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PHYSICO-CHEMICAL ASPECTS OF WATER-BASED EMULSION PAINTS

by

Guifo Joseph KAYEM

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology, September 1978

Supervisor: Dr M J Jaycock
Department of Chemistry

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DECLARATION OF ORIGINALITY

The work described in this thesis has not been submitted in full or in part to this or any other institution for a higher degree.
ACKNOWLEDGEMENTS

It is my pleasure to register my immense gratitude and appreciation firstly, to Dr Michael Jaycock for his inspiring supervision, patience and encouragement during this project; and secondly to BTP Tioxide Limited who gave generous financial assistance towards this undertaking.

I am also thankful to Dr L Simpson, Messrs J Clark and R Blakey of BTP Tioxide Limited for their help, interest and useful discussions all through this work; the government of the United Republic of Cameroon for permitting me to undertake this project; Professor R F Phillips for providing research facilities; the several technicians of the Chemistry Department who have at some stage facilitated the progress of my work; and finally to Mrs Janet Smith for working so hard to type this thesis quickly.
Dedicated to

My parents who have endured with patience and understanding my long sojourn in Europe, and to

My wife whose patience and support has made this research possible.
SUMMARY

An investigation has been performed with a view to elucidating the factors affecting storage stability and particle flocculation during drying of a water-based emulsion paint, by using a model system of polyvinyl acetate latex and a rutile pigment, where the latex was stabilized with sodium dodecyl sulphate and the pigment with polyphosphate (sodium hexametaphosphate).

In particular, the studies have concentrated on the influences of sodium dodecyl sulphate (SDS), and polyphosphate on particle stability and film formation. It has been shown that sodium dodecyl sulphate (SDS) improves the stability of the latex and pigment, while polyphosphate improves pigment stability but reduces latex stability. In the absence of SDS the polyphosphate causes the latex to flocculate when the polyphosphate concentration is $5 \times 10^{-4}$M or higher. SDS has been shown to be capable of solubilizing the latex when the free SDS concentration exceeds the critical micelle concentration in the particular solution. The ability of the SDS to solubilize the PVAc latex leads to improvement in film formation by the paint, whereas the ability of the polyphosphate to flocculate the latex leads to poor film formation.

The DLVO (Derjaguin, Landau, Verwey and Overbeek) theory of colloid stability has been applied to the model emulsion paint system and it has been shown to have some success at predicting flocculation preferences during drying. With respect to the storage stability of the paint, the application of the DLVO theory is limited
by the fact that chemical reactions occurring during storage alter the initial values of the parameters on which the DLVO theory calculations are based.

It has also been proposed that for a polyvinyl acetate/rutile emulsion paint system, in addition to the usual mechanisms (viscous flow and autohesion) of film formation; a mechanism deriving from latex solubilization should be taken into account when SDS is present in the system.
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CHAPTER 1

INTRODUCTION
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INTRODUCTION

1.1 Water-based Emulsion Paints

In the United Kingdom these paints are commonly called emulsion paints or latex paints. It is understood that these designations exclude non-aqueous dispersions. In the following text wherever latex paint or emulsion paint appears, it should be assumed to be synonymous with water-based emulsion paint.

A water-based emulsion paint is essentially a colloidal dispersion of polymer particles and pigment (inorganic oxide) particles in an aqueous phase. It is prepared by mixing an aqueous pigment dispersion (prestabilized by a polyelectrolyte) with a polymer latex (prestabilized by an emulsifier). The paint is made to a pH within the range 7-9 and a solids content of 40-60% wt/wt. Other additives are incorporated either to prevent microbial spoilage and foaming or to improve the film forming ability of the paint. The pigment stabilizer is usually a polyphosphate, although in recent years organic polyelectrolytes (polymers) have also been utilised. The emulsifier stabilizing the polymer latex can be any of the following:

(a) anionic emulsifiers such as organic polyelectrolytes; SDS and SDBS;

(b) nonionic emulsifiers - such as polyvinyl alcohol (88%), or poly(ethylene) oxides (pluronics).

* SDBS is Sodium dodecyl benzene sulphonate
Generally a mixture of emulsifiers is used. The paint pH 7-9 is achieved by adding ammonium hydroxide and it is presumed that during drying the ammonium hydroxide evaporates along with the water.

1.2 The Purpose of this Project

The formulation of emulsion paints has been more of an art than a science. The formulators have been very successful at preparing emulsion paints to meet consumer needs, by applying their knowledge of latex film formation and rudimentary colloid chemistry. However, problems have been encountered in paint storage stability and pigment distribution in dried paint films. A stage has been reached where further advances are only possible if fundamental investigations are performed with a view to elucidating the major factors affecting stability during storage and particle flocculation during drying. The purpose of this project was to carry out such investigations.

In order to perform any of the investigations mentioned above, it is necessary to select a model emulsion paint system. Since the most important components in an emulsion paint are: the pigment; the pigment stabilizer; the polymer latex; and the latex stabilizer, the choice of a model system is reduced to selecting the four components named. However, the selection of these four components has to be guided by commercial factors and the colloid chemistry of the paint system. The following factors guided the selection: the type of stabilization desired in the paint system; the availability; the extent of use in paint formulation, commer-
cial importance; purity and the ease with which it (product) can be characterised.

Generally commercial emulsion paint particles are stabilized by a combination of electrostatic (charge) stabilization and steric stabilization. In view of the present state of knowledge on both types of stabilization it was evident that only an electrostatically stabilized system would lend itself to a quantitative or semi-quantitative theoretical analysis and interpretation. Not enough is known about steric stabilization particularly in aqueous systems to be able to apply it even in a semi-quantitative way to the paint system. Consequently, it was decided that the particles in the model emulsion paint should be stabilized electrostatically. Colloid chemical and commercial considerations imposed a model system similar to a gloss emulsion paint; a gloss emulsion paint being a high reflectance, low chalking paint with a particle size distribution of 0.15-0.5 μm; 0.2-0.3 μm being ideal. The components of the model paint system were selected as described below.

As the pigment component of the system, an experimental pigment (AT-rutile) available from BTP Tioxide Ltd was chosen. A rutile type pigment was selected because of gloss paint requirements and commercial importance. The selected pigment, AT-rutile had been surface treated with alumina to modify its colloidal and chalking behaviour with respect to commercial rutile, for as Kempfer (1973) states, "a completely untreated rutile pigment provides high reflectance, whiteness and opacity but it lacks the
the qualities required in the many and varied special applications for which rutile is used'. Some of the qualities that Kempfer means are the poor dispersal in water and poor resistance to chalking by pure untreated rutile. The alumina coating diminishes these defects while not significantly affecting reflectance, opacity and whiteness.

The pigment stabilizer selected was a polyphosphate, commonly called Calgon. The polyphosphate is an anionic stabilizer of undefined molecular weight and purity. It was chosen because of its frequent use in industry and also because other pigment stabilizers had the same defects and were less commonly used.

The selection of the polymer latex and its stabilizer posed more difficult problems. Commercial latices designed for emulsion paints are often based on polyvinyl acetate either as a homopolymer or a copolymer, most of these latices also contain ester-type polymers which are very similar to polyvinyl acetate. Therefore polyvinyl acetate was chosen to be the latex component of the model system. Unfortunately there was no commercial polyvinyl acetate latex available which contained one emulsifier only, and no additives. It was therefore inevitable that the polyvinyl acetate, PVAc, latex had to be prepared in the laboratory.

Having selected an anionic stabilizer for the pigment, the latex stabilizer also had to be anionic, of which there are several available. However, purity and the necessity of well defined characteristics, led to the selection of SDS as the anionic stabilizer for the PVAc latex.
A latex forms a good film only if its constituent polymer has a very high molecular weight (usually several million). For a gloss emulsion paint the latex particle size should be in the region of 0.2-0.5 μm, and for paint preparation the latex should have an initial solids content of at least 40% wt/wt.

In summary the model water-based emulsion paint was as follows:

- **latex** = polyvinyl acetate (PVAc)
- **pigment** = alumina treated rutile (AT-rutile)
- **pigment stabilizer** = polyphosphate = Calgon; (SHMP)
- **latex stabilizer** = sodium dodecyl sulphate (SDS)
- **pH adjuster** = ammonium hydroxide
- **stabilization mechanism** = electrostatic (anionic)
- **type of paint** = gloss emulsion paint

In this formula of the model emulsion paint the only soluble components are the stabilizers. Now, this project was aimed at elucidating the main factors affecting paint storage stability and particle flocculation during drying. Hence, the project was reduced to a study of the separate and combined effects of the stabilizers (dispersants) on the pigment and the latex during storage and during drying.

It is well known that emulsion paint stability is highly pH dependent, hence the narrow pH range 7-9 in which most commercial emulsion paints are made. The project was therefore extended to include pH as a variable. The necessity then arose to define a
pH range and select pH variants. The pH range 3-10 was considered appropriate because:
1) the pH 10 is just outside the paint preparation region; and
2) the pH 3 is just below the lowest pH operative in commercial latices used in emulsion paints.

The pH's 5.0 and 8.0 were selected as key pH's because pH 8.0 was in the centre of the paint preparation region and pH 5.0 was considered the lowest pH that an emulsion pH could attain either during drying or storage. As pH variants, ammonium hydroxide and sulphuric acid were chosen. The reason for using ammonium hydroxide has been given previously in Section 1.1. Sulphuric acid was selected because sulphates and sulphuric acid constitute the main ionic decomposition products - from persulphate initiators - during the preparation of a polymer latex, see Section 3.4.4.

Thus in the final analysis, the project was directed at studying the influence of pH, and dispersants on the stability and flocculation of the pigment and latex components of the model PVAc/AT-rutile emulsion paint.

1.3 Previous Related Work

As far as is known at the moment this is the first project directed at a comprehensive fundamental study of the emulsion paint system. All previous related work has been aimed at studying the electrokinetic properties of one of the solid components of the emulsion paint system.

The very early studies of Munro and Sexsmith (1953) measured the electrophoretic mobility of PVAc latex in several stabilizers
and also investigated the effect ionic strength had on the electrophoretic mobility. The PVAc latex used by Munro and Sexsmith was a commercial latex destined for emulsion paint preparation. They showed that the stability of the polyvinyl acetate (PVAc) latex was very sensitive to ionic strength and decreased with increasing ionic strength, and that the latex decreased in stability and even flocculated in the presence of an emulsifier of opposing charge.

With respect to the pigment component of an emulsion paint system, the literature contains a dearth of publications on the electrokinetic properties of inorganic oxides; however the work related to this project has been published recently by Cremer (1977). Cremer studied surface treated rutile pigments containing various amounts of alumina coating and has shown that the alumina coating affects the electrokinetic properties of the rutile pigment and also the extent of adsorption of a stabilizer on the rutile pigment. In water the alumina coating improves the positive charge contribution on the surface of the rutile pigment and thus makes the pigment less negatively charged. He has also shown that the alumina coating on the rutile pigment improves the ability of the pigment to adsorb triethanolamine, and adsorption of this chemical raises the negative electrokinetic potential of the pigment and presumably the stability of the pigment is improved thereby.

The investigations of Cremer (1977) and of Munro and Sexsmith (1953) demonstrably highlight the usefulness of colloid and surface chemistry in the study of an emulsion paint system.
CHAPTER 2

APPLICATION OF COLLOID AND SURFACE CHEMICAL
THEORY TO THE WATER-BASED EMULSION PAINT SYSTEM
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THEORY TO THE WATER-BASED EMULSION PAINT SYSTEM

2.1 The Electrochemical Double-Layer

The early researches on electrokinetic phenomena by Quincke (1859, 1861), Dorn (1880) and others established the existence of charge on the surface of a solid in contact with a liquid such as water. It was reasoned that since immersion of a solid in water could only be attended by a redistribution of charges between the aqueous phase and the solid surface, the interface (boundary phase) acquired charges of opposite sign but equal in magnitude. The system of charges set up in the interface constitutes an electrochemical double-layer and there is a potential difference between the solid surface (wall) and the aqueous phase.

The discovery of electrokinetic phenomena and consequently the electrochemical double-layer, set the stage for experimental studies and theoretical developments on double-layer structure and potentials.

2.2 Electrochemical Double-Layer Theory

2.2.1 Double-Layer Structure Models

The simplest model of the double-layer was proposed by Helm- Holtz (1879) who regarded the system as consisting of two slabs (planes) of opposing charges and visualised the potential variation as falling linearly from the surface (wall) down to zero at the edge
of the double-layer (boundary phase). Later Perrin (1904) suggested that the double-layer could be regarded as a molecular capacitor, consisting of two plane parallel sheets of charges separated by a distance of the order of molecular dimensions.

Gouy (1910) and Chapman (1913) considered the effect of thermal motion on ions and suggested that thermal motion should produce a certain diffusiveness of charge on the solution side of the double-layer. They retained the Helmholtz-Perrin concept of the flat-double-layer and considering the charges as point charges, deduced that potential should not fall to zero but should decay exponentially from the surface into the solution phase. The Gouy-Chapman model however did not take account of the effects of specific adsorption, polarization and ionic size.

Stern (1924) modified the Gouy-Chapman model by taking account of specific adsorption and introducing the concept of a plane of closest approach of the counter ions to the surface (wall). Thus Stern split the double-layer into two parts - (1) the Stern layer consisting of an immobile layer of ions held strongly close to the wall and (2) the Gouy-Chapman layer on the solution side of the interface. In the Stern model the potential decays linearly in the Stern layer and exponentially in the Gouy-Chapman layer.

Grahame (1947) in his studies of the mercury/solution interface showed that in the Stern layer only anions were chemisorbed with partial destruction of their hydration shells; whereas the cations remained hydrated and were bound to the surface only by electrostatic forces. He distinguished between the inner Helmholtz
plane where the centres of chemisorbed anions were located and the outer Helmholtz plane which was the locus of the centres of cations closest to the wall. Beyond the outer Helmholtz plane the distribution of charge and the potential variation followed the Gouy-Chapman model.

The Gouy-Chapman-Stern-Grahame model of the double-layer has remained essentially unchanged. More modern investigations have led to small refinements of the model to include hydration of the wall and polarisation of water in the Helmholtz layers. The most detailed picture of the double-layer is due to Bockris et al (1963) and is given below, Figure 2.1. The physical properties of the double layer, viz, potentials, solvent viscosity and dielectric constant, will be considered in detail in the following sections, however coverage will be restricted to the essentials only since adequate and detailed treatment of the said topics has been provided by Dukhin and Derjaguin (1974).

2.2.2 Double-layer Potentials

Gouy (1910,1917) and Chapman (1913) were the first to attempt to find mathematical expressions for the variation of potential in the double-layer. They considered the problem from a theoretical standpoint, regarding the charge on the solid surface (wall) as a plane of 'smeared' out point charges and proceeded to examine potential variation from the compensating layer outwards into solution. Gouy and Chapman applied the apparatus of statistical physics to the resolution of this potential variation, and demonstrated that electrical neutrality of the double-layer is the...
FIGURE 2.1  The structure of the double-layer after Bockris et al (1963)
conditio sine qua non for equilibrium between the double-layer and the bulk electrolyte.

Given the electrical neutrality of the double-layer it follows from the laws of statistical physics that the distribution of charge across the double-layer obeys the Boltzmann distribution law; also the Coulombic interactions between charges can be described by Poisson's equation. For the distribution of ions we have:

\[ n_i = n_{i0} \exp\left(-\frac{z_i e \psi}{kT}\right) \]  \hspace{1cm} (2.1)

where \( n_i \) is the concentration of ions of type \( i \) at a point where the potential is \( \psi \); \( n_{i0} \) is the bulk concentration of electrolyte; \( z_i \) is the valency of the type \( i \) ions; \( e \) is the proton charge; \( k \) is Boltzmann's constant; and \( T \) is absolute temperature. The potential distribution is given by the Poisson equation:

\[ \nabla^2 \psi = -\frac{4\pi \rho}{\varepsilon} \]  \hspace{1cm} (2.2)

\( \nabla^2 \) is Laplace's operator which in Cartesian coordinates is \( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \); \( \rho \) is the space charge density, and \( \varepsilon \) is the dielectric constant of the medium.

Since \( \rho = \sum z_i e n_i \) \hspace{1cm} (2.3)

combining equations (2.1), (2.2) and (2.3) we obtain:

\[ \nabla^2 \psi = -\frac{4\pi}{\varepsilon} \sum z_i e n_{i0} \exp\left(-\frac{z_i e \psi}{kT}\right) \]  \hspace{1cm} (2.4)
This is the well known Poisson-Boltzmann equation, which is the starting point of all double-layer calculations.

Regarding the solid surface as a plane and applying Cartesian coordinates, equation (2.4) can be solved analytically. For a binary symmetrical electrolyte in solution, the potential, $\psi$ at a distance $H$ perpendicular to the plane surface is given by:

$$\psi = \frac{2kT}{\kappa z_e} \ln \left( \frac{\{\exp(ze\psi_o/2kT) + 1\} + \{\exp(ze\psi_o/2kT)-1\} \exp(-\kappa H)}{\{\exp(ze\psi_o/2kT) + 1\} - \{\exp(ze\psi_o/2kT)-1\} \exp(-\kappa H)} \right)$$

(2.5)

where $\kappa$ is the Debye-Huckel parameter and is given by:

$$\kappa^2 = \frac{4\pi e^2}{ckT} \sum n_i n_j \sigma_{ij}$$

(2.6)

In equation (2.5), $\psi = \psi_o$ at $H = 0$ (surface of the plane). Expanding equation (2.5) in the manner applied by Debye and Huckel in the theory of strong electrolytes, it can be shown that for small surface potentials ($ze\psi_o/kT << 1$), equation (2.5) reduces to:

$$\psi = \psi_o \exp(-\kappa H)$$

(2.7)

In all the above equations the potential relationships are based on the Gouy-Chapman model of the double-layer, but in view of the later modifications of the Gouy-Chapman model by Stern, Grahame and Bockris et al (see Section 2.2.1) it must be emphasised that these
potential relationships apply only to the Gouy-Chapman layer, diffuse double-layer. Therefore, in the above equations the potential $\psi_0$ may be replaced by $\psi_d$, the maximum Gouy-Chapman potential, which obtains at the outer Helmholtz plane (Stern plane).

When the charged surface is a sphere rather than a plate, the Poisson-Boltzmann equation cannot be integrated analytically without making some approximations. For a weakly charged spherical particle (i.e. $ze\psi_0/kT << 1$), the linearized Poisson-Boltzmann equation had already been solved by Debye and Huckel (1923) and has the form:

$$\psi = \psi_0 \frac{R}{R + H} \exp (-\kappa H)$$

(2.8)

where $R$ is the radius of the sphere.

Solutions of the nonlinearized Poisson-Boltzmann equation for a spherical interface have been proposed by several workers namely: (1) Gronwall (1927) and Gronwall et al. (1928), who obtained an approximate analytical solution and found good agreement with the linearized solution, equation (2.8) for $\kappa R << 1$.

(2) Muller (1928) used a graphical method and suggested that equation (2.8) was reasonably accurate up to $ze\psi_0/kT = 4$ and $\kappa R = 2$.

(3) Hoskin (1953, 1956) used numerical integration and found good agreement with equation (2.8) only for $ze\psi_0/kT < 1$ and $\kappa R < 1$. At high potentials and $\kappa R > 1$ the numerical solution diverged largely from the approximate solution, equation (2.8).
Loeb et al (1961) used numerical methods and the facility of an electronic computer to obtain solutions over a wider range of potentials and $kR$ values for symmetrical and asymmetrical electrolyte solutions, and confirmed Hoskin's observations.

The validity of all the above mentioned theoretical calculations on the double-layer depends on the applicability of the Poisson-Boltzmann equation as expressed in equation (2.4). Ever since Fowler (1927) pointed out the fundamental incorrectness of this equation there have been a number of corrections introduced, and since the subject has been adequately discussed by Bolt (1955), Sparnaay (1958, 1962, 1972) and by Bell and Levine (1966), only the essential points will be mentioned here. The corrections introduced have been aimed at taking account of one or more of the following:

1) finite size of ions
2) dielectric saturation in the double-layer
3) polarization of ions and solvent in the double-layer
4) self atmosphere and discreteness of charge effect.

Bolt (1955) has shown that for moderate potentials and ionic concentrations ($< 60$ mV and $0.01M$) the corrections become insignificant through a process of self-compensation. Bell and Levine (1960) also conclude that the effect of electrostriction on diffuse double-layer structure is negligible for low and moderate potentials, this being valid for a 1:1 electrolyte up to 75 mV and 0.1M concentration.
2.2.3 *Surface Charge Density*

In order that the double-layer be neutral the surface charge must be equal and opposite to the total space charge in solution; and under these conditions:

\[
\sigma = - \int_{0}^{\infty} \rho \, dH
\]  \hspace{1cm} (2.9)

where \( \sigma \) is the surface charge density, and \( \rho \) is the space charge density.

The relation between \( \sigma \) and the surface potential, \( \psi \), can be obtained by using the Poisson-Boltzmann equation. For a flat double-layer and a binary symmetrical electrolyte in solution, \( \sigma \) is given by

\[
\sigma = \sqrt{\frac{\varepsilon nkT}{2\pi}} \left| \exp(ze\psi_o/2kT) - \exp(-ze\psi_o/2kT) \right| \]  \hspace{1cm} (2.10)

On expansion equation (2.10) reduces (for small surface potentials) to:

\[
\sigma = \frac{\varepsilon n\psi_o}{4\pi} \]  \hspace{1cm} (2.11)

With respect to the surface charge density for a spherical double-layer, it has already been stated that the Poisson-Boltzmann equation has to be solved numerically, and Loeb et al. (1961) have tabulated data from numerical calculations for the spherical double-layer. It can be shown that for a low surface potential \((ze\psi_o \ll 1)\)
using a linearization method $Q$ the surface charge is given by:

$$Q = eR\psi_0 (1 + kR) \quad (2.12)$$

2.2.4 The Origin of Charge

Acquisition of surface charge by particles in an aqueous medium can occur by several mechanisms namely:

1) Adsorption of ionic species from solution, and this can involve the exclusive adsorption of ions of one charge type, or unequal adsorption of ions of opposing charge. In particular for the model emulsion paint system, this may involve adsorption of stabilizers and, or H\(^+\) or OH\(^-\) ions.

2) Dissociation or ionisation of surface groups, usually involving a reaction with the aqueous phase. This mechanism is exemplified by the ionisation of -COOH groups on proteinic molecules or latex particles at high pH.

3) Unequal dissolution of oppositely charged ions of which the particle may be composed; as illustrated by the negative charge on hydrosols of silver halides.

Having described the general mechanisms of charging of a solid surface in aqueous medium, it is pertinent to examine the charging of the surfaces of the pigment and latex components of our model emulsion paint system. The pigment (AT-rutile) and the latex (PVAc) will be considered separately.
Ignoring the impurities in the AT-rutile, the pigment can be regarded as a metallic oxide, and therefore the mechanism of charging of its surface will be similar to that of other metallic oxides. Generally it is accepted that in the absence of specifically adsorbable ions, the metallic oxides acquire charge by adsorption of H⁺ or OH⁻ ions from the aqueous phase, and this mechanism can be represented as follows:

\[
\begin{align*}
M-\text{OH} & \quad H^+ & \quad M-\text{OH}_2^+ \\
&, & \quad \text{OH}^- & \quad M-(\text{OH})_2^- \\
& & & M = \text{metal}
\end{align*}
\]

Parks and de Bruyn (1962) have suggested an alternative mechanism for the charging of oxide surfaces. They propose that the charging process involves the formation of hydroxo-complexes in solution and the transfer of these complexes across the interface. For Fe₂O₃, for example, the adsorbed species are postulated to be Fe(OH)⁶⁺ and FeO₂⁻, whose concentrations in solution are considered to be pH dependent. It is thought that from a purely thermodynamic standpoint, it is not possible to distinguish between the stated mechanisms of charging, although the mechanism of Parks and de Bruyn would seem unacceptable when the oxide is TiO₂ since hydroxo-complexes of titanium are very unstable. Nevertheless the general mechanism above indicates that the sign of charge on a metallic
oxide surface is pH dependent and also that at most pH's there will be two types of groups on the oxide surface - \( M-OH_2^+ \) and \( M-OH \); or \( M-(OH)_2^+ \) and \( M-OH \).

Now considering the charging of metallic oxide surfaces in the presence of phosphate is very complex, so only the reactions between the surface and phosphate will be considered. It is common experience that in the presence of phosphate \( H^+ \) and \( OH^- \) cease to be potential determining ions because of specific adsorption of phosphate. It is postulated in the scheme of reactions that phosphate can adsorb on or react with the metallic oxide surface. The postulate of chemical reaction (bond formation) derives from the very early studies of Johansen and Buchanan (1957), where it was found that phosphate adsorption on alumina could not be reversed completely within reasonable time. It is worth noting that Johansen and Buchanan themselves never suggested chemical adsorption was involved. The generally accepted schemes of reactions between orthophosphate and metallic oxide surfaces are as follows:

\[
\begin{align*}
M-OH + HPO_4^{2-} & \rightarrow M-OHPO_3^- + OH^- \quad (2.13) \\
M-OH_2^+ + HPO_4^{2-} & \rightarrow M-OHPO_3^- + H_2O \quad (2.14) \\
M-OH_2^+ + H_2PO_4^- & \rightarrow M-OH_2PO_3^+ + H_2O \quad (2.15)
\end{align*}
\]
It is evident from the above reaction schemes that only reactions 2.13 and 2.14 will result in an acquisition of charge by the surface.

With respect to the latex component of the paint system the mechanism of charging in the absence of SDS does not involve any adsorption of ions from the aqueous phase. The preparation of the latex involves ion radicals (see Section 3.4.4) and the resultant latex particles thus acquire a permanent surface charge. It will be seen later (Section 3.4.6) that the surface groups are acidic (SO₄⁻, SO₃⁻ and CO₂⁻) and so theoretically the particles can be regarded as being charged through dissociation of ionogenic surface groups. As the latex particles are permanently negatively charged, it may be expected that in the presence of SDS the surface charge might be increased by adsorption of dodecyl sulphate ions (DS⁻).

2.3 Stern Theory and the Adsorption of Ions at the Solid/Solution Interface

Since the stabilizers of the paint particles, SDS and polyphosphate, are ionising electrolytes in the aqueous phase, it is useful to consider the application of Stern theory to the adsorption of ions at the solid/solution interface. Stern (1924) was the first to analyse specific adsorption of ions at the solid/solution interface. He used a method analogous to the derivation of the Langmuir isotherm and obtained the following expression for the charge density \( \sigma_1 \) in the Stern plane:
\[ \sigma_1 = \frac{N_1 z_+ e}{1 + \frac{N_A}{n_+ M} \exp \left( \frac{z_+ e \psi_d + \phi_+}{kT} \right)} \]

\[ \frac{-N_1 z_- e}{1 + \frac{N_A}{n_- M} \exp \left( \frac{-z_- e \psi_d - \phi_-}{kT} \right)} \]

where \( N_1 \) is the available number of adsorption sites per cm\(^2\), \( z_+ \) and \( z_- \) are the valencies of ions of concentration \( n_+ \) and \( n_- \) respectively, \( \psi_d \) is the Stern plane potential and \( \phi_+ \) and \( \phi_- \) are the specific adsorption potentials of the ions; \( M \) is the molecular weight of the solvent, and \( N_A \) is the Avogadro number. Proceeding from equation (2.16) the following relationship can be obtained between the \( \sigma_1 \) and the free energy of adsorption \( \Delta G_o \), for dilute solutions, and only counter ion adsorption:

\[ \sigma_1 = n_1 ez = \frac{N_1 ez}{1 + \exp \left( \frac{\Delta G_o}{kT} \right)} \]

where \( n_1 \) = number of ions adsorbed per cm\(^2\); and \( x \) is mole fraction.

The free energy of adsorption can be split into two parts as follows:

\[ \Delta G_o = \Delta G + ze \psi_d \]

where \( \Delta G \) is the chemical component and \( ze \psi_d \) is the electrical component.
Guggenheim (1936) has criticised this artificial splitting of the free energy of adsorption pointing out that the interdependence between various terms makes it impossible to achieve such a split. Nevertheless, if the Stern theory is to be of any help in interpreting ionic adsorption then such a split is inevitable.

From equation (2.18) it emerges that even when the electrical term \( z e \psi_d \) is positive (i.e. adsorbing ion and the surface have the same charge sign) it is still possible for adsorption to occur, so long as the chemical term, \( \Delta G \), is negative and larger than the electrical term. Also if the chemical term is positive, adsorption is only possible if the approaching ion is oppositely charged with respect to the surface. When the terms \( z e \psi_d \) and \( \Delta G \) are both negative then there would be cooperative adsorption enabled by van der Waals and electrostatic (Coulombic) forces.

Stern's approach has been criticized for ignoring (a) the effects of lateral repulsion between adsorbed ions, (b) the discreteness of charge effect and (c) the influence of the absorbed ions on the dielectric constant of the material, 'medium' in the Stern layer. Also the use of the Langmuir equation implies that the adsorbed ions are immobile. The most important of the above effects is the discreteness of charge effect, the others being regarded as not very important in calculations. Levine et al (1962, 1965) have introduced a correction into the Stern-Langmuir equation to take into account the discreteness of charge effect. It is notable that the discreteness of charge effect only affects the electrical terms \( z e \psi_d \) in the Stern-Langmuir equation, equation...
2.16. It is proposed to use the Stern theory in the discussion of the adsorption of polyphosphate (SHMP) and SDS in Chapter 5.

2.4. The Zeta Potential

The discussion of the double-layer theory in Section 2.2. dwelt on the surface potential $\psi_0$, of the colloidal particle, however this surface potential is not accessible experimentally. Since electrokinetic phenomena involve relative tangential displacement between two phases (solid/liquid for our system) it follows that the potential of immediate interest experimentally in a colloidal dispersion, is the potential operative at the slipping plane between the solid and solution. The potential at the slipping plane is called the zeta potential ($\zeta$).

Since the Stern layer is considered to be immobile, the slipping plane is located in the diffuse part of the double-layer (the Gouy-Chapman layer). The relation between the $\zeta$-potential and the Stern potential, $\psi_d$ is dependent on the position of the slipping plane relative to the outer Helmholtz plane (Stern plane). Generally $\zeta$ is directly proportional $\psi_d$, and $\zeta = \psi_d$ when the Stern plane and the slipping plane coincide. Usually $\psi_d$ and $\zeta$ are unequal when there is considerable solvent immobilization in the Stern layer — see Lyklema and Overbeek (1961).

The potential $\psi_d$ is not equal to the surface potential $\psi_0$, however $\psi_d$ is regarded as the effective surface potential because (1) $\psi_d$ derives from the presence of specifically adsorbed ions in the Stern layer, and (2) when two charged particles approach each
other, it is the Stern plane potential, \( \psi_d \) which is actually 'seen' by each particle. Therefore by determining \( \zeta \) and assuming \( \zeta = \psi_d \) (i.e. slipping plane coincident with the Stern plane) it is possible to calculate the surface charge density of the Stern plane.

The \( \zeta \)-potential of a colloid particle can be obtained by electrophoresis, which is discussed in Chapter 4. The \( \zeta \)-potential is usually obtained by measuring electrophoretic mobility and then using one of the several formulae available to calculate the \( \zeta \)-potential. The discussion of the various equations for calculating \( \zeta \)-potentials has been adequately done by Overbeek (1952) and more recently Dukhin and Derjaguin (1974) have thoroughly reviewed the subject. Therefore the discussion of the equations will be brief and they will be presented in chronological order.

Helmholtz (1879) derived the first equation relating mobility and \( \zeta \)-potential but this equation was later modified by Smoluchowski (1903) and is now referred to as the Smoluchowski equation:

\[
V_e = \frac{\varepsilon \zeta X}{4 \pi \eta} \tag{2.19}
\]

where \( V_e \) is the velocity of the particle under an applied electric field of intensity \( X \) in a solution of viscosity \( \eta \). The quotient \( V_e/X \) is called the mobility (U) of the particle and is described as the electrophoretic mobility when this mobility has been obtained by electrophoresis. It can be shown that in aqueous solution at 25°C, \( \zeta \)-potential is given by:
\[ \zeta = 12.83U \]  
\[ (2.20) \]

where \( \zeta \) is in mV and \( U \) is in \( \text{m} \text{s}^{-1} \text{V}^{-1} \times 10^8 \). The Smoluchowski equation \((2.19)\) only applies when the double layer thickness is small compared to the radius of the particle; that is \( \kappa R \gg 1 \) and in practice only for \( \kappa R \geq 500 \).

When the double layer thickness is much larger than the radius of the particle (i.e. \( \kappa R \leq 0.1 \)) the \( \zeta \)-potential may be obtained from the Debye-Huckel equation:

\[ V_e = \frac{\varepsilon \zeta X}{6\pi \eta} \]  
\[ (2.21) \]

In addition to the limitation on the range of \( \kappa R \) values in which the Smoluchowski equation \((2.19)\) and the Debye-Huckel equation \((2.21)\) apply, the equations are valid only for nonconducting particles.

Henry (1948) has shown that the equations \((2.19)\) and \((2.21)\) are only limiting forms of the more general equation:

\[ U = \frac{\varepsilon \zeta}{6\pi \eta} \left[ 1 + \Lambda f(\kappa R) \right] \]  
\[ (2.22) \]

in which \( \Lambda = \frac{\lambda_o - \lambda}{2\lambda_o - \lambda} \)

where \( \lambda_o \) is the electrical conductivity of the electrolyte and \( \lambda \) that of the particle. For a nonconducting particle \( \lambda = 0 \) and \( \Lambda = 0.5 \).
Although the Henry equation (2.22) takes into account electro-
not phoretic retardation on the particle, it does not correct for the relaxation effect. The subject of the relaxation correction has been treated by Overbeek (1943, 1950), Booth (1950), Loeb et al (1961) and Wiersema et al (1966); and the following conclusions can be drawn:

1) relaxation correction is negligible for small potentials, 
\( \zeta < 25 \text{ mV} \)

2) for \( \kappa R \) between 0.1 and 100 the relaxation effect may be very important and is especially serious for \( \zeta > 10 \text{ mV} \) and \( 0.2 < \kappa R < 50 \).

3) for very large \( \kappa R \) usually \( \geq 500 \) the relaxation effect is negligible.

Generally the relaxation effect depends almost totally on the valency of the counterion and is usually a positive relaxation effect (decrease in mobility). However when there are multivalent coions of low mobility present a negative relaxation effect (increase in mobility) may result - see Wiersema et al (1966).

Overbeek and Booth found the mathematical treatment of the relaxation effect to be very difficult and they were forced to make analytical approximations to obtain expressions relating \( U \) to \( \zeta \) as a power series in \( \zeta \). Since Booth's solutions are limited to a symmetrical electrolyte, the solutions of Overbeek will be given here. Ignoring terms in higher powers than \( \zeta^3 \) Overbeek's equations are as follows:
Symmetrical electrolyte:

\[ E = y_0 f_1(\kappa R) - y_0^2 (z^2 f_3(\kappa R) + 0.5 (m_+ + m_-) f_4(\kappa R)) \]  \hspace{1cm} (2.23)

where \( E \equiv \frac{6 \pi n e U}{kT} \) \hspace{1cm} (2.24)

\[ y_0 \equiv \frac{e \zeta}{kT} \] \hspace{1cm} (2.25)

\[ m_\pm = \frac{N_A e kT z_\pm}{6 \pi n \lambda_0^\pm} \] \hspace{1cm} (2.26)

\( m_\pm \) is a friction factor; \( N_A \) is Avogadro number; \( \lambda_0^\pm \) is the limiting conductance of an ion of valency \( z_\pm \).

For an asymmetrical electrolyte:

\[ E = y_0 f_1(\kappa R) - y_0^2 (z_- - z_+) f_2(\kappa R) \]

\[ - y_0^3 \left[ \frac{z^+ m_+ + z^- m_-}{z_+ + z_-} \right] f_4(\kappa R) \] \hspace{1cm} (2.27)

All terms retain the same meanings as given for the case of a symmetrical electrolyte. The \( f(\kappa R) \) functions are plotted in figure 2.2, as a function of \( \kappa R \).

Although Overbeek indicates that his equations are exactly applicable only for \( \zeta < 25 \text{ mV} \), Wiersema et al (1966) have shown that
FIGURE 2.3 $f_n$ functions in Overbeek's equations (2.23) and (2.27).
for a 1:1 electrolyte Overbeek's equation (2.23) holds good for up to 70 mV. Generally Overbeek's solutions are reasonably good up to 50 mV.

Loeb et al (1961) applied numerical methods to solve the Poisson-Boltzmann equation exactly and used a computer to obtain results for various \( kR \) values and \( \zeta \)-potentials up to 150 mV. They did calculations for symmetrical and unsymmetrical electrolytes and tabulated all their results. Later they published an extract of their calculations (see Wiersema et al (1966)) for \( 0.2 < kR < 50 \), and indicated that their results are applicable to a 1:1 electrolyte for \( \zeta \)-potentials up to 150 mV, but for unsymmetrical electrolytes up to 60 mV. It turns out that the range of \( kR \) values where the solution applies is greater than that stated above.

The numerical solution of Loeb et al (1961) is very complicated and Wiersema et al (1966) advise that it should be used only as a last resort. It is proposed to use the Overbeek equations (2.23 and 2.27) in calculating zeta potentials in our model emulsion paint system because \( kR \) ranges from 1 to 100 in general and one of the stabilizers, the polyphosphate (see Section 3.2) is an unsymmetrical electrolyte.

One important drawback in the solutions of Overbeek and Loeb et al is that they are limited to a single electrolyte in solution, whereas our model emulsion paint system will contain a mixture of electrolytes. This problem necessitates that in Chapter 5 calculations are only performed for systems containing one type of electrolyte.
So far the discussion on the transformation of mobilities into \( \zeta \)-potentials has assumed that \( \varepsilon \) and \( \eta \) have the same value in the double layer and in the solution phase. When the applied electric field is sufficiently high it can cause a decrease in \( \varepsilon \) and or an increase in \( \eta \) in the slipping plane such that the plane of slip is replaced by a finite slipping layer - see Lyklema and Overbeek (1961). These authors have analysed the problem and conclude that the effect on \( \varepsilon \) is very small but the effect on \( \eta \) can be as much as 20\% at high \( \zeta \)-potential. However Stigter (1964) pointed out that Lyklema and Overbeek overestimated the viscoelectric effect and Smith (1969) has suggested that the error factor may be as high as 50 to 100. Because of the controversy on the variations in \( \eta \) and \( \varepsilon \) and the uncertainty about the correction factors which apply for these variations, no allowance will be made for these effects in the calculation of zeta potentials in Chapter 5.

2.5 Interaction of Electrochemical Double Layers

The mutual approach of two colloidal particles is accompanied by a repulsive energy arising from the overlap of their diffuse double layers. The treatment of this repulsive energy requires certain simplifying assumptions, and depends on the geometry of the particles. In our model emulsion the particles are spherical or roughly so, therefore the discussion on the repulsive energy \( V_R \), will be restricted to sphere-sphere interaction.

The mathematical treatments available differentiate between identical and dissimilar (non-identical) double layers, where identity
implies equality of surface potentials or charge densities. Most methods are based on constant potential interactions but Overbeek (1977) in a review has pointed out that the kinetics of charge adjustment during an encounter would seem to favour the constant charge treatment. The more common constant potential equations will be discussed first and later (Section 2.5.2). The constant charge approach will be discussed briefly.

2.5.1 Sphere-sphere interaction at constant potential

The discussion of this interaction will be split into two parts - (1) interaction of identical double-layers and (2) interaction of dissimilar double-layers.

Generally because of the number of parameters involved in the analysis, mathematical treatment is very difficult so that only approximate solutions are available.

2.5.1.1 Sphere-sphere interaction at constant equal potentials

The interaction of two spherical double-layers of equal potentials has been competently discussed by Verwey and Overbeek (1948), therefore only the important equations will be summarized, making comments where pertinent.

Derjaguin (1934, 1940) obtained an expression for the repulsive energy $V_R$ between two identical spheres by extrapolating from the infinitely large plate approach. He treated each sphere as a series of rings each of radius $h$ and thickness $dh$, and obtained that the
interaction of two rings is \( 2\pi hV(H)\) where \( V(H) \) is the interaction energy of two plates per cm\(^2\). By integration he obtained the following relation for \( V_R \):

\[
V_R = \pi R \int_{H_0}^{\infty} V(H) dH
\] (2.28)

where \( H \) is separation, \( H_0 \) is the minimum separation and \( R \) is the radius of the particle. For small potentials equation 2.28 can be solved to give the general Derjaguin equation:

\[
V_R = \frac{\varepsilon R \psi^2}{2} \ln \left[ 1 + \frac{2R}{2R + H} \exp(-\kappa H) \right] \left[ 1 + \frac{\sinh(\kappa R) \exp(-\kappa R) \exp(-\kappa H)}{\kappa (2R + H)} \right]
\] (2.29)

when \( \kappa R \gg 1 \) and \( \kappa H \gg 1 \) equation 2.29 reduces to the more familiar equation:

\[
V_R = \frac{\varepsilon R \psi^2}{2} \ln \left[ 1 + \exp(-\kappa H) \right]
\] (2.30)

when \( H \) is comparable to \( R \), a simpler form of equation 2.29 (as quoted by Nazir, 1978) is:

\[
V_R = \frac{\varepsilon R \psi^2}{2} \ln \left[ 1 + \frac{2R}{2R + H} \exp(\kappa H) \right]
\] (2.31)

It will be seen later that equations (2.30) and (2.31) are only
coincident at very small separations, as proposed by Derjaguin.

### 2.5.1.2 Sphere-sphere interaction at constant unequal potentials

Derjaguin (1954) was the first to examine the interaction of dissimilar double-layers and indicated some of the problems which may arise in the study of heteroflocculation. He showed that in interaction at unequal potentials it is possible for transition to occur from repulsion to attraction at very short separations. A maximum repulsion energy exists at a finite separation which is dependent only on the magnitude of the lower potential. It is not possible to test Derjaguin's deductions because there are no exact equations available.

Following Derjaguin's publication (1954) there have been several on dissimilar double-layers but the equation relevant to us is that of Hogg et al (1966). The equation of Hogg et al was derived, by following Derjaguin's method (Section 2.5.1.1) and is therefore subject to the same restrictions and assumptions. For two spheres of radii $R_1$ and $R_2$, $V_R$ is given by

$$V_R = \frac{2\pi R_1 R_2}{R_1 + R_2} \int_{H}^{\infty} V(H)dH$$

(2.32)

This integral was solved analytically by Hogg et al to give:

$$V_R = \frac{e R_1 R_2}{4(R_1 + R_2)} \left(\psi_{01}^2 + \psi_{02}^2\right) + \frac{2}{\psi_{01}^2 \psi_{02}^2} \ln \frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)}$$

+ $\ln (1 - \exp(-2\kappa H)}$  

(2.33)
Equation (2.33) reduces to the Derjaguin equation (2.30) for identical spheres, when \( \psi_{01} = \psi_{02} = \psi_0 \), and \( R_1 = R_2 = R \).

This statement was tested in this laboratory by computer programming (see Appendix for the program), and found to be correct, however, the identity rather surprisingly holds throughout that is, it is not dependent on \( H \). In Figure 2.3 is shown a plot of the ratios of \( V_R \) from Hogg et al. (equation 2.33) to \( V_R \) Derjaguin for identical spheres, (equation 2.30) and the corresponding ratio of \( V_R \) from the two Derjaguin equations (2.30), and (2.31). Evidently, since equation (2.30) is restricted to \( kR \gg 1 \) and \( kH \gg 1 \), it follows that given the identity between \( V_R \) from Hogg et al. for equal potentials, and \( V_R \) from equation (2.30), the equation of Hogg et al. (2.33), should be restricted to \( kR \gg 1 \), and \( kH \gg 1 \), i.e. small separations only. Figure 2.3 also indicates that for our system \( R = 1300 \Omega \), equations (2.30), and (2.33), overestimate \( V_R \) by 10% or more when \( H \geq 250 \Omega \). These observations serve as a reminder that the equation of Hogg et al. needs refinement.

2.5.2 Sphere-sphere Interaction at Constant Charge

Weise and Healy (1970) have derived the following expression for interaction at constant surface charge between spherical double layers:

\[
V_R^o = V_R^\psi - \frac{e}{2} \left( \frac{R_1}{R_1 + R_2} \frac{R_2}{R_1 + R_2} \right) \ln \left( 1 - \exp(-2kH) \right) \quad (2.34)
\]

where \( V_R^\psi \) is the repulsive energy for interaction at constant potential.
$\kappa = 10^6 \text{ cm}^{-1}; \ \psi_0 = \psi_{02} = \psi_0 = 20; 30, 40 \text{ mV}$

The ratios are potential independent.

$V_R (\text{Hogg et al})$ - equation (2.33)

$V_R (\text{Derjaguin, } R >> H)$ - equation (2.30)

$V_R (\text{Derjaguin, } H \rightarrow R)$ - equation (2.31)

$\frac{V_R (\text{Derjaguin, } R >> H)}{V_R (\text{Derjaguin, } H \rightarrow R)}$

$R_1 = R_2 = R = 1300 \text{ Å}$

FIGURE 2.3 Ratio of $V_R$ from Hogg et al to $V_R$ from Derjaguin for $R >> H$ and $H \rightarrow R$. Constant $\kappa$, equal potentials, sphere-sphere interaction.
According to Frens and Overbeek (1972) the difference between $V_R^\sigma$ and $V_R^\psi$ tends to decrease with surface potential however, for small potentials $V_R^\sigma$ deviates markedly from $V_R^\psi$ for $\kappa H < 1$.

For $\kappa H < 0.5$, $V_R^\sigma$ becomes increasingly higher than $V_R^\psi$ as $H$ decreases. Generally $V_R^\sigma$ is larger than $V_R^\psi$ and the two are only identical at large separations. Jones and Levine (1969) have concluded that neither the constant charge nor the constant potential approach is applicable at $\kappa H < 0.5$. The choice between the two approaches is so controversial that Kar et al (1973) have worked out an equation combining both methods but their equation does not seem a significant improvement.

In the study of our model emulsion paint system the constant potential approach would be adopted because of two reasons (1) the complexity of the system makes it doubtful that choice of approach makes a significant difference, (2) the large separations operative in an emulsion paint mean that $V_R^\sigma$ and $V_R^\psi$ will probably be equal anyway.

2.6 Attractive Energy of Interaction, $V_A$

In addition to the repulsive energy, $V_R$, there is an attractive energy, $V_A$, between interacting colloidal particles, which derives from three sources: (1) permanent-dipole-permanent dipole interaction - (Keesom forces), (2) permanent dipole-induced dipole interaction (Debye forces) and (3) induced dipole-induced-dipole interaction (London - van der Waals forces). Of the three types of forces, the London - van der Waals forces make the main contribution to
intermolecular attraction energy, and it is these forces which will be further discussed because of their importance in colloid science.

2.6.1 London - van der Waals forces

Van der Waals (1873) established that attraction between neutral atoms (molecules) can occur because an instantaneous dipole can be formed in an atom (molecule) as a result of instantaneous variations in the electronic configuration around the atom or molecule, and this dipole can induce other dipoles in neighbouring molecules, and the interaction between the dipoles results in attraction. London (1930) formulated the expression relating this attractive energy with the distance of separation between the molecules. He showed the energy to be proportional to the inverse 6th power of the separation distance, \( r \). However at large separations Casimir and Polder (1948) have shown that \( V_A \) decreases as \( r^{-7} \) instead of \( r^{-6} \). The relation obtained by Casimir and Polder is merely a consequence of the fact that London-van der Waals' forces are of electromagnetic origin and require time for transmission. So that there can be a retardation (time lag) between emission of a wave by molecule \( X \) to molecule \( Y \), and the reception by \( X \) of the wave re-emitted by \( Y \), with the result that the electronic configuration around \( X \) changes between emission and reception. The effect of retardation is to reduce the magnitude of the attractive energy.

There are several expressions for the attractive energy between colloid particles, and these can be divided into two groups:
(1) Solutions applicable to unretarded attraction only, which are considered to be valid for the separations $H < \lambda/2$ where $\lambda$ is the characteristic wavelength of the molecule; (2) Solutions applicable throughout, while allowing for retardation effects. These solutions are usually said to hold for $H \geq \lambda/2$. It is proposed to discuss the two groups of expressions separately.

2.6.2 Unretarded Attraction Between Spheres

Hamaker (1937) has used an integration to obtain the following analytical solutions for unretarded attraction between two spheres of radii $R_1$ and $R_2$ separated by a distance, $H$:

$$V_A = -\frac{A}{12} \left[ \frac{y}{x^2 + xy + x} + \frac{y}{x^2 + xy + x + y} + 2 \ln \left( \frac{x^2 + xy + x}{x^2 + xy + x + y} \right) \right]$$

where $x = H/(R_1 + R_2)$

$$y = R_2/R_1; \quad R_2 > R_1$$

$A$ is Hamaker constant (to be discussed in Section 2.6.4).

When $R_1 = R_2 = R$ equation (2.35) reduces to equation (2.36) below:

$$V_A = -\frac{A}{6} \left[ \frac{2R^2}{H(H + 4R)} + \frac{2R^2}{(H + 2R)^2} + \ln \frac{H(H + 4R)}{(H + 2R)^2} \right]$$

According to Verwey and Overbeek (1948) when $R \gg H$ equation (2.36) has the approximate form:
The above equations only apply for small separations where $H \ll \lambda/2$. Making the reasonable assumption that $\lambda = 1000 \, \text{Å}$ for particles in our model emulsion paint, it can be shown that in the paint $H \geq \lambda$; for example assuming a particle concentration of $10^{12}$ particles $\text{cm}^{-3}$ and a cubic lattice $H$ works out to be $2500 \, \text{Å}$. Moreover we are interested in the possible existence of secondary minima (see Section 2.9) and these tend to occur at $H > \lambda/2$. Therefore the unretarded equations are unsuitable for our system.

2.6.3 Retarded Attraction Between Spheres

Since the equations applicable to retarded attraction apply for all separations they are appropriate for our model paint system.

Schenkel and Kitchener (1960) proposed equations which are supposed to take account of retardation and these have been extensively used probably because of their simplicity. However Vincent (1973) has pointed out the inadequacy of the equation of Schenkel and Kitchener and also indicated that for small particles especially, the equation is in greater error than the unretarded Hamaker equation (2.35).

For sphere-sphere interaction the equations useful to us are those due to Vincent (1973) because of their simplicity relative to the exact but very complicated solutions of Clayfield et al (1969). Vincent's equations are based on the original equation of Vold (1961) given as:

\[
V_A = \frac{-AR}{12H} \tag{2.37}
\]
\[ V_A = \frac{-1}{12} \sum_{i,j} f(A_i) H_j \] (2.38)

for interacting particles with solution sheaths or adsorbed layers of various Hamaker constants. In equation (2.38), \( f(A_i) \) is a function of the various Hamaker constants involved and \( H_j \) is a function of the geometry of the system, which in our case is a sphere. In view of the separations involved in our model emulsion paint system it is proposed to ignore the effect of adsorbed layers since \( V_A \) is insensitive to their effect at large separations. In the absence of adsorbed layers equation (2.38) can be written as:

\[ V_A = \frac{-1}{12} f(A_i) \sum f(H)_j \] (2.39)

Vincent breaks down the \( H \) functions into two parts \( H^L \) and \( H^S \) where \( H^L \) applies at long range interaction and \( H^S \) applies for short range interactions. He claims a smooth transition from \( H^L \) to \( H^S \), throughout, however, it will be shown in Section (2.6.3.1) that this is not always true. Furthermore Nazir (1978) has found that the polynomials given by Vincent for calculating the critical separation \( \Delta^* \) for cross-over are grossly incorrect and should not be used. In this text \( \Delta^* \) has been determined graphically from computer calculations for which the program is given in the appendix.

2.6.3.1 Vincent's \( H^S \) and \( H^L \) functions for sphere-sphere interaction

Using an integration method similar to that of Hamaker (1937) Vincent derived the following expressions for \( H^S \) and \( H^L \):
\[ H^S = a \left[ \frac{y}{u} + \frac{y}{u+y} + 2 \ln \left( \frac{u}{u+y} \right) \right] + \]

\[ + \frac{8b}{c} \frac{R^2}{1} \left[ 2y + (2u+y) \ln \left( \frac{u}{u+y} \right) \right] \]  \hspace{1cm} (2.40)

\[ H^L = \frac{a'}{10c} \left[ \frac{y(1+y)^2}{u^2} + \frac{y(1-y)^2}{(u+y)^2} - \frac{2(y^2+y+1)}{u} \right] + \]

\[ + \frac{2(y^2-y+1)}{u+y} + 4 \ln \left( \frac{u+y}{u} \right) \]

\[ + \frac{b'}{60} \frac{R^2}{1} \left[ \frac{2}{u+y} - \frac{2}{u} + \frac{y^2+y+1}{u^2} - \frac{y^2-y+1}{(u+y)^2} \right] \]

\[ - \frac{y(1+y)^2}{u^3} - \frac{y(1-y)^2}{(u+y)^2} \]  \hspace{1cm} (2.41)

In the above equations (2.40 and 2.41) a, a', b, b' are constants which have the values:

\[ a = 1.01; \quad b = 0.14 \left( \frac{2\pi}{\lambda} \right) \]

\[ a' = 2.45 \left( \frac{\lambda}{2\pi} \right) \quad b' = 2.04 \left( \frac{\lambda}{2\pi} \right)^2 \]

The variable u, c, x, and y are defined as follows:
\[ u = x^2 + xy + x; \quad c = R_1 + R_2 + \Delta; \]

\[ x = \Delta/2R_1 \quad \text{and} \quad y = R_2/R_1, \quad \text{and} \]

since there are no adsorbed layers \( \Delta = H \). The characteristic wavelength, \( \lambda \), has been included in some of the constants above, so that when the two spheres are of different materials of significantly differing \( \lambda \)'s then it is not certain what value to assign to \( \lambda \). Therefore it is evident that the Vincent equations implicitly assume identical or very close \( \lambda \)'s. Fortunately in our system the \( \lambda \) values are very close and \( \lambda \) has been assumed to be 1000 Å in all calculations.

Equations 2.40 and 2.41 were tested for smoothness of cross-over for equal and unequal radii and the results are given in figures (2.4, 2.5, 2.6, 2.7 and 2.8). In figure 2.4 it can be seen that the smoothness of cross-over deteriorates as the radius of the particle radius increases, when \( R_1 = R_2 = R \) and seems that for \( R_1 = R_2 = R > 2500 \) Å the smoothness of transition breaks down completely. The breakdown in transition (cross-over) smoothness is a serious handicap because it can lead to a serious overestimation of the height of the primary barrier \( V_T(\text{max}) \), if \( V_T(\text{max}) \) occurs at a value of \( H \) in the region where the transition takes place. However, it is fortunate that for our system the cross-over is smooth as can be seen from figures 2.5 and 2.6.

Another interesting point about the Vincent functions can be deduced from figures 2.7 and 2.8 which show interaction for unequal radii where \( R_1 = 500 \) Å and \( R_2 \) varies from 500 Å to 5000 Å. In spite
FIGURE 2.4 $\Delta^*$ for spheres of equal radii

$\Delta^*$ is the value of $H$ at which $H^S$ crosses $H^L$
$R_1 = R_2 = 1250 \, \text{Å}$

**FIGURE 2.5**  $\Delta^*$ for spheres of equal radii

$\Delta^*$ is the value of $H$ at which $H^S$ crosses $H^L$. 

$H^S$ and $H^L$ represent two sets of data points plotted on a graph with a logarithmic scale for $H/H^L$. The graph shows a decrease in $\log (H^S/H^L)$ as $H$ increases from 100 Å to 400 Å.
FIGURE 2.6 $\Delta^\#$ for spheres of equal radii

$\Delta^\#$ is the value of $H$ at which $H^S$ crosses $H^L$.
FIGURE 2.7 \( \Delta \) for spheres of unequal radii

\( \Delta \) is the value of H at which \( H^S \) crosses \( H^L \)
$$R_1 = 500 \, \text{Å} \; ; \; \; \; R_2 = 5000 \, \text{Å}$$

$\Delta^*$ is the value of $H$ at which $H^S$ crosses $H^L$.

FIGURE 2.8 $\Delta^*$ for spheres of unequal radii
of the 10-fold variation in the ratio $R_2/R_1$ the cross-over is smooth throughout. So, it seems that the smoothness of transition is mainly dependent on the radius of the smaller particle.

2.7 The Calculation of Hamaker Constants

Gregory (1969) and Visser (1972) have reviewed the calculation of Hamaker constants extensively, so that only a summary will be given here.

There are two basic methods of calculating Hamaker constants, known as microscopic and macroscopic approximations respectively. The microscopic approach is based on the additivity of dispersion forces while the macroscopic approach is founded on the theory of electrodynamics. The microscopic approach has been criticized for assuming additivity of dispersion forces, however in spite of the correctness and greater accuracy of the macroscopic approach, the large amount of optical data required by this method limits its usefulness.

2.7.1 The Microscopic Approximation

This method is due to Hamaker (1937). The Hamaker constant, $A_{11}$ for two bodies of materials 1, interacting across vacuum is given by:

$$A_{11} = \pi^2 q_1^2 \beta_{11}$$  \hspace{1cm} (2.42)

where $q_1$ is the number of atoms or molecules per cm$^3$ and $\beta_{11}$ is the
constant in London's (1930) equation:

\[ V_{11} = \frac{\beta_{11}}{r^6} \]  

(2.43)

where \( V_{11} \) is the attractive energy between the molecules at a distance \( r \) apart.

For two dissimilar materials 1, 2, the Hamaker constant is given by:

\[ A_{12} = \pi^2 q_1 q_2 \beta_{12} \]  

(2.44)

where \( \beta_{12} \) is a composite London constant.

Provided that \( \beta_{12} = (\beta_{11} \beta_{22})^{\frac{1}{2}} \)  

(2.45)

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

(2.46)

It must be noted that equation (2.45) only holds exactly when the ground state electronic frequencies of the molecules are equal.

The Hamaker constant \( A_{132} \) for two bodies of material 1, and 2 embedded in medium 3 is given by:

\[ A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \]  

(2.47)

and for identical materials equation (2.47) reduces to:

\[ A_{131} = A_{11} + A_{33} - 2 A_{13} \]  

(2.48)
Schenkel and Kitchener (1960) have suggested that the right hand side of equations (2.47) and (2.48) be divided by $\varepsilon$, the dielectric constant of the medium. However it will be seen later (Section 2.7.2) that this is wrong (Visser - 1972).

It is apparent from equations (2.42) and (2.43) that the London constant must be known in order to calculate the Hamaker constant of a material. Considerable effort has been made to find appropriate expressions for determining $\beta_{11}$, the London constant, and these are adequately discussed by Gregory (1969) and Visser (1972). Notable among these expressions is that due to Slater and Kirkwood (1931):

$$
\beta_{11} = \frac{3}{4} z^{\frac{3}{2}} h \nu_o \alpha_o^2
$$

(2.49)

where $z$ is the number of electrons in the outer shell of the molecule; $h$ is Planck's constant; $\nu_o$ is the frequency of the electron in the ground state; $\alpha_o$ is the static polarizability of the molecule. Moelwyn-Hughes (1961) replaced $\nu_o$ by $\nu$, the characteristic frequency of the molecule, to give:

$$
\beta_{11} = \frac{3}{4} z^{\frac{3}{2}} h \nu \alpha_o^2
$$

(2.50)

Moelwyn-Hughes' equation (2.50) tends to give high Hamaker constants and Gregory has criticized it, but Visser claims to find good agreement between Hamaker constants obtained from the macroscopic approach and those from equation (2.50).

There are more direct methods for estimating Hamaker constants by the microscopic approximation which do not need the London constant.
Notable among these methods are the static dielectric constant approach of Tabor and Winterton (1969) and Gregory (1970), and the interfacial tension method of Fowkes (1968). According to Gregory, Tabor and Winterton the Hamaker constant of a material \( i \), is given by:

\[
A_{11} = \frac{27}{64} \hbar \nu \left( \frac{\varepsilon_{10} - 1}{\varepsilon_{10} + 2} \right)^2 \tag{2.51}
\]

where \( \varepsilon_{10} \) is the static dielectric constant of the material, obtained from the square of the refractive index at the characteristic frequency \( \nu \).

Fowkes (1968) gives the following equations for calculating Hamaker constants:

\[
A_{11} = 12.2 \frac{d^2}{\lambda} \gamma^d/\lambda \tag{2.52}
\]

and

\[
A_{131} = \frac{12.2}{k_3 \lambda_{13}} \frac{d_1 (\gamma_1^d)^{\frac{1}{2}} - d_3 (\gamma_3^d)^{\frac{1}{2}}}{\lambda_{13}} \tag{2.53}
\]

where \( \gamma^d \) is the dispersion contribution to surface tension of solids \( 1,3 \); \( d \) is the separation of atomic centres at contact and is 4.0 Å for inorganic materials, 4.3 Å for water, 4.6 Å for organic molecules; \( \lambda_{13} = 0.9 \) and \( k_3 \) is the dielectric constant of material 3; when material 3 is water \( k_3 \lambda_{13} = 1.6 \).

2.7.2 Macroscopic Approach

According to Lifshitz (1956) and Dzyaloshinskii et al (1960) the interaction constant for two bodies of material 1 and 2 separated
by a medium 3 is given by:

\[ \hbar \tilde{\omega}_{132} = \hbar \int_0^\infty \frac{\varepsilon_1(i\xi) - \varepsilon_3(i\xi)}{\varepsilon_1(i\xi) + \varepsilon_3(i\xi)} - \frac{\varepsilon_2(i\xi) - \varepsilon_3(i\xi)}{\varepsilon_2(i\xi) + \varepsilon_3(i\xi)} \cdot d(i\xi) \quad (2.54) \]

where \( \varepsilon_i(i\xi) \) is the dielectric constant of material \( i \) along the imaginary frequency axis \( (i\xi) \) and decreases monotonically from \( \varepsilon_0 \) the static dielectric constant at \( \xi = 0 \) to \( 1 \) at \( \xi = \infty \).

\( \hbar \tilde{\omega}_{132} \) is the Lifshitz-van der Waals constant, and is related to the Hamaker constant by the equation:

\[ A_{132} = \frac{3}{4\pi} \hbar \tilde{\omega}_{132} \quad (2.55) \]

According to Visser (1972) the numerical results of Krupp (1972) indicate that equations 2.46 and 2.47 should be rewritten as:

\[ A_{131} = c_1(A_{11} + A_{33} - 2A_{13}) \quad (2.56) \]

\[ A_{132} = c_2(A_{12} + A_{33} - A_{13} - A_{23}) \quad (2.57) \]

where \( c \) is a constant equal to 1.6 when material 3 is water. So that the suggestion of Schenkel and Kitchener to divide by \( \varepsilon \) is very much in error.
2.7.3 **Hamaker Constants Used in our System**

In this text AT-rutile will be referred to as material 1, PVAc as material 2 and water as 3. As AT-rutile is primarily rutile, ignoring the impurities in the pigment (see Chapter 3) the Hamaker constant of rutile can be used for our pigment. With respect to PVAc there was no literature value available so it had to be calculated. Since the available constant for rutile had been calculated by the Fowkes method, - see Visser (1972) - it was decided for the sake of consistency to calculate the Hamaker constant of PVAc by the Fowkes approach: In our system

\[ A_{11} = 31 \times 10^{-20} \text{J}, \quad A_{33} = 5.45 \times 10^{-20} \text{J}, \quad \text{and} \quad A_{22} = 6.94 \times 10^{-20} \text{J}. \]

2.8 **Total Energy of Interaction, \( V_T \)**

According to Derjaguin and Landau (1941), Verwey and Overbeek (1948), the DLVO theory, the total energy of interaction \( V_T \) between colloidal particles is given by a summation of the repulsive and the attractive energies of interaction:

\[ V_T = V_A + V_R \]  \( (2.58) \)

So the magnitude of \( V_T \) is dependent on the relative values of \( V_R \) and \( V_A \). At very short distances of approach the combination of short range repulsive forces and van der Waals' attraction leads to a deep minimum, called the primary minimum. At high surface potentials and low ionic strength \( V_R \) is dominant and a maximum occurs on
the $V_T/H$ curve at intermediate separations and this maximum, $V_T(max)$ is called the primary barrier to flocculation into the primary minimum. Since $V_R$ falls more rapidly than $V_A$ at large distances of separation it is possible for a second minimum to occur in the $V_T/H$ curve; this is designated the secondary minimum and its depth is measured by $V_T(min)$. It is obvious that whenever $V_R > V_A$, there is a barrier to flocculation into the primary minimum. Since at a given separation $V_A$ is constant, the magnitude of $V_T$ will depend largely on $V_R$ and therefore on the surface potential and ionic strength.

The relation between $V_T(max)$, $V_T(min)$ and flocculation will be discussed in the next section.

2.9 Stability and Flocculation

It was the main objective of this project to study stability during storage and flocculation during drying in our model emulsion paint system. Stability is meant to imply no change in particle concentration with time, while flocculation is meant to imply any process of particle aggregation whether it be in the primary or secondary minimum. Since we are interested mainly in predicting the conditions for stability or flocculation and not the rate of the flocculation the kinetics of flocculation will only be mentioned briefly.

It can be shown - Fuchs (1934), Derjaguin (1940) - that the stability ratio $W$ of a system having a barrier to flocculation is given by:
\[
W = 2R \int_{0}^{\infty} \frac{\exp(V_T/kT)}{(H + 2R)^2} \, dH
\]  

(2.59)

where \( W \) is the factor by which the rapid rate of flocculation is reduced by the presence of a repulsive force; the rapid rate being given by Smoluchowski (1917) as:

\[
N_t = \frac{N_0}{(1 + k_0 N_0 t)}
\]

(2.60)

where \( N_t \) is the number of particles at time \( t \); \( N_0 \) is the initial number of particles; \( k_0 \) is the rate constant. For slow flocculation \( k_0 \) may be replaced by \( k_0/W \) in equation (2.60).

Equation (2.59) can only be solved exactly by numerical integration, but Overbeek (1952) has given the following approximate form:

\[
W = \frac{\exp[V_{T(max)}/kT]}{2kR}
\]

(2.61)

For fast flocculation \( V_{T(max)} \to 0 \) and therefore \( W = 1 \); while for slow flocculation \( W \) is higher and \( W \) increases with \( V_{T(max)} \). So that the tendency to flocculation recedes as \( V_{T(max)} \) increases.

Using Overbeek's equation above it can be shown that assuming \( K = 10^6 \text{ cm}^{-1} \), a particle concentration = \( 10^{14} \) particles \( \cdot \) cm\(^3\); for \( V_{T(max)} = 15 \text{ kT}, W = 1.26 \times 10^5 \) and \( t_{\frac{1}{2}} = 0.58 \) days; for \( V_{T(max)} = 30 \text{ kT}, t_{\frac{1}{2}} > 1 \) year. A graph of \( V_{T(max)} \) versus \( t_{\frac{1}{2}} \) is shown in figure 2.9.
For a volume fraction of 50% the initial particle concentration in our system is $7 \times 10^{12}$ particles $\cdot$ cm$^{-3}$.

$V_{T(\text{max})}$ versus $\log_{10} t_{\frac{1}{2}}$ for three values of $N_0$.

1. $N_0 = 10^{12}$ particles $\cdot$ cm$^{-3}$
2. $N_0 = 10^{13}$ particles $\cdot$ cm$^{-3}$
3. $N_0 = 10^{14}$ particles $\cdot$ cm$^{-3}$

$R = 1250 \, \AA$

$\kappa = 10^6 \, \text{cm}^{-1}$
The DLVO theory does not allow evaluation of flocculation into the secondary minimum, but the depth of the minimum can be calculated by the DLVO theory. Bagchi (1975) has derived an expression for flocculation into the secondary minimum and showed that flocculation into the secondary only obtains when $V_{T(\text{min})} > 1 \ kT$ and the rate of flocculation into the secondary minimum increases with the depth of the minimum.

The DLVO theory is limited insofar as it neglects viscosity effects, - Spielman (1970); hydrodynamic factors - Honig et al (1971); and solvation layers - Ottewill (1977). Since in any case these effects tend to slow down flocculation, ignoring them in our quantitative calculations is not too serious as we are looking for maximum stability in the paint system.
CHAPTER 3

MATERIALS PREPARATION
AND CHARACTERISATION
CHAPTER 3
MATERIALS PREPARATION AND CHARACTERISATION

3.1 General

It would be tedious to write on all the compounds and materials used in the studies performed. So, coverage will be restricted to only the most important, directly involved in the surface and colloid chemical studies. Other materials will be considered in those sections where they are involved in experiments.

3.2 Chemicals

These are the soluble components in the paint system and consist of the compounds used in the stabilization of solid components, and the chemicals used to vary the pH of the dispersions.

The pH variants were ammonia and sulphuric acid and both were Analytical grade reagents. The stabilizers, sodium dodecyl sulphate, (SDS) and sodium hexametaphosphate, (SHMP), were technical grade reagents. Hence details about the specifications of the stabilizers are necessary.

Two samples of SDS were used, one of which was "cycloryl 599" from Cyclo Chemicals Limited, England, and the other sample was from Cambrian Chemicals Limited, England. It was ascertained that both samples were of identical purity and critical micelle concentration (cmc). The SDS was of very high purity, as determined by the methylene blue complexation technique, Joly (1963). It gave a
small minimum \((5 \times 10^{-3} \text{ N m}^{-1})\) at the \(c_{\text{mc}}\) \((7.03 \times 10^{-3} \text{ mol dm}^{-3})\)

\[
\text{CH}_3-(\text{CH}_2)_{11}\text{OSO}_3\text{Na}
\]

Sodium dodecyl sulphate (SDS).

Sodium hexametaphosphate (SHMP) was from BDH Chemicals Ltd., England and was described as mainly \((\text{NaP}_0_3)_6\). This description is pertinent as there is no such thing as pure SHMP because it is a polymeric glass. Commercial SHMP is commonly called "Calgon®". Toy (1973) states that it consists mainly of linear polyphosphates and is of formula \(-\text{(NaP}_0_3)_n\) where \(n\) is 15-20. The designation \((\text{NaP}_0_3)_6\) is therefore incorrect. From the value of \(n\) the molecular weight of SHMP would be between 1700 and 2100. In view of the BDH description of their product, it was decided to use 1700 as the molecular weight of our SHMP sample. The high molecular weight of SHMP suggests it could behave as a polyelectrolyte if highly dissociated in water. However, the degree of dissociation of SHMP like that of polyphosphoric acids is only about 30% - Toy (1973) and Such (1971). So that our SHMP can be regarded as something between a 1:3 and a 1:5 electrolyte.

\[
\text{Na}_3\text{P}_0_4-\text{(NaP}_0_3)_n\text{-P}_0_4\text{Na}_3 \quad n = 15-20
\]

Sodium hexametaphosphate (SHMP).

Calgon is a trade mark of Hagan Chemicals and Control Systems Inc., Pittsburgh, USA.
3.3 Pigments

Three pigments were studied. These were alumina treated rutile (AT-rutile), untreated (bare) commercial rutile (CD-rutile), and alumina (Hydral® 705). No description of the manufacturing processes for the pigments will be given, however, the physical and chemical properties of the dried pigments will be covered, because these properties determine the colloidal behaviour of the pigments.

AT-rutile and CD-rutile were supplied by courtesy of BTP Tioxide Ltd, England, and Hydral 705 was supplied by the Aluminium Company of America (Alcoa). The surface areas of the pigments were determined by the nitrogen absorption BET method, taking the molecular area of nitrogen as 0.162 nm². The particle size of AT-rutile was actually determined but that of Hydral 705 was given by Alcoa. The chemical compositions of the pigments as given hereafter are as specified by the manufacturers.

3.3.1 Alumina treated rutile (AT-rutile)

The surface area of this pigment was 15.63 m²g⁻¹. The particle diameters were respectively \( d_n = 0.25 \pm 0.03 \) µm, from Transmission Electron Micrograph (TEM) photographs, and \( d_w = 0.28 \) µm, determined by X-ray sedimentation, courtesy of BTP Tioxide Central Laboratories. The chemical composition of AT-rutile is as follows:

© Hydral is a trade mark of Aluminium Company of America.
Alumina is deliberately added to the rutile in the final step of manufacture in order to modify the dispersing properties of the rutile. All the other additives, except TMP, are used at some stage to facilitate processing of the pigment. TMP is added to ease grinding, hence TMP and alumina are surface additives whereas the other compounds are imbibed in the pigment particles.

Figure 3.1 is the TEM photograph of AT-rutile. It clearly shows the polydispersity of the pigment, and the rather ellipsoidal shape of the particles. The bottom picture shows the alumina surface coating, visible as crowns on the particles. Figure 3.2 shows the particle size distribution of the pigment.

3.3.2 Bare rutile (CD-rutile) TS33820

The surface area of this pigment is 8.05 m²g⁻¹. The particle size was not determined because there would be no calculations
Figure 3.1: Transmission electron Micrograph of AT-rutile
\( d_n = 0.25 \pm 0.03 \, \mu m \)

Surface area = 15.63 m\(^2\) g\(^{-1}\) (BET)

Breadth of distribution = 5.06

**FIGURE 3.2** Particle size distribution of AT-rutile pigment
involving this pigment, however it would be similar in size to AT-rutile. The chemical analysis of the pigment is as follows:

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total TiO₂ %</td>
<td>98</td>
</tr>
<tr>
<td>Soluble TiO₂ %</td>
<td>0.35</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>0.53</td>
</tr>
<tr>
<td>SiO₂ %</td>
<td>0.04</td>
</tr>
<tr>
<td>P₂O₅ %</td>
<td>0.19</td>
</tr>
<tr>
<td>Sb₂O₃ %</td>
<td>0.24</td>
</tr>
</tbody>
</table>

All the additives in the above list were used only to facilitate processing. The final pigment was obtained by micronising, so the actual location of any or all of the additives is unknown.

3.3.3 Alumina (Hydral 705)

The surface area of this pigment is 13.65 m²g⁻¹. Alcoa gives the following particle sizes for the pigment: \( d_n = 0.30 \mu m \) and \( d_w = 0.38 \mu m \), both obtained from TEM photographs. The chemical composition of the pigment is as follows:

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ %</td>
<td>64.1</td>
</tr>
<tr>
<td>SiO₂ %</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>0.01</td>
</tr>
<tr>
<td>Na₂O (total)%</td>
<td>0.60</td>
</tr>
<tr>
<td>Na₂O (soluble)%</td>
<td>0.22</td>
</tr>
<tr>
<td>Moisture (110°C)%</td>
<td>0.60</td>
</tr>
</tbody>
</table>
There is no indication from the manufacturers (Alcoa) whether the impurities are on the surface or in the interior of the pigment. Williams (1973) describes the pigment as alumina trihydrate. So, taking into account the coordination between hydroxyl ions and aluminium ion in the crystal lattice, the pigment formula would be $\text{Al}_2\text{(OH)}_3$. Hydral 705 consists of hexagonal platelets of average size 0.4 μm, hence the particle diameters given by Alcoa are of no significance.

3.4 Polyvinyl Acetate (PVAc) Latex

The required properties of the PVAc latex were stated in Chapter 1 as:

- A polymer molecular weight of several million
- A latex particle size in the range 0.2 - 0.5 μm
- A solids content of 40% wt/wt or higher.

Emulsion polymerisation was the only obvious suitable preparative technique.

Emulsion polymerisation is essentially a free-radical reaction in which the reaction initiating radicals are separated from the monomer (reagent) by an interface. When the polymerisation is carried out in water, the initiator is in the aqueous phase while the monomer is partitioned between emulsifier micelles and droplets stabilized by emulsifier.

Napper (1971) published an important review on the theory of emulsion polymerisation and more recently Blackley (1975) has thoroughly reviewed and documented the theory and practice. The qualitative basis of emulsion polymerisation theory was laid by
Harkins (1947, 1950). Smith and Ewart (1948) proposed a quantitative theory based on Harkins' observations. There have been some modifications of the Smith-Ewart theory by Stockmeyer (1957), O'Toole (1965), and more recently by Gordon (1970). The observation that several monomers deviated from the Smith-Ewart theory led Medvedev and Sheinker (1954) to propose an alternative theory. The most important difference between the two theories concerns the locus of polymerisation after the initiation stage. In the Smith-Ewart theory the locus of propagation (polymerisation) is in the monomer swollen micelles; whereas in the Medvedev-Sheinker theory the locus of propagation is in the interface between the organic (monomer containing) phase and the aqueous phase. The consequence of this fundamental difference is that the two theories predict different polymerisation kinetics. It is generally agreed that the emulsion polymerisation of vinyl acetate does not obey the Smith-Ewart theory. However, there is no indication whether the Medvedev-Sheinker theory is obeyed.

A review by Lindemann (1967) shows that vinyl acetate emulsion polymerisation theory is a very controversial subject. The controversy on theory will be avoided, but it will be shown how points of general agreement were used to formulate the required latex.
3.4.2 High polymer molecular weight (> $10^6$)

As in free radical polymerisation, termination reactions in emulsion polymerisation occur either by combination or by disproportionation. For the vinyl acetate/water system it is generally agreed that above 70°C termination is exclusively by disproportionation, while combination is predominant below 40°C. Termination by combination produces a molecular weight which is double that produced by disproportionation. Hence a reaction temperature below 40°C would favour high molecular weight formation. In fact 35°C was selected as a reasonable polymerisation temperature; too low a reaction temperature would seriously impede the generation of radicals. It can also be shown that:

$$\bar{X}_n \propto [M]$$

$$\bar{X}_n \propto [I]^{-\alpha}$$

where $\bar{X}_n$ = number average degree of polymerisation; [M] = monomer concentration; [I] = initiator concentration, and $\alpha$ is a constant. Obviously, high monomer concentration and low initiator concentration, would favour the formation of a high molecular weight polymer. Both requirements can be met by keeping the locus of polymerisation in the organic phase. Now for homogeneous emulsion polymerisation, the initial polymerisation occurs in the aqueous phase. When $\bar{X}_n$ exceeds 50 the growing oligomer precipitates and is stabilized by emulsifier. Beyond 40% conversion no new parti-
cles are formed, the particles absorb all the monomer and the locus of polymerisation shifts from the aqueous to the organic phase. Therefore homogeneous emulsion would not give the high molecular weight required. Seeded emulsion polymerisation seemed the only reasonable option left and in fact actually gave the high molecular weight required (Section 3.4.7).

3.4.3 Latex particle size (0.20 - 0.50 μm)

Dunn and Taylor (1965) have shown that homogeneous emulsion polymerisation of vinyl acetate in SDS solutions generates very small particles (0.16 - 0.03 μm). In the absence of emulsifier: Priest (1952) obtained larger particles (0.16 - 0.42 μm). Unfortunately emulsifier-free lattices of high solids content are very unstable. Litt et al. (1970) have shown that it is possible to systematically grow particles to a desired size in the presence of SDS as emulsifier if a seeded system is used. They also state that no new (secondary) particles are formed. In fact experimentation demonstrated that secondary particle formation is only avoidable if the particle concentration in the seed latex is such that after dilution the effective particle number in the polymerisation recipe is at least $10^{13} \text{ cm}^{-3}$ of the aqueous phase.

3.4.4 Initiator system and latex particle surface charge

A redox initiator system was considered the most suitable as it would produce a latex of the same surface charge type as
commercial PVAc latex. The selected initiator system consisted of ammonium persulphate and sodium metabisulphite. Metabisulphite ions hydrolyse in water to give bisulphite ions.

\[ S_2O_5^{2-} + H_2O \rightarrow 2HSO_3^- \]

Persulphate can break down either by thermal dissociation or by bisulphite activation.

\[ S_2O_8^{2-} \xrightarrow{\Delta H} 2SO_4^2- \]

sulphate ion radical

\[ S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_3^2^- + HSO_3^- \]

Other side reactions proposed by Katayama and Ogoshi (1956) are:

\[ SO_3^- + HSO_3^- \rightarrow SO_3^{2-} + HSO_3^- \]

\[ 2HSO_3^- \xrightarrow{} H_2S_2O_5 \]

Given, the radicals generated in the above reactions, it is clear that sulphate (SO_4^2-) and sulphonate (SO_3^-) groups will be incorporated into the polymer chains. Also, the reaction system will become acidic through the generation of hydrogen ions by bisulphite ions. Litt et al (1970) have shown that it is possible for an internal cyclisation reaction to occur along the polymer chain to give:
Hydrolysis of the cyclic ester would produce a carboxyl (CO\(_2\)) group. In fact it will be seen later (Section 3.4.6) that the latex prepared has weak acid and strong acid groups on the particle surface.

3.4.5 Preparation of PVAc paint formula latex

3.4.5.1 Chemicals

Vinyl acetate monomer was obtained from ICI through the courtesy of Dr E L Zichy. It was of AR grade but contained an inhibitor. It was purified by drying over calcium chloride for 4 days and then distilling; and the fraction distilling over at 72-73\(^\circ\)C was collected and used. The water used in the latex preparation was triple-distilled, the last two stages being from an all quartz apparatus. SDS was as described previously (Section 3.2), and was used without further purification. Ammonium persulphate (initiator) and sodium metabisulphite (redox agent) were both AR grade.

3.4.5.2 Polymerisation recipe

Seed latex (d\(_n\) = 0.11 ± 0.01 \(\mu\)m) 100.0g
Water (tri-distilled) 300.0g
SDS 3.3g
Vinyl acetate monomer (inhibitor) 251.6g ≈ 270 cm\(^3\) free
Ammonium persulphate (initiator) 15.0 cm$^3$ of 2% w/v solution
Sodium metabisulphite (redox agent) 2.0 cm$^3$ of 2% w/v solution

3.4.5.3 Method of latex preparation

The seed latex and about half the total amount of water was weighed into a four-necked reactor vessel. The reactor was then clamped in a water bath at 35 ± 0.2°C, with a twin blade stirrer down the middle of the reactor vessel. A water-cooled Liebig condenser and a 100°C thermometer were fitted to the reactor. The stirrer was turned to 100 rpm and nitrogen gas allowed to bubble through the latex in the reactor vessel at a slow and steady rate. After purging for 15 mins, the redox agent was added to the reactor, followed by the monomer. After 10 mins, an SDS solution (made from the remaining portion of water) was added to the mixture. About 15 mins were allowed to elapse and then the first portion of the initiator solution (10 cm$^3$) preheated to over 70°C, was added to the reaction mixture. Polymerisation was then allowed to proceed after raising the stirrer speed to 300-400 rpm, with the nitrogen still bubbling through.

After 18 hours, the second portion of hot initiator solution (5cm$^3$) was added to the system and the run was continued for a further 6 hours. The waterbath was removed and replaced by a heating mantle and the reactor temperature was slowly raised to 80 ± 2°C and held there for 30 mins. Finally, the system was allowed to cool to room temperature and the latex was filtered to remove any coagulum present.
3.4.6 PVAc latex characterisation

The particle-size of the latex was determined from TEM photographs to be $0.26 \pm 0.02 \mu m$. The complete particle size distribution is shown in Figure 3.3; while Figure 3.4 is a TEM photograph of the latex.

The surface charges of the latex particles was determined as follows. A sample of the latex was exhaustively dialysed against tri-distilled water, using a Visking dialysis tube. An ion exchange resin (Dowex 50W-X4) supplied by BDH Chemicals Ltd., was cleaned and prepared as suggested by Vanderhoff et al (1970) to make it cationic. The dialysed latex was diluted to 0.5g dm$^{-3}$ and 100 cm$^3$ of this latex was added to 10g of the cation-exchanger. The mixture was shaken for 12 hours and then allowed to settle. A 40 cm$^3$ portion of the cation-exchanged latex was placed in a Shedlovsky cell at 20 ± 0.2°C. The latex was then titrated conductimetrically against carbonate-free 0.025M sodium hydroxide.

The graph of conductance versus the volume of added sodium hydroxide is shown in Figure 3.5. There are two breaks in the graph. The first break which is similar to strong acid strong base titration is attributed to sulphate ($SO_4^{2-}$) and sulphonate ($SO_3^-\) groups; the two being indistinguishable in conductimetry. The second break in the graph which is similar to weak acid strong base titration is attributed to carboxyl ($CO_2^-$).

3.4.7 Polymer characterisation

The number average molecular weight, $\overline{M}_n$, of the polymer was determined by high pressure membrane osmometry using the Hewlett
\[ d_n = 0.26 \pm 0.02 \, \mu m \]

Surface area = 19.2 m² g⁻¹

Breadth of distribution = 2.01

FIGURE 3.3 Particle size distribution of PVAc latex prepared in the laboratory
Figure 3.4: Transmission electron Micrograph of PVAc latex
cm$^3$ of 0.025 mol dm$^{-3}$ sodium hydroxide added

FIGURE 3.5 Conductimetric titration of surface groups on PVAc latex particles
Packard 502 HP membrane osmometer. The polymer solutions used were made from degassed and filtered AR grade toluene. $\bar{M}_n$ was found to be $1.09 \times 10^6$. Now, the upper limit of the instrument for accurate determinations was given as $1 \times 10^6$. Therefore the value of $\bar{M}_n$ obtained is only of qualitative significance, but certainly $\bar{M}_n$ is greater than $1 \times 10^6$.

The viscosity average molecular weight, $\bar{M}_v$, was measured by using an Ubbelohde viscometer thermostated to 25.00 ± 0.02°C. The polymer solutions were made up in dry acetone. $\bar{M}_v$, was calculated from the Staudinger equation using constants determined by Clarke et al (1961) for PVAc in acetone at 25°C. The, $\bar{M}_v$, obtained was $2.84 \times 10^6$. Hence the molecular weight of the polymer was several million as required.

The glass transition temperature, $T_g$, of the polymer was measured with a Du Pont 900 DTA instrument and found to be $31.6^\circ C$. This value compared favourably with the $T_g$ value of 28-31°C given for pure, linear PVAc in the Encyclopaedia of Polymer Science and Technology (1971).

Finally, an IR spectrum of the polymer was obtained by scanning a thin film cast from an acetone solution. This spectrum is shown as the larger spectrum in Figure 3.6. The insert sample spectrum for pure PVAc confirms that the polymer prepared was entirely PVAc and that any hydrolysis to polyvinyl alcohol during latex preparation was negligible.
Fig. 11. Infrared spectrum of poly(vinyl acetate). Courtesy F. Klebacher, Mobil Chemical Co.

FIGURE 3.6 Infrared spectrum of PVAc prepared in the laboratory
CHAPTER 4

COLLOID AND SURFACE CHEMICAL EXPERIMENTAL STUDIES
CHAPTER 4

COLLOID AND SURFACE CHEMICAL EXPERIMENTAL STUDIES

4.1 Choice of Experimental Approach

As the purpose of the project was to investigate the stability of the paint during storage, and the flocculation of solid components during drying, it was convenient to split the experimental studies into two parts. The first part was concerned with the wet paint system and the second part was on dry film studies. Because it was not possible to study mixed colloid systems in the wet, it was decided to study pigment dispersions and PVAc latex systems separately.

In wet systems it is useful to study the influence of all important ions on particle stability. Given the dearth of literature on oxide dispersions in water as well as latices such as polystyrene, an electrokinetic method of investigation would seem the ideal technique. The most convenient electrokinetic method available is microelectrophoresis, which was used. It is also necessary to know certain physical properties such as viscosity and ionic strength of the interparticle fluid, in order to perform theoretical calculations. By measuring the adsorption of dispersants on the particles it is possible to obtain information on the protective effect of each dispersant and also the ionic strength of the equilibrium solutions (interparticle fluids).

Examination of dry latex and paint films, yields information on film formation and flocculation (homoflocculation and hetero-
flocculation) of particles during drying. Microscopy is the simplest and most convenient method of studying dry films, and both optical and scanning electron microscopy (SEM) were used.

4.2 Wet System Experimental Studies

These studies consisted in the measurement of electrophoretic mobilities of particles; the adsorption of dispersants on latex and pigments; and the viscosity of dispersant solutions. Two different microelectrophoresis instruments were used in the measurement of mobilities. One was a standard (conventional) flat cell microelectrophoresis apparatus (Pearson 1973), and the other was the Pen Kem Inc., USA, model 400 Laser-Zee Meter. The cell employed on both instruments was of rectangular cross-section. Nearly all the mobilities to be discussed in Chapter 5 were obtained from the Laser Zee Meter (LZM) after standardizing the apparatus. The preference for the LZM was dictated by speed and convenience.

4.2.1 Microelectrophoresis

The theory of microelectrophoresis has been adequately treated by Overbeek (1952), Smith (1969) and Dukhin (1972). Consequently, only a brief aperçu of the subject will be given, paying attention mainly to aspects relevant to the experimental work described in here.

Overbeek has shown that for a cell of circular cross-section (cylindrical cell), of radius, $r$, the net liquid velocity, $V$, at
a distance \( y \) from the middle of the cell is given by:

\[
V = V_{eo} \left( \frac{2y^2}{r^2} - 1 \right) \quad (4.1)
\]

where \( V_{eo} \) is electro-osmotic velocity.

So that at the centre of the cell, where \( y = 0 \), \( V = -V_{eo} \) and at the cell wall where \( y = r \), \( V = V_{eo} \). It is thus obvious that the liquid velocities at the centre and the wall of the cell are equal but opposite in direction. The stationary layer is located at \( V \) equal to zero, that is, at \( 2y^2 = r^2 \). In effect the stationary layer is a cylindrical shell located at \( 2y^2 = r^2 \).

For a cell of rectangular cross-section (flat cell) the velocity relationships are difficult to analyse. Using the nomenclature in Figure (4.1) below, Komagata (1933) has shown that:

\[
V_{x=0} = V_{eo} - 1.5 V_{eo} \frac{(1 - y^2/b^2)}{(1 - 192b/\pi^5 a)} \quad (4.2)
\]

where \( V_{x=0} \) is the liquid velocity along the line \( x = 0 \).

**FIGURE 4.1**
The stationary layer is located at

\[ y = b \left[ 2(0.5 + 192b/\pi^2a)/3 \right]^{\frac{1}{2}} \]

The liquid velocity at a given level in the cell is superimposed on the electrophoretic velocity of particles. Hence the observed particle velocity \( V_{\text{obs}} \) is given by:

\[ V_{\text{obs}} = V_{x=0} + V_{\text{ee}} \]

where \( V_{\text{ee}} \) is the electrophoretic velocity of particles. The derivation of equation (4.2) assumes that the cell walls in the \( y \) direction have equal charges. This condition is necessary in order to have a parabolic velocity profile, where the parabola is symmetrical about the line \( x = 0, y = 0 \). For a flat cell fulfilling the said condition, a plot of \( V_{\text{obs}} \) versus \( y^2/b^2 \) should give two straight lines intersecting on \((x=0, y=0)\). Any flat cell used in microelectrophoresis has to be checked for this linearity. The two cells used in this project were checked and found to be satisfactory as will be seen later.

4.2.2 Standard Flat Cell Microelectrophoresis Apparatus

The cell and apparatus were similar to those shown by Pearson (1973). The cell was constructed by attaching silica tubes to a flat spectrophotometric cell of 1 mm internal thickness, and the \( a/b \) ratio of the cell was 8:1. The cell was immersed in a perspex water thermostated tank (25.0 ± 0.2°C) mounted on the stage of a Patholux Ultramicroscope. A double electrode system was used so as to avoid polarization errors which would arise with a single electrode system. All electrodes were made of platinum and they were carefully blackened with platinizing solution.
The microelectrophoresis cell was calibrated as follows: the cell was cleaned by immersion in chromic acid for 24 hours followed by thorough steam cleaning. Two solutions (0.01 and 0.1 Bemal*) of potassium chloride were prepared by using dry AR grade reagent and tri-distilled water. The cell was filled with one of the solutions and placed in an oil bath at 25.00 ± 0.02°C. The electrodes were slotted in and the conductance of the solution was measured with a Wayne Kerr B224 bridge. The process was repeated using the other solution and an average effective cell length was calculated from the two determinations. The cell length was 8.49 cm. The next step in the cell calibration was the determination of the cell parabola and for this purpose a dispersion of AT-rutile in water (0.1g dm⁻³) was prepared. The cell was filled with the dispersion and mounted in position on the microscope. Electrodes were slowly lowered into the cell taking care to exclude any air bubbles. The depth (apparent) of the cell was measured in microscope scale units, by determining the distance between the inner front and inner back wall along the line x = 0 (see Figure 4.1). With the microscope focused at the inner back wall a suitable potential was applied to the cell, and the time taken by an AT-rutile particle to cross one square on a calibrated eye piece graticule was measured with a stopwatch. 20 particles were timed in each direction, reversing the polarity after each reading. The procedure was repeated at various levels in the cell, advancing a constant number units into the cell from the back towards the front wall. The average mobility, U, \( \left( \frac{V_{obs}}{divided by \text{the potential gradient}} \right) \) was calculated for each level in the cell and a plot of U versus \( y^2/b^2 \) was made. It can be seen in Figure 4.2

FIGURE 4.2 Parabola of standard flat microelectrophoresis cell using AT-rutile dispersion
that two good straight lines were obtained. The intersection of the lines is close to the line \( x = 0, y = 0 \). The cell deviates from ideality by about 3% and at worst 5%, hence the cell was considered suitable for microelectrophoresis. A final check on the cell was done by measuring the mobility of a negative AgI sol at the front and back stationary levels. From the Komagata formula the stationary layers were located at 0.189 times the apparent depth of the cell. The mobilities obtained for the AgI sol were -3.11 and -3.08 thus confirming the suitability of the cell.

### 4.2.3 The Laser Zee Meter (LZM)

This instrument is essentially a flat cell microelectrophoresis apparatus except for two important refinements. Illumination is by laser light and mobility is measured by matching the speed of a galvanometer controlled prism to the velocity of particles in the stationary layer.

The instrument used was the model 400 supplied by Pen Kem Inc. and it is shown in Figure 4.3. The microelectrophoresis cell of the LZM was mounted on the stage of a Nikon ultra-microscope of very sharp focus and a depth of view of 5 \( \mu \text{m} \). Illumination was by a 0.5 milliwatt helium-neon laser of beam thickness 5 \( \mu \text{m} \) and width 650 \( \mu \text{m} \). The laser beam entered the cell perpendicular to the direction of viewing and illuminated the whole field of view. The thickness of the laser beam (5 \( \mu \text{m} \)) and the depth of focus of the microscope (5 \( \mu \text{m} \)) were deliberately matched so that when the microscope was focused at the stationary layer in the cell, any particles not
Figure 4.3: The Laser-Zee Meter
in the stationary layer were out of focus. This constitutes an important advantage over conventional microelectrophoresis instruments which use white light for illumination.

The microscope of the LZM housed a galvanometer controlled rotating prism which was situated between the objective lens and the eye piece. The galvanometer caused the prism to undergo a flip back cyclic rotation, such that the image seen through the microscope scanned in one direction and then reset repeatedly. The rate and direction of motion of the prism was variable and can be adjusted by the operator.

Mobility of particles was measured by adjusting the speed control of the prism rotation until the field of view appeared to be stationary. A digital display of the average zeta potential of the particles was then read. The zeta potentials displayed by this instrument were calculated by Pen Kem Inc. from the Smoluchowski equation, assuming an operative temperature of 20°C. Mobility could therefore be obtained by dividing the displayed zeta potential by the factor 14.2, provided the cell behaved ideally. In conventional microelectrophoresis mobility is measured by timing 20-60 particles and calculating an average. The rotating prism appliance makes it possible to get an average mobility for very many particles (over 1000 particles are in the microscope field but probably only 200-300 are effectively averaged by the eye) in just one measurement. This is a great advantage not only in terms of time but also in terms of statistical accuracy. The advantages of the LZM over the conventional microelectrophoresis apparatus, recommended it, so long as its accuracy could be demonstrated to
be as good as or even better than that of the conventional instrument. Experimental studies were performed to ascertain the suitability of the LZM. The work was carried out in collaboration with Nazir (1978).

The manufacturers of the LZM had designed the cell with a 'single' electrode system, so that input and output of potential was through the same pair of electrodes. This raised questions about polarization effects on output potential. Furthermore, the electrodes were dissimilar; the cathode was platinum while the anode was molybdenum. The molybdenum electrode tended to oxidise and it was necessary to clean it frequently with a cleaning paste supplied by Pen Kern Inc. At our request a modified cell was supplied. The modified cell still housed the two original electrodes (Pt/Mo) but now incorporated two 'sensing' electrodes (Pt/Pt). Hereafter the (Pt/Mo) electrode system will be called outer electrodes and the (Pt/Pt) 'sensing' electrodes the inner electrodes.

As the LZM cell was constructed in acrylic plastic (Plexiglas II) it could not be cleaned by conventional methods. Pen Kern Inc. supplied a cleaning solution and an ultrasonic bath for cleaning the cell. For standardization of the instrument, the cell and the electrodes were cleaned as recommended by Pen Kern Inc., and rinsed several times with triple distilled water. The cell was then filled with an AT-rutile dispersion at 25°C, and mounted in position on the microscope stage of the LZM. Various depths in the cell were focused and the zeta potential determined at each depth as described previously. A plot of zeta potential versus $\gamma^2/b^2$ was made. The cell was then cleaned again and filled with a negative AgI sol. Zeta
FIGURE 4.4  Parabola of L2M cell using AT-rutile dispersion
Figure 4.5 Parabola of LZM using AgI solution in $10^{-4}$ mol dm$^{-3}$ KI.
potential was measured at various depths and a plot of zeta potential versus $y^2/b^2$ was made. Figures 4.4, and 4.5 show the results. It can be seen that within experimental error the cell gives a good parabola. Hence it would seem to be suitable for microelectrophoresis.

If the cell was not polarising during microelectrophoresis then the ratio of input to output voltage would be equal to the ratio of the cell length between the outer electrodes to the cell length between the inner electrodes. Now, when a potential is applied to the outer electrodes (Pt/Mo) the lines of conduction are parallel in the region where the inner electrodes (Pt/Pt) are located. Consequently the inner electrode cell length cannot be measured with a Wayne Kerr bridge as, the bridge would apply a (small) potential to the electrodes and so cause a distortion of conduction lines and give an erroneous cell length. The circuit shown below (Figure 4.6) was used to determine the inner electrode cell length.

![Diagram of Laser-Zee Meter Cell](image)
P = power supply (D.C) with constant voltage output.
R = external resistor of known value.

The cell was filled with 0.01M KCl solution at 25°C. A voltage was applied to the outer electrodes and the voltage across R, \( V_R \), and the voltage across the inner electrodes, \( V_i \), was measured with a high impedance Keithley electrometer. The measurements were repeated for several applied voltages. It can be shown that the inner electrode cell length, \( \lambda_i \), is given by:

\[
\lambda_i = \frac{V_i \lambda_s a R}{V_R} \quad (4.3)
\]

where: 
- \( a = \) X-sectional area of the cell = 1.48 x 0.151 cm²
- \( \lambda_s = \) specific conductance of the KCl solution.
- \( R = \) resistance, \( R \), in the circuit.

\( \lambda_i \) was determined by substituting values into equation (4.3) and from five measurements \( \lambda_i \) was found to be 5.08 ± 0.01 cm. Having determined \( \lambda_i \), the next step was to measure the cell length between the outer electrodes, \( \lambda_o \). In this case a Wayne Kerr B224 bridge employing 58 mV rms at 1592 Hz was used because it was thought that the potential, (58 mV) applied by the bridge would have no significant effect on the observed cell length, \( \lambda_o \), and \( \lambda_o \) was found to be 10.67 cm. Whence the ratio of outer electrode cell length \( \lambda_o \) to inner electrode cell length \( \lambda_i \), is \( \lambda_o/\lambda_i = 2.10 \).

Having determined the ratio of cell lengths, the ratio of potential at the outer electrodes to the voltage at the inner electrodes could be measured. During the determination of the cell
parabola, it had been observed that the LZM gave a stable output read out only for potentials above 10V. For potentials in the range 10-300V the LZM voltmeter was checked with a Solatron DVM and good agreement was obtained over the whole range. It was decided that in the study of the ratio of potentials the Solatron would be used to measure applied voltage for potentials below 10V whereas the LZM itself would be used for potentials greater than 10V. The ratio of potential between the outer electrodes to the potential between the inner electrodes was studied by applying various voltages (0.1-300V) to the outer electrodes and then measuring the output at the inner electrodes with the Keithley electrometer mentioned previously. The LZM cell was found to have a rest potential (no applied voltage) of -0.534V between the outer electrodes and 0.023V between the inner electrodes. A plot of the ratio of the potentials versus the potential applied at the outer electrodes is shown in Figure 4.7. It can be seen that the ratio increases continuously with applied potential and attains a constant value (2.09 ± 0.02) in the range 15-300V. Thus the ratio of potentials compares favourably with the ratio of cell lengths (2.10) determined previously.

The final step in the standardization of the Laser Zee Meter (LZM) was to calculate mobilities from the zeta potentials displayed by the instrument and compare these mobilities to mobilities obtained by conventional microelectrophoresis. If the speed of the rotating prism was accurately matched to the velocity of particles in the stationary layer, then the LZM should give the same results as conventional microelectrophoresis for applied potentials of
FIGURE 4.7 Ratio of applied potential at outer electrodes to output potential at inner electrodes versus applied potential at outer electrodes.
15-300 volts. To check the mobilities obtained from the LZM the PVAc latex mentioned in Chapter 3 was used. The mobility of the latex was determined at pH 8.0 and 25°C by standard (timing) microelectrophoresis using the apparatus mentioned in Section 4.2.2. The LZM cell was filled with the PVAc latex at 25°C and mobility was determined by timing particles in the cell and also by the prism rotation technique. The following results were obtained:

\[ U_m = -2.88 \pm 0.12 \, \text{m}^2 \, \text{s}^{-1} \, \text{V}^{-1} \times 10^8 \] (conventional method)

\[ U_{L1} = -2.80 \pm 0.10 \, \text{m}^2 \, \text{s}^{-1} \, \text{V}^{-1} \times 10^8 \] (LZM by timing)

\[ U_{L2} = -2.41 \pm 0.08 \, \text{m}^2 \, \text{s}^{-1} \, \text{V}^{-1} \times 10^8 \] (LZM prism rotation).

It is clear that within experimental error, \( U_m \) is equal to \( U_{L1} \). That is, timing in the LZM cell gave the same result as the conventional microelectrophoresis. The difference of about 3% compares favourably with the percentage error involved in conventional microelectrophoresis. The difference can be attributed to the fact that the LZM cannot be thermostated whereas in the conventional method the cell is thermostated. Comparing \( U_{L2} \) to \( U_{L1} \) and \( U_m \) it is evident that there is a large difference which is beyond experimental error. The ratio \( U_{L1}:U_{L2} = 1.16 \), indicates an error of 16% between the mobility obtained by timing in the LZM cell and the mobility obtained by the rotating prism method. Measurements on the PVAc latex in the pH range 3-10 demonstrated that the 16% error was consistently prevalent throughout the pH range. Further determinations on AT-rutile and negative AgI sol confirmed the 16% error - see Table 4.8. It was concluded that the LZM was suitable for
TABLE 4.8

Comparison of mobilities obtained on Laser-Zee Meter

\[ U_{z1} = \text{mobility obtained by timing} \]

\[ U_{z2} = \text{mobility obtained by prism rotation technique} \]

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>( U_{z1} \times 10^8 )</th>
<th>( U_{z2} \times 10^8 )</th>
<th>( U_{z1}/U_{z2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI (negative)</td>
<td>-3.09</td>
<td>-2.66</td>
<td>1.162</td>
</tr>
<tr>
<td>AT-rutile</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 8.0</td>
<td>-2.65</td>
<td>-2.27</td>
<td>1.167</td>
</tr>
<tr>
<td></td>
<td>+1.35</td>
<td>+1.165</td>
<td>1.159</td>
</tr>
<tr>
<td></td>
<td>+1.25</td>
<td>+1.075</td>
<td>1.163</td>
</tr>
<tr>
<td></td>
<td>-3.00</td>
<td>-2.59</td>
<td>1.158</td>
</tr>
<tr>
<td>PVAc Latex</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 8.0</td>
<td>-2.80</td>
<td>-2.41</td>
<td>1.161</td>
</tr>
<tr>
<td></td>
<td>-2.82</td>
<td>-2.45</td>
<td>1.151</td>
</tr>
<tr>
<td></td>
<td>-1.95</td>
<td>-1.67</td>
<td>1.168</td>
</tr>
</tbody>
</table>
microelectrophoresis provided a correction of 16% was applied to the mobilities obtained by the rotating prism technique. It must be emphasised that this correction factor is only valid for ionic strengths giving $\kappa$ values not exceeding $10^6$ cm$^{-1}$. For higher $\kappa$ values the ratio of applied outer electrode potential to measured inner electrode potential must be determined and the following equation (4.4) used to calculate the mobility:

$$U = \frac{\zeta \times 1.16 \times \text{ratio of potentials}}{14.2 \over 2.10}$$  \hspace{1cm} (4.4)

$\zeta$ = zeta potential

for $\kappa \leq 10^6$ cm$^{-1}$ $\equiv 10^{-3}$ mol dm$^{-3}$ I:I electrolyte

$$U = \frac{\zeta \times 1.16}{14.2}$$  \hspace{1cm} (4.5)

The necessity for the correction factor given in equation (4.5) implies an error in the calibration of the Laser Zee Meter. According to the manual of Pen Kem Inc., the LZM is calibrated with a standard sol of known mobility, predetermined by conventional microelectrophoresis. If the standard sol should deteriorate and it is used to calibrate a LZM then it is certain that a constant error will be introduced into all the mobilities obtained on such a LZM. It is suggested that the calibration error of our LZM probably derives from a defective calibration sol.
4.2.4 Measurement of Mobility on the Laser Zee Meter

The LZM cell is rinsed twice using about $20\text{cm}^3$ of dispersion each time. By means of a plastic syringe the cell is filled with the dispersion taking care to exclude any air bubbles. The cell is then placed in position on the microscope stage of the LZM and the microscope is focused at the stationary layer (220 μm from the wall). A suitable potential (> 15V) is applied and the speed of the rotating prism is adjusted to give a stationary field. The zeta potential, and the applied potential at the outer electrodes are read from the instrument. Although the display voltage is only accurate to ± 1V, the actual applied voltage is fed to the integrated circuit performing the comparison between the electrode voltage and the ramp speed driving the prism. The ζ-potential output is electronically stable to 0.1 mV. The overall accuracy in measurement is usually limited by other factors. The (output) potential between the inner electrodes is measured with the Keithley electrometer mentioned previously and the mobility of the particles in the dispersion is then calculated from equation (4.4) or (4.5) as appropriate.

4.2.5 Mobility Studies on PVAc Latex

The prepared PVAc latex contained SDS and some undesirable ions. In order to study the effect of ionic strength and dispersants on the mobility of the latex, it was necessary to remove the SDS and the undesirable ions so as to know accurately the concentrations involved.
The latex was cleaned by exhaustive dialysis as follows. After preparation the PVAc latex was allowed to stand for 48 hours and it was then filtered through a fine mesh gauze to remove any residual coagulum. About 200 cm$^3$ of the latex was placed in a Visking dialysis tube and the dialysis tube was sealed at both ends. The dialysis tube was placed in a tank containing 3 dm$^3$ of tri-distilled water at room temperature (22 ± 2°C). The water was changed every 24 hours until the conductance and pH of the latex were reasonably constant. About 12 days were enough for complete dialysis after which the latex was ready for mobility measurements.

The investigations carried out on the latex were:

1) Mobility as a function of pH in the absence of dispersants (SDS, SHMP);
2) Mobility as a function of SDS concentration;
3) Mobility as a function of SHMP concentration;
4) Mobility as a function of the concentration of mixed dispersants (SDS and SHMP).

For the study of mobility as a function of pH in the absence of dispersants, a portion of the dialysed latex was diluted with tri-distilled water to give a one dm$^3$ dispersion of 0.05 gdm$^{-3}$. The diluted latex was then thermostated at 25.0±0.2°C in a water bath for about 2 hours. Mobility studies were performed by taking 80 cm$^3$ of latex, adjusting the pH with AR grade ammonium hydroxide or sulphuric and measuring the mobility by proceeding as described in Section 4.2.4.
pH was measured with the Radiometer PHM62 standard pH meter.

The effect of SDS concentration on the mobility of the PVAc latex was studied as follows: A portion of latex to give a final dispersion concentration of 0.05 gdm$^{-3}$ was diluted to 500 cm$^3$ with tri-distilled water in a volumetric flask. A volume of SDS from a stock solution (0.025 mol dm$^{-3}$) was added to the diluted latex and the resultant latex was made up to one dm$^3$ with tri-distilled water. The volume of stock SDS solution used was chosen to give a predetermined concentration of SDS in the final working latex. Several lattices were prepared in this manner and thermostated at 25°C for 24 hours. For mobility measurement about 80 cm$^3$ of a given latex was taken and pH adjusted as before, then mobility was measured by proceeding as described in Section 4.2.4. For each latex containing SDS, mobility was determined as a function of pH.

In the study of the effect of SHMP concentration on the mobility of the PVAc latex a slightly different method was used in preparing the working lattices. The reason for this modification is given in Chapter 5. A volume of stock SHMP solution (0.02 mol dm$^{-3}$) was diluted to 400 cm$^3$ with tri-distilled water. A portion of stock dialysed latex was diluted to 500 cm$^3$ in a one dm$^3$ volumetric flask. The diluted SHMP solution was then added to the flask and the resultant latex was made up to the mark with tri-distilled water. Several lattices containing known concentrations of SHMP were prepared in this manner and were thermostated at 25 ± 0.2°C. For mobility studies the procedure was the same as that described above for lattices containing SDS.
For mobility studies in mixed dispersant solutions, the latex was stabilized with SDS prior to the addition of SHMP. The procedure was the same as that adopted above for the effect of SHMP concentration, except for the following: after dilution of the stock latex to 500 cm$^3$, a volume of stock SDS solution was added and the latex was thermostated at 250 ± 0.2°C for 12 hours. Diluted SHMP solution was then added and after making up to one dm$^3$, the latex was thermostated at 250 ± 0.2°C for a further 12 hours.

4.2.6 Mobility Studies on Pigments

All the pigments selected for investigation were available in dry form. Aqueous dispersions of the pigments were prepared by ultrasonic disintegration. The instrument used for this purpose was the model A180G Rapidis of Ultrasonics Ltd., England, shown in Figure 4.9. It consisted of a generator capable of producing up to 180 watts at 20 kHz, and a disintegrator head housing a magnetostriction transducer. The disintegrator head was housed in a soundproof cabinet and was designed to accept titanium probes of various tip sizes. For pigment dispersion it was found that a 19 mm tip titanium probe was the most effective in breaking down the aggregates. To disperse any of the pigments a weighed amount (0.05g - 0.15g) was placed in a 100 cm$^3$ beaker and about 75 cm$^3$ of triple distilled water or dispersant solution was added. The suspension was then subjected to ultrasonic dispersal and was finally made up to one dm$^3$ with tri-distilled water or dispersant solution.
Figure 4.9: The Ultrasonic Disintegrator
For mobility studies on the pigments it was found that the appropriate pigment concentration in the working dispersions were: 0.05 g dm\(^{-3}\), for AT-rutile and CD-rutile; and 0.15 g dm\(^{-3}\) for Hydral 705, because of the larger size of Hydral particles and increased difficulty of dispersion. As will be seen in Chapter 5, it was found that pigment dispersion at maximum ultrasonic level (60 \(\mu\)m with the 19 mm tip probe) gave mobilities which were independent of the amount of ultrasonic energy put in, for dispersion times exceeding 2 minutes. The following mobility studies were performed on all the pigments, except as otherwise stated.

1) Mobility as a function of pH in the absence of dispersants;
2) Mobility as a function of SHMP concentration;
3) Mobility as a function of SDS concentration;
4) Mobility as a function of concentration in mixed dispersant solutions;
5) Mobility of AT-rutile in dissolved PVAc latex.

In the investigations (1), (2) and (3) the pigment dispersions were prepared as described previously, using maximum (60 \(\mu\)m) ultrasonics for 5 minutes. The prepared dispersions were thermostated at 25.0±0.2°C for 6 hours in investigation (1), 12 hours in study (2) and 24 hours in study (3). Samples were then taken and pH adjusted with sulphuric acid or \(\text{NH}_4\) hydroxide and mobility studies were performed by proceeding in the manner described in Section 4.2.4. For mobility studies in mixed dispersant solutions pigment was dispersed in SHMP solution, made up to 500 cm\(^3\) in a one dm\(^3\) volumetric
flask and thermostated at 25±0.2°C for 12 hours. SDS solution was then added to raise the volume to one dm³ and the dispersion was thermostated for a further 12 hours. Samples were then taken, pH adjusted and mobility measured. Two investigations were done in mixed dispersant solutions - mobility at constant SHMP concentration but variable SDS concentration, and mobility as a function of concentration at a fixed ratio of SHMP to SDS.

The study of the mobility of AT-rutile in dissolved latex was performed as a consequence of results obtained on the effect of SDS on latex. It will be seen later (Chapter 5) that SDS can cause PVAc latex to dissolve. Latex was dissolved in SDS solution, and then a dispersion of AT-rutile in water or in SHMP solution was added, and the mixture was made up to one dm³ in a volumetric flask. This dispersion mixture was designed to contain 0.05 g dm⁻³ of pigment; 0.025 mol dm⁻³ SDS and 5x10⁻⁵ mol dm⁻³ (polyphosphate) SHMP. Dispersions containing various amounts of dissolved latex were prepared while keeping the pigment, SDS and SHMP concentrations constant. The dispersions were kept at 25±0.2°C for 24 hours and mobilities were measured at pH 8.0.

4.2.7 Viscosities of Dispersant Solutions

The use of SDS in PVAc latex, and SHMP in pigment stabilization raised questions about the viscosity of interparticle fluids in those colloids. Conversion of mobilities into zeta potentials could not be done without knowing the viscosities of the dispersant solutions. Solution viscosity was measured as a function of dispersant concentration. An Ubbelohde viscometer thermostated to
25.00±0.02°C was used for this purpose. Tri-distilled water was placed in the viscometer and the time, $t_o$, taken by the water to flow between two points in the capillary was measured with a stopwatch. Three measurements were made and the average time was calculated. The procedure was repeated with dispersant solutions and the time, $t$, for each solution was determined. The viscosity of a dispersant solution relative to water was then given by $t/t_o$.

4.2.8 Adsorption of Dispersants from Solutions

As mentioned in Section 4.1 the ionic strength of the dispersions as well as the protective ability of each dispersant could only be determined by measuring the adsorption of dispersants on the particles. Adsorption was determined as a function of concentration at constant pH. Measurements were performed at pH 5.0 and pH 8.0, keeping the temperature at 25.0±0.2°C in all cases. Although the adsorption of SDS and SHMP on all the three pigments was measured, experimental problems limited work on PVAc to the adsorption of SDS only. In all determinations SDS in the equilibrium solutions was analysed by the methylene blue dye complexation method for low concentrations of anionic surfactants (see Joly 1963). The methylene blue was obtained from Analytical Supplies, and it was found to have an extinction coefficient at 665 nm of $7.2 \times 10^4$. It was used without further purification. Analysis for SHMP was done by the vanado-molybdate method for total phosphate as described by SCOPE (1975) and by APHA, AWWA and WPCF (1971). For centrifugation of the dispersions a MSE 25 controlled temperature high speed centri-
fuge and 50 cm$^3$ plastic (polycarbonate) tubes supplied by MSE were used. The tubes in which the samples were held during the equilibration at 25°C, were made of borosilicate glass (50 cm$^3$ or 100 cm$^3$ volume) and were stoppered. As in all adsorption studies the cleaning of equipment was very important. The borosilicate glass tubes and all glassware was subjected to chromic acid and steam cleaning. The centrifuge tubes were cleaned by shaking in an ultrasonic bath containing tri-distilled water.

Adsorption of SDS on PVAc latex was determined in the following manner. Aliquots (30 cm$^3$) of freshly dialysed latex (40% wt/wt) were placed in the (50 cm$^3$, stoppered borosilicate tubes. Volumes of SDS from a stock solution (0.025 mol dm$^{-3}$) were added to the tubes with gentle stirring. Tri-distilled water was then added as necessary to lower the solids content to 30% wt/wt. The tubes were then held at 250 ± 0.2°C for 24 hours after which 40 cm$^3$ of each latex was centrifuged at 12,000g in the MSE 25 centrifuge. The speed of centrifugation was selected to prevent the formation of a firm deposit. After centrifuging 10 cm$^3$ of supernant was drawn off and SDS determined. All determinations were performed in duplicate. Whenever necessary the equilibrium solution was diluted and a portion of the diluted solution analysed for SDS.

Adsorption of SDS on pigments was carried out as follows: stoppered borosilicate glass tubes (100 cm$^3$) were cleaned as said previously and an amount of pigment to give a final dispersion concentration of 60 g dm$^{-3}$ was weighed into each tube. A predetermined volume of SDS solution from the stock solution was added to each tube and the resultant suspension was dispersed ultrasonically and
diluted with tri-distilled water as necessary to give 60 g dm$^{-3}$. The tubes were then stoppered and kept at 25.0±0.2°C for 24 hours with frequent inversion of each tube to avoid settling. 40 cm$^3$ of each dispersion was centrifuged and SDS in 10 cm$^3$ of supernatant was determined as said previously. It was not possible to avoid the formation of a firm deposit except for Hydral 705 because of the density of the pigments.

The procedure for measuring the adsorption of SHMP on pigment was the same as that used for SDS adsorption except as stated below. Only 12 hours were required for equilibration at 25.0±0.2°C and SHMP (polyphosphate) was determined by the vanado-molybdate method. In all the adsorption measurements described above, each set of determinations included duplicate blanks on the dispersions in the absence of adsorbate (SDS, SHMP).

4.3 Dry Film Studies

These studies were performed on latex and paint films, the purpose being to investigate the effect of SDS and SHMP on film formation and flocculation.

Aliquots (30 cm$^3$) of dialysed PVAc latex (40% wt/wt) were placed in beakers and predetermined volumes of SDS or SHMP from stock solution were added to the latices with gentle stirring. 25 cm$^3$ of each latex was poured into a petri dish and a clean glass microscope slide was immersed in the latex in each petri dish. The dishes were placed in a dust-free air thermostated cupboard and allowed to dry at 22.0±0.1°C (room temperature). Air was circulated in the cupboard by a fan. When the latices had dried out the micro-
scope slides were cut out. Each slide was placed on the stage of a Cooke, Troughton and Sims M3520 optical microscope with a Vickers' camera system and photographs of the interior of the dry latex film were taken. The arrangement used is shown in Figure 4.10. In addition, a representative section of each film was cut out and an SEM photograph was taken of the surface of the film.

For paint film studies the following operations were performed. Concentrated aqueous dispersions (26% wt/wt) of AT-rutile were prepared by adding SHMP. Of the dispersions prepared, one contained no dispersant while another contained only SDS. PVAc latices containing various amounts of SDS were also prepared. Paint was made by mixing AT-rutile dispersion with PVAc latex. The paints were formulated to have a solids content of 20% wt/wt and a polymer to pigment ratio of 1.5. After preparation the paints were treated in the same manner as for PVAc latices above, however because of the opacity of the films and the optical microscope available only SEM photographs could be taken.
CHAPTER 5

RESULTS AND DISCUSSION
CHAPTER 5

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5.1 Properties of the Dispersion Media

Addition of any of sulphuric acid, SDS or SHMP to water has the effect of altering the Debye-Hückel parameter, \( \kappa \), equation (2.6). In view of the small concentrations involved in the experiments described previously, the influence of ammonium hydroxide or sulphuric acid on solution parameters other than \( \kappa \) can be ignored. However, the nature of SDS and SHMP of necessity raise questions about their effect on the viscosity and Hamaker constant of the medium.

5.1.1 Solution Viscosity

The viscosities of SDS and SHMP solutions were measured as described previously (section 4.2.7) and the results are shown in tables 5.1a and 5.1b. The viscosities are expressed relative to water at 25°C, since it was not possible (equipment not being available) to measure absolute viscosities for solutions of such low concentrations.

It is evident from the tables that SHMP has the greater effect on solution viscosity and this can be explained by the fact that SHMP is a polymer \( (M_r = 1700) \). For concentrations below the cmc of SDS \( (7.03 \times 10^{-3} \text{ mol dm}^{-3}) \), the viscosity of the SDS solutions is indistinguishable from that of water. Above the cmc the increase in viscosity with concentration may be ascribed to micellar influence.
Viscosities of stabilizer (dispersant) solutions relative to water at 25°C.

Operative temperature = 25.00 ± 0.02°C

**TABLE 5.1a - SDS Solutions**

<table>
<thead>
<tr>
<th>Concentration $m^2 s^{-1} v^{-1} \times 10^8$</th>
<th>$\eta_r$ (relative viscosity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.005</td>
</tr>
<tr>
<td>1.00</td>
<td>1.006</td>
</tr>
<tr>
<td>2.00</td>
<td>1.008</td>
</tr>
<tr>
<td>4.99</td>
<td>1.008</td>
</tr>
<tr>
<td>9.98</td>
<td>1.014</td>
</tr>
<tr>
<td>19.96</td>
<td>1.033</td>
</tr>
</tbody>
</table>

**TABLE 5.1b - SHMP (Polyphosphate) Solutions**

<table>
<thead>
<tr>
<th>Concentration $m^2 s^{-1} v^{-1} \times 10^8$</th>
<th>$\eta_r$ (relative viscosity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.016</td>
</tr>
<tr>
<td>1.0</td>
<td>1.021</td>
</tr>
<tr>
<td>2.0</td>
<td>1.028</td>
</tr>
<tr>
<td>5.0</td>
<td>1.043</td>
</tr>
<tr>
<td>10.0</td>
<td>1.073</td>
</tr>
<tr>
<td>20.0</td>
<td>1.123</td>
</tr>
</tbody>
</table>
The use of viscosity arises in the calculation of zeta potentials from electrophoretic mobilities. Generally, the average error involved in the determination of mobilities is about 2-5%. Given this error margin, it would seem reasonable to use the viscosity of water for SHMP solutions up to $2 \times 10^{-3} \text{ mol dm}^{-3}$. For higher concentrations of SHMP it would be necessary to use the experimentally determined viscosities. As a general comment, it may be said that for a latex paint containing only SDS and SHMP as dispersants, the viscosity changes during drying will be mainly controlled by SHMP.

5.1.2 Hamaker Constant of Solutions

Vincent (1973) has given a formula for estimating the Hamaker constant of a binary mixture. From this formula it can be deduced that for an aqueous solution, high solute concentrations ($> 0.1 \text{ mol dm}^{-3}$) have to be reached before deviation from the Hamaker constant of water exceeds 10%. The foregoing deduction is confirmed by Vincent's own plot on the polyvinyl alcohol/water system. Now, given the errors ($> 10\%$ usually) involved in the estimation of Hamaker constants, it would seem that for the low concentrations of SDS and SHMP solutions, the Hamaker constants would be fairly close to that of water, but not in the case of a drying paint film. An attempt was made to verify this prediction by measuring the refractive indices of SDS and SHMP solutions and working out Hamaker constants therefrom. An Abbé refractometer and a tungsten lamp were used; the refractometer being thermostated at $250 \pm 0.1^\circ\text{C}$. 
It was found that departure from the Hamaker constant of water was small throughout (± 1% for a 0.02 mol dm\(^{-3}\) solution)

5.1.3 Debye-Hückel Parameter, \(\kappa\), and Double Layer Thickness

Adding ammonium hydroxide, sulphuric acid, SDS or SHMP to water increases ionic strength and leads to a compression of the double layer around particles in the medium. Also, if any of the ions are adsorbed they may alter the electrokinetic properties of the particles. The relationship between adsorption and electrokinetic properties will be discussed later.

As stated previously, ammonium hydroxide and sulphuric acid were used to vary pH, for pH 3-10. It can be shown that for the given pH range \(\kappa\) lies between \(10^4\) cm\(^{-1}\) and \(10^6\) cm\(^{-1}\) and particularly for the paint system (pH 7-9), \(\kappa\) would be \(10^4\) cm\(^{-1}\) - \(10^5\) cm\(^{-1}\) in the absence of other ions (e.g. SDS and SHMP). The particle diameters of PVAc latex and AT-rutile were 0.26 \(\mu\)m and 0.25 \(\mu\)m respectively; whence for dispersions of these particles, \(\kappa R\) (\(R =\) radius) in the given pH range would be approximately 0.1-15.

The operative dispersant (SDS and SHMP) solution concentrations were in the range \(10^5\) to \(2 \times 10^2\) mol dm\(^{-3}\). SHMP is a complex electrolyte of uncertain description in contrast to SDS which can be regarded as a 1:1 electrolyte. As explained in Chapter 3, SHMP is a polymer and may be treated as a 1:3, 1:4 or 1:5 electrolyte. The \(\kappa\) value of a given SHMP solution is therefore dependent on whichever of the foregoing relations is selected. It will be seen later that all three combinations have been considered in the calculation.
of zeta potentials. For SHMP solutions of concentration $10^{-5}$-$2 \times 10^{-2}\text{mol dm}^{-3}$, $\kappa$ lies between $10^5$ and $2 \times 10^8 \text{cm}^{-1}$, and for PVAc and AT-rutile particles in these solutions $\kappa R$ ranges from 1 to 250. In fact most of the $\kappa R$ values are between 1 and 100, and especially for the concentration region ($< 2 \times 10^{-3}\text{mol dm}^{-3}$) operative in a latex paint, $\kappa R$ ranges from 1 to 80.

For SDS solutions $\kappa$ values vary from $10^5$ to $10^7 \text{cm}^{-1}$ and $\kappa R$ for PVAc and AT-rutile from 1 to 60 for concentrations $10^{-5}$ to $2 \times 10^{-2}\text{mol dm}^{-3}$. For concentrations not exceeding $2 \times 10^{-3}\text{mol dm}^{-3}$, $\kappa R$ is $1 \approx 40$.

It is evident that generally, irrespective of the type of electrolyte most $\kappa R$ values for the systems studied lie between 0.1 and 100, which is in the middle of the region where relaxation effects have the greatest influence on electrophoretic mobility. Consequently difficulties will be experienced in transforming mobilities into zeta potentials by calculation (see Section 5.14).

5.2 Electrokinetic Properties of Pigments in Water

Three pigments were studied - AT-rutile, CD-rutile and Hydral 705, - the pigment of central interest being AT-rutile, while the others were used for the purpose of elucidating the behaviour of AT-rutile. As AT-rutile had a surface coating of alumina it was necessary to ascertain the effect of ultrasonic dispersion on the alumina coating. For this purpose the mobility of AT-rutile as a function of pH was studied at various levels of ultrasonic dispersing energy. From these studies the appropriate dispersion conditions were determined and then mobility studies as a function of
pH were performed on CD-rutile and Hydral 705.

5.2.1 Effect of Ultrasonic Dispersion on AT-rutile Coating

In Figure 5.2 is shown the plot of the mobility of AT-rutile as a function of pH at various levels of dispersing energy. Generally the effect of ultrasonics seems to be to enhance the positive charge contribution on the pigment surface. This is evident from the reduction in the magnitude of the negative mobilities and a shift in i.e.p. from pH 6.0 to pH 6.55. The foregoing observations are explainable as follows: In the final processing of AT-rutile an organic compound TMP, is used and this compound is obviously adsorbed on the alumina coating already on the pigment surface. Now, removal of the TMP will expose more of the pigment surface to the aqueous medium and since the pigment surface so exposed is alumina, it tends to acquire a positive charge in the pH range 3-9; hence the changes in mobility and i.e.p. Actually it was observed that a thin film (presumably TMP) formed on the surface of the dispersion after ultrasonic dispersion.

When the maximum level of ultrasonics is maintained beyond 2 minutes there is no change in mobility or i.e.p. with increasing dispersing time. This probably indicates that virtually all of the TMP has been eliminated from the pigment surface. Consequently it is reasonable to assume that the dispersing time of 5 minutes (time for preparing working dispersions) was sufficient to remove any variable effect on mobilities deriving from ultrasonics.
Ultrasonic amplitude  

<table>
<thead>
<tr>
<th>Ultrasonic amplitude</th>
<th>Time</th>
<th>i.e.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>△ 10 μm (minimum)</td>
<td>2 mins</td>
<td>6.0</td>
</tr>
<tr>
<td>○ 60 μm (maximum)</td>
<td>2 mins</td>
<td>6.55</td>
</tr>
<tr>
<td>□ 60 μm (maximum)</td>
<td>5 mins</td>
<td>6.55</td>
</tr>
<tr>
<td>+ 60 μm (maximum)</td>
<td>10 mins</td>
<td>6.55</td>
</tr>
</tbody>
</table>

**FIGURE 5.2** Effect of ultrasonics on the mobility of AT-rutile
5.2.2 Effect of pH on the Mobility of the Pigments

An oxide dispersion in water in the presence of hydrogen (H₃O⁺) or hydroxyl (OH⁻) ions acquires a charge generally by ion exchange with the solution. The mechanisms of charging of the oxide surface have already been discussed in Chapter 2. Nevertheless, a schematic recapitulation of the process will be useful.

\[
-M\text{-OH} \quad H_3O^+ \quad M\text{-O}^+ \quad + \quad H_2O
\]

\[
OH^- \uparrow \quad \downarrow
\]

\[
-M\text{-(OH)}_2^-
\]

M = metal atom.

The foregoing chemical equations should not be presumed to imply that the mere presence of net hydrogen ions (pH<7) or net hydroxyl ions (pH>7) would confer on the oxide a net positive or negative charge accordingly. The net surface charge of the oxide (pigment) is determined by the balance between the processes generating negative and positive surface charge respectively. The two processes exactly cancel each other at the isoelectric point (i.e.p) with the negative and positive charges being equal.

The results of the mobility studies as a function of pH are plotted in Figure 5.3 for all the three pigments investigated. The i.e.p's of the pigments are respectively 6.55 for AT-rutile; 5.2 for CD-rutile and 9.35 for Hydral 705. The i.e.p. of CD-rutile
FIGURE 5.3 Mobility of pigments as a function of pH
is lower than 6.2 (the i.e.p of hydrous rutile) because of the presence of some phosphate on its surface. AT-rutile was obtained from CD-rutile by precipitating hydrous alumina onto the surface of the latter. Evidently the surface treatment of CD-rutile with alumina to give AT-rutile shifts the i.e.p of the rutile to a higher pH. It may be recalled from Chapter 3 that the composition of the pigments indicate the presence of several impurities. If the impurities should become available at the pigment surface they would affect the i.e.p and the mobility (electrokinetic potential) of the pigment. Phosphate and silica impurities would shift the i.e.p. to lower pH's by increasing the negative charge on the pigment, while alumina impurity raises the i.e.p to higher pH by increasing the positive charge on the pigment. It is important to note that the presence of alumina on the surface of AT-rutile does not produce a mobility curve similar to that of alumina (Hydral 705). In fact the mobility curves for CD-rutile and AT-rutile are reasonably - surprisingly - parallel to each other. The similarity in shape between the two curves mentioned can be explained by either of the following postulates: (1) the surface treatment process gives only a partially alumina covered AT-rutile surface; (2) the surface coverage with alumina is complete in the dry state but some of the alumina dissolves in aqueous solution leaving a partly uncoated (bare) rutile surface. It is generally known that alumina is relatively very soluble in water and this solubility is pH dependent. The experimental studies of Dezelic et al (1971) show that a plot of the total concentration of aluminium species in solution versus pH has a plateau at pH 6.4 - 8.3, and total aluminium species concentration of $2 \times 10^{-4}$ mol dm$^{-3}$. Outside the
foregoing pH range the concentration of aluminium species in solution increases as the pH moves away from the plateau region (e.g. $7 \times 10^{-3} \text{mol dm}^{-3}$ at pH 5 and $4 \times 10^{-4}$ at pH 9).

5.3 Adsorption of Polyphosphate (SHMP) on the Pigments

The adsorption of the polyphosphate, SHMP, on the pigments (AT-rutile, CD-rutile, Hydral 705) was investigated at constant pH 5.0 and 8.0. The isotherms derived from these studies are shown in figures 5.4 and 5.5 for pH 5.0 and pH 8.0 respectively. Comparing the two figures mentioned it is evident that all the three pigments adsorb more SHMP at pH 5.0 than at pH 8.0. However the pH effect is less marked for Hydral 705. The increase in adsorption with decrease in pH suggests that the isotherms are of the high affinity type. The same observation has been recorded by Balzer and Lange (1975) for the adsorption of several phosphates on γ-alumina, by Lyklema and Breeuwsma (1973) for orthophosphate adsorption on Haematite, and by Chen et al (1973) for orthophosphate adsorption on α-alumina. The differences in adsorption of SHMP by AT-rutile and CD-rutile at pH's 5.0 and 8.0 can be explained by the fact that these pigments are positively charged at pH 5.0 but negatively charged at pH 8.0. The negative surface charge at pH 8.0 imposes an electrostatic barrier to adsorption by the negatively charged polyphosphate (SHMP) molecule.

As stated in Chapter 2, the adsorption of phosphate at the metal oxide/solution interface is postulated to involve both chemical and physical adsorption. The shapes of the isotherms such as those in figures 5.4 and 5.5 are presumed to support this postu-
Equilibrium concentration, $C_e$, of SHMP, polyphosphate $\times 10^3$ mol dm$^{-3}$

**FIGURE 5.4** Adsorption isotherms of SHMP on pigments at pH 5.0 ± 0.05
FIGURE 5.5 Adsorption isotherm of SHMP on pigments at pH 8.0 ± 0.05

Equilibrium concentration, $C_e$, of SHMP (polyphosphate) $\times 10^3$ mol dm$^{-3}$

Hydral 705
AT-rutile
CD-rutile
late. The isotherms probably indicate that chemical terms in the Stern equation considerably favour adsorption. So, at pH 8.0 the main drive is from the chemical effects while at pH 5.0 chemical and electrical effects are cooperative. Seeing that all the three pigments studied are positively charged at pH 5.0 it is evident that they will adsorb SHMP both chemically and physically at this pH. At pH 8.0, Hydral 705 will still experience chemical and physical adsorption of SHMP because it is still positively charged; whereas CD-rutile being negatively charged can only adsorb SHMP physically. It is not possible to state with absolute certainty what type of adsorption of SHMP occurs on AT-rutile at pH 8.0. As AT-rutile is negatively charged at pH 8.0 it might apparently adsorb SHMP only physically. However remembering that there may be alumina on the surface of AT-rutile, and that alumina is positively charged at pH 8.0, it is conceivable that chemical adsorption occurs on those parts of the surface where alumina is present, in spite of the net surface charge on AT-rutile being negative. After all the sign of surface charge as indicated by electrophoretic mobility is only the result of the balance between negative and positive charges on the AT-rutile.

Generally speaking the isotherm for adsorption on AT-rutile lies between those for adsorption on CD-rutile and on Hydral 705 at both pH 5.0 and 8.0. So that adsorption of SHMP is greater on AT-rutile than on CD-rutile. The fact that Hydral 705 exhibits the greatest adsorption among the pigments is explainable by the fact that it is positively charged at both pH's. The difference between AT-rutile and CD-rutile arises because CD-rutile has some phosphate on its surface and furthermore AT-rutile has some alumina surface
coating. Evidently the extent of SHMP adsorption increases with the amount of alumina on the pigment surface. This is consistent with the fact that the positive charge on the pigment surface increases with the alumina present.

It is common in literature to compare experimental isotherms for adsorption from solution with the Langmuir type isotherm. Such a comparison is of dubious value and can be very misleading when the adsorbing species are ions. The very basis of the derivation of the Stern-Langmuir isotherm requires that the term \( \left( z e \psi_d + \phi \right) \) is constant in the Stern equation (2.16). Notwithstanding, some of the publications on phosphate adsorption, Chen et al (1973), Huang (1975) and Muljadi et al (1966) have made the aforementioned comparison. Actually Muljadi et al (1966) have characterised three different adsorption regions corresponding to "at least three energetically different reactive sites": (I) Orthophosphate concentration less than \( 10^{-4} \text{ mol dm}^{-3} \) a steep Langmuir isotherm essentially irreversible; (II) \( 10^{-4} \) to \( 10^{-2} \text{ mol dm}^{-3} \) a more gently rising Langmuir isotherm, reversible on a time-scale of days; (III) orthophosphate concentration exceeding \( 10^{-2} \text{ mol dm}^{-3} \) a linear reversible isotherm. The linear isotherm of region (III) is attributed by Muljadi et al to "penetration of the phosphate into amorphous regions" of the sorbents. In regions (I) and (II) this mechanism is said to be superimposed on a Langmuir adsorption on two different types of surface sites. The three adsorption regions were found for Kaolinite, Gibbsite; and Pseudoboehmite. It is important to note that careful examination of phosphate isotherms in the literature, for the concentrations lower than \( 10^{-2} \text{ mol dm}^{-3} \) clearly
shows that the isotherms are not of the Langmuir-type—vide Lyklema and Breeuwsma (1973), Balzer and Lange (1975), Chen et al (1973), Takimoto et al (1977) and Huang (1975). So that the question of examining the isotherms in figures 5.4 and 5.5 in the light of the proposals of Muljadi et al (1966) does not arise. Moreover the phosphate (SHMP) involved in the studies reported in here is a polymer and is highly unlikely to undergo "penetration into the amorphous regions" of the adsorbent as suggested by Muljadi et al, for orthophosphate. It is worth noting that the isotherms reported in here are similar to those obtained by Lyklema and Breeuwsma (1973) for orthophosphate on Haematite, and by Balzer and Lange (1975) for adsorption of several phosphates on γ-alumina.

5.4 The Mobility of the Pigments in Polyphosphate (SHMP) Solutions

It has already been shown that the pigments adsorbed polyphosphate (SHMP) ions to a considerable extent. Therefore it is to be expected that the electrokinetic properties of the pigments would undergo considerable alteration in the polyphosphate (SHMP) solutions. The effect of SHMP concentration on the electrophoretic mobility of the pigments is shown in figure 5.6 for pH 5.0, and figure 5.7 for pH 8.0.

Irrespective of pH the mobility curve for each individual pigment shows the same features — the mobility increases negatively, goes through a maximum and then falls as the concentration of the polyphosphate (SHMP) increases. Balzer and Lange (1975) obtained mobility curves with similar features for γ-alumina in trisodium
FIGURE 5.6 Mobility of pigments in SHMP solutions at pH 5.0 ± 0.05.
FIGURE 5.7 Mobility of pigments in SHMP solutions at pH 8.0 ± 0.05
polyphosphate solutions. The observed features can be explained as follows: the rising part of the mobility curves corresponds to an initial adsorption region where double-layer compression is outweighed by adsorption effects; the falling part of the mobility curves corresponds to the region where adsorption is outweighed by double-layer compression and increasing solution viscosity. It may be recalled that the viscosity of SHMP solutions deviated considerably from the viscosity of water when the SHMP concentration exceeded $2 \times 10^{-3}$ mol dm$^{-3}$ (see table 5.1b). Also, a plot of $\kappa R$ versus SHMP concentration shows that $\kappa R$ increases slowly in the region where the mobility curves rise, whereas it rises much more rapidly in the region where mobility falls, with increasing phosphate concentration - viz. $\kappa R = 3 \approx 50$ at $10^{-5} - 10^{-3}$ mol dm$^{-3}$ and $50 \approx 225$ at $10^{-3} - 2 \times 10^{-2}$ mol dm$^{-3}$. An interesting facet about these mobility curves is the parallelism between the curves for AT-rutile and CD-rutile. Seeing that AT-rutile was supposed to have a surface coating of alumina, one would have expected the observed parallelism to be between AT-rutile and Hydral 705. Actually, the mobility curves for AT-rutile do not resemble those for Hydral 705, at all. The parallelism between the mobility curves for AT-rutile and CD-rutile was previously mentioned in Section 5.2 and it is proposed that the explanation offered in Section 5.2 is still valid for mobilities in SHMP (polyphosphate) solutions. The mobilities of CD-rutile are higher than those of AT-rutile, this may be so because CD-rutile actually has some phosphate on its surface prior to adsorbing the SHMP (polyphosphate).
Figures 5.6 and 5.7 show that upon adsorbing the negative polyphosphate ions, Hydral 705 undergoes charge reversal at pH 5.0 and 8.0 whereas AT-rutile and CD-rutile only experience charge reversal at pH 5.0. The foregoing observation is consistent with the sign of charge on the pigments at pH 5.0 and 8.0 in the absence of polyphosphate. Evidently, in polyphosphate (SHMP) solutions OH\(^-\) and H\(^+\) ions cease to be the potential determining ions because of the specific adsorption of the polyphosphate ions. Comparing mobility curves for the same pigment in figures 5.6 and 5.7 it is apparent that pH has a negligible effect on the magnitudes of the mobilities in polyphosphate solutions. When the pigments are positively charged, charge reversal by polyphosphate occurs very quickly and at very low polyphosphate concentrations.

The general reactions between an oxide surface and an orthophosphate were discussed in Chapter 2, Section 2.2.4, and bearing these reactions in mind, the following schematic representations are proposed for the charging of the pigment surfaces by polyphosphate (SHMP) adsorption:

<table>
<thead>
<tr>
<th>Pigment</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydral 705</td>
<td>5.0 ; 8.0</td>
</tr>
<tr>
<td>AT-rutile</td>
<td>5.0</td>
</tr>
<tr>
<td>CD-rutile</td>
<td>5.0</td>
</tr>
</tbody>
</table>
2. Surface charge = negative
   Pigment         pH
   AT-rutile       8.0
   CD-rutile       8.0

5.5 Adsorption of SDS on the Pigments

Adsorption of SDS on the pigments - AT-rutile, CD-rutile and Hydral 705 was studied at constant pH, 5.0 and 8.0. The isotherms for adsorption at pH 8.0 are shown in figure 5.9.

All the three isotherms in figure 5.9 are more or less S-shaped, indicating a two-step adsorption process. The isotherms are
FIGURE 5.9 Adsorption isotherms of SDS on pigments at pH 8.0 ± 0.05

Equilibrium concentration $C_e$ of SDS $\times 10^3$ mol dm$^{-3}$

Amount of SDS adsorbed $\times 10^6$ mol m$^{-2}$
flat when the equilibrium concentration, \( C_e \), of SDS exceeds the cmc \((7.0 \times 10^{-3} \text{ mol dm}^{-3})\). Using the plateau region to calculate the molecular area of SDS on the pigments, the following values are obtained: on Hydral 705, 67.8 \( \text{\AA}^2 \); on AT-rutile 118.6 \( \text{\AA}^2 \) and on CD-rutile 138.4 \( \text{\AA}^2 \). Now the area occupied per head group in the surface of a micelle of SDS is 58 \( \text{\AA}^2 \) - Tartar (1955).

It is evident that only the surface of Hydral 705 is completely saturated and there may be more than one molecular layer on its surface. As far as AT-rutile and CD-rutile are concerned it is unlikely that the surface coverage exceeds a monolayer.

It is generally accepted that a two step adsorption isotherm is indicative of two types of adsorption sites on the solid surfaces. As regards Hydral 705 these sites are \( \text{Al}^{+\text{OH}}_2 \) and \( \text{Al}^{\text{OH}} \) at pH 8.0. On such a surface the isotherm probably indicates that in the two stage adsorption - the first stage corresponds to electrostatic adsorption and the second stage to adsorption enabled by van der Waals' forces. Given the heterogeneity of the surfaces of AT-rutile and CD-rutile, it is not clear what the surface sites are on these pigments. It is probable that some of the surface sites on AT-rutile are \( \text{Al}^{+\text{OH}}_2 \) and \( \text{Al}^{\text{OH}} \) derived from the alumina surface coating on this pigment. Hence it is possible that at pH 8.0 adsorption on AT-rutile proceeds under the influence of electrostatic and van der Waals' forces. Tamamushi and Tamaki (1957) have reported an S-shaped isotherm for adsorption of SDS on alumina at 20°C.

The isotherms for the adsorption of SDS on the pigments (Hydral 705, AT-rutile and CD-rutile) at pH 5.0 are shown in figure 5.10. By comparison with the isotherms in figure 5.9 (for pH 8.0) it is clear that all the pigments adsorb considerably more SDS at pH 5.0.
FIGURE 5.10 Adsorption isotherms of SDS on pigments at pH 5.0 ± 0.05
than at 8.0. Also, the isotherms are continuous without any
breaks or stops. Hydral 705 and AT-rutile continue to adsorb
SDS at \( C_e \) greater than the cmc. Adsorption on CD-rutile attains
a platform at \( C_e \) lower than the cmc. The estimated molecular
area of SDS on CD-rutile at pH 5.0 is 59.3 \( \text{Å}^2 \) so that the SDS
molecule is adsorbed laterally on this pigment. The inability of
CD-rutile to adsorb SDS in the manner of AT-rutile and Hydral 705
beyond the cmc may be because of the presence of some phosphate
on the surface of CD-rutile.

The isotherms of AT-rutile and Hydral 705 suggest multilayer
adsorption at pH 5.0. The following schematic diagram borrowed
from Dobias (1978) explains the mechanism of such a multilayer
adsorption process:

![Schematic diagram](image)

This mechanism which involves a hemicilicelle formation on the pig-
ment surface has been used by Jaycock (1963) to explain the adsorp-
tion of SDS on a positive AgI sol; and by Dobias (1978) to explain:
the adsorption of SDBS on an alumina sol. Adsorption into the first layer occurs under electrostatic forces and involves an ion exchange process between the solid surface and the solution. When adsorption into the first layer is complete the surface is non-polar and van der Waals' attraction then enables adsorption by hydrocarbon-hydrocarbon interaction. The surface becomes charged as this second layer is formed. Evidently the adsorption process involves a reversal of the surface charge. It is not to be presumed that the foregoing adsorption mechanism implies that in practice adsorption into the second layer does not occur until the first layer is complete. It will be seen later (section 5.6) that for the pigments involved here, adsorption into the second layer probably occurs before the first layer is complete.

5.6 The Electrophoretic Mobility of the Pigments in SDS Solutions

The electrophoretic mobility of the pigments (Hydral 705; AT-rutile and CD-rutile) was studied as a function of SDS concentration at constant pH 5.0 and 8.0. The mobility-concentration curves are shown in figures 5.11 and 5.12 for pH 5.0 and 8.0 respectively.

For dispersions at pH 5.0 (figure 5.11) all the pigments experience a reversal of charge. The SDS concentration at which reversal of charge occurs is well below 10^{-5} mol dm^{-3}. It may be recalled that in section 5.5 the charge reversal on Hydral and AT-rutile was attributed to a two stage adsorption process; the first of which was surface neutralisation and the second was charging of the surface by oriented adsorption of SDS molecules. The rapid charge reversal probably indicates that at pH 5.0 both terms (chemical and electrical)
Figure 5.11: Mobility of pigments in SDS solution of pH 5.0 ± 0.05
FIGURE 5.12 Mobility of pigments in SDS solutions at pH 8.0 ± 0.05
in the Stern equation (2.16) are favourable to adsorption. Under these conditions it is possible for adsorption into the second layer to occur before the completion of adsorption into the first layer and so produce a very fast charge reversal.

For AT-rutile and CD-rutile at pH 5.0, the mobility increases with the concentration of SDS after charge reversal; goes through a maximum at about $5 \times 10^{-3} \text{ mol dm}^{-3}$ and then falls. The features of the curves can be explained thus: initially after charge reversal \( \kappa \) is very low and adsorption effects predominate so mobility rises. The sudden jump in mobility after $5 \times 10^{-4} \text{ mol dm}^{-3}$ may be indicative of a reorientation of molecules on the surface. Beyond $5 \times 10^{-3} \text{ mol dm}^{-3}$ mobility falls. In figure 5.10 this corresponds to the region of saturation adsorption (plateau) on CD-rutile and only small increases in adsorption on AT-rutile with increasing SDS concentration. In this region \( \kappa \) has become fairly high and so double-layer compression outweighs any adsorption.

The mobility curve for Hydral 705 at pH 5.0 is distinguished by the two maxima on it. The first maximum (concentration $< 10^{-4} \text{ mol dm}^{-3}$) may be due to fast adsorption of SDS with charge reversal. After this maximum, the mobility falls. As the fall is too steep to be attributable to increases in \( \kappa \) only, it is proposed that readsoption of dissolved aluminium ions (see Section 5.2.2) is responsible for the decrease in negative charge. Beyond $2 \times 10^{-4} \text{ mol dm}^{-3}$ SDS, the mobility increases with concentration until the second plateau is attained. The second plateau probably corresponds to an equilibrium between the opposing influences of adsorption and double-layer compression (increasing \( \kappa \)). It is worth noting that the range of con-
entration covered in the adsorption studies (figure 5.10) did not include the region in which the first maximum on the Hydral 705 mobility curve occurred.

The effect of SDS on the mobility of the Hydral 705, AT-rutile and CD-rutile is shown in figure 5.12 for pH 8.0. The curve for Hydral 705 bears the same features as in figure 5.11, so it is proposed that the explanation offered previously is still valid (Hydral 705 is positively charged at pH 5.0 and 8.0). As regards AT-rutile and CD-rutile, mobility falls initially because of poor adsorption (the surfaces are negatively charged), and increasing \( \kappa \). The remaining features on the AT-rutile and CD-rutile curves can be explained in the same manner as was done for the corresponding curves in figure 5.11.

Comparing mobility curves for identical pigments in figures 5.11 and 5.12, it can be seen that pH is a great influence on the magnitudes of the mobilities in SDS for concentrations below \( 5 \times 10^{-4} \text{ mol dm}^{-3} \). The foregoing observation does not apply to Hydral 705, which is positively charged at both pH's and the differences in mobility arising from pH are small throughout the SDS concentration range covered.

5.7 The Electrophoretic Mobility of Dialysed PVAc Latex

The mobilities were studied as a function of pH in the range pH 3.0 - 10.0 and the results of these measurements are plotted in figure 5.13.

All the mobilities are negative because the latex surface carries sulphate, sulphonate and carboxyl groups - see Section 3.4.6.
FIGURE 5.13 Mobility of dialysed PVAc latex versus pH
There are two parts to the mobility-pH curve: a rising part between pH 3.0 and 5.0, and a flat part between pH 5.0 and 10.0. The flat portion of the curve corresponds to the region where all the surface groups are ionised because they are above their pK\textsubscript{a}. Below pH 5.0 the mobility-pH curve falls with decreasing pH. As the pK\textsubscript{a} of carboxyl groups lies between pH 4.0 and 6.0 it is proposed that the fall in mobility arises because the carboxyl groups on the latex surface are being protonated and therefore cease to contribute to the surface charge.

5.8 Adsorption of SDS on PVAc Latex

The adsorption isotherm of SDS on PVAc latex was determined at pH 5.0 and 8.0 as described in Section 4.2.8. The results are plotted in figure 5.14 as one composite isotherm because the pH difference had only a marginal effect on adsorption. The insensitivity of the adsorption to pH for pH 5.0 and 8.0 is due to the fact that these pH's are on the flat part of the mobility-pH curve of the latex, see figure 5.13. Since the latex is negatively charged throughout the pH range, only physical adsorption of the dodecyl sulphate (DS\textsuperscript{-}) ion is possible. Hydrocarbon-hydrocarbon interaction favours oriented physical adsorption of the DS\textsuperscript{-} ion on the latex surface with the sulphate group in the aqueous phase.

In figure 5.14 the adsorption isotherm is seen to rise linearly and then flatten as the equilibrium concentration, C\textsubscript{e} of SDS increases. The plateau on the isotherm is reached at C\textsubscript{e} less than the cmc of SDS. This behaviour has been reported for the adsorption of SDS on poly-
Equilibrium concentration of \( C_\text{eq} \), of SDS \( \times 10^3 \) mol dm\(^{-3}\)

**FIGURE 5.14** Adsorption isotherm of SDS on PVAc latex at pH 5.0 and 8.0

The work required to remove a DS$^-$ ion from solution on to the surface of the latex can be split into two parts: (1) electrostatic and (2) chemical. As the adsorption is physical it can be safely assumed that the chemical work will be constant throughout. The electrostatic work is related to the surface potential and hence the surface charge density. Adsorption of DS$^-$ ion increases the surface charge density and thus the electrostatic work increases with adsorption of SDS. So that the activation energy for adsorption on the latex surface will increase as SDS is adsorbed. This violates the Langmuir premise that the activation energy for adsorption on any surface site is independent of the fractional coverage of the surface, as it would be if the term $(ze \psi_d + \phi)$ is constant in the Stern equation (2.16). Consequently, the isotherm (figure 5.14) has not been analysed to see if it fits the Langmuir equation.

Assuming that the flat portion of the isotherm corresponds to monolayer coverage, it was calculated that the adsorption area per SDS molecule on the latex surface at saturation was 49 $\AA^2$. Other workers report the following molecular areas for DS$^-$: 58 $\AA^2$ for SDS in a micelle - Tartar (1955); 53 $\AA^2$ for SDS on poly-n-butylmethacrylate latex and 58.5 $\AA^2$ on polystyrene latex - Brodnyan and Kelley (1969).
5.9 The Mobility of PVAc Latex in SDS Solutions

The influence of SDS concentration on the electrophoretic mobility of PVAc latex is shown in figure 5.15. The mobility of the latex increases with SDS concentration and reaches a maximum (-5.0 units) at $10^{-3}$ mol dm$^{-3}$ The increase in mobility is due to the adsorption of $\text{DS}^-$ ions from solution. Sieglaff and Mazur (1962) obtained a mobility-concentration curve of similar shape with a maximum for polystyrene latex in potassium laurate solutions. The maximum on the mobility curve in figure 5.15 occurs at an SDS concentration ($10^{-3}$ mol dm$^{-3}$) lower than the concentration ($6 \times 10^{-3}$ mol dm$^{-3}$) - see figure 5.14) at which saturation adsorption obtains. It is proposed that attainment of the maximum mobility at a concentration lower than expected is due to influence of $\kappa$ which increases with concentration.

The point indicated by "solubilization", corresponds to an SDS concentration at which the latex particle concentration was seen to be considerably reduced without any flocculation in the system. The dispersion was highly transparent after solubilization. It is to be noted that the solubilization of latex occurred only when $C_e$ was greater than the cmc of SDS ($7.03 \times 10^{-3}$ mol dm$^{-3}$).

5.10 The Mobility of PVAc Latex in Polyphosphate (SHMP) Solutions

In figure 5.16 is shown the mobility of the PVAc latex as a function of polyphosphate concentration. The mobility of the latex decreases as the concentration of the polyphosphate (SHMP) increases until finally the latex is flocculated at $C_e > 2 \times 10^{-4}$ mol dm$^{-3}$.
FIGURE 5.15  Mobility of PVAc latex in SDS solutions.
FIGURE 5.16 Mobility of PVAc in SHMP (polyphosphate) solutions
The considerable decrease in mobility effected by the polyphosphate cannot be explained by double layer compression (\( \Xi \) increasing \( \kappa \)) only. The highly polar nature of the polyphosphate and its negative charge (\( Z_- \geq 3 \)) precludes adsorption of the polyphosphate ion on the negatively charged latex surface because of unfavourable electrostatic and chemical interactions. In contrast to the polyphosphate ion, it is favourable electrostatically for sodium ions to be adsorbed into the inner double layer of the latex-solution interface. Any such sodium ion adsorption will reduce the negative charge on the latex surface and hence reduce the mobility of the latex. The rapid drop in latex mobility as the polyphosphate concentration increases occurs because at any given polyphosphate concentration the sodium ion concentration is on average about four times the expressed polyphosphate concentration.

5.11 The Mobility of PVAc Latex and the Pigments in Mixed Electrolytes

In the previous sections it has been seen that generally SDS increases the mobility of the pigments and the latex, whereas the polyphosphate raises the mobility of the pigments and lowers the mobility of the latex. The pernicious effect of polyphosphate concentration on the mobility of the latex prompted studies on mobilities in mixed dispersant (SDS, SHMP) solutions. In all such studies the pigment or latex was prestabilized in its normal stabilizer prior to adding the other dispersant - i.e. pigment predispersed in polyphosphate (SHMP) and then SDS added; latex prestabilized in SDS and then polyphosphate added. Two types of mobility
studies were performed: (1) Mobility as a function of opposing dispersant concentration but constant normal stabilizer concentration; (2) Mobility as a function of total dispersant concentration at various ratios of SDS to SHMP.

1. Mobilities measured at constant normal stabilizer concentration and variable opposing dispersant concentration, are shown in figures 5.17 for the pigments, and 5.18 for the latex. In figure 5.17 the mobilities of the paint pigment AT-rutile, and the CD-rutile fall first and rise later as the concentration of SDS increases. The initial fall is probably a double layer compression effect ($\kappa$ increasing) in a region where DS$^-$ adsorption is unfavourable because of high negative surface charge. The rising parts of the two mentioned mobility curves are assumed to indicate adsorption of DS$^-$ on the pigments. The mobility curve for Hydral 705 is markedly different from the curves for AT-rutile and CD-rutile. The mobility of the Hydral 705 increases to a maximum and then drops as SDS concentration increases. The general shape of this curve can be explained by the opposing effects of adsorption of DS$^-$ and double layer compression. An important feature of the mobility curves in figure 5.17 is the parallelism between AT-rutile and CD-rutile. The reason for this similarity has been given previously in section 5.2.2.

In figure 5.18 the mobility of the PVAc latex prestabilized in SDS is seen to decrease as the concentration of polyphosphate increases. In fact comparison of figures 5.18 and 5.16
Oxides were predispersed so that after addition of SDS the final concentration was \(5 \times 10^{-5} \text{ mol dm}^{-3}\) in polyphosphate.

**FIGURE 5.17** Mobility of pigments (prestabilized in \(5 \times 10^{-5} \text{ mol dm}^{-3}\) polyphosphate) versus SDS concentration.
FIGURE 5.18 Mobility of PVAc latex (prestabilized in 5x10^-4 mol dm^-3 SDS) versus SHMP concentration
shows that the effect of SDS is to shift the mobility curve and raise the polyphosphate concentration at which flocculation occurs.

2. The investigations on mobilities as a function of total dispersant concentration were performed only on AT-rutile and the PVAc latex. The results of these studies are shown in figures 5.19 for AT-rutile and 5.20 for PVAc latex. The ratios of SDS to polyphosphate were selected to fit those encountered in paint formulae. In practice the SDS/SHMP ratio is 2:1 to 10:1 but 2:1 - 5:1 is more common. The abscissae of the graphs are in total dispersant concentration because any other choice of concentration would mask some features of the curves.

From figure 5.19 the mobility of the pigment AT-rutile is generally not seriously affected by SDS. The dominant effect on the pigment is from the polyphosphate. The differences between mobilities in mixed solutions and those in "polyphosphate only" solutions can be explained by changes in viscosity and ionic strength. The general shift to higher mobilities in mixed solutions arises because of the lower viscosities and ionic strengths of such solutions compared with polyphosphate solutions at the same concentration.

In figure 5.20 the mobility of the latex in mixed solutions is observed to be lower than that measured in 'pure' SDS solutions. Although the decrease in mobility involves adsorption of sodium ions into the inner double layer other factors are now involved; the presence of polyphosphate raises both $\kappa$ and viscosity, relative
AT-rutile was always prestabilized in SHMP before adding SDS.

FIGURE 5.19 Mobility of AT-rutile in mixed dispersant solutions. Fixed ratio of SHMP to SDS.
Latex was prestabilized in SDS before adding the SHMP.

![Graph showing mobility of PVAc latex in mixed dispersant solutions, fixed ratio of SDS to SHMP.](image)

**FIGURE 5.20** Mobility of PVAc latex in mixed dispersant solutions, fixed ratio of SDS to SHMP.
to SDS at the same concentration. It is notable that for the SDS/SHMP ratios involved in figure 5.20 no flocculation occurs in the mixed solutions. However, the point of latex solubilization moves to lower SDS concentrations as the proportion of phosphate increases. This observation is discussed later in section 5.15.

5.12 The Effect of Dispersants on Paint Stability

Since measurements of mobilities were not possible in a mixed colloid system, the influence of the dispersants, SDS and SHMP, on stability was studied by making mobility measurements on latex and pigment dispersions as separate systems. All measurements relevant to the paint system were performed at pH 8.0 (paints are prepared at pH 7-9).

In figure 5.21 is shown the mobility of AT-rutile, paint pigment, as a function of concentration in 'pure' dispersant, SDS or SHMP. Ignoring concentrations higher than $10^{-2} \text{mol dm}^{-3}$ both dispersants SDS and SHMP increase the mobility of AT-rutile pigment above its value at pH 8.0 in water. For an SHMP concentration of $5\times10^{-5} \text{mol dm}^{-3}$ the mobility of AT-rutile is -5.20 units compared to -2.50 units at pH 8.0; so the mobility of the pigment has been effectively doubled by the SHMP (pigment dispersant). Making the reasonable assumption that mobility is proportional to surface potential and hence to the repulsive energy of interaction, $V_R$, a substantial increase in mobility implies a considerable increase in $V_R$ and thus a significant improvement in stability. As the dispersants, SDS and SHMP are seen to increase the mobility of AT-rutile,
pH = 8.0 ± 0.05

FIGURE 5.21 Mobility of AT-rutile versus dispersant concentration, to show the separate effects of the dispersants.
it can be said that they improve the stability of the pigment dispersion.

The influence of SDS and SHMP on the mobility of the PVAc latex is shown in figure 5.22. Evidently the two electrolytes have opposing effects on the mobility and hence the stability of the latex. SDS improves stability whereas SHMP is detrimental to the stability of the latex.

The two points indicated by "solubilization" and "flocculation" have been explained previously. However the solubilization serves as a reminder that even the SDS concentration in a paint needs to be controlled carefully.

In the above discussions, the pigment and the latex were studied in 'pure' dispersant solutions. In practice an emulsion paint is made by combining the pigment prestabilized in polyphosphate (SHMP) solution with the latex prestabilized in emulsifier (SDS). So that an appropriate parameter to monitor is the stability of the particles in the presence of "opposing dispersant". Such a study was carried out and the results are plotted in figure 5.23. The shape of the mobility curves in figure 5.23 has already been explained in section 5.11. Generally, the mobility of AT-rutile is not adversely affected by SDS, in fact it is improved, therefore SDS has a positive effect on pigment stability even when the pigment has been prestabilized in SHMP. On the other hand SHMP depresses the mobility of the latex considerably in spite of the presence of SDS on the latex surface. Thus the SHMP is unfavourable to the stability of the latex, and actually flocculates the SDS stabilized latex at
FIGURE 5.22 Mobility of PVAc latex in single dispersant solutions to show the separate effects of the dispersants.
FIGURE 5.23 Mobility of AT-rutile and PVAc latex versus opposing dispersant concentrations.
\( C_e = 5 \times 10^3 \text{ mol dm}^{-3} \text{ in SHMP}. \) Evidently it is useful to keep the polyphosphate (SHMP) concentration as low as possible, taking into account the minimum concentration required for pigment stability.

5.13 Total Potential Energy of Interaction in the PVAc/AT-Rutile Paint

In Chapter 2 it was explained how the DLVO theory can be used to predict stability and flocculation of particles in a colloidal dispersion. In order to apply the DVLO theory to the paint system it has been assumed that all interactions occur at constant surface potential, \( \psi_o \). The repulsive energy of interaction, \( V_R \), has been calculated by means of the Hogg-Healy-Fuerstenau equation (equation 2.33), and the attractive energy of interaction, \( V_A \), was calculated from the Vincent equation for sphere-sphere interactions (equation 2.39). The assumptions and approximations pertinent to each of the said equations have already been discussed in Chapter 2. The calculation of the total potential energy of interaction, \( V_T \), was performed by computer and the appropriate program is given in the appendix.

Although \( V_T \) is a summation of \( V_A \) and \( V_R \), \( V_A \) is constant at any given distance of separation, \( H \), between particles. Thus variations in \( V_T \) are totally dependent on variations in \( V_R \) and since \( V_R \) is mainly dependent on surface potential, \( \psi_o \) and ionic strength as measured by \( \kappa \), \( V_T \) will be mainly influenced by changes in \( \kappa \) and \( \psi_o \). Calculations were performed for the following situations: (1) constant \( \kappa \), variable surface potential, \( \psi_o \); (2) constant surface potential, \( \psi_o \), variable \( \kappa \). In all graphs \( V_T \) is in kT units.
1. $V_T$ at constant $\kappa$ and variable $\psi_0$ is applicable to a stored paint, assuming no chemical changes take place. The ionic strength of an emulsion paint system gives $\kappa$ value between $5 \times 10^5$ cm$^{-1}$ and $3 \times 10^6$ cm$^{-1}$. Assuming $\kappa = 10^6$ cm$^{-1}$ as equivalent to a reasonable ionic strength, $V_T$ curves were calculated for various potentials of interaction between particles in the paint system. Figures 5.24, 5.25, 5.26 and 5.27 show the $V_T$ curves for the three possible interactions, viz: pigment-pigment, latex-latex and pigment-latex.

For particles of the size involved here (~ 0.25 µm) it is generally accepted that rapid flocculation can be prevented if the maximum barrier to flocculation into the primary minimum, $V_T(\text{max})$ is at least 15 kT units (see Chapter 2). Thinking in terms of storage stability in a paint, one would want a value of $V_T(\text{max})$ which allows a "pot life" of at least one year. So the required $V_T(\text{max})$ in a paint should be greater than 30 kT units. Inspection of the $V_T$ curves in figures 5.24, 5.25, 5.26 and 5.27 indicates that at $\kappa = 10^6$ cm$^{-1}$ the following forms of fast flocculation will be prevented if the surface potentials are as indicated: pigment-pigment homoflocculation $\psi_1 = \psi_2 = \psi_0 \geq 30$ mV; latex-latex homoflocculation $\psi_1 = \psi_2 = \psi_0 \geq 20$ mV; latex-pigment heteroflocculation $\psi_1 = \psi_2 = \psi_0 \geq 25$ mV or $\psi_1 = 20$ mV and $\psi_2 = 30$ mV. It is apparent that in comparison to the pigment the latex is more easily stabilized. A plot of $V_T(\text{max})$ at equal surface potentials - figure 5.28, shows that in a paint the preferred order of flocculation is as follows at constant $\kappa$: pigment-
FIGURE 5.24 $V_T$ versus $H$ for the interaction AT-rutile/
AT-rutile at constant $\kappa$, equal, variable potential

$\kappa = 10^5$ cm$^{-1}$

$\psi_{01} = \psi_{02} = \psi_0$

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<td>4</td>
<td>40</td>
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<td>5</td>
<td>50</td>
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</table>
\[ \psi_{01} = \psi_{02} = \psi_0 \]

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

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<th>No</th>
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<td>4</td>
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**FIGURE 5.25**  \( V_T \) versus \( H \) for the interaction PVAc/PVAc at constant \( \kappa \), equal variable potentials.
\( \kappa = 10^4 \text{ m}^{-2} \)

\( \psi_{01} = \psi_{12} = \gamma \)

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FIGURE 5.26 \( V_T \) versus \( \varphi \) for the interaction PVAc/AT-rutile at constant \( \kappa \), equal, variable potential.
\[ \kappa = 10^5 \text{ cm}^{-1} \]
\[ \psi_{01} = 30 \text{ mV (PVAc)} \]

<table>
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<tr>
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<th>( \psi_{02} ) (mV)</th>
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<td>4</td>
<td>50</td>
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</table>

**FIGURE 5.27** \( V_T \) versus \( H \) for the interaction PVAc/At-rutile at constant \( \kappa \); unequal, variable potentials
$\kappa = 10^6 \text{ cm}^{-1}$

$\psi_{01} = \psi_{02} = \psi_0$

**FIGURE 5.28** $V_{T(max)}$ versus $\psi_0$ for various interactions at equal potentials and constant $\kappa$. 
pigment > latex-pigment > latex-latex. So that in a paint, effort should be concentrated on stabilizing the pigment component.

2. Calculation of $V_T$ curves at constant potential and variable $\kappa$, ionic strength is an attempt to simulate the situation in the initial stages of drying in a paint film. Such a calculation is only a first approximation since it does not take into account other factors involved in paint film formation. However $V_T$ calculated for the said conditions allow predictions on the types of flocculation which will be favoured during drying. The resistance or tendency towards flocculation in the primary minimum is measured by the height of the primary barrier, $V_T(\text{max})$, and the tendency towards flocculation in the secondary minimum is measured by $V_T(\text{min})$.

In figure 5.29 is shown a plot of $V_T(\text{max})$ and $V_T(\text{min})$ as a function of $\kappa$ for interaction at 30 mV surface potential. The 30 mV potential was considered as the minimum potential required for stability during storage. In figure 5.29 it is evident that the pigment-pigment interaction is highly sensitive to changes in ionic strength, also, the pigment can undergo secondary minimum flocculation. The latex-latex interaction is not very sensitive to changes in $\kappa$. No secondary minima were found in the $V_T$-$H$ curves for latex-latex interaction. Generally figure 5.29 shows that the tendency towards flocculation in the primary or secondary minimum, during drying will be as follows:
FIGURE 5.29  $V_{T}(\text{max})$ and $V_{T}(\text{min})$ versus $\kappa$ for various interactions, at equal potentials, $\psi_0 = 30 \text{ mV}$
FIGURE 5.30 $V_{T\text{max}}$, and $V_{T\text{min}}$ versus $\kappa$, for various interactions at equal potential $\psi_0 = 50 \text{ mV}$.
Another calculation of $V_{T(\text{max})}$ and $V_{T(\text{min})}$ versus $\kappa$ was performed for $\psi_0 = 50$ mV and these interaction curves as shown in figure 5.30. The curves confirm the deductions made from figure 5.29. Therefore, generally, when the latex and the pigment have equal surface potentials the pigment will homoflocculate earlier than the latex. Furthermore, if heteroflocculation is considered as desirable then at equal surface potentials the pigment will tend to homoflocculate into the primary minimum before the drying film attains a $\kappa$ value which allows heteroflocculation to occur.

It is the desire of emulsion paint formulators that in dried paint films the pigment should be finely distributed. This objective might be achieved by designing the paint such that either heteroflocculation of pigment-lateX is favourable, or the pigment is maintained in a highly deflocculated state during film formation. As stated above, latex-pigment heteroflocculation is less favourable than pigment-pigment homoflocculation when the latex and the pigment have equal surface potentials. It would seem that heteroflocculation might be favourable if the surface potential of the pigment is considerably higher than the latex surface potential. A calculation of $V_{T(\text{max})}$ and $V_{T(\text{min})}$ versus $\kappa$ was performed for interactions where the pigment surface potential is 50 mV and the latex surface potential is 30 mV, and the resultant interactive curves are shown in figure 5.31. It is clear from figure 5.31 that even for these unequal potentials (50 mV/30 mV) pigment-lateX heteroflocculation is always less favourable than the other types of homoflocculation. In fact when $\kappa > 3.5 \times 10^6$ cm$^{-1}$, the preferred order of flocculation is exactly identical to the situation at equal pigment-pigment > pigment-latex > latex-latex
\[ \psi_0 = \text{PVAc} = 30 \text{ mV} \]
\[ \psi_0 = \text{AT-rutile} = 50 \text{ mV} \]

**FIGURE 5.31** \( V_T(\text{max}) \) and \( V_T(\text{min}) \) versus \( \kappa \), for interactions where AT-rutile and PVAc differ in potential
surface potentials, namely: pigment-pigment > latex-pigment > latex-latex.

5.14 Zeta-Potentials of Particles in the Emulsion Paint

In the discussion in section 5.13 above, the surface potentials were selected arbitrarily, and it would be useful to know the surface potentials operative in the emulsion paint. As explained previously, although surface potentials are used in the calculations based on the DLVO theory, only zeta ($\zeta$) potentials are accessible experimentally. $\zeta$-potential is accessible experimentally in so far as it can be calculated from electrophoretic mobility by one of the methods discussion in Section 2.4. Of the said methods, the Overbeek equations (equations (2.23) and (2.27)) are the most suitable for the model emulsion paint system, because of the electrolyte systems involved.

Applying the Overbeck equations to the latex and pigment dispersions in water at pH 8.0, in the absence of SDS and polyphosphate (SHMP), the following table of mobility/$\zeta$-potentials was obtained:

\[
\text{pH} = 8.0 \\
T = 298.15 \text{ K} \\
\kappa = 3.29 \times 10^5 \text{ cm}^{-1}.
\]

<table>
<thead>
<tr>
<th>Particle</th>
<th>KR</th>
<th>Mobility $m^2 s^{-1} V^{-1} x , \Omega^{-1}$</th>
<th>$\zeta$-potential $\text{mV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT-rutile</td>
<td>0.41</td>
<td>-2.65</td>
<td>-52</td>
</tr>
<tr>
<td>PVAc latex</td>
<td>0.43</td>
<td>-2.80</td>
<td>-58</td>
</tr>
</tbody>
</table>
ammonium hydroxide Electrolyte = \& i.e. |Z_+| = |Z_-| = 1

m_+ = 0.1752; m_- = 0.0651

m_+ was calculated by using \( \lambda_0^+ = \lambda_0^{OH^-} \) from Bockris (1970) and \( \lambda_0^+ = \lambda_0^{NH_4^+} \) from McInnes (1938). The value of \( \kappa \) given is only approximated, since the natural pH of the latex and pigment dispersions was 6-6.2 and \& was added to raise the pH to 8.0.

Since \( \zeta \)-potential is proportional to surface potential, \( \Psi_d \), the table suggests the pigment and latex dispersions should be stable at pH 8.0. In practice the latex was seen to be reasonably stable but the pigment settled completely within a few days. The instability of the pigment dispersion might be explained by postulating edge-edge flocculation of particles, such as is obtained in clay systems. AT-rutile particles are more or less ellipsoidal in shape - see figure 3.1 and their surfaces are alumina treated. At pH 8.0 in water the pigment has a net negative surface charge; however the surface charge is a summation between positive (alumina sites) and negative (bare-rutile sites) surface charges. Given the shape of the particles and the types of surface sites available it is energetically favourable for contact to occur between sites of opposite charge on different particles.

As stated above the \( \zeta \)-potentials of interest are those operative in the paint system. Now the paint contains a mixture of ammonium hydroxide electrolytes - SDS, SHMP and \& and as explained previously (Section 2.4), \( \zeta \)-potentials cannot be calculated for mixed electrolyte systems. This problem was circumvented by assuming that the \( \zeta \)-potentials operative in the separate systems viz. PVAc
latex/SDS and AT-rutile/SHMP would be indicative of the magnitude of ζ-potentials to be expected in the emulsion paint. Experience from paint formulation suggested the following electrolyte concentrations: (a) PVAc/SDS: SDS = 5 \times 10^{-4} \text{ mol dm}^{-3} (b) AT-rutile/SHMP: SHMP = 5 \times 10^{-5} \text{ mol dm}^{-3}

The terms \( \kappa \) and \( m_\pm \) involved in ζ-potential calculations have to take into account the nature of the electrolytes. SDS is a 1:1 electrolyte, however the SHMP is any of 1:3, 1:4 or 1:5 electrolyte, and these properties were taken into account in the calculations of \( \kappa \). The calculation of \( m_\pm \) terms gave the following results:

\[
m_\pm = 12.86 \frac{z_\pm}{\lambda_\pm^0} \text{ at } T = 298.15 \text{ K}
\]

SDS |\( Z_+ \)| = |\( Z_- \)| = 1

\[
m_+ = m_{N_3} = 0.26 \quad m_- = m_{DS^-} = 0.59
\]

\( \lambda^0_{N_3} \) was obtained from Bockris (1970) and \( \lambda^0_{DS^-} \) from Smith (1969).

SHMP (polyphosphate).

|\( Z_+ \)| = 1 \quad |\( Z_- \)| = 3, 4 or 5

\[
m_+ = 0.26
\]

\[
\begin{array}{ccc}
|Z_-| & m_- \\
3 & 0.15 \\
4 & 0.14 \\
5 & 0.12 \\
\end{array}
\]
\( \lambda^0 \) values were obtained from Koryta (1970).

In calculating zeta-potentials by the Overbeek method, it is mathematically more convenient to assign zeta potentials, calculate the mobilities, plot a graph of mobility/zeta potential and then by interpolation find the zeta-potential corresponding to the observed electrophoretic mobility. The aforementioned graph (mobility/\( \zeta \)-potential) was obtained by a computer program given in the appendix. For PVAc latex in \( 5 \times 10^{-4} \text{ mol dm}^{-3} \text{ SDS} \) and AT-rutile in \( 5 \times 10^{-5} \text{ mol dm}^{-3} \text{ polyphosphate} \), the mobility - zeta potential graphs are given in figures 5.32 and 5.33 respectively. The experimental mobility of PVAc latex in \( 5 \times 10^{-4} \text{ mol dm}^{-3} \text{ SDS} \) is \(-4.90 \) units, and the mobility of AT-rutile in \( 5 \times 10^{-5} \text{ mol dm}^{-3} \) polyphosphate (SHMP) is \(-5.20 \) units.

Inspection of figures 5.32 and 5.33 indicates these mobilities would probably give zeta-potentials above 80 mV. It is unfortunate that the magnitude of the expected zeta-potentials are so high because this means that the observed mobilities cannot be converted into zeta-potentials by the Overbeek method. Proper, exact calculation of the \( \zeta \)-potentials might be achieved by using the numerical methods of Wiersema et al (1966). However the computer program used by Wiersema et al was not available. Also the methods of these authors are limited to a maximum ionic valency of 3 and would therefore not apply to AT-rutile in polyphosphate. Nevertheless the Overbeek method does indicate that for the mobilities observed, the PVAc latex and the AT-rutile probably have comparable (if not equal) surface potentials, \( \psi_d > 80 \) mV.
FIGURE 5.32 Calculated mobilities versus zeta potential for PVAc latex in SDS. Calculations used the Overbeek equation (2.23).
AT-rutile in SHMP (polyphosphate) solution,
SHMP concentration = $5 \times 10^{-5}$ mol dm$^{-3}$
\(\kappa R = 7.115\)

**FIGURE 5.33** Calculated mobilities versus zeta potential

using Overbeek equation (2.27)
5.15 Solubilization of PVAc Latex by SDS

While performing mobility studies on PVAc latex in the presence of SDS - Section 5.9 - it was observed that the latex dissolved when the concentration of SDS was around or higher than the cmc ($cmc = 7.03 \times 10^{-3} \text{ mol dm}^{-3}$). Further mobility studies in mixed dispersant (SDS/SHMP) solutions - Section 5.11 - indicated that the concentration of SDS at which noticeable latex dissolution occurred, tended to decrease with increasing polyphosphate (SHMP) concentration. The foregoing observations suggested that latex solubilization might be linked to micelle formation by the SDS. Consequently the effect of polyphosphate (SHMP) on the cmc of SDS was studied and the results are shown in figure 5.34. The cmc of SDS is clearly seen to fall as the concentration of polyphosphate increases, thus suggesting that it is reasonable to link PVAc latex solubilization with micelle formation by SDS.

Having linked PVAc latex solubilization to micelle formation by SDS, it was immediately apparent that this would have important implications regarding latex or paint stability and also film formation during drying. Previous publications on latex solubilization - Sata and Saito (1952), Saito (1953), Isemura and Imanishi (1958), Isaacs and Edelhauser (1966) and Edelhauser (1969) - indicated that the emulsifier concentrations required for latex solubilization should be very high indeed, (generally $> 0.02 \text{ mol dm}^{-3}$). Isemura and Imanishi (1958) suggested that micelles were not responsible for the solubilization and proposed that oriented physical
FIGURE 5.34 The cmc of SDS as a function of SHMP polyphosphate concentration
adsorption of the emulsifier at the latex-solution interface made to latex particles hydrophilic. They considered this hydrophilizing effect to be responsible for the solubilization. The solubilized polymer retained virtually all the adsorbed emulsifier and behaved as a polyelectrolyte. Isaacs and Edelhauser (1966) agreed with Isemura and Imanishi (1958) and proposed the following scheme for the solubilization process:

The adsorbed emulsifier molecule bores into the polymer particle entraining water with it. The entrained water causes the particle to swell, and so more water and emulsifier are absorbed into the particle. The process of swelling and inhibition continues until the particle distinigrates and dissolves.

While the evidence for the polyelectrolyte behaviour of the dissolved latex is incontrovertible, the proposed mechanisms of solubilization are highly questionable. How does one explain the link between solubilization and micelle formation as observed in the laboratory? Also, if the mechanism of Isaacs and Edelhauser is right then there is no reason why solubilization should not occur at equilibrium concentrations below the cmc. Yet there is no report indicating solubilization occurs at equilibrium concentrations lower than the cmc.

Therefore an alternative mechanism of solubilization will be proposed, which, it is felt will, explain not only the link between cmc and solubilization, but also the observation that cationic emulsifiers invariably do not cause solubilization of PVAc latex
whereas anionic emulsifiers do.

5.15.1 The Mechanism of Solubilization of PVAc Latex

The publications on latex solubilization have been devoted either exclusively to PVAc latex or revolved around PVAc latex. All PVAc latices are prepared by emulsion polymerisation and so they are invariably anionic (negatively charged). The schematic diagrams below show the possible arrangement of ionising surface active molecules on the surface of a PVAc latex particle.

Figure 5.35: Latex solubilization mechanism

\[ C_e < \text{cmc} \]

\[ C_e \geq \text{cmc} \]

\[ \text{micellar type arrangement} \]
In process A → C all the surface active molecules are oriented with their hydrocarbon section on the latex surface. So that it is possible in this process, A → C, to envisage a progressive crowding of the latex surface until virtually all the water molecules are squeezed out and the polymer (latex) particle is trapped in a hydrocarbon (organic) core. Such a crowding is only attainable in a micellar solution as the core of micella is essentially organic. If the hydrocarbon core (organic phase) has a suitable dielectric constant and is compatible with the polymer constitution of the latex particle, the hydrocarbon tails of the surface active molecules may diffuse into the latex particle. The latex particle will then progressively soften up and dissolve in the manner that a polymer dissolves in an organic solvent. So, the solubilization of the latex particle by the anionic emulsifier will be diffusion controlled and also dependent on the particle size of the latex. As solubilization occurs by diffusion of the hydrocarbon tails of the emulsifier into the latex particle, these tails will be entangled in the polymer network and so the dissolved polymer will be held in a sort of micelle. The entanglement of the hydrocarbon tails of the emulsifier molecules in the polymer network, explains why Isemura and Imanishi (1958) observed that even after solvation the polymer retained the adsorbed emulsifier molecules.

As regards process B → D in figure 5.35, there is no stage at which the latex particle can be completely engulfed in a hydrocarbon core. The presence of the positively charged head group of the emulsifier on the particle surface ensures that water will be eternally present at the latex particle surface. Also, the
arrangement shown in D means that even at maximum coverage only half the surface area of the particle will be in contact with the hydrocarbon tails of the emulsifier. Hence even in a micellar solution of the cationic emulsifier the latex particle cannot be trapped in a totally hydrocarbon (organic) phase and so solubilization of the anionic latex by a cationic emulsifier is inherently unlikely.

The above schemes, $A \rightarrow C$ and $B \rightarrow D$, explain why it has been found that PVAc, polyvinyl formal, polyvinyl acetals, and polymethylacrylate anionic latices dissolve in SDS and SDBS but not in cetyl pyridinium chloride.

5.15.2 **Effect of Latex Solubilization on Particle Stability and Flocculation in Paints**

Having established that solubilization of PVAc latex occurs when SDS forms micelles in solution, it is useful to consider what advantages and disadvantages can derive from latex solubilization in an emulsion paint.

When PVAc latex is dissolved by SDS the solubilized polymer behaves as a polyelectrolyte. Hence the dissolved latex might be expected to affect the mobility and the stability of particles in an emulsion paint system if it adsorbs on the particles. Inspection of figure 5.20 shows that whenever solubilization occurs the mobility of the residual latex particles jumps to a much higher value. The jump in mobility can only be explained by postulating that the dissolved latex (polyelectrolyte) is swept up (adsorbed) by residual latex particles and the mobility of the residual latex...
particles is thereby increased. Now, since the latex particles can adsorb the dissolved latex, it is possible in a concentrated latex system for the dissolved latex to cause flocculation by a 'bridging' mechanism. In this laboratory, it was found that PVAc latices in which free SDS concentration approached the cmc tended to gel after a few weeks. The gel network was fairly loose because the entrapped water oozed out and accumulated on the top of the gel. The fact that the dissolved latex can cause flocculation means that latex solubilization is undesirable in a paint during storage. Since solubilization only occurs when the cmc of SDS is achieved, the concentration of free SDS in the PVAc latex and in the PVAc latex-AT-rutile emulsion paint should be kept as low as stability requirements will allow. The graph of cmc of SDS versus the concentration of polyphosphate—figure 5.34—indicates that the free SDS concentration should preferably be kept below $2 \times 10^{-3} \text{ mol dm}^{-3}$.

The effect of dissolved latex on the AT-rutile was studied by measuring the mobility of the pigment in dissolved latex solutions. Tables 5.36 and 5.37 show the mobility of the AT-rutile as a function of the amount of dissolved latex. In table 5.36 where there is no polyphosphate present, the mobility of the AT-rutile is seen to be manifestly dependent on the amount of dissolved latex. In table 5.37 where the AT-rutile has been prestabilized in polyphosphate solution, the mobility of the pigment is reasonably independent of the amount of dissolved latex. This observation suggests that the dissolved latex does not adsorb on AT-rutile stabilized by polyphosphate (SHMP).
AT-rutile pigment in dissolved PVAc latex solutions; mobility versus amount of dissolved latex.

Operative SDS concentration ~ $2.5 \times 10^{-2}$ mol dm$^{-3}$

Pigment concentration = 0.05 g dm$^{-3}$

TABLE 5.36  No Phosphate (SHMP) Present

<table>
<thead>
<tr>
<th>Amount of dissolved latex</th>
<th>Mobility of Pigment $\mu^{2}$ s$^{-1}$ V$^{-1}$ x $10^{8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NONE (a)</td>
<td>-4.67</td>
</tr>
<tr>
<td>0.0125</td>
<td>-5.20</td>
</tr>
<tr>
<td>0.025</td>
<td>-5.68</td>
</tr>
<tr>
<td>0.05</td>
<td>-5.33</td>
</tr>
<tr>
<td>* 0.10</td>
<td>-5.10</td>
</tr>
</tbody>
</table>

* This pigment dispersion was visibly flocculated yet upon re-dispersing ultrasonically no change in mobility was observed.

(a) Pigment dispersed in $2.5 \times 10^{-2}$ mol dm$^{-3}$ of SDS
AT-rutile pigment in dissolved latex solutions: mobility versus amount of dissolved latex.

Operative SDS concentration = $2.5 \times 10^{-2}\text{mol dm}^{-3}$

Pigment concentration = $0.05\text{ g dm}^{-3}$

TABLE 5.37 Phosphate (SHMP) Present

<table>
<thead>
<tr>
<th>Amount of dissolved latex g</th>
<th>Mobility of Pigment $m^2\text{s}^{-1}\text{V}^{-1}\times10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NONE</td>
<td>-5.20 (pigment in phosphate only)</td>
</tr>
<tr>
<td>0.0125</td>
<td>-5.07</td>
</tr>
<tr>
<td>0.025</td>
<td>-5.13</td>
</tr>
<tr>
<td>0.05</td>
<td>-5.26</td>
</tr>
<tr>
<td>0.10</td>
<td>-5.06</td>
</tr>
</tbody>
</table>

The pigment was always pre-dispersed in SHMP before adding to dissolved latex solution. The final operative concentration of SHMP was $5 \times 10^{-5}\text{mol dm}^{-3}$
In a drying paint film at some stage the concentration of free SDS must react and pass the cmc. Thus solubilization of latex particles is certain to occur in the drying paint film and it is therefore pertinent to consider how solubilization of latex affects the predictions of the DLVO theory regarding the preferred order of flocculation during drying.

In Section 5.14 it was seen that the latex and pigment could be regarded as having almost equal zeta-potentials. It is therefore appropriate to assume equal surface potentials for the pigment and latex, and a surface potential of 50 mV was considered a reasonable potential to expect in the model PVAc latex - AT-rutile emulsion paint. For the surface potential of 50 mV, $V_{T(\text{max})}$ and $V_{T(\text{min})}$ was calculated for variable $K$, with the purpose of simulating the drying paint film, and the plot of $V_{T(\text{max})}$ and $V_{T(\text{min})}$ versus $K$ is shown in figure 5.38. A second abscissa (solids content, % wt/wt) has been appended in order to help indicate the region of $K$ values at which flow in the film probably stops. When solubilization of latex occurs, the interaction curves for PVAc/PVAc and PVAc/AT-rutile disappear from figure 5.38 and only two curves are left, and both pertain to AT-rutile. In the absence of solubilization all the four interaction curves in figure 5.38 have to be taken account of in deciding the sequence of events that occur during drying.

As water evaporates from a drying paint film, the solids concentration increases, the viscosity of the interparticle fluid rises and the diffusion of particles is slowed down. This trend of events proceeds until flow in the film stops at some stage.
\( \psi_0 = 50 \text{ mV}; \quad \text{SDS} = 5 \times 10^{-4} \text{ mol dm}^{-3} \) (initially)

\( \text{SHMP} = 5 \times 10^{-5} \text{ mol dm}^{-3} \) (initially)

Assumptions: Hamaker constant invariable; beyond cmc \( C_e \) of SDS is always \( 7.03 \times 10^{-3} \text{ mol dm}^{-3} \)

**FIGURE 5.38 Interactions in drying paint film**
When flow by diffusion stops, the interparticle separation will be dependent on viscosity and double-layer interactions.

Using the interaction curves shown in figure 5.38 the following trend of events can be predicted to occur in the drying paint film: as the paint film dries out the AT-rutile pigment particles will tend to slide into a secondary minimum, but the rate of descent into the minimum (secondary) will be slowed down by the increasing viscosity of the interparticle liquid. At about 80-90% wt/wt solids, diffusive flow probably stops. The pigment particles are now in a secondary minimum of about -1 to -2 kT units, and they are about 100-200 Å apart. It is also at about this stage that the latex begins to dissolve. Now, it has been seen previously in this section that dissolved PVAc does not adsorb on AT-rutile pigment predispersed in polyphosphate, and since there is polyphosphate on the AT-rutile in the paint, the dissolving latex will not adsorb on the AT-rutile pigment. However because of the distance of separation between the pigment particles (100-200 Å) in the secondary minimum, the dissolving latex can distribute itself in the spaces between the pigment particles. This distribution of dissolved latex between the pigment particles will mean that as the final water leaves the paint film, the pigment particles will be entangled in a network of polymer chains and will thereby be prevented from homoflocculating, and hence the pigment particles will be finely distributed in the polymer network.

If there was no latex solubilization in the scheme of events described above, the pigment particles will simply slide into an
ever deeper secondary minimum and finally flocculate, forming scattered aggregates. The latex particles will be on their own and since the pigment particles are no longer available for hereto-flocculation to occur, the latex particles will coalesce and form a film in which the pigment aggregates will be distributed.

It follows from the foregoing discussions that latex solubilization would result in paint films which are better in quality (i.e. gloss, pigment distribution) relative to those in which no latex solubilization occurs. It will be seen later (Section 5.17) that this prediction is confirmed by paint film studies. Thus the DLVO theory has some success in predicting flocculation in the model PVAc/AT-rutile emulsion paint.

5.16 Comparison of Charge Densities from Adsorption and Electrophoresis

The adsorption of ionic species as described by the Stern theory has already been discussed in Chapter 1. In spite of the refinements on the Stern theory and the splitting of the Stern layer into the inner and outer Helmholtz layers, the Stern approach will be used because of its simplicity. The charge density in the Stern plane (from adsorption) is described by the Stern equation (2.17), which corresponds to the adsorption of counter ion only; while correspondingly the Gouy-Chapman approach gives the charge density (from potential measurements) according to equation (2.10). By comparing the charge densities from the two methods, it is possible to make some deductions regarding the mode of adsorption of stabilizers on the solid components of our model paint system.
In view of the polymeric nature of the phosphate (SHMP = pigment stabilizer) it would be inappropriate to examine charge densities deriving from adsorption of the polyphosphate since certain basic assumptions in the Stern theory will be violated. On the other hand it should be possible (and is indeed desirable) to discuss the case for adsorption of SDS in AT-rutile and PVAc latex. For this purpose the data has been extracted from figure 5.9 (adsorption) and figure 5.12 (mobility measurements). In order to calculate the charge density from the Gouy-Chapman approach the zeta-potentials have been obtained by using the Henry equation (2.22) and assuming \( \zeta = \psi_d \). The charge densities obtained by the two methods stated above, are presented in table 5.39a for SDS on AT-rutile and table 5.39b for SDS on PVAc latex, where \( \sigma_s \) is the charge density according to the Stern approach and \( \sigma_d \) is the charge density from the Gouy-Chapman approach.

Comparing \( \sigma_s \) and \( \sigma_d \) in any of the tables it is evident that \( \sigma_s \) is greater than \( \sigma_d \) by several orders of magnitude, whereas theoretically they should be comparable, or equal. The large discrepancy between \( \sigma_s \) and \( \sigma_d \) can only be explained postulating:

1. That adsorption of SDS on AT-rutile and PVAc latex involves adsorption of \( \text{DS}^- \) and \( \text{Na}^+ \) ions (co-ion and counter-ion adsorption) into the Stern layer. Since the particles are negatively charged prior to adsorption of SDS, it means that the chemical terms \( \phi \) in the Stern equation (2.16) are considerable.

2. The plane of shear is a considerable distance further from the locus of the head groups, because of the length of the hydrocarbon chain in the SDS molecule, so that \( \psi_d \neq \zeta \).
Comparison of charge densities from adsorption and electrophoresis.

**TABLE 5.39a** - AT-rutile in SDS Solution: \( \text{pH} = 8.0 \pm 0.05 \)

<table>
<thead>
<tr>
<th>SDS Concentration ( 10^{-3} \text{ mol dm}^{-3} )</th>
<th>Amount of SDS adsorbed ( 10^{-6} \text{ mol m}^{-2} )</th>
<th>( \sigma_s ) (adsorption) ( \mu C \text{ m}^{-2} )</th>
<th>( \psi_d ) mV</th>
<th>( \sigma_d ) electrophoresis ( \mu C \text{ m}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.125</td>
<td>1.206</td>
<td>-50</td>
<td>0.084</td>
</tr>
<tr>
<td>1.0</td>
<td>0.15</td>
<td>1.447</td>
<td>-58</td>
<td>0.145</td>
</tr>
<tr>
<td>5.0</td>
<td>0.375</td>
<td>3.619</td>
<td>-62</td>
<td>0.357</td>
</tr>
</tbody>
</table>

**TABLE 5.39b** - PVAc Latex in SDS Solution: \( \text{pH} = 8.0 \pm 0.05 \)

<table>
<thead>
<tr>
<th>SDS Concentration ( 10^{-3} \text{ mol dm}^{-3} )</th>
<th>Amount of SDS adsorbed ( 10^{-6} \text{ mol m}^{-2} )</th>
<th>( \sigma_s ) (adsorption) ( \mu C \text{ m}^{-2} )</th>
<th>( \psi_d ) mV</th>
<th>( \sigma_d ) electrophoresis ( \mu C \text{ m}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.313</td>
<td>3.015</td>
<td>-78</td>
<td>0.161</td>
</tr>
<tr>
<td>1.0</td>
<td>0.781</td>
<td>7.539</td>
<td>-75</td>
<td>0.213</td>
</tr>
<tr>
<td>2.0</td>
<td>1.563</td>
<td>15.01</td>
<td>-73</td>
<td>0.289</td>
</tr>
<tr>
<td>5.0</td>
<td>3.073</td>
<td>29.65</td>
<td>-70</td>
<td>0.310</td>
</tr>
</tbody>
</table>
It is not possible to prove postulate (2) experimentally, however postulate (1) may be tested by working with a 'clean' surface of known charge density prior to adsorption and using radiolabelled SDS. Our system does not permit such an undertaking and therefore one can only speculate about the reasons for $\sigma_s \neq \sigma_d$. It is notable that if postulate (1) above is valid for SDS then it is even more probable that it will be valid for polyphosphate (SHMP) adsorption on AT-rutile, so that adsorption of polyphosphate ions will be accompanied by the adsorption of large amounts of sodium ions into the Stern layer.

5.17 The Mechanism of Film Formation by Latices

The film forming component of an emulsion paint is the (polymer) latex. Therefore, factors that affect film formation by a latex will also affect paint film formation.

There are three theories aimed at describing the mechanisms of film formation by latexes and these theories are: the Dillon-Matheson-Bradford, the Brown and the Voyutskii theories. Historically the theories appeared in the order given here and each was an advancement. Dillon et al (1951) considered film formation only from the stage where the latex particles were in contact. They proposed that coalescence of particles occurred by viscous flow according to the Frenkel equation for coalescence of spheres:

$$\Theta = \frac{3\gamma_t}{2\pi \eta}$$  (5.1)
where: $\theta$ is the half angle of coalescence.

$\gamma$ = surface tension

$r$ = particle radius

$\eta$ = polymer viscosity.

$t$ = time

Two criticisms can be levelled at the Dillon-Matheson-Bradford theory. First of all the theory says nothing about the events preceding contact between particles. Secondly some of the terms in Frenkel equation as assigned by Dillon et al are not clearly defined. It is not certain which surface tension is meant: is $\gamma$ the water-air interfacial tension or the polymer-water interfacial tension? What does polymer viscosity mean?

Brown (1956) noted the above defects of the Dillon-Matheson-Bradford theory and worked out a more quantitative theory. He considered the stage just before contact, and the situation after contact. He introduced colloid chemical forces into the discussion and defined $\gamma$ as the polymer-water interfacial tension. Brown postulated capillary forces as the driving force towards coalescence and argued that coalescence can only occur when the capillary forces exceed the shear forces of the polymer constituting the latex particles. He also introduced the concept of the minimum film formation temperature. However as regards the mechanism of coalescence Brown retained the Dillon et al proposal of coalescence by viscous flow.

In spite of the considerable quantitative advances of Brown, the fate of stabilizers or emulsifiers was not considered.
Voyutskii (1958) accepted the Dillon-Matheson-Bradford and Brown mechanism of coalescence by viscous flow through the action of capillary forces. He extended Brown's treatment of the drying latex film to include the beginning of drying and proposed a three step process for film formation, viz:

1. Particles are concentrated under the action of surface tension forces, as water evaporates from the film. This process continues until an equilibrium separation of particles is reached, where free diffusion of particles stops.

2. Under the action of Brown's capillary forces, the particles are forced closer together until surface-surface contact is made.

3. By means of van der Waals and capillary forces the particles are sintered. During this final stage the stabilizer molecules are displaced from parts of the surface of the particles and accumulate in islands in interparticle spaces. Sintering of particles occurs through autohesion as bare surfaces meet. During latex coalescence if the stabilizer is compatible with the polymer then it will dissolve in the polymer network, otherwise the stabilizer accumulates in islands.

In the mechanisms proposed in the foregoing theories latex solubilization is not considered. In fact Vanderhoff (1970) reviewed the theories and presented evidence to show that emulsifier is exuded during film formation, but discounted solubilization as a contributive mechanism in film formation. He stated that SDS did not affect film formation by PVAc latex. Evidence will be
presented to show that SDS solubilizes PVAc latex during drying and improves film formation. Also it will be shown that when a stabilizer is incompatible with the latex, it causes poor film formation.

The influence of SDS and polyphosphate (SHMP) on PVAc latex and on PVAc latex/AT-rutile paint was studied by optical and scanning electron microscopy as described in Section 4.3. All PVAc films were cast from 30% wt/wt dispersions, while paint films were from 20% wt/wt dispersions.

In figure 5.40 is shown the photographs of a film cast from dialysed PVAc latex. Clearly a poor film is produced, and the interior of the film as shown by the optical microscope picture is poorly coalesced. Addition of SDS to the latex produces very considerable improvement in coalescence as shown in figure 5.41 and the improvement in film formation increases with the SDS concentration. All SDS concentrations were kept below 0.4% wt/wt based on latex, because at higher concentrations no structure would be found anywhere in the film. When polyphosphate is added to the PVAc latex the films formed are very heterogeneous, (fig. 5.42). Since the polyphosphate is highly polar it is incompatible with the PVAc. Also it was seen previously that the polyphosphate does not adsorb on PVAc, hence the polyphosphate will be exuded from the latex film during drying. The disruptive effect of the polyphosphate increases with concentration. Photographs (see figure 5.43) of PVAc latex films containing a mixture of SDS and polyphosphate indicate that the SDS reduces the disruptive effect of the polyphosphate. The improvement caused by SDS increases with the ratio of SDS to polyphosphate.
Figure 5.40: Latex Film containing no dispersants
Figure 5.41: Effect of SDS on latex films
SHMP = 0.05% wt  SHMP = 0.10% wt  SHMP = 0.20% wt

Optical Microscope: Magnification = 350 for all

SHMP = 0.05%  SHMP = 0.10%  SHMP = 0.20%

Scanning Electron Micrograph

Figure 5.42: Effect of SHMP on Latex Films
Optical Microscope; Magnification = 350 for all

Scanning Electron Micrograph

Figure 5.43: Latex film containing SDS and SHMP

Effect of increasing SDS concentration
The above experiments were repeated with an AT-rutile/PVAc latex paint but only SEM photographs were taken of the paint films. Figure 5.44 shows a photograph of the paint with no dispersant. The film is brittle and cracked at several places on the surface. When the paint is made with SDS as the only stabilizer all the cracks disappear from the film and a high quality film is obtained. No paint was made with polyphosphate as the only stabilizer, because the paint flocculated very quickly. Paints made with a mixture of SDS and polyphosphate gave films whose quality improved as the SDS:phosphate ratio increased, see figure 5.45.

All these preceding observations lead to the conclusion that SDS causes good film formation while polyphosphate is bad for film formation. The effects of the polyphosphate are reduced and sometimes even totally removed when SDS is present. These observations are explained by the fact that the SDS solubilizes the latex whereas the polyphosphate flocculates it. Solubilization by SDS is the only explanation possible in mixed electrolytes (SDS/polyphosphate) since the amount of SDS is too small to cause such extensive improvements in the film by mere plasticization.

It is therefore proposed that based on this evidence of solubilization of PVAc latex by SDS, the mechanisms proposed for latex film formation should include solubilization. The photographs shown here tend to suggest that PVAc latex solubilization by SDS may be the sole mechanism of film formation in the model emulsion paint (AT-rutile/PVAc latex).
Figure 5.44: Scanning Electron Micrograph of Artificial Paint films.
Containing no dispersants

"Artificial" = not useable
Figure 5.45: Scanning Electron Micrograph of "Artificial" paint films containing SDS and SHMP. Effect of increasing SDS concentration.
5.18 Time Dependent Chemical Changes in the Emulsion Paint

Stability and flocculation have been discussed both in terms of experimental observations and in terms of the DLVO theory. However it would be inappropriate to close the discussion without considering one of the imponderables of the system namely: time dependent chemical changes. This is an important factor in the pot life of a paint. The following chemical reactions can and do occur during the storage of the paint.

1. Hydrolysis of residual vinyl acetate monomer left over during the emulsion polymerisation.

\[ \text{CH}_2=\text{CH-OCOCH}_3 + \text{OH}^- \rightarrow \text{CH}_3 \text{COOH} + \text{CH}_3\text{CHO} \]

2. Hydrolysis of the polyvinyl acetate side chain

\[
\begin{align*}
\text{CH}_2-\text{CH} & \quad + \text{OH}^- \\
\text{OH} & \\
\text{C=O} & \\
\text{CH}_3 & \\
\text{n}
\end{align*}
\]

3. Hydrolysis of SDS to dodecyl alcohol.

\[ \text{CH}_3-(\text{CH}_2)_{11}-\text{OSO}_3^- + \text{OH}^- + \text{CH}_3(\text{CH}_2)_{11}-\text{OH} \rightarrow \text{SO}_4^{2-} \]

According to Such (1971), linear polyphosphates such as SHMP readily hydrolyse to give initially cyclic phosphates and eventually orthophosphate.

5. Hydrolysis of carboxyl and sulphate end groups on the latex surface. That this occurs was demonstrated by measuring the mobility of the PVAc latex as a function of time. In figure 5.46 is shown a plot of mobility versus time for dilute PVAc latex in SDS and in the absence of SDS. The mobility curves fall with increasing time and the drop in mobility for the dialysed latex must be due to loss of charge by hydrolysis.

All the 5 reaction schemes result in an increase in ionic strength, so that during storage the ionic strength of the paint will rise significantly. In fact the paint could become very acidic. The increase in ionic strength has two effects: (a) $V_{T_{\text{max}}}$ is lowered and (b) the cmc of SDS drifts to a lower concentration. Thus chemical reactions during storage increase the probability of latex solubilization and lower the resistance to destabilization. Reactions (3) and (5) have a more dramatic effect on stability because they result in loss of surface charge.

It would be useful to know the extent to which the above chemical reactions affect the stability of paint but so far one can only conjecture on their impact on stability.
Mobility of undialysed latex soon after preparation

Mobility of dialysed latex after completion of analysis

Undialysed latex (SDS present)

Dialysed latex (SDS free)

FIGURE 5.46 Mobility of dialysed and undialysed PVAc latex versus time
CHAPTER 6

CONCLUSIONS

6.1 The Stability of the Model AT-rutile/PVAc Emulsion Paint

Electrophoretic mobility measurements have shown that in the pH range of paint preparation (pH 7-9, the pigment (AT-rutile) and the latex (PVAc) are negatively charged, having mobilities at pH 8.0 of \(-2.65\) and \(-2.80 \text{ m s}^{-1} \text{V}^{-1} \text{cm}^{-1}\) respectively. The DLVO theory predicts that for such mobilities the pigment and latex may be stable in the aqueous phase without needing stabilizers. However experimental observations show this to be true of the latex but not the pigment. The instability of the pigment has been postulated to derive from the presence of positive and negative charge sites on the pigment surface.

From the studies of the pigment and latex in single and mixed dispersants (SDS and SHMP) solutions the following points emerge:

1) SHMP improves the mobility (negative) of the pigment considerably by adsorbing on it. However SHMP does not adsorb on the latex and produces a considerable decrease in the mobility of the latex, flocculating the latex at \(5 \times 10^{-4} \text{ mol dm}^{-3}\) in the absence of SDS.

2) SDS improves the mobility of the pigment and the latex by adsorbing on them; the effect being pH dependent in the case of the pigment. When the equilibrium concentration of SDS is above the cmc, the latex tends to dissolve, and it
has been shown that solubilization of the latex occurs whenever the ionic strength permits micellization to occur.

3) Since SHMP can flocculate the latex, while SDS can solubilize it, it is necessary to keep the concentrations of these dispersants as low as possible, taking into account the minimum concentrations required for paint stability. In our system the following concentration ranges are advisable: SHMP, \(2 \times 10^{-5} - 10^{-4}\ \text{mol dm}^{-3}\); SDS, \(5 \times 10^{-4} - 2 \times 10^{-3}\ \text{mol dm}^{-3}\).

4) Assuming SHMP concentration of \(5 \times 10^{-5}\ \text{mol dm}^{-3}\) and an SDS concentration of \(5 \times 10^{-4}\ \text{mol dm}^{-3}\) the mobilities of the pigment (AT-rutile) and PVAc latex are respectively \(-5.20 \ \text{m}^2 \text{s}^{-1} \text{V}^{-1} \ \text{cm}^{-1}\) and \(-4.90 \ \text{m}^2 \text{s}^{-1} \text{V}^{-1} \ \text{cm}^{-1}\). Therefore it may be assumed that the zeta potentials of the pigment and the latex are comparable, and for the stated mobilities the \(\zeta\)-potentials are in excess of 80 mV.

Although the DLVO theory predicts high stability and a long pot life for the paint, it turns out that chemical reactions intervene to reduce the pot life of the paint. The latex tends to lose charge by hydrolysis of SDS and surface end groups, while the polyphosphate breaks down to give ultimately orthophosphate, which is less effective as a pigment stabilizer. These chemical reactions ensure that the paint decreases in stability progressively because of loss of surface charge, and increasing ionic strength. The final destabilization probably occurs by solubilization of the latex since the cmc of SDS is lowered by increased ionic strength and latex solubilization occurs when the cmc is reached or passed.
6.2 Flocculation and Film Formation

Theoretical calculations based on the DLVO theory indicate that among the paint components the pigment is very sensitive to destabilization (flocculation) by increasing ionic strength. It has been shown that the preferred order of flocculation during drying is as follows: pigment-pigment homoflocculation > pigment-latex heteroflocculation > latex-latex homoflocculation; in the absence of latex solubilization.

Experimental studies show that the viscosity of the system will rise considerably during drying and that SDS causes the latex to solubilize. When the DLVO theory takes into account these observations it is predicted that solubilization of latex should lead to improved distribution of pigment distribution in the dried paint film.

Microscopic investigations on dried latex and paint films have shown that the polyphosphate (SHMP) causes poor film formation, while the SDS considerably improves film formation by dissolving the latex. When SHMP and SDS are both present in the latex or paint, the quality of the film formed improves as the ratio of SDS to SHMP (polyphosphate) increases, and the effect of SHMP is completely removed when the SDS to SHMP ratio is high.

6.3 Suggestions on Future Work

It seems that the stability of a water-based emulsion paint is controlled mainly by the chemical reactions that occur after formulation. Therefore if the objective of the formulator is to
obtain high stability during storage, it will be necessary to look for recipes that minimize the chemical reactions during storage. The following actions might be helpful:

1) reduce the esteric function in the latex by using a non-esteric monomer in the polymerization recipe.

2) replace the inorganic phosphate by an organic phosphate as the pigment stabilizer. The experimental investigations of Balzer and Lange (1975) indicate that organic phosphates are as effective as inorganic polyphosphates in raising the zeta potential of a γ-alumina. Also compatibility between organic phosphate and polymer latex will make it unlikely that the latex will be destabilized by the organic phosphate, in contrast to inorganic polyphosphate which tends to destabilize the latex.

The DLVO theory predicts that good pigment distribution in the dry paint film is unlikely because of the high preference of the pigment for homoflocculation, at an earlier stage during drying. However if latex solubilization occurs then poor pigment distribution can be averted. It may seem at first sight a good idea to use as much solubilizing emulsifier as possible, but this is not advisable because it would cause problems in storage stability. A probable but difficult answer is to use an amphoteric latex in the paint formulation, arranging that, when the pH of drying film falls below a certain value, charge reversal on the latex occurs and heteroflocculation takes place. It is possible that using an organic phosphate as pigment stabilizer, would reduce the tendency of the pigment to
homoflocculate. There is also the added bonus that an organic phosphate would encourage compatibility between pigment and latex, since it may be recalled that pigment pre-dispersed in inorganic polyphosphate, does not adsorb dissolved latex.

It is clear that to the emulsion paint formulator, storage problems are mainly related to the latex, while problems on flocculation during drying are linked with the pigment, and in the reconciliation of this divergence lies the way to a model emulsion paint.
MASTER REPULSIVE ENERGY

* PROGRAM CALCULATES VR, REPULSIVE ENERGY OF INTERACTION FOR
* IDENTICAL SPHERES USING THE DERJAGUIN EQUATIONS FOR SMALL AND
* LARGE SEPARATIONS, AND ALSO FROM THE HOGG ET AL. EQUATION; AND
* COMPARES RATIOS OF VR FROM THESE EQUATIONS.

* READING INPUT FILES
* READ (1,10) EPS, TEMP, H, HSTEP, NSTEP
10 FORMAT(4F0.0,10)
WRITE(2,66) EPS, TEMP, H, HSTEP, NSTEP
66 FORMAT(1H1,5X,4HEPS=,F10.4,5X,5HTEMP=,F10.4,5X,2HH=,F10.4,5X,6HHST
1EP=,F10.4,5X,6HSTEP=,16//)

* HIN = H/(10.0**8)
HSTEP = HSTEP/(10.0**8)

99 H = HIN

* READING PARAMETERS
* READ(1,30) R, CAPPA, PSI
30 FORMAT(F0.0,E0.0,F0.0)
WRITE(2,33) R, CAPPA, PSI
33 FORMAT(/,1UX,2HR=,F10.3,10X,6HCAPPA=,E11.4,10X,4HPSI=,F10.3,//)
WRITE(2,44)
44 FORMAT(6X,15HRV(DERJAGUIN),4X,13HRV(DERJAGUIN),4X,14HRV(HOGG,ET,AL
1)4X,16HRV(R>>H)/VR(R>>H),4X,17HRV(HOGG)/VR(R>>H),4X,16HSEPARATION
2IST.,/6X,6H(R>>H),8X,17MH COMPARABLE TO R,/
PSI = PSI/(299.8*1000.0)
R = R/(10.0**8)

*
DO 200 N = 1,NSTEP  
VD1 IS DERJAGUIN'S VR EQUATION FOR SMALL SEPARATIONS.  
VD2 IS DERJAGUIN'S VR EQUATION FOR LARGE SEPARATIONS.  
VF IS HOGG ET AL. EQUATIONS FOR SPHERES OF EQUAL RADII, AND

\[
VD1 = 0.5 \epsilon \sigma \rho \omega (1 + \exp (\sigma \alpha H))
\]

\[
VD1kt = VD1 \times (10^{16}) / (1.3805 \times \text{TEMP})
\]

\[
VD2 = 0.5 \epsilon \sigma \rho \omega (1 + 2.0 \exp (\sigma \alpha H) / (2.0 + H))
\]

\[
VD2kt = VD2 \times (10^{16}) / (1.3805 \times \text{TEMP})
\]

\[
VF = 0.25 \epsilon \sigma \rho \omega (1 + \exp (\sigma \alpha H)) \times (1 - \exp (-2 \times \sigma \alpha H))
\]

\[
VFKT = VF \times (10^{16}) / (1.3805 \times \text{TEMP})
\]

\[
\text{RAT1} = VD1kt / VD2kt
\]

\[
\text{RAT2} = VFKT / VD1kt
\]

\[
\text{HA} = H \times (10^{-8})
\]

WRITE(2,77) VD1kt, VD2kt, VFKT, RAT1, RAT2, HA

77 FORMAT(7X, E11.4, 5X, E11.4, E11.4, 9X, F10.4, 11X, F10.4, 10X, F10.4)

H = H + HSTEP

200 CONTINUE

READ(1,11) L

11 FORMAT(10)

IF(L)22,22,99

22 CONTINUE

STOP

END

FINISH

****
MASTER DELS SPSP

*****************************************************************************
* CALCULATION OF HS AND HL FUNCTIONS TO DETERMINE DELS (DEL STAR) OF VINCENT FOR SPHERE-SPHERE (SPSP) *
* SPHERE-SPHERE INTERACTION -- Eqs. 10 AND 11 OF VINCENT -- REF. *
* VINCENT JOURNAL OF COLLOID AND INTERFACE SCIENCE 42,270,(1973) *
REAL LAMDA
DIMENSION DAR(1),DBR(1)
READ (1,2) H,HSTEP,NSTEP,LAMDA
2 FORMAT (2F0.0,10,F0.0)
WRITE (2,21) H,HSTEP,NSTEP,LAMDA
21 FORMAT (10X,1HH,14X,5HHSTEP,8X,5HNSTEP,8X,5HLAMDA,/2(5X,F10.3),9X,113,5X,F10.3,/) 

* LAMDA IS CHARACTERISTIC WAVELENGTH OF THE MOLECULE IN ANGSTROM UNITS AND IS USED TO CALCULATE NUMERICAL CONSTANTS IN HS AND HL Eqs. OF VINCENT *
* RA AND RB ARE PARTICLE RADII IN ANGSTROMS RA BEING THE LESSER *
* ADSORBED LAYERS ARE IGNORED SO DEL = H *
* 
MIN = H/10.**8
HSTEP = HSTEP/10.**8
LAMDA = LAMDA/10.**8
22 READ (1,3) RA,RB
3 FORMAT (2F0.0)
WRITE (2,31) RA,RB
31 FORMAT (1X,3HRA=,F10.3,2X,3HRB=,F10.3,/) 

*****************************************************************************
M = 1
DAR(M) = RA/10.**8
DBR(M) = RB/10.**8
H = HIN
WRITE (2,52)
  52 FORMAT (7X,1HH,15X,2HHS,15X,2HHL,13X,6HLOG(H),10X,7HLOG(HS),
     1   10X,7HLOG(HL),/)
HDIFOLD = 0
RA = DAR(M)
RB = DBR(M)
DO 101 N=1,NSTEP
X = H/(2.*RA)
Y = RB/RA
U = X*X + X*Y + X
C = RA + RB + H
A = 1.01
B = 0.142_*3.1416/LAMDA
T1 = A*(Y/U + Y/(U*Y) + 2.*ALOG(U/(U + Y)))
T2 = 8.*RA*RA*B*(2.*Y + (2.*U + Y)*ALOG(U/(U + Y)))/C
HS = T1 + T2
AP = 2.45*LAMDA/(2.*3.1416)
BP = 2.04*LAMDA*LAMDA/(4.*3.1416*3.1416)
S1 = AP*(Y*(1.+Y)/(U*U)+Y*(1.-Y)*(1.-Y)/(U+Y)*(U+Y))
S2 = AP*(2.*(Y*Y-Y+1.)/(U*U)-2.*(Y*Y-Y+1.)/U + 4.*ALOG((U+Y)/(U)))
S3 = BP*(2./U+Y-2./U+(Y*Y+Y+1.)/(U*U)-(Y*Y-Y+1.)/(U+Y)*(U+Y))
S4 = BP*(Y*(1.+Y)*(1.+Y)/(U*U*U)+Y*(1.-Y)*(1.-Y)/(U+Y)*(U+Y))
HL = (S1 + S2)/(10.*C) + (S3-S4)/(60.*RA*RA)
HDIF = HS-HL
IF (HDIF*HDIFOLD) 91,93,93
  91 WRITE (2,92)
  92 FORMAT (100X,4HDELS)
  93 CONTINUE
C
HDFOLD = HDIFF
HA = H*(10.**8)
H = H + HSTEP
HAL = ALOG10(HA)
HSL = ALOG10(ABS(HS))
HLL = ALOG10(ABS(HL))
WRITE (2,99) HA, HS, HL, HAL, HSL, HLL
99 FORMAT (1X,F10.3,5X,2(E12.4,5X),3(3X,F7.3,7X))
101 CONTINUE
READ (1,103) I
103 FORMAT (I0)

* ***************************************************** *
 C
* IF I = 0 , PROGRAM ENDS
* IF I = 1 , NEW RA AND RB VALUES ARE READ IN AND PROGRAM
* REPEATS
* ***************************************************** *

IF (I) 106,106,22
106 CONTINUE

C
C
C
STOP
END
FINISH
****
MASTER NONIDENTICAL SPHERES INTERACTION

******************************************************************

PROGRAM CALCULATES THE TOTAL POTENTIAL ENERGY OF INTERACTION VT,
FOR DISSIMILAR SPHERES - UNEQUAL POTENTIALS, RADI, AND HAMAKER
CONSTANTS.
VR, IS DETERMINED BY THE HOGG ET AL. EQUATION AND VA BY VINCENT'S
EQUATION.

******************************************************************

REAL LAMDA
DIMENSION IEGTN(2),DAR(1),DBR(1)
DATA IS/1HS/,IL/1HL/

* *
READ(1,34) H,HSTEP,EPS,TEMP,NSTEP
34 FORMAT(4F0.0,10)
WRITE(2,43) H,HSTEP,EPS,TEMP,NSTEP
43 FORMAT(1H1,10X,1HH,15X,5HSTEP,15X,3HEPS,15X,4HTEMP,15X,5HSTEP,/,1
READ(1,24) AS1,AS2,AM,LAMDA
24 FORMAT(3E0.0,F0.0)
WRITE(2,42) AS1,AS2,AM,LAMDA
42 FORMAT(10X,5HAS1,15X,3HAS2,15X,2HAM,15X,5HLAMDA,/,3(6X,E12,4),6X,
1 F10.3)

HIN = H/(10.0**8)
HSTEP = HSTEP/(10.0**8)
LAMDA = LAMDA/(10.0**8)
A = 1.01
B = 0.14*2.1416/LAMDA

*
```c
A12 = SQRT(AS1*AS2)
A13 = SQRT(AS1*AM)
A23 = SQRT(AS2*AM)
A132 = 1.6*(A12 + AM - A13 - A23)
44 READ(1,50) RA,RB,CAPPA,PSI1,PSI2,DELS
50 FORMAT(2F0.0,E0.0,3F0.0)
WRITE(2,404) RA,RB,CAPPA,PSI1,PSI2,DELS
404 FORMAT(/,10X,2HRA,15X,2HRB,15X,5HCAPPA,15X,4HPSI1,15X,4HPSI2,15X,
1 4HDELS,6X,F10.3,7X,F10.3,7X,E12.4,8X,F10.3,2(9X,F10.3))

H = HIN
PSI1 = PSI1/(299.8*1000.0)
PSI2 = PSI2/(299.8*1000.0)
DELS = DELS/(10.0**8)
M = 1
DAR(M) = RA/(10.0**8)
DBR(M) = RB/(10.0**8)
WRITE(2,55)
55 FORMAT(/,15X,1HH,9X,5HVT/KT,8X,5HVA/KT,8X,5HVR/KT,21X,2HVT,13X,
1 2HVA,13X,2HVR,/)```

```c
C******************************************************************
C
00 100
N = 1,NSTEP
RA = DAR(M)
RB = DBR(M)
X = H/(2.0*RA)
Y = RB/RA
U = X*X + X*Y + X
C = RA+RB+H
FAC1 = EPS*RA*RB*(PSI1*PSI1+PSI2*PSI2)/(4.0*(RA+RB))
FAC2 = 2.0*PSI1*PSI2/(PSI1*PSI1+PSI2*PSI2)
C`
TR1 = FAC1*FAC2*ALOG((1.+EXP(-CAPPA*H))/(1.-EXP(*CAPPA*H)))
TR2 = FAC1*ALOG(1.-EXP(-2.*CAPPA*H))
VR = TR1 + TR2
IF(II-DELS) 11,11,77
   T1=A*(Y/U*Y/(U+Y)+2.*ALOG(U/(U+Y)))
   T2=8.*RA*RA*B*(2.*Y/(2.*U+Y)*ALOG(U/(U+Y)))/C
   HS = T1 + T2

HFUN IS VINCENT'S H FUNCTIONS
IEQTN(N):EXPRESSION MAKES THE PROGRAM TO STATE THE VINCENT H FUNCTION BEING USED IN THE PARTICULAR CALCULATION

IEQTN(1) = IS
IEQTN(2) = IO
HFUN = HS
GO TO 88

AP = 2.45*LAMDA/(2.*3.1416)
BP = 2.04*LAMDA*LAMDA/ (4.*3.1416*3.1416)
S1=AP*(Y*(1.+Y)*(1.+Y)/(U+U)+Y*(1.-Y)/(U+Y)*(U+Y))
S2=AP*(2.*Y*Y+1.)/(U+U)+2.*Y*Y+1.)/(U+4.*ALOG(U+U)/U)
S3=BP*(2./(U+Y)-2./U+(Y*Y+1.)/(U+U)-(Y*Y-Y+1.)/(U+Y)*(U+Y))
S4=BP*(Y*(1.+Y)*(1.+Y)/(U+U)*U)+Y*(1.-Y)/(U+Y)*(U+Y))
HL = (S1+S2)/(10.*C) + (S3-S4)/(60.*RA*RA)

IEQTN(2) = 1L
IEQTN(1) = IO
HFUN = HL
88 VA = A132*HFUN*(-1./12.)
VT = VA + VR
VTKT = VT*(10.**16)/(1.3805*TEMP)
VAKT = VA*(10.**16)/(1.3805*TEMP)
VRKT = VR*(10.**16)/(1.3805*TEMP)

WRITE(2,66) H,VTKT,VAKT,VRKT,VT,VA,VR,IEQTN

66 FORMAT(10X,8PF10.3,3X,0PG10.3),10X,3(3X,G12.5),5X,2A1
  H = H + HSTEP
100 CONTINUE
  READ(1,200) L
200 FORMAT(10)
  IF(L)33,33,44
33 CONTINUE

STOP
END
FINISH
MASTER INTERACTION OF IDENTICAL SPHERES

* *****************************************************************
* CALCULATION OF TOTAL POTENTIAL ENERGY OF INTERACTION, VT, FOR
* SPHERES OF IDENTICAL POTENTIALS, RAII, AND HAMAER CONSTANTS.
* VR IS DETERMINED BY THE HOGG ET AL. EQUATION AND VA BY THE VINCENT
* EQUATION.
* *****************************************************************

* REAL LAMDA
DIMENSION IEQTN(2), RA(1)
DATA IS/1HS/, IL/1HL/

READ(1,1) AS, AM, H, HSTEP, NSTEP, LAMDA, CAPPA, R, EPS, PSI, TEMP, DELS
1 FORMAT(2E0.0, 2F0.0, 0.10, F0.0, 5F0.0)
WRITE(2,11) AS, AM, H, HSTEP, NSTEP, LAMDA, CAPPA, R, EPS, PSI, TEMP, DELS
11 FORMAT(1H1, 9X, 2HAS, 15X, 2HAM, /2(5X, E12.4), /10X, 1HH, 14X, 5HHSTEP, 8X,
1 5HHSTEP, /X, 5HLAMDA, /2(5X, F10.3), 9X, 13X, 5X, F10.3, /8X, 5HCAPPA,
2 13X, 1HH, 15X, 3HEPS, 12X, 3HPSI, 10X, 4HTEMP, /5X, E12.4, 3(5X, F10.3),
3 6X, F7.2, //7X, 5HDELS = F10.3)

4 HIN = H/10.8
HSTEP = HSTEP/10.8
LAMDA = LAMDA/10.8
AS = SQRT(AS)
AM = SQRT(AM)
51 H = HIN
PSI = PSI/(299.8*1000.)
DELS = DELS/10.8
R = R/10.8
C M = 1
RACM) = R
WRITE (2,52)
52 FORMAT (10X,1H,N,9X,HVT/KT,8X,HVA/KT,8X,HVR/KT,21X,HVT,13X,
1 2HVA,13X,2HVR)
C *****************************************************
C DO 101 N=1,NSTEP
DEL = H
X = H/(2,R)
U = X**2,R
VR=0.25 EPS*R*PSI*PSI ALOG ((1,EXP (-CAPPA*H))* (1,EXP (-2,CAPPA*H
1 ))/(1,EXP (-CAPPA*H)))
IF (DEL-DELS) 8,8,9
8 HS=1,01*(1,U+1.)/(U+1.)+2,ALOG(U/(U+1.))+(/U+1.))+((7.03717*R(M)**2)/(U+1.)
1((2.*R(M)+DEL)*(LAMDA))*(2,*U+1.)*ALOG(U/(U+1.)))
C HFUN IS VINCENT'S H FUNCTIONS
IEQTN(1)=15
IEQTN(N)= EXPRESSION MAKES THE PROGRAM TO STATE THE VINCENT H
FUNCTION BEING USED IN THE PARTICULAR CALCULATION
C IEQTN(2)=10
HFUN = HS
C ******************************************************
GO TO 12
C 9 HL=((0.38993*LAMDA)/(2,R(M)+DEL))*(4./(U**2)/(U+2.)/(U+1.))+4. *
1*ALOG(U+1.)/U)+0.00086123*((LAMDA/R(A(M))*2))/(U+1.)/(U+1.)*23./(U**3)
IEQTN(1)=10
IEQTN(2)=IL
HFUN = HL
12 VA = (-1./12.)*HFUN* (AS-AM)*(AS-AM)*1.6  

VT = VA+VR
VTKT = VT*10,**16/(1.3805*TEMP)
VAKT = VA*10,**16/(1.3805*TEMP)
VRKT = VR*10,**16/(1.3805*TEMP)
WRITE(2,102) H, VTKT, VAKT, VRKT, VT, VA, VR, IEQTN
102 FORMAT (5X, 8PF10.3, 3(3X, 0PG10.3), 10X, 3(3X, G12.5), 5X, 2A1)

H = H + HSTEP

CONTINUE
READ (1, 103) I
103 FORMAT (10)
IF (I) 106, 106, 104
READ (1, 105) R, CAPPA, PSI, DELS
105 FORMAT (F0, 0, E0, 0, 2F0.0)
WRITE (2, 109) R, CAPPA, PSI, DELS
109 FORMAT (///7X, 2HR, =, F10.3, 6X, 6HCAPPA, =, E12.4, 6X, 4HPsi =, F10.3, 6X,
5HDELS =, F10.3, /)
GO TO 51
106 CONTINUE

CONTINUE
STOP
END
FINISH

***
C PROGRAM CALCULATES MOBILITIES FROM GIVEN ZETA POTENTIALS USING THE OVERBECK EQUATIONS
F1, F2, F3, F4 ARE THE OVERBECK F FUNCTIONS.

DIMENSION CAPC10, F1C10), F2(10), F3(10), F4(10), ZETA(15), Y(15)
NCAT AND NAN ARE CATION ANION VALENCE
LAMDA IS LIMITING CONDUCTANCE
REAL LAMDA1, LAMDA2, NCAT, NAN
READ(1,99) (ZETA(I), I=1,15)
99 FORMAT(5F0,0)

CONST = 1,3328/(10.0**4)
88 READ(1,1) RADIUS, NCAT, NAN, LAMDA1, LAMDA2
1 FORMAT(5F0,0)
WRITE(2,28) RADIUS, NCAT, NAN, LAMDA1, LAMDA2
28 FORMAT(1H1, SX, 7HRAADIUS:, F8,3,3X, 15HCATION VALENCE:, F3,0,3X, 14HANION VALENCE:, F3,0,11X, 15HCONDUCTANCE:, F8,3,3X, 18HANION CONDUCTANCE:, F8,3,/)  
CM1 AND CM2 ARE FRICTION FACTORS OF CATION AND ANION RESPECTIVELY.
CM1 = 12,86*NCAT/LAMDA1
CM2 = 12,86*NAN/LAMDA2
IF(NCAT.NE.NAN) GO TO 100
222 READ(1,33) (CAP(J), F1(J), F3(J), F4(J), J =1,7)
33 FORMAT(4F0,0)

C
C
C
C
C
C
C
C
C
C
* ****************************************************************** *
  DO 77 J=1,7
      WRITE(2,11) CAP(J),F1(J),F3(J),F4(J)
  11 FORMAT(/,5X,'KAPPA*RADIUS=',F10.5,5X,'F1=',F11.7,5X,'F3=',F11.7,5X,'F4=',F11.7,/) 
      WRITE(2,31)
  31 FORMAT(10X,'ZETA POTENTIAL',5X,'APPROX=HENRY',5X,'PART 10VERBEK',5X,'FULL OVERBEK',5X,'RATIO(U3/UDH)',/,'16X',3HMVS, 
        210X,'18MICRON/SEC/VOLT/CM',5X,'18MICRON/SEC/VOLT/CM',4X,'18MICRON/SEC/VOLT/CM',6X,'NO UNITS')
  DO 30 I=1,15
      Y(I) = ZETA(I)/25.69
      U1 = Y(I)*CONST*F1(J)
      T1 = CONST*Y(I)*Y(I)*Y(I)*(NAN*NAN*F3(J))
      U2 = U1 - T1
      T2 = CONST*Y(I)*Y(I)*Y(I)*(CM1+CM2)*0.5*F4(J)
      U3 = U2 - T2
      U1 = U1*(10.0**4)
      U2 = U2*(10.0**4)
      U3 = U3*(10.0**4)
      RATIO = U3*19.26/ZETA(I)
      WRITE(2,49) ZETA(I),U1,U2,U3,RATIO
  49 FORMAT(12X,'ZETA',10.4,9X,'F11.6',10X,'F11.6',12X,'F11.6',8X7'F11.6')
  DO 30 I=1,15
      Y(I) = ZETA(I)/25.69
      U1 = Y(I)*CONST*F1(J)
      T1 = CONST*Y(I)*Y(I)*Y(I)*(NAN*NAN*F3(J))
      U2 = U1 - T1
      T2 = CONST*Y(I)*Y(I)*Y(I)*(CM1+CM2)*0.5*F4(J)
      U3 = U2 - T2
      U1 = U1*(10.0**4)
      U2 = U2*(10.0**4)
      U3 = U3*(10.0**4)
      RATIO = U3*19.26/ZETA(I)
      WRITE(2,49) ZETA(I),U1,U2,U3,RATIO
  49 FORMAT(12X,'ZETA',10.4,9X,'F11.6',10X,'F11.6',12X,'F11.6',8X7'F11.6')
  CONTINUE
  77 CONTINUE
* *
  GO TO 60
  100 READ(1,55) (CAP(J),F1(J),F2(J),F4(J),J=1,7)
  55 FORMAT(4F0.0)
* *
* ****************************************************************** *
*
DO 111 J=1,7
WRITE(2,101) CAP(J),F1(J),F2(J),F4(J)
101 FORMAT(/,5X,14H KAPPA*RADIUS=,F10.5,5X,3HF1=,F11.7,5X,3HF2=,F11.7,
15X,3HF4=,F11.7,/) WRITE(2,200)
200 FORMAT(10X,14HZETA POTENTIAL,5X,16HU1(APPROX-HENRY),5X,17HU2(PART
OVERBEEK),5X,17HU3(FULL OVERBEEK),5X,13HRATIO(U3/UDH),/16X,3HMVS,
210X,18MICRON/SEC/VOLT/CM,3X,18MICRON/SEC/VOLT/CM,4X,18MICRON/SE
3C/VOLT/CM,6X,8HNO UNITS)
DO 90 I = 1,15
Y(I) = ZETA(I)/25.69
U1 = Y(I)*CONST*F1(J)
S1 = Y(I)*Y(I)*CONST*(NCAT)*F2(J)
U2 = U1-S1
S2 = Y(I)*Y(I)*Y(I)*CONST*((NCAT*CM1*CM2*NCAT)/(NCAT+NCAT))*F4(J)
U3 = U2 -S2
U1 = U1*(10.0**4)
U2 = U2*(10.0**4)
U3 = U3*(10.0**4)
RATIO = U3*19.26/ZETA(I)
WRITE(2,122) ZETA(I),U1,U2,U3,RATIO
122 FORMAT(12X,F10.4,9X,F11.6,10X,F11.6,12X,F11.6,8X,F11.6)
90 CONTINUE
111 CONTINUE
60 READ(1,37)N
37 FORMAT(10)
IF(N) 44,44,88
44 CONTINUE
C STOP
END
FINISH
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