AGGREGATE MORPHOLOGY IN
MIXED COLLOIDAL DISPERSIONS

by

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ABSTRACT

Scanning electron microscopy has been used to study the morphology of aggregates formed in mixed colloidal dispersions, specimens being prepared for observation by quench-freezing followed by thin-film freeze-drying. The results of this method were corroborated using optical microscopy and particle sedimentation. The adsorption of anionic polystyrene and poly(vinylidene chloride) latex particles onto larger cationic polystyrene latex particles was studied as a function of particle size ratio, particle concentration ratio, electrolyte concentration and the absence/presence of poly(vinyl alcohol). Pseudo-equilibrium fractional particle coverages ($\theta_{eq}$) were shown to increase with increasing size of the adsorbing particles, and with increasing electrolyte concentration, with remarkably even distributions of adsorbed particles being observed. For particles with physisorbed PVA, $\theta_{eq}$ increased until a critical electrolyte concentration was reached, above which a dramatic decrease in $\theta_{eq}$ was noted. These results can be rationalised in terms of the balance between attractive (normal) and repulsive (lateral) interparticle interactions. A model has been developed which allows calculation of the energy of approach of an adsorbing particle, and hence prediction of $\theta_{eq}$; the predictions of the model are in reasonable agreement with the experimental results. Initial rate constants for particle adsorption in these systems were found to increase with decreasing sizes of the adsorbing particles and with decreasing electrolyte concentration. The observed rates were greater than those predicted by a Smoluchowski-Fuchs type model.

Aggregation in mixtures of similarly-sized rutile titanium dioxide and either anionic or amphoteric polystyrene latex particles was studied using an intrusive sampling sedimentation rate technique, in which aliquots of dispersion were analysed for their polystyrene content. This allowed both the aggregate size distribution and composition to be determined. Ranges of pH have been identified for which homoaggregation and heteroaggregation occur in such mixtures.
I should like to express my gratitude to my supervisors, Dr. Dudley Thompson and Dr. Brian Vincent, for their guidance and encouragement throughout this work. The helpful comments of Dr. Paul Mills, Dr. David Sutton and Dr. David Taylor of I.C.I. were also greatly appreciated.

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To Mum and Dad,

with thanks for all
their help and
encouragement
DECLARATION

The work contained in this thesis was carried out between October 1985 and September 1988, in the Department of Physical Chemistry, University of Bristol, and in the laboratories of I.C.I. (Corporate Colloid Research Group, Runcorn). The work was supervised by Dr. D.W. Thompson and Dr. B. Vincent.

Except where indicated by reference, this is the original work of the author, and has not been submitted for any other degree.

S. HARLEY
# CONTENTS

## CHAPTER 1 - INTRODUCTION

<table>
<thead>
<tr>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

## CHAPTER 2 - THEORY

| 2.1 Introduction | 9 |
| 2.2 "van der Waals" Interactions | 9 |
| 2.2.1 The Microscopic Approach | 10 |
| 2.2.2 The Macroscopic Approach | 11 |
| 2.3 Electrostatic Interactions | 12 |
| 2.3.1 The Electrical Double Layer | 12 |
| 2.3.2 Interaction of Similar Double Layers | 18 |
| 2.3.3 Interaction of Dissimilar Double Layers | 21 |
| 2.3.4 Constant Surface Charge versus Constant Surface Potential Models | 28 |
| 2.4 Polymeric Stabilisation | 31 |
| 2.4.1 Effect of Adsorbed Polymer on the Electrical Double Layer | 32 |
| 2.4.2 Effect of Adsorbed Polymer on van der Waals Attraction | 33 |
| 2.4.3 "Steric" Interactions | 33 |
| 2.5 The Total Interaction Energy | 35 |
| 2.6 Electrophoretic Mobility and Zeta-Potential | 35 |
| 2.7 Kinetics of Aggregation | 37 |

## CHAPTER 3 - SPECIMEN PREPARATION FOR ELECTRON MICROSCOPY

| 3.1 Introduction | 43 |
| 3.2 Freezing | 43 |
| 3.3 Freeze-Fracture and Freeze-Etch Microscopy | 48 |
| 3.4 Principles of Freeze-Drying | 48 |
3.5 Thin-Film Freeze-Drying: Experimental 53
  3.5.1 Thin-film Formation 53
  3.5.2 Freezing 54
  3.5.3 Drying 54
  3.5.4 Mounting and Gold Coating 62
  3.5.5 Observation 62

3.6 Freeze-Drying: Results and Discussion 62
  3.6.1 Brass-Block Freeze-Dryer 62
  3.6.2 Stainless Steel Chamber 65
  3.6.3 Miscellaneous Freeze-Drying Results 66

3.7 Cryo-SEM 67

3.8 Conclusions 68

CHAPTER 4 - DISPERSION PREPARATION AND CHARACTERISATION 69

4.1 Preparation of Polystyrene Latexes 69
  4.1.1 Anionic Latexes 69
  4.1.2 Cationic Latexes 70
  4.1.3 Amphoteric Latex 72

4.2 Preparation of Poly(vinylidene chloride) Latex 74

4.3 Latex Characterisation 75
  4.3.1 Solids Content 75
  4.3.2 Particle Size Analysis 75

4.4 Adsorption of PVA onto Polystyrene Latexes 76

4.5 Electrophoresis Measurements 77
  4.5.1 The Influence of Electrolyte (KCl) Concentration on the Electrophoretic Mobility of Uncoated Latexes 80
  4.5.2 The Influence of Electrolyte (KCl) Concentration on the Electrophoretic Mobility of PVA-coated Latexes 81
  4.5.3 The Influence of pH on the Electrophoretic Mobility of Uncoated Latex and Titanium Dioxide 81
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>84</td>
</tr>
<tr>
<td>5.2</td>
<td>Specimen Preparation</td>
<td>85</td>
</tr>
<tr>
<td>5.3</td>
<td>Determination of Particle Coverage</td>
<td>87</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Freeze-Drying/SEM</td>
<td>89</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Optical Microscopy</td>
<td>93</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Particle Sedimentation</td>
<td>93</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Electrophoresis</td>
<td>95</td>
</tr>
<tr>
<td>5.4</td>
<td>Pseudo-Equilibrium Particle Adsorption Results</td>
<td>97</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Comparison of Techniques</td>
<td>97</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Fractional Coverage versus Concentration of Small Particles</td>
<td>102</td>
</tr>
<tr>
<td>5.4.3</td>
<td>Fractional Coverage versus Electrolyte Concentration</td>
<td>104</td>
</tr>
<tr>
<td>5.4.4</td>
<td>The Effect of Adsorbed PVA</td>
<td>106</td>
</tr>
<tr>
<td>5.4.5</td>
<td>Electrokinetic Studies of Heteroaggregates</td>
<td>111</td>
</tr>
<tr>
<td>5.5</td>
<td>Models for Particle Adsorption In Mixed Latex Systems</td>
<td>115</td>
</tr>
<tr>
<td>5.5.1</td>
<td>A Kinetic Model for Particle Adsorption</td>
<td>115</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Comparison of Experimental Results with Predictions of the Kinetic Model</td>
<td>120</td>
</tr>
<tr>
<td>5.5.3</td>
<td>Application of the Kinetic Model to PVA-Coated Systems</td>
<td>123</td>
</tr>
<tr>
<td>5.5.4</td>
<td>Discussion of the Kinetic Model</td>
<td>125</td>
</tr>
<tr>
<td>5.5.5</td>
<td>A Thermodynamic Model for Particle Adsorption</td>
<td>132</td>
</tr>
<tr>
<td>5.6</td>
<td>Kinetics of Particle Adsorption</td>
<td>136</td>
</tr>
<tr>
<td>5.6.1</td>
<td>The Effect of Particle Concentration Ratio</td>
<td>140</td>
</tr>
<tr>
<td>5.6.2</td>
<td>The Effect of Particle Size Ratio</td>
<td>140</td>
</tr>
<tr>
<td>5.6.3</td>
<td>The Effect of Electrolyte Concentration</td>
<td>140</td>
</tr>
<tr>
<td>5.6.4</td>
<td>The Effect of Adsorbed PVA</td>
<td>145</td>
</tr>
<tr>
<td>5.6.5</td>
<td>An Electrophoretic Study of Particle Adsorption Kinetics</td>
<td>145</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION
INTRODUCTION

Mixed colloidal dispersions, in which more than one type of particle is present, exhibit significantly more complicated aggregation behaviour than dispersions which contain only one type of particle. One reason for this is that in mixed systems the possibility of different types of particle-particle interaction arises. In the simplest case, of a binary dispersion which contains particles of type A and B, aggregation may occur by the formation of A-A, B-B and A-B contacts. The formation of predominantly A-A and/or B-B contacts is referred to as homoaggregation, whereas the formation of A-B contacts is referred to as heteroaggregation. In aqueous media, the aggregation behaviour of mixed systems is influenced by a number of factors. These include the magnitude and sign of the surface electrical potentials of the particles, the particle sizes and concentrations, the concentration of electrolyte in the dispersion medium, and the presence of adsorbed species at the particle surfaces. The work presented in this thesis represents an investigation of some of these factors, especially with respect to the morphology of the aggregates formed.

Mixed colloidal dispersions play a vital rôle in many technologies. For instance, the gloss and "hiding power" of an "emulsion" paint are largely determined by the morphology of particle aggregates formed as the paint dries.\(^1\) Homoaggregation of pigment particles leads to the occurrence of agglomerates of pigment in the final film, causing a poor finish. In contrast, if heteroaggregation between pigment and polymer particles is predominant, the pigment
will remain well-dispersed in the dry film, giving good gloss and "hiding" properties. Similar considerations apply in ceramics processing, where the particulate structure of the product determines its mechanical properties.\(^2\) In the field of medicine, heteroaggregation of polymer latex particles, whose surfaces have been modified by attachment of antigens or antibodies, is used in diagnostic immunoassays for rheumatism, pregnancy and many other conditions.\(^3\) Latex particles with attached DNA fragments are also used for DNA and RNA fractionation and characterisation.\(^4\)

Particle deposition onto surfaces is a limiting case of heteroaggregation where the size ratio between two species of particle is essentially infinite. Common applications of particle deposition onto surfaces include the manufacture of pigment-coated paper,\(^5\) and the filtration of potable water and beverages to remove suspended particles such as bacteria.\(^6\) In nature, bacterial deposition onto teeth\(^7\) and onto plant roots\(^8\) is important in tooth decay and nitrogen fixation, respectively.

If heteroaggregation and particle deposition are to be controlled and exploited efficiently, a fundamental understanding of the colloid science of these processes is necessary. A number of workers have addressed themselves to this problem and a brief review of the most important literature will be presented below.

The earliest theoretical treatments of the electrostatic interactions between dissimilar surfaces were carried out by Derjaguin\(^9\) and by Devereux and de Bruyn,\(^10\) who considered flat
parallel plates of dissimilar surface potentials. This work was extended by Hogg, Healy and Fuerstenau,\textsuperscript{11} who derived an analytical expression for the potential energy of interaction between spherical particles of dissimilar surface potential and size. Kitchener and co-workers\textsuperscript{12,13} obtained experimental results for the deposition of carbon black and of anionic polystyrene latex particles onto rotating discs coated with various polymers. They found qualitative agreement with the predictions of Hogg et al.\textsuperscript{11} for particles and surfaces carrying electrical charges of opposite sign. Agreement with the theoretical predictions was, however, rather poor for particles and adsorbent surfaces carrying charges of the same sign.

Many of the early experimental investigations of heteroaggregation were carried out using combinations of metal oxide particles.\textsuperscript{14-18} It was observed, however, that the rate and extent of aggregation in these systems was greatly affected by the solubility of the particles. The more soluble oxide species tended to dissolve and reprecipitate at the surfaces of less soluble particles. This gave rise to behaviour which was dependent upon the time allowed for equilibration prior to aggregation. The dissolution and reprecipitation process resulted in two sets of particles of different bulk composition, but similar surface characteristics, and it was thus difficult to compare the behaviour of these systems with theoretical predictions.

The problem of partial dissolution of particles has been circumvented in other work by the use of polymer latex particles.
For example, the rate of aggregation of amphoteric and anionic polystyrene latex particles of the same size was determined by James et al.,¹⁹ who monitored the change in turbidity of the mixed dispersion as a function of time. Aggregation rates obtained from this study were found to be in reasonable agreement with those predicted by the theory of Hogg et al.¹¹

Several workers have studied heteroaggregation between particles of appreciably different size, a process which may also be considered as the adsorption of small particles onto large ones. In most cases, the extent of adsorption was determined by centrifugation, to effect sedimentation of the large particles plus adsorbed small particles, followed by an assay for unadsorbed small particles remaining in the supernatant solution. Cheung²⁰ studied the adsorption of cationic polystyrene latex particles (radius 0.21 \( \mu \text{m} \)) onto anionic polystyrene particles (radius 1.07 \( \mu \text{m} \)). High affinity particle adsorption isotherms were observed, the number of adsorbed small particles per large particle rising with increasing electrolyte concentration. In a series of papers, Vincent and Young²¹,²² reported the results of experimental studies made on systems similar to those investigated by Cheung, but with both latex species carrying physically adsorbed poly(vinyl alcohol). In this case, the equilibrium concentration of small particles remaining in the supernatant solution after centrifugation was determined turbidimetrically. Below a critical electrolyte concentration, high affinity particle adsorption isotherms were observed, whereas above the critical concentration,
low affinity ("S-shaped") isotherms were observed. Particle adsorption in the latter case was readily reversible. These results were rationalised in terms of the balance between the attractive force operating between oppositely charged large and small particles, and the lateral force between adsorbed small particles. The lateral force may be either repulsive or attractive, depending upon the extension of the adsorbed poly(vinyl alcohol) layers and the electrolyte concentration. For the low affinity systems, it was proposed that net attraction between small particles at the surface of a large particle leads to the formation of two-dimensional "raft-like" structures. This was tentatively supported by observations made using electron microscopy. Further work by Vincent, Luckham et al.,23-25 on the same systems, led to the identification of particle concentration regimes in which small particles acted as bridging agents for the aggregation of large particles.

Matijević and co-workers26 also considered heteroaggregation in mixtures of large and small particles. In this case, the extent of adsorption was determined by centrifugation followed by angular light scattering measurements on the supernatant dispersions. Hansen and Matijević27 studied mixtures of anionic poly(methyl methacrylate) particles (radius 40 nm), and either alumina (radius 250 nm) or hematite (radius 275 nm), in dispersions having pH values at which the oxide materials carried a positive net surface charge. These mixtures gave rise to high affinity particle adsorption isotherms, based upon which these authors concluded that the equation of Hogg et
al. greatly overestimated the electrostatic ("double layer") forces acting between the particles. This led to the derivation of an alternative expression for the energy of electrostatic interaction between dissimilar spherical particles, which was claimed to fit closely the observations of Hansen and Matijević.

In a recent publication by Furusawa and Anzai, high affinity particle adsorption isotherms, determined by centrifugation and dry weight analysis of the supernatant solutions, were presented. The particles used in this case were amphoteric polystyrene latex (radius 125 nm) and silica (radii in the range 150 to 800 nm). The fraction of the large particle surface covered by small particles, θ, was again shown to rise with increasing electrolyte concentration, and also with increasing particle size ratio (silica/latex). These authors made no attempt, however, to rationalise their results in terms of the colloidal forces involved in the aggregation process.

In the aforementioned work, particle aggregation was studied using methods which provided no direct information regarding the morphology of heteroaggregates formed. Morphology has a major influence on the properties of an aggregated product, however, and is thus an important area for study. In order to obtain structural information, microscopy has been used, especially electron microscopy in the case of sub-micron colloidal particles. A popular technique by which specimens are prepared for observation using the transmission electron microscope is freeze-etching. This method has
been applied most often in the study of single dispersions, but has disadvantages in the study of mixed systems, in that a carbon replica of a two-dimensional section through a dispersion is observed. This makes difficult both the identification of individual particle type, and the interpretation of the image in terms of a three-dimensional structure. In view of such problems, it was deemed desirable to develop an alternative technique by which colloidal dispersions, especially aggregating mixed systems, may be prepared for observation using the electron microscope. The development of this technique ("thin-film freeze-drying for scanning electron microscopy") is described in chapter 3 of this thesis.

In chapter 2, theories describing particle interactions in aqueous media are discussed, with emphasis on interactions between dissimilar particles. As stated above, chapter 3 describes the techniques used to prepare samples for examination by electron microscopy, whilst chapter 4 describes the preparation and characterisation of the dispersions used in the subsequent aggregation studies. In chapter 5, results are presented relating to the aggregation of small anionic polystyrene latex particles with larger cationic polystyrene particles. The rate and final extent of aggregation, together with the morphologies of the aggregates formed, were studied using thin-film freeze-drying/SEM, in conjunction with optical microscopy. A theoretical model for the aggregation process is proposed and assessed in the light of the experimental results.
Finally, chapter 6 comprises a report of results obtained using a sedimentation rate analytical method. This was used to study aggregation in mixtures of similarly sized polystyrene latex and rutile titanium dioxide particles. This work has led to the identification of conditions under which heteroaggregation and homoaggregation occur in these systems.
CHAPTER 2

THEORY
2.1 Introduction

The adsorption of small, charged particles onto large, oppositely charged particles, in aqueous electrolyte solutions, is essentially governed by three types of interparticle force:

a) "van der Waals" forces, due to electromagnetic effects,

b) electrostatic forces, due to the overlap of electrical double layers around particles, and

c) "steric" forces, arising from chemical species present at the particle-solution interface.

These forces will be discussed below, followed by consideration of electrokinetic phenomena and the kinetics of particle aggregation.

2.2 "van der Waals" Interactions

Attraction between electrically neutral molecules can arise in three ways:

a) mutual orientation of permanent dipoles (the Keesom force),

b) induction of dipoles by permanent dipoles (the Debye force), and

c) co-operative polarisation of non-polar molecules due to fluctuations in their charge distribution (the London dispersion force).

The van der Waals attraction between colloidal particles is accounted for almost exclusively by the London dispersion force. Two theoretical methods, the "microscopic" and "macroscopic" approaches, can be used to calculate such forces.
2.2.1 The Microscopic Approach

This approach, which was originated by Kallmann and Willstätter\(^3\) and extended by de Boer\(^3\) and by Hamaker\(^3\), assumes that the interactions between the individual atoms or molecules comprising the particle are additive. The total van der Waals energy of interaction, \(V_A\), is then calculated by summation (or integration) over all pairs of molecules in any two interacting particles. For the case of two spherical particles of radii \(a_1\) and \(a_2\), separated, in vacuo, by a surface to surface distance \(H_0\), Hamaker\(^3\) derived the following expression.

\[
V_A = -\frac{A}{12} \left[ \frac{y}{x^2+xy+x} + \frac{y}{x^2+xy+x+y} + 2\ln \left( \frac{x^2+xy+x}{x^2+xy+x+y} \right) \right] \quad (2.1)
\]

In this expression \(x = \frac{H_0}{2a_1}\) and \(y = \frac{a_2}{a_1}\).

In equation (2.1), \(A\) is the "Hamaker constant" which is related to the polarisability of the atoms or molecules comprising the particles, as described by equation (2.2).

\[
A = \frac{3}{4} \pi^2 q^2 \alpha_0^2 h\nu_0 \quad (2.2)
\]

In this equation, \(q\) is the number density of the constituent molecules, \(\alpha_0\) is the polarisability of the molecule, \(h\) is Planck's constant, and \(\nu_0\) is the frequency of electronic fluctuations of the material. Hamaker\(^3\) also showed that if particles are separated by a liquid medium the net Hamaker constant is given by:
\[ A = (A_{11} - A_{22})^2 \] (2.3)

where \( A_{11} \) and \( A_{22} \) are the Hamaker constants for the particle and medium, respectively.

Casimir and Polder,\(^{34}\) followed by Schenkel and Kitchener,\(^{35}\) extended the above treatment to allow for the finite time required for propagation of the electromagnetic field between the two particles. This "retardation effect" reduces the attraction and becomes important for \( \lambda_0 > \) the wavelength of the field.

Despite the retardation correction, the accuracy of the microscopic approach is limited because of inherent assumptions. These include the pairwise additivity of intermolecular forces, the dominant contribution of a single characteristic frequency (usually in the ultraviolet region), and the modulation of the electromagnetic radiation in the liquid medium by the inclusion of a single, high frequency dielectric constant.

2.2.2 The Macroscopic Approach

A more rigorous and physically realistic model, proposed by Lifshitz,\(^{36}\) is the macroscopic approach, in which the interacting particles and intervening medium are treated as continuous phases. This approach accounts for many-body interactions, and \( V_A \) is derived from a knowledge of the bulk optical/dielectric properties of the particle and medium over the complete electromagnetic spectrum. The calculation of \( V_A \) by this method is much more complicated than that using the microscopic approach, especially with respect to particle size and shape,\(^{37,38}\) and will not be discussed here. The macroscopic
approach generally predicts somewhat smaller values of $V_A$ than the microscopic approach, particularly for the retarded region.

The interparticle attractions operating in the mixed systems studied in this work predominantly are due to "electrical double layer" forces, rather than to van der Waals attractions. Hence the simpler, if less rigorous, microscopic approach (equation 2.1) has been used in subsequent calculations of $V_A$.

2.3 Electrostatic Interactions

2.3.1 The Electrical Double Layer

When an electrically charged surface is in contact with an electrolyte solution, ions of opposite sign of charge to that of the surface (counter-ions) are attracted towards the surface, whereas ions of like charge (co-ions) are repelled away from the surface. Thermal diffusive mixing tends to oppose these effects. The resulting region of perturbed ionic atmosphere in the vicinity of the surface is commonly termed the "electrical double layer" (EDL).

Stern proposed that the EDL consists of distinct inner, and outer ("diffuse") regions. The inner part (or "Stern layer") comprises tightly bound ions, sufficiently strongly attached to the surface by electrostatic and/or van der Waals forces to be unaffected by thermal motion. The ionic distribution in the diffuse region is determined by a combination of electrostatic and thermal mixing forces. The arrangement of ions in the EDL, together with the consequent electrical potential, $\Psi$, is presented schematically in Figure 2.1.
Figure 2.1. Schematic Representation of the Structure of the Electrical Double Layer.

- Inner Helmholtz Plane
- Stern Plane
- Surface Plane of shear

Potential

\[ \zeta \quad \psi_d \quad \psi_0 \]

Distance
The "inner Helmholtz plane", first proposed by Grahame,\textsuperscript{43} lies at a distance from the surface equal to the radius of specifically adsorbed ions which are dehydrated on adsorption (at least in the direction of the surface). The "outer Helmholtz plane", or "Stern plane", lies at a distance from the surface equal to the radius of adsorbed hydrated ions. Within the Stern layer, the electrical potential falls from $\psi_0$ at the surface, to $\psi_d$ at the Stern plane. The plane of shear and zeta-potential, $\zeta$, will be discussed in section 2.6.

A quantitative description of the diffuse EDL is presented below, largely based upon the models of Gouy\textsuperscript{44} and Chapman,\textsuperscript{45} Derjaguin and Landau,\textsuperscript{46} and Verwey and Overbeek.\textsuperscript{47}

Ions in the diffuse region adopt a Boltzmann distribution, according to equation (2.4).

\[
n^+ = n_0^+ \exp \left( \frac{-z^+ \psi}{kT} \right) \quad \text{and} \quad n^- = n_0^- \exp \left( \frac{z^- \psi}{kT} \right) \quad (2.4)
\]

In this equation $n^+$ and $n^-$ are the respective numbers of positive and negative ions per unit volume, at a given point in the solution phase. $\psi$ is the corresponding electrical potential at that point, $n_0^+$ is the bulk concentration of each ionic species, and $z^\pm$ is the valence of each ionic species.

The relationship between $\psi$ and the net volume charge density, $\rho$, is given by Poisson's equation (2.5).

\[
\nabla^2 \psi = \frac{-\rho}{\varepsilon \varepsilon_0} \quad (2.5)
\]
\( \nabla^2 \) is the Laplacian operator, \( \varepsilon \) is the relative permittivity of the medium, and \( \varepsilon_0 \) is the permittivity of free space. \( \rho \) is also given by equation (2.6).

\[
\rho = e(z^+n^+ - z^-n^-) \quad (2.6)
\]

Combination of equations (2.4), (2.5) and (2.6) lead to the Poisson-Boltzmann (PB) equation (2.7).

\[
\nabla^2 \psi = \frac{-e}{\varepsilon \varepsilon_0} \left( z^+n^+ \exp\left[-\frac{z^+e\psi}{kT}\right] - z^-n^- \exp\left[\frac{z^-e\psi}{kT}\right] \right) \quad (2.7)
\]

Full solutions of the PB equation are very complex and, consequently, simplifications are commonly introduced.

For a flat surface and symmetrical electrolyte \((z^+=z^-)\), a one-dimensional PB equation can be derived (equation (2.8)).

\[
\frac{d^2 \psi_x}{dx^2} = \frac{-ze\alpha}{\varepsilon \varepsilon_0} \left( \exp\left[-\frac{ze\psi_x}{kT}\right] - \exp\left[\frac{ze\psi_x}{kT}\right] \right) \quad (2.8)
\]

Equation (2.8) can also be written in the following form.

\[
\frac{d^2 \psi_x}{dx^2} = \frac{2ze\alpha}{\varepsilon \varepsilon_0} \sinh\left[\frac{ze\psi_x}{kT}\right] \quad (2.9)
\]

The solution of equation (2.9), for the boundary conditions \( \psi_x = \psi_0 \) when \( x = 0 \), and \( \psi_x = \frac{d\psi_x}{dx} = 0 \) when \( x = \alpha \); takes the form

\[
\psi_x = \frac{2kT}{ze} \left[ \frac{1 + \gamma \exp[-\alpha \psi]}{1 - \gamma \exp[-\alpha \psi]} \right] \quad (2.10)
\]
where

\[
\gamma = \frac{\exp[ze\psi_o/2kT] - 1}{\exp[ze\psi_o/2kT] + 1}
\]  

(2.11)

and

\[
\kappa = \left\{ \frac{2e^2 n_o z^2}{\varepsilon \varepsilon_0 kT} \right\}^{1/2}
\]  

(2.12)

For small values of \(\psi_o\) the Debye-Hückel (DH) approximation\(^{48}\) may be applied; this simplifies (or "linearises") equation (2.9) by using the relationship

\[
\sinh y = y + \frac{y^3}{6} + \frac{y^5}{120} + \ldots \quad \text{for } y < 1
\]  

(2.13)

where \(y = ze\psi/kT\). It follows that, for \(ze\psi_o < 25.6 \text{ mV}\) (whereby \(y < 1\), at 25°C), the "linearised", one-dimensional PB equation takes the form shown in equation (2.14).

\[
\psi_x = \psi_o \exp[-\kappa x]
\]  

(2.14)

Thus, the potential in the diffuse layer decays exponentially with the distance from the surface. \(\kappa^{-1}\) has the units of distance, and is often loosely referred to as the "double layer thickness" or "Debye length".

For a spherical interface, the three-dimensional form of the PB equation reduces to equation (2.15), for symmetrical electrolytes.

\[
\nabla^2 \psi_r = \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d\psi_r}{dr} \right] = \frac{2ze\psi_o}{\varepsilon \varepsilon_0 kT} \sinh \left[ \frac{ze\psi_r}{kT} \right]
\]  

(2.15)
In this equation $r$ is the radial distance from the centre of a sphere of radius $a$. Equation (2.15) cannot be integrated analytically, but, by applying the DH approximation once more, equation (2.16) can be derived.

$$\psi_r = \psi_0 \frac{a}{r} \exp[-\kappa(r-a)] \quad (2.16)$$

The surface charge density, $\sigma_0$, can be equated with the net volume charge density in the diffuse double layer, according to equation (2.17).

$$\int_{x=0}^{x=\infty} \varphi \, dx = -\sigma_0 \quad (2.17)$$

For the one-dimensional case, it can be shown, using the Poisson equation (2.5), that

$$\sigma_0 = \varepsilon \varepsilon_0 \left[ \frac{d\psi_x}{dx} \right]_{x=0} \quad (2.18)$$

which, via the integrated form of the one-dimensional PB equation for symmetrical electrolytes, leads to equation (2.19).

$$\sigma_0 = (8n_0 \varepsilon \varepsilon_0 kT)^{1/2} \sinh \left[ \frac{2e\psi_0}{2kT} \right] \quad (2.19)$$

For small $\psi_0$, equation (2.19) reduces to the following expression.

$$\sigma_0 = \varepsilon \varepsilon_0 \kappa \psi_0 \quad (2.20)$$
In calculating the charge density for spherical interfaces, the problem of solving the three-dimensional PB equation (2.7) arises once more. For small $\psi_0$ and symmetrical electrolytes, equation (2.21) is applicable.

$$c_0 = \varepsilon \varepsilon_0 \psi_0 \left( \frac{1}{\alpha} + \kappa \right)$$

(2.21)

The equations given in the foregoing pages are applicable only in the diffuse part of the double layer. Whilst they were derived using the surface potential, $\psi_0$, since the advent of Stern’s theory it is common to replace $\psi_0$ in the above expressions with $\psi_d$ (the potential at the Stern plane).

2.3.2 Interaction of Similar Double Layers

As two similar charged surfaces approach in electrolyte solution, the diffuse parts of their electrical double layers eventually overlap. Such overlap causes repulsion between the surfaces. This repulsion is due to a combination of repulsion between like-charged counter-ions, and a rise in osmotic pressure caused by an increase in ionic concentration between the surfaces as they approach. As in the case of a single double layer (section 2.3.1), it is necessary to introduce approximations if manipulable quantitative expressions are to be derived for such interactions.

The approach of infinite identical flat plates was considered by Derjaguin and by Verwey and Overbeek, who independently derived an
expression for the electrostatic potential energy of interaction \((V_E)\), as a function of the separation between the plates, \(H\). In the case of constant and small \(\psi_o\), this expression takes the following form.

\[
V^f_P = \frac{64 n_0 k T \gamma^2}{\kappa} \exp (-\kappa H) \tag{2.22}
\]

In this expression, \(\gamma\) and \(\kappa\) are defined by equations (2.11) and (2.12) respectively, and the superscript \(f_P\) refers to flat plates.

In the case of interactions between curved surfaces, no exact analytical solutions to the PB equation are known, even on application of the DH approximation. This problem was circumvented by Derjaguin\(^{49}\), who extended his theory for flat plates to the approach of identical spheres. This he did by considering each sphere to be made up of infinitesimally small concentric rings, each of which can be treated as a flat plate (see Figure 2.2). The energy of approach of the spheres, \(V^S\), is then given by equation (2.23)

\[
V^S = \pi a \int_{H_0}^{\infty} V^f_P(H) \, dH \tag{2.23}
\]

This geometrical treatment is only valid for small double layer extensions relative to the particle size \((\kappa a > 10)\), and small inter-particle separations \((H_0 < a)\). Substitution of equation (2.22) into (2.23) leads to the following expression for the energy of approach of identical spheres of low surface potential \((\psi_o < 25 \text{ mV})\).

\[
V^S = 2\pi \epsilon_0 \omega \psi_0 \ln(1 + \exp[-\kappa H_0]) \tag{2.24}
\]
Figure 2.2. Schematic representation of the principle of the Derjaguin approximation.
2.3.3 Interaction of Dissimilar Double Layers

The approach of two surfaces which possess charge of dissimilar magnitude or sign, or both, was considered by Derjaguin\(^9\), and later by Devereux and de Bruyn\(^10\). The full PB equation (2.7) was used to calculate the force between approaching dissimilar infinite flat plates. The resulting formulae must, however, be solved numerically.

For systems of small surface potentials (< 25 mV) and symmetrical electrolyte, an analytical expression for the energy of interaction between flat plates was derived by Hogg, Healy and Fuerstenau\(^11\) (HHF) (equation (2.25)).

\[
V_{EP} = \frac{\varepsilon \varepsilon_0 K}{2} \left[ (\psi_{01}^2 + \psi_{02}^2)(1 - \coth(\kappa H)) + 2\psi_{01} \psi_{02} \coth(\kappa H) \right]
\]  

(2.25)

In this equation \(\psi_{01}\) and \(\psi_{02}\) are the surface potentials of the two plates. Values of \(V_{EP}\) calculated using equation (2.25) agree well with the exact numerical values of Devereux and De Bruyn,\(^10\) even up to \(\psi_{01}, \psi_{02} \approx 75\) mV,\(^11\) despite equation (2.25) being strictly valid only for low (and constant) surface potentials.

Hogg et al.\(^11\) extended the above treatment to dissimilar spheres \((\psi_{01} \neq \psi_{02}, a_1 \neq a_2)\) by applying Derjaguin's geometrical method,\(^49\) giving equation (2.26).

\[
V_E^S = \pi \varepsilon \varepsilon_0 a_1 a_2 \left( \frac{\psi_{01}^2 + \psi_{02}^2}{a_1 + a_2} \right) \left( \frac{2\psi_{01} \psi_{02}}{(\psi_{01}^2 + \psi_{02}^2)} \right) \ln \frac{1 + \exp[-\kappa H_0]}{1 - \exp[-\kappa H_0]}
\]

+ \ln(1 - \exp[-2\kappa H_0])

(2.26)
Again, this equation is strictly valid only for small and constant $\psi_{01}$ and $\psi_{02}$, and for $ka_1, ka_2 > 10$ and small $H_0$ ($< a_1, a_2$).

In order to improve the accuracy of the HHF equation (2.26) for larger $H_0$, the use of Derjaguin's geometrical method was circumvented by Bell, Levine and McCartney (BLM), who obtained the following expression,

\[
V_{E}^{\infty} = \left[\frac{kT}{e}\right]^2 \frac{2\pi \varepsilon_0 a_1 a_2 (r-a_1)(r-a_2)}{r[r(a_1+a_2)-a_1^2-a_2^2]} \left\{ (\Phi_1 + \Phi_2 + \Lambda \Phi_1 \Phi_2) \ln (1 + \exp[-\kappa r]) + (\Phi_1^2 + \Phi_2^2 - \Lambda \Phi_1 \Phi_2) \ln (1 - \exp[-\kappa r]) \right\} \tag{2.27}
\]

where $r = a_1 + a_2 + H_0$,

\[
\Lambda = \frac{a_2(r-a_2)}{a_1(r-a_1)} + \frac{a_1(r-a_1)}{a_2(r-a_2)} \tag{2.27}
\]

\[
\Gamma = \frac{a_1 a_2}{(r-a_1)(r-a_2)} \exp[\kappa(a_1+a_2)] ,
\]

\[
\Phi_1 = \frac{ze\psi_{01}}{kT} \quad \text{and} \quad \Phi_2 = \frac{ze\psi_{02}}{kT} .
\]

For large separations a linear superposition approximation was used, by which it is assumed that the potential at a point equidistant between the sphere centres is the sum of the potentials of the two spheres considered in isolation. At small separations equation (2.27) reduces to the HHF equation (2.26).
A weakness of all the treatments of inter-particle interactions discussed so far is that the PB equation (2.7) is solved for a one-dimensional parallel plate model (i.e. for the decay of $\psi$ in the $x$-direction only). The cylindrical symmetry of two approaching spheres means that the use of a two-dimensional PB equation is more rigorous, since this accounts for lateral contributions to the force of interaction. In this case the PB equation has the following form.

$$
\left[ \frac{1}{r} + \frac{6}{6r} \left( \frac{r}{6} \right) + \frac{6^2}{6x^2} \right] \psi = \frac{2ze_n}{\varepsilon \varepsilon_0} \sinh \left[ \frac{2e\psi}{kT} \right]
$$

(2.28)

In this equation $r$ is the radial distance from the centre of sphere 1, and $x'$ is the co-ordinate connecting the centres of the two spheres.

Equation (2.28) has been solved by Barouch et al.\textsuperscript{28} (BMRF) for the case of dissimilar spheres of constant surface potential, at small separations, without using Derjaguin's geometrical method. The resulting expression takes the form,

$$
V_E = \left[ \frac{kT}{e} \right] \left[ -\pi a_1 \varepsilon \varepsilon_0 2^H \int_0^{Ka_1} \Phi_1 [(a_1\kappa)^2 - R^2]^{-1/2} \cosh \Phi_1 - \Phi(R) \right]^{1/2} R dR
$$

$$
- \pi a_2 \varepsilon \varepsilon_0 2^H \int_0^{Ka_2} \Phi_2 [(a_2\kappa)^2 - R^2]^{-1/2} \cosh \Phi_2 - \Phi(R) \right]^{1/2} R dR
$$

(2.29)

where $\Phi_1 = \frac{ze\psi_1}{kT}$, $R = kr$ and $\Phi(R)$ is the cosh value of the minimum potential of interaction between the particles. Clearly, this expression is more complicated than the analytical HHF equation (2.26), and must be solved numerically. Barouch et al.\textsuperscript{28} compared
the "BMRF" and "HHEF" methods and found that smaller energies of interaction are predicted by the former, as shown in Figure 2.3. Further comparisons were presented by Barouch and Matijević, together with an explanation for the deviations between the two methods, which they showed to be significant for $\kappa H_0 < 4$.

The mathematical correctness of the BMRF method has been the subject of considerable debate in the literature and has still to be generally accepted. It is clear, however, that a full mathematical treatment of the interaction between dissimilar spheres is extremely complex. Although the equations of HHEF (2.26) and BM (2.27) must be regarded as approximate, especially in the case of large surface potentials, the appeal of these expressions lies in their relatively simple analytical form.

Irrespective of which model is used, all constant surface potential solutions to the PB equation predict an attraction, at small distances of separation, between surfaces with potentials of like sign but unequal magnitude. No such attraction is predicted when $\psi_1 = \psi_2$. These features are illustrated in Figure 2.4, which shows $V_E$ (calculated using equation (2.26)) versus $H_0$, for several combinations of $\psi_1$ and $\psi_2$, and particle sizes $a_1 = 1.0 \mu m$ and $a_2 = 0.1 \mu m$, in $5 \times 10^{-4}$ mol dm$^{-3}$ KCl.

The attraction between surfaces of like-sign can be rationalised in the following way. Consider the case of two parallel, flat plates where $\psi_1 \neq \psi_2$. Figure 2.5 shows the dependence of $\psi(x)$ on $\kappa x$, cal-
Figure 2.3. Potential Energy of Interaction, $V_E$, of Two Dissimilar Spherical Double Layers Calculated using the HHF, BLM and BMRF Equations.

For each case,

- $a_1 = 1 \mu$m ; $\phi_{os} = 25$ mV
- $a_2 = 2 \mu$m ; $\phi_{oa} = 50$ mV
Figure 2.4. $V_E$ versus $H_o$ curves computed using HHF equation (2.26) for spherical particles of dissimilar size ($a_1 = 1.0 \mu m; a_2 = 0.1 \mu m$) and a range of surface potentials.

**KEY**

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FIGURE 2.5.

POTENTIAL VERSUS DISTANCE CURVES FOR TWO PARALLEL PLATES OF UNEQUAL SURFACE POTENTIAL, AT THREE SEPARATION DISTANCES (redrawn from Overbeek).
culated using equation (2.25). When the distance between the plates is relatively large (Figure 2.5a) a minimum in potential occurs at a distance $\kappa d_1$ from plate 1. Consequently the potential gradients, and hence the charges (via equation (2.18)), at the surfaces of the plates are of the same sign, and a repulsion is predicted. As $H$ decreases a point is reached (Figure 2.5b) when the potential minimum lies on surface 1; in this case $\sigma_{01} = 0$ (since $(d\psi_x/dx)_{x=0} = 0$), and $\sigma_{02}$ is positive, but the surfaces still repel. At yet smaller $H$, $\sigma_{01}$ becomes negative (Figure 2.5c), and at sufficiently small $H$ the electrostatic attraction between the negative and positive surface charges outweighs the repulsive osmotic pressure term. In these circumstances overall attraction results. For two spherical particles, only the regions close to the axis of symmetry may show such charge reversal, and hence the force between spheres changes sign at much smaller separations than for plates.

2.3.4 Constant Surface Charge versus Constant Surface Potential Models

The models for the interaction between electrical double layers described in the previous sections were derived using the boundary condition of constant surface potential to solve the PB equation. This implies that the surface charge, $\sigma_0$, must change as $\kappa$ changes, or as two surfaces approach, according to equations (2.18) to (2.21).

Constant surface charge may be used as an alternative boundary condition to solve the PB equation. Conversely, this condition implies that $\psi_0$ must vary as $\kappa$ and/or $H$ change. An analogous ex-
pression to the HMF equation for spheres (equation (2.26)) was derived by Wiese and Healy\textsuperscript{62} using the constant charge model, and is given by equation (2.30).

\[
V_{E} = \frac{\pi\varepsilon_{0}a_{1}a_{2}}{(a_{1}+a_{2})} \left[ \frac{2\psi_{01}\psi_{02}}{(\psi_{01}^{2}+\psi_{02}^{2})} \right] \ln \left\{ \frac{1+\exp(-K_{H_{0}})}{1-\exp(-K_{H_{0}})} \right\} - \ln(1-\exp(-2K_{H_{0}}))
\]

(2.30)

In this case \(\psi_{01}\) and \(\psi_{02}\) are the potentials of the two surfaces at infinite separation.

Figure 2.6 shows \(V_{E}^{S}\) versus \(H_{0}\) curves calculated using equation (2.30) for various combinations of \(\psi_{01}\) and \(\psi_{02}\) (c.f. Figure 2.4 for the corresponding constant potential model). In this case repulsion is predicted between surfaces where \(\psi_{01}\) and \(\psi_{02}\) are of opposite sign. Again this may be explained in terms of a balance between electrostatic and osmotic forces.\textsuperscript{60}

Although coinciding at large \(H_{0}\), the predictions of constant surface potential and constant surface charge models clearly differ in a qualitative sense as \(H_{0}\) becomes small. This raises the question of which model is physically realistic. On one hand, if the surface charge results from adsorption of potential determining ions, \(\psi_{0}\) will remain constant, providing that adsorption equilibrium is maintained. Alternatively, if the surface charge results from ionisation of surface chemical groups then the equilibrium will shift as particles approach. Consider, for example, the approach of two polymer latex particles whose surface charge arises from the dissociation of acidic
Figure 2.6. $V_E$ versus $H_0$ curves computed using constant surface charge equation (2.30) for spherical particles of dissimilar size ($a_1 = 1.0\mu m$; $a_2 = 0.1\mu m$) and a range of surface potentials.

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(e.g. sulphate) groups. As the particles approach, the volume between them decreases and the counter-ion concentration between them tends to increase to preserve electroneutrality. In particular, the concentration of $H_2O^+$ ions near the surfaces will increase, causing a shift in the acid/base dissociation equilibrium, thereby changing $\sigma_0$, and consequently $\psi_0$. In addition, Overbeek\textsuperscript{63} and Frens et al.\textsuperscript{64} have observed that the approach of two colloidal particles typically is too fast for ion adsorption equilibrium to be maintained. Thus, in general, neither $\sigma_0$ or $\psi_0$ remain constant as $H_0$ decreases, the true situation being intermediate between the two cases.

A full description of the problem requires a solution of the PB equation using boundary conditions which account for the dissociation equilibria of surface ionisable groups. Such calculations have been performed for identical plates,\textsuperscript{65-67} but again the situation is much more complicated for dissimilar surfaces. Prieve and Ruckenstein\textsuperscript{60,61} have considered such systems using numerical methods, and once more predict repulsion between oppositely charged surfaces at small separations. No analytical equation is currently available, however, for a model of this type.

2.4 Polymeric Stabilisation

Adsorbed polymer molecules can impart stability upon colloidal particles by preventing them from approaching close enough for van der Waals forces to become effective. This phenomenon is generally referred to as "steric stabilisation". In addition, adsorbed polymer may modify both the electrical double layer and van der Waals forces of the substrate particles.
2.4.1 Effect of Adsorbed Polymer on the Electrical Double Layer

Modification of the electrical double layer around particles, and hence their electrostatic interaction energy, $V_E$, by adsorbed polymer, may arise from a combination of effects. Firstly, polymer segments adsorbed in "trains" (series of segments adsorbed closely at the surface) may affect the surface charge density, $\sigma_0$. Secondly, polymer "loops" and "tails" may affect the distribution of counterions in the diffuse region of the double layer. A simple treatment, proposed by Vincent, is to calculate $V_E$ for distances of separation $H_0 > 2S$, where $S$ is the thickness of the polymer layers. In this case $\psi_0$ or $\psi_1$ are replaced in the standard equations, given in section 2.3, by the potential at the outside of the polymer layer, $\psi_S$, which is usually equated with the zeta-potential, $\zeta_S$. In addition, the interparticle distance, $H_0$, must be replaced by $H_0 - 2S$. For example, in the case of polymer-coated particles, equation (2.24) for similar double layers is replaced by equation (2.31).

$$V_E^S = 2\pi \varepsilon_0 (a+S) \zeta_S^2 \ln(1+\exp[-\kappa(H_0-2S)])$$

(2.31)

In cases where $H_0 < 2S$, the expression for the electrostatic interaction energy is more complicated. Under these conditions, however, $V_E$ is usually much smaller than the interaction energy due to "steric" forces, and therefore need not be considered in detail.
2.4.2 Effect of Adsorbed Polymer on van der Waals Attraction

Vold's treatment for composite particles has been extended by Vincent to the case of particles with adsorbed polymer. The polymer layer, plus associated solvent, is considered to have a uniform Hamaker constant, $A_{33}$, which modifies equation (2.3). The exact relationship is rather complicated and will not be discussed here, except to observe that if $A_{33} = A_{22}$ one can treat the polymer layer as a sheath of solvent of thickness $\delta$. If, however, $A_{33}$ is either greater or less than $A_{22}$, $V_A$ is increased in magnitude. This effect is usually quite small in the case of high molecular weight adsorbed polymer.

2.4.3 "Steric" Interactions

When two surfaces carrying adsorbed polymer approach to a distance $H < 2\delta$, a "steric" interaction between the polymer layers occurs. This interaction can be envisaged as arising from three effects:

i) The "elastic" or "volume restriction" effect. The conformations of the adsorbed chains are perturbed, causing a loss of configurational entropy. This effect is always repulsive ($V_{el}$ is positive).

ii) The "adsorption" effect. If the polymer coverage, $\Gamma$, is low, the approach of two particles may lead to bridging of polymer chains between them. If this effect is present, $V_{ads}$ is negative.
iii) The "osmotic" or "mixing" effect. Displacement of solvent from the interfacial region to the bulk occurs as $H$ decreases. The resulting interaction energy, $V_{mix}$, can be either positive or negative, depending upon the polymer-segment/solvent interaction energy, defined in terms of the Flory-Huggins parameter ($\chi$)\textsuperscript{71}. For a "good" solvent ($\chi<0.5$) $V_{mix}$ is positive, whereas for a "poor" solvent ($\chi>0.5$) $V_{mix}$ is negative.

The total steric interaction energy, $V_S$, may be regarded as the sum of the three terms discussed above (equation (2.32)).

$$V_S = V_{el} + V_{ads} + V_{mix} \quad (2.32)$$

The evaluation of these contributions to $V_S$ has been the subject of many theories. These have been reviewed by Napper,\textsuperscript{71} and by Vincent and Whittington,\textsuperscript{72} and will not be discussed here.

The splitting of $V_S$ into separate contributions, whilst conceptually simple, is somewhat artificial. More recent theories, particularly that of Scheutjens and Fleer\textsuperscript{73} (SF), have avoided this splitting. The SF treatment is based upon a lattice model for polymer adsorbed at a planar surface, and has been extended to the case of two such interacting surfaces. A mean field, i.e. a uniform segment density distribution in any layer parallel to the surface, is assumed. An iterative procedure is used to minimise the free energy of the system, thereby predicting an optimum polymer-segment density distribution normal to the surface. This method has been applied to
interacting spherical particles\textsuperscript{74} using Derjaguin's geometrical method. The SF theory predicts experimental trends well, but the problem of scaling lattice dimensions to absolute distances remains unresolved.

2.5 The Total Interaction Energy

Derjaguin and Landau,\textsuperscript{46} and Verwey and Overbeek\textsuperscript{47} independently proposed that the total interaction energy between two surfaces, $V_T$, may be regarded as the sum of the van der Waals interaction energy, $V_A$, and the interaction energy due to overlap of electrical double layers, $V_E$:

$$V_T = V_A + V_E$$ \hspace{10cm} (2.33)

The so-called DLVO theory is central to the subject of colloid stability, and is usually interpreted in terms of $V_T$ versus $H$ curves (for example see Shaw\textsuperscript{75} (Figures 8.2-8.4)).

Where polymeric species are present at either or both of the surfaces "steric" forces also contribute to $V_T$, leading to equation (2.34).

$$V_T = V_A + V_E + V_S$$ \hspace{10cm} (2.34)

2.6 Electrophoretic Mobility and Zeta-Potential

The electrokinetic phenomena of electrophoresis, electro-osmosis, streaming potential and sedimentation potential occur when attempts are made to separate the diffuse part of the electrical double layer
from the parent charged surface. Electrophoresis is the movement of
a charged particle, plus attached material (e.g. adsorbed polymer)
relative to stationary solvent, in an applied electric field.
Electrophoretic mobility, \( u \), is defined as follows,

\[
  u = \frac{v_e}{E} \tag{2.35}
\]

where \( v_e \) is the velocity of the particle in the applied field, and \( E \)
is the applied field strength.

Electrokinetic phenomena are usually interpreted in terms of a
"zeta-potential", \( \zeta \), which is the electrical potential at the plane
of shear between the phases in relative motion. The exact location
of the plane of shear is uncertain, since this is a region of rapidly
changing viscosity. In general, however, the (experimentally
determined) zeta-potential is usually regarded as a good approxi-
mation, or slight underestimate, of the (theoretical) Stern
potential, \( \Psi_d \). Figure 2.1 (section 2.3) illustrates this point. Li
and de Bruyn\(^76\) have shown that \( \zeta \approx \Psi_d \) is a good approximation for \( \Psi_d \)< 100 mV and electrolyte concentration (I) less than 10\(^{-2}\) mol dm\(^{-3}\).

The relationship between electrophoretic mobility and \( \zeta \)-potential
shows a rather complicated dependence upon \( \kappa \alpha \).\(^77\) Two limiting cases,
\( \kappa \alpha \gg 1 \) and \( \kappa \alpha \ll 1 \), are relatively simple and are described by the
Smoluchowski equation\(^78\) (2.36) and Hückel equation \(^79\) (2.37),
respectively.

\[
  (\text{For } \kappa \alpha \gg 1) \quad u = \frac{e\varepsilon_0 \zeta}{\eta} \tag{2.36}
\]
In these equations \( \eta \) is the viscosity of the dispersion medium.

For many systems of practical importance, however, the conditions of large or small \( \kappa a \) do not hold, and more complicated expressions must be used. Corresponding values of \( \zeta \)-potential and electrophoretic mobility were computed by Wiersema et al.\(^80\) for a wide range of \( \kappa a \) values, and presented in a graphical form by Ottewill and Shaw.\(^81\) These calculations were based upon the full PB equation and accounted for the "relaxation effect" (the retarding force exerted on a moving particle by the asymmetry of the mobile part of the electrical double layer). More recently O'Brien and White\(^82\) reanalysed the whole problem of calculating \( \zeta \)-potentials from mobility measurements. The results of their computations are in good agreement with those of Wiersema et al., but cover a much wider range of \( \zeta \)-potential. These results are shown in Figure 2.7. The mobility maxima for \( \kappa a > 3 \) are a result of the relaxation effect increasing at a faster rate with \( \zeta \) than does the electrophoretic driving force (particle charge multiplied by field strength).\(^82\)

2.7 Kinetics of Aggregation

The rate of aggregation of a dispersion is determined by the frequency of encounters between particles, and the probability that such encounters lead to permanent interparticle contacts. The latter probability depends upon the form of the potential energy versus distance curve.
FIGURE 2.7
THE RELATIONSHIP BETWEEN ELECTROPHORETIC MOBILITY AND ZETA-POTENTIAL FOR SPHERICAL COLLOIDAL PARTICLES IN AQUEOUS KCl SOLUTIONS: a) $K_e \gg 3$; b) $K_e \ll 2.75$ (reproduced from O'Brien and White (1978)).
Consider a fixed central particle (type 1) being approached by particles of type 2, where \( r \) is the distance from the centre of the fixed particle. Under steady state conditions, the flux \( (J) \) of particles towards, and hence the rate of encounters with, the central particle is given by Fick's First equation (2.38).

\[
J = D_2 4\pi r^2 \frac{dn_2(r)}{dr}
\]  
(2.38)

In this equation \( D_2 \) and \( n_2 \) are the diffusion coefficient and number concentration of type-2 particles, respectively.

The effect of attractive and of repulsive interparticle interactions upon the particle flux are considered in turn below.

a) Interparticle Attraction

A purely attractive interaction may, to a first approximation, be considered as a "square-well potential", whereby no interaction is present for \( r>R \), but for \( r<R \) attraction is infinite. This model was first proposed by von Smoluchowski, who applied it to "rapid coagulation", where van der Waals attraction is the dominant interparticle force. The model also includes the conditions,

\[
\begin{align*}
    n_2 &= n_{02} \quad \text{for } r>R \\
    n_2 &= 0 \quad \text{for } r<R
\end{align*}
\]  
(2.39)

where \( n_{02} \) is the bulk concentration of species 2. In this case the solution to equation (2.38) is given below.

\[
J = 4\pi RD_2 n_{02}
\]  
(2.40)
In reality, the central particle (1) is also subject to Brownian motion, and the diffusion coefficient in equation (2.40) should describe the relative motion of the particles. It can be shown\(^{84}\) that

\[ D_{12} = D_1 + D_2 \]  
(2.41)

where \( D_{12} \) is the mutual diffusion coefficient of species 1 and 2. The individual diffusion coefficients are calculated using the Stokes-Einstein equation (2.42).

\[ D_i = \frac{kT}{6\pi\eta a_i} \]  
(2.42)

In this equation \( \eta \) is the viscosity of the dispersion medium.

The initial rate of disappearance of species 2 per central particle, is equal to the flux, \( J \), and is given by equation (2.43).

\[ -\frac{dn_2}{dt} = 4\pi RN_1(D_1 + D_2)n_0^2 \]  
(2.43)

Thus, the overall initial rate of disappearance of species 2 is

\[ -\frac{dn_2}{dt} = 4\pi RN_1(D_1 + D_2)n_0^2 \]  
(2.44)

where \( n_0 \) is the initial number concentration of species 1.

For dispersions of only one particle type, equation (2.44) reduces to

\[ -\frac{dn}{dt} = 8\pi RDn_0^2 \]  
(2.45)

where \( D = D_1 = D_2 \), and \( n_0 = n_{01} = n_{02} \).
As aggregation proceeds, equations (2.44) and (2.45) increasingly become less accurate because they do not account for collisions of aggregates, either with primary particles or other aggregates. von Smoluchowski\textsuperscript{83} extended the treatment to later stages during aggregation.

b) Interparticle Repulsion

The case where a potential energy barrier must be overcome before particles come into contact was considered by Fuchs.\textsuperscript{85} He showed that for "slow aggregation" the flux, $J'$, of particles towards a central particle is given by equation (2.46).

$$J' = \frac{4\pi(D_1+D_2)n_0}{a_1+a_2} \int_a^\infty \exp \left[ \frac{V_T(r)}{kT} \right] \frac{dr}{r^2} \tag{2.46}$$

For a homodispersion this expression reduces to equation (2.47).

$$J' = \frac{8\pi Dn_0}{2a} \int_0^\infty \exp \left[ \frac{V_T(r)}{kT} \right] \frac{dr}{r^2} \tag{2.47}$$

The "degree of stability" of dispersions is sometimes expressed in terms of the ratio, $W$, between the rates of rapid and slow aggregation. For the case of a homodispersion (where $R = 2a$), combination of equations (2.45) and (2.47) leads to the following expression.

$$W = 2a \int_2^\infty \exp \left[ \frac{V_T(r)}{kT} \right] \frac{dr}{r^2} \tag{2.48}$$
An approximate form of equation (2.48), which is more simple to calculate, was proposed by Reerink and Overbeek:

\[ W = \frac{1}{2kT} \exp \left( \frac{V_{\text{max}}}{kT} \right) \]  

(2.49)

In this equation, \( V_{\text{max}} \) is the maximum on the \( V_T \) versus \( r \) curve.
CHAPTER 3

SPECIMEN PREPARATION

FOR

ELECTRON MICROSCOPY
3.1 Introduction

The study of morphology in both colloidal and biological systems is hindered by the fact that specimens must usually be dry if they are to be examined using electron microscopy. A simple method of specimen preparation is air-drying, but this is inadequate for all but the most robust samples, due to the creation of a large surface tension at the drying front. Consequently much effort has been expended in the development of alternative drying procedures. A summary of the main techniques in current use is presented in Figure 3.1.

After a discussion of the aspects of freezing, freeze-fracture and freeze-drying most relevant to colloidal systems, the technique of thin-film freeze-drying will be described and its value in the study of the morphology of colloidal dispersions assessed.

3.2 Freezing

Rapid freezing is essential if good preservation of specimen morphology is to be achieved. This is a consequence of the fact that formation of ice crystals causes material (e.g. colloidal particles) to be pushed to the areas (eutectic phase) around these crystals, hence disrupting specimen morphology. Figure 3.2 shows that ice crystal growth occurs between 270 and 130K, and therefore that this temperature range must be traversed as quickly as possible. In practice, the critical cooling rate necessary for freezing to vitreous water has rarely been achieved. The size of the ice
FIGURE 3.1.
SPECIMEN PREPARATION TECHNIQUES
FOR ELECTRON MICROSCOPY

TEM

AIR-DRY

SEM

AQUEOUS SPECIMEN

FREEZE

CRYO-SEM
(direct observation of frozen specimen)

FREEZE-DRY

GOLD or CARBON COAT

SEM (observation of dry specimen)

FREEZE-FRACTURE/
FREEZE-ETCH

REPLICATE

TEM (observation of replica)

CRITICAL-POINT DRY

SOLVENT-EXCHANGE
Figure 3.2. Rate of Crystallisation of Ice in Relation to Temperature (after Moor 89)
crystals formed depends on the cooling rate; for instance Menold et al.\textsuperscript{93} reported that cooling rates of ca. 100 K s\textsuperscript{-1} gave rise to crystals 4-5 μm in diameter, while rates of several thousand K s\textsuperscript{-1} gave crystals of 1-2 μm. It is clear from Figure 3.2 that ice crystals also form if an initially well frozen specimen is allowed to warm above the recrystallisation point (\(T_r = 130\)K).

The freezing rate attained in practice depends upon three factors:

a) Size and shape of the specimen. Ice is a poor conductor of heat\textsuperscript{94} and hence small specimens, preferably with at least one dimension in the region of 10 μm,\textsuperscript{95} are desirable if fast freezing is to be achieved. In addition a small specimen support of high thermal conductivity is advantageous.\textsuperscript{96} The support chosen, however, must be strong enough to withstand mechanical processes such as plunging into liquid cryogen.

b) Choice of cryogen. The most commonly used cooling agents are liquid cryogens, although cold metal blocks have also been employed.\textsuperscript{97,98} A number of authors have determined cooling rates for a range of liquid cryogens\textsuperscript{95,99-103} (Table 3.1); liquid propane is generally regarded as the best commonly available cryogen.

c) Method of immersion. The cooling rate rises with increasing rate of immersion,\textsuperscript{100} and is also affected by the depth of immersion,\textsuperscript{99} it being advantageous to continually bring the specimen into contact with fresh cryogen. A fast rate of entry also minimises the possibility of slow freezing due to pre-
Table 3.1 Comparative Cooling Rates Observed for a Range of Liquid Cryogens and Immersion Techniques

<table>
<thead>
<tr>
<th>Immersion Method</th>
<th>Immersion Velocity (m s⁻¹)</th>
<th>Liquid Propane</th>
<th>Freon 22</th>
<th>Freon 12</th>
<th>Liquid Nitrogen Slush</th>
<th>Liquid Nitrogen</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1.4</td>
<td>19,100</td>
<td>9,000</td>
<td>6,580</td>
<td>1,700</td>
<td>800</td>
<td>95</td>
</tr>
<tr>
<td>&quot;Rubber Band&quot;</td>
<td>-</td>
<td>5,860</td>
<td>3,980</td>
<td>2,940</td>
<td>-</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>-</td>
<td>0.49</td>
<td>98,000</td>
<td>66,000</td>
<td>47,000</td>
<td>21,000</td>
<td>16,000</td>
<td>100</td>
</tr>
<tr>
<td>&quot;Dipped&quot;</td>
<td>-</td>
<td>1,800</td>
<td>-</td>
<td>740</td>
<td>1,000</td>
<td>720</td>
<td>101</td>
</tr>
<tr>
<td>&quot;Free-fall&quot;</td>
<td>-</td>
<td>4,116</td>
<td>2,621</td>
<td>2,503</td>
<td>-</td>
<td>128</td>
<td>102</td>
</tr>
<tr>
<td>&quot;Dipped&quot;</td>
<td>-</td>
<td>2,432</td>
<td>609</td>
<td>-</td>
<td>364</td>
<td>125</td>
<td>103</td>
</tr>
<tr>
<td>&quot;Jet-freezing&quot;</td>
<td>-</td>
<td>18,000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>103</td>
</tr>
</tbody>
</table>
cooling of the specimen by a layer of cold gas above the cryogen. Fast immersion methods have been reported in which specimens enter liquid cryogen by means of gravity, spring or rubber band propulsion, or electromagnetic actuation.

3.3 Freeze-Fracture and Freeze-Etch Microscopy

These closely related techniques involve the observation of a replica produced by the shadowing of a section through a frozen specimen. They are summarised in Figure 3.3.

Originally developed by biologists, freeze-etching has commonly been used in the study of colloidal dispersions and emulsions. Although of considerable value in such applications, the technique has a number of drawbacks. For example the observation of a replica, rather than the particles themselves, may make difficult differentiation of species in mixed systems. The interpretation of essentially two-dimensional images of three-dimensional structures is also problematical, although possible using stereological techniques; again this is more difficult for mixed systems. The rather large sample volumes and particle volume fractions employed (typically ~10 μl and 0.1, respectively) are also unfavourable for good freezing.

3.4 Principles of Freeze-Drying

The term freeze-drying refers to the freezing of a specimen (section 3.2) and the subsequent vacuum sublimation of solvent. For drying to occur two basic requirements must be fulfilled: i) input of energy to supply the latent heat of sublimation, and ii) maintenance
Figure 3.3. Freeze-Fracturing and Freeze-Etching

PREPARATION STEP

(i) Mount Sample in Holder

(ii) Freeze (eg. in liquid Propane)

(iii) Fracture

(iv) Etch (Freeze-Etching Only)

(v) Shadow with metal

(vi) Replicate

(vii) Thaw Specimen and Clean Replica
of a vapour concentration gradient to enable solvent to diffuse away from the specimen.

The latent heat of sublimation can be supplied either by conductive or radiant heating. In the former, heat is transferred from a temperature-controlled support to the drying surface via the bulk of the frozen specimen. Since the drying surface is cooled by the sublimation process itself, there will exist a temperature gradient within the specimen, the base being warmer than the surface (Figure 3.4a). The constraint that the temperature in no part of the specimen should rise above the ice recrystallisation temperature thus limits the rate of heat input to the drying surface.

Radiant heating, on the other hand, transfers heat directly to the drying surface, leading to a temperature gradient of the form shown in Figure 3.4b). Thus the temperature at the drying surface can be higher than for conductive heating, without causing ice re-crystallisation. The nature of the specimen is important in determining whether radiant heating is a viable method in practice. After drying has proceeded for a time, there will exist a layer of dried material between the drying boundary and heat source. This layer may be highly insulating, thus increasing the heat input required to maintain sublimation. In turn the temperature of the dried material may be increased to an unacceptable level. This problem is most acute for biological specimens and explains why relatively few freeze-dryers have employed radiant heating.115

The second main criterion in determining the rate of sublimation is the concentration gradient of water vapour with respect to
Figure 3.4. Temperature Profiles Encountered During Freeze-Drying

a) Conductive Heating:

b) Radiant Heating:
distance from the drying surface. For efficient drying to occur it is necessary for a steep concentration gradient to be maintained. This is generally achieved by the use of cold shields, to which sublimed water molecules adhere. The diffusion of vapour may, however, be hampered by the build up of dry material at the surface of the specimen ("blocking effect"). Cold shields also serve to protect the specimen from contamination by pump oil and other extraneous material. The function of the vacuum system is to maintain a pressure at which the mean free path of vapour molecules is greater than the distance from specimen to cold shield.

Umrathtabulated theoretical drying rates versus temperature, assuming infinitely efficient removal of water vapour from the specimen. These data are reproduced, in part, in Table 3.2. Slower rates may be achieved in practice due to the blocking effect, inefficient trapping and poor vacuum.

Table 3.2 Theoretical Freeze-Drying Rates at Different Temperatures (after Umrats)
3.5 Thin-Film Freeze-Drying: Experimental

In order to determine whether thin-film freeze-drying is a suitable technique for studying the morphology of colloidal aggregates, it was necessary firstly to assess if artefacts were introduced during specimen preparation. This was achieved by freeze-drying aqueous dispersions which were stable towards aggregation at room temperature. The freeze-dried specimens were examined using scanning electron microscopy, and their state of aggregation/dispersion noted.

The following stable aqueous dispersions were used: i) PSL(-3), prepared as described in chapter 4.1, and ii) Silica S1, as described in appendix 1. In each case a particle volume fraction (\(\phi\)) of \(1 \times 10^{-4}\) was used; at this concentration minimal aggregation theoretically would be caused by particles settling vertically onto underlying ones as drying proceeds.

3.5.1 Thin-film formation

Each specimen was supported using a sheet of freshly cleaved muscovite mica, of approximate dimensions 6 mm x 4 mm x 10 \(\mu\)m. Such a sheet was dipped into the sample dispersion using fine tweezers; upon withdrawal the mica was drained by dabbing one side on a piece of filter paper. Findlay\(^{118}\) determined by weighing that drained aqueous films 20±5 \(\mu\)m deep are produced by this technique. This thickness was confirmed by observation of such films using a Nikon Optiphot microscope. Optical microscopy was also used to demonstrate that aggregation of particles did not take place at either the liquid/air interface, or at the mica surface. This was
true provided that excessive air-drying was not allowed to occur; complete air-drying of a thin film took approximately 8 minutes at 20°C.

3.5.2 Freezing

Liquid propane was freshly condensed before use into a steel vessel cooled by liquid nitrogen (LN₂), as illustrated in Figure 3.5. Upon standing, a sheet of filter paper was placed over the vessel to prevent excessive condensation of water vapour into the propane.

A thin film of dispersion on mica was frozen within 5 seconds of drainage, by immersion in liquid propane. The mica, held at one corner by tweezers, was rapidly plunged into the cryogen and left submerged for 10 seconds before transfer to the drying apparatus.

3.5.3 Drying

Drying was carried out using one of the two pieces of apparatus described below.

(1) Brass-block freeze-dryer:
This apparatus is illustrated in Figure 3.6. The block was cooled by immersion in LN₂ in an expanded polystyrene box. When the LN₂ ceased to boil the block was opened and the LN₂ level adjusted to approximately 1 cm above the height of the base. Frozen mica-supported samples were then rapidly transferred from the liquid propane and mounted as shown in Figure 3.6. When all the samples were in place (up to 10 could be accommodated) the LN₂ was topped up in order to re-cool the upper section, which was then lowered, trapping approximately 1/3 of each mica support.
Figure 3.5. Propane Condensation

Small flow of Propane Gas

Liquid Propane

Liquid Nitrogen

Steel Vessel

Dewar Vessel

Expanded Polystyrene Block
Figure 3.6. Brass-Block Freeze-Dryer
After sample loading the block was transferred to a vacuum chamber. Either an Edwards "Speedivac 12E6/903" coating unit or an Edwards "E306A" coating system was used; in both cases a rotary pump gave a pressure of ca. $10^{-3}$ torr. The block was allowed to warm up gradually by means of conduction from the base of the vacuum chamber. The temperature profile during warming was determined by attachment of copper/constantan thermocouples to both the upper and lower sections of the block. In addition, a thermocouple was attached to a mica sheet using graphite paste; this was then frozen and mounted in the usual way. The corresponding temperature profiles are shown in Figure 3.7.

(ii) Stainless steel chamber:

The chamber, which is illustrated in its assembled state in Figure 3.8, consisted of three sections - base, lid and specimen holder (S in Figure 3.8). The temperature of the specimen and the shield (D) could be varied independently, allowing either conductive or radiant heating methods to be employed. The basic operating sequence for the chamber is shown in Figure 3.9. Up to 4 samples were held in place in the specimen holder (Figure 3.10) by clamps which were individually tightened.

During drying the temperatures of the specimen holder and the shield were regulated by balancing heating by the cartridge heaters with cooling by the LN$_2$ reservoirs. Three classes of temperature profile were investigated -
Figure 3.7. Temperature versus Time Profile for Brass-Block Freeze-Dryer

- Mica
- Base of block
- Top of block
FIGURE 3.8
STAINLESS STEEL FREEZE-DRYER.
(NOTE: LOWER LIQUID NITROGEN RESERVOIR (E), AN EXPANDED POLYSTYRENE BOX SURROUNDING DRYER UP TO LEVEL C, OMITTED FROM DIAGRAM)
FIGURE 3.9
OPERATIONAL SEQUENCE FOR STAINLESS-STEEL FREEZE-DRYER

CHAMBER

Attach lid to base without specimen holder inside

Evacuate chamber using rotary pump

Cool lid using lower LN$_2$ reservoir

Warm flange (G) using hot-air dryer

Vent with dry nitrogen gas and remove lid

Charge legs (H) with 5Å molecular sieves

Evacuate using rotary pump

Isolate from pump (when mol. sieves used)

Control temperature of base and lid for required time and monitor pressure

Warm to room temperature using heaters or natural warming

Isolate vacuum pump (when sieves not used)

Vent to air and detach lid

Remove sample holder

Bake out sieves under vacuum to remove moisture

SPECIMEN

Cool holder (S) in separate LN$_2$ bath

Mount pre-frozen specimens in holder under LN$_2$

Transfer to chamber using forceps

Mount holder (S) in chamber

Cease venting and attach lid

Evacuate using rotary pump

Evacuate using oil-diffusion pump

Control temperature of base and lid for required time and monitor pressure

Warm to room temperature using heaters or natural warming

Isolate vacuum pump (when sieves not used)

Vent to air and detach lid

Remove sample holder

Dismount specimens, Gold coat and observe using SEM

(Note. Letters refer to Figure 3.8.)
Figure 3.10. Specimen Holder for Stainless-Steel Freeze-Dryer

PLAN VIEW

SECTION
(Composite A-A, B-B)
(1) Mimicking of the brass-block conditions.

(2) Conductive heating, with specimen holder (S) at a constant temperature (in the range -70 to -105°C) and shield (D) colder (-120 to -140°C).

(3) Radiant heating, with cold specimen holder (S) (-150±20°C) and heated shield (D) to give temperature at specimen surface of -95±5°C for up to 5 days.

In the latter case the temperature at the drying surface was estimated by clamping a copper/constantan thermocouple in the holder and monitoring its temperature at different shield (D) temperatures. The calibration graph is shown in Figure 3.11.

3.5.4 Mounting and Gold Coating

After removal from the freeze-dryer each specimen was mounted on a 25 mm x 5 mm x 0.5 mm copper "boat" using graphite paste. They were then sputter-coated with gold using an Edwards "Speedivac 12E6/903" coating chamber.

3.5.5 Observation

Specimens were examined using a Jeol JEM 100CX TEMSCAN instrument in the scanning mode. Images were recorded using Ilford FP4 film.

3.6 Freeze-Drying: Results and Discussion

3.6.1 Brass-Block Freeze-Dryer

On many occasions freeze-drying using the brass-block resulted in a uniform distribution of "singlet" particles, an example being shown
Figure 3.11. Temperature Calibration Curve for Radiant Heating in Stainless-Steel Freeze-Dryer
Such results, however, were not found to be consistently reproducible. In some cases aggregation was observed to take the form of a large scale "cell structure" (Plate 3.1b)). A likely explanation for this effect is ice crystal formation, either at the initial freezing stage, or during the drying process. In these circumstances large numbers of particles were aggregated in "strings", which probably correlate with the eutectic zones around ice crystals. Another possible explanation for this effect is the formation of bubbles of vapour which burst out of the ice layer causing particles to be pushed together.

It was noted that adjacent samples often showed considerably different extents of aggregation. A possible reason for this phenomenon is that the samples were not individually clamped in the block and, in consequence, there may have been a temperature difference between them. Another commonly observed feature was the greater extent of aggregation (and also contamination) on the areas of mica formerly trapped by the block (Plate 3.2a)). This may have been caused by restricted escape of water vapour, resulting in temperatures well in excess of the ice-recrystallisation point being reached before drying was completed.

Aggregates were often found in association with extraneous material. This phenomenon was investigated by Findlay, who considered vacuum pump oil to be a major source of contamination, a feature also noted in freeze-etching. Gas-liquid chromatography was used to confirm the presence of traces of pump oil on bare mica.
Plate 3.1.a)

A Freeze-Dried PSL(-3) Sample
Showing Mainly "Singlets"

Plate 3.1.b)

A Freeze-Dried PSL(-3) Sample
Showing "Cell-Structure"
Plate 3.2.a)
A Freeze-Dried PSL(-3) Sample
Formerly Trapped by the Brass-Block

Plate 3.2.b)
A Freeze-Dried PSL(-3) Sample
Showing "Cracks"
sheets freeze-dried in the usual way. In order to establish if such contamination contributed to aggregation, two oil-free pumping systems were investigated - a) a LN$_2$-cooled molecular sieve pump, and b) a Seiko SE105 turbomolecular pump (electromagnetically levitated; "roughing out" of chamber using molecular sieve pump). In neither case was the extent of aggregation reduced significantly, despite oil contamination being eliminated.

3.6.2 Stainless Steel Chamber

The use of the stainless steel chamber allowed freeze-drying to be carried out at controlled temperatures. Of the three classes of temperature control outlined in section 3.5c), none, including radiant heating gave consistently better results than the brass-block dryer. Use of the stainless steel chamber sometimes gave rise to lines on mica sheets devoid of particles (Plate 3.2b)). This may have been caused by frozen samples cracking on application of the large tension used to fix them in the specimen holder. This effect was noted much less often for brass-block drying.

Despite individual clamping of samples in the specimen holder (Figure 3.10), it was often observed that they remained only loosely clamped after drying. This was probably due to sublimation of the ice layer originally trapped beneath the clamp. Attempts to overcome this problem by hollowing out the clamps (Fig. 3.10J), thereby making them more springy, were only partially successful. The inefficiency of the clamping method may have had an adverse effect upon temperature control of the specimens.
3.6.3 Miscellaneous Freeze-Drying Results

Freeze-drying of non-aqueous dispersions of silica particles (kindly supplied by Mr. S. Emmett of this University) was also carried out. These particles, stabilised by chemically-grafted stearyl alcohol chains, were dried from both dimethylformamide and ethanol, using the brass-block apparatus. Again aggregation was observed, suggesting that its occurrence may be caused by factors other than, or in addition to, ice crystal formation. For solvents more volatile than water, freeze-drying at lower temperatures may be desirable; if drying occurs too quickly it may be possible for lateral movement of particles to be caused by a "wind" of vapour. This mechanism was proposed by Anderson for the disruption of virus specimens.

No correlation was observed between aggregation and pressure in the drying chamber. This is not surprising since it is the vapour pressure in the immediate vicinity of the specimen which critically affects the drying rate (section 3.4). This local pressure is difficult to measure experimentally, although Wildhaber did so by using mass spectrometry to determine the vapour pressure of deuterium oxide above a deuterated ice layer.

The most successful application of thin-film freeze-drying proved to be in the study of large polystyrene latex particles (PSL(+21), dia. = 2.1 µm) in the presence of smaller latex particles of opposite surface charge. These studies are described in chapter 5 of this thesis. The samples were dried using the brass-block apparatus. The large size of the PSL(+21) particles is thought to have contributed
to a reduction in disruption, as discussed by Menold et al.\textsuperscript{93} Disruption of the local arrangement of small particles at the large particle surface was probably minimised by the large attractive force between the two types of particle.

3.7 Cryo-SEM

It is possible to directly observe freeze-drying using a scanning electron microscope equipped with cryogenic sample stage. Such an observation was made on a frozen aqueous dispersion of PSL(-3) ($\phi=0.01$) using an Hitachi S 650 SEM. The specimen was viewed uncoated at a temperature of $-60\pm20^\circ$C. Accurate control and access to lower temperatures was limited by the equipment available. Drying appeared to occur rapidly, with particles suddenly emerging from the ice layer as it receded. In addition, bubbles of water vapour, apparently formed deep in the ice layer, were seen to burst out of the specimen. This constitutes a mechanism by which particles could be pushed together to form aggregates. Lateral movement of particles lying on top of the frozen layer also occurred; this was possibly a manifestation of the water vapour "wind" mentioned previously.

It should be noted that this technique is not directly comparable with thin-film freeze-drying for the following reasons. Firstly, the specimen temperature control was poor and drying undoubtedly took place at a higher temperature than in either the brass-block or stainless steel chamber. Secondly, considerable beam damage may have occurred due to localised heating by the electron beam. These observations do, however, demonstrate that artefacts may be caused by bubbling and by vapour "wind".
3.8 Conclusions

Maintenance of the spatial distribution of particles in colloidal dispersions by the technique of thin-film freeze-drying is clearly problematical, especially in the case of sub-micron particles. A likely explanation for the artefactual aggregation encountered is ice crystal formation at the initial freezing stage. The freezing rate would be difficult to increase, however, since more complicated sample mounting and propulsion techniques may exacerbate the problem of air-drying of the thin films.

Ice crystal formation subsequent to initial freezing has not been ruled out, improvements in specimen clamping and temperature control being desirable in this respect.

Cryo-SEM observations tentatively support the theory that rapid freeze-drying may cause artefacts due to the formation of water vapour bubbles in the ice layer, and to "wafting" by a vapour "wind". Reduction of these effects may be achieved in future by prolonged drying at temperatures below -100°C. Radiant heating may yet prove to be a valuable technique if drying temperature and specimen configuration can be optimised.
CHAPTER 4

DISPERSION PREPARATION

AND

CHARACTERISATION
4.1 **Preparation of Polystyrene Latexes**

The method of preparation of the polystyrene latexes was similar to that described by Goodwin et al.\textsuperscript{122} Most of the water to be used was placed in a three-necked, round-bottomed flask, fitted with a water-cooled Leibig condenser. This was heated to 70°C using a thermostatically-controlled oil bath, and the styrene (plus seed latex and sodium chloride, where appropriate) was added. The mixture was stirred, under an atmosphere of nitrogen, for approximately 30 minutes. The initiator was dissolved in approximately 20 cm\(^3\) of water, at room temperature, then added swiftly to the reaction vessel via a funnel. The mixture was stirred at 70°C, under nitrogen, for 24 hours, after which the resulting latex was filtered through glass wool to remove coagulum. It was then decanted into well-boiled "Visking" dialysis tubing, and dialysed for 2 weeks against distilled water, the dialysate being changed every 24 hours.

4.1.1 **Anionic Latexes**

The free radical initiator used in the preparation of anionic latexes was potassium persulphate. The formulations used, and the resulting particle diameters are summarised in Table 4.1.
Table 4.1 Anionic Polystyrene Latexes

<table>
<thead>
<tr>
<th>Latex Reference No.</th>
<th>Volume of Styrene (cm$^3$)</th>
<th>Volume of Water (cm$^3$)</th>
<th>Weight of NaCl (g)</th>
<th>Weight of K$_2$S$_2$O$_8$ (g)</th>
<th>Number Average Mean Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSL(-1)</td>
<td>80</td>
<td>600</td>
<td>0</td>
<td>0.200</td>
<td>696 ± 10</td>
</tr>
<tr>
<td>PSL(-3)</td>
<td>18</td>
<td>600</td>
<td>0</td>
<td>0.103</td>
<td>180 ± 6</td>
</tr>
<tr>
<td>PSL(-4)</td>
<td>20</td>
<td>600</td>
<td>0</td>
<td>0.095</td>
<td>320 ± 11</td>
</tr>
<tr>
<td>PSL(-7)</td>
<td>20</td>
<td>600</td>
<td>0</td>
<td>0.096</td>
<td>330 ± 20</td>
</tr>
</tbody>
</table>

4.1.2 Cationic Latexes

Cationic latexes were prepared using the initiator azo-bis-(isobutylamidine)dihydrochloride (ABA.2HCl), which has the structure shown below.

![Chemical Structure](attachment:image)

ABA.2HCl dissociates, with the loss of nitrogen, leading to the presence of $-C(CH_3)_2-C(NH_2)_2^@$ groups at the particle surface.

The preparative formulations and particle diameters of the cationic latexes are summarised in Table 4.2. In all cases glassware was used which had been hydrophobed by rinsing with a solution of dichlorodimethylsilane in 1,1,1-trichloroethane, followed by thorough washing with water. In addition the latexes were stored in polyethylene sample bottles which had been thoroughly washed and soaked in water. Untreated glassware was not used in association with cationic
<table>
<thead>
<tr>
<th>Latex Reference No.</th>
<th>Volume Styrene (cm³)</th>
<th>Volume Water (cm³)</th>
<th>Weight NaCl (g)</th>
<th>Seed Latex</th>
<th>Volume Seed (cm³)</th>
<th>Weight of ABA·2HCl (g)</th>
<th>Number Average Mean Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSL(+1)</td>
<td>37</td>
<td>800</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0.174</td>
<td>305 ± 20</td>
</tr>
<tr>
<td>PSL(+5)</td>
<td>40</td>
<td>800</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0.033</td>
<td>320 ± 20</td>
</tr>
<tr>
<td>PSL(+20)</td>
<td>30</td>
<td>600</td>
<td>0.50</td>
<td>PSL(+5)</td>
<td>60</td>
<td>0.30</td>
<td>826 ± 46</td>
</tr>
<tr>
<td>(as made)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSL(+21)</td>
<td>40</td>
<td>600</td>
<td>0.50</td>
<td>PSL(+20)</td>
<td>60</td>
<td>0.30</td>
<td>2170 ± 250</td>
</tr>
<tr>
<td>(as made)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
latexes owing to the problem of contamination by anionic polysi-
licates, which can be leached from glass and adsorb on cationic
particles, thus reducing their net charge.

Hydrolysis of the amidine surface groups can also lead to
reduction in charge of cationic latex particles. The hydrolysis
which can be acid or base catalysed, leads to the formation of
carboxylic acid groups at the particle surface (Figure 4.1). In
order to reduce the rate of hydrolysis the latexes were stored in a
refrigerator.

4.1.3 Amphoteric Latex

An amphoteric latex, PSL(±3), was prepared by the method of
Homola and James. Styrene was co-polymerised with methacrylic
acid (MA) and dimethylaminoethylmethacrylate (DMAM), which gave rise
to anionic and cationic surface groups, respectively. A non-ionic
surface active agent, "Triton X-100" (iso-octylphenoxypolyethoxy-
ethanol, containing 10 ethylene oxide units per chain), was used to
regulate the size of the particles. The reaction was carried out at
a temperature of 80°C, using the following formulation.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>600 cm³</td>
</tr>
<tr>
<td>DMAM</td>
<td>5.98g</td>
</tr>
<tr>
<td>MA</td>
<td>3.34g</td>
</tr>
<tr>
<td>Styrene</td>
<td>60 cm³</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>1.60g</td>
</tr>
<tr>
<td>Hydrochloric acid to pH 1.2</td>
<td></td>
</tr>
<tr>
<td>Potassium persulphate</td>
<td>1.20g</td>
</tr>
</tbody>
</table>
FIGURE 4.1.

BASE-CATALYSED HYDROLYSIS OF CATIONIC (AMIDINIUM) LATEX SURFACE GROUPS

\[
\begin{align*}
\text{OH}^- & \quad \text{Rate limiting step} \\
\text{OH}^- & \quad \text{NH}_3 \\
\text{NH}_3 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{OH}^- \\
\end{align*}
\]
The number average mean diameter of the resultant latex was 176 nm ± 8.

4.2 Preparation of Poly(vinylidene chloride) Latex

Vinylidene chloride (VDC) was polymerised using essentially the same apparatus and method as described for the polystyrene preparations. Potassium persulphate was used as the initiator, but in this case the polymerisation was carried out at 35°C to prevent dehydrochlorination of the PVDC product. These conditions necessitated the use of a redox couple to activate the persulphate. A sodium metabisulphite/iron(II) couple was used, the iron(II) species being present as a 0.01% impurity in the metabisulphite. Free-radical formation by the redox system is summarised below.

i) \[ S_{2}O_{8}^{2-} + H_{2}O \rightarrow HS_{2}O_{3}^{-} + OH^{-} + SO_{2} \]

ii) \[ S_{2}O_{8}^{2-} + Fe^{2+} \rightarrow SO_{4}^{2-} + SO_{4}^{2-} + Fe^{3+} \]

iii) \[ HS_{2}O_{3}^{-} + Fe^{3+} \rightarrow Fe^{2+} + HSO_{3}^{-} \]

The presence of sulphate and bisulphite radicals gives rise to sulphate and sulphonate groups, respectively, at the particle surface.

The formulation used in the preparation of latex PVDC(5) was as follows.
Water 500 cm³
VDC 50 cm³
69% Nitric Acid 0.3 cm³
Sodium dihexylsulphosuccinate 0.76g
Sodium metabisulphite 0.36g
Potassium persulphate 0.70g

The sodium metabisulphite and potassium persulphate were dissolved together in 20 cm³ of water, and added to a stirred mixture of the remaining reagents. Stirring was continued for 24 hours at a temperature of 35°C, after which the latex was filtered and dialysed in the manner described for the polystyrene latexes.

Latex PVDC(5) had a number average mean particle diameter of 116 nm ± 4.

4.3 Latex Characterisation

4.3.1 Solids Content

The solids concentration of each latex dispersion was determined by evaporating to dryness a known weight of dispersion, at a temperature of 70°C. The drying temperature was below the temperature of thermal decomposition of polystyrene (300°C127).

4.3.2 Particle Size Analysis

Transmission electron micrographs of the latexes were recorded using a Jeol JEM-100CX TEMSCAN electron microscope. The micrographs were enlarged and printed onto Kodak P84 photographic paper, and size analysis carried out using a Carl-Zeiss TGZ3 analyser. A minimum of 500 particles were counted for each sample.
4.4 Adsorption of PVA onto Polystyrene Latexes

Isotherms were determined for the adsorption of poly(vinyl-alcohol) (PVA, viscosity molar mass ≈ 22,000) onto latexes PSL(+21) and PSL(-1). Samples of latex were diluted into a series of PVA solutions of known concentration and allowed to equilibrate. Centrifugation, followed by an assay for unadsorbed PVA remaining in the supernatant solutions allowed the weight of PVA adsorbed per square metre of latex particle surface, \( \Gamma_{PVA} \), to be calculated. The experimental details are given below.

Approximately 2 cm\(^3\) of latex of known volume fraction (\( \phi = 0.05 \)) was accurately weighed into a centrifuge tube, and to this was added 20 cm\(^3\) of PVA solution in the concentration range 20 to 1,000 ppm. The tube was sealed and rotated end-over-end for 24 hours to attain equilibrium. Centrifugation at 5,000G for 45 minutes (using an MSE21 centrifuge) removed latex particles, plus adsorbed PVA, from the PVA solution. The supernatant solution was carefully removed from the sediment.

The concentration of PVA in the supernatant solutions was determined using the following assay technique. A solution of potassium iodide (0.30g), iodine (0.153g), and boric acid (3.96g) in water (100 cm\(^3\)) was prepared. 4 cm\(^3\) of this "indicator" solution was added to 6 cm\(^3\) of supernatant solution, and gently inverted to ensure mixing. In the presence of PVA a dark green complex formed, due to the adoption by PVA of a helical structure, enclosing iodine molecules.\(^{128}\) This complex exhibited a peak in absorbance at a wavelength of 670 ± 5 nm, which was measured using a Pye-Unicam
SP1800 Spectrophotometer. The concentration of PVA in the supernatant solution was then calculated by comparison with an absorbance versus PVA concentration calibration graph (Figure 4.2). Quantitative dilution of the supernatant PVA solutions was used to ensure that their concentrations fell in the range 0-50 ppm of PVA, for which the calibration graph was linear.

The $\Gamma_{PVA}$ versus equilibrium concentration of PVA adsorption isotherms thus determined are shown in Figure 4.3. The results are similar to those determined by other workers for the adsorption of PVA onto both anionic and cationic latexes. 129,130

4.5 Electrophoresis Measurements

Electrophoretic mobilities were measured using either a "Rank Brothers Mark II" microelectrophoresis apparatus, or a "Penkem System 3000" automated electrokinetics analyser. Practical aspects of these techniques are described elsewhere. 131,123 Good agreement between the two techniques was observed, except for cationic latexes, whose mobilities were smaller when measured using the "Rank" apparatus. This was almost certainly due to contamination of the particles by polysilicate anions leached from the walls of the electrophoresis cell, as reported by Young. 130 The "Penkem" equipment facilitated quicker measurements upon more concentrated samples, thus reducing the probability of contamination, and was used for all measurements on cationic latexes reported here.
Figure 4.2. Absorbance versus Concentration Calibration Curve for PVA Analysis.
Figure 4.3. Adsorption Isotherm for the Interaction of PVA with latexes PSL (+21) (□) and PSL (-1) (○) in aqueous KCl ($10^{-3}$mol dm$^{-3}$) at pH 6.0.
Samples were prepared for use in the "Penkem" apparatus by dilution of approximately 100 µl of stock latex dispersion (~0.5% w/v) with 10 cm³ of standard KCl solution. The pH was adjusted using dilute hydrochloric acid or potassium hydroxide solutions, as required.

4.5.1 The Influence of Electrolyte (KCl) Concentration On the Electrophoretic Mobility of Uncoated Latexes

The electrophoretic mobility of latexes PSL(+21), PSL(-1), PSL(-3) and PSL(-4) was measured as a function of KCl concentration, at a temperature of 25°C and pH 6±1. The results are shown in Figure 4.4. It proved impossible to obtain data for latex PVDC(5) due to its weak light scattering.

The reduced magnitude of electrophoretic mobility at high electrolyte concentration is due to compression of the electrical double layer, causing the zeta-potential to fall. This effect, however, does not explain the observed maxima in the mobility versus electrolyte concentration curves. Such maxima have been reported for many colloidal systems, especially polystyrene latexes. A number of explanations for this phenomenon have been proposed, such as anomalous surface conductance, adsorption of co-ions into the inner Helmholtz plane, the presence of a polymeric gel layer at the latex surface, and counter-ion exchange in the Stern layer. These mechanisms will not be described further here.

The method of O'Brien and White (section 2.7) was used to compute zeta-potentials from the mobility data; the results are shown in Table 4.3.
Table 4.3 Zeta-Potentials (mV) of Polystyrene Latex Particles at Three Electrolyte (KCl) Concentrations

<table>
<thead>
<tr>
<th>Latex</th>
<th>KCl Concentration/mol dm$^{-3}$</th>
<th>1 x 10$^{-5}$</th>
<th>5 x 10$^{-4}$</th>
<th>5 x 10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSL(+21)</td>
<td></td>
<td>+101</td>
<td>+88</td>
<td>+62</td>
</tr>
<tr>
<td>PSL(-1)</td>
<td></td>
<td>-84</td>
<td>-100</td>
<td>-97</td>
</tr>
<tr>
<td>PSL(-4)</td>
<td></td>
<td>-92</td>
<td>-105</td>
<td>-96</td>
</tr>
<tr>
<td>PSL(-3)</td>
<td></td>
<td>-74</td>
<td>-102</td>
<td>-85</td>
</tr>
</tbody>
</table>

4.5.2 The Influence of Electrolyte (KCl) Concentration On the Electrophoretic Mobility of PVA-coated Latexes

Electrophoretic mobility versus KCl concentration curves are shown in Figure 4.4, for PVA-coated latexes PSL(+21), PSL(-1) and PSL(-3), equilibrated with PVA as described in section 5.2. In this case, the mobilities are smaller than for the corresponding uncoated particles, consistent with the plane of shear being displaced away from the particle surface by the adsorbed polymer layer.

4.5.3 The Influence of pH On the Electrophoretic Mobility of Uncoated Latex and Titanium Dioxide

The electrophoretic mobility of latexes PSL(-7) and PSL(-3) and of rutile titanium dioxide R-SM3, was measured as a function of pH, at a temperature of 25°C, in 5 x 10$^{-3}$ mol dm$^{-3}$ KCl solution. The results are shown in Figure 4.5. The iso-electric points of PSL(+3) and Rutile R-SM3 were pH 7.1±0.1, and pH 4.3±0.2, respectively. PSL(-7) showed little variation in mobility in the range pH 4-8, which is consistent with the presence of strongly acidic surface groups.
Figure 4.4. The Influence of Electrolyte (KCl) Concentration on the Electrophoretic Mobility of Latexes $PSL(\pm 21)(\square), PSL(-1)(\circ), PSL(-3)(\times)$ and $PSL(-4)(\Delta)$ at pH 6.0.
Figure 4.5. The Influence of pH on the Electrophoretic Mobilities of Latex and Rutile Particles Dispersed in Aqueous KCl ($5 \times 10^{-3}$ mol dm$^{-3}$)
CHAPTER 5

PARTICLE ADSORPTION IN
MIXED LATEX SYSTEMS
PARTICLE ADSORPTION IN MIXED LATEX SYSTEMS

5.1 Introduction

In a series of papers, Vincent and co-workers discussed the adsorption of small (radius $= 0.1 \ \mu m$) cationic polystyrene latex particles onto larger (radius $= 1.0 \ \mu m$) anionic polystyrene latex particles. The extent of adsorption in these systems was determined using centrifugation (to effect sedimentation of the large particles plus adsorbed small particles) followed by a turbidimetric assay for unadsorbed small particles. For particles without adsorbed PVA or PEO, "high-affinity" fractional particle coverage ($\Theta$) versus equilibrium small particle volume fraction ($\Phi_{eq}$) isotherms were observed. Such adsorption was found to be irreversible upon dilution of the unadsorbed small particles. The "plateau" value of $\Theta$ was proposed to be determined by a balance between the (normal) electrostatic attraction between the large and small particles, and the (lateral) electrostatic repulsion between neighbouring adsorbed particles.

For PVA- and PEO-coated particles two distinct classes of adsorption behaviour were reported. Below a threshold electrolyte concentration ($I_{crit}$), high-affinity isotherms were observed, similar to those discussed above for systems without PVA or PEO. However, above $I_{crit}$ "low-affinity" or "S-shaped" isotherms were observed, for which adsorption was reversible upon dilution of the unadsorbed small particles. This behaviour was rationalised in terms of a small normal attraction between the large and small particles, coupled with an overall attraction between adsorbed small particles. This
proposal was tentatively supported by electron microscopic observations of "raft-like" two-dimensional aggregates of adsorbed small particles. Isotherms of the high- and low-affinity types are shown schematically in Figure 5.1.

The work reported in this Chapter relates to the adsorption of small anionic latex particles onto larger cationic polystyrene latex particles. Both the extent and rate of adsorption were determined using freeze-drying/scanning electron microscopy, with optical microscopy and particle sedimentation being used to assess the value of freeze-drying for such studies. The effects upon pseudo-equilibrium fractional coverage ($\theta_{eq}$) and particle adsorption rate of particle size ratio, particle concentration ratio, presence or absence of PVA, and electrolyte concentration, were studied.

5.2 Specimen Preparation

In all cases the substrate species for the adsorption process was the cationic latex PSL(+21) (radius = 1.08 μm). Two stock dispersions of this latex were prepared, one of uncoated particles and one with enough PVA present for the plateau level of PVA adsorption to be attained (see Figure 4.3). The two dispersions were of identical particle concentration, which was chosen to give the optimum sample preparation conditions for freeze-drying/SEM (as discussed in Chapter 3).
Figure 5.1  Schematic Representation of High-and Low-Affinity Particle Adsorption Isotherms

\[ \theta_{cp} - \]

\[ \theta \]

\[ I < I_{crit} \]

\[ I > I_{crit} \]

\[ \phi_{eq} \]
Four different species of adsorbate particle were used, namely PSL(-1), PSL(-3), PSL(-4) and PVDC(5). Like the cationic latex above, two dilute dispersions of each anionic latex were prepared, one without PVA and one with. Details of the stock latex dispersions are presented in Table 5.1.

The general method of preparation of mixed dispersions was the same irrespective of which technique was to be used to determine the extent of adsorption. A 10 cm³ sample of standard KCl solution was measured into a plastic "Sterilin" centrifuge tube. To this solution was added 20 µl of stock PSL(+21) dispersion, using a "Gilson" micropipette. The tube was inverted to ensure homogeneous dispersion. Between 20 and 500 µl of stock anionic latex dispersion was then added, and the tube inverted once to mix the specimen thoroughly. A faster mixing technique, such as stopped-flow, was deemed unnecessary in view of the very low particle concentrations used. The sample was kept at room temperature for a time, t, after mixing the latexes. The extent of particle adsorption was then determined.

5.3 Determination of Particle Coverage

For each mixed dispersion the extent of particle adsorption at time t was determined using freeze-drying/SEM. In some instances the following techniques were also used:

a) Optical Microscopy
b) Particle Sedimentation
c) Electrophoresis
### Table 5.1

**Stock Latex Dispersions Used In Particle Adsorption Studies**

<table>
<thead>
<tr>
<th>Latex Species</th>
<th>Particle Diameter (nm)</th>
<th>% wt. Fraction</th>
<th>Volume Fraction, φ</th>
<th>Particle Number Concentration (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSL(+21)</td>
<td>2170 ± 250</td>
<td>0.20</td>
<td>1.89 x 10⁻³</td>
<td>3.52 x 10⁸</td>
</tr>
<tr>
<td>PSL(-1)</td>
<td>696 ± 10</td>
<td>0.67</td>
<td>6.34 x 10⁻³</td>
<td>3.53 x 10¹⁰</td>
</tr>
<tr>
<td>PSL(-4)</td>
<td>320 ± 11</td>
<td>0.51</td>
<td>4.82 x 10⁻³</td>
<td>2.81 x 1⁰¹¹</td>
</tr>
<tr>
<td>PSL(-3)</td>
<td>180 ± 6</td>
<td>0.12</td>
<td>1.14 x 10⁻³</td>
<td>3.73 x 1⁰¹¹</td>
</tr>
<tr>
<td>PVDC(5)</td>
<td>116 ± 4</td>
<td>0.45</td>
<td>2.55 x 10⁻³</td>
<td>3.12 x 1⁰¹²</td>
</tr>
</tbody>
</table>

* Calculation based on the following densities of solid polymers\textsuperscript{127}:

\[
\rho(PSL) = 1.057 \text{ gcm}^{-3}
\]

\[
\rho(PVDC) = 1.77 \text{ gcm}^{-3}
\]
5.3.1 Freeze-Drying/SEM

A thin film of mixed latex dispersion was quench-frozen in liquid propane. The sample was then freeze-dried, mounted on a copper specimen support, sputter-coated with gold and examined using a Jeol JEM-100CX TEMSCAN electron microscope. A full description of this technique is given in Chapter 3 of this thesis.

An electron micrograph of a freeze-dried PSL(+21) particle carrying adsorbed PSL(-1) particles is shown in Plate 5.1. The total number of small particles adsorbed per PSL(+21) particle \( \Gamma_a \) was greater than the number actually observed using SEM \( \Gamma_{EM} \). This discrepancy was due to the "eclipse" of small particles lying beneath the large particle, and to "obscuration" of adsorbed particles by their neighbours, primarily around the circumference of the heteroaggregates. The conventions adopted for quantifying \( \Gamma_{EM} \) were chosen in order to maximise the surface area of PSL(+21) particles accounted for, whilst minimising errors due to obscuration. This balance led to different counting conventions being used for differently-sized adsorbing particles, as illustrated in Figure 5.2, and described below.

(i) Adsorbed PSL(-3) or PVDC(5):

Only particles wholly within the circumference of the large particle were counted (positions a' to a" and above, in Figure 5.2).

(ii) Adsorbed PSL(-4):

Only particles on and above the circumference of the large particle were counted (positions b' to b" and above in Figure 5.2).
Plate 5.1

A Freeze-Dried
PSL(+21)/PSL(-1) Heteroaggregate
Figure 5.2. Diagram of Procedures Used for Counting $\tau_{em}$
(relative sizes of particles not to scale)
Relatively few PSL(-4) particles were observed to lie precisely on the circumference, and hence the error due to two-fold contribution of such particles to $\Gamma_a$ is thought to be small.

(iii) Adsorbed PSL(-1):

Only completely eclipsed particles were not counted (c' to c" and below in Figure 5.2).

In order to calculate $\Gamma_a$ from $\Gamma_{EM}$, "counting correction factors" (C) were used, where

$$\Gamma_a = C \times \Gamma_{EM} \quad (5.1)$$

Calculations of C for the four mixed latex systems used here are presented in Appendix 2; the results are summarised in Table 5.2.

In the forthcoming section, the extent of particle adsorption is commonly expressed as a "fractional particle coverage" ($\theta$) as defined by equation (5.2).

$$\theta = \frac{\Gamma_a}{\Gamma_{cp}} \quad (5.2)$$

In the above equation, $\Gamma_{cp}$ is the number of small particles which theoretically could be hexagonally close-packed on one large particle. The calculation of $\Gamma_{cp}$ for each mixed system used here is shown in Appendix 3; the results are summarised in Table 5.2.

All $\Gamma_{EM}$ and $\theta$ results presented later in this chapter are mean values, which are based upon observations of at least ten hetero-aggregates for each mixed dispersion. The standard deviation of the observed values is given in each case.
Table 5.2
Counting Correction Factors and Theoretical Close-Packed Coverages
For Different Latex Species Adsorbed On PSL(+21)

<table>
<thead>
<tr>
<th>Adsorbing Species</th>
<th>Counting Correction Factor, $C$</th>
<th>Theoretical Close-Packed Coverage, $\Gamma_{cp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSL(-1)</td>
<td>1.08</td>
<td>58.9</td>
</tr>
<tr>
<td>PSL(-4)</td>
<td>2.0</td>
<td>217</td>
</tr>
<tr>
<td>PSL(-3)</td>
<td>4.25</td>
<td>616</td>
</tr>
<tr>
<td>PVDC(5)</td>
<td>3.56</td>
<td>1406</td>
</tr>
</tbody>
</table>
5.3.2 Optical Microscopy

The resolution of an optical microscope (a Nikon Optiphot, with differential interference contrast facility) was sufficient to allow the number of PSL(-1) particles adsorbed per PSL(+21) particle to be observed directly.

A drop of the specimen was placed on a Helber bacteria counting cell (Figure 5.3), and a glass cover-slip placed over it. This type of cell has two advantages over a standard microscope slide: a) a recessed ring around the central portion of the cell allows a reservoir of liquid to be retained, which considerably slows the drying of specimens, and b) an etched graticule (20 μm x 20 μm squares) in the centre of the cell facilitates particle counting. For reasons of image clarity, observations were made directly using the microscope, rather than from optical micrographs.

Once more, the observed number of adsorbed particles (Γ_{OM}) was an underestimate of the true number adsorbed (Γ_a), due to the eclipse of small particles by the large ones. The same counting correction factor (C) was applied as for PSL(+21)/PSL(-1) systems observed using SEM. Similarly, all Γ_{OM} results are mean values based on observations of at least ten heteroaggregates per mixed dispersion.

5.3.3 Particle Sedimentation

For a mixed dispersion of PSL(+21) and PSL(-3), θ was determined by centrifugal sedimentation of the large particles plus adsorbed small particles. The concentration of unadsorbed small particles remaining in the supernatant dispersion was determined turbidi-
Figure 5.3 Helber Bacteria Counting Cell
metrically, allowing calculation of the number adsorbed, and hence θ. This method has been used previously by Vincent and co-workers21-25.

After mixing and equilibration (Section 5.2), specimens were centrifuged for 1 hour at ca. 1000G using an "MSE Centaur 2" centrifuge. Approximately 3 cm³ of supernatant dispersion was transferred to a sample cell and its absorbance at a wavelength of 400 nm (A₄₀₀) measured using a "Pye-Unicam SP1800" spectrophotometer. The concentration of unadsorbed PSL(-3) particles was determined by comparison with a calibration curve of A₄₀₀ versus PSL(-3) concentration (Figure 5.4). A control experiment was performed using only PSL(+21), which showed that virtually all the PSL(+21) particles were sedimented under the centrifugation conditions described.

Particle sedimentation studies were carried out only for the mixed dispersion PSL(+21)/PSL(-3), since the sedimentation rate disparity between the two latex species was large in this case. The larger density of PVDC (c.f. polystyrene) prevented efficient separation of PSL(+21) particles from PVDC(5) particles, despite the small size of the latter.

5.3.4 Electrophoresis

Electrophoretic mobility measurements were made for a number of mixed latex dispersions, using either a "Penkem 3000" system or a "Rank Brothers Mark 1" microelectrophoresis apparatus. These techniques have been described in Section 4.5 of this thesis.
Figure 5.4 Calibration Graph of Absorbance versus Volume Fraction of PSL(-3)
5.4 **Pseudo-Equilibrium Particle Adsorption Results**

The extents of adsorption of PSL(-1), PSL(-3), PSL(-4) and PVDC(5) particles onto PSL(+21) particles were determined for a range of experimental conditions, at effectively infinite time after mixing of the latexes. This extent of adsorption is referred to subsequently as the "pseudo-equilibrium" level. True equilibrium was not achieved since particle adsorption was shown to be irreversible, and to increase, albeit very slowly, for a considerable time after mixing (see Section 5.6).

5.4.1 **Comparison of Techniques**

Pseudo-equilibrium particle adsorption results obtained using optical microscopy and particle sedimentation were compared with those obtained using freeze-drying/SEM, in order to assess the latter technique.

5.4.1.1 **Comparison of Optical Microscopy and Freeze-Drying/SEM**

ΓOM and ΓEM for the adsorption of PSL(-1) onto PSL(+21) particles were determined as a function of the total volume fraction (φ) of PSL(-1), at t = 5 hours. At an electrolyte concentration of 5 x 10^{-4} mol dm^{-3} KCl, in the absence of PVA, the isotherms shown in Figure 5.5 were obtained. In Figure 5.6 analogous results for PVA-coated particles in 1 x 10^{-5} and 5 x 10^{-3} mol dm^{-3} KCl are shown.

These results demonstrate a close correlation between (uncorrected) ΓOM and ΓEM values for systems where the particle coverage was below ca. 12. For higher coverages, ΓEM was always greater than ΓOM. This discrepancy was almost certainly due to the
Figure 5.5 Number of Adsorbed PSL(-1) Particles per PSL(+21) Particle (in $5 \times 10^{-4}$ mol dm$^3$ KCl), Observed Using Optical Microscopy (■) and Freeze-Drying/SEM (×)

\[ \Gamma \]

\[ \phi \text{ (PSL (-1))} / 10^{-4} \]
Figure 5.6 Number of Adsorbed PSL (-1) Particles per PSL (+21) Particle (both PVA-coated) Observed Using Optical Microscopy (■) and Freeze-Drying/SEM (×)
necessity of operating close to the limit of resolution of the optical microscope. In such cases, it became difficult to distinguish individual PSL(-1) particles around the circumference of heteroaggregates, and the probability of undercounting was large. Such observational difficulties were not encountered for these systems when electron microscopy was used.

It may be concluded that observations made using optical microscopy suggest that the process of freeze-drying did not affect the number of adsorbed particles in mixed PSL(-1)/PSL(+21) latex dispersions. The form of the isotherms shown in Figures 5.5 and 5.6 will be discussed in Section 5.4.2.

5.4.1.2 Comparison of Particle Sedimentation and Freeze-Drying/SEM

These techniques were used to determine fractional particle coverage ($\Theta$) versus $\phi_{eq}(PSL(-3))$ isotherms for the adsorption of PSL(-3) onto PSL(+21) particles, where $\phi_{eq}(PSL(-3))$ is the pseudo-equilibrium volume fraction of unadsorbed PSL(-3) particles. In $5 \times 10^{-4}$ mol dm$^{-3}$ KCl solution, in the absence of PVA, the isotherms thus determined took the form shown in Figure 5.7. Good agreement between the two techniques was observed, which suggests once more that minimal disruption was caused to heteroaggregates by the process of freeze-drying. The estimated errors for the particle sedimentation method are larger than for freeze-drying/SEM, especially for the higher values of $\phi_{eq}(PSL(-3))$. This is due to the relatively small difference between the total concentration of PSL(-3) particles and the pseudo-equilibrium concentration of unadsorbed particles, in combination with the greater inaccuracy of the absorbance versus $\Phi(PSL(-3))$ calibration curve (Figure 5.4) at higher volume fractions.
Figure 5.7 Pseudo-Equilibrium Particle Adsorption Isotherm for PSL(+21)/PSL(-3)/5x10^{-4} mol dm^{-3} KCl Determined Using Particle Sedimentation (□) and Freeze-Drying/SEM (●)
5.4.2 Fractional Coverage versus Concentration of Small Particles

Particle adsorption isotherms were determined using freeze-drying/SEM for mixtures of each of the four anionic latexes with PSL(+21). $\Theta$ versus $\phi_{eq}$ results are shown in Figure 5.8, where $\phi_{eq}$ is the pseudo-equilibrium volume fraction of unadsorbed anionic latex particles. In each case, the volume fraction of PSL(+21) was $3.6 \times 10^{-5}$, no PVA was present, the electrolyte concentration was $5 \times 10^{-4}$ mol dm$^{-3}$ KCl, and the dispersion was frozen at $t=5$ hours.

All four mixed systems exhibited "high-affinity" isotherms, with a plateau coverage ($\Theta_{eq}$) which did not rise as the concentration of anionic latex was increased. This type of isotherm has been observed for similar systems by Vincent and co-workers$^{21-25}$. Plates 5.2 and 5.3 show scanning electron micrographs of typical heteroaggregates in systems corresponding to the plateau regions of the isotherms. A notable feature of these micrographs is the remarkably uniform distribution of the small particles upon the large ones. This suggests that electrostatic repulsion between the small particles plays an important rôle in determining the morphology of such heteroaggregates.

Another feature of the adsorption isotherms shown in Figure 5.8 is the rise in $\Theta_{eq}$ as the radius of the adsorbing species increases. This trend cannot be explained without recourse to calculations of the electrostatic forces involved in heteroaggregate formation. Such calculations are discussed in Section 5.5 of this thesis.
Figure 5.8 Pseudo-Equilibrium Fractional Coverage ($\theta$) versus Volume Fraction, for the Adsorption of Anionic Latex Particles onto PSL (+21) in $5 \times 10^{-4}$ mol dm$^{-3}$ KCl solution, in the absence of PVA.
Plate 5.2

Pseudo-Equilibrium Heteroaggregates

Formed In \(5 \times 10^{-4} \text{ moldm}^{-3}\) KCl Solution

a) PSL(+21)/PVDC(5)

b) PSL(+21)/PSL(-3)
Plate 5.3

Pseudo-Equilibrium Heteroaggregates

Formed In $5 \times 10^{-4}$ moldm$^{-3}$ KCl Solution

a) PSL(+21)/PSL(-4)

b) PSL(+21)/PSL(-1)
5.4.3 Fractional Coverage versus Electrolyte Concentration

A simple method of changing the range of particle interactions in aqueous media is to vary the electrolyte concentration (I). The scanning electron micrographs presented in Plate 5.4 a)-d) illustrate the effect upon the pseudo-equilibrium aggregate morphology of varying I. It is uncertain whether the aggregation between PVDC particles at the surface of the larger PSL(+21) particle shown in Plate 5.4 d), for \( I = 5 \times 10^{-3} \text{ mol dm}^{-3} \), is a real effect or an artefact caused by short range lateral movement during specimen preparation. Such an artefact would be most obvious for hetero-aggregates with a high fractional coverage.

\( \theta_{eq} \) versus \( \kappa \) curves for all four mixed systems are shown in Figure 5.9, where \( \kappa \) is defined by equation (2.12). It is clear that \( \theta_{eq} \) rises as \( \kappa \) is increased, as previously noted for similar systems\(^{20,130}\). This effect can be rationalised in terms of a balance between lateral repulsion (between adsorbed small particles) and normal attraction (between the large and small particles). As I, and hence \( \kappa \), increases, the ranges of both these forces are reduced. Reduction in the lateral repulsion allows small particles to pack more closely on the surface of the large particles, whilst reduction in the normal attraction reduces the tendency for small particles to adsorb at all. The balance between these forces clearly is affected by electrolyte concentration, with the normal forces becoming more dominant as I is increased. A model will be presented in Section 5.5 which can be used to predict \( \theta_{eq} \) as a function of \( \kappa \) for these systems.
Plate 5.4

Pseudo-Equilibrium PSL(+21)/PVDC(5) Heteroaggregates Formed In Solutions Of Different KCl Concentrations (I)

a) $I = 1 \times 10^{-5}$ mol dm$^{-3}$  

b) $I = 1 \times 10^{-4}$ mol dm$^{-3}$

c) $I = 5 \times 10^{-4}$ mol dm$^{-3}$

d) $I = 5 \times 10^{-3}$ mol dm$^{-3}$
Figure 5.9 Pseudo-Equilibrium Fractional Coverage, $\theta_{eq}$, versus K for the Adsorption of Anionic Latex Particles onto PSL (+21), in the Absence of PVA
5.4.4 The Effect of Adsorbed PVA

θ versus κ curves obtained for PVA-coated particles (at single values of θ_eq, and t=5 hours) differed qualitatively from those for uncoated particles, as shown in Figure 5.10 a)-d). Below a threshold value of κ (κ_{crit}) the curves for corresponding coated and uncoated systems coincide. Above κ_{crit}, however, θ for the PVA-coated particles falls dramatically, owing to a reduction in the normal electrostatic attraction between the large and small particles. It is proposed that this reduction is caused by compression of the electrical double layer of the particles to within the PVA sheath. This is supported by electrophoretic mobility versus electrolyte concentration data for the PVA-coated particles (Figure 4.4), which show a reduction in mobility of both anionic and cationic latexes to approximately zero for I > 5x10^{-3} mol dm^{-3} (κ > 2.3 x 10^{8} m^{-1}). In addition, κ_{crit} for all four mixed systems studied here was in the range 1-2 x 10^{8} m^{-1}, which corresponds to an "effective double layer thickness" (κ^{-1}) in the range 5-10 nm; this is approximately half of the value, determined by Garvey et al.,^{129} for the extension (S) of a sheath of PVA (of molecular weight ≈ 25,000) adsorbed on polystyrene latex particles. In the range used in this study, electrolyte concentration has been shown to have little effect upon S_{138}.

Since the θ versus κ curves shown in Figure 5.10 were obtained only for a single value of θ_eq in each case, the four sets of data are not directly comparable where κ > κ_{crit}. No evidence of "raft-like" two-dimensional aggregation of adsorbed particles was found for any of the PVA-coated systems where κ > κ_{crit}; it is possible that such structures exist only for higher values of θ_eq.
Figure 5.10 Fractional Coverage (\( \theta \)) versus \( K \) for the Adsorption of Anionic Latexes onto PSL (+21); \( x \) = uncoated particles, \( o \) = PVA-coated

a) PSL (+21) / PVDC (5) \( (\phi(\text{PVDC (5)}) = 4.9 \times 10^{-5}) \)
Figure 5.10 b) PSL (+21) / PSL (-3) (Φ(PSL (-3)) = 2.17 × 10^{-5})
Figure 5.10 c) PSL (+21) / PSL (-4) \( (\Phi (\text{PSL} (-4)) = 9.3 \times 10^{-5} ) \)
Figure 5.10 d) $\frac{\text{PSL}(+21)}{\text{PSL}(-1)}$ $(\phi (\text{PSL}(-1)) = 1.22 \times 10^{-4})$
5.4.5 Electrokinetic Studies of Heteroaggregates

Electrophoretic mobilities of pseudo-equilibrium heteroaggregates were determined for a range of electrolyte concentrations. In each case, no PVA was present and the heteroaggregates were formed in conditions corresponding to the plateau regions of \( \Theta \), as shown in Figure 5.8. The electrophoresis results are presented in Table 5.3, and may be compared directly with the \( \Theta \) versus \( \kappa \) results for identical systems, which are given in Section 5.4.3 and reproduced, in part, in Table 5.3.

The electrokinetic potentials of all the heteroaggregates studied were found to be of negative sign. For \( 5 \times 10^{-3} \) and \( 5 \times 10^{-4} \) mol dm\(^{-3} \) KCl solutions, the electrophoretic mobility values were close to those of the corresponding anionic latex dispersions, whereas for \( 1 \times 10^{-5} \) mol dm\(^{-3} \) KCl solutions they were somewhat smaller. This suggests that the large cationic particle has little effect upon the electrophoretic mobility of the heteroaggregate, unless \( \Theta \) is small (\( \leq 0.25 \)). A likely explanation for this observation is that the shear plane around a heteroaggregate, although undoubtedly complicated in shape, must lie much closer to the small anionic particles than to the large cationic particle, especially when \( \Theta \) is large. Hence, the zeta-potential predominantly will reflect the electrical potential close to the adsorbed particles. Further evidence in support of this assertion is provided by the following calculation:
Table 5.3
Electrokinetic Measurements for Mixed Latex Systems in KCl Solutions (in the Absence of PVA)

<table>
<thead>
<tr>
<th>Mixed Latex System</th>
<th>KCl Conc. (mol dm(^{-3}))</th>
<th>Electrophoretic Mobility (10(^{-8}) V(^2) m(^{-1}) s(^{-1}))</th>
<th>(\theta_{eq})</th>
<th>(\theta_{Q=0})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Hetero-aggregate</td>
<td>Anionic Latex Only</td>
<td></td>
</tr>
<tr>
<td>PSL(+21)/PSL(-3)</td>
<td>1 x 10(^{-5})</td>
<td>-2.5 ± 0.6</td>
<td>-3.4 ± 0.7</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>5 x 10(^{-4})</td>
<td>-3.9 ± 0.5</td>
<td>-4.0 ± 0.6</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>5 x 10(^{-3})</td>
<td>-5.1 ± 0.3</td>
<td>-5.0 ± 0.9</td>
<td>0.40</td>
</tr>
<tr>
<td>PSL(+21)/PSL(-4)</td>
<td>1 x 10(^{-5})</td>
<td>-2.9 ± 0.4</td>
<td>-4.8 ± 0.4</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>5 x 10(^{-4})</td>
<td>-6.0 ± 0.4</td>
<td>-6.3 ± 0.5</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>5 x 10(^{-3})</td>
<td>-4.3 ± 0.4</td>
<td>-4.6 ± 0.6</td>
<td>0.43</td>
</tr>
<tr>
<td>PSL(+21)/PSL(-1)</td>
<td>1 x 10(^{-5})</td>
<td>-3.4 ± 0.6</td>
<td>-3.8 ± 0.5</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>5 x 10(^{-4})</td>
<td>-5.0 ± 0.7</td>
<td>-5.5 ± 0.4</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>5 x 10(^{-3})</td>
<td>-6.4 ± 0.6</td>
<td>-6.8 ± 0.3</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Consider a central cationic particle (radius $a_1$) of total charge $Q_1$, upon which are adsorbed $r_a$ anionic particles (radius $a_2$) each of charge $-Q_2$. For overall electroneutrality of the heteroaggregate

$$Q_1 = r_a Q_2$$  \hspace{1cm} (5.3)

and hence

$$r_a = \left[ \frac{a_1}{a_2} \right]^2 \frac{\sigma_1}{\sigma_2}$$  \hspace{1cm} (5.4)

where $\sigma_1$ and $\sigma_2$ are the surface charge densities of species 1 and 2 respectively. No measurements of surface charge densities were made for the latex species studied here, but $\sigma_1/\sigma_2$ can be estimated from electrokinetic data in the following way.

It is reasonable to assume that

$$\frac{\sigma_1}{\sigma_2} = \frac{\sigma_{1,el}}{\sigma_{2,el}}$$  \hspace{1cm} (5.5)

where $\sigma_{1,el}$ and $\sigma_{2,el}$ are the charge densities at the shear planes of species 1 and 2 respectively. These charge densities can be estimated using an equation analogous to equation (2.19) of Chapter 2,

$$\sigma_{el} = (8n_0 \epsilon \epsilon_0 kT)^{1/2} \sinh \left[ \frac{ze\zeta}{2kT} \right]$$  \hspace{1cm} (2.19a)

which for small potentials reduces to

$$\sigma_{el} \approx \epsilon \epsilon_0 k \zeta$$  \hspace{1cm} (2.20a)
For the mixed systems considered here, $\kappa$ is identical for species 1 and 2, and hence equations (5.5) and (2.20a) reduce to

$$\frac{c_1}{c_2} = \frac{c_1}{c_2}.$$  \hspace{1cm} (5.6)

Combination of equations (5.2), (5.4) and (5.6) gives the following equation (5.7) for the fractional particle coverage of a heteroaggregate possessing zero net charge ($\Theta_{Q=0}$).

$$\Theta_{Q=0} = \frac{\left[\frac{a_1}{a_2}\right]^2 c_1}{a_2 c_2} \frac{C_2}{\Gamma_{cp}}.$$  \hspace{1cm} (5.7)

Values of $\Theta_{Q=0}$ are presented in Table 5.3, together with experimental values of $\Theta_{eq}$, for three of the mixed latex systems studied here. Two important points emerge from these calculations. Firstly, the system PSL(+21)/PSL(-3)/1x10^{-5} mol dm^{-3} KCl showed a negative zeta-potential, where a positive overall charge is calculated (since $\Theta_{eq} < \Theta_{Q=0}$). This supports the previously stated conclusion that the zeta-potential of the heteroaggregates is largely dependent upon the potential of the adsorbed particles, rather than on the overall charge of the heteroaggregates. The other major conclusion is that in KCl solutions of concentrations $\geq 5 \times 10^{-4}$ mol dm^{-3}, the fractional particle coverages determined by freeze-drying/SEM were well in excess of those required for electro-neutrality of the heteroaggregates.
5.5 Models For Particle Adsorption In Mixed Latex Systems

Two models have been developed which may be used to predict "pseudo-equilibrium" fractional particle coverages for mixed latex systems, such as those reported in Section 5.4. These will be referred to as the "kinetic" and "thermodynamic" models.

In the kinetic model, the energy of approach of a small particle towards a larger particle (already carrying adsorbed particles) is calculated. The predicted fractional coverage ($\Theta_{\text{model}}$) is defined as that for which further adsorption is opposed by an energy barrier greater than a threshold value of 15 kT. (It will be shown later that the precise value of threshold energy does not affect significantly the predictions of the model).

In the thermodynamic model, the enthalpy of adsorption is treated as the sum of the enthalpies of normal attraction (between an adsorbed particle and the large particle) and lateral repulsion (between neighbouring adsorbed particles). This model takes no account of the energy of approach of adsorbing particles. $\Theta_{\text{model}}$ in this case is defined as the fractional coverage for which the chemical potential of an adsorbed small particle is equal to that of an unadsorbed one.

5.5.1 A Kinetic Model for Particle Adsorption

For the purposes of this model, a hexagonal array of adsorbed small particles was assumed (on the basis of experimental observations of uniform distributions, as illustrated in Plates 5.1 to 5.4). Two variations on the basic hexagonal geometry were considered:
Figure 5.11a. Case 1 Geometry of Approach of a Small Particle Toward a Larger One

Side View:

Top View:
Figure 5.11 b). Case 2 Geometry of Approach of a Small Particle Towards a Larger One.

Side View:

Top View:
Case 1 (Figure 5.11a)

Adsorbed particles arranged in a hexagonal array with a single unoccupied space, into which an approaching particle fits.

Case 2 (Figure 5.11b)

Adsorbed particles arranged in a hexagonal array with no unoccupied spaces; an approaching particle fits into a triangular gap in this array.

The physical implications of the two cases will be discussed in Section 5.5.4.

For each geometry, the surface-to-surface distance between the approaching particle and its nearest adsorbed neighbours ($h$) was calculated as a function of the surface-to-surface distance between the approaching particle and the large particle ($H$), the radii of the two types of particle ($a_1$ and $a_2$), and the distance of separation between the adsorbed particles ($c$). Note that $c$ is the distance between particles on either side of the unoccupied space (case 1 geometry), rather than the distance between nearest neighbours in the array (which is designated $b$, as shown in Figure 5.11). Calculations of $h$ in terms of $H$ are described fully in Appendix 4.

The total potential energy of approach of a small particle ($V_{ads}(H)$) was calculated by summation of its interactions with its nearest adsorbed neighbours and with the large particle, as described by equation (5.8).

$$V_{ads}(H) = \left[ z \cdot V_{22}(h) \right] + V_{12}(H) \tag{5.8}$$
In this equation $V_{22}(h)$ is the sum of the electrostatic and van der Waals interaction energies for two small particles, and $V_{12}(H)$ is the analogous sum for one large and one small particle. Electrostatic interactions were calculated using the expressions of Bell, Levine and McCartney\textsuperscript{50} (equation (2.27)) and of Hogg, Healy and Fuerstenau\textsuperscript{11} (equation (2.26)), where the surface potentials ($\Psi_1$ and $\Psi_2$) were approximated by zeta-potentials ($\zeta_1$ and $\zeta_2$, respectively). van der Waals attractive interactions were calculated using equation (2.1); a value for the net Hamaker constant ($A$) of $7.75 \times 10^{-21}$J was used, as calculated by Cheung\textsuperscript{20} and by Gingell and Parsegian\textsuperscript{139}, for the polystyrene/water system.

In equation (5.8), $z$ is the number of adsorbed neighbours nearest to the incoming particle. For case 1 geometry $z = 6$, whereas for case 2 geometry $z = 3$. The effect of more distant adsorbed particles was ignored.

The final fractional particle coverage ($\theta_{\text{model}}$) will, by definition, be that for which further adsorption takes place at a negligible rate. In accordance with Reerink and Overbeek's approximation\textsuperscript{86} (Section 2.7), the rate of adsorption ($k_{\text{ads}}$) was assumed to be inversely proportional to the height of the maximum in the corresponding $V_{\text{ads}}$ versus $H$ curve ($V_{\text{max}}$). An iterative procedure was used to determine the adsorbed particle spacing ($c_{\text{model}}$) for which $V_{\text{max}} = 15$ kT. This threshold value of $V_{\text{max}}$ was chosen since aggregation rates typically become negligible when $V_{\text{max}} \geq 10\text{--}15$ kT. The method used to calculate $\theta_{\text{model}}$ from $c_{\text{model}}$ is described in Appendix 5, which also includes $\theta$ versus $c$ calibration graphs for the four mixed systems studied here.
In summary, this method was used to predict the fractional coverage, $\theta_{\text{model}}$, for which further adsorption is opposed by a potential energy barrier of height $15 \ kT$.

The calculations described in this section were carried out using an Opus II personal computer; the programs used to calculate $V_{\text{ads}}$ versus $H$ curves are shown in Appendix 6.

5.5.2 Comparison of Experimental Results with Predictions of the Kinetic Model

Predicted $\theta_{\text{model}}$ versus $\kappa$ curves are shown in Figure 5.12, together with experimental $\theta_{\text{eq}}$ results, all for systems with no PVA. For three values of $\kappa$, results are presented in Table 5.4, which includes predicted and experimental values for adsorbed particle spacings. These results were calculated using the "BLM" equation (2.27) for electrostatic interactions; no significant differences were observed when the "HFE" equation (2.26) was used instead.

Qualitative agreement between the predicted and observed coverages is reasonable - the experimentally observed increase in $\theta$ with increasing $\kappa$ is predicted. For case 1 geometry, the observed rise in $\theta$ with increasing adsorbed particle size ($a_2$) is also predicted, but the opposite effect is predicted for case 2 geometry. Although quantitative agreement is fair at small values of $\kappa$ the disparity between both cases of the model and the experimental results increases as $\kappa$ rises. This point will be discussed in Section 5.5.4, as will the large differences between "case 1" and "case 2" predictions.
Figure 5.12 Predicted and Experimental Equilibrium Fractional Coverage, $ \theta $, versus $ K $ (in the absence of PVA)

- **Predicted (Case 1 Geometry)**
- **Experimental**
- **Predicted (Case 2 Geometry)**

- $ \Delta $ PSL(-1), $ a_1 = 348 \text{ nm} $
- $ \square $ PSL(-4), $ a_2 = 160 \text{ nm} $
- $ \bigcirc $ PSL(-3), $ a_2 = 90 \text{ nm} $
- $ \times $ PVDC (5), $ a_2 = 58 \text{ nm} $
Table 5.4  Comparison of Experimental Pseudo Equilibrium Adsorption Results with Predictions of the Kinetic Model

<table>
<thead>
<tr>
<th>Adsorption Parameter</th>
<th>PSL(+21)/PVDC(5)</th>
<th>PSL(+21)/PSL(-3)</th>
<th>PSL(+21)/PSL(-4)</th>
<th>PSL(+21)/PSL(-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-7} \times \kappa (m^{-1})$</td>
<td>1.0   7.4    23.3</td>
<td>1.0   7.4    23.3</td>
<td>1.0   7.4    23.3</td>
<td>1.0   7.4    23.3</td>
</tr>
<tr>
<td>$\theta_{eq}$ (nm)</td>
<td>0.13  0.25  0.32</td>
<td>0.18  0.31  0.40</td>
<td>0.20  0.33  0.43</td>
<td>0.26  0.40  0.45</td>
</tr>
<tr>
<td>$\theta_{eq}$ (nm)</td>
<td>520   350   295</td>
<td>650   460   380</td>
<td>1020  750  630</td>
<td>1610  1290  1200</td>
</tr>
<tr>
<td>$b_{eq}$ (nm)</td>
<td>205   118   90</td>
<td>240   144   104</td>
<td>380   230   165</td>
<td>595   340   280</td>
</tr>
<tr>
<td>$\theta_{model}$ (nm)</td>
<td>0.32  0.49  0.75</td>
<td>0.31  0.57  0.80</td>
<td>0.33  0.68  0.86</td>
<td>0.48  0.82  0.93</td>
</tr>
<tr>
<td>$\theta_{model}$ (nm)</td>
<td>295   215   151</td>
<td>460   290   220</td>
<td>750   440   360</td>
<td>1150  775   690</td>
</tr>
<tr>
<td>$b_{model}$ (nm)</td>
<td>92    50    18</td>
<td>144   58    22</td>
<td>230   70    25</td>
<td>290   70    25</td>
</tr>
<tr>
<td>$\theta_{model}$ (nm)</td>
<td>0.23  0.22  0.25</td>
<td>0.16  0.20  0.26</td>
<td>0.12  0.22  0.28</td>
<td>0.10  0.19  0.23</td>
</tr>
<tr>
<td>$\theta_{model}$ (nm)</td>
<td>460   380   340</td>
<td>700   610   500</td>
<td>1350  970   850</td>
<td>2350  1840  1710</td>
</tr>
<tr>
<td>$b_{model}$ (nm)</td>
<td>175   134   115</td>
<td>270   222   165</td>
<td>575   350   270</td>
<td>~1400  790   670</td>
</tr>
</tbody>
</table>

Notes. All figures refer to systems without PVA

Interparticle spacings b and c are defined in Figure 5.11a).
An example of a set of $V_{\text{ads}}$ versus $H$ curves (calculated for case 1 geometry) for the system PSL(+21)/PSL(-4)/1 $\times 10^{-5}$ mol dm$^{-3}$ KCl is shown in Figure 5.13. It was noted that for small changes in $\theta$, the height of the energy barrier for adsorption ($V_{\text{max}}$) changed dramatically. Conversely, this indicates that $\theta_{\text{model}}$ is rather insensitive to the threshold value of $V_{\text{max}}$ ($V_{\text{crit}}$) used to define it, and that the (somewhat arbitrary) choice of $V_{\text{crit}}^{\text{max}} = 15 \, kT$ did not unduly influence the $\theta_{\text{model}}$ results.

Setting $A=0$ in equation (2.1) effectively removed van der Waals interactions from the model. This made no discernible difference to the $V_{\text{ads}}$ versus $H$ curves, and thus demonstrated that van der Waals interactions play an insignificant rôle in the determination of $\theta_{\text{model}}$, at least in the range of electrolyte concentrations studied here ($I \leq 5 \times 10^{-3}$ mol dm$^{-3}$ KCl).

5.5.3 Application of the Kinetic Model to PVA-Coated Systems

A simple modification was made to the kinetic theory in order to predict the behaviour of PVA-coated particles. A "hard-wall" barrier was introduced as a model for the "steric" repulsion, whereby $V_{12}(H) \rightarrow \infty$ for $H \leq 2S$ and $V_{22}(h) \rightarrow \infty$ for $h \leq 2S$, with a value of $S = 15$ nm being estimated for the thickness of the PVA sheath (see Section 5.4.4). The geometry of particle approach and calculation of $\Gamma_{\text{cp}}$ were also modified to account for the PVA sheath (see Appendix 4). The surface potentials of the PVA-coated particles were assumed to be equal to those of the equivalent uncoated particles; the effect of adsorbed PVA upon surface charge density and charge distribution
Figure 5.13 Predicted Energy of Approach of a PSL (-4) Particle Towards a PSL (+21) Particle as a Function of Fractional Coverage, $\theta$ (Case 1 Geometry)
in the electrical double layer were ignored (c.f. Section 2.4.1). Nevertheless, this approximation should not affect the balance between the normal and lateral interparticle forces, and hence the qualitative predictions of the theory.

Examples of predicted $V_{ads}$ versus $H$ curves for PVA-coated particles are shown in Figure 5.14. Figure 5.15 shows experimental and predicted $\theta$ versus $\kappa$ curves for both PVA-coated and uncoated PSL(+21)/PSL(-3) systems. At low electrolyte concentrations, slightly higher values of $\theta_{model}$ were predicted for the PVA-coated system, whereas the experimental results showed insensitivity to the presence of PVA. This discrepancy may have been due to the use of "unmodified" surface potentials for the PVA-coated particles. At electrolyte concentrations above a critical value ($I_{crit}$), the $V_{ads}$ versus $H$ curve becomes purely repulsive (Figure 5.14c)) and no adsorption is predicted. In this case, the exact value of $I_{crit}$ is very sensitive to the value of $\varepsilon$ used in the calculations.

5.5.4 Discussion of the Kinetic Model

Possible reasons for the disparity between the predictions of the model and the experimentally observed fractional particle coverages, can be split into two categories: inadequacies in the treatment of the "mixed double layer" around a heteroaggregate, and shortcomings in the geometrical description of the adsorption process. These features will be considered below.
Figure 5.14 Predicted $V_{ads}$ versus $H$ curves for PVA-coated PSL(+21)/PSL(-3) Mixtures ($d = 15$ nm)

1x10^{-5} \text{ mol dm}^{-3} \text{ KCl}

\[ \frac{V_{ads}}{kT} \]

<table>
<thead>
<tr>
<th>CURVE</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
</tr>
</tbody>
</table>

5x10^{-4} \text{ mol dm}^{-3} \text{ KCl}

\[ \frac{V_{ads}}{kT} \]

\[ V_{min} \]

<table>
<thead>
<tr>
<th>CURVE</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>0.73</td>
</tr>
<tr>
<td>2</td>
<td>0.64</td>
</tr>
<tr>
<td>3</td>
<td>0.55</td>
</tr>
</tbody>
</table>

5x10^{-3} \text{ mol dm}^{-3} \text{ KCl}

\[ \frac{V_{ads}}{kT} \]

<table>
<thead>
<tr>
<th>CURVE</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.91</td>
</tr>
<tr>
<td>2</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Figure 5.15 Comparison of Experimental and Predicted (Case 1 geometry) Fractional Coverage versus K for PSL(+21) / PSL(-3).

(o = PVA-coated particles (d=15nm); x = uncoated)
i) Treatment of the Mixed Double Layer

The distribution of ions close to a heteroaggregate, which is comprised of both cationic and anionic particles in a complicated spatial arrangement, will undoubtedly be complex. The model describes this situation by assuming additivity of the contributions of each of the particles in the heteroaggregate. Clearly this is a rather simplistic approach, but one which is difficult to assess in the absence of a solution for a Poisson-Boltzmann equation for such a complicated multi-body problem. An indication of the accuracy of the approach adopted may be gained, however, by studying the discrepancy between $\theta_{\text{model}}$ and $\theta_{\text{eq}}$ as a function of $\kappa$. For small values of $\kappa$ extensive overlap of the double layers of particles comprising the heteroaggregate would be expected, whereas for large values of $\kappa$ less overlap will occur. Therefore simple additivity is expected to be most accurate for large $\kappa$. Comparison of $\theta_{\text{model}}$ and $\theta_{\text{eq}}$ show the opposite effect, however, for both model geometries. Whilst not implying that simple additivity is accurate, this observation nevertheless does suggest that the model may require other improvements.

In the work reported thus far, constant surface potential equations were used to describe the double layer interactions. Use of a constant surface charge equation (2.30) did not lead to significantly different predictions for the systems studied here. Significant differences would be expected, however, if the magnitude of $|\psi_{01}|$ and $|\psi_{02}|$ differed greatly; in that case, pairwise repulsion
between the oppositely charged large and small particles would be predicted (at small distances of separation) by the constant charge model (see Figure 2.6), whereas the constant potential model (equation (2.26), Figure 2.4) would predict attraction.

It was decided not to incorporate the BMRF equation (2.29) in the model since this would have added greatly to the complexity of the calculations, whilst not addressing the question of additivity.

ii) Geometrical Considerations

The two cases of the kinetic model place very different constraints on particle adsorption, despite both being based on an essentially hexagonal geometry.

Case 1 geometry (Figure 5.11a)) implies that the relaxation of a hexagonal lattice of adsorbed particles occurs prior to the approach of an adsorbing particle. The result is a completely uniform hexagonal array of adsorbed particles (which concurs with experimental observations, at least when \( a_1 \gg a_2 \)). This model can be criticised on the following grounds. Firstly, the adsorbed particles in reality are only likely to rearrange to accommodate an incoming particle under its repulsive influence (rather than before it approaches, as the model implies). Consequently the model will underestimate the energy barrier to adsorption (and thus overestimate \( \theta \)), because the adsorbed particles of the model are constrained to be further away from the incoming particle than they would be in reality. In addition, the model assumes that the adsorbed particles are completely free to move laterally at the surface, in the timescale of the approach of a "new" particle from the bulk dispersion.
The implications of case 2: geometry (Figure 5.11b)) are very different. Here a complete hexagonal array of adsorbed particles already exists and does not relax as the adsorbing particle approaches; the adsorbing particle must fit into a "triangular" gap in the array. If the energy barrier to adsorption in this configuration was below the threshold value ($V_{\text{crit}}$), then adsorption into all the equivalent triangular gaps would occur, and a "quantum jump" in coverage would be predicted. An alternative way of regarding this version of the model is to consider that after adsorption of a particle into a triangular gap, the whole array then relaxes to a new hexagonal configuration into which the next incoming particle then attempts to fit. The distinction between these two stages (the first with no relaxation, the second with unopposed relaxation) is somewhat artificial, and probably results in an overestimate of the energy barrier to adsorption, due to the adsorbed particles being constrained to be too close to the incoming one.

A physically more realistic model, which still retains the essentially hexagonal symmetry of the original model, would be one in which the initial configuration is identical to case 2 geometry, but which allows the adsorbed array to rearrange under the repulsive influence of the incoming particle. In this case the final fractional coverage would be determined by a balance of the following terms:

1) "normal" attraction between the incoming particle and the large particle (the same as for case 1 and case 2 geometry),
2) repulsion between the incoming particle and its \( z(=3) \) nearest adsorbed neighbours, which are displaced laterally (similar to case 2 of the model except that a more complicated relationship between distances \( h \) and \( H \) would exist as the array relaxes),

3) "second-order" repulsion between the \( z \) displaced particles and their neighbours (this "knock-on" effect may radiate from the adsorbing particle for a considerable distance),

4) a frictional force, acting between adsorbed particles and the large particle, which will oppose rearrangement of the array and be proportional to the strength of the normal attraction (and thus presumably influenced by the presence of adsorbed PVA).

It would also be instructive to develop a model based upon those discussed above, but which does not involve the constraint of adsorbed particles to a hexagonal array. This would be especially advantageous for systems where the radius ratio \( (a_1/a_2) \) is small, making hexagonal packing of adsorbed spheres on a large sphere difficult to achieve on geometric grounds. A random, non-hexagonal, array could be computer-generated by a method similar to that of Vold\(^{140}\). In this simulation, a succession of small particles would be linearly projected, from random directions, towards a fixed large central particle of opposite charge. The energy of approach of each successive small particle would be calculated in a similar manner to that described in Section 5.5.1, except that the geometry of approach would now be dictated by the positions of the previously simulated particles. Each small particle would be permanently fixed where it
had first "struck" the large particle, i.e. no rearrangement of the array could take place. The final coverage (θ_{model}) would be attained when all the sites for which V_{max} < \nu_{crit} had been filled. This simulation would be repeated many times to generate an average value for θ_{model}. It would be of interest to compare the heteroaggregate morphologies predicted by this method with a hexagonal array, and with the experimental (freeze-drying/SEM) results.

5.5.5 A Thermodynamic Model for Particle Adsorption

In order to investigate the effect of various parameters upon the expected equilibrium value of θ, the following simplistic thermodynamic model was devised.

At equilibrium, the chemical potentials of adsorbed and unadsorbed small particles will be equal, as described by equation (5.9).

\[ \mu^\sigma = \mu^d \]  

(5.9)

In this equation \( \mu^\sigma \) is the chemical potential per adsorbed small particle, and \( \mu^d \) is the chemical potential per unadsorbed small particle.

By definition, equation (5.9) can be written in the following form,

\[ u^\sigma - T s^\sigma = u^d - T s^d \]  

(5.10)

where \( u \) and \( s \) are the enthalpy and entropy, respectively, of a small particle. For the purposes of this model, only configurational entropy (s_{config}) terms will be considered, and it will be assumed
that the thermal entropy is the same for adsorbed and unadsorbed particles. In addition, if the adsorbed particles are assumed to be fixed in position \( s_{\text{config}}^a \) will be zero. Assuming that \( u_d = 0 \) (i.e. there is no enthalpic contribution from interparticle interactions, since the bulk concentration of small particles used was very small), equation (5.10) reduces to the following expression.

\[
\zeta^2 = -T_s s_{\text{config}}^d \tag{5.11}
\]

\( \zeta^2 \) is the sum of the (normal) energy of attraction between a small and large particle (\( V_{12} \) when \( H=0 \)), and the (lateral) energy of repulsion between neighbouring adsorbed particles (\( V_{22} \) when \( h=b \)). These parameters have been discussed previously in relation to the kinetic model (Section 5.5.1).

Assuming a hexagonal array of adsorbed particles (i.e. \( z=6 \)), equation (5.11) can be re-written in the following form.

\[
V_{12}(H=0) + 6V_{22}(h=b) + T_s s_{\text{config}}^d = 0 \tag{5.12}
\]

For the kinetic model \( V_{12}(H) \) and \( V_{22}(h) \) were calculated using equation (2.26) or (2.27). However, both these equations predict that \( V_{12} \to \infty \) as \( H \to 0 \), and consequently the following approximate expression was used.

\[
V_{12}(H=0) = 4\pi \varepsilon \varepsilon_0 (a_1 + 5) \xi_1 \xi_2 \tag{5.13}
\]

Equation (5.13) is a limiting case of equation (2.26) where \( \exp(-\kappa H) \ll 1 \) (i.e. double layer overlap is small) and \( a_1 \gg a_2 \). The first of these conditions clearly does not hold when \( H=0 \).
Similarly $V_{22}(h=b)$ may be described by equation (5.14), when $\exp(-\kappa b) \ll 1$.

$$V_{22}(h=b) = 2\pi \varepsilon_0 (a+b) \zeta_2^2 \exp(-\kappa b) \quad (5.14)$$

The configurational entropy of an unadsorbed particle, $s^d_{\text{config}}$, may be estimated very approximately (for dilute dispersions) using equation (5.15)\textsuperscript{141}.

$$s^d_{\text{config}} = k \ln \frac{V}{v} \quad (5.15)$$

In this equation, $v$ is the volume of a "small" latex particle (species 2), and $V$ is the total volume which that particle can occupy, i.e. the volume of dispersion. For the purposes of the calculations presented below, $V$ was taken to be 10 cm$^3$, although the predicted value of $\theta$ was not critically dependent upon $V$.

Combination of equations (5.12) to (5.15) allows prediction of the equilibrium adsorbed particle spacing ($b$), and hence the equilibrium fractional particle coverage ($\theta$).

Predicted equilibrium values of $b$ and $\theta$ for the system PSL(+21)/PSL(-3)/no PVA are presented in Table 5.5, together with analogous predictions of the kinetic model, as well as experimental data. Equilibrium coverages predicted by the thermodynamic model rise with increasing $\kappa$, but are in excess of experimentally observed coverages and the predictions of case 1 of the kinetic model. Despite the very approximate expressions used to calculate $V_{12}$ and $V_{22}$ in the thermodynamic model, these results seem to support the proposition that the extent of particle adsorption is determined kinetically rather than thermodynamically.
Table 5.5

Comparison of Experimental Pseudo-Equilibrium Adsorption Results with Predictions of the Thermodynamic and Kinetic Models, for the System PSL(+21)/PSL(-3)/no PVA

<table>
<thead>
<tr>
<th></th>
<th>$10^{-7} \times \kappa \ (\text{m}^{-1})$</th>
<th>$b \ (\text{nm})$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Results</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1.0</td>
<td>240</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>144</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>23.3</td>
<td>104</td>
<td>0.40</td>
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<tr>
<td><strong>Thermodynamic Model</strong></td>
<td></td>
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<tr>
<td>1.0</td>
<td>78</td>
<td>0.49</td>
<td></td>
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<tr>
<td>7.4</td>
<td>17</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>23.3</td>
<td>1</td>
<td>0.99</td>
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<tr>
<td><strong>Kinetic Model (Case 1)</strong></td>
<td></td>
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</tr>
<tr>
<td>1.0</td>
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<tr>
<td>7.4</td>
<td>58</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>23.3</td>
<td>22</td>
<td>0.80</td>
<td></td>
</tr>
</tbody>
</table>
5.6 Kinetics of Particle Adsorption

The kinetics of particle adsorption was studied as a function of particle concentration and size ratios, and electrolyte concentration, for both PVA-coated and uncoated latex particles. The characteristic shape of all the $\Gamma_a$ versus time curves, as determined by freeze-drying/SEM, is depicted in Figure 5.16. Plate 5.5 a)-c) illustrates the increase of $\Gamma_a$ with time, for the system PSL(+21)/PSL(-4)/5 x 10^{-4} \text{ mol dm}^{-3} \text{ KCl/no PVA}.

The kinetic data were treated on the basis of a Langmuir-type model\textsuperscript{142}, which accounts for the reduction in surface area available for adsorption as fractional coverage increases. In the case of irreversible gas adsorption, this model takes the form

$$- \frac{dn}{dt} = kn(1 - \Theta)$$ \hspace{1cm} (5.16)

where $n$ is the number of unadsorbed gas molecules, and $k$ is the rate constant for adsorption. The $(1 - \Theta)$ term is sometimes referred to as a "blocking factor". By analogy with equation (5.16), particle adsorption onto a surface (or larger particle) can be described by equation (5.17).

$$\frac{d\Gamma_a(t)}{dt} = k_{\text{ads}} \cdot \left[n_0 - N_+ \Gamma_a(t) \right] \cdot \frac{1 - \frac{\Gamma_a(t)}{\Gamma_{\text{eq}}}}{\text{concentration "blocking term" factor}}$$ \hspace{1cm} (5.17)

In this equation -

$\Gamma_a(t) = \text{the number of small particles adsorbed per large particle at time } t$
Figure 5.16 Characteristic $T_a$ versus Time Curve
Plate 5.5

Evolution With Time (t) Of PSL(+21)/PSL(-4) Heteroaggregates Formed In 5x10^{-4} moldm^{-3} KCl Solution

a) $t = 1$ minute  

b) $t = 10$ minutes

c) $t = 300$ minutes
\[ n_0 = \text{the initial number concentration of small particles} \]
\[ N_+ = \text{the number concentration of large particles (assumed to be invariant with } t) \]

\[ \Gamma_{eq} = \Gamma_a(t) \text{ as } t \to \infty ("\text{pseudo-equilibrium coverage}"). \]

\( k_{ads} \) was determined (using the non-integral form of equation (5.17)) by determining \( \Gamma_a \) and \( d\Gamma_a/dt \) directly from the \( \Gamma_a \) versus \( t \) curve. An integral form of equation (5.17) was used by Vincent et al., and took the form

\[
\ln \left[ \frac{n}{n-n_f} \right] = \ln \left[ \frac{n_0}{n_0-n_f} \right] + \left[ \frac{n_f}{n_0-n_f} k_{ads} N_+ t \right] \quad (5.18)
\]

where

\[ n = \text{the number concentration of unadsorbed particles at time } t \]
\[ n_f = n \text{ as } t \to \infty. \]

In this case a plot of \( \ln(n/n-n_f) \) versus \( t \) should give a straight line of slope \( (n_f/n_0-n_f)N_+k_{ads} \). However, it was found for the results reported here that this approach did not yield linear plots, but rather ones of the form shown schematically in Figure 5.17. The initial decrease in slope (and hence \( k_{ads} \)) may be due to a decrease in electrostatic attraction between large and small particles as \( \Gamma_a \) increases. The subsequent increase in slope is thought to be an artefact caused by the \( n/(n-n_f) \) term rising sharply as \( n \) approaches \( n_f \). This makes the treatment very sensitive to the value of \( n_f \), the accuracy of which is limited by the fact that \( \Gamma_{eq} \) (and hence \( n_f \)) are determined for large, but not infinite, \( t \).
Figure 5.17 Kinetic Results for System PSL(+21) / PSL(-4) / 5 x 10^{-4} \text{ mol dm}^{-3} \text{ KCl}, Plotted According to Equation (5.17)
5.6.1 The Effect of Particle Concentration Ratio

The kinetics of adsorption in the system PSL(+21)/PSL(-4)/5 x 10^-4 mol dm^-3 KCl/no PVA was studied for three initial concentrations of anionic latex (n_0) whilst keeping the concentration of PSL(+21) (N_+) constant. All three small particle concentration regimes corresponded to the "plateau region" of the θ versus PSL(-4) concentration isotherm (Figure 5.8).

The three Γ_a versus t curves obtained are shown in Figure 5.18, and a corresponding k_ads versus θ graph is shown in Figure 5.19. The apparent independence of the latter plot on n_0 is noteworthy.

5.6.2 The Effect of Particle Size Ratio

Γ_a versus t results were obtained for the adsorption of PSL(-1), PSL(-4), PSL(-3) and PVDC(5) onto PSL(+21), all in 5 x 10^-4 mol dm^-3 KCl solution, in the absence of PVA. Corresponding k_ads versus θ plots are presented in Figure 5.20. Two main features are noteworthy:

i) there is an approximately linear decrease of k_ads with increasing θ;
ii) the initial rate constant (k_ads as θ → 0) increases with decreasing diameter of the adsorbing particle. This trend is expected since the diffusion constant for the adsorbing species (D_2) is proportional to a_2^-1 (see Section 2.7).

5.6.3 The Effect of Electrolyte Concentration

Γ_a versus t curves for the system PSL(+21)/PSL(-3)/no PVA at four different electrolyte concentrations (I), are shown in Figure 5.21.
Figure 5.18 Effect of Small Particle Concentration ($n_o$) on $\Gamma_t$ versus $t$ Curves for the System PSL (+21) / PSL (-4) / 5.0 x 10^{-4}$ mol dm$^{-3}$ KCl (no PVA) ($N_+ = 6.86 \times 10^6$ cm$^{-3}$).
Figure 5.19 Particle Adsorption Rate Constant, $k_{ads}$ versus $\theta$ for the Adsorption of PSL (-4) onto PSL (+21) in $5 \times 10^{-4}$ mol dm$^{-3}$ KCl at 3 different PSL (-4) concentrations (no PVA)
Figure 5.20 Particle Adsorption Rate Constant, $k_{\text{ads}}$, versus $\theta$ for the Adsorption of Four Anionic Latexes onto PSL(+21) in $5 \times 10^{-4}$ mol dm$^{-3}$ KCl (no PVA)

$10^{-11} \times k_{\text{ads}}$ /cm$^3$ s$^{-1}$

- $\triangle$ PVDC, $a_2 = 58$ nm
- $\square$ PSL(-3), $a_2 = 90$ nm
- $\times$ PSL(-4), $a_2 = 160$ nm
- $\circ$ PSL(-1), $a_2 = 348$ nm
Figure 5.21 Particle Coverage, $\Gamma_a$, versus Time for the Adsorption of PSL (-3) onto PSL (+21) at a range of KCl concentrations (no PVA).

($N_+ = 6.81 \times 10^6 \text{ cm}^{-3}; n_o = 7.17 \times 10^9 \text{ cm}^{-3}$)
As I is increased the initial rate of particle adsorption falls and the final coverage ($\Gamma_{eq}$) increases (as discussed in Section 5.4.3). Corresponding $k_{ads}$ versus $\theta$ plots are shown in Figure 5.22.

The observed relationship between initial adsorption rate and I can tentatively be ascribed to the range of the electrostatic attraction between the large and small particles. At low I attraction begins at greater interparticle separations than at higher I, making "reactive collisions" more frequent.

5.6.4 The Effect of Adsorbed PVA

Figure 5.23 shows $\Gamma_a$ versus t curves for the system PSL(+21)/PSL(-4)/5 x 10^{-4} mol dm^{-3} KCl both in the presence and absence of adsorbed PVA. Similar results were obtained for the adsorption of PSL(-1) onto PSL(+21). $k_{ads}$ versus $\theta$ plots for PVA-coated and uncoated PSL(+21)/PSL(-4) and PSL(+21)/PSL(-1) mixtures are shown in Figure 5.24.

The reduced rate of adsorption in the presence of adsorbed PVA is probably due to the smaller diffusion coefficients of PVA-coated particles, compared with uncoated ones. This point is discussed in Section 5.6.7, below.

5.6.5 An Electrophoretic Study of Particle Adsorption Kinetics

In addition to freeze-drying/SEM, the kinetics of particle adsorption was observed indirectly by following the change with time of the electrophoretic mobility of the large particles. The mobilities of species present in a mixture of PSL(+21) and PSL(-1) were measured using a "Penkem 3000 electrokinetics analyser". This
Figure 5.22 Particle Adsorption Rate Constant, $k_{ads}$, versus $\theta$ for the Adsorption of PSL (-3) onto PSL (+21) at a range of KCl concentrations (no PVA).

$10^{14} \times k_{ads}$ (cm$^3$ s$^{-1}$)

- $\Delta = 1 \times 10^{-3}$ mol dm$^{-3}$ KCl
- $\circ = 1 \times 10^{-4}$ mol dm$^{-3}$ KCl
- $\square = 5 \times 10^{-4}$ mol dm$^{-3}$ KCl
- $\times = 1 \times 10^{-5}$ mol dm$^{-3}$ KCl

$\theta_{eq}$ values

($\theta_{eq}$ for $5 \times 10^{-3}$ mol dm$^{-3}$ = 0.45)
Figure 5.23 Particle Coverage, $\Gamma_a$, versus Time for the Adsorption of PSL(-4) onto PSL(+21) in $5 \times 10^{-4}$ mol dm$^{-3}$ KCl solution. ($N_+ = 6.81 \times 10^6$ cm$^{-3}$; $n_0 = 5.40 \times 10^9$ cm$^{-3}$)
Figure 5.24 Particle Adsorption Rate Constant, $k_{ads}$, versus $\theta$ for the Adsorption of PSL(-1) and of PSL(-4) onto PSL(+21) in $5 \times 10^{-4}$ mol dm$^{-3}$ KCl, both in the presence and absence of PVA.

$10^{11} \times k_{ads}$

$/$ cm$^3$ s$^{-1}$

$\Delta$ + 21/-4

○ + 21/-4/PVA

□ + 21/-1

× + 21/-1/PVA

$\theta$
combination of particles was used because both species could be detected simultaneously; in contrast, light scattered by smaller adsorbing particles (PSL(-4), PSL(-3) and PVDC(5)) was obscured by that from the larger particles. Figure 5.25 shows the evolution with time of the probability versus electrophoretic mobility histogram for the system PSL(+21)/PSL(-1)/5 x 10^{-4} mol dm^{-3} KCl/no PVA. As adsorption proceeds, the peak due to bare PSL(+21) particles disappears, and a "heteroaggregate peak" moves towards negative mobilities. This heteroaggregate peak eventually superimposes upon the peak due to individual PSL(-1) particles. In contrast to the corresponding freeze-drying/SEM results (Section 5.6.2), the electrophoresis data suggest that a wide range of particle coverages (Γ_a) can occur at a given time. This may be due to ongoing aggregation during mobility measurements (which each took approximately 1 minute); additionally, mobility may be very sensitive to small changes in Γ_a in this region.

Particle adsorption rates were not quantified using electrophoresis, for the following reasons: i) a time delay of approximately three minutes between measurements was unavoidable, making it difficult to study the early stages of adsorption; ii) as described in Section 5.4.5 the mobility of a heteroaggregate is difficult to relate to θ, especially for high coverages; and iii) the hydrodynamic characteristics within the "feed line" from the sample container to the electrophoresis cell were ill-defined and may have affected the rate of adsorption.
FIGURE 5.25

ELECTROPHORETIC MOBILITY HISTOGRAM FOR
PSL(+21) / PSL(-1) / 5x10^{-4} mol dm^{-3} KCl / NO PVA
AT A SERIES OF TIMES AFTER MIXING

$t= 3$ minutes

$PSL(-1) ightarrow PSL(+21)$

$t= 12$ minutes

$t= 25$ minutes

$t= 80$ minutes

$-1.00E-07$ to $1.00E-07$
5.6.6 Prediction of Adsorption Rate Constants

Predictions of the rate of adsorption of small particles onto larger ones be made using Smoluchowski's treatment (Section 2.7). For a "square-well" attractive potential, the initial rate of aggregation of particles of type 2 with a single particle of type 1, is given by equation (2.43), which is reproduced below.

\[
\frac{-dn_2}{dt} = 4\pi R(D_1+D_2)n_0 \quad (2.43)
\]

In the above equation, R is the distance between the centres of the aggregating particles at the onset of attraction.

Equation (2.43) can be applied directly to the adsorption of small anionic latex particles (type 2) onto a single large cationic latex particle (type 1). In this case equation (5.18) holds.

\[
\frac{-dn_2}{dt} = \frac{d\Gamma_a}{dt} \quad (5.18)
\]

Combination of equations (5.18) and (2.43) with the Langmuirian rate equation (5.16) leads, in the limit as \( t \to 0 \), to the following expression for the initial rate constant for adsorption.

\[
(k_{ads})_{t=0} = 4\pi R(D_1+D_2) \quad (5.19)
\]

Comparisons between predicted initial rate constants, calculated using equation (5.19), and experimentally determined values are shown in Table 5.6. For the purposes of these calculations values of R were estimated using equation (5.20).
Table 5.6

Predicted and Observed Initial Rate Constants for Particle Adsorption

<table>
<thead>
<tr>
<th>Latex Mixture</th>
<th>KCl Concentration (mol dm⁻³)</th>
<th>(k_{ads})t=0 (x 10^{11} cm³s⁻¹)</th>
<th>Predicted</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>x = 4*</td>
<td>x = 10*</td>
</tr>
<tr>
<td>PSL(+21)/PSL(-1)</td>
<td>5 x 10^{-4}</td>
<td>1.74</td>
<td>1.84</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>PSL(+21)/PSL(-4)</td>
<td>5 x 10^{-4}</td>
<td>2.83</td>
<td>3.05</td>
<td>7.0 ± 0.5</td>
</tr>
<tr>
<td>PSL(+21)/PSL(-3)</td>
<td>5 x 10^{-5}</td>
<td>4.56</td>
<td>4.86</td>
<td>7.0 ± 1</td>
</tr>
<tr>
<td>&quot;</td>
<td>5 x 10^{-4}</td>
<td>5.78</td>
<td>7.92</td>
<td>14.0 ± 2</td>
</tr>
<tr>
<td>&quot;</td>
<td>5 x 10^{-3}</td>
<td>4.42</td>
<td>4.52</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>PSL(+21)/PVDC(5)</td>
<td>5 x 10^{-4}</td>
<td>6.71</td>
<td>7.17</td>
<td>11.0 ± 3</td>
</tr>
</tbody>
</table>

PSL(+21)/PSL(-1)/PVA

| S = 15 nm                     | 5 x 10^{-4}                   | 1.68                             | 1.77       | 1.2 ± 0.4|
| S = 30 nm                     | 5 x 10^{-3}                   | 1.63                             | 1.72       |          |

PSL(+21)/PSL(-4)/PVA

| S = 15 nm                     | 5 x 10^{-4}                   | 2.65                             | 2.81       | 5.0 ± 0.5|
| S = 30 nm                     | 5 x 10^{-3}                   | 2.46                             | 2.62       |          |

Note: * x is the assumed range of double layer interactions, in "Debye Lengths" (see equation 5.20).
Values of $x = 4$ and $x = 10$ were assumed. This represents the onset of attraction at interparticle distances of 4 and 10 "double layer thicknesses" (or "Debye lengths"), respectively; a distance of approximately $7/\kappa$ is predicted by classical expressions such as the HHH equation (2.26).

Diffusion coefficients were calculated according to the Stokes-Einstein equation (2.42), except for PVA-coated particles, where a modified form was used (equation 5.21).

\[
D_i = \frac{kT}{6\pi n (a_i + \delta)}
\]

Calculations were carried out based on adsorbed PVA-layer thicknesses ($\delta$) of 15 nm and 30 nm.

5.6.7 Discussion of the Adsorption Rate Data

Agreement between the observed and predicted initial adsorption rate constants is reasonable. The observed decrease in $(k_{ads})_{t=0}$ with increasing diameter of the adsorbing particle is predicted, as is the decrease in rate constant with increasing electrolyte concentration. However, the observed rate constants were larger than predicted. An explanation may be that the range of electrostatic attraction between oppositely-charged particles is considerably greater than predicted by classical double layer theory, and is of the order of tens of Debye lengths.
Hydrodynamic forces (e.g. those introduced by stirring) could also, in principle, cause the disparity between the predicted and experimental initial rate constants. Whereas Smoluchowski's treatment assumes that aggregation is purely diffusion-controlled, Spielman and Cukor\textsuperscript{143} showed that the imposition of an external hydrodynamic force can increase the rate of capture of small particles by larger ones. However, in the mixing conditions used in this work, such forces would exist only for a very short time, and it thus seems unlikely that they account for the observed rates. It is noteworthy that hydrodynamic forces can also cause a decrease in the rate of aggregation, because liquid must drain from between particles as they approach. Spielman\textsuperscript{144}, and Honig \textit{et al.}\textsuperscript{145}, showed that for this reason aggregation rates may typically be two to three times slower than predicted by Smoluchowski's theory.

The smaller rate of adsorption of PVA-coated particles, compared with uncoated ones, is also predicted by the modified Smoluchowski theory, although the observed size of this effect was larger than predicted.

In principle it would be possible to combine the models for the initial adsorption rate and pseudo-equilibrium coverage, in order to predict adsorption rates at intermediate times. This could be achieved using Fuchs' modification to Smoluchowski's treatment of diffusion-controlled aggregation\textsuperscript{85} (Section 2.7). The adsorption rate for any given $\Theta$ will depend on the form of the analogous $V_{\text{ads}}$ versus $H$ curve, calculated according to the "kinetic" model for pseudo-equilibrium coverage. Owing to the steep rise in the predicted energy barrier to
adsorption as \( \theta \) increases (as illustrated in Figure 5.13), \( k_{\text{ads}} \) is predicted to be invariant with \( \theta \) up to a threshold coverage, above which it falls rapidly to zero. In contrast, an approximately linear decrease in \( k_{\text{ads}} \) with increasing \( \theta \) was observed experimentally. This qualitative difference between predicted and experimental data suggests that additional factors may influence the rate of adsorption.

A possible reason for the disparity between predicted and experimental data is the decrease in the diffusion coefficient of a large particle as the number of adsorbed small particles increases; this effect is likely to be small, however, since the relative diffusion coefficient \( D_{12} \) is dominated by the diffusion coefficient of the smaller particle. A more plausible explanation is that the electrostatic attraction between a heteroaggregate and an incoming small particle is reduced in proportion to the overall charge on the heteroaggregate. As discussed in Section 5.4.5, however, adsorption continues well beyond the point of overall charge reversal. Therefore, the relationship between particle adsorption rate and overall charge is not simple, which serves to emphasise the complicated nature of the charge distribution around a heteroaggregate.
5.7 Conclusions and Suggestions for Further Work

The results presented in this chapter demonstrate the value of freeze-drying/SEM for the study of particle adsorption in mixtures of oppositely-charged particles of different sizes. The technique is particularly advantageous in the study of adsorption kinetics, since the process can be "stopped" virtually instantly, and at any time, simply by freezing a small aliquot of dispersion. In this respect it is a preferable technique to particle sedimentation, for example, wherein aggregation may still be occurring during the determination of $\Theta$.

Theories have been presented in the foregoing Sections which allow prediction both of initial rates of adsorption and "pseudo-equilibrium" fractional particle coverages. In both cases, the main experimental trends were predicted, but in neither case was quantitative agreement good. As previously discussed, both the "initial rate" and "pseudo-equilibrium" theories are limited by the accuracy of the equations used to model electrostatic double layer interactions. Kinetic data indicate that attractive interactions may be of longer range than would be predicted classically. Additivity of double layer interaction energies must also be questionable, especially when $\Theta$ is large.

Further information regarding aggregate morphology, especially the ability of adsorbed particles to move laterally, would be useful in the development of a comprehensive model for particle adsorption. This would indicate whether the proposed modification to the "kinetic" model for pseudo-equilibrium adsorption, whereby adsorbed
particles "relax" to accommodate an incoming one, is physically realistic. Such morphological studies may best be carried out by observing adsorption of particles onto a plane surface (a polymer-coated glass slide, for example) using optical microscopy. This would allow real-time observations of lateral movements of adsorbed particles; such observations are impossible using freeze-drying/SEM. In addition, observation and interpretation of spatial arrangements of adsorbed particles on a plane surface would be much easier than on spheres. This would allow the proposal that particles adsorb in essentially hexagonal arrays to be tested, and may lead to the development of a model in which no regular symmetry is imposed.

A number of mixed particle systems closely related to those reported in this Chapter could fruitfully be studied using freeze-drying/SEM. Examples include:

i) binary mixtures where insufficient small particles are present to cover the large particles to their "plateau level", thereby leading to particle bridging aggregation\textsuperscript{24,146}, and

ii) systems exhibiting two-dimensional "raft-like" aggregation of adsorbed particles.
CHAPTER 6

A STUDY OF SEDIMENTATION
IN MIXED DISPERSIONS
A STUDY OF SEDIMENTATION IN MIXED DISPERSIONS

6.1 Introduction

The distribution of particles in a quiescent colloidal dispersion is affected by their rate of sedimentation, and hence by the size of the particles and/or the aggregates which they form. Determination of the particle distribution, in the form of a concentration versus depth profile, can lead, via an incremental method of size analysis,\textsuperscript{147} to an aggregate size distribution for the dispersion.

In the experiments reported here, concentration versus depth profiles were determined using an intrusive sampling technique, by which aliquots were simultaneously removed from four different depths in a column of dispersion. The total particle concentrations of the samples were determined by dry weight analysis.

Sedimentation behaviour of a rutile titanium dioxide dispersion, and of mixed dispersions of rutile and polystyrene latex (either anionic or amphoteric), was studied for a range of pH values. In the case of the mixed dispersions, the polystyrene content of each aliquot was determined using u.v./visible spectroscopy, thus allowing both aggregate size and composition to be investigated.

6.2 Incremental Particle Size Analysis\textsuperscript{147}

Consider a small horizontal volume element, at depth $h$, in a dispersion with an invariant particle (or aggregate) size distribution. Let the particle concentration in this element be $C(h, t)$, where $t$ is the time since the onset of sedimentation. For an initially homogeneous dispersion, the concentration in the element is
equal to the total particle concentration of the dispersion \( (C_0 = C(h, O)) \). As sedimentation proceeds, particles and/or aggregates are lost from the element according to their rates of sedimentation. Thus, the fraction \( C(h, t)/C(h, O) \) represents the proportion of particles or aggregates which sediment with velocities less than \( h/t \).

For dilute dispersions (in practice less than ca. 1% w/w) of spherical particles, a relationship between sedimentation velocity and particle size is given by equation (6.1).

\[
\frac{dh}{dt} = \frac{2a_s^3(e_2-e_1)g}{9\eta}
\]  

In this equation \( \frac{dh}{dt} \) is the terminal sedimentation velocity of a spherical particle of radius \( a_s \) and density \( \rho_2 \), sedimenting in a medium of density \( \rho_1 \) and viscosity \( \eta \), under the influence of a local acceleration \( g \) (due to gravity or an applied centrifugal acceleration).

A plot of \( C(h, t)/C(h, O) \) versus \( a_s \) thus represents a cumulative probability versus size distribution. In the context of an aggregated dispersion, however, \( a_s \) does not represent an absolute aggregate dimension, but rather the radius of a spherical particle of identical density which would sediment at the same rate as the aggregate. As such, \( a_s \) is usually referred to as the "equivalent Stokes radius".

The calculation of equivalent Stokes radii for heteroaggregates is somewhat more complicated than for homoaggregates, owing to the fact that a "composite density" must be ascribed to the former. If the species comprising the heteroaggregates are of unequal density,
this composite density will depend upon the proportion of each species within the aggregates. For any given set of conditions, a range of compositions may exist, but for the purposes of the calculations presented here, average compositions were assumed. In this case, the proportions (by weight) of rutile and latex in the aggregates which have disappeared from depth h (P_R and P_L, respectively), are given by equation (6.2).

\[
P_L = 1 - P_R = \frac{C_L(h,0) - C_L(h,t)}{C_T(h,0) - C_T(h,t)} \quad (6.2)
\]

In this equation C_L and C_T refer to latex concentration and total particle concentration, respectively. The composite density (P_2) is then given by

\[
P_2 = \frac{1}{(P_L/P_L) + (P_R/P_R)} \quad (6.3)
\]

where P_L and P_R are the densities of latex and rutile, respectively.

6.3 Experimental

A 280 cm³ sample of dispersion, at a pH at which it was stable, was placed in a 300 cm³ beaker. The pH of this dispersion was then adjusted by addition, with stirring, of dilute hydrochloric acid or potassium hydroxide solution, as required. Aliquots of the dispersion were withdrawn at up to three different times, using the apparatus illustrated in Figure 6.1, in the following way. With Hofmann clips 1-4 closed, the beaker was raised to the position shown in Figure 6.1 using a "lab-jack". Clips 1-4 were then slowly opened
Figure 6.1. Sedimentation Sampling Apparatus

- 25ml syringe
- Rubber tubing
- Sampling pipette (volume of each bulb ≈ 3cm³)
- Reference level
- 300cm³ beaker
- Lab jack
- Position of Hofmann clip 5
- Position of Hofmann clips 1-4
in sequence, allowing dispersion to enter the capillary tubes. Gentle suction was applied using the syringe, causing the bulbs on each arm of the sampling pipette to be filled slowly and without creating appreciable turbulence in the sample. Clips 1-5 were then closed and the beaker lowered away from the pipette. The four aliquots were drained into vials and their weights were noted. These samples were dried at 70°C and reweighed, and the weight fraction of solids in each aliquot was calculated.

Polystyrene contents of the aliquots were determined in the following manner. 7 cm$^3$ of dichloromethane was added to a known weight (between 4 and 12 mg) of dried material and then sonicated for several minutes to aid dissolution of the polystyrene. Suspended rutile was removed by centrifugation at 120G using an MSE 18 bench-top centrifuge. The polystyrene content of the supernatant solution was determined by measurement of the absorbance of the solution at a wavelength of 262 nm (using a Pye-Unicam SP1800 Spectrophotometer) followed by comparison with an absorbance versus polystyrene concentration calibration curve (Figure 6.2).

When calculating the polystyrene content of the aliquots using the analytical data, account was taken of the adsorption of polystyrene onto rutile particles from dichloromethane (and therefore its removal from the supernatant solution). In order to determine the size of this effect a known weight of rutile was dispersed in a polystyrene/dichloromethane solution of accurately known concentration. This dispersion was rotated end-over-end for 1 hour to prevent settling of the rutile, and to allow equilibration. Centri-
Figure 6.2. Absorbance versus concentration calibration graph for polystyrene dissolved in dichloromethane.
fugation followed by assay for polystyrene (as described above) allowed the amount of polystyrene adsorbed to be calculated. It was found that $0.005 \pm 0.002$ mg of polystyrene adsorbed per 1 mg of rutile (equivalent to a coverage of $0.75 \pm 0.3$ mg/m$^2$). Thus, in most cases, the size of the correction was small in comparison with the polystyrene content of the samples. In addition, when calculating the rutile content of the aliquots, account was taken of their electrolyte content.

6.4 Results

The conditions used for the sedimentation studies fall into four categories, as summarised in Table 6.1.

Table 6.1 Sedimentation Experiment Conditions

<table>
<thead>
<tr>
<th>Experiment Set</th>
<th>Initial Particle Concentration (% w/w)</th>
<th>pH Range</th>
<th>KCl conc$^n$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO$_2$(R-SM3) PSL(-7) PSL(±3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.18</td>
<td>3.3-6.9</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>6.6-7.6</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>0.18 0.16</td>
<td>3.5-5.1</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>0.18</td>
<td>3.5-7.6</td>
<td>$5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

6.4.1 Sedimentation of Rutile Titanium Dioxide

Concentration versus depth profiles for a rutile dispersion at pH 6.9 are shown in Figure 6.3. No significant change in the profile was noted for $t \leq 4$ hours (where $t$ is the time between pH adjustment and sampling), although a depletion in particle concentration at
small depths was detected for measurements made after a period of 24 hours. At pH 5.6 sedimentation was more rapid, as is illustrated in Figure 6.4.

Cumulative probability versus equivalent Stokes radius curves are shown in Figure 6.5 for dispersions at pH 6.9 and at pH 5.6. Corresponding aggregate size distributions are presented in Figure 6.6. A rather narrow size distribution was obtained for the pH 6.9 system, with a mean equivalent Stokes radius, $\bar{a}_S$, of 0.20±0.03 $\mu$m. This value is somewhat larger than that determined for the primary particles using transmission electron microscopy, which indicated a mean particle radius of 0.1±0.03 $\mu$m. This discrepancy may be due to the rutile particles being incompletely dispersed (by ultrasonication) at the beginning of the experiment, or due to slow aggregation at pH 6.9, with a consequent gradual increase in aggregate size during the course of the experiment. The good agreement between the cumulative probability results for samples taken at different times (Figure 6.5) suggests, however, that the size distribution was probably invariant during the pH 6.9 experiment. In contrast, the cumulative probability results for the dispersion at pH 5.6 show poor overlap between data from different sampling times, which probably reflects an increase in aggregate size during the experiment.

Much faster sedimentation was observed for pH values in the range 4.9 to 3.3, as indicated by the concentration profiles for t=2 minutes, which are presented in Figure 6.7. The observed increase in sedimentation rate as the iso-electric point of the rutile particles (pH (i.e.p) = 4.3±0.1) is approached, is in qualitative accordance
Figure 6.3. Concentration versus depth profiles for TiO$_2$ at pH 6.9

Figure 6.4. Concentration versus depth profiles for TiO$_2$ at pH 5.6
Figure 6.5. Cumulative Aggregate Size Distributions for TiO$_2$ at pH 6.9 and 5.6

Figure 6.6. Aggregate Size Distributions for TiO$_2$ at pH 6.9 (□) and pH 5.6 (○)
Figure 6.7. Concentration versus Depth Profiles at \( t = 2 \) minutes, for TiO\(_2\) at pH 3.3 (x), pH 3.9 (□), pH 4.2 (o) and pH 4.9 (Δ).

Figure 6.8. Concentration versus Depth Profiles for PSL (± 3) at pH 7.0.
with the theory of Fuchs\textsuperscript{85}, as described in section 2.7 of this thesis.

6.4.2 Sedimentation of Amphoteric Polystyrene Latex PSL(\pm3)

The sedimentation behaviour of latex PSL(\pm3) was studied for pH values 6.6, 7.1 and 7.6. For dispersions at pH 6.6 and 7.6 no significant sedimentation was detected during a period of 24 hours. However, at pH 7.0, close to the iso-electric point of PSL(\pm3) (pH (i.e.p) = 7.1 \pm 0.1) sedimentation was detected, as is illustrated in Figure 6.8. The corresponding cumulative aggregate size distribution is shown in Figure 6.9, which indicates a median equivalent Stokes radius of ca. 17 $\mu$m for aggregates under these conditions.

No detectable sedimentation occurred for PSL(-7) dispersions with pH values in the range 3.3-6.9.

6.4.3 Sedimentation in Mixed Dispersions of Rutile Titanium Dioxide and Anionic Polystyrene Latex (PSL(-7))

Concentration profiles obtained for a mixture of rutile (0.18\% w/w) and PSL(-7) (0.16\% w/w) at pH 3.5 are shown in Figure 6.10a); sedimentation of both species of particle was detected for t>1 minute. In comparison with results obtained for dispersions of rutile and of PSL(-7) alone, this behaviour is consistent with heteroaggregation between the positively-charged rutile particles and negatively-charged PSL(-7) particles. The proportions of the two species in the aggregates are shown in Table 6.2a). The small range of values of $P_R$ suggests that composition does not vary significantly with aggregate size, which provides some justification for the use of
Figure 6.9. Cumulative Aggregate Size Distribution for PSL (±3) at pH 7.0
Table 6.2  Composition of TiO$_2$/PSL(-7) aggregates in mixed dispersions at pH 3.5, 4.3 and 5.1

<table>
<thead>
<tr>
<th>pH</th>
<th>Depth, h (cm)</th>
<th>Time, t (secs)</th>
<th>$P_R$ (=1-$P_L$)</th>
<th>$10^{-3} \times \rho_2$ (kg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 3.5</td>
<td>2</td>
<td>2100</td>
<td>0.65 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>14400</td>
<td>0.58 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2100</td>
<td>0.64 ± 0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>14400</td>
<td>0.56 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2100</td>
<td>0.61 ± 0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>14400</td>
<td>0.65 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Mean composition</td>
<td></td>
<td></td>
<td>0.62 ± 0.05</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>b) 4.3</td>
<td>2</td>
<td>1800</td>
<td>0.73 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1800</td>
<td>0.71 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>64800</td>
<td>0.64 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1800</td>
<td>0.74 ± 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1800</td>
<td>0.89 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Mean composition</td>
<td></td>
<td></td>
<td>0.74 ± 0.2</td>
<td>2.8 ± 0.6</td>
</tr>
<tr>
<td>c) 5.1</td>
<td>2</td>
<td>1800</td>
<td>0.88 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1800</td>
<td>0.94 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1800</td>
<td>0.91 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1800</td>
<td>0.81 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Mean composition</td>
<td></td>
<td></td>
<td>0.90 ± 0.1</td>
<td>3.2 ± 1.0</td>
</tr>
</tbody>
</table>
an average composition in calculation of composite density $\rho_2$.

Results obtained for a similar mixture at pH 4.3 (close to the iso-electric point of rutile) also provided evidence of hetero-aggregation, as shown in Figure 6.10b) and Table 6.2b). In this case sedimentation was somewhat slower than at pH 3.5. In addition, the proportion of latex in the aggregates ($P_L$) was smaller than that found for the lower pH dispersion medium, which is consistent with homoaggregation of rutile taking place concurrently with hetero-aggregation.

Concentration versus depth profiles obtained for a rutile/PsL(-7) dispersion at pH 5.1, where both species carry a negative surface charge, are illustrated in Figure 6.10c), with the corresponding aggregate compositions being shown in Table 6.2c). In this case, the value of $P_R$ was larger than those obtained for analogous dispersions at pH 3.5 and 4.3, and was close to that expected for homoaggregation of rutile (for which $P_R = 1$).

Cumulative aggregate size distributions for dispersions at the three different pH values are shown in Figure 6.11. A significant feature of these data is the very broad aggregate size distribution at pH 3.5, which suggests that large, possibly ramified, aggregates form when "fast" aggregation occurs between oppositely-charged particle species. Smaller aggregates appear to form when the interparticle attraction is reduced.
Figure 6.10. Concentration versus Depth Profiles for TiO$_2$/PSL(-7) mixtures

a) pH 3.5:

TiO$_2$. PSL(-7) Concentration /% w/w

Depth, h /cm

$C_R(h, 0) = 0.18\%$

$C_L(h, 0) = 0.16\%$

b) pH 4.3:

TiO$_2$. PSL(-7) Concentration /% w/w

Depth, h /cm

$C_R(h, 0) = 0.21\%$

$C_L(h, 0) = 0.16\%$
Figure 6.11. Cumulative Aggregate Size Distributions for TiO$_2$/PSL(-7) mixtures at pH 3.5 (o), pH 4.3 (o) and pH 5.1 (x).
6.4.4 Sedimentation in Mixed Dispersions of Rutile Titanium Dioxide and Amphoteric Polystyrene Latex (PSL(±3))

Concentration versus depth profiles were obtained for rutile/PSL(±3) dispersions at pH 3.5, 6.6, 7.1 and 7.6. At both pH 3.5 (where both particle species carried a positive charge) and pH 7.6 (where both species carried a negative charge) these profiles were invariant, within experimental error, for t≤4 hours. The absence of detectable sedimentation indicates complete dispersion stability in these systems.

At pH 6.6 (between the iso-electric points of rutile and PSL(±3)) the concentration versus depth profiles shown in Figure 6.12a) were obtained. Table 6.3a) shows corresponding values of $P_R$. In comparison with the behaviour of dispersions of rutile and PSL(±3) alone at pH 6.6, these results indicate that heteroaggregation occurred under these conditions. An analogous cumulative aggregate size distribution is shown in Figure 6.13. This distribution is less broad than for mixtures of oppositely-charged rutile and PSL(-7) particles (Figure 6.11), although the median equivalent aggregate radius is ca. 4 μm in both cases; the reason for this difference is not apparent.

Figure 6.12b) shows concentration versus depth profiles for a mixed rutile/PSL(±3) dispersion at pH 7.1 (close to the iso-electric point of PSL(±3)). These results provide a clear indication that heteroaggregation occurred, since homoaggregation of rutile is not expected under these conditions (see section 6.4.1). The proportion of rutile in the aggregates, $P_R$, was smaller in this case than for
Figure 6.12. Concentration versus Depth Profiles for TiO$_2$ / PSL(±3) mixtures

a) pH 6.6:

TiO$_2$, PSL (±3) Concentration /% w/w

Depth, h / cm

KEY: TiO$_2$  
PSL(±3) (Arrows indicate sediment of concentration >0.25%)

$C_R(h,0) = 0.24\% \pm 0.02$
$C_L(h,0) = 0.13\% \pm 0.01$

t = 1 min

t = 3 mins

t = 30 mins

b) pH 7.1:

TiO$_2$, PSL(±3) Concentration /% w/w

Depth, h / cm

$C_R(h,0) = 0.21\% \pm 0.02$
$C_L(h,0) = 0.18\% \pm 0.01$

t = 10 mins

t = 30 mins

t = 2 mins
Figure 6.13. Cumulative Aggregate Size Distributions for TiO$_2$ /PSL(±3) mixtures at pH 6.6 (×) and pH 7.1 (○)
Table 6.3 Composition of TiO$_2$/PSL(±3) aggregates for mixed dispersions at pH 6.6 and 7.1

<table>
<thead>
<tr>
<th>pH</th>
<th>Depth, h (cm)</th>
<th>Time, t (secs)</th>
<th>$P_{R (±1-P_L)}$</th>
<th>10$^{-3} \times \rho_2$ (kgm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 6.6</td>
<td>2</td>
<td>180</td>
<td>0.66 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1800</td>
<td>0.62 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>180</td>
<td>0.67 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1800</td>
<td>0.62 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>180</td>
<td>0.57 ± 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1800</td>
<td>0.62 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>Mean composition</td>
<td></td>
<td></td>
<td>0.63 ± 0.10</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>b) 7.1</td>
<td>2</td>
<td>180</td>
<td>0.53 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1800</td>
<td>0.41 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>180</td>
<td>0.42 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1800</td>
<td>0.42 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>180</td>
<td>0.58 ± 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1800</td>
<td>0.42 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Mean composition</td>
<td></td>
<td></td>
<td>0.46 ± 0.10</td>
<td>1.8 ± 0.1</td>
</tr>
</tbody>
</table>
the equivalent dispersion at pH 6.6 (see Table 6.2), which suggests that homoaggregation between PSL(±3) particles took place in addition to heteroaggregation. By analogy with the results for a homodispersion of PSL(±3) (section 6.4.2) this behaviour is expected. The aggregate size distribution for the rutile/PSL(±3) dispersion at pH 7.1 is shown in Figure 6.13. In this case, the median aggregate size is 10±1 μm, which is between the median sizes determined for rutile/PSL(±3) heteroaggregation (at pH 6.6) and PSL(±3) homoaggregation, and supports the proposition that both hetero- and homo-aggregation occur at pH 7.1.

6.5 Discussion

The results presented in the preceding section demonstrate that sedimentation analysis may successfully be used to study aggregation in a binary dispersion, especially with respect to aggregate composition and size. Unfortunately, proposed experiments to verify these parameters by electron microscopic observation proved non-viable for the reasons outlined in chapter 3 of this thesis.

Although the sedimentation analysis graphs agree well in a qualitative sense with the predictions of classical electrical double layer theory, care must be exercised with regard to their quantitative evaluation. The sedimentation technique used in this work can be criticised on several grounds, not least of which is the ongoing nature of aggregation during sedimentation. This inevitably introduces errors into the aggregate size distributions; nevertheless, comparative studies can still yield useful information. Such
errors would be reduced considerably if a quenching technique such as dilution by electrolyte solution, was used to slow the rate of aggregation; sedimentation analysis could then be used to determine the aggregate size distribution at the time of quenching. However, this method would necessitate very sensitive analytical techniques for the determination of the small particle concentrations involved.

The accuracy of the size distribution results, especially in the sub-micron size range, may also be affected by diffusion and convection currents in the sample, which oppose sedimentation. This problem is compounded by the intrusive nature of the sampling technique, which although carried out carefully in this work, inevitably led to some disruption of the samples. In this respect, a non-intrusive method of sedimentation analysis, such as the ultrasound technique developed by Howe et al.,\textsuperscript{148} may prove advantageous. It is uncertain, however, if it would be possible to study mixed dispersions in this way, since density matching of one species of particle with the dispersion medium would be necessary if aggregate compositions were to be determined. Such matching, by means of varying solvent composition, may in itself perturb the experimental system.\textsuperscript{149}
APPENDICES
APPENDIX 1

Materials and Reagents

Water: Doubly-distilled from an all-Pyrex apparatus, or obtained from a "milli-Q" water filtration system.

Potassium Chloride: B.D.H. analytical grade reagent

Potassium Persulphate: B.D.H. analytical grade reagent

Sodium Metabisulphite: B.D.H. analytical grade reagent

Azo-bis-(isobutylamidine)dihydrochloride: ("V-50"), Wako Chemicals.

Dihexylsulphosuccinate: Aldrich Chemicals

Styrene: B.D.H. reagent. Supplied stabilised by 100-200 ppm t-buylcatechol; distilled under vacuum prior to use.

Vinylidene Chloride: Aldrich Chemicals. Supplied stabilised by ~200 ppm 4-methoxyphenol; used as supplied.

Poly(vinyl alcohol): PVA GLO5 ex-Nippon Ghosei Ltd; viscosity average molecular weight = 22,000. Kindly supplied by Mr R. Croot of this University.

Silica dispersion (Si): Kindly made and supplied by Mr. S. Emmett of this University, by method of Stöber et al. Number average size = 0.60 μm ± 0.05.

Rutile Titanium Dioxide: R-SM3 ex-Tioxide Ltd., kindly supplied by Dr. D. Greenwood, ICI Paints Division.
APPENDIX 2

Calculation of Counting Correction Factors (C)

The requirement for correction factors (C) when counting the number of PVDC(5), PSL(-3) or PSL(-1) particles adsorbed on a PSL(+21) particle (using either SEM or optical microscopy) is discussed in Section 5.3.1. In particular, Figure 5.2 should be referred to in conjunction with this Appendix.

The surface area of a PSL(+21) particle which can be occupied by "counted" PVDC(5) or PSL(-3), or "uncounted" PSL(-1) particles can be calculated in the following way (see Figure A.2). By inspection

\[
\sin \rho = \frac{a_1 - a_2}{a_1 + a_2}, \quad \text{and hence} \quad \cos \rho = \frac{2\sqrt{a_1 a_2}}{a_1 + a_2}. \tag{A2.1}
\]

The area of the solid ring in Figure A.2 is \(2\pi a_1 \sin \rho \cdot a_1 \, d\phi\) and hence the area of the shaded portion of the large sphere (\(SA'\)) is given by

\[
SA' = 2\pi \int_0^\rho a_1^2 \sin \rho \, d\phi = -2\pi a_1^2 \left[ \cos \rho \right]_0^\rho \tag{A2.2}
\]

The ratio (P) of the shaded area to the total surface area of the large sphere is given by

\[
P = \frac{SA'}{4\pi a_1^2} = -\frac{1}{2} \left[ \cos \rho \right]_0^\rho \tag{A2.3}
\]

which in combination with equation (A2.1) leads to

\[
P = \frac{1}{2} - \frac{\sqrt{a_1 a_2}}{a_1 + a_2} \tag{A2.4}
\]
Figure A.2 Geometry for Calculation of Counting Correction Factors

Direction of Observation
(Adsorbed PVDC(5), PSL (-3))

Direction of Observation
(Adsorbed PSL (-1))
Counting correction factors ($C$) are defined as follows:

i) for adsorbed PSL(-1)

$$C = \frac{1}{1-P}$$ 
(A2.5)

ii) for adsorbed PVDC(5), PSL(-3)

$$C = \frac{1}{P}$$ 
(A2.6)
PAGE NUMBERING AS ORIGINAL
APPENDIX 3

Calculation of Theoretical Close-Packed Coverage ($\Gamma_{cp}$)

It can be shown that the fraction of a plane surface which can be occupied by close-packed spheres ($\theta_p$) is given by equation (A3.1).

\[ \theta_p = \frac{\pi}{2\sqrt{3}} = 0.907 \]  (A3.1)

However, this equation will adequately describe the packing of spheres on a sphere only when $a_2/a_1$ tends to zero. Princen and DeVena-Peplinski\textsuperscript{14} considered the case when $a_2/a_1 > 0$, and their method forms the basis for the following calculations.

Consider an array of hexagonally packed discs on the surface of a sphere of radius $a_1+a_2$. In this case the maximum number of small particles which may surround a large one ($\Gamma_{cp}$) can be estimated by equation (A3.2).

\[ \Gamma_{cp} = \frac{2\pi}{\sqrt{3}} \frac{(a_1+a_2)^2}{a_2^2} \]  (A3.2)

This equation is only valid for $a_2/a_1 \to 0$, i.e. packing on a plane, and in reality overestimates the true value of $\Gamma_{cp}$.

A correction can be made to equation (A3.2) by considering hexagonal close-packing of discs onto a sphere of radius $(a_1+a_2-\beta)$, where $\beta$ is defined by Figure A.3. In this case

\[ \Gamma_{cp} = \frac{2\pi}{\sqrt{3}} \frac{(a_1+a_2-\beta)^2}{a_2^2} \]  (A3.3)
Figure A.3. The Geometry of Close-Packing of Small Spheres on a Larger Sphere.
and (by similar triangles)

\[ \beta = \frac{a_2^2}{(a_1 + a_2)} \]  \hspace{1cm} (A3.4)

Now consider the situation where \( a_1 = a_2 \), for which equation (A3.2) predicts \( \Gamma_{cp} = 14.5 \) and equation (A3.3) predicts \( \Gamma_{cp} = 8.2 \). It is clear, however, that for \( a_1 = a_2 \) the true value of \( \Gamma_{cp} \) is 12 (the value for hexagonal close-packing). Equation (A3.3) can be weighted by a factor, \( f \), yielding equation (A3.5).

\[ \Gamma_{cp} = \frac{2\pi}{\sqrt{3}} \frac{(a_1 + a_2 - f\beta)^2}{a_2^2} \]  \hspace{1cm} (A3.5)

For the conditions \( a_1 = a_2 \), \( \Gamma_{cp} = 12 \), it can be shown that \( f = 0.363 \). A more rigorous derivation may reveal that \( f \) is itself a function of \( a_1/a_2 \), but for the purpose of this work the above value was used throughout.

For PVA-coated systems \( a_1 \) and \( a_2 \) in the above equations were substituted by \( (a_1 + \delta) \) and \( (a_2 + \delta) \) respectively, where \( \delta \) is the "thickness" of the adsorbed layer.
APPENDIX 4

Geometry of Approach of a Small Sphere Towards a Larger Sphere with Adsorbed Small Spheres

The model for particle adsorption proposed in Section 5.5 requires that the distance of approach of an adsorbing particle be calculated in terms of both the large/small particle separation (H) and the small/small particle separation (h). This situation is illustrated in Figure A4.1.

It can be seen from Figure A4.1 that the following relationships hold:

\[ AE^2 = AB^2 - EB^2 \]  (A4.1)
\[ AE = AD - ED \]  (A4.2)
\[ ED = EC - DC \]  (A4.3)
\[ EC^2 = BC^2 - EB^2 \]  (A4.4)

Substitution of (A4.4) into (A4.3) gives

\[ ED = (BC^2-EB^2)H - DC \]  (A4.5)

and substitution of (A4.5) into (A4.3) gives

\[ AE = AD - [(BC^2-EB^2)H-DC] \]  (A4.6)

Combination of (A4.6) and (A4.1) gives

\[ AB^2 = [AD-[(BC^2-EB^2)H-DC]]^2 + EB^2 \]  (A4.7)

Inserting known quantities into (A4.7) yields

\[ h = \{[(H+a_2)-([(a_1+a_2)^2-S^2]K-a_1)]^2+S^2\}^H - 2a_2 \]  (A4.8)
Figure A.4.1. The Geometry of Approach of a Small Particle Towards a Larger One.
In the calculations described in Section 5.5, the parameter \( c \) was used to describe the distance between the adsorbed particles, as illustrated by Figure 5.11. This distance is related to distance \( S \) of equation (A4.8) by the following equations, which can be derived using simple geometry:

i) For case 1 geometry

\[
S = \frac{c + 2a_2}{2} \quad (A4.9)
\]

ii) For case 2 geometry

\[
S = \frac{c + 2a_2}{4 \cos 30^\circ} \quad (A4.10)
\]

An analogous derivation allows calculation of \( h \) as a function of \( H \) for PVA-coated particles (equation (A4.11)). The geometry of approach in this case is illustrated in Figure A4.2.

\[
h = \left\{ [(H+a_2) - ((a_1+a_2+2S)^2-SS^2)^{1/2}-a_1)]^2+SS^2 \right\}^{1/2} - 2a_2 \quad (A4.11)
\]
Figure A.4.2. The Geometry of Approach of a Small Particle Towards a Larger One in the Presence of Adsorbed PVA.
APPENDIX 5

The Relationship Between Fractional Particle Coverage (θ) and Spacings (b and c) Between Adsorbed Particles

i) Relationship Between θ and b

θ is defined by equation (5.2) to be equal to \( \Gamma_a/\Gamma_{cp} \), where \( \Gamma_a \) is the number of adsorbed particles and \( \Gamma_{cp} \) is the maximum number of small spheres which theoretically could pack around a larger sphere. A method of calculating \( \Gamma_{cp} \) has been outlined in Appendix 3. An extension of this method allows \( \Gamma_a \) to be calculated as a function of particle sizes \( a_1 \) and \( a_2 \), and the adsorbed particle spacing \( b \) (as defined by Figure 5.11). The resulting equation is

\[
\Gamma_a = \frac{2\pi}{\sqrt{3}} \left( \frac{(a_1+a_2-f\beta_0)^2}{(a_2+\frac{b}{2})^2} \right) \tag{A5.1}
\]

where

\[
\beta_0 = \frac{(a_2+\frac{b}{2})^2}{(a_1+a_2)} ; \quad f = 0.363 \text{ (see appendix 3)}
\]

Combination of equations (A5.1) and (A3.5) leads to the following expression for fractional particle coverage.

\[
\theta = \frac{\left( \frac{(a_1+a_2-0.363\beta_0)^2}{(a_2+\frac{b}{2})^2} \right)}{\left( \frac{(a_1+a_2-0.363\beta)^2}{a_2^2} \right)} \tag{A5.2}
\]

where

\[
\beta = \frac{a_2^2}{(a_1+a_2)}
\]
194

Θ versus b calibration curves for the four mixed systems studied here are shown in Figure A5.1. For systems with adsorbed PVA, $a_1$ and $a_2$ were replaced in the above equations by $(a_1+s)$ and $(a_2+s)$ respectively, where $s$ is the adsorbed layer thickness.

ii) Relationship Between Interparticle Spacings $b$ and $c$

Parameters $b$ and $c$ are defined, in plan view, by Figure 5.11a). In the limit as $a_1/a_2 \to \infty$ the two interparticle spacings are simply related according to equation (A5.3).

$$c = 2(b+a_2)$$ (A5.3)

This equation must be modified, however, for the systems studied here, where $a_1/a_2$ was in the range 3.1 to 18.7.

A side elevation of three particles adsorbed on one large particle is shown in Figure (A5.2). By simple geometry, $b$ and $c$ can be shown to be related according to equation (A5.4).

$$(b+2a_2)^2 = \left(\frac{c}{2} + a_2\right)^2 + \left[a_1+a_2 - \left((a_1+a_2)^2-(\frac{c}{2} + a_2)^2\right)^{1/2}\right]^2$$ (A5.4)

iii) $Θ$ versus $c$ Calibration Curves

$Θ$ versus $c$ calibration curves were computed using a program which combined equations (A5.2) and (A5.4). These curves are shown in Figure A5.3 (and refer to uncoated particles, i.e $s=0$).
Figure A.5.1. \( \theta \) versus \( b \) Calibration Curves.
Figure A.5.2. Geometrical Relationship Between Interparticle Spacings $b$ and $c$. 
Figure A.5.3. \( \theta \) versus \( c \) Calibration Curves
Appendix 6. Programs Used To Compute $V_{ads}$ versus $H$ Curves.

Appendix 6.1. Electrostatic Energy Calculated Using HHF Equation (2.26) (For Constant Potential) or Wiese and Healy Equation (2.30) (For Constant Charge).

```
10 DIM VPLOT(10,200)
20 KEY OFF :CLS
30 PRINT "HHF Calculation ( particle adsorption )"
31 INPUT "const.potential (1) or const.charge (0)"; REG
34 INPUT "No.of curves"; NC
40 INPUT "Large Sphere Radius (microns)"; AL
50 INPUT "Small Sphere Radius (microns)"; AS
60 AL=AL*.000001: AS=AS*.000001
65 INPUT "Polymer thickness (nm)"; DEL
66 DEL=DEL*1E-09
70 INPUT "Large Sphere Zeta Potential (mV)"; ZL
80 INPUT "Small Sphere Zeta Potential (mV)"; ZS
90 ZL=ZL*.001: ZS=ZS*.001
100 INPUT "Temperature (K)"; T
110 INPUT "Kappa (/metre ¥K 1e7)"; K
1^_iß K=K*1E+07
115 INPUT "Furthest distance (nm)"; HF
120 INPUT "Hamaker Constant (Joules*1e21)"; A
125 A=A*9.999999E-22
130 INPUT "Step in Ho (nm)"; ST
140 INPUT "Geometric Factor, z"; Z
170 FOR CURVE=1 TO NC
180 INPUT "Surface Interparticle Separation (microns)"; Sa
190 SA=SA*.000001
200 CLS
210 LL=1
215 IF REG=0 THEN 216: IF REG=1 THEN 217
216 PRINT "Const.charge"
217 PRINT "Const.potential"
220 PRINT "a(large)/microns=", AL, "a(small)/microns=", AS, "Zl(mV)=", ZL,
230 PRINT "Zs(mV)=", ZS, "T=", T, "Kappa (m/)", K, "Hamaker A(J)=", A, "z=", Z,
240 PRINT "Surface Separation, c (microns)=", SA, "Polymer del (nm)=", DEL*1E+09
250 PRINT "h(nm)	Vls/kT	Vss/kT	V_{ads}/kT"
260 PRINT "H	V_{ls}/kT	V_{ss}/kT	V_{ads}/kT"
280 FOR H=.01 TO HF STEP ST; HO=H*1E-09
290 REM HHH electrostatic energy (large/small)
300 T1=AL*AS*(ZL^2+ZS^2)/(AS+AL)
310 T2=2*ZS*ZL/(ZS^2+ZL^2)
320 EXPH=EXP(-1*K*HO)
330 T3=LOG((1+EXPH)/(1-EXPH))
340 EXPHH=EXP(-2*K*HO)
350 T4=LOG(1-EXPHH)
355 IF REG=0 THEN T4=-T4
360 VE=CST*Ti*((T2*T3)+T4)
370 REM vdW attraction (large/small)
380 X=HO/(AS+AL): Y=AS/AL
390 AA=Y/(X^2+(X*Y)+X)
400 AB=Y/(X^2+(X*Y)+X+Y)
410 AC=(X^2+(X*Y)+X)/(X^2+(X*Y)+X+Y)
420 AD=2*LOG(AC)
430 VA=(-1*A/12)*(AA+AB+AD)
450 REM polymer int. (hard wall)
460 IF HO<=2*DEL THEN VTKT=1000
470 GOSUB 1000
480 VADS=VTKT+VTSS: VPLOT(CURVE, LL) = VADS
490 LL=LL+1
500 PRINT USING "H	V_{ls}/kT	V_{ss}/kT	V_{ads}/kT"
```

USING " +£.££$";VSS ;: PRINT USING " +£.££$";VADS
600 NEXT H
605 NEXT CURVE
610 PRINT "Display Graph? Y or N"
620 IF INKEY$<"" THEN 620
630 K$=INKEY$ : IF K$ = "" THEN 630
640 IF K$="Y" OR K$="y" THEN GOSUB 2010
650 LOCATE 23,50: INPUT "Another Separation? Y or N",K$
660 IF (K$="Y")OR (K$="y")THEN SCREEN 0 : GOTO 175
690 SCREEN 0
700 END
1000 REM geometry for particle approach
1010 SS=(SA/2)+AS
1020 GA=HO+AS: GB=(AS+AL+(-*DEL))^2: GC=SS^2
1030 GD=SQRT(GB-GC): GE=(GD-AL)
1040 GF=(GA-GE)^2: GG=SQRT(GF+GC)
1050 REM HOO=appr. sp-ads. sp distance
1060 H00=1-370-(2*AS)
1070 REM HHF electrostatic energy (small/small)
1080 TT1=AS*AS*(2*ZS^2)/(2*AS)
1090 TT2=1
1100 EXPHS=EXP(-I*K*HOO)
1110 TT3=LOG((1+EXPHS)/(1-EXPHS))
1120 EXPHSS=EXP(-2*K*HOO)
1130 TT4=LOG(1-EXPHSS)
1140 VE =CST*TT1+((TT2*TT3)+TT4)
1150 REM van der Waals attraction (small/small)
1160 XX=H00%(2*AS)
1170 TA=(XX^2)+(2*XX)
1180 TB=T6+1
1190 TC=(1/TA)+(1/TB)
1200 TD=2*LOG(TA/TB)
1210 TE=TC+TD
1220 VVA=(-1*A/12)*TE
1230 VSS=VVA+VESS
1240 VSS=VSS/(T*1.3807E-23)
1250 VTSS=VSS*Z
1254 REM polymer int. (hard wall)
1255 IF HOO<=(2*DEL) THEN VTSS=1000
1260 RETURN
1270 STOP
2000 REM graphics routine
2010 SCREEN 2 : CLS
2020 LINE (50,110)-(550,110)
2030 LINE(50,10)-(50,190)
2040 LOCATE 15,68 : PRINT HF ;"nm"
2050 LOCATE 2,1 : PRINT"100 kT"
2055 FOR CURVE=1 TO NC
2060 LL=1
2070 FOR H = .01 TO HF STEP ST
2080 Y=INT(VPLOT(CURVE,LL) +.5)
2090 X=INT(500*H/HF +.5)
2095 IF Y<199 THEN Y=250
2097 IF Y<0 THEN Y=-1
2100 IF H>.01 THEN PSET (X,Y) ELSE LINE -(X,Y)
2110 LL=LL+1
2120 NEXT H
2125 NEXT CURVE
2130 RETURN
Appendix 6.2. Electrostatic Energy Calculated Using BLM Equation (2.27)

10 DIM VPLOT(10,200)
20 KEY OFF:CLS
30 PRINT "Blm/DLVO Calculation ( particle adsorption )"
34 INPUT "No.of curves";NC
40 INPUT "Large Sphere Radius (microns)";AL
50 INPUT "Small Sphere Radius (microns)";AS
60 AL=AL*.000001: AS=AS*.000001
65 INPUT "Polymer thickness (nm)";DEL
66 DEL=DEL*1E-09
70 INPUT "Large Sphere Zeta Potential (mV)";ZL
80 INPUT "Small Sphere Zeta Potential (mV)";ZS
90 ZL=ZL*.001: ZS=ZS*.001
100 INPUT "Temperature (K)";T
110 INPUT "Kappa (/metre * le7)";K
120 K=K*1E+07
170 INPUT "Furthest distance (nm)";HF
180 INPUT "Surface Interparticle Separation (microns)";SA
190 SA=SA*.000001
200 CLS
210 LL=1
220 PRINT "a(large)/microns="AL*1000000!, "a(small)/microns="AS*1000000!, "Zl(mV)="ZL*1000!, "Zs(mV)="ZS*1000!, "T="; T, "Kappa(/m)="; K, "Hamaker A(J)="; A, "z="; Z
230 PRINT "h(nm) Vls/kT Vss/kT Vads/kt"
240 PRINT "f=-(AS*(R-AS)/((AL*(R-AL))))
100 F=AS*ADD/(ADD+AL)
150 BG=SGR(F)+SGR(1/F)
200 I=AL*AS/(AS+AL)
250 DL=(AL*AL)*T
300 DL=(AL*AL)*T
350 EA=AL*AS/(AS+AL)
400 EE=(R*(AL+AS)-(AL^2+AS^2))
450 EC=EA/EB
500 EX=EXP(-1*K*HO)*SGR(I)
550 EY=BG/EB
600 ED=DL^2+OS^2+2+EY
650 EE=LOG(EX+1)
700 EF=DL^2+OS^2-2-EY
750 EB=LOG(1-EX)
800 EH=(ED*EE)+(EF*EB)
850 REM vdW attraction (large/small)
900 X=HO/(AS+AL): Y=AS/AL
950 AA=Y/(X^2+(X*Y)+X)
1000 AB=AA/(X^2+(X*Y)+X)
1050 AC=(X^2+(X*Y)+X)/(X^2+(X*Y)+X)
1100 AD=2*LOG(AC)
1150 VA=(-1*K*HO)*LOG(1-EX)
1200 EH=(ED*EE)+(EF*EB)
1250 REM polymer int. (hard wall)
1300 IF HO<=(2*DEL) THEN VTKT=1000
1350 IF HO<=(2*DEL) THEN VTKT=1000
560 GOSUB 1000
570 VADS=VTKT+VTSS : VPLT(CURVE, LL) = VADS
580 LL=LL+1
590 PRINT USING " +.£££. £"; H,: PRINT USING " +£.££££££££; VTF : PRINT USING " +£.££££££££; VADS
600 NEXT H
605 NEXT CURVE
610 PRINT "Display Graph? Y or N"
620 IF INKEY$<>"" THEN 620
630 K$=INKEY$ : IF K$ = "" THEN 630
640 IF K$ = "Y" OR, K$ = "y" THEN GOSUB 2010
650 LOCATE 23,50: INPUT "Another Separation? Y or N", K$
660 IF (K$ = "Y") OR (K$ = "y") THEN SCREEN 0: GOTO 175
670 SCREEN 0
680 END
1000 REM geometry for particle approach
1010 SS=(SA/2)+AS
1020 GA=HO+AS: GB=(AS+AL+(2*DEL))^2: GC=SS^2
1030 GD=SQR(GB-GC): GE=(GD-AL)
1040 GF=(GA-GE)^2: GG=SQR(GF+GC)
1050 REM HOO=appr. sp-ads. sp distance
1060 HOO=GG-(2*AS)
1070 REM BLM electrostatic energy (small/small)
1080 RR=HOO+(2*AS)
1090 SB=(AS*(RR-AS))/(2*RR)
1100 SC=AS/(RR-AS)
1110 SF=SC*EXP(-1*K*HOO)
1120 SH=LOG(1+SF)
1130 SI=4*(DS^2)*SH
1140 VE=SB*SI*(T^2)*3.264E-17
1150 REM vdW attraction (small/small)
1160 XX=HOO/(2*AS)
1170 TA=(XX^2)+(2*XX)
1180 TB=TA+1
1190 TC=(1/TA)+(1/TB)
1200 TD=2*LOG(TA/TB)
1210 TE=TC+TD
1220 VVA=(-1*A/12)*TE
1230 VE=VEA+VVF
1240 VE=VEA/(T+1.3807E-23)
1250 VTSS=VSS*T
1254 REM polymer int. (hard wall)
1255 IF HOO<=(2*DEL) THEN VTSS=1000
1260 RETURN
1270 STOP
2000 REM graphics routine
2010 SCREEN 2: CLS
2020 LINE (50,110)-(50,190)
2030 LOCATE 15,68 : PRINT HF ; "nm"
2050 FOR CURVE=1 TO NC
2060 LL=1
2070 FOR H= .01 TO HF STEP ST 
2080 XPOINT = 110 - INT(VPLOT(CURVE, LL) +.5)
2090 YPOINT = 50 + INT(500*H/HF +.5)
2095 IF YPOINT>199 THEN YPOINT=250
2097 IF YPOINT<0 THEN YPOINT=0
2100 IF H=.01 THEN PSET (XPOINT,YPOINT) ELSE LINE -(XPOINT,YPOINT)
2110 LL=LL+1
2120 NEXT H
2125 NEXT CURVE
2130 RETURN
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>net Hamaker constant</td>
</tr>
<tr>
<td>A_{ij}</td>
<td>Hamaker constant of a particle</td>
</tr>
<tr>
<td>A_{22}</td>
<td>Hamaker constant of a dispersion medium</td>
</tr>
<tr>
<td>A_{33}</td>
<td>Hamaker constant of a polymer layer plus associated solvent</td>
</tr>
<tr>
<td>a_i</td>
<td>radius of particle species i</td>
</tr>
<tr>
<td>a_s</td>
<td>Stokes' equivalent radius</td>
</tr>
<tr>
<td>b</td>
<td>surface to surface distance between adsorbed small particles</td>
</tr>
<tr>
<td>C</td>
<td>counting correction factor</td>
</tr>
<tr>
<td>c</td>
<td>surface to surface distance between adsorbed small particles (defined by Fig. 5.11)</td>
</tr>
<tr>
<td>C(h,t)</td>
<td>concentration of particles at depth h in a column of dispersion, at time t</td>
</tr>
<tr>
<td>D_i</td>
<td>diffusion coefficient of particles of species i</td>
</tr>
<tr>
<td>D_{ij}</td>
<td>mutual diffusion coefficient of species i and j</td>
</tr>
<tr>
<td>E</td>
<td>applied electrical field strength</td>
</tr>
<tr>
<td>e</td>
<td>fundamental unit of electronic charge</td>
</tr>
<tr>
<td>g</td>
<td>acceleration due to gravity</td>
</tr>
<tr>
<td>H</td>
<td>distance between flat plates or concentric rings</td>
</tr>
<tr>
<td>H_0</td>
<td>surface to surface distance between two spheres</td>
</tr>
<tr>
<td>h</td>
<td>surface to surface distance between an adsorbed small particle and an incoming one</td>
</tr>
<tr>
<td>h</td>
<td>depth in a column of dispersion (Ch. 6 only)</td>
</tr>
<tr>
<td>I</td>
<td>electrolyte concentration</td>
</tr>
</tbody>
</table>
\( J \) - flux of particles towards a fixed central particle

\( J' \) - \( J \) in presence of a repulsive interparticle force

\( k \) - Boltzmann's constant

\( k_{\text{ads}} \) - particle adsorption rate constant

\( M_w \) - weight average molecular weight

\( N_+ \) - number concentration of PSL(+21) particles

\( n \) - concentration of unadsorbed particles at time \( t \)

\( n_0 \) - concentration of unadsorbed particles at \( t = 0 \)

\( n_f \) - concentration of unadsorbed particles at \( t \to \infty \)

\( n^+ \) - concentration of cations

\( n^- \) - concentration of anions

\( n_0^\pm \) - bulk concentration of each ionic species

\( P_L \) - proportion (by weight) of latex in mixed aggregates

\( P_R \) - proportion (by weight) of rutile in mixed aggregates

\( Q_i \) - total charge carried by a particle of species \( i \)

\( q \) - number density of molecules

\( R \) - interparticle centre to centre distance at the onset of attraction

\( r \) - radial distance from the centre of a fixed particle

\( S^\circ \) - entropy of an adsorbed small particle

\( S_d \) - entropy of an unadsorbed small particle

\( S_{\text{config}} \) - configurational entropy

\( S_{\text{th}} \) - thermal entropy

\( T \) - temperature

\( T_{\text{r}} \) - ice recrystallisation temperature

\( t \) - time
u - electrophoretic mobility
\( u^e \) - net interparticle interaction energy of an adsorbed particle
\( u^d \) - interparticle interaction energy of an unadsorbed particle
V - volume of dispersion
\( V_A \) - van der Waals interaction energy
\( V_{ads} \) - predicted energy of approach of a small particle
\( V_E \) - electrostatic interaction energy
\( V_{Efp} \) - electrostatic interaction energy between infinite parallel plates
\( V_{Es} \) - electrostatic interaction energy between spheres
\( V_{el} \) - elastic (volume restriction) interaction energy
\( V_{ij} \) - total interaction energy between particles of species i and j
\( V_{max} \) - maximum on \( V_{ads} \) versus H curve
\( V_{crit} \) - threshold value of \( V_{max} \)
\( V_{mix} \) - osmotic (mixing) interaction energy
\( V_S \) - total steric interaction energy
\( V_T \) - total interaction energy
v - volume of a small particle
\( v_e \) - velocity of a particle in an applied electric field
W - degree of stability
x - distance
\( y_i \) - reduced surface potential of species i
z - number of nearest neighbour adsorbed particles
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z^+$</td>
<td>valence of a cation</td>
</tr>
<tr>
<td>$z^-$</td>
<td>valence of an anion</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>molecular polarisability</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>number of adsorbed small particles per large particle</td>
</tr>
<tr>
<td>$\Gamma_a$</td>
<td>true value of $\Gamma$</td>
</tr>
<tr>
<td>$\Gamma_{cp}$</td>
<td>value of $\Gamma$ for close-packed small particles</td>
</tr>
<tr>
<td>$\Gamma_{EM}$</td>
<td>$\Gamma$ as observed using electron microscopy</td>
</tr>
<tr>
<td>$\Gamma_{eq}$</td>
<td>pseudo-equilibrium value of $\Gamma_a$</td>
</tr>
<tr>
<td>$\Gamma_{OM}$</td>
<td>$\Gamma$ as observed using optical microscopy</td>
</tr>
<tr>
<td>$\Gamma_{PVA}$</td>
<td>weight of physically adsorbed PVA per unit surface area of particles</td>
</tr>
<tr>
<td>$\nabla^2$</td>
<td>Laplacian operator</td>
</tr>
<tr>
<td>$s$</td>
<td>thickness of a physically adsorbed PVA layer</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>relative permittivity of a dispersion medium</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>permittivity of free space</td>
</tr>
<tr>
<td>$\zeta_i$</td>
<td>zeta-potential of particle species $i$</td>
</tr>
<tr>
<td>$\zeta_S$</td>
<td>zeta-potential of a particle species carrying adsorbed PVA</td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity of a dispersion medium</td>
</tr>
<tr>
<td>$\theta$</td>
<td>fractional particle coverage</td>
</tr>
<tr>
<td>$\theta_{cp}$</td>
<td>$\theta$ for close-packed small particles on a larger particle</td>
</tr>
<tr>
<td>$\theta_{eq}$</td>
<td>pseudo-equilibrium value of $\theta$</td>
</tr>
<tr>
<td>$\theta_{model}$</td>
<td>predicted value of $\theta$</td>
</tr>
<tr>
<td>$\theta_p$</td>
<td>$\theta$ for particles close-packed on a planar surface</td>
</tr>
<tr>
<td>$\theta_{Q=0}$</td>
<td>$\theta$ for a heteroaggregate of zero net charge</td>
</tr>
</tbody>
</table>
\( \kappa \) - electrical double layer decay parameter
\( \kappa_{\text{crit}} \) - value of \( \kappa \) at the border of high- and low-affinity particle adsorption regimes
\( \mu^0 \) - chemical potential of adsorbed small particles
\( \mu^d \) - chemical potential of unadsorbed small particles
\( \nu_0 \) - frequency of electronic fluctuations
\( \varrho \) - net volume charge density
\( \rho_1 \) - density of a dispersion medium
\( \rho_2 \) - density of a particle
\( \rho_L \) - density of latex particles
\( \rho_P \) - density of rutile particles
\( \sigma_{oi} \) - surface charge density of particle species \( i \)
\( \sigma_{el} \) - charge density at the plane of shear
\( \vartheta \) - volume fraction
\( \phi_{\text{eq}} \) - pseudo-equilibrium volume fraction of unadsorbed small particles
\( \chi \) - Flory-Huggins interaction parameter
\( \psi \) - electrical potential
\( \psi_0 \) - electrical potential of a surface
\( \psi_{oi} \) - electrical potential of a surface of species \( i \)
\( \psi_d \) - electrical potential at the plane of shear
\( \psi_r \) - electrical potential at radial distance \( r \) from the centre of a particle
\( \psi_X \) - electrical potential at a perpendicular distance \( x \) from a planar surface, or from a surface of a sphere

(in the above cases, subscripts \( i \) and \( j \) refer to particle or surface species \( i \) and \( j \), where \( i = 1 \) or 2 and \( j = 1 \) or 2).
BLM - Bell, Levine and McCartney
BMRF - Barouch, Matijević, Ring and Finlan
DLVO - Derjaguin, Landau, Verwey and Overbeek
DH - Debye-Hückel
EDL - Electrical Double Layer
HHF - Hogg, Healy and Fuerstenau
LN₂ - Liquid Nitrogen
PB - Poisson-Boltzmann
PSL - Polystyrene Latex
PVA - Poly(vinyl alcohol)
PVDC - Poly(vinylidene chloride)
SEM - Scanning Electron Microscopy
SF - Scheutjens and Fleer
TEM - Transmission Electron Microscopy