuous ink jet technology (figure 1.2).
Modern day ink jet technology, although evolved from continuous ink jet printing, is different and uses drop-on demand (DOD) technology and has superseded continuous ink jet printers in the office and home markets. Zoltan\textsuperscript{8}, Kyser and Sears\textsuperscript{9} are among the inventors of the DOD printing system. In this type of printer, ink droplets are ejected by a pressure wave created from the mechanical motion of the piezoelectric ceramic.

![Figure 1.2 Schematic representation of a continuous ink jet printer.\textsuperscript{10}](image)

Ink jet printing has a wide range of potential applications. Figure 1.3 shows the current ink jet technology that exists in today’s market and will be discussed in greater detail in the following sections. The two main categories; continuous and DOD can further be subdivided.

### 1.1.2 Continuous ink jet printing\textsuperscript{11}

Figure 1.2 illustrates a schematic representation of a continuous ink jet printer. In this system\textsuperscript{11}, fluid under pressure is ejected out of an orifice with a typical diameter of about 50-80\textmu m. The jet stream is then broken up into uniform droplets by the amplification of capillary waves induced onto the jet. This is usually done by an electromechanical device that causes pressure oscillations to propagate through the fluid. The drops, as they break off from the jet in the presence of an electrostatic field (provided by the charge electrode) acquire an electrostatic charge. The charged drops then travel through the deflection plates. These drops can either end up in the catcher (and recycled) or on the print substrate. This system is termed ‘continuous’ because drops are continuously produced and their trajectories are varied by the applied charge. Continuous ink jet can be divided into ‘binary’ or ‘multiple’
depending on the drop deflection method used. In a binary system, the charged drops are used for printing on the media while the uncharged drops are caught by the catcher and recycled. In a multiple deflection method, the charged drops are deflected on to the media at different levels and the uncharged drops are recycled. Both methods are used extensively in industrial coding, marking and label marking. In addition to the above two methods, Hertz’s continuous print system has a unique way of obtaining gray scale through a burst of small drops. This concept is used in printers such as Iris Realistic for the graphic art market and Scitex’s digital press for high speed on demand printing.¹¹

Figure 1.3 Ink jet technologies and suppliers available in 1998.¹¹

1.1.3 Drop-on-demand ink jet printers¹¹

The second category of ink jet printing, the drop-on-demand (DOD) is shown schematically in figure 1.4. In a DOD system, every ink droplet produced is used and no ink is wasted or returned to the reservoir because drops are only produced when
required to form a dot on the medium. The droplets are not charged and are fired in a straight line on to the substrate.

![Figure 1.4 Schematic of a DOD print system.](image)

The printhead is placed quite close to the substrate so that the droplet does not have far to travel, giving accurate positioning of the dots leading to better quality prints. Therefore, DOD printers are more efficient and environmentally friendly than the continuous type. DOD printers can be divided to 4 major types: piezoelectric, thermal bubble jet, electrostatic and acoustic ink jet. The latter two types are in late stages of development\cite{12-17} and will not be discussed further in this report. Thermal printers\cite{11} are the most successful in the market today. Depending on its configuration, a thermal printer can be a roof shooter (orifice is located on top of the heater) or a side shooter (orifice is on a side located nearby the heater). The ink is superheated to a critical temperature for bubble nucleation. The water vapour bubble instantaneously expands to force a droplet of ink out of the nozzle. The whole process of the bubble formation and collapse takes place in less than 10 $\mu$s. The ink then re-fills back into the chamber and the process is ready to begin again (figure 1.5).

![Figure 1.5 Drop formation process of a thermal ink jet printer.](image)
In a piezoelectric DOD method, deformation of the piezoelectric material causes the ink volume to change in the pressure chamber generating a pressure wave that propagates towards the nozzle. This acoustic pressure wave overcomes the viscous pressure loss in a small nozzle and the surface tension forces lead to ink drop formation at the nozzle. When the drop is formed, the pressure must be sufficient to expel the droplet towards the recording media.

1.1.4. Applications of ink jet printing

Ink jet printers started out in the office/home market where the primary medium used is paper. The low cost and good print quality has made the ink jet printers suitable for other applications including the textile industry, for making colour filters for liquid crystal displays (LCD) and in electronic photography. Table 1.1 summarises different market segments and key players in each of the fields that use ink jet printing technology.

In the past, hard copies were produced using impact printers such as typewriters, the daisy wheel and the dot-matrix printer. In general, these are slow and noisy. With the arrival of computers and word processors in the 1980s, offices underwent a major change and electronically controlled non-impact printers such as laser and ink jet printers were introduced. These are fast, almost silent, can produce both text and graphics and show full-colour capabilities. The main advantage of ink jet systems is their low cost and simplicity, but, as they use water-based inks the dry time of the print is longer than the laser jet printers.

Textile printing under conventional technology involves several stages, starting with manual tracing of the original pattern, engraving screen or roller for colour that will be used, production of several prints in different colours for customer approval and finally, bulk printing. The time scale for sample production is roughly 2-8 weeks and if bulk production is to be carried out, this can be extended to about 12 weeks. The development of Computer Aided Design (CAD) in the 1980s has simplified the process by allowing designs to be scanned into the system and the
resultant images to be manipulated and optimised. Initially, samples generated by CAD were printed onto paper, but, with the advancement of printing technology, the designs can now be printed directly onto fabrics, thus saving time, cost and materials.

Ink jet printing of colour filters in LCDs uses appropriate coloured inks that are deposited on to glass and coated with a special transparent ‘receiver layer’. Materials that are used as receiver layer include resins, polymers such as polyamides and polyvinyl alcohols.

<table>
<thead>
<tr>
<th>Markets and Applications</th>
<th>Market/Application</th>
<th>Key player</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current</strong></td>
<td>Small home or small office</td>
<td>Hewlett-Packard, Canon, Epson</td>
</tr>
<tr>
<td></td>
<td>Office network</td>
<td>Tektronix, Hewlett-Packard</td>
</tr>
<tr>
<td></td>
<td>Graphic Arts</td>
<td>Iris, Tektronix, Epson</td>
</tr>
<tr>
<td></td>
<td>Industrial/postal marking</td>
<td>VideoJet, Marsh, Image, Willet</td>
</tr>
<tr>
<td></td>
<td>Large Format</td>
<td>ColourSpan, Encad, Hewlett-Packard, Mimaki</td>
</tr>
<tr>
<td><strong>Emerging</strong></td>
<td>Home photo</td>
<td>Hewlett-Packard, Epson, Canon</td>
</tr>
<tr>
<td></td>
<td>Colour copier</td>
<td>Hewlett-Packard, Canon</td>
</tr>
<tr>
<td></td>
<td>Multifunction</td>
<td>Hewlett-Packard, Canon</td>
</tr>
<tr>
<td></td>
<td>Digital colour press</td>
<td>Scitex, ACS, Tektronix</td>
</tr>
<tr>
<td></td>
<td>Grand format</td>
<td>Idanit, Vutek, Nur, ColourSpan, Mutoh</td>
</tr>
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<td></td>
<td>Textile</td>
<td>Canon, Seiren, Stork, Toxot</td>
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<td></td>
<td>Medical imaging</td>
<td>Iris, Sterling Diagnostic</td>
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<tr>
<td></td>
<td>3-D printing</td>
<td>3D system, Z Corporation</td>
</tr>
<tr>
<td></td>
<td>Computer-to-plate</td>
<td>Polychrome, Iris</td>
</tr>
</tbody>
</table>

Table 1.1 Applications of ink jet printing.
The recent introduction of affordable, good quality digital cameras has revolutionised the photographic industry. Instead of using conventional silver halide photography, consumers are now able to print their photographs using ‘photorealistic’ ink jet printers. This also makes it possible to print the photographs directly from the computer and not have to wait for days to get the prints back from the photo-developers. Currently, the ‘photorealistic’ dyes have poor image durability, especially light fastness when printed on standard paper.  

1.2 Ink

A very important aspect of ink jet printing is the chemistry of the inks, which not only dictates the quality of the printed image, but also affects the drop ejection characteristics and the reliability of the print system. Many different types of ink have been made and used (figure 1.6).

Aqueous based inks are commonly used in home and small office ink jet printers. Phase change inks are also known as hot melt or solid inks as they are solid at room temperature, but become a liquid when heated to about 60-125 °C. The ink is squirted out from the nozzle as a molten liquid and solidifies as soon as the droplet lands on the recording media. This prevents the ink from spreading, smearing and penetrating the recording media. Non-aqueous solvent-based inks are commonly used in industry for marking or coating applications on non-porous media such as plastic, metal or glass. Oil-based inks are used in large format printers and UV-curable inks are used to produce sharp, durable images on non-absorbent substrates such as metal, glass or plastics. Factors such as the availability of low-toxicity monomers and photoinitiators and printhead capabilities have hindered the progress and further development of these inks.
1.2.1 Ink development

For a printer to work at high speed and efficiency and at the same time achieve high quality hard copy, the ink must be designed to match the technology used and be compatible with the type of printer and the substrate used.

Both the common DOD printers in the office and the printers that are used in generating high quality photographic images for the emerging high value markets (table 1.1) use water-based inks and therefore will be the main focus in this thesis. They contain colourants (pigments or dyes), humectants (for viscosity control), deionised water (the carrier medium), surfactants (present for wetting and better penetration), biocides (to prevent biological growth), buffers (for pH control) and other additives such as chelating agents, defoamers and solubilisers.

Figure 1.6 Ink jet technology map
For a dye to be of use it must have intense colour, good light and wet fastness and high solubility. Intense colour depends on the presence of a chromophore with one or more polar substituents, the auxochromes. Auxochromes are functional groups on chromophores which influence the colour of the compound. The chromophore absorbs ultra violet (UV) radiation and therefore on its own is a weakly coloured compound. The auxochromes shift the absorption peaks from the UV to the visible range by stabilising the resonance forms of the structure. One of the most important chromophores is the azo group and the auxochrome most favoured is the sulfonic acid group.

In commercial applications, the colour of a dye is best defined by its position in 'three-dimensional (3-D) colour space'. There are several models of 3-D colour space (figure 1.7). The model used most widely is the L*a*b model, in which, the colours are arranged in a colour circle around the a and b axes, while 'lightness' which is the degree of 'whiteness' ranges from L=0 (zero 'whiteness' or total 'blackness') to L=100 (total 'whiteness') represents the perpendicular axis. A 2-D slice version of the colour space is called a colour map and an example of which is shown in figure 1.7. The brighter colours are found at the edge and the chroma (brightness of colour) is the distance from origin (a=0, b=0).

Figure 1.7 Colour map (x) and a 2-D colour slice (y)

1.2.2 Light fastness

Light fastness is a measure of a dye's ability to withstand exposure to light without undergoing degradation. There are many factors that bring about photodegradation.
For example, spectral light sources, \(^{27,28}\) atmospheric composition, \(^{27,29}\) humidity, \(^{27-31}\) and temperature, \(^{23,27,32}\) aggregation, \(^{27,28,30}\) dye concentration, \(^{27-30}\) and substrate influence. \(^{33-35}\) However, the most important factors that bring about dye degradation are light, atmospheric composition and aggregation. Light fastness of dyes is often assessed under accelerated test condition using Xenon or high-pressure mercury lamps. The UV light provided by these lamps accelerates dye fading. Atmospheric composition and humidity are important factors because they often relate to the presence of singlet oxygen (\(^1\text{O}_2\)), which is known to promote fading in dyes. \(^{36-37}\)

Increasing the temperature, as with most chemical reactions will increase rate, but in addition will promote the fading of a dye by increasing the ease with which moisture and/or oxygen diffuse into the substrate. Aggregation of dye molecules on the substrate plays an important part in photofading. Studies have shown that aggregated dyes are more light fast than fully dispersed dyes. In cellulose, it appears that the dyes build-up and in multilayers rather than discrete particles and lower layers of dye are protected from incident light through loss of sacrificial upper layers.

### 1.2.2.1 Dye fading mechanism

Azo dyes undergo photo-oxidation or photo-reduction depending upon the nature of the dye, substrate used and the atmospheric conditions. \(^{38-40}\) Those with electron-withdrawing groups such as CO\(_2\)H, NO\(_2\) and Cl are less light fast because strength of the azo link is decreased whilst electron-donating groups such as OH, CH\(_3\), C\(_6\)H\(_5\) and OCH\(_3\) enhance the light fastness. \(^{27,38,41}\) Figure 1.8 compares the general oxidative and reductive pathways, which are thought to occur in azo dye degradation. The reductive route has been confirmed for textiles but the oxidative step has yet to be verified. \(^{27,40}\) In the reductive route, the azo group abstracts a hydrogen from the polymer to give a hydrazo intermediate which eventually forms anilines while the oxidative route produces an azoxy group. Recent studies have elucidated an oxidative route which involves an active singlet oxygen (figure 1.9) which interacts with the dyes to produce quinines. \(^{27,42}\)
Chapter 1 Introduction

![Diagram of oxidative and reductive degradation pathways in dye degradation.]

Figure 1.8 Oxidative and reductive pathways in dye degradation.²⁷

![Diagram of oxidative degradation of azo phenols by singlet oxygen, leading to quinone products.]

Figure 1.9 Oxidative degradation of azo phenols by singlet oxygen, leading to quinone products.²⁷

Anthraquinone dyes also undergo oxidative and reductive decay.²⁷,⁴³ Substituents adjacent to the carbonyl group are capable of intramolecular hydrogen bonding as shown in figure 1.10. Absorption of light can change the ground state keto form into an enolic form in the excited state. The enol releases the absorbed energy in the form of heat, to return to the keto form with the chromophore intact. Research²⁹,⁴⁴ has shown that light fastness of hydroxy anthraquinones decreases as the number of
hydroxy groups increases. It also has been reported\textsuperscript{27} that 1-amino derivatives show poor light fastness in comparison to 1-hydroxy derivatives. This suggests that the hydrogen bond plays a vital role in photodegradation and a strong bond gives the anthraquinones dyes a better light fastness.

Figure 1.10 light promoted keto-enol conversion for hydroxy substituted anthraquinone dyes.\textsuperscript{27}

Triphenylmethane dyes, in the presence of oxygen, undergo photo-oxidation initiated by the ejection of an electron when the dye is excited to its triplet state (scheme 1.1).\textsuperscript{27,45-47} The radical di-cation and the solvated electron can recombine to restore the original dye or they can enter separate reactions as shown. Hydrogen peroxide was detected as a product of the fading reaction.

\begin{align*}
1^\text{D}^+ & \longrightarrow 3^\text{D}^+ \\
3^\text{D}^+ + \text{substrate or solvent} & \longrightarrow \text{D}^{++} + \text{e}^- (\text{solvated}) \\
\text{D}^+ + \text{e}^- (\text{solvated}) & \longrightarrow \text{D}^+ + \text{solvent} \\
2\text{D}^+ + \text{H}_2\text{O} & \longrightarrow \text{DH} + \text{D}^+ + \text{OH}^- \\
\text{e}^- (\text{solvated}) + \text{O}_2 & \longrightarrow \text{O}_2^- + \text{solvent} \\
\text{O}_2^- + \text{H}_2\text{O} & \Leftrightarrow \text{HO}_2^- + \text{OH}^- \\
2\text{HO}_2^- & \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{D}^+ + \text{H}_2\text{O}_2 & \longrightarrow \text{Oxidation products}
\end{align*}

Scheme 1.1 Reactions involved in the photofading of cationic triphenylmethane dyes\textsuperscript{27}
1.2.3 Ozone Fastness

Air pollutants such as NO\textsubscript{x}, SO\textsubscript{x} and O\textsubscript{3} can cause fading of the dye.\textsuperscript{48} However, ozone is responsible for most of the observable gas fading which eventually results in the destruction of the chromophore.\textsuperscript{48} The ability of a dye to withstand fading brought about by the presence of ozone (in ambient air) is termed as ozone fastness (OF).

Many factors\textsuperscript{48} contribute to the OF of the dye, however they all centre around a common factor, protecting the dye from ambient air.

- Print media- the OF of dyes are much better on polymeric prints rather than microporous prints. On this type of media, the dyes are protected from the outside environment and there's a lesser chance of the dye coming into contact with ozone present in the ambient air.
- Ink- the ink formation is important because it determines the penetrative depth of the dye. If the dye is deep within the media, once again, there's a reduced chance of the dye coming into contact with ambient air-borne ozone. Some ink formations also contain additives such as anti-oxidising agents that prevent, to a certain extent, the ozone from attacking the dye.
- Colorant- different dye types have different physio-chemical properties which in turn can determine how it behaves in the presence of ozone.

Most ink jet dyes are based on azo compounds. Matsui \textit{et al} studied\textsuperscript{49} the reaction of azo benzene with ozone and found that ozone causes fading by inserting into the azo link and in subsequent reactions, causing the azo link to break.

1.2.4 Wet fastness

A water-based ink depends on penetration and adsorption for its drying mechanism (figure 1.11).\textsuperscript{11} Some evaporation of water takes place, but this method of drying is slow and thus results in poor colour density and spot-resolution on paper. If the fibres
are coated with a water-receiving layer this can lower the wetting delay and control both ink spreading and penetration to improve colour density and resolution.

Figure 1.11 Dye spreading resulting from delayed wetting and slow evaporation.¹¹

The final print should be wet-fast so that if the paper gets wet, or rubbed with moist fingers, smudging does not occur. This is the main challenge in producing good aqueous inks. Initially, the dye should be highly water-soluble in the ink, but once printed on to the paper should effectively be water insoluble.

Figure 1.12 Use of pH dependent solubility to achieve both high dye solubility and high wet fastness.¹⁸,⁵₀,⁵¹

One of the effective ways of achieving high wet fastness is by using the concept of ‘differential solubility’¹⁸,⁵₀,⁵¹. A dye having substituents with appropriate pKₐ value can show high solubility in ink but low solubility on paper because water-based inks typically have a value pH 6.0 – 10.0 and papers are slightly acidic (pH 4.5 – 6.5). Thus, if the dye has a pKₐ of about 6.5 - 8.0, then it can have high water solubility in
an alkaline ink and be insoluble on acidic paper if the acidic form of dyes has low solubility. Figure 1.12 illustrates this concept.

The ‘smelling salts principle’\(^{18,50,51}\) is used to achieve wet fastness levels approaching 100%. Smelling salt is \((\text{NH}_4)_2\text{CO}_3\), the salt of a weak acid, carbonic acid and a weak base, ammonia. This salt is unstable and readily decomposes into its gaseous components, water vapour, carbon dioxide and ammonia (eq 1 in figure 1.13). This principle can be incorporated to obtain the dye as an ammonium salt of a carboxylate, which is unstable and loses ammonia by evaporation, producing the free carboxylic acid (figure 1.13). However, evaporation takes several hours and is associated with the smell of ammonia. This approach is used in making Pro-Jet Fast Black 2 (figure 1.14). The two approaches outlined above are used in producing wet fast cyan, magenta and yellow dyes, which are used commercially.

\[
\begin{align*}
\text{(NH}_4\text{)}_2\text{CO}_3 & \rightarrow 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad \text{Eq 1} \\
[\text{Dye}]-\text{CO}_2^+\text{NH}_4 \, (\text{soluble}) & \rightarrow [\text{Dye}]-\text{CO}_2\text{H} \, (\text{insoluble}) - \text{NH}_3
\end{align*}
\]

**Figure 1.13** The smelling salt approach to creating high wet fastness.\(^{3,18}\)

**Figure 1.14** Structure of Pro-jet fast black 2 dye.\(^{3,51}\)
Current research is directed towards making inkjet dyes that have instantaneous 100\% wet fastness, whilst at the same time retaining their image intensity (chroma), light fastness and reliability. One of the ways of tackling this problem is to create a dye that gives a very insoluble zwitterionic form at the pH of the paper surface.\(^{51}\) This is achieved by using a system which contain piperazino units, which have sulfonamido groups bonded directly or linked via a spacer group and sulfonic acid groups. Under alkaline conditions, the dyes are very soluble because the sulfonates are in their ionised form and the amines neutral. The dye becomes wet fast on the paper when both the sulfonate and protonated amino groups exist in a charged form as a zwitterion which is very insoluble in contact with cellulose due to the strong hydrogen bonding between dye and cellulose fibre (figure 1.15).

![Figure 1.15](image)

**Figure 1.15** High wet-fastness by zwitterionic dye design to formulate a dye that once bound to cellulose, is wet fast.\(^{3,51}\)

Good edge sharpness and non-bleed are essential features in ink formulation. An ink with low surface tension can be adsorbed rapidly onto the substrate without any lateral spread and is known as a penetrating ink. Non-penetrating inks, on the other hand, are mainly used in printing text when no adjacent colours are present. The behaviour of penetrating and non-penetrating inks is shown in figure 1.16
1.2.4 Colourants

There are two types of colourants: pigments (insoluble) and dyes (soluble). The chemical nature of the colourant largely determines the nature and extent of its interaction with the substrate\textsuperscript{18,21}

Non-penetrating inks

<table>
<thead>
<tr>
<th>Colour</th>
<th>Black</th>
<th>Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>Good optical density</td>
<td>Poor bleed</td>
</tr>
</tbody>
</table>

Penetrating ink

<table>
<thead>
<tr>
<th>Colour</th>
<th>Red</th>
<th>Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Moderate optical density</td>
<td>Good bleed</td>
</tr>
</tbody>
</table>

**Figure 1.16** Schematic representation of penetrating and non-penetrating inks.\textsuperscript{3}

Dyes can be further divided into 5 types: acid, direct, modified direct, reactive and disperse dyes\textsuperscript{52}. Acid and direct dyes\textsuperscript{52}, commonly used in the desktop ink jet printers, are ionic by nature. The early dyes were relatively small in size with low molecular weight and high aqueous solubility resulting in poor image durability. But, acid dyes are still used because of their high image intensity (chroma). Direct dyes\textsuperscript{52} are also widely used for printing. These dye molecules are much larger than the acid dyes and have an increased affinity for the substrate (paper). Direct dyes are quite soluble with a lower chroma in comparison to acid dyes. However, these dyes have a much better light and moderate to low wet fastness. Modified direct dyes\textsuperscript{52} are dyes with added functionality to enhance the interaction with media leading to improved performance on cellulose and thereby improve its wet and light fastness.

Reactive dyes\textsuperscript{52} contain groups that can react with cellulosic and protein substrates to form covalent bonds. They work under high temperature and pH and therefore are unsuitable for printing on paper or film.
Disperse dyes are insoluble dyes and are applied as finely dispersed aqueous inks on to the substrate. These dyes have high chroma, good image durability and are currently used on hydrophobic substrates such as polyester.

Pigments are insoluble colourants that are applied as fine particle dispersions. These dyes have high chroma and image durability, but they do not have any affinity to the substrate they are fired on to leading to rub fastness problems with the printed image.

1.2.5 Dyes

The dye colours required for ink jet printing are black and three subtractive primary colours: yellow, cyan and magenta. Light cyan and light magenta are used in photorealistic ink jet printing to achieve better skin tones. Mixing of these primary colours can produce any colour required.

Since earliest known history, colour has been used in all manner of decoration. Neanderthal man used red ochre to paint the corpses and coloured paintings adorn the walls of many caves in France, the earliest, dates back ca. 30,000 years. Egyptian mummies have been found wrapped in cloth dyed from the madder plant and Alexander the great is supposed to have deceived the Persians into thinking that his army was wounded, by sprinkling his soldiers with a red dye, probably madder juice, which contains the dye alizarin. A legend recorded on coins attests that Hercules, the god of strength, discovered Tyrian purple. His dog bit a snail, which stained its jaws purple. Mark Antony's flight from the crucial naval battle of Actium was especially conspicuous because he fled in Cleopatra's barge, which was carrying snails, known for their color royal purple.

Until the middle of the 19th century, all dyes available to man came from natural sources. Most of these were vegetable extracts and a few were animal products. The vegetable dyes that were used were Madder (red dye), Indigo (blue), Saffron (yellow), Weld (yellow) and Logwood.
In 1771 Woulfe\textsuperscript{54,57} prepared picric acid by the action of nitric acid on indigo and showed that it dyed silk in bright yellow shades. Laurent\textsuperscript{54,57} in 1842 converted phenol into picric acid and Perkin\textsuperscript{54,57} in 1856 discovered Mauve, the first synthetic dye to be manufactured and used for practical dyeing. Faraday\textsuperscript{54,57} discovered benzene in 1825 and Hofmann\textsuperscript{54,57} isolated it from coal tar in 1845.\textsuperscript{54,57} By 1869 Kekule\textsuperscript{54,57} established the structure of benzene. It paved the way for the systematic study of aromatic compounds and for the manufacture of synthetic dyes.

1.2.5.1 Black Dyes

Because of the large amount of text that is printed, black is a very important colour in ink jet printing. CI Food Black 2 (figure 1.17) was initially the black dye of choice because of its high water solubility leading to stable ink formulations.

![Figure 1.17 CI Food Black 2 (a) and Improved CI Food Black 2 with increased wet fastness (b)\textsuperscript{21}](image)

CI Food Black 2 gave good neutral shades of black,\textsuperscript{18,58} but, its high solubility results in poor wet fastness. Wet fastness was not improved until the late 1980s when the concept of differential solubility was applied\textsuperscript{21} (section 1.2.4) and some of the sulfonic acid groups were replaced with carboxylic acids.\textsuperscript{59,60} Figure 1.17 illustrate examples of the improved dyes.

Diaz\textsuperscript{61} (figure 1.18, 1), triazo\textsuperscript{62} (figure 1.18, 2) and tetrakisazo\textsuperscript{63} (figure 1.18, 3) dyes with a higher proportion of carboxylic acid groups have been developed for even
greater wet fastness. These employ the smelling salt principle (section 1.2.4), where the dyes exist as ammonium salts of all carboxylate and sulfonate groups.

To accommodate more groups, it proved necessary to lengthen the dye by incorporating more azo linkages. By coupling a larger aromatic diamine, the conjugation within the molecule is extended and this produces good neutral black shades.\textsuperscript{21} Diazo dyes are preferred over triazo and tetrakisazo dyes such as 2 and 3, the structures of these dyes are much more complex and therefore pose many synthetic problems.\textsuperscript{21} Metallised diazo dyes\textsuperscript{21} have also been proposed for ink jet printing as they have improved light fastness properties. But, these dyes often need to be mixed with a small amount of yellow dye to attain the required shade of black.\textsuperscript{64}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.18.png}
\caption{Improved black dyes used for printing.\textsuperscript{21}}
\end{figure}
1.2.5.2 Magenta dyes

There are a variety of magenta dyes in use. These either have high chroma or good light fastness and it has not yet been possible to incorporate both desirable characteristics together.

Magenta dyes can be divided into H-acid based dyes (arylazonaphthol) and gamma acid-based dyes (arylamine based structure). Tautomerism has a marked effect on the properties of the dyes. H-acid based dyes exist preferentially in the hydrazo form. In comparison, gamma acid-based dyes exist exclusively in the azo form (figure 1.19).

![Figure 1.19 Tautomerism in aryazonaphthol (A) and arylamine-based (B) dyes](image)

The H- acid type has been used for many years in the preparation and fine tuning of magenta dyes. They are bright, bluish-red with good water solubility and a moderate light fastness. The differential solubility approach has been used to improve their wet fastness. But, the synthesis of the magenta dyes requires the use of intermediates with a certain number of sulfonic acid groups. Thus, the effect of differential solubility is therefore greatly reduced.
Gamma acid derivatives tend to be more hypsochromic (shift to a shorter wavelength in the absorption spectrum) with a lower chroma and superior light fastness in comparison with the corresponding H-acids.

Light fastness of magenta can be improved by protecting the vulnerable azo linkage by complexing the dye with a metal such Cu$^{2+}$. Unfortunately, this is accompanied by reduction of chroma and water solubility brought about by dye aggregation.

There are a few non-azo magenta dyes used in aqueous ink systems; but they are all variations on the Xanthene structure. These dyes produce very bright inks, but have poor light and wet fastness properties.

1.2.5.3 Yellow dyes

Yellow dyes used in aqueous inks are almost exclusively azo dyes of two types, carbocyclic azo dyes and heterocyclic azo dyes. Carbocyclic azo dyes can be based on phenyl azo components (figure 1.20 A), napthyl azo components (figure 1.20 B) or it can be synthesised to have mixed chromophores (figure 1.20 C).

The heterocyclic dyes are all derived from carboxylic diazo analogues that are coupled to heterocyclic systems. There are two types of heterocyclic dyes and these are azopyrazolones and azopyridones. Azopyrazolones are bright, greenish yellow dyes with poor wet fastness and less than optimum light fastness (these dyes exist as the hydrazone tautomers) values. Wet fastness has been improved by creating larger molecules with greater substrate affinity through the use of diamino diazo components to link the molecules such as shown in figure 1.21.
Figure 1.20 Yellow dyes that are used commercially.\(^{21}\)

Figure 1.21 A diazo yellow dye\(^{21}\)

Azopyridone\(^{71}\) dyes like azopyrazolones, give bright, strong, greenish-yellow prints. These exist in a tautomeric equilibrium between the azo and the hydrazo form, with the latter being favoured. Figure 1.22 shows a yellow dye made from pyridone intermediates.
Figure 1.22 Yellow dye prepared from approach 2 using pyridone intermediates, which show good wet and light fastness.\textsuperscript{21}

1.2.5.4 Cyan dyes

Two main chromophores are used in making cyan dyes; triphenylmethanes and copper phthalocyanines.\textsuperscript{21} The triphenylmethanes were very popular in the early development of ink jet printing due to their bright colour of dye and most importantly because of the reliability of ink formulations. The main problem associated with these dyes was their poor photostability (i.e. light fastness).\textsuperscript{21} Phthalocyanines (figure 1.23), on the other hand, offer not only good colour, strength and reliability, but, also a significantly greater light fastness.\textsuperscript{38} Carboxylated phthalocyanine derivatives in the ammonium salt form are used for improved wet fastness.

Figure 1.23 CI direct blue shows improved light fastness.\textsuperscript{21}

1.3 Paper used in ink jet printing

The origins of paper have been traced to China in about AD 105. It reached Central Asia by 751 and Baghdad by 793 and by the 14\textsuperscript{th} century there were paper mills in several parts of Europe. The invention\textsuperscript{72} of the printing press around 1450 greatly
increased the demand for paper and at the beginning of the 19th century wood and other vegetable pulps began to replace rags as the principal source of fibre for papermaking.

Around 1798, Nicholas-Louis Robert constructed the first papermaking machine. Using a moving screen belt, paper was produced one sheet at a time by dipping a frame or mold with a screen bottom into a vat of pulp. A few years later, the process was improved by the brothers Henry and Sealy Fourdrinier and in 1809 John Dickinson invented the first cylinder machine.

Although almost all steps in papermaking have become highly mechanised, the basic process has remained essentially unchanged. First, the fibres are separated and wetted to produce the paper pulp, or stock. The pulp is then filtered on a woven screen to form a sheet of fibre, which is pressed and compacted to squeeze out most of the water. The remaining water is removed by evaporation and the dry sheet is further compressed and, depending upon the intended use, coated or impregnated with other substances.

The quality of a print is dependent on the ink used and the surface onto which the dye is applied. To obtain high quality images from aqueous-based dyes, it is necessary that the printing surface have properties, which allow controlled penetration of the water-based ink. This is complicated by the fact that the drying of the ink is accomplished by adsorption onto the paper. Instead of spreading on the paper in a regular fashion, the ink can travel along a cellulose fibre. This causes a problem called feathering, in which the drop spreads in an irregular fashion. If the ink penetration can be controlled, then drops of known dimension can be printed and they retain their regular shape. The spot diameter depends not only on the surface smoothness and the water absorptivity, but also on the ink jet nozzle diameter, ink pressure and physical properties of the dye such as viscosity, specific gravity of the ink, etc.
To obtain colour quality or maximum colour gamut, an opaque paper with a white, bright surface is required\(^7^5\). Plain paper, which consists simply of cellulose and filler, adsorbs the dye onto the surface. When light is shone on the paper, the reflection from the fibre/air interface limits the maximum optical density obtainable. This is because the white light the eye receives has not travelled through the ink layer. With uncontrolled spreading and feathering, the resolution of the print is further affected and the overall result is poor colour quality prints.

If a coating such as the swellable polymer, polyvinyl alcohol (PVA) polymer is applied on to the paper, the water-based ink stays on the surface after printing. The first surface reflection becomes specular and results in increased optical density and better saturation (figure 1.24). The light going through the ink layer must also be reflected\(^7^5\)

![Figure 1.24 Specular and diffuse surface reflections\(^7^5\)](image)

**1.3.1 Fillers\(^7^6\)**

Fillers were first added to the paper matrix to lower the cost. Today, however, fillers are added to improve the quality of the paper\(^7^6\). Fillers can perform various functions depending on amount added on to paper. These functions are as follows,

- Improving sheet formation by filling any empty areas around fibre crossings
- Provide a smooth and uniform surface
- Increase opacity and brightness
- Improving ink receptivity and reducing ink penetration
- Improve dimensional stability
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- Lower cost- fillers can replace higher cost fibre

Refractive index, particle morphology, particle size, specific surface area, brightness and particle charge are some of the important characteristics of fillers that have a great impact on the optical and physical behaviour of the paper.

Refractive index is a fundamental property of filler and is determined by its chemical composition and molecular structure. When light hits a filler particle, its is refracted from its path (light scattering), A high refractive index indicates a greater amount of reflected light, which in turn increases the opacity (proportional to light scattering) of the paper.

The shape, size and distribution of the particle are also important as they determine the way that light is reflected. This in turn affects the overall optical performance of the filler. Mie theory\textsuperscript{76} for light scattering predicts that maximum scattering is obtained by spherical particles (plastic particles, titanium dioxide and certain types of spherical calcium carbonate) one half the wavelength of light or between 0.2 - 0.3 μm in diameter. Particles that do not fall into this category scatter light less efficiently. Fillers with non-spherical particles (kaolin and talc) do not behave according to Mie theory. The shape of the particle also affects the packing ability of the dye, which in turn affects the sheet bulk and porosity.

Shape, size and distribution of the filler have a huge impact on the specific surface area. The filler's surface area affects not only light scattering, but also the strength and printing properties of the paper. High surface area fillers enhance the printing characteristic of the paper, but reduce the strength of the paper.

Whiteness and ‘brightness’ are measurements used in characterising fillers. Aluminium trihydroxide show the highest brightness followed by plastic pigments, precipitated calcium carbonates, precipitated silicas and sodium silicoaluminates.
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Particle charge is important for dispersion and retaining the filler within the paper. Van der Waals, electrostatic and steric (between adsorbed molecules or polymers) forces can affect the filler and determine whether filler remains dispersed or flocculated.

Abrasion is another important characteristic of fillers. Fillers that increase the abrasive character will cause excessive wear and tear of printing plates, paper machine wires and etc. Abrasiveness is due to crystalline nature of the filler (impurities, strength of atomic bonds, spatial arrangements) and its physical characteristics (size, shape, surface area).

The most commonly used fillers are clay, calcium carbonate, titanium dioxide, kaolin clays and talc. Amorphous silica and silicates, aluminium trihydroxides, barium sulfates and calcium sulfates are some of the fillers that are used for special applications.76

Since being introduced in the 1940s, the use of aluminium trihydroxide as a filler has grown rapidly. In 1992, the worldwide use of this filler was estimated around 10 000 tons. Aluminium trihydroxides increase brightness, ink receptivity and flame retardancy of paper. The raw material for the filler is bauxite ore, which is a mixture of various mineral forms aluminium hydrate, silica, iron oxide, titanium dioxide, clay and other impurities. The physical and performance properties of aluminium trihydroxide are outline in table 1.2 and further discussed in the following section.

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<thead>
<tr>
<th></th>
<th>Ground (natural)</th>
<th>Precipitated (synthetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index</td>
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<td>1.57</td>
</tr>
<tr>
<td>Specific gravity (g/m³)</td>
<td>2.42</td>
<td>2.42</td>
</tr>
<tr>
<td>TAPPI brightness (%)</td>
<td>97</td>
<td>100</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Einlehnner abrasion²</td>
<td>2-3</td>
<td>1-2</td>
</tr>
<tr>
<td>Particle size, sedigraph &gt; 5μm(%)</td>
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<td>-</td>
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</tbody>
</table>
Chapter 1 Introduction

<table>
<thead>
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<th>80</th>
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<tbody>
<tr>
<td>Particle size, sedigraph mean (μm)</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

*174000 rev

Table 1.2 Typical physical properties of aluminium trihydroxide fillers.\(^{96,77}\)

### 1.4 Aluminium hydroxides\(^{78,79,80}\)

Aluminium forms a wide range of oxides and hydroxides. Some of these are well characterised crystalline compounds, while others are amorphous and ill-defined. There are three main types of aluminium oxide/hydroxide, aluminium oxide \([\text{Al}_2\text{O}_3]\), aluminium oxy/hydroxide \([\text{Al}(\text{O})(\text{OH})]\) and aluminium hydroxide \([\text{Al}(\text{OH})_3]\), each of which can be subdivided into \(\alpha\) and \(\gamma\) forms (table 1.3). Other forms such as tohdite \((5\text{Al}_2\text{O}_3.\text{H}_2\text{O})\) exist but are less well documented.

<table>
<thead>
<tr>
<th>Oxide/hydroxide</th>
<th>(\alpha)-form</th>
<th>(\gamma)-form</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
<td>corundum</td>
<td>(\gamma)-alamina</td>
</tr>
<tr>
<td>(\text{Al}(\text{O})(\text{OH}))</td>
<td>diaspore</td>
<td>boehmite</td>
</tr>
<tr>
<td>(\text{Al}(\text{OH})_3)</td>
<td>bayerite</td>
<td>gibbsite</td>
</tr>
</tbody>
</table>

Table 1.3 Common forms of aluminium oxide/hydroxides

The structure of corundum is composed of hexagonal close-packed layers of oxygen ions with two-thirds of the octahedral holes occupied statistically by aluminium ions. This is the most thermodynamically stable of the aluminium oxide/hydroxides and is the final product of thermal or dehydroxylation treatments of all the oxides/hydroxides. It has a Mohs’ hardness of 9 and a density of 3.98 g cm\(^{-3}\).

\(\gamma\)-Alumina has no single defined structure and instead represents a collection of phases which are based on a defective spinel \((\text{M}^{2+}\text{M}^{3+}_2\text{O}_4)\) structure where the oxygen atoms are essentially cubic close packed and the aluminium ions are disordered within this lattice. A substantial number of these transition phases are
observed before ultimate reconstruction of the lattice to that of corundum (figure 1.25).

![Diagram of phase changes](image)

**Figure 1.25** Phase changes of aluminium oxide/hydroxides on heating\textsuperscript{78-80}

Diaspore (figure 1.26) is isostructural with \(\alpha\)-Fe(O)(OH) (goethite) and contains two independent oxygen atoms (\(O_1\) oxo and \(O_{1\parallel}\) hydroxyl). All aluminium ions are octahedral and bound to three \(O_1\) and three \(O_{1\parallel}\) (Al-\(O_1\) 1.85 Å and Al-\(O_{1\parallel}\) 1.98 Å). The resulting octahedra share edges to form “double rutile strings”. These are connected to each other by corner shared oxygens forming a 3-D network.

![Structure of diaspore](image)

**Figure 1.26** Structure of diaspore.\textsuperscript{78-80}

The structure of boehmite (figure 1.27) as a whole is not close packed, but the oxygen atoms within a layer are cubic close packed. As in diaspore there are two types of oxygen (\(O_1\) oxo and \(O_{1\parallel}\) hydroxyl). The structure can essentially be regarded as an Al/\(O_1\) sheet backbone with \(O_{1\parallel}\)H on the periphery of the sheet hydrogen bonded to \(O_{1\parallel}\)H of the adjacent sheet.
All forms of aluminium trihydroxide are built around the same basic unit, layers of \( \{\text{Al(OH)}_3\}_n \), and the differences between them result from the nature of the stacking of these layers. The layer can be described as a system of Al(OH)\(_6\) octahedra each sharing three edges, or as close-packed sheets of hydroxide ions stabilised by aluminium ions situated in two-thirds of the octahedral interstitial holes.

Bayerite contains approximately hexagonal close-packed anions with an interlayer spacing of 4.72 Å. The structure is monoclinic.

In the structure\(^{81}\) of gibbsite (figure 1.28) the layers are open-packed with neighbouring pairs, with the whole structure having approximately hexagonal symmetry. The interlayer spacing is larger than in bayerite at 4.85 Å. Gibbsite is usually monoclinic, but a triclinic form also exists\(^{78,79}\)
Nordstrandite represents an intermediate case of the two main aluminium trihydroxide structures with an interlayer spacing of 4.79 Å.

The Bayer process produces aluminium oxides and hydroxides, with most of the annual production going to make aluminium metal. Approximately 3.6 million tonnes of aluminium hydroxide per year is used outside of aluminium metal production. Much of this is used to make other aluminium compounds including, zeolites, aluminium sulfate for use in paper making and water treatment, aluminium fluoride, aluminium nitrate, aluminium chloride, poly(aluminium silicate sulfate), sodium aluminate, catalysts and titania pigment coating.

There are also many direct applications of aluminium hydroxide, which account for several hundred thousand tonnes annually. Approximately 200,000 tonnes per year worldwide is used as the basis of fire retardants in plastics. The fire retardant properties of aluminium hydroxide are due to its interference with the primary combustion stage. On heating to above 200 °C it decomposes to give alumina and water vapour (scheme 1.2). This reaction is strongly endothermic, absorbing 1.97 kJ g⁻¹ of aluminium hydroxide, thus removing heat from the reaction zone of the polymer and slowing the rate of decomposition. The water vapour (34.6 % by wt of Al(OH)₃) released also dilutes any combustible gases evolved and hinders the access of oxygen to the polymer thereby suppressing the fire.

\[
2 \text{Al(OH)}_3(s) \xrightarrow{>200°C} \text{Al}_2\text{O}_3(s) + 3 \text{H}_2\text{O}(g)
\]

Scheme 1.2 Mechanism of fire retardance of Al(OH)_3.

Toothpastes can contain up to 50 % by weight of aluminium hydroxide, as an abrasive filler. Aluminium hydroxide is particularly good in this regard as it has excellent cleansing properties but causes less damage to tooth enamel than other commonly used fillers such as chalk and calcium diphosphate. The degree of abrasivity and cleaning properties can be controlled by choice of particle size. Its non-toxicity, insolvability and compatibility with fluorides also enhance its suitability.
The paper industry uses\textsuperscript{76} aluminium hydroxide as both a filler and a coating. It has very high retention and dispersibility characteristics during paper manufacture and improves the retention behaviour of other fillers and pigments. As a coating it imparts high brightness, high opacity, high gloss and good ink receptivity.

Aluminium hydroxide is used as a cheaper alternative to titania in paint formulations\textsuperscript{82,83} It has been shown\textsuperscript{84} that a 25\% replacement of the titania can be made without loss of opacity.

High purity amorphous aluminium hydroxide gel is used\textsuperscript{85} in the pharmaceutical industry in antacid preparations and in medicines for the control of phosphate levels.

Alumina ceramics have superb resistance to heat, wear and chemicals, which means that they have a multiplicity of application in many areas of industry. These include laboratory ware (e.g. crucibles), spark plugs, electronics (e.g. integrated circuits), bioceramics (e.g. bone substitutes in joints and dental implants), armour (e.g. bullet-proof jackets), tableware and cutting tools\textsuperscript{83,84}.

High purity aluminas\textsuperscript{84,85} are used in the manufacture of synthetic gemstones such as rubies and yttrium aluminium garnets for lasers and sapphires for instrument windows and lasers.

1.5 Dye adsorption

Although both chemisorption and physisorption play\textsuperscript{25} an important role in dye adsorption, chemisorption presides over physisorption in the adsorption of dyes on the surface.
1.5.1 Interfacial Tension

Molecules in the surface or interfacial regions are subject to attractive forces from adjacent molecules, which result in an attraction into the bulk phase. This attraction tends to reduce the number of molecules in the surface region. Hence, work must be done to bring the molecules from the interior to the interface.

In water, the intermolecular interactions that produce surface tension are essentially composed of (a) London-Van Der Waals forces and (b) Hydrogen bonding. It is estimated that about one third of the interfacial tension is due to Van der Waals attraction and the remainder is due to hydrogen bonding. The interfacial tension between two phases is subject to the resultant force field made up of compounds arising from attractive forces in the bulk of each phase and forces operating across the interface.

The Gibbs Equation (Eq 5) relates the extent of adsorption at an interface to the change in interfacial tension. The equation predicts that substances, which reduce the surface (interfacial) tension \((\delta\gamma/\delta\ln a_i) < 0\), will be adsorbed at the interface. Electrolytes have the tendency to increase surface tension \((\gamma)\) and organic molecules with surface-active molecules (i.e. long chain fatty acids) to decrease surface tension.

\[
\Gamma_i = -\frac{1}{R} \left( \frac{\delta\gamma}{\delta\ln a_i} \right)_{T, P}
\]

Eq 5

Where

- \(\Gamma_i\) = surface concentration \((\text{mol m}^{-2})\)
- \(T\) = Absolute temperature
- \(\gamma\) = surface tension \((\text{Jm}^{-2})\)
- \(a_i\) = activity of species I
- \(R\) = gas constant
Chapter 1 Introduction

At solid-water interfaces, the orientation of hydrophilic and hydrophobic groups depends on the relative affinities for water and for solid surfaces.

1.5.2 Dye-substrate forces

There are many types of dye-fibre interactions and the strength of these interactions determines both the quality and durability of a particular print. The different forces that can exist between the dye molecule and the paper surface are:\(^87,88\)

- **Van der Waals forces** These define the size and shape specificity of the interactions and are the sum of dispersion and repulsive energies. The thermodynamic strength of these interactions is less than 8 kJ mol\(^{-1}\).

- **Electrostatic interactions** between static molecular charges. Hydrogen bonds between dye and cellulosic fibres are the predominant type of interaction present when printing on paper. Hydrogen bond strengths vary considerably, but for neutral molecules, these are with the range 10-65 kJ mol\(^{-1}\) and for ionic compounds, they increase up to 40-190 kJ mol\(^{-1}\).\(^87-90\)

- **Induction forces** due to the interaction between molecular charge distribution of one molecule and the proximity-induced charge of the other; such forces are small and can be disregarded when looking at dye-substrate interactions.\(^87\)

- **Charge transfer stabilisation** due to interactions of ground state (AB) with an excited state (A\(^+\)B\(^-\)). These forces are rather weak and can be discounted.

- **Solvophobic and hydrophobic interactions** which are crucial when determining dye uptake by substrate and wet fastness of the print.

- **Covalent bonds in reactive dyes** Cellulose-O-Dye is a strong bond. Common in textile dyes.
Vickerstaff suggested\textsuperscript{91} that hydrogen bonds were formed when the dye and cellulose were closely aligned. He confirmed this theory by dichroism. Further work\textsuperscript{92} by Arshid in 1956 showed that dyes were unlikely to form hydrogen bonds with simple solutes in water, because the cellulose had a firmly bound water layer and it would seem unlikely that the dye could get close enough to form hydrogen bonds. This hypothesis was confirmed by further evidence supported\textsuperscript{93-95} by Taylor & Rowlindson, Preston & Tawde and Allingham et al.

A form of hydrogen bonding in which the cellulosic hydroxyl groups are attracted by the $\pi$-electron system of the dye molecule was suggested\textsuperscript{96} by Bamford and later examined\textsuperscript{97} by Yoshida et al. This form of bond also requires close face-to-face alignment of the carbohydrates and the planar dye molecules. The bond involves multiple adjacent protons in the carbohydrates and $\pi$-electron system of the dye and seems to be effective even in the presence of water. This type of bonding is present in all dye molecules except azo dyes. The absence of $\pi$-bonding in this type of dye could be due to azo group reducing the electron density of the aromatic nuclei on either side and prevent bonding with carbohydrates.

In conclusion, the type of binding displayed by dyes is dependent on several factors, the structure of the dye itself, the ink solvent and the media being printed on.

When the fibrous cellulose layer is coated with an inorganic oxide such as silica or alumina, a porous structure\textsuperscript{98-100} of broad pore distribution can be formed. Pores of a specific radius selectively adsorb the dye in the ink and uniform optical density and dot diameter can be obtained without the dye bleeding, ink beading or ink repulsion regardless of whether hydrophilic or hydrophobic dyes are used. When using a porous layer with a particle radius greater or less than the range used (average particle diameter range 1-50 nm and pore volume range of 0.4-0.6 cm$^3$ g$^{-1}$), the ability of adsorbing the dyes is lowered and bleeding and beading of the dye is likely to take place. Also, the pore structure of the ink-receiving layer does not depend only on the kind of oxide used, but also on the production conditions such as type.
and mixing ratio of binder; the concentration, viscosity and dispersion state of coating liquid, the coating apparatus, the type of coating head, the coating amount etc.

1.6 Adsorption Isotherms

In this project, adsorption isotherms are to be used to investigate the strength of binding of model dyes to metal-oxides.

Adsorption can be considered in terms of isotherms, which show the relationship between the activity of adsorbate (substance in solution that becomes adsorbed at the surface of the solid) and the amount at constant concentration. These are used to study adsorption systems where the amount adsorbed is plotted against concentration at constant temperature under equilibrium conditions. The initial slope indicates the rate of change of site availability with increase in solute adsorbed. As more solute is taken up, the chance of an adsorbate molecule finding a suitable site to be adsorbed becomes increasingly difficult. Adsorption isotherms can provide information about (1) equilibrium constant for adsorption/desorption (2) no of sites available on the surface for monolayer coverage (3) binding strength of the ligand (4) surface coverage by one ligand (if “surface area” of ligand is known) (5) orientation of the ligand on the surface.

1.6.1 Isotherm types\textsuperscript{102,103}

Isotherms can be divided into four main classes $S$, $L$, $H$ and $C$ and further into several sub-groups 1, 2, 3, etc. (figure 1.29). The initial slope of the graph is used to classify the main classes of the isotherm with sub-group defined by the shape further from the origin.
The initial slope of an isotherm depends on the rate of change of site availability with increase in solute adsorbed.\textsuperscript{80,102,103} As more solute is adsorbed, there is usually progressively less chance that an approaching solute molecule will find a suitable site on which it can adsorb. This case applies in normal \textit{L} curves and in the latter stages of \textit{S} and \textit{H} curves. For the initial slope of \textit{S} curves the opposite condition applies and the more solute already adsorbed makes it easier for additional solute molecules to adsorb. This implies cooperative behaviour of the adsorbed molecules on the surface. In the case of \textit{C} curves the availability of adsorption sites remains constant at all concentrations up to saturation. The probable causes for these effects are described below.

In the \textit{S} curve, adsorption becomes easier as concentration is increased. To obtain this type of curve, the conditions (figure 1.30) that need to be fulfilled are that the solute molecule must be (1) monofunctional (such ligands are likely to be more weakly bound than polyfunctional and therefore more likely to experience significant competition from solvent molecules. For a strongly bound ligand competition from solvent would be negligible.), (2) show moderate intermolecular attractions allowing it to pack vertically in a regular array on the
surface and (3) compete for binding sites with solvent molecules or other adsorbed species.

The $L$ curve shows that as more sites in the substrates are filled, it becomes increasingly difficult for a solute molecule to find an available vacant site. In this type of system, the solute molecule is most likely to be adsorbed parallel to the substrate, or alternatively has little or no competition from solvent molecules. This type of adsorption systems can experience very strong intermolecular attraction. It is quite possible in these cases for the adsorbed ions to become associated in very large clusters just before adsorption takes place.\textsuperscript{102,103}

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure130.png}
\caption{Conditions for S curve isotherms - the solute molecule is more stable adsorbed at site a, adjacent to another adsorbed molecule than in isolation at site b. ii; Conditions for L curve isotherms - the bifunctional molecule is equally stable adsorbed at site a or b.\textsuperscript{80,102,103}}
\end{figure}

The $H$ curve is a special case of $L$ curve in which the solute has a very high affinity that is completely adsorbed at low concentration. Therefore, the initial slope of the curve is vertical. Examples of such solutes are ionic micelles and sulfonated dye ions that easily exchange with chloride ions (which have a lower affinity for the surface) on alumina.\textsuperscript{102,103}

The $C$ curve is characterised by the constant partitioning of solute between solution and substrate, right up to the maximum possible adsorption, where an abrupt change to the horizontal plateau takes place. The conditions that favour this type of curve are (1) porous substrate with flexible molecules and regions of differing degrees of
crystallinity, (2) solute has a higher affinity for substrate when compared with solvent and (3) solute has better penetrating powers due to condition (2). The linearity of the initial slope shows that the number of sites available for adsorption remains constant, i.e., as the vacant sites become occupied, more sites are created. Such a situation could arise when the solute penetrates the substrate, breaking inter-substrate bonds and opening up sites which were previously unavailable.

In figure 1.31, the substrate is microporous and the solute molecules (circles) have a higher affinity for the substrate than have those of the solvent. The entering molecule can be likened to a molecular wedge, forcing its way into the micropores of the substrate, which are thereby opened to access by following solute molecules. The penetration of substances is depicted in stages 1, 2 and 3. Solvent may, in some cases, accompany the solute into the pores. When the pores are filled, the solute may break into other regions and the adsorption process is then repeated.

![Diagram of C-type curve](image)

**Figure 1.31** C-type curve arising in the presence of a microporous structure. The solute can increase the number of available binding sites by penetrating into the substrate by breaking inter-substrate bonds.\(^{103}\)

The rate of adsorption is independent of any available area of substrate at any given time, because each molecule as it becomes adsorbed can generate a new vacant site. The rate is only dependent on the concentration of solute. This expansion of structure cannot continue indefinitely and a situation will arise where the primary expansion will result in secondary or even tertiary structure expansion. Examples of C-curve systems are (1) non-ionic dyes, which are highly polar, applied from water to polyethylene terephthalate which has a very low affinity for water and (2) Water
applied as a solute to wool from solution in n-butanol, which does not readily penetrate wool.

1.6.2 Interpretation of Isotherms\textsuperscript{102,103}

The simplest assumption in this study is that the adsorption sites on the surface of solid become occupied by an adsorbate from the solution. The conditions that are required for a Langmuir type adsorption equilibrium are (i) thermal equilibrium up to the formation of a monolayer, $\theta = 1$; (ii) the energy of adsorption is independent of $\theta$ (i.e., equal activity of all surface sites). Derivation of the Langmuir equation\textsuperscript{80} is shown in figure 1.32.

1) $n + [HL] \xrightarrow{K} n_A$

$n = \text{concentration of unoccupied surface sites mol}^{-1}$

$[HL] = \text{concentration of adsorbate in solution mol}^{-1}$

$n_A = \text{concentration of adsorbate on surface sites mol}^{-1}$

Applying the mass law to this equation gives:

2) $\frac{n_A}{n[HL]} = K = \exp\left(-\frac{\Delta G_{\text{ads}}^*}{RT}\right)$

The maximum concentration of surface sites $n_M$ is given by:

3) $n_M = n + n_A$

Thus:

4) $n_A = n_M \frac{K[HL]}{1 + K[HL]}$

The equation can also be written either as:

5) $\theta = \frac{K[HL]}{1 + K[HL]}$ where

6) $\theta = \frac{n_A}{n_M}$ or

7) $K[HL] = \frac{\theta}{1 - \theta}$

Figure 1.32 Derivation of Langmuir Equation.\textsuperscript{80,102,103}

The Langmuir model was developed for a solid-gas systems but can be modified for use in solid-solution systems based on the assumption that binding sites on a surface can become occupied by the solutes on a 1:1 stoichiometry. Other assumptions are that all binding sites are equivalent so that a ligand has no special preference for a
particular site and that the binding is not influenced by neighbouring bound ligands, i.e. the model does not take into account cooperative binding. If a maximum concentration of surface sites, \( n_M \) and surface of a substrate is known, then the required surface area per ligand can be calculated (figure 1.33).

\[
\text{Required surface area per molecule} = \frac{\text{surface area of substrate}}{n_M}
\]

**Figure 1.33** Equation for calculating the required surface area per molecule\(^ {80,102,103}\)

The Langmuir model\(^ {80,102,103}\) does not take into account charge, be it surface or ligand. And, as a result, the validity of the model breaks down, as the system becomes more complicated. Another limitation is that the model assumes monolayer coverage and with strongly binding ligands this can happen. This is not usually a problem, but, when dealing with weakly binding ligands, it is unlikely that monolayer coverage will be achieved and this can lead to an overestimation of the required surface area per ligand\(^ {80,102,103}\).

The model can be expanded to look at adsorbants with two binding sites at different affinities (figure 1.24).

\[
n_A = n_f \frac{K_1[HL]}{1 + K_1[HL]} + n_s \frac{K_2[HL]}{1 + K_2[HL]}
\]

**Figure 1.34** Adsorbants with two binding sites at different affinities\(^ {80,101-103}\)

Several other models have been developed for more complex behaviour. One of these is the Frumkin equation\(^ {80,101-103}\) (figure 1.35), also known as the Frumkin-Fowler-Gugenheim (FFG) equation. This takes into account lateral interactions at the surface, such as charged ions repelling each other within the adsorbed layer, by the addition to the Langmuir model of the \( \exp(-2a\theta) \) term, which reflects the extent of these interactions. An interaction coefficient of \( a > 0 \) indicates attraction, while \( a < 0 \) means repulsion.
\[ K[HL] = \frac{\theta}{1-\theta} \exp(-2a\theta) \]

**Figure 1.35** The Frumkin equation\(^{80,101-103}\)

### 1.7 Overview

This project will deal with the design, synthesis and evaluation of ink jet dyes to bind to inorganic oxide surfaces particularly that of aluminium oxide. Chapter 1 provides an overview on the ink jet printing industry but focusing mainly on printing on paper, ink development, papers required for printing, dyes and adsorption isotherms. ‘Simple’ azo dyes are considered in chapter 2 and binding of these dyes to aluminium trihydroxide [Al(OH)\(_3\)] will be examined. Dyes with different acidic functional groups will be applied to different papers via ink jet method and the prints will be analysed for their light, ozone and humidity fastness properties to determine the effect of these acidic functional groups on ink jet test properties. Chapter 3 will discuss the design and synthesis of complex phosphonic acid azo dyes and the corresponding binding and ink jet properties and lastly chapter 4 will consider the effects cyclodextrin on binding strength and ink jet tests results.
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CHAPTER 2

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2.1 Introduction

Phosphoric acid is used extensively in treatment of aluminium. Phosphonic and phosphinic acids have also been studied as corrosion inhibitors/adhesion promoters and there are a number of patents in this area. Adler et al studied a number of surface ligating groups for improving corrosion inhibition and adhesion properties and found that phosphorus-based ligating groups showed the best results by forming a structural layer on the aluminium surface. The adsorption of phosphonic groups on aluminium surfaces involves an acid base reaction, the driving force of which is the formation of an insoluble surface salt, with the phosphonic/phosphinic acid being able to bind through all available oxygen donors.

2.2 Synthesis and characterisation of ‘simple’ dye systems

The dye systems prepared in this chapter are shown (table 2.1). Full experimental details and characterisations for all compounds are given in section 2.3.

<table>
<thead>
<tr>
<th>Structure</th>
<th></th>
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<tr>
<td>4-(4'-hydroxylphenylazo)benzene sulfonic acid</td>
<td>1</td>
</tr>
<tr>
<td>4-(4'-hydroxyphenylazo)benzoic acid</td>
<td>2</td>
</tr>
<tr>
<td>4-(4'-hydroxyphenylazo)phenyl phosphonic acid</td>
<td>3</td>
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</tbody>
</table>

54
<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical Structure</th>
<th>Name</th>
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<td>3-(4'-hydroxyphenylazo)phenyl phosphonic acid</td>
</tr>
<tr>
<td>5</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>4-(4'-hydroxyphenylazo)benzyl phosphonic acid</td>
</tr>
<tr>
<td>6</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>3-(4'-aminophenylazo)phenyl phosphonic acid</td>
</tr>
<tr>
<td>7</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>3-(4'-hydroxyphenylazo)phenyl phosphinic acid</td>
</tr>
<tr>
<td>8</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>bis[(4-hydroxyphenylazo)phenyl] phosphinic acid</td>
</tr>
<tr>
<td>9</td>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>4-(4'-hydroxyphenylazo)phenyl boronic acid</td>
</tr>
<tr>
<td>10</td>
<td><img src="image7.png" alt="Structure 7" /></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.1 Dyes used for surface binding studies in this chapter.

2.2.1 Preparation of azo-dyes via diazotisation

Conversion of aniline derivatives to azo dyes is a well established reaction.\textsuperscript{11,12} Diazotisation is achieved through sodium nitrite acting on aromatic amine under acidic conditions at 0-4 °C.\textsuperscript{12} The overall process in which the diazonium ion is formed is outlined in section 2.1

\[
\text{NaNO}_2(aq) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{HNO}_2(aq)
\]

in the presence of $\text{H}^+$,

\[
\text{HO—N=O} + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}^+—\text{N=O}
\]

\[
\text{H}_2\text{O}^+—\text{N=O} \rightleftharpoons \text{H}_2\text{O} + \text{N}=\ddots
\]

\[
\begin{align*}
\text{NH}_2 & + \text{NH—N=} \\
\text{NH—N=O} & \rightleftharpoons \text{NH—NOH}
\end{align*}
\]

\[
\begin{align*}
\text{NH—N=} & \rightleftharpoons \text{NH—N=OH} \\
\text{NH—N=OH} & \rightleftharpoons \text{NH—N=OH}
\end{align*}
\]

\[
\text{X} + \text{H}_2\text{O} \rightleftharpoons \text{X} + \text{H}^+
\]

Scheme 2.1 Reaction of nitrous acid with aryl amines form arene diazonium salts that are stable at ice-bath temperatures.\textsuperscript{11}
A low temperature for this reaction is used for two reasons. First, the solubility of free nitrous acid is greater resulting in less nitrous gases escaping from the solution and the diazotisation of the aryl compound taking place more readily. Secondly, the instability of the diazonium salt requires the reaction to be carried out at low temperatures.

### 2.2.2 Preparation of azo dyes 1-10

Scheme 2.2 outlines the synthetic procedure used in the preparation of both the sulfonic and carboxylic azo dyes, 1 and 2 respectively. The yields were low because the dyes were in their sodium salt form, which made isolation difficult. Many attempts were made to purify the compounds and obtain them in their acid form. Synthetic details and characterisation data can be found in the experimental section. $^1$H and $^{13}$C NMR spectra of both compounds were as expected and details are given in the experimental section 2.3. The dyes decomposed before a melting point could be measured and these were recorded.

![Scheme 2.2 Synthetic procedure for preparation of 4-(4'-hydroxyphenylazo)-benzene acid dyes 1 and 2.](attachment:image.png)

**Scheme 2.2** Synthetic procedure for preparation of 4-(4'-hydroxyphenylazo)-benzene acid dyes 1 and 2.

The preparation of the 4-(4'-hydroxyphenylazo)benzenephosphonic acid dye (3) was difficult, as little synthetic work has been reported on phosphonic acid-substituted aromatics. Several routes were attempted before a workable method was found. The first attempt at making the $p$-phosphonic acid is outlined in scheme 2.3. It is assumed
that the palladium species used in the reaction undergoes oxidative addition with aryl bromide to give the intermediate aryl palladium complex, [ArPdBr(PPh$_3$)$_2$]. This intermediate is highly reactive and the phosphonic acid ester is inserted in place of the bromide. The catalyst is re-generated in the presence of triethylamine. The purified nitrobenzenephosphonic acid ester was reduced to the amine by a mixture of triethylamine and formic acid in the presence of palladium-carbon catalysts (scheme 2.4).

Scheme 2.3 First attempt to prepare 4-(4'-hydroxy-phenylazo)benzene phosphonic acid.\textsuperscript{13}

Scheme 2.4 Reduction of p-nitrophenylphosphonate using Pd/C and triethylammonium formate.\textsuperscript{14-16}

Although nitro groups have been reduced\textsuperscript{14-16} in this manner, the mechanism by which palladium catalyses the reaction is unknown. However, formate (HCO$_2^-$) is an
excellent source of $\text{H}^-$ and triethylammonium ($\text{Et}_3\text{N}^+$) can provide $\text{H}^+$ ions.$^{14-16}$ Therefore, the reduction of the nitro group can involve single electron transfer on the surface of the Pd in a mechanism that could possibly be analogous to the reduction of nitro groups involving Pd/C and $\text{H}_2$.

The $R$-aminophosphonic acid ester was hydrolysed using excess concentrated HCl to obtain the acid. Ethanol was added to aid dissolution. It was impossible to obtain the $p$-aminophenylphosphonic acid as a solid and it was thought that the final acid product might exist as a zwitterion. Further experimental work was not carried out using this method, as the yield each step was low.

The second method is outlined in scheme 2.5. In order to attach the phosphorus atom, the first step is to create a good leaving group such as bromide. Acetanilide was reacted with bromine at low temperature to produce $p$-bromoacetanilide. The acetamide group directs bromination to the paras position by sterically hindering the ortho positions on the aromatic ring. The procedure for the preparation$^{17}$ of aromatic phosphonates is an extension of the known Arbuzov reaction (also known as Michaelis-Arbuzov rearrangement) using a Ni catalyst.

\[ \begin{align*}
\text{amine} & \xrightarrow{\text{Br}_2, \text{acetic acid}} \text{Br-acetanilide} \\
\text{Br-acetanilide} & \xrightarrow{\text{P(OEt)}_2, \text{NiCl}_2} \text{P(OEt)}_2 \text{Br-acetanilide} \\
\text{P(OEt)}_2 \text{Br-acetanilide} & \xrightarrow{\text{HCl, reflux}} \text{P(OEt)}_2 \text{Br-acetanilide} \\
\text{P(OEt)}_2 \text{Br-acetanilide} & \xrightarrow{\text{NaNO}_2/\text{H}^+, \text{PhOH/McOH}} \text{P(OEt)}_2 \text{Br-acetanilide}
\end{align*} \]

Scheme 2.5 The synthesis of 4-($4'$-hydroxy-phenylazo)phenylphosphonic acid (3).$^{18}$

Previous studies$^{19}$ carried out on NiBr$_2$ with trialkyl phosphites and bromobenzene showed that the reactions were not inhibited when a radical scavenger was added. This means that the reaction does not proceed via a radical mechanism to replace the
bromine atom. Further work by Jensen\textsuperscript{20} reported a deeply coloured (blue-violet) compound, $X_2\text{Ni}\{(P(\text{OR})_3)_2$ when $X=\text{Br, Cl}$, which was later isolated. Based on this, it was thought that the catalysis proceeds through the elimination of a mixture of chloroethane or bromoethane to form a coordinatively unsaturated complex as shown in scheme 2.6. This is highly reactive and reacts with the aryl halogenate which is present in excess. The halogen is transferred to the Ni and at the same time a diethyl phosphonate group is generated, PO(OR)$_2$ which reacts with the aryl group reforming the catalyst. The ethyl halide which is generated early in the experiment can be collected in a short Dean-Stark apparatus, giving an indication of the progress of the reaction. Recrystallisation from ethyl acetate afforded crystals of a quality suitable for X-ray diffraction. The crystal structure is shown in figure 2.1\textsuperscript{21} and data are presented in Appendix.

Scheme 2.6 Possible mechanism for the NiCl$_2$ catalysis of bromide substitution.
In the solid state, 4-acetylaminophenyl-phosphonic acid diethyl ester forms hydrogen bonds between the amide nitrogen N-H and the P=O oxygen of a neighbouring molecule giving N...O contact of 2.910 Å as seen in figure 2.2 and figure 2.3.

Figure 2.1 The crystal structure of 4-acetylaminophenyl-phosphonic acid diethyl ester. Oxygen, phosphorus and nitrogen atoms are shown as red, purple and blue respectively.\(^{21}\)

Figure 2.2 Crystal structure of 4-acetylaminophenylphosphonic acid diethyl ester showing the hydrogen bond.\(^{21}\)
4-Acetylamino phenyl phosphonic acid diethyl ester was refluxed in excess conc. HCl for 3 days to deprotect the amino and phosphonic acid groups. Diazotisation of the \( p \)-aminophenyl)-phosphonic acid to form the azo dye 3 was carried out as described previously (scheme 2.2) and the dye was purified by Soxhlet extraction.

\( m \)-Aminophenyl phosphonic acid was prepared by nitration of phenyl phosphonic acid followed by reduction with \( H_2 \) using 10\% Pd/C (scheme 2.7)\(^{18}\). \( m \)-Aminophenylphosphonic acid was coupled to either aniline or phenol to prepare 3-(4\'-hydroxyphenylazo)phenyl phosphonic acid (4) and 3-(4\'-aminophenylazo)phenyl phosphonic acid (6) respectively, as described above for 1-3.
Scheme 2.7 Synthesis of 3-(4'-hydroxyphenylazo)phenylphosphonic acid (4) and 3-(4'-amino-phenylazo)phenylphosphonic acid (6).\(^1\)

Scheme 2.8 Synthesis of 4-(4'-hydroxyphenylazo)benzylphosphonic acid, 5.\(^2\)

Scheme 2.8 shows the steps involved in making 4-(4'-hydroxyphenylazo)benzyl phosphonic acid, 5 from commercially available 4-nitrobenzylbromide. This was phosphorylated and the nitro group reduced with ammonium formate and Pd/C. 4-Aminobenzylphosphonic acid ester was deprotected with conc. HCl. 4-(4'-hydroxyphenylazo)benzyl phosphonic acid, 5, was obtained as a ‘dull orange’ powder in a similar manner to 1-4.
Scheme 2.9 Synthesis of 3-(4'-hydroxy-phenylazo)phenylphosphinic acid, 7.\(^\text{18}\)

3-(4'-hydroxy-phenylazo)benzenephosphinic acid was prepared from commercially available phenylphosphinic acid as illustrated in scheme 2.9.\(^\text{18}\) \(m\)-Aminophenylphosphinic acid was coupled to phenol to generate 3-(4'-hydroxy-phenylazo)phenylphosphinic acid (7).

Scheme 2.10 Synthesis Bis[(4-hydroxyphenylazo)phenyl]phosphinic acid (8).\(^\text{23}\)

4-(4,4'-bishydroxyphenylazo)benzenephosphinic acid was prepared in a similar manner to 8 from commercially available biphenylphosphinic acid as outlined in scheme 2.10.\(^\text{23}\)
**Scheme 2.11** Synthesis of 4-(4'-hydroxy-phenylazo)phenylboronic acid, 9.\(^{24}\)

4-(4'-hydroxyphenylazo)phenylboronic acid was synthesised in a one-pot reaction from the commercially available 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and phenol as illustrated in scheme 2.11 using a similar method to DiCesare *et al.*\(^{24}\)

**Scheme 2.12** Synthesis of 4-(4'-hydroxy-phenylazo)phenylarsionic acid, 10.

4-(4'-hydroxy-phenylazo)benzenearsonic acid was obtained in a single step from commercially available 4-aminophenylarsionic acid as indicated in scheme 2.12.
2.2.3 NMR

A combination of spectroscopic techniques were used to characterise 1-10. The proton NMR spectrum of 3 and the atom labelling scheme used for interpretation are shown in figure 2.4.

Figure 2.4 Atom labelling scheme for the interpretation and the \( ^1H \) NMR proton spectra obtained for 3.

Figure 2.4 illustrates the structure of 3, and the protons that will be seen are labelled from \( a \) to \( h \). In the structure illustrated, \(-N=N-\) has the highest electron withdrawing properties. This is followed by the phosphonic acid group which is more electron withdrawing than the hydroxyl group. The proton peaks corresponding to \( a \) and \( d \) is at the far left of the nmr spectrum with the highest chemical shift. Protons \( b \) and \( c \) should ideally show \(^1H-^{31}P\) coupling. However, the peaks overlap with each other, and the final peak shows line broadening and it is impossible to see coupling or the \( a \) and \( d \) protons.
For 4 (figure 2.5), the protons $c$ and $d$ adjacent to the phosphonic acid group also give rise to multiplets through coupling to $^{31}\text{P}$ and the peaks appear at a slightly higher ppm value than in 3. The $^{31}\text{P}$ NMR spectrum gives a peak at 8.84 ppm (slightly lower than the p-substituted analogue, 3).  

$^{13}\text{C}$ NMR spectra were consistent with the proposed shielding for 3-10. Spectra were assigned with the aid of program gNMR©. The lower symmetry of the $m$-phosphonic acid substituted dye 4, as expected, leads to a larger number of peaks in comparison to 3 (table 2.2).

For all $^1\text{H}$ spectra for 3-10 dyes, the protons closest to phosphonic acid/phosphinic acid groups show multiplets through $^{31}\text{P}-^1\text{H}$ coupling with phosphorus. The phosphorus signal in $^{31}\text{P}$ spectra of the dyes falls in the range 8.8 - 9.2 ppm, slightly lower than in the parent aniline, e.g. $p$-aminophenylphosphonic acid.

Assignment of most of the $^{13}\text{C}$ spectra in 3-10 are shown in table 2.2 and figure 2.5. Entries are grouped according to whether the phosphorus acid groups are orientated para- (dyes 3, 5, 9, 10) or meta- (dyes 4, 6, 7, 8) relative to the azo substitution. Good agreement between observed chemical shift and those calculated using gNMR© programme was observed.
Figure 2.5 Carbon atom labelling scheme for interpretation of the $^{13}$C NMR of 3-10.
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Table 2.1 Comparison of calculated and observed chemical shifts for $^{13}$C NM spectra of 3-10.
2.2. 4 Electronic spectra of 1-10

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Table 2.1 Electronic spectra for dyes in NaHPO₃ buffer at pH 8 at 25 °C.

As all dyes 1-10 are observed to have similar colours, orange-dark orange, it is not surprising that these electronic spectra recorded in the range 300-500 nm in aqueous solution are similar.

![Absorption spectra of 3 and 8 recorded in water.](image)

Figure 2.1 Absorption spectra of 3 and 8 recorded in water.

Absorption spectra similar to 3 were obtained for all other dyes, apart from 8, regardless of functionality, position of head group or the type of tail group used. 8 is a biphenyl dye and display an additional shoulder in the visible region. This is due to
the presence of the second aromatic group. Absorption spectroscopy is based on transitions of \( n \) or \( \pi \) electrons to the \( \pi^* \) excited state. These transitions need an unsaturated group in the molecule to provide the \( \pi \) electrons. Biphenyl phosphinic acid (8) has two aromatic groups (unsaturated group) which can each give rise to separate \( \pi \rightarrow \pi^* \) transitions each. The errors involved in calculating the extinction coefficient were obtained from the Origin software package which was used to plot the absorbance against wavelength to determine the extinction coefficient.

2.3 Adsorption Isotherms

Adsorption isotherms to follow the uptake of dyes 1-10 from aqueous solution onto high surface area aluminium trihydroxide (ATH) were determined using procedures developed from earlier work at the University of Edinburgh.\(^{25,35}\)

As discussed in section 1.6, an adsorption isotherm plot can provide information on surface coverage and binding strength. Binding strength is displayed by the steep gradient of the initial part of the curve. When the curve reaches a plateau region, this signifies complete surface coverage or saturation point.

Numerical values for the surface coverage and equilibrium adsorption constant from adsorption isotherms were achieved by applying the Langmuir model using Origin software package and carrying out a curve fitting on the isotherm plot in a similar procedure used by other researchers.\(^{22,25}\)

2.3.1 Sulfonic and Carboxylic acid dyes, 1 and 2

The adsorption isotherms were determined as described in the experimental section and isotherm plots for 1 and 2 are illustrated in figure 2.7. Isotherm plot for 1 was determined using ICP whilst the plot for 2 was determined using UV-Vis to determine the residual concentration of ligand in solution (section 2.6.3).
The plots for 1 and 2 (figure 2.7) are almost linear and characteristic\(^2\) of very weak adsorption. There is also some indication that at very low residual concentration, dye 2 shows an 'S-type curve' (section 1.6.1)\(^2\) and 'cooperative adsorption', where when one molecule is adsorbed onto the surface site, some form of secondary bonding encourages the next molecule to bind on to the surface, at higher concentrations.

The isotherm plots 1 and 2 do not reach an upper limit (a plateau), associated with saturation of the surface with dye. Consequently it is not possible to obtain a value for the total surface coverage. We were unable to fit the sulfonic or the carboxylic acid azo dye (1 and 2) adsorption data to either a Langmuir or double Langmuir curve fitting equation due to the pseudo linear plots and 'S-type' behaviour at low concentrations.

![Figure 2.2 Adsorption isotherm plots for uptake of 1 and 2 on ATH at pH 8 and 25\(^\circ\) C.](image)

### 2.3.2 Phosphorus containing dyes

Aluminium complexes of phosphinic acids were first synthesised in 1964 by Coates and Murkherjee.\(^2\) From cryoscropic measurements they were found to be dimeric in solution and IR studies indicated that the phosphinates act as three atom bridges (1, 3 bridging mode) between the aluminium atoms. Many structures have been synthesised\(^2\) since, however, they all contain the phosphinate ligand binding in a
1,3 bridging fashion, indicating that it is the preferred coordination mode for aluminium.

In the diverse range of structures observed for these aluminium phosphonates, there are two predominant binding modes for phosphonates to aluminium. The first involves bonding of all three oxygen atoms to three separate aluminium atoms and occurs when the phosphonate is fully deprotonated \((\text{RPO}_3^{2-})\). In the second mode, the phosphonate is singly deprotonated \((\text{RPO}_3\text{H}^+)\) and only two oxygen atoms find two separate aluminium atoms forming a 1,3 bridge similar to that found in aluminium phosphinate chemistry. Both of these modes are common in metal phosphonate chemistry. Figure 2.8 illustrates the two predominant binding modes for phosphonate to aluminium.

![Figure 2.8](image)

**Figure 2.3** Potential binding modes\(^{35}\) of sulfonic, carboxylic and phosphonic acid groups.

Phosphinic and phosphonic acids have also been studied as corrosion inhibitors/adhesion promoters\(^{36,37}\) for metal/metal oxide surfaces and there are a number of patents\(^{38-44}\) in these areas.

In summary, previous research done on phosphonic acids, suggest that they have a high affinity for aluminium/oxides and the tendency of these acids is to form strong metal complexes.
2.3.2.1 Phosphonic acid dyes

A typical isotherm of phosphonic acid (3) is shown in figure 2.9. The isotherm plot is characterised by an initial steep slope indicating that the dye has a high affinity (strong binding strength) to ATH, probably 'H' type binding (chapter 1.6). 3 has a required surface area of 58 (12) Å² molecule⁻¹, calculated from monolayer coverage determined by the Langmuir model. Maximum surface coverage of 3 was calculated to be 20 (2) x 10⁻⁶ mol g⁻¹ and the equilibrium adsorption constant of was determined to be 821 (100) L mol⁻¹.

Figure 2.4 Adsorption isotherm plot for 3 (A) and a enlarged view of the adsorption at low concentrations (B).

A high binding strength as observed for 3 could be indicating that the phosphonic ligand/dye is forming polymeric metal complexes with the aluminium oxide.

Figure 2.10 illustrates the proposed acid-base interactions on the aluminium surface by Adler et al.⁴⁵ It is quite possible that 3 can interact as shown in fig 2.8 to bind through its multi-site attachments forming the polymeric metal complexes on surface which are highly stable. However, it is less likely that 1 and 2 form as stable multi-site attachments on the surface.
Another factor that is important in surface binding is anionic charge on the ligand. The phosphonic ligand (RPO$_3^{2-}$) has a higher charge than sulfonates (RSO$_3^-$) and carboxylates (RCO$_2^-$) and will thereby be more ‘basic’ and take part readily in the acid-base interactions as illustrated in figure 2.10.

In conclusion, absorption isotherms of phosphonic acid (3) shows much stronger binding in comparison to its sulfonic (1) and carboxylic (2) analogues. Such a result can be rationalised by recognising the key factors such as increased anionic charge, the tendency to form stable polymeric complexes with metals, especially aluminium oxide and the higher stability of the complexed species in solution.

Figure 2.11 illustrates the adsorption plots obtained for mono-phosphorylated dyes 3, 4 and 5. Data for 4 was fitted using Langmuir model as previously carried out for 3. However, 5 was fitted using double Langmuir model, which is a ‘two site’ model. Use of double Langmuir model suggests that there are two possible competing species (chapter 1.6). It is possibly that 5 in solution, at pH 8, can exist in two forms of deprotonated species, each with a strong affinity for ATH or that the flexibility afforded by the methyl link can lead to different orientations of the ligand on the surface.
On initial observations, the plots appear to show that all three monophosphonic acid dyes exhibit similar binding strengths (illustrated by the initial steep slope) but the surface coverage of the meta-substituted acid dye, 4, is significantly lower than the para-phosphonic acid and para-methylphosphonic acid analogues, 3 and 5. It is possible that the meta orientation of the functional group prevents 4 from binding approximately perpendicular to the surface (figure 2.12) in contrast to 3 and 4 and consequently much less efficient packing is achieved. Dye 4 has a surface coverage of $7.4 \times 10^{-6}$ mol g$^{-1}$ and the area occupied by a single molecule is $157 (30)$ Å$^2$. The equilibrium adsorption constant of 4 is $3210 (500)$ L mol$^{-1}$.

![Figure 2.6 Comparison of adsorption plots of 3, 4, 5 at pH 8 and 25 °C.](image)

Dye 5, which was fitted using double Langmuir model, has an equilibrium adsorption constant of $5000 (400)$ L mol$^{-1}$ and $5888 (900)$ L mol$^{-1}$ and surface coverage is $1.0 (4) \times 10^{-5}$ and $7.5 (1) \times 10^{-6}$. The area occupied by a molecule is $116 (55)$ Å$^2$ and $155 (45)$ Å$^2$. 
Dyes 4 and 6 differ only in the nature of the substituents (OH or NH$_2$) in their 'tail' group. 6 was once again fitted using double Langmuir model as illustrated in figure 2.15 to obtain a surface coverage of 30 (5) x 10$^{-6}$ mol g$^{-1}$ and 5.4 (1) x 10$^{-6}$ mol g$^{-1}$ and the area obtained by a single molecule is 39 (8) Å$^2$ molecule$^{-1}$ and 215 (50) Å$^2$ molecules$^{-1}$. The equilibrium adsorption constant of 6 is 3.3 (150) x 10$^{4}$ and 588 (0.1) x 10$^{3}$ L mol$^{-1}$. The values obtained for 4 and 6 suggest that whilst the binding strength of species remained the same, the surface coverage of 6 has doubled. Assembly of a 'double layer' of 6 based on a combination of electrostatic and hydrogen bonding between the partially deprotonated phosphonate groups in head groups of 6 and the protonated amino tails already tethered to the surface figure 2.13 (B) could account for the higher surface coverage.
2.3.3.2 Phosphinic acid dyes

The effect of changing the head group from dibasic phosphonic acid to monobasic phosphonic acid can be examined by comparing isotherms of the meta substituted dyes.

Figure 2.9 illustrates the adsorption isotherms obtain for 7, 8 and the comparison against phosphonic analogue, 4. Both isotherm plots were fitted with Langmuir model using Origin software. Surface coverage observed for 7 is 20 (2) x 10^{-6} \text{ mol g}^{-1} and the area occupied by a single molecule 58 (25) \text{ Å}^2 \text{ molecule}^{-1}. In comparison, 8 shows a surface coverage of 10 (1) x 10^{-6} \text{ mol g}^{-1} and the area occupied by a single molecule is 116 (75) \text{ Å}^2 \text{ molecule}^{-1}. The equilibrium adsorption constant of 7 and 8 are 418 (68) and 716 (171) \text{ L mol}^{-1} respectively.

Analysis of 7 and 8 against 4 (figure 2.14) reveals that the binding strengths of the phosphonic acid is smaller 418 (68) \text{ L mol}^{-1} for 7 compared against 3210 (500) \text{ L mol}^{-1} observed for 4 as expected. Phosphinic acids have only two oxygen donors and are monobasic. Therefore the electrostatic contribution is expected to be smaller. However, the overall surface coverage by 7 is higher than the surface coverage by 4.

![Figure 2.9 Adsorption isotherm plot for 4, 7 and 8 at pH 8 at 25°C.](image)

The results suggest that the phosphinic acid’s binding mode (using two oxygens instead of 3) allows a different orientation relative to the surface (more nearly
perpendicular) than the phosphonic acids. Such an arrangement is likely to lead to slightly weaker binding of 7. Due to the orientation of 7 on the surface (nearly perpendicular), the ligands will be able to pack more efficient and thereby increase the surface coverage.

7 and 8 have similar binding strength that is slightly smaller than the binding strength displayed by other dye molecules. The dye is monobasic, can only bind through two oxygens, but unlike 7, 8 cannot orientate itself on surface as described above due to its increased steric bulk (figure 2.15). This results in decreased surface coverage.

![Figure 2.10 Schematic representation of the orientation of 8 and 7.](image)

2.3.3 Boronic and arsonic acid dyes

The absorption isotherm for the para-substituted boronic acid dye, 9 and para-substituted boronic acid dye, 10, are compared with the phosphonic acid analogue in figure 2.16.

Due to problems with solubility, it was only possible to determine the isotherm for 9 at residual concentration $2 \times 10^{-3}$ mol dm$^{-3}$. The plot (figure 2.16 A) shows an almost linear form similar to that of carboxylic acid, 2 and even weaker bonding.
Figure 2.11 Adsorption isotherm plots comparing 3 and 9 (A) and 3 and 10 (B) at pH 8 and 25 °C.

The arsenic acid dye, 10, shows a very similar isotherm plot to that of its phosphonic acid analogue (figure 2.16 B). The surface coverage of 20 (2) x 10⁻⁶ mol⁻¹ g and the area occupied by a molecule is 58 (13) Å² molecule⁻¹. The equilibrium adsorption constant of 10 is 1178 L mol⁻¹. Arsonic and phosphonic acids have similar physio-chemical properties and therefore 10 was expected to have similar surface coverage to its phosphonic acid analogue, 3. This is observed in fig 2.16 (B).

The determination of the isotherms 1-10 gives an indication of what functionalised groups on what soluble dyes will lead to strong binding at aluminium oxide treated papers. The following section considers how variation in binding strength influences can influence the performance of ink jet dyes.
2.4 Performance of the model dyes when printed on paper

Tests to evaluate the performance of the model dyes, 1-10, when printed on a variety of papers are described in section 2.4.1. All the equipment for this work was located at Avecia's Laboratories in Blackley, Manchester which was used whilst on secondment. Many of the tests (see experimental section and acknowledgements) were carried out by Avecia staff.

2.4.1 Humidity fastness

Humidity fastness (HF) of dyes 3-4 were measured by exposing text prints (figure 2.17) of the individual dyes under humid conditions on different types of paper. The prints were observed and compared, by eye, against control prints used by Avecia under optical microscopy. The extent of dye migration was noted and scaled from 1-10, where 1 is excellent HF and 10 is poor HF. The results of the dyes are noted in table 2.4.

Non-commercial media is a development media with 80% alumina coating and PGPP is a premium glossy paper with 80% silica coating. HG 201 and PR 101 are white opaque films with alumina coated top layers.

<table>
<thead>
<tr>
<th>Paper</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG 201</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PR 101</td>
<td>2-3</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PGPP</td>
<td>2</td>
<td>2-3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Non-commercial media</td>
<td>1</td>
<td>7</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2.2 Humidity fastness values for 1-4 are measured on a 1-10 scale where 1 is good HF and 10 is poor HF.
Before and after humidity fastness test. Figure 2.12 Optical microscopic (x5 magnification) pictures of text prints of carboxylic acid dye, 2, before and after humidity fastness test.

Based on the adsorption isotherm results (section 2.3), 1 and 2 are expected to bind more weakly to alumina coated surface than 3 and 4. Table 2.4 indicates that dye 2 migrates easily on non commercial media with high alumina content. This is most likely to be due to the weak interactions between the dye and media resulting in poor weakly bound dyes that move easily (Poor HF). Surprisingly, 1 shows equally good humidity fastness on the alumina treated papers, non commercial media, HG 201 and PR 101. However, the test doesn’t discriminate between 1, 3 and 4- all show ‘scores’ in top/second best ranking. 1 and 2 also show poor performance on silica coated paper, PGPP and 3 and 4 show good performance in all papers.

In conclusion, results are consistent with the hypothesis that phosphonate functionalization of dyes improve their binding to alumina treated papers and possibly also to other oxides (e.g. silica). More discriminating tests are required to determine whether position of the functionalised groups has any effect on the overall humidity fastness and to distinguish between humidity fastness of sulfonic acids and phosphonic acids on high alumina content media.

Humidity fastness tests were not carried out for other dyes. For the purpose of humidity fastness, control of ink projection and lay down is essential as the test looks for dye migration from point of origin. However, a new test was designed to
accommodate the insolubilities of cyclodextrin (chapter 4) in the ink solution (high throughput screen which is a contact method of ink laydown-HTS). Unfortunately, control of ink projection is not feasible with this method, as the prints usually have too much dye making it difficult to measure dye migration accurately.

Overall, the results of the humidity fastness test indicate that phosphonic aside can bind strongly and thereby become water fast. It is assumed that phosphinics and arsonics have similar properties as their chemical behaviour is quite similar.

Light and ozone fastness of dyes with high binding strength is difficult to predict. Sections 2.4.2 and 2.4.3 discuss the light and ozone fastness of phosphonate dyes.

### 2.4.2 Light fastness

Table 2.5 shows the paper types used for ink jet test studies in this study. SEC Epson Premium Photo paper is a type of microporous glossy photo paper. It consists of a 20 μm silica /alumina (graded Al at top) layer, a 10 μm layer of carboxymethyl cellulose (CMC), 15 μm filled polythene, 100 μm of cellulose and 15 μm polythene + some inorganic components.

Canon PR 101 is also a type of microporous glossy photo paper which has a 20 μm alumina + CMC, 2 μm Ba₂SO₄, 100 μm cellulose, 3 μm of Ba₂SO₄ and 100 μm inorganic oxide and CMC. Barium sulfate is added to smooth the surface and give the paper a high optical reflectivity. The polymer layer ensures that the water based ink remains on the surface.

Canon HG 201 is a type of microporous white opaque film. This paper is quite acidic having a pH value of around 3.1-3.6. It consists of 30 μm alumina and 120 μm of Melinex/ Ba₂SO₄. Melinex is a type of polyester film used by photographic companies, combined with their own ink jet coatings, to produce supergloss prints. Polyester film has a mirror-like smooth surface that maximises the reflected light.
HP Premium Plus paper is a swellable acidic (pH 4.4) photo paper consisting of four layers. The first layer is a 30 μm layer of modified polyvinylacetate (PVA) and polyvinylphosphate (PVP) with inorganics, followed by 20 μm of polyethylene, 180 μm cellulose and 30 μm of polyethylene and silica (backing coat).

Ilford Printasia is a microporous glossy photo paper, consisting of 5 layers, with a pH of 6.4. The outer layer is gelatin + silica layer, followed by a polythene layer, cellulose, polythene and gelatin + silica layer.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Commercial name</th>
<th>Description</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEC Premium</td>
<td>Epson Premium Glossy Photo Paper</td>
<td>Silica coating</td>
<td>microporous</td>
</tr>
<tr>
<td>PR 101</td>
<td>Canon Photo Paper Pro</td>
<td>Alumina coating</td>
<td>microporous</td>
</tr>
<tr>
<td>HG 201</td>
<td>High Gloss Photo Film</td>
<td>Alumina coating</td>
<td>microporous</td>
</tr>
<tr>
<td>HP Premium</td>
<td>HP Premium Plus Photo Paper</td>
<td>Polymer coating</td>
<td>swellable</td>
</tr>
<tr>
<td>Printasia Paper</td>
<td>Ilford Printasia Photo Glossy Paper</td>
<td>polymer coating</td>
<td>swellable</td>
</tr>
<tr>
<td>PGPP Paper</td>
<td>Epson Premium Glossy Photo</td>
<td>silica</td>
<td>microporous</td>
</tr>
<tr>
<td>Non Development media</td>
<td>alumina</td>
<td>microporous</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3 Paper types used for ink jet tests

Some background to the measurement of light fastness in evaluating the performance of dyes was given in section 1.2.2. Procedures to evaluate the model dyes 1-10 in this chapter are described in some detail in the experimental section.

Light fastness (LF) is assessed using an accelerated test that determines the dye fading properties. Prints were tested on a Hewlett Packard UV weatherometer. Figure 2.18 shows internal layout of a typical weatherometer. An average office
illuminance is about 450 lux and a print in real life would be exposed to $450 \times 12 \times 365 = 1.971 \text{ Mlux hour.}^{48}$ The prints were exposed for an average of 20094 klux under a bank of fluorescent tubes which equates to about 9 years of exposure. Any dyes that exceed 35% ROD % loss within the study will be considered as 'failed' dyes. 35% density loss is considered the end point, objectionable fade, for a yellow and the end limit for magenta is 25%. These 'failure' points are set somewhat arbitrarily by ISO (International Organisation for standardization) and ANSI (American National Standards Institute) standards for photographic images. Commercial yellow dyes generally have chroma ~100, hue ~90 and ROD at 100% depth >1.9. Commercial dyes commonly last for about 10 years. Direct Yellow 86 and Direct Yellow 132 have a LF about 15 years and Acid Yellow 23 (not used in inkjet printing much as it has poor LF) fades to failure in less than 2 years. ROD % loss can be calculated by Eq 1. $^{48}$

$$\text{ROD } \% \text{ loss} = 100 \times (1-\text{Fade rod/initial rod}) \quad (\text{Eq 1})$$

Hue, along with saturation and brightness make up the three distinct attributes of colour (as defined in the colour space). The terms "red" and "blue" are primarily describing hue and therefore related to wavelength for spectral colours. Chroma, also known as saturation relates to the white amount and is used in describing purity of colours. A colour that is 100 percent saturated contains no white (monochromatic colours). A colour that has 0 percent saturation is white. $^{49}$ A more general discussion about colour maps, hue and chroma can be found in section 1.2.1.
The ROD values for the model dyes under study are quite low, when compared to commercial dyes which have some chromophores and several auxochromes resulting in intensely coloured compounds. The dyes under study are mainly composed of a single chromophore and two auxochromes and are therefore less intensely coloured. These dyes are more hypsochromic than commercial yellow dyes, meaning that much of their absorbance in the UV region of the spectrum and so does not contribute to the colour or density. Generally speaking it is straightforward to move the absorption of an azo dye by adding auxochromes - electron donating and withdrawing groups.

Solubility problems with the boronic acid dye meant that it was not used in the ink jet tests because solutions of high enough concentrations could not be prepared to give sufficiently high ROD values to allow accurate differences in ROD to be measured.

Analysis of the spectra of all dyes show that generally SEC premium (silica coated) and HP premium (polymeric coat) prints show high levels of LF whilst PR 101
(alumina coating) and HG 201 (alumina coating) prints show poor LF properties. These results are summarised in table 2.6 which highlights the best and worst performance on paper for each dye 1-8 and 10.

<table>
<thead>
<tr>
<th>Dye</th>
<th>ROD</th>
<th>Hue</th>
<th>Chroma</th>
<th>Best LF performance*</th>
<th>Worst LF performance**</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1.64-</td>
<td>91-37</td>
<td>103-64</td>
<td>HP Premium paper</td>
<td>PR 101 (alumina coat, sonic)</td>
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<tr>
<td></td>
<td>0.83</td>
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<td>(alumina coat, microporous)</td>
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<td>PR 101 (alumina coat, microporous)</td>
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<td>(silica coat, microporous)</td>
<td>(alumina coat, microporous)</td>
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<td>79-41</td>
<td>SEC premium glossy paper</td>
<td>PR 101 (alumina coat, microporous)</td>
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<tr>
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<td>0.047</td>
<td></td>
<td></td>
<td>(silica coat, microporous)</td>
<td>(alumina coat, microporous)</td>
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<td>4</td>
<td>0.59-</td>
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<td>24-16</td>
<td>Printasia (polymer coating)</td>
<td>PR 101 (alumina coat, microporous)</td>
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<td></td>
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</tr>
<tr>
<td>5</td>
<td>1.01-</td>
<td>59-38</td>
<td>97-35</td>
<td>SEC premium glossy paper</td>
<td>HG 201 (alumina coat, microporous, acidic)</td>
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<tr>
<td></td>
<td>0.48</td>
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<td>(silica coat, microporous)</td>
<td>(alumina coat, microporous)</td>
</tr>
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<td>6</td>
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<td>SEC premium glossy paper</td>
<td>PR 101 (alumina coat, microporous)</td>
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<tr>
<td></td>
<td>0.73</td>
<td></td>
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<td>(alumina coat, microporous)</td>
</tr>
<tr>
<td>7</td>
<td>0.16-</td>
<td>114-107</td>
<td>13-5</td>
<td>PR 101 (alumina coat, microporous)</td>
<td>HG 201 (alumina coat, microporous, acidic)</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td>(alumina coat, microporous)</td>
</tr>
<tr>
<td>8</td>
<td>1.24-</td>
<td>94-84</td>
<td>70-39</td>
<td>PR 101 (alumina coat, microporous)</td>
<td>HG 201 (alumina coat, microporous, acidic)</td>
</tr>
<tr>
<td></td>
<td>0.63</td>
<td></td>
<td></td>
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<td>(alumina coat, microporous)</td>
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<tr>
<td>9</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>10</td>
<td>2.06-</td>
<td>34-26</td>
<td>89-77</td>
<td>HP Premium paper</td>
<td>HG 201 (alumina coat, microporous, acidic)</td>
</tr>
<tr>
<td></td>
<td>1.89</td>
<td></td>
<td></td>
<td>(polymeric coat, swellable)</td>
<td>(alumina coat, microporous)</td>
</tr>
</tbody>
</table>

Table 2.4 Summary of LF properties for dyes 1-10

* Lowest ROD % loss (when there is no significant loss in ROD after 9 years, the highest initial ROD is chosen)

** Highest ROD% loss
Previous work\textsuperscript{51,52} has shown that LF is greatly dependent on the dye-media interactions. PR 101 and HG 201 are microporous media with an alumina oxide coating. Adsorption isotherm studies indicated that phosphonate dyes bind strongly to ATH. When printed, these dyes can bind strongly to ATH (confirmed by the high humidity fastness on inorganic oxide media) and possibly form polymeric metal complexes that will be stable on the surface. Consequently, these dyes will be attacked by oxidative and reductive species and will undergo fading. It is possible that phosphonate dyes do not bind that strongly with silica oxides and therefore only leaves a smaller number of dye molecules on the surface to be attacked (the remaining dye molecules might seep through cavities of the microporous layer and be contained within the paper). Hence, the dye might appear to have a better LF. HP Premium and Printasia have polymeric layers that swell up to encompass the dye and then effectively seal the dye within.

Figure 2.19 compares the light fastness of 3 on different papers at increasing levels of intensity. During the scope of the study, dyes printed on PR 101 and HG 201 lose 80\% of their ROD. Comparatively, the dyes printed on SEC and HP premium only lose 30\% of their ROD. Research carried out by Vikman \textit{et al}\textsuperscript{53} on kaolin coated papers suggests that LF is affected by physical and chemical properties of the coating. Therefore, it is possible that the difference in fading is due the strong binding of 3 to alumina paper. However, due to the limited knowledge on fastness properties on coated paper, it is difficult to suggest that the difference is solely due to difference in binding to the paper. However, it is quite likely that binding strength is an associated factor in the fading process.

Dyes 1-8 and 10 show fading, although on certain papers, the ROD\% loss is small. On some graphs, there is an increase in ROD after a short exposure. This could be due to the dye 'spreading' from the point of deposition to an area of lower concentration. This phenomenon is most common for SEC premium and HP premium papers, where dye interactions with media are small.
Figure 2.14 A comparison of the light fastness of 3 on different papers (see table 2.5 for the composition of these), based on the plots of percentage loss of ROD against total exposure in klux. (The dashed red line illustrates the fade limit of 35% of ROD% loss).

The absorption/reflection spectrum of the dye is dependant on the environment. It can change in different solvents (solvotochromism) and on different media. The electronic environment can change the position of the absorption band, the intensity and the shape of the band. Reflection/absorption spectra can differ in intensity due to surface roughness. The spectrodensitometer is set to measure only diffuse reflections and to exclude any specular reflections. Rough surfaces (microporous surfaces seen for HG 201, SEC premium and PR 101) contain less specular reflections and the detector sees these reflections as white light which effectively dilutes the diffuse spectrum, which appears lighter. For smoother surfaces, specular light is caught by the detector and the spectrum is therefore more saturated. The reflectance/absorption for any individual dye can differ from medium to medium in two ways. Firstly, because the electronic environment is different and secondly, because of the amount of white light measured in the detector caused by variations in the surface roughness of the medium.

Reflectance data for 3 was measured at 0, 34.8, 417, 4440, 12030, 20094 klux at wavelength 360-720 nm. Lux is a flux of light across an area per unit time and klux
is total quantity of light exposure. The reflectance values were then converted to absorbance values using Beer Lamberts Law (Equation 2.2). The absorption results for the dye prints should illustrate any electronic changes taking place for the dye as it decomposes and also indicates the concentration of remaining dye with exposure.

\[ A = \log_{10}(1/R) \]  

Equation 2.2

Figure 2.20 and figure 2.21 shows the effect of increasing exposure on dye 3 absorption at wavelengths 300-500 nm. The plots illustrate that SEC and HP and Printasia have similar absorption spectra that narrow with increasing intensity. In contrast, PR 101 and HG 201 display broad peaks that undergo dramatic reduction in absorption as the study progresses.

The spectra suggest that some degradation of dye is taking place in all dye prints. This is shown by the loss of density across the whole spectrum and the change in spectrum shape. However, the degradation seems quite slow on Printasia (E) which is a swellable polymeric coat. The more intense, broader spectrum on PR 101 (B) also loses density more quickly and the absorption maximum moves from \(~390\) nm to somewhere in the UV that is not monitored, suggesting a decomposition pathway to a chromophoric intermediate system.

In summary, the results indicate that the LF properties largely depend on the type of media and not the details of the dye design. However, more radically different dyes will have very different lightfastness. All dyes show significantly poor LF when printed onto the aluminium treated microporous papers, PR 101 and HG 201 paper, which could be due to the strong interactions between media and dye.
Figure 2.15 Comparison of absorption spectra of 3 on SEC premium (A), PR 101 (B), HG 201 (C).
2.4.3 Ozone fastness

The OF test is an accelerated ozone fade test, the conditions were that the concentration of ozone in the machine was 1ppm (compared to ambient indoor levels of several parts per billion) and the duration of the test was 24 hours. This test roughly equates to 250 days exposure. The composition of papers used in this study are defined in table 2.5 and figure 2.22 illustrates the OF of dyes 1-
8 and 10. Pr 101 and HG 201 show poor OF fastness (over 35% ROD loss). However, SEC and HP premium prints show better OF and they will be used for comparison. SEC premium prints seem to have better ozone fastness on dye 2 than other dyes (which could be associated to the poor binding to surfaces exhibited by the dye. Most dyes show very good OF on HP premium. This is due to the dyes being protected from the ambient air borne ozone by the polymeric coating of the media.

Figure 2.17 Comparison of OF for dyes 3-7 and 8 where the prints were generated in the ink lay down method. (The dashed red line illustrates the fade limit of 35% of ROD% loss).

Dye 8 shows the best OF. This could be due to the dye having two chromophores and losing one is less likely to have an adverse effect on the ROD compared to other dyes.

Figure 2.23 illustrates the OF of dyes 3 and 4 printed using ink jet method. The overall OF of all prints for 3 shows a much lower ROD % loss compared to the values obtained in the ink lay down method. In the ink lay down method, there is no control over how much ink is put down on the print. Therefore, we often see an excess of ink on the print. However, aggregation normally improves OF. Therefore,
the high OD loss are more likely due to some other factor. Ink jet printing delivers uniform spread of ink on the print and we get a more accurate indication of the OF of the dyes. However, both methods show the same trends and patterns of dye behaviour.

![Graph](image)

**Figure 2.18** Comparison of OF for dyes prints of 3 and 4 generated using the ink jet method. (The dashed red line illustrates the fade limit of 35% of ROD% loss).

All dye prints show good OF and 4 displays a better OF than 3 on most papers.

### 2.5 Conclusions

Strong binding of ATH is a good indication of a dye that would perform well in humidity fastness tests on inorganic oxide treated papers. It is possible that this strong binding has a detrimental effect on light fastness and ozone. Therefore it is necessary to find other means of improving the light and ozone fastness (Chapter 4).
2.6 Experimental

2.6.1 Chemicals and Instrumentation.

All reagents were used as obtained from Aldrich, Acros. Solvents were used as received. High surface area "superfine Al(OH)$_3$" was supplied by Alcan. Water was distilled before use.

$^1$H, $^{13}$C and $^{31}$P NMR were obtained using Bruker WP200 and AC250 spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent protons as internal standards. NMR spectra were interpreted with the aid of gNMR 4.1.0 (demo version) © 1995-1999 IvorySoft. Fast atom bombardment mass spectrometry (FABMS) was carried out using a Kratos MS50TC spectrometer a 3-nitrobenzyl alcohol (NOBA) or thioglycerol matrix. Electro Spray (ESI) mass spectra were obtained on a Thermoquest LCQ spectrometer in methanol. Electronic spectra were measured on an ATI UNICAM UV/vis spectrometer with 1cm path length quartz cuvettes. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed on a Thermo Jarrell Ash Iris ICP-AES spectrometer.

Curve fitting were performed using the programs Origin 5.0 © Microcal Software Inc and SigmaPlot 2000 (demo version) © 1986-2000 SPSS Inc.

Crystal data were collected on a Bruker Smart APEX CCD area detector equipped with an Oxford Cryosystems low-temperature device.

Ink jet tests were carried out at Avecia Labs in Blackley, Manchester. Lighfastness was tested on Atlas Ci5000 weatherometer and Ozone fastness was measured on Hampden 903 ozone cabinet.
2.6.2 Dye Synthesis

4-(4'-Hydroxy-phenylazo)benzenesulfonic acid (1)\(^{12}\)

An aqueous solution of sodium nitrite (0.759 g in 10 cm\(^3\)) was added to a solution of \((p\)-aminobenzene\)-sulfonic acid (1.53 g, 1.0 \(\times\) 10\(^{-2}\) mol) in conc. HCl (520 cm\(^3\)) at 0 \(^\circ\)C. The reaction mixture was stirred for 30 min at 0 \(^\circ\)C, then transferred to an addition funnel and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\(^3\)) at 0 \(^\circ\)C. The reaction mixture was stirred for 1 hour, the precipitate collected by filtration and dried under vacuum. The filtrate was retained, solvent removed and the residue dried under vacuum. Soxhlet extractions using ethanol were carried out on both crude products for 72 hours, solvent removed and the orange powder dried under vacuum. Combined yield (1.8 g, 65 \%). mp 282-285 \(^\circ\)C (dec) (lit.\(^{12}\) 283\(^\circ\)C). \(^1\)H NMR (250MHz, D\(_2\)O) \(\delta\) 7.80 (d, 2H), 7.60-7.78 (m, 4H), 6.98 (d, 2H). \(^13\)C NMR (90 MHz, D\(_2\)O) \(\delta\) 157.6, 152.5, 145.2, 139.4, 133.9, 122.6, 124.1, 116.1; ES (-ve ion), m/z peak 277.

4-(4'-Hydroxy-phenylazo)benzoic acid (2)\(^{12}\)

An aqueous solution of sodium nitrite (0.759 g in 10 cm\(^3\)) was poured into a solution of \((p\)-aminophenyl\)-carboxylic acid (1.53 g, 1.0 \(\times\) 10\(^{-2}\) mol) and conc. HCl (520 cm\(^3\)) at 0 \(^\circ\)C. The reaction mixture was stirred for 30 min at 0 \(^\circ\)C and added dropwise into a solution of phenol (6.9 g, 0.07mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\(^3\)) at 0 \(^\circ\)C. The reaction mixture was stirred for 1 hour, the
precipitate collected, stirred in methanol, rotary evaporated and dried under vacuum. The filtrate was retained, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were carried out on both products for 72 hours and dried under vacuum. The powder obtained (1.6 g, 66 %) had an mp 275-277 °C (dec) (lit., 54  277-279 °C). \(^1\)H NMR (250MHz, D\(_2\)O) \(\delta\) 7.98 (d, 2H) 7.76-7.84 (m, 4H), 6.98 (d, 2H). \(^{13}\)C NMR (90 MHz, D\(_2\)O) \(\delta\) 183.0, 157.6, 157.3, 145.2, 133.1, 130.4, 122.6, 124.1, 116.1. ES (- ve ion), m/z peak 241.

**p-Bromoacetanilide**

Acetanilide (27.0 g, 0.2 moles) was dissolved in acetic acid (90 cm\(^3\)) and the solution cooled to 10 °C in an ice/water bath. A solution of bromine (3.4 g, 0.212 moles) in acetic acid (90 cm\(^3\)) was added dropwise with stirring. The mixture was then stirred at room temperature for 30 min and poured into water (900 cm\(^3\)). The colour was removed by the addition of a small amount of sodium bisulfite. The solid was collected by filtration, washed with water and dried in a vacuum oven at 50 °C. The white crystals were obtained in high yield (42.5 g, 99.3 %). mp 165-7 °C (lit., 55  168. °C. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 9.16 (s, 1H), 7.70 (m, 4H), 4.05 (m, 4H), 2.17 (s, 3H), 1.28 (t, 6H); \(^{13}\)C NMR (90 MHz, CDCl\(_3\)) \(\delta\) 168.6, 114.5, 120.8, 138.8, 131.5, 24.2. FABMS m/z 215 (M+H\(^+\)).

**4-Acetylyaminophenyl) phosphonic acid diethyl ester**

\(p\)-Bromoacetanilide (50 g, 0.21 mol) and NiCl (3.5 g, 0.03 mol) were heated to 190 °C. Once the solid had melted, triethyl phosphite (44.8 cm\(^3\), 0.26 mol) was added dropwise with stirring, keeping the temperature between 180 - 200 °C throughout the addition. The bromoethane formed during the reaction was collected in a short Dean - Stark apparatus, fitted with a solid CO\(_2\) condenser. After complete addition, the
reaction was allowed to cool to 150 °C and stirred at this temperature for 30 min. The solution was cooled and stirred with 40/60 petroleum ether to give a fine grey solid which was collected, washed with 40/60 petroleum ether and dried in air. Recrystallisation from ethyl acetate gave colourless crystals. These crystals were of high purity and suitable for X-ray crystallography. (29.4 g, 51%); mp 134 °C; \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 9.16 (s, 1H), 7.70 (m, 4H), 4.05 (m, 4H), 2.17 (s, 3H), 1.28 (t, 6H), \(^1\)C NMR (90 MHz, CDCl\(_3\)) \(\delta\) 169.3, 142.55, 132.53, 121.81, 119.07, 62.06, 24.33, 16.12. \(^3\)P (90 MHz, CDCl\(_3\)) \(\delta\) 20.14 (1P); FABMS m/z 272 (M+H\(^+\)).

(4-Aminophenyl)-phosphonic acid

(4-Acetylamino phenyl)-phosphonic acid diethyl ester (28.1 g, 0.10 mol) was stirred at reflux in conc. HCl (700 cm\(^3\)) and ethanol (100 cm\(^3\)) overnight. The solution was cooled, concentrated to ~200 cm\(^3\) and placed in the fridge for 48 hours. The resulting precipitate was collected and dried in air (Batch 1, 12.6 g). The filtrate was concentrated further (~50 cm\(^3\)) and placed in the fridge overnight. The solid was collected and dried (Batch 2, 1.2 g). Solid remaining in the flask from the first filtration was washed out with acetone, the volume reduced and NaOH added to ca pH 7. The precipitate was filtered and dried to give Batch 3 (1.3g). All three batches decomposed at the same temperature. (15.1 g, 81 %); mp 251-252 °C (lit. 7; 254-256 °C) \(^1\)H NMR (250MHz, D\(_2\)O) \(\delta\) 7.40 (m, 2H), 6.69 (m, 2H); \(^1\)C NMR (90 MHz, D\(_2\)O) \(\delta\) 160.93, 131.91, 131.04, 115.68. \(^3\)P NMR (90 MHz, D\(_2\)O) \(\delta\) 13.55 (1P); FABMS m/z 174 (M+H\(^+\)).

4-(4'-Hydroxyphenylazo)-phenyl phosphonic acid (3)

\[ \text{H}_2\text{O}_3\text{P} \quad \text{N} \quad \text{N} \quad \text{O} \quad \text{OH} \]
A solution of sodium nitrite (4.6 g in water 10 cm$^3$) was added to a solution of (p-aminophenyl)-phosphonic acid (12.6 g, 0.07 mol) and conc. HCl (520 cm$^3$) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm$^3$) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, stirred in methanol, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were carried out on both products for 72 hours and the resultant powder was dried under vacuum. (9.4 g, 48 %); mp 277- 280 °C (dec); (Found: C, 49.6; H, 4.0; N, 8.5 %; C$_{12}$H$_{11}$N$_2$O$_4$P requires C, 51.8; H, 4.0; N, 10.1 %); $^1$H NMR (250 MHz, D$_2$O) $\delta$ 7.89 (d, 2H), 7.76-7.84 (m, 4H), 6.98 (d, 2H); $^{13}$C NMR (90 MHz, D$_2$O) $\delta$ 161.7, 153.5, 145.3, 140.5, 131.8, 125.19, 121.6, 116.2. $^{31}$P NMR (90 MHz, D$_2$O) $\delta$ 11.75. ES (−ve ion), m/z peak 277.

(3-Aminophenyl)-phosphonic acid

Phenylyphosphonic acid (25.0 g, 0.144 mol) was dissolved in conc. H$_2$SO$_4$ (102 cm$^3$) at 0-5 °C. Once all the solid had dissolved, H$_2$SO$_4$:HNO$_3$ (19.0 g:18.1 g) mixture was added dropwise with stirring at 0-5 °C. the solution was maintained at this temperature for 2 h and drowned in ice (300 g). The white precipitate (18.0 g, 61.5%) of m-nitrophenylphosphonic acid was recrystallised with hot acetic acid and reduced under H$_2$ for 6h using catalytic amounts of 10% Pd/C (0.3g). Yield 8.5g, 55.6%; mp (decomp) 290 °C (lit. 315 °C); $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.02 (d, 1H), 6.60 (d, 1H) 6.40 (d, 2H); $^{13}$C NMR (90 MHz, CD$_3$OD) $\delta$ 150.1, 117.4, 137.9, 121.8, 129.1, 112.3. $^{31}$P (90 MHz, CDCl$_3$) $\delta$ 25.0. FABMS m/z 174 (M+H$^+$$)$. 

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3-(4'-hydroxy-phenylazo)benzenephosphonic acid (4)\(^\text{18}\)

An aqueous solution of sodium nitrite (4.6 g in 10 cm\(^3\)) was poured into a solution of (m-aminophenyl)-phosphonic acid (12.6 g, 0.07 mol) and conc. HCl (520 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were carried out on the precipitate to give an orange powder. (2.6 g, 13 %); mp 268-261 °C (dec) \(^1\)H NMR (250MHz, CD\(_3\)OD) \(\delta\) 7.73-7.93 (m, 4H), 7.55 (m, 2H) 6.84 (d, 2H). \(^{13}\)C NMR (90 MHz, CD\(_3\)OD) \(\delta\) 162.0, 151.3, 144.9, 132.8, 128.3, 124.7, 122.5, 116.2. \(^{31}\)P NMR (90 MHz, CD\(_3\)OD) \(\delta\) 16.2. ES (-ve ion), m/z peak 277.

3-(4'-amino-phenylazo)phenylphosphonic acid (6)\(^\text{18}\)

(3-aminophenyl)-phosphonic acid was prepared as outlined above. An aqueous solution of sodium nitrite (4.6 g, 10 cm\(^3\)) was poured into a solution of (m-aminophenyl)-phosphonic acid (12.6 g, 0.07 mol) and conc. HCl (520 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of aniline (6.5 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were carried out on the precipitate. (2.6 g, 13 %); mp 268-261 °C (dec). \(^1\)H NMR (250 MHz, CD\(_3\)OD) \(\delta\) 7.02(d, 2H), 7.44(t, 1H), 7.78 (d, 2H), 7.72-7.84 (m, 2H), 8.2 (d,
1H). $^{13}$C NMR (90 MHz, CD$_3$OD) $\delta$ 116.24, 122.53, 122.16, 124.74, 131.79, 145.28, 161.71. $^{31}$P NMR (90 MHz, CD$_3$OD) $\delta$ 16.2. ES (-ve ion), m/z peak 276.

4-Nitrobenzylphosphonic acid diethylester$^{23}$

4-Nitrobenzyl bromide (4.85g, 0.022 mol) was stirred with triethyl phosphite (4.5 g, 0.025 mol) under N$_2$ and heated at 110 °C for 2h. The bromoethane formed during the reaction was collected in a short Dean and Stark apparatus, fitted with a CO$_2$ condenser. Reaction was followed by TLC (ethyl acetate:hexane on silica) and when the reaction was complete, the solution was cooled and excess triethyl phosphite was distilled off under vacuum. NMR and Mass spec showed that no starting materials were present and reaction had gone to completion (3.0 g, 50 %) bp 180-183 °C [lit. Error! Bookmark not defined. 183-187 (0.5 Torr) °C]. $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 8.14 (d, 2H), 7.38 (d, 2H), 3.8 (d, 4H), 3.5 (m, 8H), 1.8 (m, 12H). $^{13}$C NMR (90 MHz, D$_2$O) $\delta$ 164.7, 148.5, 127.9, 120.8, 27.3, 18.1, 10.3. $^{31}$P (90 MHz, CDCl$_3$) $\delta$ 25.0 (1P); FABMS m/z 274 (M+H$^+$).

4-Aminobenzyl phosphonic acid$^{23}$

Formic acid (6.8 cm$^3$, 0.00176 mol) was added dropwise to a stirred mixture (13.91 g, 0.05 mol) of 4-nitrobenzylphosphonic ester (31 cm$^3$, 0.002 mol) of triethylamine and 0.25 g of 5% Pd/C. The mixture was refluxed for 6 hrs, poured into water and extracted with dichloromethane. The combined organic layers were washed with brine, dried with MgSO$_4$ and rotary evaporated to get the desired compound (yellow-white solid; 6.0 g, 49 %). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 6.8 (d, 2H), 6.5 (d, 2H), 3.82 (d, 2H), 3.5 (m, 8H), 1.5 (m, 12H). $^{13}$C NMR (90 MHz, CDCl$_3$) $\delta$ 149.0, 129.7, 127.8 112.3, 48.0, 18.0, 11.0. $^{31}$P (90 M Hz, CDCl$_3$) $\delta$ 20.91. FABMS m/z 244
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(M+H⁺); p-aminobenzylphosphonic acid ester was hydrolysed in conc. HCl (500 ml) overnight and cooled to room temperature to obtain a pale yellow solid, p-aminobenzylphosphonic acid (3.0 g, 65 %) \(^1\)H NMR (250 MHz, MeOH) \(\delta\) 6.9 (d, 2H), 6.65 (d, 2H), 3.82 (d, 2H). \(^{13}\)C NMR (90 MHz, MeOH) \(\delta\) 148.5, 130.7, 128.0, 113.1. 16.6. FABMS m/z 188 (M+H⁺).

4-(4'-Hydroxyphenylazo)-benzylphosphonic acid (5)\(^{12}\)

An aqueous solution of sodium nitrite (4.6 g, 0.07 mol) was poured into a solution of p-aminobenzylphosphonic acid (13.1 g, 0.07 mol) and conc. HCl (520 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, stirred in methanol, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were carried out on both products for 72 hours and dried under vacuum (5.0 g, 24%). mp 272-285 °C (dec). \(^1\)H NMR (250 MHz, MeOH) \(\delta\) 7.8 (d, 2H), 7.70 (d, 2H), 7.3 (d, 2H), 6.19 (d, 2H), 3.2 (d, 2H). \(^{13}\)C NMR (63 MHz, MeOH) \(\delta\) 157.6, 151.3, 145.2, 143.7, 127.4, 122.1, 121.4, 116.1, 18.1. \(^{31}\)P (101 MHz, MeOH ) \(\delta\) 20.14. FABMS m/z 293 (M+H⁺).

3-Aminophenylphosphinic acid

Phenylphosphinic acid (25.0 g, 0.144 mol) was dissolved in conc. H\(_2\)SO\(_4\) (102 cm\(^3\)) at 0-5 °C. Once all the solid had dissolved, H\(_2\)SO\(_4\):HNO\(_3\) (19.0 g:18.1 g) mixture was added dropwise with stirring at 0-5 °C. the solution was maintained at this
temperature for 2 h and drowned in ice (300 g). The white precipitate, m-nitrophenylphosphinic acid was recrystallised from hot acetic acid and reduced under H₂ for 5 h using catalytic amounts of 10% Pd/C (0.3 g). Yield 20.0 g, 74 % mp 237 °C. (lit. 58 240-244 °C). ¹H NMR (250 MHz, CD₃OD) δ 8.5 (s, 1H), 8.3 (d, 1H), 8.1 (d, 1H), 2.17 (s, 3H), 7.5 (d, 1H). ¹³C NMR (63 MHz, CD₃OD) δ 150.1, 121.8, 137.9, 117.4, 129.1, 112.3. ³¹P (101 MHz, CD₃OD) δ 26.6. FABMS m/z 158 (M+H⁺).

3-(4'-Hydroxyphenylazo)phenylphosphinic acid (7)₁⁸

An aqueous solution of sodium nitrite (4.6 g, 0.07 mol) was poured into a solution of (m-aminophenyl)-phosphinic acid (11.0 g, 0.07 mol) and conc. HCl (520 cm³) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm³) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were carried out on the precipitate. (2.6 g, 14 %); mp 268-261 °C (dec) 7.02 (d, 2H), 7.6 (t, 1H), 7.78 (d, 2H), 7.72-7.84 (m, 2H), 8.2 (d, 1H). ¹³C NMR (63 MHz, CD₃OD) δ 157.6, 152.4, 145.2, 135.8, 137.5, 127.8, 128.7, 122.7, 124.7, 116.2. ³¹P NMR (101 MHz, CD₃OD) δ 16.2.; ES (- ve ion), m/z peak 261.
**Bis(3-aminophenyl)phosphinic acid**

Phenylphosphinic acid (25.0 g, 0.144 mol) was dissolved in conc. H₂SO₄ (102 cm³) at 0-5 °C. Once all the solid had dissolved, H₂SO₄:HNO₃ (19.0 g:18.1 g) mixture was added dropwise with stirring at 0-5 °C. the solution was maintained at this temperature for 2 h and drowned in ice (300 g). The white precipitate was purified from hot acetic acid and reduced under H₂ for 5h using catalytic amounts of 10% Pd/C (0.3 g) and recrystallised from ethanol to give a white powder (10.0 g 22%). mp 278-280 °C (dec) (lit. 23 287-289 °C). (dec) ^1^H NMR (250 MHz, CDCl₃) δ 8.6, (d, 2H) 8.5,(d, 2H), 8.1(d, 2H), 7.7 (d, 2H). ^13^C NMR (63 MHz, CDCl₃) ^13^C NMR (63 MHz, CD₂OD) δ 165.8, 140.6, 129.2, 120.8, 138.0, 125.9. ^31^P (101 MHz, CDCl₃) δ 20.1. FABMS m/z 309 (M+H⁺).

**Bis[4-hydroxy(phenylazo)phenyl]phosphinic acid (8)**

An aqueous solution of sodium nitrite (4.6 g, 0.07 mol) was poured into a solution of Bis(3-aminophenyl)phosphinic acid (21.6 g, 0.07 mol) and conc. HCl (520 cm³) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm³) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. Soxhlet extractions in ethanol were
carried out on the precipitate. (8.6 g, 27 %); mp 281-288 °C (dec) \(^1\)H NMR (250 MHz, CD\(_3\)OD) \(\delta\) 7.73-7.93 (m, 4H), 7.55-7.47 (m, 4H), 7.14 (D, 2H) 6.84 (d, 2H). \(^1\)C NMR (63 MHz, CDCl\(_3\) \(^1\)C NMR (63 MHz, CD\(_3\)OD) \(\delta\) 157.6, 152.4, 145.2, 135.8, 122.7, 128.7, 137.5, 127.8, 121.4, 116.1. \(^3\)P NMR (101 MHz, CD\(_3\)OD) \(\delta\) 16.2 (1P); ES (- ve ion), m/z peak 457.

### 4-(4'-Hydroxyphenylazo)-phenylboronic acid (9)

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5.0 g, 0.0228 mol) was obtained from Aldrich. An aqueous solution of sodium nitrite (4.6 g, 0.07 mol) was poured into a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12.6 g, 0.07 mol) and conc. HCl (520 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\(^3\)) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, stirred in methanol, rotary evaporated and dried under vacuum. The filtrate was kept, rotary evaporated and dried under vacuum. The boronic dye was de-protected by refluxing in 25% conc. HCl for 48 hours. Soxhlet extractions in methanol were carried out on both products for 72 hours and dried under vacuum Yield (1.5 g, 9%). mp 279-283 °C (dec) \(^1\)H NMR (250MHz, CD\(_3\)OD) \(\delta\) 7.68 (d, 2H), 7.60-7.4 (m, 4H), 6.98 (d, 2H). \(^1\)C NMR (250 MHz, CD\(_3\)OD) ES (- ve ion), m/z peak of 241. \(^1\)C NMR (63MHz, CD\(_3\)OD) \(\delta\) 157.0, 152.5, 145.2, 130.7, 128.8, 122.7, 124.1, 116.1; ES (- ve ion), m/z 241.
4-(4'-Hydroxyphenylazo)-phenylarsonic acid (10)\textsuperscript{12}

4-Aminophenylarsonic acid (5.0 g, 0.0228 mol) was obtained from Aldrich. An aqueous solution of sodium nitrite (4.6 g, 0.07 mol) was poured into a solution of 4-aminophenylarsonic acid (12.6 g, 0.07 mol) and conc. HCl (520 cm\textsuperscript{3}) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and added dropwise into a solution of phenol (6.9 g, 0.07 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm\textsuperscript{3}) at 0 °C. The reaction mixture was stirred for 1 hour, the precipitate collected, stirred in methanol, rotary evaporated and dried under vacuum and purified using Soxhlet extractions to get an orange powder. Yield (4.1, 18 %). mp 288-289 °C (dec) \textsuperscript{1}H NMR (250MHz, CD\textsubscript{3}OD) \textit{δ} 7.70 (d, 2H), 7.50-7.6 (m, 4H), 6.90 (d, 2H). \textsuperscript{13}C NMR (63MHz, CD\textsubscript{3}OD) \textit{δ} 157.6, 152.5, 145.2, 130.7, 128.8, 122.7, 124.1, 116.1; \textsuperscript{31}P NMR (90 MHz, CD\textsubscript{3}OD) \textit{δ} 11.75 (1P); ES (-ve ion), \textit{m/z} 320.

2.6.3 Adsorption isotherm measurements

A stock solution of a known concentration of dye in distilled water was prepared to the concentration 5 x 10\textsuperscript{-3} M in a standard flask. A series of solutions were prepared by removing known aliquots of stock solution at pH 8 (0.3) and making up to 10 ml with distilled water. Known amounts (ca. 0.4 g) of ATH were placed in 15 polycarbonated centrifuge tubes to which the diluted stock was added and stirred at 25 °C in a water bath for 2 h to allow the reaction to reach equilibrium. The tubes were centrifuged for 10 mins and the supernatant was filtered through Pasture pipettes fitted with glass wool to filter any residual ATH. Residual concentration was determined by ICP and isotherm plot was obtain when the residual concentration of dye was plotted against the amount of dye adsorbed by ATH using Microsoft Origin software package.\textsuperscript{22,25}
Carboxylic acid dyes could not be detected by ICP methods, therefore a UV/vis method was chosen where the absorption of each solution was measured at an appropriate wavelength to determine the residual concentration. The preparation of solutions for analysis were identical to that of the ICP technique. To obtain the isotherm plot, residual concentration of 2 was plotted against the amount adsorbed.25

2.6. 4 Ink Jet test methods

The inks were prepared according to a generic screening protocol ink preparation method.

2.6.4. 1 Ink preparation

The dye (0.35 g) was placed in a glass vial and dissolved in mixture of glycerol (0.75 g), thiodiglycol (0.75 g), urea (0.75 g), Surfynol 465 (0.1 g) and distilled water (7.3 g). The mixture was stirred for 30 mins and brought up to pH 8.5-9.5 by the addition of lithium hydroxide solution.

The ink solution was micro-filtered through a 0.45 µm syringe filter and the filtrate was placed in a ‘nib’ which was used in generating the prints using High Throughput Screen test (HTS) which is a contact method of ink laydown. This method was used in generating the prints for dyes 1-8 and 10.

Ink jet printing method was used for dyes 3 and 4 to obtain prints for OF. Preparation of the ink solution was identical to that used in HTS method. The ink solution was micro-filtered through a 0.45 µm syringe filter and injected (3-7 ml) into a clean BC21 monochrome ink cartridge. A small volume of ink was pulled through using a vacuum line and the cartridge was inserted into HP560 printer to generate prints.
2.6.4. 2 Print testing

2.6.4.2.1 Colour measurements

Reflected optical density (ROD), L, a, b, C and h of the prints were measured using Gretag Macbeth spectrodensitometer 24 h after printing.

2.6.4.2.2 Light fastness

The cards were mounted and were faded in Atlas Ci5000 weatherometer for the period of 100 hours. The print was measured before and after fading with Gretag Macbeth spectrodensitometer.

The Atlas Ci5000 weatherometer has a xenon arc lamp. Relative humidity and temperature are controlled in this machine. The lamp is held in a vertical position in the machine and the samples are placed in holders in circles around the lamp (there are 3 rows of samples, or 3 circles around the lamp). The samples sit below the lamps. The light intensity varies with age so before and during fade, the light intensity is monitored so how much light the samples have received is known and the illumination per hour is calculated. Heat and humidity is not controlled in this machine.

Lamp: Atlas 12000 W Xenon Burner. The lamp is changed after 2500 hours use to maintain near constant level of illumination.
Power: 0.8 W/m² - measured at 420nm.
Black Panel Temperature: 63 °C.
Relative Humidity: 50 %
Wavelength: 340 nm - no light passage <300 nm
Lamp Filters: Borosilicate inner; soda lime outer - combination results in simulation of exposure behind window glass in continuous light.
Exposure Time: Standard 100 hours
2.6.4.2.3 Humidity fastness

Expose a portion of text from the prints in a sealed humidity jar for 16 h at 60 °C. The prints were then analysed under optical microscopy and colour bleed into non-printed areas was evaluated qualitatively and the humidity fastness was determined by comparing the prints with control prints used by Avecia.

2.6.4.2.4 Ozone fastness

The ozone machine is a Hampden 903 ozone cabinet which generates ozone by UV light. The conditions used to test the dyes are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
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<td>Ozone Concentration:</td>
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<tr>
<td>Temperature:</td>
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</tr>
<tr>
<td>Relative Humidity:</td>
<td>50%</td>
</tr>
<tr>
<td>Exposure Time:</td>
<td>Standard 24 hours</td>
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</tbody>
</table>

The gas flow is controlled in the chamber, light is occluded and the samples are placed on holders on a carousel. There is a rotor at the centre of a X shape - at the end of each arm, there is a carousel so there are 4 carousels in total in the chamber. The rotor controlling the carousels moves the arms (the X) around the chamber and each carousel rotates thus each sample should see the same amount of ozone as they will all pass the same spaces in the chamber and the movement will ensure air movement to all areas in the chamber.

In all cases, the colour properties of the printed samples are measured before the test; they are mounted onto the required holder and placed in the machine.
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2.7 References

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49 http://www.sapdesignguild.org/resources/glossary_color/index1.html
50 http://www.screenweb.com/graphics/cont/weatherelementsbl.html
CHAPTER 3
Polyphosphonic acid dyes
Chapter 3 Polyphosphonic acid dyes

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3.1 Introduction

Given the high equilibrium adsorption constant to aluminium trihydroxide shown by the phosphonic acid-substituted dyes discussed in chapter 2, a range of dyes with more than one phosphonic group was targeted for study. It was hoped that extra phosphonic acid functionalities would also be able to attach to the oxide surface, thereby increasing the overall equilibrium adsorption constant of the dye. Ink jet tests would be carried out to determine the effect multi-phosphonic acid substituents have on their performance as dyes.

A variety of potentials dyes containing multiple substituents were designed for the study. Purification of the multiphosphonic acid dyes proved to be difficult. These are highly water-soluble and therefore recrystallisation of the crude product is complex. Column chromatography is difficult due to the close retention times for the side products. Lastly, the use of size-selective permeable membrane to remove salt and other impurities was attempted. However, due the small size of the polyphosphonic molecules (compared to commercial dyes), the dye is able to move through the smallest mesh. Due to the problems with purification of these dyes, attention was focused on those dyes which could be conveniently synthesised. These are listed in table 3.1.

<table>
<thead>
<tr>
<th>Structure</th>
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<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>11</td>
</tr>
<tr>
<td>4-(4-hydroxyphenylazo)phenol-2,6-bis methylphosphonic acid</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>12</td>
</tr>
<tr>
<td>4-(4-hydroxyphenylazo)phenyl-2,6-bis methylphosphonic acid</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.1 Dyes with more than one phosphonic acid substituents targeted for study (15 was supplied from Avecia).
3.2 Synthesis and attempted synthesis of polyphosphonic acid dyes, 11 and 12

Full experimental details for the preparation of and spectroscopic data used in characterisations of 11 and 12 are given in section 3.5.

Dye 11 which would have both a phenolic hydroxyl group and phosphonic acid groups available for binding to inorganic oxide surface was chosen as the methyl analogue 4-methyl-2,6-bis(phosphonomethyl)phenol has been shown to bind strongly to ATH\(^1\) and has proved to be an effective anti-corrosion agent for aluminium.\(^2\) Preparation of the aniline precursors, 5-Amino-2-hydroxy-3-phosphonomethylbenzylphosphonic acid and its tetraethyl ester, for the dye 11 proceeded smoothly using reaction outlined in scheme 3.1. 2, 6-(Bisbromomethyl)-4-nitrophenol and the related esters were prepared by methods described by De Mendoza \textit{et al}\(^3\) and Nation\(^4\). Reduction to the aniline followed a procedure developed earlier for \textit{meta}-aminophenyiphosphinic acid (section 2.5.2). Diazotisation of the diphosphonic acid or its tetraethyl ester and coupling to phenol appeared to proceed successfully, being accompanied by the generation of an intensely coloured solution. However, any attempt at purifying the crude dye to an acceptable standard proved unsuccessful due to dye solubility problems. Mass spec and NMR indicated that the dye was present and the result was confirmed by ICP-OES which gave an indication of the phosphorus (expected 415 ppm, found 375 ppm) concentration in stock solution. In the absence of starting and intermediate materials (not observed in Mass Spec or NMR), the phosphorus concentration gave an indication of the \(\geq 90\%\) purity of the dye and the remaining impurities was considered to be salts. UV-Vis, showed a broad peak in the visible region around 351 nm corresponding to the dye. Consequently the impure material was used in the determination of on adsorption isotherm on ATH (section 3.3).

Preparation of azo dye 12 analogous to 11 but carrying no phenolic OH from the surface binding functional group set was attempted using the reactions outlined in scheme 3.2. 2,6-(Bisbromomethyl)-4-nitrobenzene and the related esters were
prepared in a similar method to that described by Jacobson et al. Reduction to the aniline followed procedures developed earlier for meta-aminophenylphosphinic acid (section 2.5.2).

Scheme 3.1 Preparation of 4-(4-hydroxyphenylazo)phenol-2,6-bis methylphosphonic acid (11).³,⁴

Scheme 3.2 Preparation of 4-(4-hydroxyphenylazo)phenyl-2,6-bis methylphosphonic acid (12).⁴
Diazotisation of the diphosphonic and its tetra ethyl ester appeared to proceed successfully with a pronounced colour change from orange to brown upon the addition of phenol in MeOH/H2O. All attempts at purifying the crude compound to an acceptable level, by recrystallisation, sohxlet extraction and dialysis, proved unsuccessful. Mass spec (ES (- ve ion) m/z (crude product) 385) revealed a small peak corresponding to the dye and UV-Vis of the crude product in phosphate buffer (pH 8) revealed that the desired dye was present.

### 3.3 Attempted preparation of triazine based dyes

Full experimental details for the preparation of and spectroscopic data used in characterisations of 13 and 14 are given in section 3.5.

1,3,5- triazines have been known for over two hundred years, they are six membered heterocyclic rings with nitrogens in 1,3,5 positions. The most common starting material for the synthesis of the triazine derivatives is cyanuric chloride. It has been demonstrated previously that cyanuric chloride can be derivatised in a step-wise manner with the displacement of one, two or three chloride groups with nucelophiles via control of reaction temperature and/or pH.

Triazine groups are commonly used in dyestuff chemistry to combine chromophores and introduce tethering groups. Reactive dyes for cotton contain these triazine groups with two of the three chlorides replaced with chromophores or tethering groups. The remaining chloride reacts with the cellulosic fibres to firmly tether the dye on the textile.

Scheme 3.3 indicates the reaction mechanism for the one-pot synthesis of both 13 and 14. Attempts to replace the remaining chloro groups on the triazine unit with 2-aminomethyl phosphonate ester or diethyl {[(diethyloxyphosphorylmethyl)amino]methyl}phosphonate were monitored by TLC and deemed successful. However, isolation of the desired dye from its starting
Chapter 3 polyphosphonic acid dyes

Materials using column chromatography proved unsatisfactory due to very similar retention times of the side products generated in the reaction.

Scheme 3.3 Preparation of diphosphonic acid using cyanuric chloride.¹¹

Scheme 3.4 Dye 15 from Avecia research labs
Of the candidates di-, tri- and tetra- phosphonic acid-substituted dyes listed in table 3.1, 11 was the most readily prepared and a sample of 15 was produced by Avecia. These were used in the determination of adsorption isotherms to compare the strength of binding to ATH with the monophosphonic acid dyes (section 2.3.2.1). As there was no major increase in surface binding it was decided not to carry out additional work to develop effective routes 11-15.

3.4 Adsorption Isotherms

Stock solutions of 11 and 15 were prepared as outlined in section 2.5.3 and absorption isotherms to determine the equilibrium adsorption constant of 11 and 15 to ATH were measured in a similar manner.

Fitting the results presented on a Langmuir isotherm indicates that the equilibrium adsorption constant of 11, 870(80) L mol⁻¹ is similar to that of the monophosphonic acid dye 3, 821 (50) L mol⁻¹. The similarity of equilibrium adsorption constant and surface coverage {[20 (0.8) and 20 (5)] x 10⁻⁶ mol g⁻¹ for 3 and 11 respectively} is somewhat suprising and may indicate that only one phosphonic acid group in 11 is used in binding to the surface. However, the area occupied by 3 and 11 are comparable. This suggests that 11 is bound through all functional groups and is achieving monolayer coverage. However, 3 has yet to reach monolayer coverage. Previous work at Edinburgh on the methyl analogue gave similar results under different conditions but using the same ATH batch. Area occupied by 11 was calculated to be 58 (1) Å and is in good comparison with the methyl analogue which which was calculated to be 65(4) Å. The area occupied by 3 is 58 (5) Å.
Figure 3.1 Comparison of the adsorption isotherm plots of 3, 11 and 15.

The much larger dye molecule 15 which contains three phosphonic acid substitutes, show a similar equilibrium adsorption constant on ATH of 710 (70) L mol$^{-1}$ compared to 680 (50) L mol$^{-1}$ obtained for 3, again suggesting that possibly only one phosphonic acid group interacts with the surface. In this case, surface coverage shown by 15 is $10 \times 10^{-6}$ mol g$^{-1}$ which is approximately half that shown by 3 which is consistent with its significantly larger bulk.

3.5 Conclusion

The binding constant data obtained for 11 and 15 suggest that there is no significant benefit in incorporating more than one phosphonic acid surface-ligating group per dye molecule. Consequently it was decided that no further work would be undertaken to develop synthetic routes to the other dyes listed in table 3.1.
3.6 Experimental

3.6.1 Chemicals and Instrumentation

All reagents were used as obtained from Aldrich, Acros or Lancaster. Dye 15 was obtained from Avecia. Solvents were used as received. Water was distilled before use. Melting points was determined using a Gallenkamp melting point apparatus and are uncorrected.

3.6.2 Synthesis

8-Acetoxymethyl-6-nitro-1,3-benzodioxane

![Chemical Structure](image)

4-Nitrophenol (20 g, 0.14 mol) was added to a heated mixture (55-60 °C) of paraformaldehyde (17.3 g, 0.58 mol), acetic acid (100 cm³) and conc. H₂SO₄ (160 cm³) and the reaction maintained at this temp for 48 h. The mixture was allowed to cool to room temp and water (300 cm³) added. The solution was neutralised by slow addition of K₂CO₃ in aq. solution (ca. 0.56 mol). The colourless solid, which precipitated, was collected, washed with cold water, dried and recrystallised from ethanol to give 8-acetoxymethyl-6-nitro-1,3-benzodioxane (28.3 g, 80 %). M.p. 121-122 °C (lit. 3 118 °C). ¹H NMR (250 MHz, CDCl₃) δ 8.2 (d, 1H), 8.1 (d, 1H), 5.7 (s, 2H), 5.0 (s, 2H), 4.7 (s, 2H), 2.1 (s, 3H). ¹³C NMR (90 MHz, CDCl₃) δ 170, 155, 141, 125, 123, 121, 120, 91, 65, 59, 20. FABMS m/z 254 (M+H⁺).

2,6-Bis(bromomethyl)-4-nitrophenol

![Chemical Structure](image)
A mixture of 8-acetoxymethyl-6-nitro-1,3-benzodioxane (12.0 g, 0.047 mol) and 48\% hydrobromic acid (360 cm$^3$) was heated under reflux for 48 h, cooled and filtered at room temperature. The solid was washed with cold water and recrystallised from chloroform to give 2,6-bis(bromomethyl)-4-nitrophenol as a pale yellow solid (12.8 g, 84\%). M.p. 143- 145 °C (lit.\textsuperscript{3} 146-147 °C). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 8.2 (s, 2H), 4.6 (s, 4H). $^{13}$C NMR (90 MHz, CDCl$_3$) $\delta$ 158.3, 126.8, 126.6, 125.6, 27.0. FABMS m/z 326 (M+H$^+$).

5-Amino-2-hydroxy-3-phosphonomethylbenzylphosphonic acid

Triethyl phosphite (5.28 g, 0.03 mol) was added to 2,6-bis(bromomethyl)-4-nitrophenol (3.9 g, 0.012 mol) under N$_2$ and the resultant solution was maintained at 120 °C for 3 h (until TLC showed that reaction had gone to completion). Excess triethyl phosphite was removed under reduced pressure to obtain dimethyl [5-nitro-3-dimethoxyphosphonylmethyl]-2-hydroxy benzyl]-phosphonate as an analytically pure dark yellow oil (2.10 g, 40\%). The oil was used in the reduction step without any further purification. $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 8.2 (s, 2H), 4.2- 4.0 (m, 8H), 3.3- 3.2 (d, 4H), $\delta$ 1.4- 1.2 (m, 12H). $^{13}$C NMR (250 MHz, CDCl$_3$) $\delta$ 160.0, 141.0, 126.3, 121.7, 63.1, 28.5, 16.5. $^{31}$P NMR (90 MHz, CDCl$_3$) $\delta$ 28.0. FABMS m/z 440 (M+H$^+$).

The nitrophosphonate ester (2.0 g, 0.004 mol) was dissolved in MeOH (40 cm$^3$) and was reduced under H$_2$ in the presence of 5\% Pd/C (0.5 g) for 5 h. the catalyst was removed and the solution reduced to a small volume on a rotary evaporator to give a yellow oil residue. $^1$H NMR (90 MHz, CDCl$_3$) $\delta$ 7.2 (s, 2H), $\delta$ 3.6- 3.5 (m, 8H), $\delta$ 1.1- 1.3 (m, 12H) $^{13}$C NMR (250 MHz, CDCl$_3$) $\delta$ 152.3, 126.4, 122.0, 121.1, 67.1, 65.5, 13.5. $^{31}$P NMR (90 MHz, CDCl$_3$) 5.0. FABMS m/z 410 (M+H$^+$).
The amino di-ester was hydrolysed by reaction with conc. HCl/MeOH (50:450 cm$^3$) under reflux for 3 days to give (5-amino-2-hydroxy-3-phosphonomethylbenzyl)phosphonic acid as an yellow-orange oil in good yield (1.1 g, 95%). $^1$H NMR (250 MHz, CD$_3$OD) $\delta$ 6.8 (s, 2H), 3.4 (d, 4H). $^{13}$C NMR (90 MHz, CD$_3$OD) $\delta$ 149.3, 140.4, 122.0, 1201.1, 15.6. $^{31}$P NMR (90 MHz, CD$_3$OD) $\delta$ 30.0. FABMS m/z 296 (M-H$^-$).

Attempted synthesis of [2-hydroxy-5-(4-hydroxyphenylazo)-3-phosphonomethylbenzyl] phosphonic acid (11)

(5-Amino-2-hydroxy-3-phosphonomethylbenzyl)phosphonic acid (1.0 g, 0.003 mol) was diazotised and reacted with phenol (0.32 g, 0.003 mol) using the method outlined for dye 1 in section 2.5.2. No precipitate was formed and the solution was concentrated. $^1$H NMR (250 MHz, CD$_3$OD) $\delta$ 7.82 (d, 2H), 7.49 (d, 2H), 7.1 (d, 2H), 3.5 (d, 4H). $^{13}$C NMR (90 MHz, CD$_3$OD) $\delta$ 157.6, 154.8, 145.2, 144.0, 129.1, 124.1, 122.0, 116.1, 20.6. $^{31}$P NMR (90 MHz, CD$_3$OD) 30.0. ES (- ve ion), m/z peak 401. Analysis by NMR proved to be inconclusive. UV-Vis showed a broad absorption band with a peak at 351 nm. ICP-OES of the dye in a known stock solution indicated that the dye had a purity level of $\geq$ 90%.

[5-Amino-3-dimethoxyphosphonylmethyl]-2-hydroxybenzyl]-phosphonate (1.0 g, 0.002 mol) was diazotised and reacted with phenol (0.22 g, 0.002 mol) using the method described for dye 1 in section 2.5.2. A precipitate was not formed, therefore the solution was concentrated and hydrolysed to give [2-hydroxy-5-(4-hydroxyphenylazo)-3-phosphonomethylbenzyl] phosphonic acid (crude) and characterisation, as above, on the residual product gave identical analysis.
3,5-Di(bromomethyl)-1-nitrobenzene

A solution of 3,5-di(hydroxymethyl)-1-nitrobenzene (9.45 g, 0.05 mol), triphenylphosphine (26.2 g, 0.1 mol) and carbontetrabromide (33.1 g, 0.1 mol) in anhydrous ether (250 cm$^3$) was stirred at 25 °C for 60 h under a N$_2$ atmosphere. After removal of solvent, the residue was purified by flash silica gel column chromatography (Hex/EtOAc = 5/1) to give a bright yellow solid (6.9 g, 45%). M.p. 109-110 °C. (lit. 12 104-105 °C). $^1$H NMR (250 MHz, CDCl$_3$) δ 7.9 (s, 2H), 7.4 (s, 1H), 4.9 (d, 4H). $^{13}$C NMR (90 MHz, CDCl$_3$) δ 148.9, 138.9, 134.7, 123, 38.0. FABMS m/z 310 (M+H$^+$).

Dimethyl[3-(diethoxyphosphonylmethyl)-5-nitrobenzyl]phosphonate

3,5-Di(bromomethyl)-1-nitrobenzene (6.5 g, 0.021 mol) was dissolved in trimethyl phosphite (100 cm$^3$) of and heated to 80 °C for 12 h under N$_2$ atmosphere. After evaporation, the residue was purified using flash silica gel chromatography (CHCl$_3$/MeOH = 30/1) to give the phosphonic diester, dimethyl-3-(diethoxyphosphonylmethyl)-5-nitrobenzyl]phosphonate, as an off-white solid (4.2 g, 55%). $^1$H NMR (250 MHz, CDCl$_3$) δ 7.9 (s, 2H), 7.6 (s, 1H), 3.4-3.3 (m, 12H), 3.2-3.1 (d, 4H). $^{13}$C NMR (250 MHz, CDCl$_3$) δ 155.0, 142.0, 126.3, 121.7, 63.1, 16.5. $^{31}$P NMR (90 MHz, CDCl$_3$) δ 28.0. FABMS m/z 368 (M+H$^+$).
[3-Amino-5-phosphonylmethyl]benzyl phosphonic acid

Dimethyl 3-(diethoxyphosphonylmethyl)-5-nitrobenzyl]phosphonate (1.5 g, 0.004 mol) and of 10 % Pd/C (0.4 g) in of MeOH (40 cm³) was stirred under H₂ (40 psi) at 25 °C for 5h. The catalyst was removed and the residue was concentrated and purified using a silica column (Silica 60, CHCl₃/MeOH = 20:1) to give a white solid (1.0 g, 74 %). ¹H NMR (250 MHz, CDCl₃) δ 7.9 (s, 1H), 7.1 (d, 2H), 3.4 (d, 4H), 3.1 (s, 6H), 4.7 (s, 2H), 3.0 (d, 4H). ¹³C NMR (90 MHz, CDCl₃) δ 150.1, 142.0, 113.9, 109.7, 59.0, 16.9. FABMS m/z 338 (M+H⁺).

The amino di-ester was hydrolysed by reaction with conc. HCl/MeOH (50:450 cm³) under reflux for 3 days to give (5-amino-3-phosphonomethylbenzyl)phosphonic acid as an yellow-orange oil in good yield. (1.0 g, 75 %). ¹H NMR (250 MHz, CD₃OD) δ 6.8 (s, 1H), 6.7 (s, 2H), 3.4 (d, 4H). ¹³C NMR (90 MHz, CD₃OD) δ 149.3, 140.4, 122.0, 1201.1, 15.6. ³¹P NMR (90 MHz, CD₃OD) 28.0. FABMS m/z 282 (M+H⁺).

Attempted azo coupling reaction of [3-Amino-5-phosphonylmethyl]benzyl phosphonic acid with phenol (12)

(5-Amino-3-phosphonomethylbenzyl)phosphonic acid (1.0 g, 0.003 mol) was diazotised and coupled with phenol (0.31 g, 0.003 mol) using the method outlined in chapter 2. No precipitate was formed and the solution was concentrated. ES (- ve ion) m/z (crude product) 385. UV-Vis of crude product in Na₂PO₄/NaHPO₄ buffer showed a peak between 300-500 nm. Isolation and purification of product to a suitable level was not possible. The reaction was abandoned.
**Diethyl (aminomethyl)phosphonate**\(^\text{13}\)

Hydrazine hydrate (4.4 g, 0.09 mol) was added to diethyl (phthalimidomethyl)phosphonate, (25.0 g, 0.08 mol) in absolute ethanol (164 cm\(^3\)) and the mixture stirred at room temperature for 4 days. The white phthaloyl hydrazide precipitate was removed and the filtrate was concentrated under reduced pressure to provide diethyl (aminomethyl)phosphonate as a pale yellow oil (13.4 g, 100%). \(^1\)H NMR (250 MHz, CDCl\(_3\)) 4.4-4.3 (m, 4H), \(\delta\) 4.06 (d, 2H), \(\delta\) 1.55 (t, 6H). \(^{13}\)C NMR (90 MHz, CDCl\(_3\)) \(\delta\) 60.8, 37.2, 13.0. FABMS m/z 168 (M+H\(^+\)).

Diethyl (aminomethyl)phosphonate was hydrolysed by reaction with conc. HCl/MeOH (250 cm\(^3\)) under reflux for 3 days to give aminomethylphosphonic acid as a white powder (7.1 g, 80%). \(^1\)H NMR (250 MHz, CD\(_2\)OD) \(\delta\) 3.6 (d, 2H). \(^{13}\)C NMR (250 MHz, CD\(_2\)OD) \(\delta\) 18.0. \(^{31}\)P NMR (90 MHz, CD\(_2\)OD) \(\delta\) 25.1. FABMS m/z 112 (M+H\(^+\)).

**Diethyl \{[(diethoxyphosphorylmethyl)amino]methyl\}phosphonate**\(^\text{14}\)

Benzyamine (9.8 g, 0.09 mol) and diethyl phosphite (25.7 g, 0.187 mol) were mixed and cooled to 0-5 °C. Aqueous 37% formaldehyde (21.0 cm\(^3\), 0.28 mol) was added dropwise maintaining the reaction temperature under 10 °C. The resulting emulsion was stirred at room temperature for 30 min and then heated to 100 °C for 1 h. Water and excess formaldehyde were removed under reduced pressure to give analytically pure tetraethyl N-benzyliminobis(methylphosphonate) as a colourless oil. (72.0 g, 95%). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 7.9-7.2 (m, 5H), 4.2-4.0 (m, 8H) 3.9 (s, 2H), 4-1.3 (m, 12H). \(^{13}\)C NMR (90 MHz, CDCl\(_3\)) \(\delta\) 141.0, 128.5, 127.8, 127.1, 60.8 48.0, 20.4, 10.3. \(^{31}\)P NMR (90 MHz, CDCl\(_3\)) \(\delta\) 24.0. FABMS m/z 408 (M+H\(^+\)).
Ammonium formate (3.36 g, 0.05 mol) dissolved in distilled water (6 cm³) was added to the N-benzyl derivative (7.32 g, 0.02 mol) dissolved in EtOH (30 cm³), followed by 10% Pd/C (0.50 g). The mixture was stirred and heated to reflux for 1 h and a second portion of ammonium formate (3.36 g, 53.6 mol) added and reflux maintained for 1 h. The catalyst was filtered off and the solution was concentrated under reduced pressure. The residue was partitioned between CH₂Cl₂ and 10% aq. Na₂CO₃. The organic layer was separated, dried over Na₂SO₄ and the solvent removed under reduced pressure to obtain diethyl [(diethyloxyphosphorylmethyl)amino]methyl]phosphonate (4.4 g, 70%).

\[ {\text{H NMR(250 MHz, CDCl₃) } \delta 4.2-4.1(\text{ m, 8H}) \delta 3.7(\text{ d, 4H}) \delta 1.4-1.2(\text{ t, 12H}).} \]
\[ {\text{13C NMR (90 mHz, CDCl₃) } \delta 62, 58.0, 16.2.} \]
\[ {\text{31P NMR (90 MHz, CDCl₃) } \delta 26.0.} \]
\[ {\text{FABMS m/z 318 (M+H⁺).}} \]

Diethyl [(diethyloxyphosphorylmethyl)amino]methyl]phosphonate was hydrolysed by reaction with conc. HCl/MeOH (250 cm³) under reflux for 3 days to give iminobismethylphosphonic acid as a white powder (2.5 g, 88%).

\[ {\text{1H NMR (250 MHz, CD₂OD) } \delta 3.8(\text{ d, 4H}).} \]
\[ {\text{13C NMR (250 MHz, CD₂OD) } \delta 17.0.} \]
\[ {\text{31P NMR (90MHz, CD₂OD) } \delta 25.0.} \]
\[ {\text{FABMS m/z 206 (M+H⁺).}} \]

4-(4-hydroxyphenyl azo) aniline

An aqueous solution of sodium nitrite (10.1 g in 30 cm³) was added to a solution of p- aminoacetanilide (20 g, 0.13 mol) in conc. HCl (520 cm³) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then transferred to an addition funnel and added dropwise into a solution of phenol (13.4 g, 0.143 mol) and sodium carbonate (100 g, 1.0 mol) in 4:1 water-methanol (250 cm³) at 0 °C. The reaction mixture was stirred for 1 h, the precipitate collected by filtration and dried under vacuum. The solid was dissolved in EtOH/HCl (450:50 cm³) and was heated under reflux for 48 h. The resultant mixture was re-concentrated and the solid formed was filtered and dried. Soxhlet extractions using MeOH were carried out on the solid product for 72
h, followed by removal of solvent removed and the magenta powder obtained was dried under vacuum (19.8 g, 70%). $^1$H NMR (250 MHz, CD$_3$OD) $\delta$ 7.8 (d, 2H), 7.7 (d, 2H), 7.0 (d, 2H), 6.7 (d, 2H). $^{13}$C NMR (90 MHz, CD$_3$OD) $\delta$ 157.6, 152.4, 147.5, 140.7, 125.0, 122.5, 118.8, 110.5. ES (- ve ion), m/z peak 215.

**Reaction of aminomethylyphosphonic acid and 4-(4 hydroxyphenylazo) aniline with cyanuric chloride (13)**

4-(4 Hydroxyphenylazo) aniline (2.0, 0.01 mol) was dissolved in acetone:water mixture (1:1, 200 cm$^3$) and added dropwise to cyanuric chloride (1.7 g, 0.01 mol) in acetone (200 cm$^3$) maintaining the pH at 6 and the reaction temperature under 10 °C. The progress of the reaction was monitored by TLC (n-proponal/methylethylketone/conc. ammonia = 1/1/1). Once the reaction was complete, aminomethylyphosphonic acid (2.2 g, 0.02 mol) was added to the reaction mixture and the temperature was raised to 35-40 °C and stirred vigorously for 4 h followed by another addition of aminomethylyphosphonic acid (2.2 g, 0.02 mol) and heated under reflux with vigorous stirring for further 4 h. The resultant mixture was cooled and concentrated. ES (- ve ion), m/z 511. Isolation and purification of the desired compound on a silica column (n-proponal/methylethylketone/conc. ammonia = 1/1/1) proved unsatisfactory.
Iminobismethylphosphonic acid (4.12 g, 0.02 mol) and 4-(4-hydroxyphenylazo) aniline (2.0, 0.01 mol) were reacted with cyanuric chloride (1.7 g, 0.01 mol) in the manner discussed for 13. The resultant mixture was cooled and concentrated. ES (-ve ion), m/z 699. Similar purification techniques were attempted with no success.

### 3.6.3 Adsorption Isotherms

The isotherm tests were carried out in the same manner for dyes 11 and 15 as described in section 2.6.3.
3.6 References

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4.1 Introduction

Recently it has been shown that enclosing the azo group of a 'reactive' dye in the cavity of α-cyclodextrin (α-CD) significantly improves its resistance to reductive, oxidative and photo bleaching when used on textiles. In order to establish whether this approach can be used on dyes 1-8 and 10 to improve their ink jet properties by forming strong inclusion complexes with cyclodextrin, it is necessary to demonstrate firstly that the dyes are capable of forming such inclusion complexes with α-CD and secondly to show that surface ligating dyes encapsulated within the cyclodextrin cavity can still bind strongly to the oxide surface through their pendant functional groups.

Cyclodextrins (CDs) are cyclic oligosaccharides built from glucopyranose rings that have a hydrophobic interior and a hydrophilic exterior due to primary and secondary hydroxyl groups on the rim. CDs consist of three main types; α- (6 glucopyranose rings), β- (7 glucopyranose rings) and γ- (8 glucopyranose rings) and the structure of α-cyclodextrin is illustrated in figure 4.1.

![Figure 4.1](image)

Figure 4.1 Structure of α-cyclodextrin (A) and illustration of the primary and secondary hydroxyl groups on CDs (B).

By the end of the 1960s, large-scale laboratory preparative methods for CDs were known. The structure, physical and chemical properties and inclusion complex
forming properties were also known and well exploited. Table 4.1 lists the important characteristics of CDs and figure 4.2 show the dimensions of the cyclodextrins.

<table>
<thead>
<tr>
<th>No of glucose units</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol wt</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Solubility in water, g 100 ml⁻¹ at RT</td>
<td>14.5</td>
<td>1.85</td>
<td>23.2</td>
</tr>
<tr>
<td>[α]₂₅°C</td>
<td>150 ± 0.5</td>
<td>162.5 ± 0.5</td>
<td>177.4 ± 0.5</td>
</tr>
<tr>
<td>Cavity diameter, Å</td>
<td>4.7 - 5.3</td>
<td>6.0 - 6.5</td>
<td>7.5- 8.3</td>
</tr>
<tr>
<td>Height of torus, Å</td>
<td>7.9 ± 0.1</td>
<td>7.9 ± 0.1</td>
<td>7.9 ± 0.1</td>
</tr>
<tr>
<td>Diameter of the outer periphery, Å</td>
<td>13.7 ± 0.4</td>
<td>15.3 ± 0.4</td>
<td>16.9 ± 0.4</td>
</tr>
<tr>
<td>Approx. volume of cavity, Å³</td>
<td>174</td>
<td>262</td>
<td>427</td>
</tr>
<tr>
<td>Crystal forms (from water)</td>
<td>Hexagonal</td>
<td>Monoclinic</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Crystal water, wt %</td>
<td>10.2</td>
<td>13.2-14.5</td>
<td>8.13-17.7</td>
</tr>
<tr>
<td>Diffusion constant at 40 °C</td>
<td>3.443</td>
<td>3.224</td>
<td>3.000</td>
</tr>
<tr>
<td>pK (by potentiometry) at 25 °C</td>
<td>12.332</td>
<td>12.202</td>
<td>12.081</td>
</tr>
<tr>
<td>Partial molar volumes in solution ml mol⁻¹</td>
<td>611.4</td>
<td>703.8</td>
<td>801.2</td>
</tr>
</tbody>
</table>

Table 4.1 Characteristics of α, β, and γ-CDs

The inclusion into a cyclodextrin’s hydrophobic cavity is driven by Van der Waals interactions, hydrophobic effects and the displacement of water from the cavity. Other factors that govern complex formation include the shape and size of the CD and the guest molecule. Exploitation of such factors has lead to an explosion in cyclodextrin research. Because of their non-toxic nature and their chemical and physical properties, these CD complexes are used commonly in control of solubility (solubilising hespiridin to remove the cloudiness in orange juice), process aids (removal of cholesterol from animal fats such as eggs and dairy products), stabilizations (slower degradation of Penicillin G), masking the effects of the guest (decreased side effects of pilocarpine), reduction of volatility (the release of
fragrances from laundry dryer sheets), directing chemical reactions (synthesis of 2, 6-Napthalenedicarboxylic acid), control of fluorescence and light adsorption, to name a few.

![Dimensions of the three common types of cyclodextrins.](image)

When a cyclodextrin is dissolved in an aqueous solution, the hydrophobic cavity is filled with water molecules. The interactions between these water molecules and the hydrophobic cavity are unfavourable (polar- non polar interactions) and therefore the water molecules can be readily substituted by a less polar guest molecule. The CD is the ‘host’ molecule and the ‘driving force’ of complex formation is the substitution of the high energy water molecules by less polar ‘guest’ molecules.

The equilibrium constant of the association of cyclodextrin (CD) and guest (G) and the dissociation of the complex (CD-G) is defined by the equation

$$
CD + G \rightleftharpoons CD - G
$$

For a 1:1 host: guest ratio, the equilibrium constant K is then

$$
K = \frac{[CD-G]}{[CD][G]}
$$

NMR and UV-Vis spectroscopy have become the two key techniques used when investigating CD complexes. For NMR, measurements of changes in chemical shift (NMR shift titration) are used in calculating the association constant, K. In UV-Vis experiments, the change in absorbance is measured to calculate K.
Host-guest encapsulation using cyclodextrins is widely studied. Cram and Warmoth showed that high energy intermediates such as cyclobutadiene, orthobenzyne and cycloheptatetraene could be stabilised when encapsulated in calixarene-based cages.\textsuperscript{11-16} Recently, work more directly related to dyestuff chemistry was reported by Anderson \textit{et al} who attempted to encapsulate dyes in cyclodextrins to determine whether encapsulation protects the conjugated \(\pi\) system from oxidative and reductive species (i.e. increases the lifetime of the dye).\textsuperscript{1} In their study, they also tried to establish whether encapsulation hindered the dye from binding to the surfaces of fabrics such as cotton and whether the encapsulated dye was more resistant to fading.

The dyes studied are reactive dyes used in the textile industry.\textsuperscript{1} These dyes react with the textile surface to create covalent bonds with the cellulosic hydroxyl groups. The reactive component of the dye is the chlorotriazine group (six membered heterocyclic ring with three nitrogens) with the chlorines imparting higher reactivity. Scheme 4.1 illustrates the preparation of the reactive dye from chlorotriazine reacting and its subsequent attachment to the cellulose surface. \(\alpha\)-Cyclodextrin was methylated to prevent the chlorotriazine reacting with hydroxyl groups in the cyclodextrin. Methylation also increases the cavity size,\textsuperscript{17} and the shielding of the dye. Although two stereoisomers are possible, depending on which way the dye is threaded between the narrow and large face, only the displayed isomer (scheme 4.1) is seen for encapsulated species.\textsuperscript{1}

An energy-minimised space-filling model of the rotaxane complex is shown in figure 4.3.\textsuperscript{1} According to the model, the azo region of the conjugated \(\pi\) system is surrounded by the cyclodextrin.

Fading of the encapsulated species and the free dye was tested using sodium dithionite which can reduce the azo link to a hydrazine and then to an amine and destroy the conjugated \(\pi\) system. Initial results showed that the encapsulated species is about 100 times less reactive to fading compared to the free dye.\textsuperscript{1} When tested with oxidising agents such as Fenton's reagent,\textsuperscript{18} the rotaxane species is also more
resistant to fading than the free dye, requiring 6 h for 90% bleaching (fading) whilst the free dye took only 50 mins to reach 90% fading.

Scheme 4.1 Preparation of an encapsulated reactive dye (RD1) and its covalent attachment to cellulose. \(^1\) a) TM-\(\alpha\)-CD, C\(_3\)N\(_5\)Cl\(_3\), H\(_2\)O, 0 °C, pH 6.5; b) 3-aminobenzenesulfonic acid, H\(_2\)O, 35 °C, pH 7.6; c) mercerized cotton, H\(_2\)O, 20 mM RD1, 0.7 M NaCl, 85 °C, pH 10, 24 h.

Figure 4.3 Energy-minimised structure of the encapsulated reactive dye, RD1. \(\alpha\)-Cyclodextrin is shown in white. \(^1\)

On cotton, the encapsulated dye (RD1) showed a paler colour (figure 4.4) suggesting that the cyclodextrin obstructs the binding by reducing the reactivity of the reactive dye. However, this effect can easily be overcome by simply increasing the concentration of the bound dye.
Figure 4.4 also shows the effect of bleaching on cotton. After 1h, the free dye is almost completely bleached whilst the encapsulated dye (RD1) remains unaffected.\textsuperscript{1} Similar results were obtained for Fenton’s reagent. Light stability tests using commercial fadometers show that free dye undergoes photobleaching ten times faster than the cyclodextrin encapsulated species.

\textbf{Figure 4.4} Photographs of cotton samples dyed with rotaxane-bound species (RD1) and free dye before (a) and after (e) bleaching sodium dithionite (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}).\textsuperscript{1}

This work and the earlier studies by Cram \textit{et al}\textsuperscript{11-16} suggest that cyclodextrin encapsulation can increase the chemical stability of the guest component and the findings indicate in particular that encapsulation protects the azo link from attack. This concept has been extended in this work to establish whether encapsulation of the ‘simple’ azo dyes described in chapter 2 improves the longevity (light fastness) of the azo chromophore. For this approach, it is necessary to show that the surface-ligating dyes form inclusion complexes with cyclodextrin and that resulting assemblies are strongly bound to the oxide surface through the pendant phosphonate or the surface-ligating group. The results are discussed in the following sections.

\section*{4.2 Molecular modelling\textsuperscript{3}}

Modelling studies were carried out first to determine whether ‘simple’ model dyes can ‘fit’ inside the cyclodextrin cavity. Modelling was carried out on \textit{para}-phosphonic acid azo dye, 3 and \(\alpha\)-CD. Dye 3 was chosen for modelling as it
performed significantly better in standard wet fastness test compared to the sulfonic and carboxylic analogues (chapter 2).

The dye 3 also carries a phenol group at the end furthest from the surface-ligating unit (figure 4.5). α-CD was chosen in preference to other types of CD because the cavity size is comparable with the width of dyes under study and would therefore be expected to form stronger inclusion complexes than with larger cyclodextrins.

![Figure 4.5 The structure of 3.](image)

A search of the Cambridge Structural Database (CSD) for cyclodextrins gave a number of hits. One of these, CDEXIA01, α-cyclodextrin para-iodoaniline trihydrate was selected for use as the base structure for this study. The additional molecules, the guest and water of solvation, in the structure were removed to leave just the cyclodextrin. This was then optimised using the Dreiding forcefield method to give the structure shown in figure 4.6 (A). A space-filling diagram of this molecule is shown in figure 4.6 (B).

From the optimised structure, the equilibrium diameter of the ring can be measured. The distance chosen was between one of the bridging oxygen atoms and its counterpart on the opposite side of the ring. For this structure, the value obtained was ~ 8.35 Å. This corresponds to the cyclodextrin in a relaxed state. Due to the flexibility of the structure, there is scope for the ring to increase in diameter to accommodate larger molecules or decrease in size to accommodate smaller molecules.

Dye 3 was first optimised using the Dreiding forcefield method and then introduced into the cavity of the cyclodextrin ring. To simplify the modelling, the dye was
defined as a rigid body, its geometry was fixed and only the cyclodextrin ring itself was allowed to flex.

Figure 4.6 The Dreiding optimised α-cyclodextrin structure (A) and space-filling diagram (B).³

There are two possible complexes that could be formed defined here by the direction in which the dye is threaded through the α-CD, i.e. which rim of the cyclodextrin is adjacent to the phosphonic acid group. For 3, there is very little difference in terms of energy between these two complexes (that with the PO₃H₂ adjacent to the primary OH ring gave minimum energy of -152 kcal mol⁻¹ whilst that adjacent to the secondary rim gave a minimum energy value of -162 kcal mol⁻¹). Given the complexity and flexibility of these molecules, it is not possible to conclude that this energy difference is statistically significant and that one complex is more favourable than the other.

An image of the complex formed between cyclodextrin and 3 with the phosphonic acid group protruding through at the secondary hydroxyl rim is shown in figure 4.7. This image highlights that cross sections of the cyclodextrin ring are no longer the same. Measurements from O...O across the ring now give values of 7.02, 9.02 and 9.60 Å. The ring has been elongated away from the edges and compressed towards the faces of the benzene rings of the dye.
Figure 4.7 The energy-minimised structure (A) and the space filling diagram (B) of the $\alpha$-CD: 3 complex with the $\text{PO}_3\text{H}_2$ group of 3 protruding through the secondary hydroxyl rim of the cyclodextrin viewed down the dye from the $\text{PO}_3\text{H}_2$ group.$^3$

The reason why there is only a small difference in energy between the complexes where the dye is threaded differently is that the portion of the dye molecule that the cyclodextrin "sees" is very similar in both cases. The phosphonic acid group is located outside the cyclodextrin and plays no part in any interactions. This is established in the space-filling diagram in figure 4.8, a side-on view of the complex with the dye molecule vertical and the phosphonic acid located out of the top of the cyclodextrin ring.

The molecular modelling studies suggest that the flexibility in the cyclodextrin ring is such that it can accommodate the azo dyes of shape and size similar to 3 readily.
4.3 Binary studies on dye: CD complexes

4.3.1 NMR

2D-ROESY (Rotating frame nuclear Overhauser Effect Spectroscopy) has been shown to be a powerful tool for examining the solution structure of cyclodextrin-encapsulated species.\textsuperscript{20-25} When a guest or a part of a guest is enclosed within the cavity of α-CD, the attached protons may display a through-space (Nuclear Overhauser Effect, NOE) with protons H3 and H5 of the cyclodextrin inner cavity (figure 4.9). In a ROESY experiment, these interactions lead to cross peaks on the spectrum. H3 protons on the cyclodextrin ring lie on the secondary end whilst H5 lies midway between primary and secondary end of the cyclodextrin ring. Thus, some indication of the orientation and/or depth of inclusion can be determined from the relative intensities of the cross peaks arising from dye protons and CD protons interactions on ROESY NMRs.
2D-NMR was chosen to study the dye/α-CD interactions in this project; dye protons of greatest interest are illustrated on figure 4.10.

As discussed in the previous section on molecular modelling, encapsulation can result in two isomers due to the conical shape of α-CD. However, only one isomer was observed when the three-dimensional geometry was investigated using COESY and NOESY experiment. This corresponds to the phosphonic acid group protruding through the wider rim with secondary hydroxyl groups.

The 600 MHz ROESY spectrum of a 0.05 M solution of 3 in D2O with equimolar amount of α-cyclodextrin at pH 8 and was recorded using WINNMR software with a mixing time of 300 ms (figure 4.11). Strong cross peaks corresponding to interaction
are between H3 and H5 from the cavity with dye protons are indicated in figure 4.11. The dye protons involved in these interactions are the protons closest to the azo group, suggesting that the azo link is contained centrally within the cavity.

Peaks corresponding to dye protons Ha-Hd are broad. This suggests that the dye: α-CD complex is in fast equilibrium with free dye and free cyclodextrin. Complexation kinetics are faster than NMR time scale and both structures, complexed and uncomplexed, are observed. This results in broad peaks.

Adamantane-1-carboxylate can form strong complexes with α-CD \( (K = 2.2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ at pH 4.39 at 25 }^\circ\text{C}) \).\(^{26}\) One equivalent of adamantane-1-carboxylate was added to the NMR mixture and the ROESY spectrum showed strong NOE interaction between H3 and H5 with adamantyl protons. Cross peaks between cavity protons and 3 were not observed. These results suggest that the dye has been pushed out of the cavity, which is now occupied by the adamantyl group.

Dye 4 protons of greatest interest are illustrated on figure 4.12. The 600 MHz ROESY spectrum of 0.05 M solution of the equivalent meta-phosphonic acid dye, 4 is illustrated in figure 4.13. Strong cross peaks between protons on 4 and cavity protons suggest that the meta dye is encapsulated within the CD cavity. The meta positioning of the phosphonic acid on the dye does not seem to hinder encapsulation and the protons closest to the azo link show strong cross peaks with H3 and H5 suggesting that the azo link is once more contained within the cavity.
Figure 4.11 Contour plot of ROESY experiment performed on a sample containing 0.05 M of 3 and equimolar amount of α-CD in D$_2$O, 298 K, 600 MHz, 300 ms mixing time. The white squares indicate the strong cross peaks between the dye protons and CD cavity protons.
Chapter 4 Dye Cyclodextrin Interactions

450 MHz 2D-ROESY NMR experiments were carried out on dyes 1-8 and 10 as 0.02 M solutions in D$_2$O with an equimolar amount of $\alpha$-CD at pH 8 and were recorded using WINNMR software. All dyes indicated cross peaks apart from 8, the biphenyl dye, which showed no cross peaks. The results suggest that due to the increased steric bulk and the lack of flexibility for rotation around the bonds prevent the biphenyl dye from forming binary complexes.

Overall, 2D-NMR studies confirm the structure for the dye: $\alpha$-CD complexes suggested by molecular modelling and in solution, all dyes are in equilibrium with $\alpha$-CD ring (except 8) and the azo link is contained within the cavity.
Figure 4.13 Contour plot of ROESY experiment performed on a sample containing 0.05 M of 4 and equimolar amount of α-CD in D₂O, 298 K, 600 MHz, 300 ms mixing time. The white squares indicate the strong cross peaks between dye protons and CD cavity protons.
4.3.2 Dye-CD interactions

In aqueous solutions an equilibrium is established between the uncomplexed molecules and inclusion complexes. The magnitude of the equilibrium constants and the degree of protection afforded to the dyes depend to a large extent on the size of the cyclodextrin cavity and the fit of the guest molecules into these cavities.

The strong absorption of azo dyes in the visible region of the electromagnetic spectrum arises from $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions associated with the azo group. The changes in the visible absorption spectrum of 3 is characterised by a maximum created at 359 nm and a shoulder at 440 nm (figure 4.14). The shoulder could be due to one of the electronic transitions mentioned above. At pH 8, the dye can exist in a protonated and deprotonated state hence the 2 peaks might be due to these different "forms". Azo dyes have been found to aggregate in aqueous solutions, with a resultant decrease in absorption and a departure from Beer Lamberts law. At dye concentrations used in this study ($7 \times 10^{-5}$ M), the absorbance was found to vary linearly with the concentration of 3.

The aromatic groups present in the dye give 3 its affinity for complexation by cyclodextrins. The absorbance of 3 at pH 8 in Na$_2$HPO$_4$ upon the addition of $\alpha$-CD was measured. In this experiment the dye concentration was fixed and the $\alpha$-CD concentration was varied. The resulting spectra of dye 3 are shown in figure 4.14. The absorption spectrum indicates that there are two peaks at 359 and at 440 nm. The first peak at 359 nm corresponds to the absorption by the chromophore and the shoulder peak corresponds to a different electronic transition. The absorption spectrum of 3 at low concentrations of $\alpha$-CD does not change greatly. It is possible that at such low concentrations of $\alpha$-CD, the dye molecules remains largely uncomplexed and the electronic environment ‘seen’ by the chromophore is unchanged and hence the spectrum remains unchanged. At high concentrations of $\alpha$-CD, a bathachromic shift is observed, possibly as a result of a decrease in dye-solvent interactions caused by complexation with $\alpha$-CD. At such high concentrations, all dye molecules in solution are most likely to exist as inclusion
complexes. This would change the electronic environment experienced by the chromophore resulting in a peak shift.

![Figure 4.14 Absorbance spectrum of 3 (7 x 10^{-5} M) alone and in the presence of \( \alpha \)-CD ranging from (1.0 x 10^{-7} to 1.0 x 10^{-2} M) in aqueous solution at pH 8.0 (Na_2HPO_4) at 25 °C.]

To calculate the thermodynamic equilibrium constant K accurately, it is necessary to measure the absorbance where the largest change takes place. Figure 4.15 compares the extinction coefficients at 359 nm and 440 nm at varying concentrations of \( \alpha \)-CD and illustrates that the biggest change in absorbance is observed at 359 nm.
Figure 4.15 Comparative plot illustrating the variations in extinction coefficients at 359 and 440 nm with α-CD for dye 3. The arrows illustrate the change in extinction coefficient at both 359 and 440 nm.

Quantitive evaluations of the equilibrium constants require the measurement of the absorption spectra of dye species in the presence of cyclodextrin. The equilibrium constant K for the formation of 1:1 complex for 3 was calculated as follows:

\[
\text{CD} = \text{Cyclodextrin} \\
\text{D} = \text{Dye} \\
\text{CD-D} = \text{Cyclodextrin- dye complex}
\]

The equilibrium is given by,

\[
\text{CD} + \text{D} \rightleftharpoons \frac{K_f}{K_i} \text{CD-D}
\]

Assuming that the solution is ideal, the equilibrium \( K_1 \) is given by

\[
K_1 = \frac{[\text{CD-D}]}{[\text{CD}][\text{D}]}, C^0
\]

Where \( C^0 = 1 \text{ mol dm}^{-3} \) is the standard concentration.
If the total concentration of cyclodextrin is,
\[ [C]_0 = [C] + [CD-D] \]

and that of the dye is,
\[ [D]_0 = [D] + [CD-D] \]

then
\[ [CD-D] = [D]_0 - [D] \]

and,
\[ [C] = [C]_0 - [CD-D] = [C]_0 - [D]_0 + [D] \]

Equilibrium constant is,
\[ K = \frac{([D]_0 - [D]) C^0}{([C]_0 - [D]_0 + [D]) [D]} \]

If \( \chi \) is the fraction of 'free' molecules, then
\[ \chi = \frac{[D]}{[D]_0} \]

And
\[ K = \frac{(1 - \chi) C^0}{([C]_0 - [D]_0)(1 - \chi) \chi} \]

Solving for \( \chi \) gives,
\[ \chi_{\text{free}} = \frac{-1 + (1 + K \Delta)^2 + (4 K [D]_0 / C^0)^{1/2}}{2 K [D] / C^0} \]

Where
\[ \Delta = \frac{[C]_0 - [D]_0}{C^0} \]

It is instructive to consider the behaviour of \( \chi_{\text{free}} \) in the simple case where \([C]_0 = [D]_0\), then \( D = 0 \) and

If \([C]_0 = [D]_0\), then \( \Delta = 0 \) and
\[ \chi = \frac{-1 + (1 + 4 K ([D]_0 / C^0)^{1/2})}{2 K [D]_0 / C^0} \]
If $[D]_0 = [C]_0$, then $X_{\text{free}} \rightarrow 1$.

If $[D]_0 = [C]_0$, then $X_{\text{free}} \rightarrow 0$.

At low concentrations of $\alpha$-CD, the molecules are free and $X_{\text{free}}$ approaches 1. However, at high concentrations of $\alpha$-CD, the dyes are complexed and hence $X_{\text{free}}$ approaches zero.

To illustrate the dye/ $\alpha$-CD complexation, UV-Vis experiments were carried out on 3 and $\alpha$-CD. The total dye concentration was fixed at $[D]_0 = 1 \times 10^{-7}$ M and $[C]_0$ was varied between $10^{-3}$ - $10^{-7}$ M. The variation of the absorbance peak in the region of $\lambda = 350$ - 400 nm with $[C]_0$ was attributed to an average of the signals from the 'free' dye with $\varepsilon = \varepsilon_{\text{free}}$ and the complexed dye with $\varepsilon = \varepsilon_{\text{complex}}$, where $X_{\text{free}}$ is give by

$$\varepsilon([C]_0) = X_{\text{free}}\varepsilon_{\text{free}} + (1 - X_{\text{free}})\varepsilon_{\text{complex}}$$

UV-Vis measurements on solutions in Na$_2$HPO$_4$ buffer at 25 °C with various amounts of $\alpha$-CD on a fixed dye solution are illustrated in figure 4.16.

The resulting fit of extinction coefficients of complexes at increasing concentrations of cyclodextrin gave the values $K = (3 \pm 1) \times 10^3$, $\varepsilon_{\text{free}}$ (359 nm) = 12100 ± 100 M$^{-1}$ cm$^{-1}$ and $\varepsilon_{\text{complex}}$ (359 nm) = 16000 ± 200 M$^{-1}$ cm$^{-1}$.

The formation of 1:1 complexes were also examined by $^1$H NMR (Figure 4.17) measurements on solutions in D$_2$O at 25 °C with various values of $\alpha$-CD concentration and fixed dye concentration. The total dye concentration was fixed at $[D]_0 = 0.05$ M and $[C]_0$ was varied between 0.4[$D]_0$ and 2[$D]_0$. The variation of a peak in a well resolved signal in the region of $\delta_f$= 7- 8 ppm with $[C]_0$ was attributed to an average of the signals from the 'free' dye with $\delta = \delta_{\text{free}}$ and the complexed dye with $\delta = \delta_{\text{complex}}$

$$\delta([C]_0) = X_{\text{free}}\delta_{\text{free}} + (1 - X_{\text{free}})\delta_{\text{complex}}$$
The resulting fit of $^1$H NMR data gave the values $K = (2 \pm 1) \times 10^3$, $\delta_{\text{free}} = 7.77 \pm 0.02$ ppm and $\delta_{\text{complex}} = 7.48 \pm 0.01$ ppm. This value is comparable with the value obtained with UV-Vis studies [$K = (3 \pm 1) \times 10^3$] suggesting that reliable equilibrium constants can be obtained by either of these methods.

Figure 4.16 Variation of the extinction coefficient ($\varepsilon$) cyclodextrin-dye complex of 3 (1 x $10^{-7}$ M) at pH 8 with concentration of $\alpha$-cyclodextrin in phosphate buffer at 25 $^\circ$C.

Figure 4.17 Variation of the chemical shift ($\delta$) of the $^1$H (7-8 ppm) signal of 3 (0.05 M) in D$_2$O with concentration of $\alpha$-cyclodextrin at pH 8 at 25 $^\circ$C.

The remaining dyes were also studied using UV-Vis and the results are tabulated in table 4.2. The K value of 4 maybe erroneous due to background noise. Dyes 1-7 have
similar equilibrium constants. Dye 8 differs as it is a biphenyl dye and due to its steric bulk and restrictions on flexibility, it cannot complex with α-CD to form the binary complex. This result was confirmed by ROESY NMR (section 4.3.1). The large errors associated with the K values largely arise from cumulative dilution errors.

<table>
<thead>
<tr>
<th>Dye</th>
<th>K</th>
<th>( \varepsilon_{\text{free}} / \text{M}^{-1} \text{cm}^{-1} )</th>
<th>( \varepsilon_{\text{complex}} / \text{M}^{-1} \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1800 (60)</td>
<td>13350 (200)</td>
<td>16500 (200)</td>
</tr>
<tr>
<td>2</td>
<td>8500 (3000)</td>
<td>14000 (60)</td>
<td>15000 (50)</td>
</tr>
<tr>
<td>3</td>
<td>3000 (700)</td>
<td>12100 (100)</td>
<td>16000 (200)</td>
</tr>
<tr>
<td>4</td>
<td>60 (100)</td>
<td>14000 (100)</td>
<td>37000 (50000)</td>
</tr>
<tr>
<td>5</td>
<td>1200 (300)</td>
<td>15000 (100)</td>
<td>18000 (200)</td>
</tr>
<tr>
<td>6</td>
<td>2400 (2000)</td>
<td>13000 (100)</td>
<td>13000 (100)</td>
</tr>
<tr>
<td>7</td>
<td>700 (400)</td>
<td>17000 (300)</td>
<td>19905 (400)</td>
</tr>
<tr>
<td>8</td>
<td>Unable to fit</td>
<td>Unable to fit</td>
<td>Unable to fit</td>
</tr>
<tr>
<td>10</td>
<td>17000 (5000)</td>
<td>14000 (50)</td>
<td>13000 (50)</td>
</tr>
</tbody>
</table>

Table 4.2 Summary of equilibrium constants and extinction coefficients of the free dye and the inclusion complex for dyes 1-8 and 10 in phosphonate buffer at pH 8 at 25 °C

The variation of the extinction plot of 10 is different to 3 and shows that \( \varepsilon_{\text{complex}} < \varepsilon_{\text{free}} \) and has a large equilibrium value. Such behavior in solution has previously been reported for phthalacyanine dyes in aqueous solutions.29

The UV-Vis studies illustrated that the experimental data fitted well with the approximation, suggesting that the solution is nearly ideal. In principle, the equilibrium constants should be calculated using activities. However, if the total dye concentration and the total cyclodextrin concentration are sufficiently low, then the respective activity coefficients could be taken as equal to unity.
The $K$ value obtained for 3 compares satisfactorily with a similar azo dye, $^{30}$ Brilliant Yellow, which has stability constant, $K_{s}$, of 2200 (50) M, pH =10 at 25 °C using similar spectrometric titrations.

![Graph](image)

**Figure 4.18** Variation of the extinction coefficient ($\varepsilon$) cyclodextrin-dye complex of 10 ($1 \times 10^{-7}$ M) at pH 8 with concentration of $\alpha$-cyclodextrin in phosphate buffer at 25 °C.

### 4.4 Ternary complexes

NMR and UV-Vis studies have demonstrated that most of the surface ligating dyes can form strong inclusion complexes with $\alpha$-CD in solution. It was then necessary to establish whether these binary complexes can bind strongly to the oxide surface through the pendant phosphonate group to form, dye-CD-oxide surface ternary complexes.

Absorption isotherms were carried out on the dyes in the presence of CDs to establish whether the ternary complexes, dye-CD-Al(OH)$_3$, is formed and light fastness and ozone fastness tests were performed to determine whether encapsulation can improve the performance of ink jet properties.
Chapter 4 Dye Cyclodextrin Interactions

4.4.1 Close packing on surfaces

In solid state chemistry, structures of identical spheres are often pictured as being formed by placing close packed layers on top of each other. In this project, the two dimensional packing of the cyclodextrin truncated cones may prove important in determining the surface coverage obtained on adsorption.

As suggested above that (with the exception of 8), the most favourable species in solution is the binary dye: α-CD complex, then it is possible that it will be the binary complex that interacts with the surface to form the ternary complex. Packing factors can determine the maximum surface coverage by the dye: α-CD complex and comparison of value with those obtained from adsorption isotherms for dye in the absence of α-CD, will enable us to judge whether a potential or full mono layer or a double layer of the ternary complexes are formed on the ATH surface. If the surface coverage of dye in the presence of α-CD is similar to the value obtained for ‘primitive’ cubic packing, it can be assumed that surface coverage is achieved by a primitive cubic packed structure of the ternary species and similar logic can be applied to with hexagonal close packing.

4.4.1.1 Primitive cubic close packing

![Diagram of primitive cubic close packing]

**Figure 4.19** Packing based on a "primitive cubic" arrangement in which centres of α-CD molecules lie on the corners of a square.

The theoretical surface coverage of α-CD on the surface can be calculated as follows:
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The area occupied by a single \( \alpha \)-CD molecule = (diameter of \( \alpha \)-CD).\(^2 \) The area defined by the centres of the \( \alpha \)-cyclodextrin molecules ABCD = AB \times BC = (2 \times radius of the larger rim)\(^2 \) = 187.7 Å\(^2 \). This square contains 4 quarters of cyclodextrin molecule therefore each \( \alpha \)-CD occupies 187.7 Å\(^2 \). If the surface area of the ATH used is 7.0 m\(^2 \) g\(^-1 \) = 7.0 \times 10^{20} \) Å\(^2 \) g\(^{-1} \) then the number of \( \alpha \)-CD molecules per gram is \( \frac{3.7 \times 10^{18}}{6.02 \times 10^{23}} \) \( \alpha \)-CD. This corresponds to \( \frac{3.7 \times 10^{18}}{Avogadro's \; \text{number} \; \text{of} \; \text{mol} \; \text{of} \; \alpha \text{-CD} = 6.2 \times 10^{-6} \). Therefore, for “primitive cubic” two dimensional arrangement for the max surface coverage on a flat surface would be 6.2 \( \times 10^{-6} \) mol of \( \alpha \)-CD g\(^{-1} \).

4.4.1.2 Hexagonal close packing

In hexagonal close packing, layers of spheres are packed so that spheres in alternating layers lie over one another. As in primitive cubic close packing, each sphere is surrounded by 6 other spheres.

![Figure 4.20](image)

**Figure 4. 20** Schematic illustration of the arrangement of hexagonal closed packed \( \alpha \)-CD spheres such that the spheres in alternate layers overlie one another.

Hexagonal close packing is more efficient and should therefore give slightly higher value for max coverage of \( \alpha \)-CD.

In a hexagonal close packed system, the area is given by \( \frac{1}{2} \times BC \times AD = \frac{1}{2} \times 13.7 \times 11.86 = 81.3 \) Å\(^2 \). The above figure corresponds to \( 3 \times 1/6 \) th molecule (or \( \frac{1}{2} \) molecule). Therefore the area covered by a single \( \alpha \)-CD is \( \frac{2 \times 81.3}{162.6} \) Å\(^2 \). Surface area of ATH = 7.0 m\(^2 \) = 7x \( 10^{20} \) Å\(^2 \) and the no. of molecules of \( \alpha \)-CD per gram of ATH = \( 7x \times 10^{20} \) Å\(^2 \) / 162.6 Å\(^2 \) = 4.305 \times 10^{18} \) molecules of \( \alpha \)-CD/g. Max surface coverage of \( \alpha \)-CD = \( 4.305 \times 10^{18} \) / Avogadro’s No = \( 4.305 \times 10^{18} / 6.02 \times 10^{23} = 7.15 \times 10^{-6} \) mol of \( \alpha \)-CD /gram.
When calculating surface coverages for hexagonal or 'primitive cubic' packing, the assumptions are that the surface is flat and the area required by the CD is defined by the perfectly circular lower rim. In practice, Al(OH)₃ is unlikely to be flat and the molecular modeling in section 4.2 suggests that α-CD is more 'oval' in shape when the binary complex formed. Any distortion from the circular cross-section of the α-CD will result in a less efficient packing and a reduction in surface coverage.

**4.4.2 Adsorption isotherms**

The isotherms were recorded on dyes 1-8 and 10 in the presence of equimolar amounts of α-CD using methodology similar to that discussed in chapter 2. It was shown in chapter 2 that phosphonic acid-substituted dyes achieved stronger binding and higher surface coverage than sulfonic and carboxylic acid analogues. Phosphinic dyes have lesser binding abilities compared to phosphonic acids, but are still more strongly surface ligating than sulfonic and carboxylic analogues. Arsonic acids, similar in its physio-chemical properties to phosphonic acids give a dye derivative with similar coverage and binding strength.

If the binary complex present in solution interacts strongly with the surface of Al(OH)₃ then the resulting ternary complex, dye-CD-Al(OH)₃, is likely to show reduced surface coverage as a consequence of the increase in bulk due to α-CD.

Polyalcohols have poor binding affinity³³ for Al(OH)₃ and as a result α-CD is unlikely to compete with the binary complex or free dye for the surface. If the dye prefers to bind as a free dye rather than encapsulated species, then there is likely to be only a small difference in the isotherm plots associated with the activity of the free dye in solution being reduced by the formation of the binary complex. In the results presented below, it appears that, apart from dye 8, it is the ternary complex which is formed in all cases.
The adsorption isotherms also reveal the binding strength of free dye and that of the encapsulated species. If the initial steep gradients are similar, this suggests that the binding strength of the functional groups has not changed and that cyclodextrin places no adverse effects on the binding. It would also reaffirm the findings of the ROESY NMR studies discussed in the earlier sections, suggesting that the CD is most likely to surround the azo link as illustrated by figure 4.21.

Adsorption isotherm measurements for 1 and 2 (figure 4.22) indicate that the sulfonic (1) and carboxylic acid (2) functionalised dyes are still taken up at the ATH surface in the presence of α-CD and that the surface density of dye is reduced. This could be due to either the formation of ternary complex, dye-CD-Al(OH)₃ complexes at the surface and the increased bulk of these reducing the overall surface coverage or due to the formation of stable inclusion dye-CD in solution reducing the effective concentration of dye. It has been shown in section 4.3.2 that 1 and 2 form such inclusion complexes in solution.

![Figure 4.21](image)

**Figure 4.21** Schematic of α-CD encapsulation where the position of α-CD as shown by A could affect the surface binding by restricting the functional group interactions with the surface whilst the position of α-CD as shown in B is less likely to show unfavourable interaction.

The reduced surface coverage observed for 1 and 2 in the presence of α-CD are similar to those observed for dyes 3-7 and 10 (figure 4.23-figure 4.28) Due to poor binding to the surface of Al(OH)₃, the isotherms for 1 and 2 do not allow us to compare strengths of binding in the absence and in the presence of α-CD.
Isotherms for the phosphonic acid 3 are much better defined (figure 4.23) as expected from the results presented in the section (section 2.3.2). The initial slope of the plot of the uptake of dye 3 in the presence of α-CD is very similar to that of the dye alone. The increased bulk of α-CD complexes leads to a significant decrease in surface coverage from $20 \times 10^{-6}$ to $6.3 \times 10^{-6}$ mol g$^{-1}$ for 3 and its α-CD complex. The data correspond to coverage of $58 \pm 12$ and $185 \pm 19$ Å$^2$ molecule$^{-1}$ respectively, based on the surface area ($7$ m$^2$ g$^{-1}$) for the Al(OH)$_3$ used. The equilibrium adsorption constant of the free dye was calculated to be $821 \pm 88$ and that of the encapsulated species $4617 \pm 800$ L mol$^{-1}$. The encapsulated species is calculated to have a higher binding strength because it reaches maximum coverage at lower concentrations. This is probably due to size of the complex which results in a lower number of ternary complexes required to cover the surface.

Figure 4.22 Adsorption isotherms showing the uptake of 1 or 2 in the absence and presence of equimolar concentrations of α-CD.
Hypothetically, if free α-CD could bind to ATH, then the theoretical maximum surface coverage, calculated from cubic close packing, would be 6.2 x 10⁻⁶ mol of α-CD/g. Since the dye fits inside the α-CD cavity and the size of the complex is similar (see modelling results section 4.2) the maximum surface coverage for the ternary complex should be similar to that of the free α-CD. The surface coverage of 3 in the presence of α-CD (6.3 x 10⁻⁶ mol of α-CD/g) is indeed very similar (within experimental error) to the theoretical surface coverage of α-CD (6.2 x 10⁻⁶ mol of α-CD/g) estimated on pages 157-158 for a cubic packed structure.

Figure 4.23 Adsorption isotherms showing the uptake of 3 in the absence and presence of equimolar concentrations of α-CD.

Dyes 4 and 7 contain the phosphonate group at a meta position in the dye. Strong binding strength is observed with a reduced surface coverage with respect to the plot obtained for dye alone (figure 2.24). Reduced surface coverage from 20 (1) x 10⁻⁶, to 6.3 (1) x 10⁻⁶ mol g⁻¹ for 3 and its α-CD complex correspond to area occupied per molecule of 58 (2) and 185 (9) Å² molecule⁻¹. In comparison, ternary meta complex dye 4 has a surface coverage that is reduced from 7.4 (1) to 3.1 (1) x 10⁻⁶ mol g⁻¹ and the area occupied by a single molecule has risen from 157 (30) to 375 (50) Å² molecule⁻¹. Dye 4, in the presence of α-CD, has not reached full monolayer coverage for hexagonal or cubic close packing which might be due to inefficient packing motif. Surface coverage for 7 is reduced from 20 (2) to 6.0 (1) x 10⁻⁶ mol g⁻¹
and the area occupied by a single molecule has increased from 58 (25) to 184 (30) Å² molecule⁻¹. Dye 7 shows a similar surface coverage to the extended maximum surface coverage of α-CD (page 157-158) for the cubic packing and to that observed for 3 in the presence of α-CD. This suggests that surface coverage is now determined by the size of α-CD and not the size of the dye or its orientation to the surface nor is it dependant on its strength of binding to the ATH.

Figure 4.24 Adsorption isotherms showing the uptake of 4 or 7 in the absence and presence of equimolar concentrations of α-CD.

The absorption isotherm of 5 was fitted with double Langmuir function, which is a 'two site' model as the data could not be fitted to the standard Langmuir function used previously. Examination of the plot at the low level of concentration of dye reveals a similar binding strength to other dyes (section 2.3.2).
Curve fitting provides two sets of values and as observed for previous dyes, the addition of \( \alpha \)-CD reduces the surface coverage from 10.0 \((1) \times 10^{-6}\) mol g\(^{-1}\) to 1.0 \((1) \times 10^{-5}\) and 6.5 \((2) \times 10^{-6}\) mol g\(^{-1}\) in the two models respectively. The area occupied by a single molecule changed from 155 \((11)\) Å\(^2\) and 116 \((19)\) Å\(^2\) molecule\(^{-1}\) to 116 \((15)\) and 178 Å\(^2\) molecule\(^{-1}\). However, the surface coverage obtained by complex 1.0 \((1)\) and 7.5 \((1) \times 10^{-6}\) mol g\(^{-1}\) is slightly higher than the value obtained for hexagonal close packed structure of \(\alpha\)-CD. Bearing this in mind, molecular modelling predicts that the \(\alpha\)-CD will lose its circular cross section (modelling predicts an ‘oval’ shape) when encapsulation is achieved. It is likely that the surface coverage of an ‘oval-shaped’ \(\alpha\)-CD will have a lower value than that calculated for hexagonal and primitive packing. The higher surface coverage could reflect a double layer formation, where the phosphonic acid head groups binds with the hydroxyl tail group to create a new layer, adding more molecules to the surface. In solution, the dye molecules exist as binary complexes. However, if all molecules are not complexed, then the free dye could compete with the ternary complex to bind with the surface.

The increased possibilities for hydrogen bonding provided by the aniline NH\(_2\) group of 6 could be responsible the formation of a multilayer which is not observed for the other dyes as discussed in chapter 2 (figure 4.27). Consequently, an elevated surface...
coverage (in comparison to 4 and 7) is observed for both free dye and the dye in the presence of α-CD. The absorption isotherm for the free dye was plotted using the double Langmuir function (it was not possible to fit the data satisfactorily with the standard Langmuir isotherm) and the dye and α-CD plots were analysed using the standard Langmuir function used for other dyes. The surface coverage of free dye changed from 30 (5) and 5.4 (1) x 10^-6 mol g^-1 to 10.0 (2) x 10^-6 mol g^-1 and the area occupied by a single molecule increased from 39 (8) and 215 (50) to 116 (12) Å² molecule^-1 the higher surface coverage (relative to dye 3 and 5) could be due to the formation of the multilayer brought about by the salt formation of the protonated amine and deprotonated phosphonic group. It is also possible that there is some free dye in solution and there is competition between the binary complex and the free dye for surface ligation.

**Figure 4.26** Adsorption isotherms showing the uptake of 6 or 10 in the absence and presence of equimolar concentrations of α-CD.
Figure 4.27 Possible multilayer formation for 6 resulting in salt formation at pH 8 and 25 °C

Adsorption isotherm of 10 illustrates that surface coverage is reduced when α-CD is added to the dye solution from 10 (2) x 10^{-6} \text{ mol} \cdot \text{g}^{-1} to 8.7 (1) x 10^{-6} \text{ mol} \cdot \text{g}^{-1} and the area occupied by a single molecule changed from 116 (13) \AA^2 \text{ molecule}^{-1} to 133 (19) \AA^2 \text{ molecule}^{-1}.

Solution studies carried out on the dye 10 in the presence of α-CD indicated possible aggregation in solution which can encourage multilayer formation on the surface. This phenomena might explain the increase in the observed surface coverage in comparison with 3 and 7.
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Figure 4.28 Adsorption isotherms showing the uptake of 8 in the absence and presence of equimolar concentrations of α-CD.

Isotherm plot for 8 (figure 4.28) show only minor differences suggesting that the complex is not formed with this dye. Previously, NMR and UV-Vis suggested that this dye might not be able to form inclusion complexes due to the steric bulk and the drop in degrees of freedom for rotation around the bonds for the phenyl rings. The surface coverage of the dye with or without α-CD present is 2.9 (0) and 3.9 (1) $\times 10^6$ mol g$^{-1}$ respectively and area occupied by a single molecule with/without α-CD present is 352 (75) and 298 (50) Å$^2$ molecule$^{-1}$ respectively.

In summary, formation of the ternary complex, dye–α-CD- oxide is observed for all dyes apart from 8. Dyes 3 and 7 appear to show ternary complex binding to the surface. Dye 6 show possible multilayer formation of the ternary complex, possibly, through the interactions of protonated amine and deprotonated phosphonic acid. Dyes 5 and 10 also indicate the possibility of multilayer formation on ATH surface.

4.5 Light and Ozone Fastness

Ink jet prints were prepared as before (chapter 2). The dye was dissolved in generic ink solution with equimolar amounts of α-CD to form the test ink. The ink was then printed on to HG 201, SEC premium, PR101, HP premium plus, Printasia and the
sample prints were analysed for their light fastness properties using an Atlas HP-UV and ozone fastness using a Hampden/Satra 903 model.

4.5.1 Light Fastness

The behaviour of dyes on each type of paper and more specifically, the interaction between dye and oxide media is discussed in more detail in section 2.4. However, the light fastness (LF) results showed that type of media on paper was more important than the design of the dye. This study was undertaken to determine whether the formation of the ternary complex, dye-CD-oxide media, results in change in LF.

In the previous section, it was noted that only dyes 3 and 7 bound to the surface with ternary complex only and the remaining dyes bound in the presence of the free dye and ternary complex. In this section, comparisons will be attempted between dyes within the same group, i.e. the dyes that bind to the surface with the ternary complex and the dyes that bind with both ternary and free dye.

ROD relates to the colour of a dye. ROD % loss is a measure of the difference between starting ROD and current value. A high ROD % loss suggests that the dye is highly susceptible to light and will 'fade' quickly. Any dyes that exceed 35% ROD % loss within the study will be considered as 'failed' dyes. 35% density loss is considered the end point, objectionable fade, for a yellow and the end limit for magenta is 25%. These ‘failure’ points are set somewhat arbitrarily by ISO (International Organisation for standardization) and ANSI (American National Standards Institute) standards for photographic images. Figure 4.29 and figure 4.30 illustrate the ROD % loss for 3 on different types of papers. The remaining ROD % loss graphs for all other dyes are contained within the appendix and the results observed will be summarised in the following paragraphs.

Figure 4.29 and figure 2.30 illustrate the ROD% loss against exposure (illuminance is how well lit something is) for the papers SEC, PR 101, HG 201 and HP premium printed using the ink lay down method. Figure 4.31 demonstrate ROD % loss over
exposure for Printasia paper printed using the ink jet printing method. Initial observations illustrate that the LF is improved with addition of CD (25% improvement in LF is observed for alumina coated media, PR101 and HG 201) and on some prints (HP and Printasia), no measurable difference is observed upon the addition of CD to the ink solution. The initial high ROD % loss observed for dye with CD is an instrumental error. All prints apart from HP and Printasia exceed the ‘failure’ point before the end of the study.

![Graph A](image1.png)

![Graph B](image2.png)

**Figure 4.29** ROD% loss against exposure [illuminance is how well lit something is] for 3 on SEC premium (A), PR 101(B) and HG 201. (The dashed red line illustrates the fade limit of 35 % of ROD % loss).
Figure 4.30 ROD % loss against exposure for 3 on HG 201 (C), HP premium (D) and Printasia (E).
Figure 4.31 compares ROD % loss against exposure for prints SEC premium obtained from the ink lay down method and ink jet printing method. The two methods differ only in the way ink is projected on to the prints and the volume of ink. Initial observations suggest that prints obtained through ink jet printing have a slightly higher light fastness compared to the prints obtained from the ink lay down method and the dye 3 with CD has improved light fastness on SEC prints when printed using ink jet printing method. This is a surprising result. Due to the design of the test, there is little control over the volume of dye ejected from the nib in the HTS ink lay down method unlike ink jet printing, where controlled amounts of ink is projected out of the nozzle and on to the medium. There will invariably be a higher concentration of dye/ink on the medium in the HTS method which can lead to dye aggregation. Previous research carried out by Giles et al. has shown that dye aggregation can enhance the light fastness of the dye. Therefore, enhanced LF displayed by prints generated through ink jet printing must be due to other factors that govern fading.

In summary, dye 3 printed on the microporous Al oxide papers show a 25 % improvement in LF. This could be due to the ternary complex where the CD effectively shields the azo link from attack and thereby improving the longevity of the dye. However, the LF of these prints are poorer than observed for the polymer coated papers (Printasia and HP) where the dyes shielded from the environment by the polymer layer. Consequently, these dyes fade much less.

Dye 4 shows a significant amount of spreading (increased ROD) upon the addition of α-CD (SEC, PR101 and HP premium) which results in increased LF. This could be due to two reasons. Firstly, α-CD may bind with media creating a surface that the dye can no longer bind on. However, isotherm studies in the previous section suggested that CD has a very weak binding affinity to aluminium oxide and is unlikely to bind with the surface. Furthermore, if α-CD was binding with the medium, spreading would be observed in all spectra containing the dye α-CD. The second factor that could cause spreading is if the ternary complex cannot bind with media as effectively. Due to the amount of spreading, the dye + α-CD prints are yet
to reach the fade level. As observed for 3, the initial ROD of 4 on prints is increased upon the addition of α-CD.

Figure 4.31 ROD % loss against exposure illuminance for 3 using SEC premium prints obtained with HTS ink lay down method (A) or ink jet printing method (B).

ROD % loss spectra for 7 indicates a slight improvement in LF properties on Al-oxide media. There is no measurable difference in ROD % loss for with/without α-CD for SEC premium prints and a slight increase in fading is observed for HP premium paper. However, most prints fade to failure before the end of the study.

In conclusion, dyes that possibly bind to the Al(OH)$_3$ through a ternary complex monolayer show improved LF on the Al-oxide coated media. The adsorption
isotherm plots of 5, 6 and 10 suggested the possibility of multi layer formation on the oxide surface. The LF of these dyes will be discussed in the following paragraphs.

5 shows improved LF on all prints save SEC premium and 6 indicate poor LF on all prints apart from HG 201. Dye 10 shows no overall change in LF with the addition of α-CD. The decrease in LF by 6 could be due to the decomposition of a top layer at the surface. However, all prints of 5, 6 and 10 ‘fail’ before the end of the study.

1 shows a vast improvement on all prints apart from the Al-oxide containing papers where only a slight improvement is observed.

Dye 8, the biphenyl dye, shows no change in its LF properties upon the addition of CD. PR101 and HG 201 prints ‘fail’ before the end of the study.

In conclusion, the ROD% loss results show that 3 and 7 have improved LF when α-CD is added. Dye 4 experiences extensive spreading when α-CD is added to the ink solution and appear to have an increased LF. Dye 8 sees no change in LF properties upon the addition of α-CD and other dyes experience variable changes in LF.

Reflectance data were measured for every dye print at 0 klux, 34.8 klux, 417 klux, 4440 klux, 12030 klux, 20094 klux at wavelength 360-720 nm. The reflectance data was converted to absorbance values using Beer Lamberts Law (Equation 4.2). The absorption results for the dye prints should illustrate any electronic changes taking place for the dye as it decomposes.

\[
A = \log_{10}(1/R)
\]

Equation 4.2

Figure 4.33 compares the absorption spectra of 3 with/without CD on various types of papers.
Figure 4.32 Comparison of absorption spectra of 3 without/with CD on SEC premium (A and B respectively) with increasing intensity.
Figure 4.33 Comparison of absorption spectra of 3 without/with CD on HG 201 (C and D respectively) with increasing intensity.
Figure 4.34 Comparison of absorption spectra of 3 without/with α-CD HP premium (E and F respectively).
Figure 4.35 Comparison of absorption spectra of 3 without/with α-CD PR 101 (G and H respectively).
Figure 4.36 Comparison of absorption spectra of 3 without/with α-CD on Printasia (I and J respectively).
All spectra (figure 4.32-figure 4.36 and spectra for other dyes) show a difference when α-CD is added to the ink solution. This effect is variable and in many cases peaks are broader and bathochromic with α-CD than without. Therefore, an increase in optical density (OD) is observed as peaks broaden and move into the visible and out of the UV region, they become more detectable by eye. Narrowed absorption peaks on the addition of α-CD can be also be interpreted as being in a state of greater symmetry and homogeneity. Decreasing peak size indicates the decomposition of the chromophore.

As discussed in chapter 2, the absorption/reflection spectrum of the dye is dependant on its environment. It can change in different solvents (solvatochromism) and on different media. The electronic environment can change the position of the absorption band, the intensity and the shape of the band. For reflection/absorption, spectra can differ in intensity to due to changes in surface roughness.

When the dye is printed with α-CD, if 100% encapsulation of dye is achieved, the intensity can vary from media to media depending on the surface type. However, the dye environment is the same for all dyes and therefore the shape of the spectrum should be the same regardless of surface type. This can then be used to decide which dyes are being encapsulated.

The change in spectra for dye (with/without α-CD) can be interpreted in two ways. Firstly, the α-CD can interact with the media creating a slightly different environment thereby altering the spectrum. Secondly, the dyes interact with α-CD, which alters the environment and thereby the spectrum appears changed.

The absorption spectrum of 8 is different because it has a different electronic environment compared to the others. The other dyes are X-Ar-N=N-Ar-X, whereas 8 is X-Ar-N=N-Ar- X-Ar-N=N-Ar-X. The additional aryl groups on the phosphinic effectively makes it a much better electron acceptor, thereby stabilising the excited state and moving the absorption band further into the visible region (bathochromic).
The spectra of 10 show low starting OD. This is most likely due to most of the dye absorption being in the UV region and tailing off into the visible region.

In summary, the absorption spectra of the dyes 1-8 and 10 suggests that if all the dyes were encapsulated in α-CD in every case and did not experience any environment from the media, then the spectrum would appear to be the same regardless of the medium. This is not observed. However, on the whole, the spectra do become more and more similar to each other when printed with α-CD suggesting that some dyes are encapsulated when printed and in some cases, multi-layer formation is achieved.

4.5.2 Ozone Fastness

The behaviour of dyes on each type of paper and more specifically, the interaction between dye and oxide media is discussed in more detail in chapter 2. However, previously, the ozone fastness (OF) results showed that type of media on paper was more important that the design of the dye. This study was undertaken to determine whether the formation of the ternary complex, dye-α-CD-oxide media, results in change in OF.

![Bar chart showing OF comparison with/without α-CD for dyes 1-3 and 10](image)

**Figure 4.37** Comparison of OF with/without α-CD for dyes 1-3 and 10 where the
prints were generated in the ink lay down method. (The dashed red line illustrates the fade limit of 35% of ROD% loss).

Figure 4.32 illustrates the OF of dyes 1-3 and 10. Pr 101 and HG 201 show poor OF. However, SEC and HP premium prints show better OF and will be used for comparisons. The addition of α-CD to 1 and 2 improves the OF of the prints. 1 sees a drop in ROD% loss from 67% to 15% for SEC and 18% to 2% on HP. Similarly, 2 sees a drop in ROD% loss from 20% to 8% for SEC. However, 3 and 10 shows a small increase in fading through ozone attack.

Figure 4.38 Comparison of OF with/without CD for dyes 3-7 and 8 where the prints were generated in the ink lay down method. (The dashed red line illustrates the fade limit of 35% of ROD% loss).

Figure 4.38 illustrates that the dyes 5-7 have slightly improved OF. 8 indicate a high OF value. This could be due to the dye having two azo links while the other dyes have only a single azo link. Decomposition of one azo link in 8 will still enable the dye to appear as coloured.
Figure 4.39 Comparison of OF with/without CD for dye prints 3 and 4 generated using the ink jet method. (The dashed red line illustrates the fade limit of 35 % of ROD % loss).

Figure 4.39 illustrated the OF of dyes 3 and 4 printed using ink jet method. The overall OF all prints for 3 show a much lower ROD % loss compared to the values obtained in the ink lay down method. In the ink lay down method, there is no control over how much ink is put down on the print. Therefore, we often see an excess of ink aggregated on the print. When exposed to ozone test conditions, the aggregated dyes will fade much slower (low ROD % loss). Ink jet printing delivers uniform spread of ink on the print and we get a more accurate indication of the OF of the dyes. Therefore, the improved LF observed for the ink jet printing method must be due to other factors. However, both methods show the same trends and patterns of dye behaviour.

OF levels of 3 on Printasia and PR 101 show an increase in fading in the presence of α-CD. Other prints show no significant change. 4, however, shows extensive spreading on most papers when α-CD is added. This lowers the ROD %.
4.6 Conclusions

This chapter has shown that dyes in the presence of α-CD form binary complexes in solution with relative ease. The complexes then interact with the ATH surface to form ternary complexes. Isotherm plots reveal that surface coverage was determined by the size of the α-CD and not the size of the dye, its orientation to the surface or its strength of binding. Some ternary complexes formed monolayers on the surface whilst others displayed a higher surface coverage than predicted indicating the possibility of double layer formation. It is possible that the higher surface coverage achieved by 6 is achieved through the interactions between the protonated tail group amine and the deprotonated head group phosphonic acid. The effect of α-CD on dye in ink jet tests is variable.

4.7 Experimental

4.7.1 Chemicals and Instrumentation

α-Cyclodextrin was obtained from Aldrich and dried under vacuum for 3 day prior to use. Solvents were used as received. Water was purified before use on Milli-Q ® water purification system.

All 2D NMR experiments (COSY and ROESY) were acquired from 1024 increments of 2 K data points and 16 scans each. The data were zero-filled twice in the $t_1$ dimension and multiplied by a squared sine bell function (SSB) in both dimensions. NMR spectroscopic data processing was carried out on a Bruker Silicon Graphics O2 station with standard UXNMR software as well as on a PC with 1D WIN NMR (960901) software (Bruker Franzen Analytic GmbH).

UV-Vis, ICP and ink jet tests were carried out on instruments previously mentioned in chapter 2.
4.7.2 Solution studies

4.7.2.1 2-Dimensional $^1$H NMR

COESY experiments on all dyes were performed in D$_2$O solutions containing 0.03 mol of dye and 0.03 moles of α-CD at pH 8, 25 °C, 250 MHz. with a mixing time of 0.3 seconds.

ROESY experiments on all dyes (adamantine-1-carboxylate) were performed in D$_2$O solutions containing 0.03 mol of dye and 0.03 moles of α-CD at pH 8, 25 °C, 400 MHz. with a mixing time of 0.3 seconds.

In the NMR experiment of dye 3, the total dye concentration was held fixed at 0.05 mol dm$^{-3}$, at pH 8, 25 °C and the cyclodextrin concentration was varied between 0.4[Dye] and 2.0[Dye].

4.7.2.2 UV-Vis

Absorbance data were collected at 1nm intervals on ATI UNICAM UV/vis spectrometer with 1cm path length quartz cuvettes. Wavelength ranges where the greatest change in absorbance occurred were selected for analysis. These ranges were 300-500 nm for all dyes.

Stock solutions of dyes at known concentrations were prepared in phosphate buffer and the absorption spectrum of the dye was measured alone and in the presence of increasing concentrations of α-CD (ranging from $1 \times 10^{-7}$ to $1 \times 10^{-2}$ mol dm$^{-3}$) at pH 8, 25 °C. To calculate equilibrium constant, the wavelength at maximum peak height for dye alone was identified and the variation of absorbance with subsequent increase in α-CD concentration at these peak height were measured.
4.7.3 Solid state studies of Dye with added α-CD

4.7.3.1 Adsorption Isotherms

The adsorption isotherms were prepared in the same manner described in section 2.6.3. with the addition of equimolar amounts of α-CD in to the dye stock solution.

4.7.3.2 Ink jet tests

Identical preparation to that described in section 2.6.4 with the addition of α-CD into ink solution.
4.8 References

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CHAPTER 5

Conclusion
The objective at the outset of the project was to determine how the uptake of watersoluble dyes on metal oxide-coated paper depends on the types and disposition of anionic pendant groups in the dye system. These could then be analysed for their ink jet properties such as humidity, light fastness and ozone fastness.

The approach taken was to use polynucelating ligands that could address arrays of metals on surface oxide structures in order to optimise the thermodynamic stability of the ‘surface complexes’ formed by ligands with a high density of donor functions were chosen hereby maximising the number of ligand-to-surface metal interactions.

Measurement of adsorption isotherms for the uptake of dyes on high surface area Al(OH)₃ proved to be an effective screening process in identifying the functional groups that bind strongly to ATH. A ranking order of head groups has been established based on work in this thesis, carboxylic acid < boronic acid < sulfonic acid << phosphinic acid< arsonic acid ≈phosphonic acid ≈multi phosphonic acids.

In addition, the shapes of the graphs gave information on the mode /modes of binding of the compounds.

Sulfonic, carboxylic and boronic acid derivatives were rejected as candidate head groups due to poor binding strength shown by the structurally related dyes and boronic acid derivatives showed poor solubility in aqueous solutions. Whilst the binding strength of a compound is a useful indicator of its likely effectiveness as a surface ligand, it has been establish within this thesis and from other work at Edinburgh that binding strength is not the only important criteria for achieving useful effects in surface complexes.

The binding studies have provided ‘structure-activity’ relationships which have contributed greatly to the understanding the ligand design features that are important for strong binding to metal oxide surface but do not always allow us to predict surface coverage because other factors allow binding to form additional layers. An example of this is that while 3-(4′-aminophenylazo)phenylphosphonic acid does not show an increased binding strength over 3-(4′-hydroxphenylazo)phenylphosphonic
acid which carries a pendant hydroxyl group, the amine functionality does help it to achieve a much higher surface coverage at higher ligand concentrations. This may be brought about multilayer arrangement on ATH surface through the salt formation between the protonated amine and deprotonated phosphonic acids.

It has been shown in this thesis that improved wet fastness is observed for dyes with “strong” surface-tethering functions when printing onto photographic quality (oxide treated) papers and performing industry-standard humidity-resistance tests. In contrast, strong binding functionalities on metal-oxide surfaces performed worse in light and ozone fastness tests after printing onto oxide-treated papers. This may result from an increased polarity in the molecule or in the medium close to the azo group in the dye. Formation of inclusion complexes of the dyes were investigated to address the problem.

The simple dyes form stable inclusion complexes with cyclodextrins (CDs) and surface coverage data from isotherms for uptake on Al(OH)₃ in the presence of α-CD demonstrate that ternary Al(OH)₃/dye/α-CD complexes are formed. Binding studies in the presence of α-CD suggested that surface coverage was determined by the size of the oligosaccaride and not the size, orientation to surface or binding strength of dye with the exception of 8 where no dye:α-CD interactions were present. The formation of these ternary complexes where intermolecular reaction of photo activated chromophores is suppressed by the protective hydrophobic CD cavity appears to result in variable light and ozone fastness properties.

Future work could consist of synthesising cyclodextrin with phosphonic acid head groups on the wider rim, allowing the cyclodextrin to firmly tether itself to the oxide surface. These cyclodextrins could then be used in conjunction with weakly binding functionalities (such as sulfonic acid groups), which can form ternary complexes, in an attempt to improve light, ozone and humidity fastness.

In a broader context the work has shown that it possible to attach the chromophores to inorganic substrates using surface ligating groups. This approach could be
extended to a number of areas to modify the properties of pigments or other photo-activated solids, e.g. in light harvesting photo materials.

Whilst it is intrinsically difficult to investigate the structures of complexes formed at oxide surfaces, the work has resulted in plausible models for the mode of action of various surface ligating groups and other surface coverage studies in particular have allowed us to propose reasonable models for the binding of dyes and their corresponding complexes with CDs. It would be appropriate to consider other techniques to analyse the ink prints with and without α-CD e.g. using Surface Enhanced Electronic Raman Spectroscopy (SEERS) to determine the nature of the surface-bound species.
CHAPTER 6

Appendix
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Folder- Ink jet results

Table 3 Light fastness test results for dyes 1-8 and 10 (HTS method)

Table 4 Ozone fastness tests results for dyes 1-3, 5-8 and 10.

Table 5 Ozone fastness test results for 3 and 4

Sub folder- Dye only

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Figure 4 ROD % loss for dye 4 on media

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