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UMI
THE ROLE OF POLYMERS AND SURFACTANTS IN FLOCCULATION AND DISPERSION OF AQUEOUS SUSPENSIONS

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences

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ABSTRACT

The dispersion of aqueous suspensions using surfactants and polymers has widespread applications. In addition to the amount adsorbed, the structure of adsorbed surfactant and polymer layers determines the interfacial properties of solid particles and thus suspension stability in these systems. Therefore, an understanding of that structure at the molecular level is very useful. The aim of this work is to study the role of adsorbed layer micro-structural properties, namely micro-polarity, micro-fluidity, and most importantly, molecular conformation and orientation at the solid/liquid interface, in controlling dispersion properties. A multi-pronged approach involving the use of fluorescence, ESR, NMR, computer simulation, along with conventional techniques to measure turbidity and the adsorption isotherm, could be used to explore surfactants/polymers at solid/liquid interfaces.

The adsorption of ionic surfactants (both cationic and anionic surfactants) on alumina in aqueous solution shows regions corresponding to different adsorption mechanisms following a 4-region model. The suspension stability also displays significant changes concomitant with changes in the structure of the adsorbed layer. When polymers are used, their conformation can be manipulated by changing solution conditions such as pH and/or by the addition of a second surfactant or polymer. Such manipulation can be used to obtain a desired level of stabilization or flocculation. In the case of mixed systems involving at least one polymer, the order of addition is found to be an important factor in determining dispersion conditions.

Novel approaches are introduced into the field of flocculation for studying floc structure and flocculation kinetics. Floc structure can be investigated indirectly by examining water signals given by conventional NMR. In addition, a computer program was
developed to simulate flocculation kinetics and floc structure for particles with heterogeneous surface properties. It is hoped that the flocculation process can be better understood from further application of these novel approaches.
# TABLE OF CONTENTS

LIST OF FIGURES .................................................................................. iii
ACKNOWLEDGMENTS .......................................................................... vii

1. INTRODUCTION ............................................................................. 1

2. BACKGROUND .................................................................................. 4
   2.1. Fundamentals of Colloidal Stability ........................................ 4
   2.2. Effect of Surfactant Adsorption on Dispersion Properties ....... 6
      2.2.1. Mechanism of inorganic surfactant adsorption on metal oxides.. 6
      2.2.2. The surface adsorption and colloidal stability .................. 10
   2.3. Effect of Polymer Adsorption on Dispersion Properties .......... 10
      2.3.1. Generals about polymer adsorption ............................... 10
      2.3.2. Mechanism of flocculation/ dispersion by adsorbed polymer 12
      2.3.3. Role of polymer conformation in flocculation and stabilization .. 16
   2.4. Summary .................................................................................. 18

3. MATERIALS AND METHODS ............................................................. 20
   3.1. Materials ................................................................................. 20
   3.2. Methods ................................................................................. 22
   3.3. Basic Principles of the Spectroscopic Methods ...................... 25
      3.3.1. Fluorescence ................................................................. 25
      3.3.2. Electron Spin Resonance (ESR) .................................... 25
      3.3.3. Nuclear Magnetic Resonance (NMR) ....................... 30
   3.4. Quality Assurance .................................................................... 32

4. RESULTS AND DISCUSSION ......................................................... 34
   4.1. Adsorption of Trimethylammonium Bromides on Negatively Charged Alumina ..................................................... 35
      4.1.1. Adsorption isotherm measurement .................................. 35
      4.1.2. Vacuum flotation ............................................................ 37
      4.1.3. ESR results ................................................................. 40
      4.1.4. Fluorescence decay of pyrene in the adsorbed layer .......... 44
      4.1.5. Conclusions .................................................................. 47

   4.2. A Study of Dual Polymer Flocculation ................................... 48
      4.2.1 Introduction .................................................................... 48
      4.2.2. Enhanced flocculation with dual polymers ..................... 49
      4.2.3. Effect of PAA molecular weight and size distribution ....... 51
      4.2.4. Effect of Percol molecular weight and charge density ...... 54
      4.2.5. Polymer conformation ................................................. 55
4.2.6. Summary .................................................. 59

4.3. Interaction Between PAA and NP-15 in Solution and at
    Alumina/Water Interface ...................................... 62
    4.3.1. Introduction ............................................ 62
    4.3.2. Interaction between PAA and NP-15 in solution ...... 63
    4.3.3. PAA-NP15 at alumina/water interface ................. 69
    4.3.4. Summary ................................................ 71

4.4. Role of Sequential Addition of PAA and SDS Mixtures and Their
    Conformation in Dispersion/Flocculation of Alumina ......... 73
    4.4.1. Introduction ............................................ 73
    4.4.2. Effect of addition mode ................................ 74
    4.4.3. Effect of amount of pre-adsorbed PAA ................. 78
    4.4.4. Stirring time effect .................................... 80
    4.4.5. Effect of time interval between additions of PAA and SDS 81
    4.4.6. Kinetics of SDS adsorption in the presence and
            Absence of PAA ......................................... 82
    4.4.7. Summary ................................................ 83

4.5. NMR Study of Water in Flocs ................................ 85
    4.5.1. Introduction ............................................ 85
    4.5.2. NMR spectra of native flocs .......................... 87
    4.5.3. Surfactant induced flocs .............................. 93
    4.5.4. Polymer flocculated particles ......................... 95
    4.5.6. Conclusion ............................................ 95

4.6. Computer Simulation for Flocculation of Particles with
    Surface Heterogeneity ...................................... 97
    4.6.1. Introduction ............................................ 97
    4.6.2. Surface coverage ..................................... 100
    4.6.3. Patch size ............................................. 104
    4.6.4. Addition mode ........................................ 107
    4.6.5. Summary .............................................. 109

5. SUMMARY AND CONCLUSIONS .................................. 111

6. SUGGESTIONS FOR FUTURE WORK ............................. 116

Appendix ....................................................... 118
LIST OF FIGURES

Figure 2.1. Particle-particle potential energy of interactions as a function of separation distance ................................................................. 6

Figure 2.2. Adsorption isotherms and structures of the surfactant aggregates on solid surfaces according to the reverse orientation model, the (surface) bilayer model, and the small surface micelle model (the x axis indicates residual concentrations of surfactants and y axis indicates adsorption densities) ........................................ 7

Figure 2.3. Evolution of the conformations of the adsorbed polymer segment ........ 11

Figure 2.4. Schematic illustration of a) bridging flocculation; b) restabilization by adsorbed polymer ................................................................. 13

Figure 2.5. "Electrostatic patch" model for the interaction of negatively charged particles ......................................................................................... 15

Figure 3.1. Typical fluorescence spectrum of pyrene showing the five vibrational lines ..................................................................................... 26

Figure 3.2. Schematic representation of the correlation of the extent of excimer formation and coiling extent of pyrene labeled polyacrylic acid ......................................................... 27

Figure 3.3. Nuclear Magnetic Resonance (NMR) .................................................. 31

Figure 4.1.1. Adsorption isotherms for alkytrimethylammonium bromides (CTAB, TTAB and DTAB) on alumina .................................................. 36

Figure 4.1.2. Correlation of alumina flotation with the adsorption isotherm of cetyltrimethylammonium bromide (CTAB) ........................................ 39

Figure 4.1.3. Rotational correlation time of CAT-16 in cetyltrimethylammonium bromide (CTAB) solloid layer along with the corresponding adsorption isotherm ..................... 41

Figure 4.1.4. Rotational correlation time of CAT-16 in tetracyltrimethylammonium bromide (TTAB) solloid layer along with the corresponding adsorption isotherm .... 42

Figure 4.1.5. Rotational correlation time of CAT-16 in dodecyltrimethylammonium bromide (DTAB) solloid layer along with the corresponding adsorption isotherm .... 42

Figure 4.1.6. Hyperfine splitting constants of CAT-16 in alkytrimethylammonium bromide solloid layers along with the corresponding adsorption isotherms .................. 43
Figure 4.1.7. Rotational correlation times of CAT-16 in solloid layers of alkyl TABs of three different chain length. .................................................. 44

Figure 4.1.8. Aggregation numbers of alkyltrimethylammonium bromide solloids of three different chain lengths on alumina .................................................. 45

Figure 4.2.1. Diagram illustrating flocculation of alumina fines with polyacrylic acid (PAA) ................................................................. 50

Figure 4.2.2. Enhanced flocculation with dual polymers: flocculation of alumina particles with polyacrylic acid (PAA) alone, Percol alone, and combination of the two polymers under two modes of addition ................................ 51

Figure 4.2.3. Effect of molecular weight of polyacrylic acid (PAA) on the flocculation of alumina ................................................................. 52

Figure 4.2.4. Effect of polyacrylic acid (PAA) molecular weight distribution on the flocculation of alumina .................................................. 53

Figure 4.2.5. Effect of Percoll molecular weight and charge density on the flocculation of alumina ................................................................. 55

Figure 4.2.6. Polyacrylic acid (PAA) conformational change and flocculation responses as a function of Percoll concentration. .................................. 56

Figure 4.2.7. Flocculation responses under different polymer addition modes, sequential addition vs. co-addition .................................................. 57

Figure 4.2.8. Polyacrylic acid (PAA) conformational changes due to Percoll addition in solution and at the alumina/water interface ......................... 58

Figure 4.2.9. A schematic representation of dual polymer flocculation ......................... 61

Figure 4.3.1. Hydrogen bonding between PAA and NP-15 and chemical shift values for PEO segment on NP-15. .................................................. 64

Figure 4.3.2. Increase in temperature will induce downfield shift of carbon atoms along the PEO segment on NP-15. .................................................. 65

Figure 4.3.3. Chemical shifts (ppm) of carbon atoms of PEO segment on NP-15 upon the addition of PAA .................................................. 66

Figure 4.3.4. The coiling of 200 ppm PAA as a function of NP-15 concentration and the
pH change due to the stronger interaction between PAA and NP-15 at higher NP-15 concentrations. ................................. 67

Figure 4.3.5. Coiling index of PAA as a function of pH in the presence/absence of NP-15 .................................................. 68

Figure 4.3.6. Effect of NP-15 micelle on PAA conformation at different pHs. ........ 69

Figure 4.3.7. Alumina suspension turbidity and PAA coiling index as a function of NP-15 concentration when PAA is added before NP-15 addition (PAA/NP-15 addition mode) .................................................. 70

Figure 4.3.8. Schematic picture for the coiling and stretching effect of NP-15 on PAA presented in Figure 4.3.7 ........................................ 70

Figure 4.3.9. Alumina suspension turbidity and PAA coiling index as a function of NP-15 concentration when NP-15 is added before PAA addition (NP-15/PAA addition mode) .................................................. 71

Figure 4.4.1. Turbidity of alumina suspension or SDS/PAA addition mode, PAA/SDS addition mode, and addition of only SDS ................................. 75

Figure 4.4.2. PAA coiling index at alumina/water interface under the SDS/PAA and PAA/SDS addition modes as well as in solution in the presence of SDS. .......... 76

Figure 4.4.3. Adsorption isotherm of SDS on alumina in the presence of pre-adsorbed PAA .................................................. 77

Figure 4.4.4. Schematic illustration for (a) SDS/PAA addition mode and (b) PAA/SDS addition mode. .................................................. 78

Figure 4.4.5. Turbidity of alumina suspension as a function of PAA concentration in the absence and presence of SDS (PAA/SDS mode) .................................................. 79

Figure 4.4.6. SDS adsorption density on alumina as a function of pre-adsorbed PAA. .... 80

Figure 4.4.7. (a) Turbidity and PAA coiling index change as a function of stirring time under SDS/PAA addition mode; (b) SDS adsorption density as a function of stirring time under SDS/PAA addition mode. .................................................. 81

Figure 4.4.8. The effect of time interval between SDS and PAA additions on alumina stability. .................................................. 82
Figure 4.4.9. The kinetics of SDS adsorption is enhanced by the presence of small amount of pre-adsorbed PAA ........................................... 83

Figure 4.5.1. Schematic representation of intra-floc water and inter-floc water as well as their expulsion processes. ................................................................. 88

Figure 4.5.2. The time effect on NMR peak ratio .............................................................. 89

Figure 4.5.3. Flocs produced by three kinds of flocculants: salt, polymer and surfactant. ................................................................. 90

Figure 4.5.4. Particle size effect for zeolite in water .............................................................. 91

Figure 4.5.5. Temperature effect for alumina and zeolite flocs .............................................................. 92

Figure 4.5.6. SDS induced flocs at different SDS concentrations .............................................................. 93

Figure 4.5.7. Time effect for dual polymer induced flocs .............................................................. 96

Figure 4.6.1. Kinetics of flocculation as a function of polymer surface coverage .............. 100

Figure 4.6.2. Relative flocculation rates for particles with different surface coverage . 101

Figure 4.6.3. Examples of floc structure for particles with polymer surface coverages of 5%, 15% and 25%. .............................................................. 102

Figure 4.6.4. Relative floc size as a function of surface coverage .............................................................. 103

Figure 4.6.5. Anisotropy ratio (A) as a function of surface coverage .............................................................. 104

Figure 4.6.6. Effect of patch size on flocculation kinetics (patch ratio is kept at 25% while patch size equals to 1/4, 1/20 or 1/40 of the particle periphery respectively) ............. 105

Figure 4.6.7. Schematic representation of hidden area of aggregates which is not available for further collision. .............................................................. 106

Figure 4.6.8. Mixing effect on flocculation kinetics .............................................................. 108

Figure 4.6.9. Mixing effect on floc structure .............................................................. 108
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Chapter 1. INTRODUCTION

Colloidal stability is a key interfacial parameter that controls the efficiency of many industries such as cosmetics, ceramics, pharmaceuticals, detergents, food, minerals, as well as processes in biological systems involving blood, kidneys and artificial organs. Adsorption of polymers and surfactants at solid/liquid interfaces will alter the interfacial properties and result in different colloidal stability.

In the presence of polymers or surfactants, a colloidal dispersion can undergo stabilization (charge or steric) or flocculation\textsuperscript{1,2}. The occurrence of these phenomena is always attributed to the type and nature of the materials (adsorbent, solvent and adsorbate), adsorption density, micro-structure and conformation of the adsorbed surfactant/polymer. Considerable attempts have been made in the past to correlate adsorption density and zeta potential to the stability characteristics of colloidal suspensions. However, there is a lack of correlation between the flocculation behavior and the microscopic characteristics of the adsorbed polymer/surfactant layer, i.e., polymer/surfactant conformation at particle/water interface. This has been primarily due to the lack of reliable techniques to monitor \textit{in situ} the minute amounts of species that adsorb on solids.

A substantial amount of \textit{in situ} research has been directed towards the study of the structure and dynamics of surfactant/polymer in solution by using spectroscopic techniques such as fluorescence\textsuperscript{3}, electron spin resonance (ESR)\textsuperscript{4,5} and nuclear spin resonance (NMR)\textsuperscript{6}. However, these techniques had not been adapted to the field of colloidal suspensions until the mid 80's\textsuperscript{7}. Over the past ten years, modern spectroscopic methods have contributed significantly to the understanding of surfactant and polymer aggregates at solid-liquid
interfaces, which have been called solloids\(^8\) (surface colloids). Solloid study was no longer limited by the empirical techniques. Despite the efforts made in the last decade, there are still numerous issues not understood and systems not well-studied. The lack of correlation between the empirical observations and a direct observation on a molecular level made it difficult to predict and control the colloidal stability of many systems. In the present investigation, flocculation and dispersion of alumina fines are studied in the presence of surfactants, polymers, and their combinations utilizing both the conventional techniques used for decades and newly-adapted spectroscopic methods.

In addition to the need to apply the newly adapted techniques to investigate different issues and systems for a molecular level understanding, there is also always a demand to continue to discover novel approaches. One of the attempts made in this study is to correlate NMR signals of water in flocs with floc structure. Although a correlation between water signals and solid/liquid suspensions has been found in the past\(^9,10\), natural floc has not been found to be studied and therefore, NMR has not been utilized directly for the study of floc structure. Among all the technologies, computer science is growing most fast in the current era as well as in the near future. It is not only seeping into every corner of our lives but every field of science as a powerful tool. For example, computational chemistry has grown into a major branch of today’s chemistry. It is hoped that the power of computer can be utilized here to tackle problems presented in colloidal stability. In the pursuit of computer simulation for flocculation, the simulation of a large number of particles with heterogeneous surface properties was made possible. While aggregation has been simulated by computer for more than 10 years, the surface heterogeneity has never been taken into account in the
previous studies.

It is hoped that this study will further the understanding of the role of polymers/surfactants in colloidal stability, with the help of a variety of tools well established, recently-adapted, and newly developed.
Chapter II BACKGROUND

2.1. Fundamentals of Colloidal Stability

Colloidal systems are composed of one or more dispersed phases and a continuous medium. The term "dispersion" often refers to the process by which the aggregates or agglomerates in the dry state are broken into smaller particles in the medium. The total energy of the system usually increases due to an increase in surface energy resulting from the increase in the surface area and possible changes in the nature of the surface. The nature and the magnitude of the surface energy are determined by the physico-chemical nature of the particles and the solvents since the particles will have a tendency to undergo aggregation to reduce surface energy. A colloidal dispersion is therefore not a thermodynamically stable system in most cases.

Colloidal particles in a dispersion medium are always engaged in Brownian motion with frequent collisions between them. Stability is thus determined by the nature of the interactions between the particles during such collisions. When attractive forces dominate, the particles will aggregate and the dispersion may be destabilized -- followed by a phase separation. When repulsive forces dominate, the system will remain in a dispersed state.

Generally, there are six types of particle-particle interaction forces possibly existing in a dispersion as summarized below.
Table 2.1. Summary of forces existing in aqueous dispersed systems\textsuperscript{11}

<table>
<thead>
<tr>
<th>Force</th>
<th>Nature</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLVO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical double layer</td>
<td>repulsive</td>
<td>surface structure and ion adsorption</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>attractive</td>
<td>universal presence</td>
</tr>
<tr>
<td>Non-DLVO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steric</td>
<td>repulsive</td>
<td>induced by adsorbed species</td>
</tr>
<tr>
<td>Hydration/solvation</td>
<td>both</td>
<td>hydration/solvation of adsorbent/adsorbate</td>
</tr>
<tr>
<td>Polymeric bridging</td>
<td>attractive</td>
<td>induced by adsorption of long chain polymer</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>attractive</td>
<td>intrinsic or induced by adsorption</td>
</tr>
</tbody>
</table>

For simple dispersions in aqueous electrolyte solutions, one can predict colloidal stability based on DLVO\textsuperscript{12,13} (Derjguin-Landau-Verwey-Overbeek) theory by considering only electrical double layer and van der Waals interactions. Typical net energy of interaction caused by the electrical double layer repulsion force \((V_R)\) and van der Waals attraction force \((V_A)\) is shown in Figure 2.1 as a function of distance \(h\). The attractive energy \(V_A\) is inversely proportional to the distance and hence increases rapidly as the particles approach each other, while the repulsive energy \(V_R\) changes relatively slowly. The total force \(V_T(V_T = V_A + V_R)\) curve shows three distinct features, a primary minimum, a maximum, and a secondary minimum. For particles to experience aggregation in the primary minimum, which is often irreversible, they have to surmount the repulsive energy barrier. This is possible if the colloidal particles have sufficient kinetic energy. The form of the curve shown in Figure 2.1 depends on the size and surface charge of the particles and the solution conditions. The height of the energy barrier can be used to quantify aggregation kinetics.

As stated in Table 2.1, besides DLVO interactions, there are 4 other forces which can affect dispersion properties. The presence of adsorbed or solvation layers on the particles...
can influence the dispersion properties by altering the van der Waals force and the electrical double layer force as well as by their own characteristic properties. The effects of both surfactant and polymer adsorption layers on colloidal stability will be discussed in the following sections.

![Diagram of Particle-particle potential energy of interaction as a function of separation distance](image)

Figure 2.1. Particle-particle potential energy of interaction as a function of separation distance\textsuperscript{14}.

2.2. Effect of Surfactant Adsorption on Dispersion Properties

2.2.1. Mechanism of ionic surfactant adsorption on metal oxides

Adsorption of ionic surfactants on charged metal oxides is a topic of great industrial and academic interest, and this has led to a large number of studies with different models proposed\textsuperscript{15,16}.

The reverse orientation model suggested by Somasundaran and Fuerstenau\textsuperscript{17} has
been particularly successful in describing anionic surfactant adsorption on alumina and rutile\textsuperscript{18}. Since the adsorption isotherms of these systems can be divided into 4 distinct regions when plotted on a log-log scale, this model is termed a 4 region model. According to this model (Figure 2.2(a)), the surfactants adsorb electrostatically as individual ions in Region I and associate into hemimicelles in Region II of the isotherm. In the hemimicelle, the surfactants are oriented with their charged headgroups toward the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.2.png}
\caption{Adsorption isotherms and structures of the surfactant aggregates on solid surfaces according to the reverse orientation model, the (surface) bilayer model, and the small surface micelle model (the x axis indicates residual concentrations of surfactants and y axis indicates adsorption densities).}
\end{figure}

solid surface, while the hydrocarbon chains protrude into the aqueous phase, thus forming hydrophobic patches on the surface. Further adsorption results in an increasing number of
surfactant aggregates, with molecules adsorbing in an opposite orientation once the surface is neutralized by the oppositely charged surfactant. Adsorption in Region III occurs through the growth of aggregates already formed in Region II without an increase in the number of aggregates. Finally, in the plateau region, Region IV, the adsorbed layer possesses the structure of a bilayer. The 4 region model is supported by in situ fluorescence, Raman and ESR studies\textsuperscript{19,20,21,22,23}. A slightly different model, the bilayer model, has been presented by Harwell\textit{ et al.}\textsuperscript{24,25} (Figure 2.2(b)). According to this model, local bilayer structures form on patches of the solid surface at a critical solution concentration without hemimicelles at lower surfactant concentrations. These patches of surfactant bilayers were called "admicelles". Admicelles were proposed to form already in Region II. By growing in number and size they will eventually form a more or less complete bilayer.

A much different model was proposed by Gu\textit{ et al.}\textsuperscript{26,27}. According to this model, the adsorption of the surfactant shows a two step characteristic, which is evident on a linear scale adsorption isotherm (Figure 2.2(b)). In the first step, the surface active species are adsorbed through interactions with the solid surface, which is the same as what is proposed for region I in the 4 region model, and in the second step, they are adsorbed through interactions between the adsorbed surfactants, such that small "surface micelles" are formed. A picture consistent with this model is that of the small micelles retaining their structure but becoming more closely packed along the adsorption isotherm. Based on the two-step adsorption model, a general adsorption isotherm equation was also derived\textsuperscript{28}. This model was later modified to allow for different aggregation numbers for the surface micelles, and this resulted in a BET type of equation\textsuperscript{29}. The equations derived have been successfully applied
to various types of adsorption isotherms for a relatively large number of systems, with the majority of studies being concerned with silica surfaces. However, there is a lack of direct experimental evidence for the formation of small micelles on the solid surface.

In order to simplify the terminology, the term "solloid" was created as a general term for surface colloids that include all sorts of adsorbed surfactant layer structures such as bilayers, monolayers, admicelles, hemimicelles and small surface micelles. Also, self-consistent field lattice theory (SCFA theory) was utilized by Böhmer and Koopal in recent years to resolve theoretical controversies. SCFA theory does not require any assumptions about the adsorbed layer structure. Results obtained with the SCFA theory show the shape of the isotherm to be quite complex and different for constant charge and constant potential (variable charge) surfaces. For metal oxides, their surface potentials are about constant at a given pH. The isotherms calculated for constant potential surfaces, plotted on a log-log scale, show the characteristic four region behavior. At constant charge surfaces and low ionic strengths, the calculated isotherm corresponds well with the 2 step isotherms found for carbon black, biotite and fluorite, polystyrene latex, PTFE latex, and some surfactant isotherms on silica.

According to the SCFA theory, the four region model and the two step model coexist and are valid under different conditions depending on the charge properties of the solid surface. The adsorption behavior of anionic and cationic surfactants on oppositely charged rutile was found to be the same with the isotherm shape consisting of four regions, as predicted by the SCFA theory. SCFA theory resolves the controversies of different models. However, it is important to test its validity further under different situations.
2.2.2. The surface adsorption and colloidal stability

The evolution of surfactant layer differs for the different models proposed, which leads to different trends of colloidal stability along the adsorption isotherms. The surface micelle model and the bilayer model warrant continuous increase or decrease in hydrophobicity along the entire adsorption isotherm, while the reverse adsorption model (4-region model) indicates a hydrophobicity maximum and thus a stability minimum somewhere in the middle of the adsorption isotherm. Therefore, in order to study the effect of surfactant adsorption on colloidal stability, it is first of all important to determine the mechanism of its adsorption.

2.3. Effect of Polymer Adsorption on Dispersion Properties

2.3.1. Generalities about polymer adsorption

Polymer adsorption onto solid surfaces can be described as a three step process. The first step is the diffusion of polymer from bulk solution to the solid surface and the attachment of the first few polymer segments to the surface. In the second step, the attached macromolecule undergoes conformational rearrangements to achieve a lower energy state. The final step is an exchange process between the adsorbed chains and the free chains in the bulk.

The structure of the adsorbed polymer layer is relevant to the surface coverage and its formation history. Figure 2.3 depicts the conformations of adsorbed polymers generally expected in different adsorption regimes. On a bare surface, polymer enjoys a maximal number of contacts with surface sites since there is no competition from other chains. So
during the initial stages of adsorption, adsorbed chains lie relatively flat on the surface, forming a "pancake" layer. Segments in direct contact with the surface are called "trains". If the bulk polymer concentration exceeds a critical value ($C_{b1}^*$ in Figure 2.3), chains interact with other chains and inter-chain competition for adsorption sites can occur. Not all of the repeating units of a single polymer can find surface sites which to attach. In this situation, there may be portions of chains with two ends attached to the surface, which form loops and portions with one free end, forming tails. The loops and tails form an extended layer, like a "brush" ($\tau_1 \rightarrow \tau_2$ in Figure 2.3). The thickness of this layer generally increases with surface coverage. When the concentration is higher than a threshold value, $C_{b2}^*$, the equilibrium surface coverage usually attains saturation and increase in the bulk polymer concentration hardly changes the equilibrium coverage ($\tau_2$ in Figure 2.3).

Figure 2.3. Evolution of the conformations of the adsorbed polymer segments.
2.3.2. Mechanism of flocculation/dispersion by adsorbed polymer

There is considerable interest, both practical and fundamental, in the effects of polymers on dispersion properties. Much of this interest is concerned with the stabilization of dispersed particles by adsorbed polymer layers. This effect is usually known as steric stabilization. With certain polymers, the opposite effect is found and particle stability can be reduced, so that flocculation occurs. Such behavior can be observed with quite small amounts of an added polymer. It is now recognized that several mechanisms can be involved in flocculation by polymers:\(^3:\)

a) Polymer bridging

b) Charge neutralization (including "electrostatic patch" effects)

c) Polymer complex formation ("network flocculation")

d) Flocculation by free polymer ("depletion flocculation")

Among them, the first two have received the most attention and are probably more significant than the other mechanisms in the majority of applications.

**Bridging flocculation**

Essentially, bridging flocculation occurs because segments of a polymer chain adsorb on more than one particle, thus linking the particles together. For adsorption to occur, some favorable interaction between polymer segments and particle surfaces is required and this can arise in a number of ways such as hydrophobic bonding, hydrogen bonding, covalent bonding, electrostatic attraction, etc. These interactions are all of very short range.

The earliest suggestion of polymer bridging appears to be by Ruehrwein and Ward in 1952\(^4\). They pointed out that typical polymer molecules might be comparable in size to
many colloidal particles (0.1 to 1 μm) and the attachment of a polymer chain to several particles could occur. Effective bridging flocculation requires the adsorbed polymer to extend far enough from the particle surface to attach to other particles and the particle to have sufficient free surface for adsorption of these extended chains. If excess polymer is adsorbed, the particles can become restabilized because of surface saturation or by steric stabilization. Bridging flocculation and restabilization are illustrated schematically in Figure 2.4 (a) and (b).

![Diagram](image)

**Figure 2.4.** Schematic illustration of a) bridging flocculation; b) restabilization by adsorbed polymer

LaMer\textsuperscript{45,46} and others\textsuperscript{47} have related the bridging efficiency factor to the fractional surface coverage of polymers. It can be predicted from the original LaMer model and subsequently modified models that bridging is most efficient when 50% of the particle is covered with polymer. However, in practice, optimum polymer dosages are often found at
much lower coverage value.

A very significant aspect of flocculation by polymers is that the resulting aggregates (flocs) can be much stronger, i.e. more difficult to break, than those produced by other means.

**Charge neutralization**

There are many practical applications where the only effective flocculants are those with a charge opposite to that of the particles. In such cases, because of the strong ionic interaction it is likely that polyelectrolytes adsorb with a rather flat configuration, which would limit the possibility of bridging. Since charged particles are stabilized by electrical repulsion, it is clear that the adsorption of oppositely charged polymers could reduce or eliminate this repulsion and cause flocculation. The restabilization of particles by excess polymers could then be the result of charge reversal.

It is worthwhile to establish the relative importance of charge neutralization and bridging in the flocculation of particles by oppositely charged polymers. For instance, if charge neutralization is the predominant effect, then there should be no need for high molecular weight polymers, which are more expensive and less convenient to use. Also, polyelectrolytes of high charge density should be most effective in such cases.

There is a considerable body of evidence suggesting that, for cationic polymers and negative particles, charge neutralization plays a large role in the flocculation process. The most direct evidence comes from measurements of electrophoretic mobility (and hence the zeta potential) of particles dosed with polyelectrolytes. With many different types of particle, including clays, latex, cellulose fibers, silica and bacteria, it has been found that the
optimum flocculation dosage of cationic polymer corresponds quite closely with the amount required to give zero electrophoretic mobility (i.e. to neutralize the particle charge).

"Electrostatic Patch" Mechanism

Although charge neutralization goes a long way towards explaining the behavior of cationic polymers in many systems of interest, there are some effects of polymer weight and ionic strength which do not fit in with this simple picture. These can be better explained by the "electrostatic patch" model\textsuperscript{48,49}. Essentially, this model applies when particles have a fairly low density of immobile surface charges and the adsorbing polymer has a high charge density. In this case, it is not physically possible for each charged group on the polymer chain to be adjacent to a charged surface site and regions of excess charge develop even though the particle as a whole may be electrically neutral. Particles having this "mosaic" type of charge distribution may interact in such a way that positive and negative "patches" come into contact giving quite strong attachment. A schematic illustration of this type of interaction is given in Figure 2.5.

![Figure 2.5. "Electrostatic patch" model for the interaction of negatively charged particles with adsorbed cationic polymer. Interactions are a and b: repulsive; c: attractive (ref:50).](image-url)
The electrostatic patch mechanism qualitatively explained a number of features commonly observed in the flocculation of negative particles by cationic polymers. A semi-quantitative account of the role of molecular weight and charge density of the polymer has been given by Mabire et al.\textsuperscript{50}

2.3.3. Role of polymer conformation in flocculation and stabilization

As discussed in the above section, a colloidal dispersion can undergo either stabilization or flocculation upon polymer addition. These phenomena are attributed to macroscopic adsorption characteristics such as polymer adsorption density, particle surface charge, and microscopic adsorption characteristics such as the conformation and orientation of the adsorbed polymer at particle/water interface. The various factors that affect the flocculation include polymer molecular weight and charge density, pH and ionic strength of the suspension, solid concentration and polymer dosage. The effect of these factors on floc characteristics are not clearly established. Although in a number of cases there have been attempts to explain the relationship between floc structural characteristics and various flocculation parameters, there is a lack of experimental evidence for such correlations. Until a correlation of adsorbed state conformation to flocculation responses such as supernatant clarity, sediment density and filterability are established, the technique of polymeric flocculation may continue to remain as an art.

Several techniques have been reported in the literature for determining conformational characteristics of adsorbed polymer, namely bound segment fraction and adsorbed layer thickness. These are based on vibrational spectroscopy, microcalorimetry.
light scattering and hydrodynamics\textsuperscript{51}.

Commonly used methods for the determination of adsorbed layer thickness are ellipsometry\textsuperscript{52}, photon correlation spectroscopy\textsuperscript{53,54,55,56}, capillary flow\textsuperscript{57} and ultracentrifugation. Ellipsometry can be used only with smooth surfaces and, therefore, cannot be used for systems involving fine particles. The latter three techniques measure the hydrodynamic thickness of the adsorbed layers. Of these, only photon correlation spectroscopy and ultracentrifugation can be used reliably for particulate systems. However, in order to obtain hydrodynamic thicknesses using these methods the particles should be maintained discrete and, therefore, they cannot be used in flocculation systems. Another recently developed technique for studying adsorbed layer conformation is small angle neutron scattering\textsuperscript{48}. This is a powerful technique since it can be used not only for determining the adsorbed layer thickness but also the spatial distribution of chain segments. However, this technique can be used only with very dilute dispersions and, therefore, is not suitable for flocculation systems.

The spectroscopic methods, which measure the fraction of the polymer segments bound to the interface, include Fourier transform infrared spectroscopy (FTIR)\textsuperscript{59,60}, nuclear magnetic resonance (NMR)\textsuperscript{61,62}, and electron spin resonance (ESR)\textsuperscript{63}. Due to the small amount of polymer used in flocculation, both FTIR and NMR are not sensitive enough for the measurements. Although ESR may have enough sensitivity, it has never been applied for \textit{in situ} flocculation studies.

In the early 90's, using pyrene labeled polyacrylic acid, Tjipangandjara and Somasundaran\textsuperscript{64,65} showed conformation of adsorbed acrylic acid to have a significant effect
on the stability of alumina suspensions. A very elegant experiment involving manipulation of polymer conformation in solution and at interfaces by shifting pH was designed with polymer conformation monitored with pyrene fluorescence emission technique. They have found that the conformation of adsorbed polymer can be altered by changing solution conditions and depending upon the adsorption density and direction of pH shift, the significant enhancement in flocculation or stabilization can be obtained.

Adaptation of fluorescence labeling technique to flocculation/dispersion makes it possible to correlate polymer conformation with suspension stability. Application of this newly-adapted technique to different complex systems could help to answer the questions that could only be speculated in the past. However, very little work has been done in this regard. In addition to the need of further investigation on the role of polymers in suspension systems, there is also a demand for the development of new methods to study flocculation and dispersion.

2.4 Summary

It is clear from the above discussion that there are major unanswered questions on the role of polymers/surfactants in determining the stability of dispersions. The knowledge on this topic has been limited by measurements on bulk properties. Although the introduction of spectroscopic methods to this field has shed much light on it during the last ten years, it is still an area far from well explored. There is a need to build up correlations between bulk properties and molecular level conformation for various systems and in various ways.
Manipulation of suspension stability can only thus be made possible.
Chapter 3. MATERIALS AND METHODS

3.1. Materials

Dispersions

Particles: Linde A alumina purchased from Union Carbide was used to make model dispersions since it is well characterized. It is specified to be 90% $\alpha$-$\text{Al}_2\text{O}_3$ and 10% $\gamma$-$\text{Al}_2\text{O}_3$, and has a mean crystal diameter size of 0.3 $\mu$m and aggregation size of 10 $\mu$m. The BET surface area was measured to be 14-15 m$^2$/g.

Media: Triply distilled water (TDW) is used to prepare solutions and dispersions. It has a specific conductivity less than 1.5 $\mu$S/cm and is organic free according to surface tension measurements.

Surfactants

The most commonly used surfactants in three different categories (cationic, anionic and non-ionic) are chosen for various model studies:

Cationic tetradecyltrimethylammonium bromide (TTAB), $[\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3]\text{Br}$, and dodecyltrimethylammonium bromide (DTAB), $[\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_2)_3]\text{Br}$. were from American Tokyo Kasei, Inc., and cetyltrimethylammonium bromide (CTAB), $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]\text{Br}$. was from Fluka.

Anionic Sodium dodecyl sulfate (SDS) was purchased from Fluka.

Non-ionic Pentadecylethoxylated nonyl phenol (NP-15), $C_{15}H_{31}C_6H_{4}O(\text{CH}_2\text{CH}_2\text{O})_{15}H$ is from Nikko Chemicals, Japan.

Surface tension measurements confirmed the high purity (>99%) of the above
surfactants and they were used as received.

**Polymers**

Anionic Polyacrylic acid (PAA) of molecular weights 10k, 90k, and 100k are from Polysciences Inc. PAA is chosen for both its importance and the availability of its pyrene-labeled form (py-PAA).

Pyrene-labeled PAA (M.W.=7.6×10^4 or 1.2×10^5) was provided by National Chemical Laboratory (NCL) of India.

Cationic Cationic copolymer of various molecular weights and cationic charge densities (Allied Colloids Inc.) were copolymers of acrylamide and dimethyl aminoethyl acrylate, the latter being fully quaternized and therefore positively charged over a wide pH range. Characteristics of the cationic polyelectrolytes are listed in Table 3.1. It is convenient to study the effects of polymer molecular weight and charge density by using this cationic copolymer.

**Table 3.1.** Polymer characterizations for cationic polyelectrolyte Percol

<table>
<thead>
<tr>
<th>Polymer</th>
<th>%Cationic*</th>
<th>Intrinsic viscosity (cm^2/g)**</th>
<th>Molecular mass (×10^6)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percol 722</td>
<td>50</td>
<td>5.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Percol 728</td>
<td>50</td>
<td>7.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Percol 757</td>
<td>80</td>
<td>5.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*given by the manufacturer  
**measured by a viscometer in 30°C water bath  
***Calculated using [\eta]=kM^* with k=3.7×10^{-2} and α=0.66
**Inorganic Reagents**

Reagent grade sodium chloride from Fisher Sci. Co. was used to adjust the ionic strength of solution (0.03 mol/l or 0.1 mol/l). pH of the solution and the suspension was adjusted using Fisher Standard hydrogen chloride and sodium hydroxide solutions.

**Probes used for surfactant solloid study**

ESR probe CAT-16 is purchased from Molecular Probes, Inc. It possess a structure of cationic surfactant and is should co-adsorb with cationic surfactants onto negatively charged surfaces. Fluorescence probe pyrene is from Aldrich Chemical Company, Inc. This highly hydrophobic probe will solubilize in the hydrophobic layers of solloids. The probes were used without further purification.

![CAT-16](image)

![Pyrene](image)

**3.2. Methods**

**Surfactant adsorption**

Adsorption experiments were conducted in capped 20ml vials. Two-gram samples of alumina were mixed with 10 ml of 0.03 M NaCl aqueous solutions for 1 hour at room temperature. The pH was adjusted as desired and the suspension allowed to equilibrate
further for 1 hour. Then 10 ml of 0.03 M NaCl solutions containing the surfactant at
different concentrations were added, and the samples were equilibrated overnight. The pH
was adjusted again using 0.1 M NaOH. The samples were equilibrated for about 3 more
hours and then centrifuged for 25 min. At 5000 rpm. The supernatant was then pipetted out
for analysis. Surfactant concentration was determined by a two-phase titration technique.
using chloroform as the organic solvent and bromophenol blue as the indicator.

**Vacuum Flotation**

The procedures for adsorption as described above were followed except that the
amount of all the reagents were doubled so that 40 ml vials could be used. The vials were
directly connected to the vacuum system (FTS systems, Inc.), the flow rate was controlled
manually, stirring done using a magnetic stirrer bar, and flotation was conducted for 5 min.

**ESR measurements**

ESR spectra were obtained using a Bruker EPR300 spectrometer at room
temperature.

**Fluorescence Measurements**

All fluorescence spectra were recorded on a Photon International PTI-LS 100
spectrometer. In the case of slurry samples, the fluorescence experiment was conducted in
a 1 cm square and 2 mm flat quartz cell. In the case of tests with surfactant adsorbed
alumina, pyrene stock solutions were prepared by stirring pyrene in concentrated surfactant
solutions for 24 hours and filtering the excess probe. Pyrene concentrations before and after
adsorption were measured by UV absorbance using an extinction coefficient of $4.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. For solution and solid samples containing pyrene-labeled polymer, the fluorescence
experiments were conducted in a 1 cm square and 2 mm flat quartz cell respectively. The relative intensities of pyrene emission peak at 373 nm (monomer) and 475 nm (excimer) obtained with excitation at 335 nm were recorded. The ratio of intensities of excimer to monomer peaks, I_e/I_m, was calculated and termed coiling index which reflects the extent of coiling of polymer chains.

*Flocculation test*

For each experiment, a certain amount of alumina (0.2g, 0.5g or 1g) was put in 40ml of 0.1 M (or 0.03 M) NaCl in a 50 ml beaker fitted with a propeller with four baffle plates and sonicated for 30 seconds with a power setting of 30 Watts (Lab-line Ultratip Labsonic System, Lab-Line Instruments, Inc.). The desired amount of polymer solution was then added to the suspension with the propeller rotating at 300 rev/min. After the stirring was stopped for a certain time, 16 ml of the supernatant from the top was transferred to a turbidimeter (HF scientific Inc.) For turbidity measurement.

*NMR measurements*

To study water signals from flocs, flocs produced from flocculation tests were carefully transferred into a standard 5 mm NMR tube and allowed to settle for a certain amount of time (the typical time scale is a few hours). The tube is filled so that the solid filled the volume of the probe coil. The ^1^H-NMR spectrum was obtained using a VXR Varian-400 M Hz NMR spectrometer. Spectra were obtained at 25°C. In all spectra, 64 scans were acquired without spinning. For all sets of measurements, floc preparation and NMR measurements were made on a parallel time scale, which ensured the same settling time for flocs in each sample.
3.3. Basic Principles of the Spectroscopic Methods

3.3.1. Fluorescence

Fluorescence emission is the radiative emission of light by an excited molecule (usually a complex organic molecule such as pyrene) returning to its ground state energy level. This phenomenon bears a wealth of information on the environment of the light absorbing species. Parameters of fundamental importance in fluorescence emission are (1) emission maximum (wavelength of maximum intensity) (2) quantum yield of fluorescence (emission efficiency measured as intensity) and (3) fluorescence lifetime (time taken by the excited state to decay to 1/e of its initial value).

The fluorescence measurements are generally carried out by a steady state fluorescence spectrofluorometer and lifetime of fluorescence by a time-resolved fluorescence lifetime instrument\textsuperscript{66}. The dependence of fluorescence intensity and lifetime on the physicochemical environment of the fluorescing molecule has been well documented\textsuperscript{67}. Such data have been applied to micellar photochemistry to understand the property of micelles\textsuperscript{68}. It has been recently adapted as a tool for solloids to obtain information on the micropolarity, microviscosity of the probe environment and the aggregation number of the surfactant at the interface\textsuperscript{69,70}.

To determine the micropolarity, a fluorescence molecule such as pyrene, which possesses a highly structured fluorescence spectrum whose vibrational lines are susceptible to intensity fluctuations brought on by polarity changes of the medium, is used. This empirical knowledge has been found to be of universal applicability and used widely to investigate the micropolarity of micelles. A properly resolved fluorescence spectrum of
pyrene in fluids has five vibrational fine structures in the region from 370 to 400 nm (Figure 2.6). The intensities of the first \( I_1 \) and the third \( I_3 \) peaks are found to be particularly sensitive to the changes in the probe environment. The ratio of these peaks \( I_3/I_1 \) sometimes referred to as the polarity parameter, changes from about 0.6 in water to a value greater than unity in hydrocarbon media.

![Intensity vs Wavelength](image)

Figure 3.1. Typical fluorescence spectrum of pyrene showing the five vibrational lines.

Information on microviscosity can be obtained by studying the excimer (excited dimer) forming capabilities of suitable fluorescence molecules like 1,3-dinaphthyl propane (DNP). The excimer, which is a complex of a ground state and an excited state monomer, has a characteristic emission frequency. The intramolecular excimer formation is a sensitive function of the microviscosity of its neighborhood.

When the concept of the monomer to excimer ratio \( I_m/I_e \) is applied to pyrene-labeled
polymer, polymer conformation can be studied. The rationale behind the use of this technique is the observation that the extent of excimer formation which depends on the interaction of an excited state pyrene of the polymer pendant group with another pyrene group on the ground state has a direct bearing upon the polymer conformation. This may be understood with reference to Figure 2.7 which shows that when a polymer is more coiled, there is a better probability for intramolecular excimer formation.

Figure 3.2. Schematic representation of the correlation of the extent of excimer formation and coiling extent of pyrene-labeled polyacrylic acid.

The dynamics of fluorescence emission of pyrene is more complex than the steady state. While the decay kinetics of monomer and excimer emissions may be derived directly for a homogeneous solution (continuous medium), statistical methods are to be applied to arrive at similar kinetics in aggregated micellar/soloidal ensembles. This stems from a
need to recognize the possibility of random multiple occupancy of the probe in the aggregates which affects the excimer forming probability within the aggregate. If the micellar/solloidal system is viewed as groups of individual aggregates with \( n \) probes, then \( P_n \), the average number of probes per micelle, may be related to \( n \) by Poisson statistics through the relation

\[
P_n = n^n \exp(-n)/n!
\]  
(3.1)

This model yields the following relation for the time dependence of monomer emission:

\[
I_{m(t)} = I_{m(0)} \exp[-k_o t + n(\exp(-k_e t) - 1)]
\]  
(3.2)

where \( k_o \) is the reciprocal lifetime of excited pyrene in the absence of excimer formation; \( k_e \) is the intra-aggregate encounter frequency of pyrene in excited and ground state; and \( I_{m(0)} \) and \( I_{m(t)} \) represent the intensity of monomer emissions at time zero and time \( t \) respectively.

Knowing \( n \), the aggregation number \( N \) can be calculated using the expression

\[
n = [P]/[\text{Agg.}] = [P]N/([S] - [S_{eq}])
\]  
(3.3)

where \([P]\) is the total pyrene concentration; \([\text{Agg.}]\) is the concentration of the aggregates; and \([S] - [S_{eq}]\) is the concentration of the adsorbed surfactant.

3.3.2. Electron Spin Resonance (ESR)

ESR studies as applied to micellar/solloidal systems rely on the sensitivity of a free
radical probe to respond to its microenvironment. Molecular species with a free electron possess intrinsic angular momentum (spin), which in an external magnetic field undergoes Zeeman splitting. For a system with \(S=1/2\), two Zeeman energy levels are possible whose energy gap \((\Delta E)\) is given by

\[
E = h \nu = gBH_0
\]

The magnetic moment of the free electron is susceptible also to the secondary magnetic moments of the nuclei and thus the Zeeman splitting will have superimposed on it the hyperfine splitting which brings about further splitting of the absorption signal. The hyperfine splitting pattern depends on the spins and the actual number of neighboring nuclei with spins. If the electron is in the field of a proton when the ESR spectrum would yield two lines of equal intensity, and similar interaction by a nucleus with \(S=1\), as in nitrogen, would produce a triplet of equal intensity. The lineshapes of ESR signals are subject to various relaxation processes (spin-lattice and spin-spin relaxations) occurring within the spin system as well as anisotropic effects due to the differentially oriented paramagnetic centers being acted upon by an external magnetic field\(^{72}\). These effects result in a broadening of the absorption lines. Three types of ESR study can be applied to probe surfactant microstructures: spin probing, spin labeling and spin trapping\(^{73}\). In the spin probe technique, a molecule with spin is externally added to the system, whereas in spin labeling a spin-bearing moiety, through covalent bonding, becomes a part of the molecule. The spin trapping techniques are mainly used for the identification of radicals produced thermally, photochemically or radiolytically by trapping the radical through chemical reactions with a
spin trap (like butyl nitroxide) and converting the radical to a free radical which can be examined by ESR.

Information on micropolarity and microviscosity can be obtained by measuring the hyperfine splitting constant $A_N$ and the rotational correlation time $\tau_c$. The latter is a measure of the time required for a complete rotation of the nitroxide radical about its axis. Its value can be defined as the time required for the nitroxide to rotate through an angle of one radian. Both $A_N$ and $\tau_c$ can be obtained from a direct ESR lineshape analysis.

3.3.3. Nuclear Magnetic Resonance (NMR)

The phenomenon of nuclear magnetic resonance was first observed in 1946 and it has found wide application in the studies of surfactant/polymer systems.

Some atomic nuclei have a nuclear spin ($I$), and the presence of a spin makes these nuclei behave rather like bar magnets. In the presence of an applied magnetic field the nuclear magnets can orient themselves in $2I+1$ ways. Those nuclei with an odd number of nucleons, of which the most important are $^1H$ and $^{13}C$, have spins of $\frac{1}{2}$. These nuclei, therefore, can take up one of only two orientations, a low energy orientation aligned with the applied field, and a high energy orientation opposed to the applied field. The difference in energy is given by:

$$\Delta E = \hbar \gamma B_0 / 2\pi \quad (3.5)$$

where $\gamma$ is the magnetogyric ratio (which is a measure of the strength of the nuclear magnets); $B_0$ is the strength of the applied magnetic field.

The number of nuclei in the low energy state ($N_o$) and the number in the high energy
state \((N_p)\) will differ by an amount determined by the Boltzmann distribution:

\[
N_\beta / N_\alpha = \exp(-\Delta E / kT) \quad (3.6)
\]

When a radio frequency signal is applied to the system, this distribution is changed if the radio frequency matches the frequency at which the nuclear magnets naturally precess in the magnetic field \(B_0\): some of the \(N_\alpha\) nuclei are promoted from the low energy state to the high energy state, and \(N_\beta\) increases (Figure 2.8\(^7\)). The frequency in Hz, the resonance frequency, is given by:

\[
\nu = \gamma B_0 / 2\pi \quad (3.7)
\]

and is therefore dependent upon both the applied field strength and the nature of the nucleus in question.

![Diagram of nuclear magnetic resonance](image)

Figure 3.3 Nuclear Magnetic Resonance (NMR)

The precise frequency at which each carbon/hydrogen comes into resonance is determined not only by the applied field, \(B_0\), but also by minute differences in the magnetic
environment experienced by each nucleus. These minute differences are caused by the variation in electron density in the neighborhood of each nucleus.

The chemical shift scale is defined by:

\[ \delta = \nu_r (Hz) - \nu_{TMS} (Hz) / \text{operating frequency} (MHz) \]  (3.8)

The parameter \( \delta \), which measures the position of the signal, will now be the same whatever machine it is measured on. It has no units and is expressed as fractions of the applied field in parts per million (p.p.m.). Tetramethylsilane (TMS) is chosen as the internal standard because it has only one signal, which comes into resonance at one extreme of the frequencies found for most carbon atoms in organic structures, and it is inert, volatile, non-toxic, and cheap.

3.4. Quality Assurance

The following steps were adopted in the experimentation and analysis of results to ensure the quality of the results ensuing from this investigation:

1. Glass ware was cleaned using the following recommended procedure: soak in chromic acid for 30 minutes to remove impurities such as oxide films, wash in distilled water 10 times and finally rinse three to four times with triply distilled water. The glassware was checked for cleanliness by steaming when necessary.

2. Water was purified by distillation in the presence of potassium permanganate in order to destroy the organic contaminants in the system. A three stage distillation which ensures very low impurity level will be adopted. A conductivity value of lower than \(10^{-6}\) mho/cm and a
surface tension of 72.8 dynes/cm at 20°c will be used as criterion for water purity.

(3) Solutions of polymers were made within one week will be used to avoid complications due to oxidation on long storage.

(4) Most experimental sets were run in duplicate.

(5) Three kinds of controls and blanks were performed when polymer/surfactant adsorption is involved:

A) Blank test: This involves measuring changes in concentration of the bulk solution in the absence of the polymer/surfactant and the solids. This will reveal any interference in the adsorption measurement from the reaction containers, water, salt used to control ionic strength, etc.

B) Positive control: This involves measuring changes in concentration of bulk solution in the presence of the solids without any added polymer/surfactant. This will reveal any interference from the solid surface on the adsorption measurement.

C) Negative control: This involves measuring changes in concentration of the bulk solution in the presence of the polymer solution without any added solid. This will reveal any depletion due to adsorption on the container, loss by precipitation due to salt addition etc.
Chapter 4. RESULTS AND DISCUSSION

The role of polymers/surfactants in colloidal stability (flocculation or dispersion) is of great academic and industrial interest. The knowledge on this topic has been obtained mainly by doing conventional measurements. Although the introduction of spectroscopic methods to this field has shed much light on it during the last ten years, it is still an area far from well explored.

This work can be divided into two parts:

1. Combine the newly adapted spectroscopic techniques, such as ESR, NMR and fluorescence, with conventional techniques, such as adsorption isotherm measurement and flocculation test, to achieve a better understanding of the role of polymer and surfactant in colloidal stability. The surfactant role is closely related to its adsorption mechanism, where considerable debate is going on, while the role of polymer on solids depends highly on its interfacial conformation, which can be manipulated not only by changing solution properties but also by adding a second species.

2. Explore some novel approaches to study colloidal stability, such as bringing in the NMR technique for floc structure study, and simulate particles with heterogeneous surfaces (such as those in patch flocculation) to study flocculation kinetics and floc structure.

Although part 1 mainly focuses on correlating bulk properties to the molecular level conformation for unknown systems while part 2 emphasizes on developing new approaches, the aims in both cases are the same: to better understand the role of polymers and surfactants in controlling colloidal stability. With this aim in mind, different experiments were designed and results have been obtained and are discussed in the following six sections.
4.1. Adsorption of Trimethylammonium Bromides on Negatively Charged Alumina

As discussed in section 2.2.1, there are a large number of studies with different models proposed for the adsorption of ionic surfactants on metal oxides. The solloid evolution differs in various models, and should result in different colloidal stability curves accordingly. Therefore, in order to understand the role of surfactant in controlling colloidal stability, we have to first of all set up a realistic picture of solloid evolution along the adsorption isotherm.

As discussed previously, according to the SCFA theory, the four-region model and the two-step model coexist and are valid under different conditions, depending on the charge properties of the solid surface. The adsorption behaviors of anionic and cationic surfactants on oppositely charged rutile were found to be the same with the isotherm shape consisting of four regions, as predicted by the SCFA theory. Alumina is often used as a substrate for the adsorption of anionic surfactants, for which the 4-region model was first discovered. If SCFA theory is valid in general, then a 4-region isotherm should also be observed for cationic surfactant adsorption on negatively charged alumina. Whether a 4-region isotherm is observed or not becomes a critical test for the validity of SCFA theory.

4.1.1. Adsorption isotherm measurement

A visual examination of the adsorption isotherms of the three cationic surfactants on alumina, given in Figure 4.1.1, suggests that they do not fall into the four region type. Specifically, Region III seems to be absent. However, from the shape of the isotherms alone, it is difficult to determine the real mechanisms controlling the adsorption in these systems.
The shape of a surfactant adsorption isotherm depends to a great extent on its critical micelle concentration (CMC) and critical hemimicelle concentration (HMC) which mark the onsets of Regions II and IV respectively. An increase in chain length is considered to decrease the Gibbs free energies of the micellization and hemimicellization resulting in a shift of CMC and HMC towards lower concentrations. Addition of a CH₂ group to the chain is known to decrease the CMC and HMC by a factor of 3 (Traube’s rule). The experimental results presented in Figure 4.1.1 exhibits such decreases well.

Assuming the same solloid structure at the plateau region, the plateau value reflects the tightness of the packing of the solloids. For alkyl TABs adsorption on alumina, the adsorption density in the plateau region is about $2-3\times10^{-6}$ moles/m². This value is lower
than the $6.5 \times 10^{-6}$ moles/m$^2$ for sodium dodecyl sulfate adsorption on the same kind of alumina at pH 6.5 in 0.1 M NaCl solution$^{75}$. Three factors are proposed to contribute to this difference. First, the head group area of alkyl TAB (about 37 Å$^2$) is larger than that of SDS (about 25 Å$^2$). Secondly, alumina particles have a lower charge density at pH 10 (about -30 mV) than at pH 6.5 (about 40 mV). Finally, 0.1 M NaCl used for SDS adsorption is more effective in reducing head group repulsion than 0.03 M NaCl used for alkyl TAB adsorption. These three factors can all result in a tighter packing of SDS; it can be concluded that alkyl TAB solloid layers on alumina are relatively loosely packed compared to SDS solloids on alumina.

The slopes of Region II and plateau values of Region IV increase slightly with chain length, which is due to the increase in hydrophobic attraction upon increasing the chain length. The stronger coherence of longer chain length was also found for C$_n$TAB series of molecules at air/water interface by neutron reflection, which compensates the increasing tilting with longer chains and results in a lack of variation of the adsorption layer thickness with chain length.$^{76}$

4.2.2 Vacuum Flotation

Flotation technique$^{77}$ is a convenient method for determining the hydrophobicity of particles. In this technique, particles in a suspension are allowed to collide with bubbles. Particles which attach to bubbles because of their hydrophobicity will levitate to the top of the container where they can be separated and measured. The floated fraction can be used as a measure of the hydrophobicity of the particles.

In this experiment, vacuum flotation, in which bubbles are generated through the
application of vacuum, was used to monitor changes in the hydrophobicity of surfactant coated alumina particles along the adsorption isotherm and the results obtained are shown in Figure 4.1.2. Increase in flotation is considered to be due to the hydrophobicity imparted to the mineral surface by surfactant adsorption, while the decrease at higher surfactant concentrations can be due to surfactant adsorption in this range with a reverse orientation as well as to mutual repulsion between the bubbles and the particles\(^7^8\). Based on the 4 region model, flotation is expected to exhibit a maximum at the transition point between Region II and III. A maximum in Figure 4.1.2 does exist somewhere on the sharp rising portion of the isotherm. The existence of Region III in the present system can hence be concluded based on flotation experiments.

The difficulty in detecting Region III in the isotherm is therefore proposed to result from the similarity of the slopes of Regions II and III. According to the original 4 region model, Region III should have a smaller slope than Region II. In Region II, adsorption is favored both by the strong electrostatic interaction between the head group and the solid surface, and the hydrophobic attraction between the tails. In Region III, only the latter attraction exists with electrostatic repulsion building up as adsorption continues. For the current system, the transition between Regions II and III is not perceptible on a conventional isotherm, which implies presence of similar forces for adsorption in these regions. To account for this, the hydrophobic attraction in Region III is proposed to be much stronger than that in Region II so as to offset the electrostatic attraction in Region II. A penetrating architecture with head-in and head-out orientations in the adsorption layers, resulting in a strong hydrophobic interaction in Region III, is proposed towards this purpose. The loose
structure of the solloid, the bulky head of the surfactants, and the moderate charge density of alumina at pH 10 all justify such a hypothesis.

![Graph](image)

Figure 4.1.2. Correlation of alumina flotation with the adsorption isotherm of cetyltrimethylammonium bromide (CTAB)

The phenomenon of a weak or merged II/III transition was observed also in the case of dodecyl pyridinium chloride adsorption/rutile adsorption when the solution pH was close to its point of zero charge (pzc)\(^9\). In view of the above discussion, the proximity of pH to its pzc results in a weak electrostatic attraction in adsorption Region II. Closer the pH value is to the pzc, smaller is the difference between the driving forces for adsorption in Region II and III, and hence weaker is the II/III transition.
From the flotation results, a process similar to what was proposed in the 4 region model can be expected to occur in the present case. Surface micelle model and bilayer model warrant continuous increase or decrease in hydrophobicity along the entire adsorption isotherm. Since such a continuous change is not observed here, they can both be excluded for the current system. Based on the above results, a loose and inter-penetrating configuration for the solloid layer is suggested for the system under study.

4.1.3. ESR results

The ESR spectra of CAT-16 were used to determine changes in environmental polarity and viscosity of solloids along the adsorption isotherms. Contributions from probe in the bulk solutions to the ESR signal intensities are negligible in all cases. The measurable parameters from these spectra include the nitrogen hyperfine splitting constant, $A_N$, and the rotational correlation time, $\tau_C$.

The nitrogen hyperfine splitting constant can be obtained from the average separation of the three lines of the ESR spectrum. Since $A_N$ does decrease with micropolarity decrease, it is a good measure of the micropolarity of the probe environment. ESR spectrum becomes increasingly anisotropic as the solvent viscosity increases as a result of the decrease in rotational mobility of the probe. The rotational correlation times can be calculated from\textsuperscript{10}

$$\tau_C = 6.5 \times 10^{-10} \Delta H \left[ \left( \frac{h_0}{h_{11}} \right)^{1/2} - 1 \right] \text{Sec.} \quad (4.1)$$

where $\Delta H$ is the peak to peak width of the central line. $h_0$ and $h_{11}$ are the heights of the central and high field lines respectively. Thus, $\tau_C$ provides a direct measurement of the microviscosity of the probe environment. Figures 4.1.3 - 4.1.5 show $\tau_C$ values of the ESR spectra obtained for the alumina in CTAB, TTAB and DTAB solutions respectively, with
isotherms also plotted in the same figure for comparison purposes. It can be seen that rotational correlation time plots correlate with the adsorption isotherms so well that they almost overlap. It is clear that the rotation of the probe molecule is severely restricted in the solloid layers as expected. The hyperfine splitting constant is found to decrease upon solloid formation on the surface (Figure 4.1.6), indicating a more hydrophobic environment for the probe.

Figure 4.1.3. Rotational correlation time of CAT-16 in cetyltrimethylammonium bromide (CTAB) solloid layer along with the corresponding adsorption isotherm.
Figure 4.1.4. Rotational correlation time of CAT-16 in tetradecyltrimethylammonium bromide (TTAB) solloid layer along with the corresponding adsorption isotherm.

Figure 4.1.5. Rotational correlation time of CAT-16 in dodecyltrimethylammonium bromide (DTAB) solloid layer along with the corresponding adsorption isotherm.
Figure 4.1.6. Hyperfine splitting constants of CTA-16 in alkyltrimethylammonium bormide solloid layers along with the corresponding adsorption isotherms.

It can be seen from Figure 4.1.7 that the plateau values of rotational correlation times vary significantly with surfactant chain length. Probes in CTAB solloids are most restricted, whereas those in DTAB solloids are most mobile. The chain length of the probe molecule is the same as that of CTAB and longer than those of TTAB and DTAB. Thus shorter the host chain length, higher is the freedom of the nitrooxide group of the probe in adsorbed layer of the surfactant.
Figure 4.1.7. Rotational correlation times of CAT-16 in solloid layers of alkyl TABs of three different chain length.

4.1.4. Fluorescence Decay of Pyrene in the adsorbed layer

The principles for determination of micelle aggregation number from data for fluorescence decay have been reviewed extensively elsewhere\textsuperscript{41,42}. However, the technique has rarely been used to obtain solloid aggregation numbers on metal oxides. The solloid aggregation numbers obtained in the current study are presented in Figure 4.1.8, which shows a change in aggregate size along the rising part of TTAB and part of the sharp rising parts of CTAB and DTAB isotherms. The average aggregation numbers, N, measured at particular adsorption densities are indicated along the isotherm. It is to be noted that at all concentrations under study, no pyrene was detected in the supernatant of each sample.
Figure 4.1.8. Aggregation numbers of alkyltrimethylammonium bromide solloids of three different chain lengths on alumina.

In general, the size of aggregate can be seen to increase with adsorption density. In the middle range of the sharp increase in the isotherm, the aggregation number stays constant as in Region II of the 4 region model. In the upper range of the sharp increase, there is a significant increase in the aggregation number, as in Region III of the 4 region model. The increase in solloid size with chain length is also to be noted. It is helpful to compare the above results with results obtained previously for the sodium dodecyl sulfonate (SDS)/alumina system:
1) The probe induces a slight increase in the adsorption of the surfactant. However, for all the systems studied, the change in adsorption upon probe addition can be considered to be insignificant.

2) A similar trend of N value increase was found for both system (N values of 66, 49, 121, 123, 128, 166, 196. 258, 356 were found for SDS solloids and those of 20, 18, 26, 49, 50, 52, 71, 78, 114 were found for TTAB solloids as shown in Figure 4.1.8). In the initial stage of Region II, the aggregation number is quite small in both cases. These aggreagtes grow from monomers in Region I and apparently serve as big hydrophobic anchors for further adsorption. It is evident that further adsorption results in an almost constant solloid size at the end of region II. This stage of Region II where N is constant indicates a process similar to micellization. It is to be noted that these constant N values are about the same as their micelle aggregation numbers. However, the solloid structure has to be different from the micelle structure. There has to be more head-on adsorption than head-out adsorption, which makes further adsorption in Region III and a maximum in flotation possible.

3) The N values for SDS solloids are considerably larger than those for alkyl trimethyl ammonium bromide of the same chain length. although the trend is almost the same. This is consistent with the higher plateau value of SDS adsorption. It can also been seen that N increases with the chain length. The slight increase in both slope and plateau values with chain length are in accord with this observation.

From the fluorescence study, a 4 region model is once again supported. It was also found that the looser structure of solloid, the lower plateau value of the adsorption isotherm, and the smaller solloid aggregation number are all closely related to one another. In
addition, solloid grows in size in the initial part of Region II without much size change in the later stage of Region II.

4.1.5. Conclusions

From the results obtained for adsorption isotherm, flotation, ESR and fluorescence, it can be concluded that the adsorption mechanism for alkyltrimethylammonium bromides on alumina is in accord with the 4 region model, although only three regions were detected on the conventional adsorption isotherms; this is suggested to be the result of a loose and inter-penetrating configuration of the colloids. The results suggest that the solloid nature, as a dominating factor in deciding the shape of adsorption isotherm, is influenced greatly by the type of surfactant, the solid, and solution conditions.
4.2. A Study of Dual Polymer Flocculation

4.2.1. Introduction

Many industrial processes such as papermaking, mineral processing, water treatment, and sludge dewatering involve solid-liquid separation using polymeric flocculants. In many of these applications, use of combinations of oppositely charged polyelectrolytes under suitable conditions enhances the flocculation \(^{83}\). Although such combinations are increasingly used as flocculants in the industry, very limited amount of mechanistic or molecular level research has been done in the past and as a result fundamentals of this complex process is far from being well understood, for example, with respect to the influence of polymer molecular weight and polymer conformation on the flocculation process.

It has been known for a while that a pair of oppositely charged polymers can produce synergism in the flocculation of paper pulp\(^{84}\). Although most studies had been empirical, some fundamental investigations have been performed in the recent years. For example, Yu and Somasundaran\(^{85}\) have investigated dual polymer flocculation of alumina particles by studying not only polymer adsorption, solution viscosity and particle zeta potential, but also the important parameter, polymer coiling index, as determined by the fluorescence label technique. Petzold et al.\(^{86}\) studied the effect of charge ratios of the two oppositely charged polymers and the influence of polymer molecular weight on flocculation. In all of the previous studies, two effects have been combined: (1) the strong adsorption and anchoring effect of highly oppositely charged polyelectrolyte of low molecular weight and (2) the bridging effect of high molecular weight polymer of similar charge to achieve enhanced flocculation.
In this study, the effect of combinations of polyacrylic acid (PAA) and a high molecular weight cationic copolymer of acrylamide and quaternary acrylate salt (Percol) was investigated. To understand the mechanism behind this dual polymer flocculation, the effects of the molecular weights of PAA and Percol as well as charge density effect of Percol were studied. PAA conformation at alumina/water interface was investigated at the molecular level by the fluorescence label methods under different polymer addition modes, i.e., sequential addition of the two polymers vs. co-addition. Polymer size distribution was also investigated. Based on the results, a flocculation mechanism is proposed for this system.

4.2.2. Enhanced flocculation with dual polymers

Single polymer flocculation has been well studied in the past. The major mechanisms proposed for single polymer flocculation was introduced in chapter 2. Compared with single polymer flocculation, flocculation involving dual polymers has received very little attention.

The flocculation of alumina suspensions with polyacrylic acid alone is illustrated in Figure 4.2.1 in terms of supernatant turbidity vs. time. Flocculation was enhanced when the concentration of 10k PAA was increased from 1ppm to 5ppm, and then decreased upon further addition of PAA. The flocculation is not strong because neither charge neutralization nor bridging is significant with 10k PAA at pH 8. The addition of Percol 757 at 5 ppm dosage causes some flocculation but less than that by the same amount of PAA (Figure 4.2.2), due to the almost negligible interactions between Percol and alumina which are both
positively charged. However, when both polymers were added to the suspension, flocculation was found to improve markedly. In addition, it can be seen that sequential addition of the two polymers produces better flocculation than co-addition. This phenomenon will be further discussed later in this paper. For the purpose of discussion, we term the flocs induced by PAA alone "primary flocs" and those formed with two polymers "binary flocs".

![Graph showing turbidity vs. time for different concentrations of PAA and without PAA.](image)

Figure 4.2.1. Diagram illustrating flocculation of alumina fines with polyacrylic acid (PAA)
4.2.2. Enhanced flocculation with dual polymers: flocculation of alumina particles with polyacrylic acid (PAA) alone, Percol alone, and combination of the two polymers under two modes of addition.

4.2.3. Effect of PAA molecular weight and size distribution

In a set of experiments, PAA was added first and was proposed to serve as the "anchor" for the adsorption of the second polymer. The addition of PAA alone produces primary flocs, which grow into binary flocs when the second polymer is added. It can be seen in Figure 4.2.3 that there is a clear PAA M.W. effect: the higher the PAA molecular weight, the less Percol 757 needed for reaching the maximum flocculation. This indicates
that larger PAA molecules produce bigger primary flocs, which requires a smaller amount of the tethering second polymer to form binary flocs. It is concluded that polymer bridging exists in the formation of primary flocs for this system.

Figure 4.2.3. Effect of molecular weight of polyacrylic acid (PAA) on the flocculation of alumina.

Most commercial polymers have wide molecular weight distributions. In order to study the effect of polymer size distribution, 10k and 90k M.W. PAA molecules were premixed at a 1:1 ratio to obtain a bimodel and broad molecular weight distribution. The flocculation responses obtained are shown in Figure 4.2.4. It can be seen that with the 1:1
mixture of 10k and 90k PAA, the Percol dosage range for good flocculation is wider. Therefore, it is proposed that a wider size distribution of PAA is preferred for flocculation in the tested molecular weight range. Possibly, a wider distribution of PAA M.W. results in a wider size distribution of primary flocs. The binary floc formation which probably involves patch model, i.e. patch adsorption and bridging, is possibly a non-equilibrium process. In single polymer flocculation, such non-equilibrium flocculation has been found to cause entrapment \textsuperscript{87,88}, this could also be expected to occur in the binary floc formation. A wider size distribution of primary flocs probably facilitates the trapping process.

![Graph](image)

Figure 4.2.4. Effect of polyacrylic acid (PAA) molecular weight distribution on the flocculation of alumina.
It has to be noted that while a wider size distribution is preferred for the first polymer added, no effect on flocculation was observed when mixtures of the second polymers of different molecular weights were tested. This effect of polymer size distribution may possess some industrial significance.

4.2.4. Effect of Percol molecular weight and charge density

As discussed earlier in this paper, the patch model fits single polymer flocculation systems containing highly charged polymers. Similarly, the patch model can be used to explain the formation of binary flocs where a highly charged large polymer is used89. For this system under study, both the dangling chains of PAA and the highly charged Percol ensure the patch adsorption of Percol.

The effect of Percol size and charge density on the flocculation process is shown in Figure 4.2.5. It can be seen that a higher charge density can reduce the polymer dosage required to achieve optimum flocculation. This reduction is approximately proportional to charge density increase, which implies charge neutralization. A larger molecule can produce bigger flocs and thus better flocculation, which suggests a bridging mechanism. The above observations illustrate the importance of both the polymer size and the charge density in forming the secondary flocs, which are in agreement with predictions made from patch model.
Figure 4.2.5. Effect of Percol molecular weight and charge density on the flocculation of alumina

4.2.5. Polymer conformation

Yu and Somasundaran employed fluorescence to investigate the conformational change of anionic high molecular weight PAA as a function of concentration of lower molecular weight cationic polymer polydiallyl dimethyl ammonium chloride (PDADMAC). PAA serves as the bridging agent and PDADMAC as the anchoring polymer. The coiling index of the larger polymer, PAA, was found to decrease continuously with the increase in
concentration of the smaller polymer. In other words, PAA is more stretched when there is more preadsorbed PDADMAC. In the present study, PAA serves as the anchoring polymer and Percol as the bridging polymer. Interestingly, it was found in this study that PAA gets stretched more with increase in concentration of the second polymer (Figure 4.2.6). In both cases, the conformation of PAA is dramatically changed. It can therefore be concluded that complexation of oppositely charged polymers does take place at the solid/water interface. As the concentration of one polymer increases, the other polymer, no matter whether it plays the role of anchoring or bridging, will become more stretched.

Figure 4.2.6. Polyacrylic acid (PAA) conformational change and flocculation responses as a function of Percol concentration.
It was seen from Figure 4.2.2 that different flocculation resulted when the polymer addition mode differed. The influence of addition mode is further illustrated in Figure 4.2.7. It can be seen that the whole curve shifted to the left with sequential addition in comparison to the co-addition mode, which means less dosage is required in the former mode. Premixing of PAA and Percol will weaken both the anchoring effect of PAA and bridging effect of Percol, since the number of anchors is decreased and the bridging chain is coiled before adsorption on the particles. Since polymer conformation does play a critical role in determining the flocculation response, an additional polymer conformation study was conducted by comparing the coiling indexes of PAA at alumina/water interface with two different addition modes (Figure 4.2.8). Conformational change of PAA due to complexation with Percol 757 in solution phase was also measured and shown on the same figure for reference.

![Graph showing flocculation response under different polymer addition modes.](image)

**Figure 4.2.7.** Flocculation response under different polymer addition modes, sequential addition vs. co-addition.
Figure 4.2.8. Polyacrylic acid (PAA) conformational changes due to Percol addition in solution and at the alumina/water interface.

In solution, PAA chains become coiled and then stretched until a constant coiling extent is reached. Coiling with Percol at low dosage is attributed to charge neutralization. With further addition of the cationic polymer, the polymer complex may become positively charged with resultant restretching. It is interesting to note that the stretching reaches a constant value when Percol concentration is above 20 ppm. This constant value is somewhat lower than that for PAA alone, and can be attributed to the higher charge density of Percol 757 relative to PAA. As expected, the polymer conformation curve for co-addition lies
between those for the solution phase and the sequential addition mode at the solid-liquid interface.

With both addition modes, there should be a competition between the particle and Percol for PAA due to their electrostatic attraction with PAA. In the case of sequential addition, PAA adsorption on the particle surface takes place first. Percol competes with the surface adsorption sites and becomes dominant at higher concentration, which results in increased stretching of PAA. In co-addition mode, PAA is first complexed with Percol and the surface adsorption sites have only the residual sites on PAA to complex with. With higher amounts of Percol concentration in the complex, the particle surface makes less impact so that the co-addition curve is more similar to that of complexation in solution and deviates markedly from the sequential addition curve. It is clear that the conformation and hence flocculation is markedly affected by the environment (free in bulk or bound on the surface) in which the two polymers encounter each other.

4.2.6. Summary

The results of the investigations reported above may be summarized as follows.

1. Flocculation can be markedly enhanced by choosing an appropriate pair of oppositely charged polymers (Figure 4.2.9). The polymer that is added first adsorbs on the alumina particles and produces primary flocs. It also serves as anchors for the adsorption of the second polymer. In addition to charge neutralization, bridging contributes to the primary floc formation for the system under study.

2. Larger PAA is preferred since bigger primary flocs can be formed which will decrease the
optimum dosage of the second polymer required. A wider molecular distribution of PAA
M.W. can also widen the optimum dosage range of the second polymer and is hence
preferred.

3. With the second polymer, bigger flocs will form with the larger polymer, and increase in
charge density reduces the optimum polymer dosage. This can be explained by patch model.

4. Increase in the concentration of one of the two polymers is found to make the other
polymer more stretched.

5. Sequential addition is a better mode than co-addition, i.e., polymer complexation should
occur after the adsorption of the first polymer, since the polymer adsorption is essentially
irreversible. In this mode, a maximum amount of the second polymer is available for
complexation coupled with bridging.
Figure 4.2.9. A schematic representation of dual polymer flocculation.
4.3. Interaction between Polyacrylic Acid (PAA) and Non-ionic Surfactant (NP-15) in Solution and at Alumina/Water Interface

4.3.1. Introduction

Surfactants and polymers are known to show marked deviations from regularity in aqueous solution. In mixed solutions major changes in the properties of the individual species may result owing to formation of complexes. In the last few years, a significant increase in research activity on the polymer-surfactant interaction has occurred. Several reviews on the development of the field have been published recently.\textsuperscript{90,91,92,93}

Polyacrylic acid (PAA) and ethoxylated nonionic surfactants are widely used detergent additives for both household and industrial applications. Typical examples are laundry agents and pretreatment chemicals used in textile dyeing\textsuperscript{94,95,96}. Whereas the surfactants serve as solubilizing and dispersing agents of oil and grease, PAA acts as "builder"\textsuperscript{97} to support the dispersing ability of the surfactants and act as scale inhibitors. Together with other detergent ingredients, surface active agents and builders constitute a multi-component system, the complex physicochemical behavior of which is far from being fully understood. A fundamental knowledge of the interacting components, however, will facilitate the development of new products which must be superior to their predecessors both in cost and performance.

The behavior of mixtures of PAA and non-ionic ethoxylated surfactant in solution has been investigated mainly by Saito \textit{et al}\textsuperscript{98,99,100,101} in the past. With viscosity measurements they showed that configurational changes in PAA were induced if non-ionic ethoxylated surfactants were added. At the same time, the CMC decreased. Interaction between the two
species was accompanied by a rise in pH. These findings were interpreted in terms of the formation of hydrogen bonds between the acid groups of the polymer and the polar head groups of the surfactants, which can only occur at low pH. Furthermore, it was proposed that the binding of surfactants to PAA does not require a whole PEO moiety for hydrogen bonding but only a certain segment close to the hydrophobic moiety. The interactions of these two components at solution/air interface were recently investigated also by Maloney and Huber\textsuperscript{102} utilizing surface tension measurements and spectroscopic ellipsometry.

The aim of this study is to further elucidate the interaction between PAA and ethoxylated non-ionic surfactant in solution, as well as to explore its effect on the stability of alumina suspension. The model system chosen towards this purpose is PAA with a molecular weight of 90,000 and pentadecylethoxylated nonyl phenol (NP-15). Pyrene labeled PAA(Py-PAA) is used for monitoring polymer conformation.

4.3.2. Interactions between PAA and NP-15 in solution

As mentioned above, it has been proposed that the binding of ethoxylated non-ionic surfactants to PAA does not require a whole PEO moiety for hydrogen bonding but only a certain segment close to the hydrophobic moiety\textsuperscript{103}. This is a speculation made from experimental observation that Tl in PAA-treated systems is a constant, being independent of the PEO moiety of the surfactants in the same homologous series (Tl is the critical surfactant concentration lower than CMC and above which PAA-surfactant complexes form and dye solubilization takes place).

Since configuration of the polymer-surfactant complex is highly dependent on their
interaction sites, it is important to obtain a direct picture as to where the specific interactions take place. A much more direct method to do this is by measuring the chemical shift values of the PEO segments by using NMR. On one hand, hydrogen bonding with PAA will downshift the PEO segments on the NMR spectrum. On the other hand, the change in packing density of NP15 in the presence of PAA will also affect chemical shift values: a higher packing density will result in a higher trans/gauche ratio and thus a downfield shift. Therefore, the changes in the chemical shifts of the PEO segments of NP15 upon the addition of PAA has to be considered as a combined result of the above two contributions.

Five $^{13}$C peaks can be observed for the PEO chains of NP-15. The designation of the peaks are shown in Figure 4.3.1. It was made with the reference to $^{13}$C NMR peak assignment for Triton-100 and verified by computer simulation.

![Chemical structure of PEO and NP15](image)

Chemical shift (ppm) 67 69 70 72 60

Figure 4.3.1. Hydrogen bonding between PAA and NP15 and chemical shift values for PEO segment on NP15
It is well known that aggregation number (i.e. packing density) of NP15 micelle increases with temperature\textsuperscript{105}. This explains the down field shifts in NMR measurements with increase in the trans/gauche ratio with the packing density \textsuperscript{106}(Figure 4.3.2). Figure 4.3.3 shows the effect of PAA-NP15 interaction on chemical shift of PEO segment. Since hydrogen bonding could only result in down field shifts, the upfield shifts observed for C1, C2 and C3 can be attributed only to decrease in packing density of NP15 aggregates upon PAA addition. The following conclusions can be drawn from this figure: (1) Down field shift is most obvious for the end groups of PEO segments; therefore, the hydrogen bonding takes place for end groups of PEO (2) In the presence of PAA, packing density of NP15 is lower which accounts for the upfield shifts observed for C1, C2 and C3.

Figure 4.3.2. Increase in temperature will induce downfield shift of carbon atoms along the PEO segment on NP15 (the number on x-axis is corresponding to C1– C5 as designated in Figure 1).
Figure 4.3.3. Chemical shifts (ppm) of carbon atoms of PEO segments on NP15 upon the addition of PAA
(The number on x-axis is corresponding to C1–C5 as designated in Figure 4.3.1)

Interactions between PAA and NP15 is associated with the conformational changes of PAA, as manifested by the change of viscosity as reported in the previous study. However, specific changes in PAA conformation have never been reported, and it is an aim of this study to examine such changes. Pyrene labeled PAA is utilized to achieve this objective.
It is shown in Figure 4.3.4 that before NP15 forms aggregates, the interaction between NP15 monomer and PAA will coil up the polymer slightly, while a drastic stretching of PAA is observed upon the NP15 aggregation formation, accompanied by a small pH increase due to the strong interaction.

![Graph showing coiling index and pH as a function of NP15 concentration](image)

**Figure 4.3.4.** The coiling of 200 ppm PAA as a function of NP15 concentration and the pH change due to the stronger interaction between PAA and NP15 at higher NP15 concentrations.

When coiling index of PAA is plotted as a function of pH in the absence of NP15, a continuous decrease in coiling index is observed as expected (Figure 4.3.5). In the presence of NP15, the coiling index is decided by both the pH effect and the effect of
hydrogen bonding between PAA and NP15, and as a result of these two contributing factors, a coiling index maximum is resulted. Interactions between PAA and NP15 as a function of pH can be evaluated from the subtraction between the curves on Figure 4.3.4. It can be seen from the curve (Figure 4.3.6) depicting this that strong interactions between NP15 micelle and PAA take place when pH is less than 5, with a much stronger interaction at lower pH. At pH values higher than 5, there is a small coiling effect of NP15 on PAA, and this is attributed to NP15 monomer interactions with PAA. No co-operative effect is involved in the complexation between PAA and NP-15 in this pH range.

Figure 4.3.5. Coiling index of PAA as a function of pH in the presence/absence of NP-15.
4.3.3. PAA-NP15 at alumina/water interface

Since interactions can exist between any pair of components in PAA/NP15/alumina suspension system, the system is very complex and difficult to study.

When PAA is added before the addition of NP15, a turbidity minimum corresponding to coiling index maximum is observed (Figure 4.3.7). The trend of the coiling index is very similar to that in solution alone, and we can draw a schematic picture based on results presented in Figure 4.3.7 (Figure 4.3.8). A very different coiling index change was observed for the addition mode where NP15 was added first (Figure 4.3.9). It is rather difficult to deduce the mechanisms since in this case there can be PAA molecule interacts with both pre-adsorbed NP15 and NP15 molecules in solution.
Figure 4.3.7. Alumina suspension turbidity and PAA coiling index as a function of NP-15 concentration when PAA is added before NP-15 addition (PAA/NP-15 addition mode)

Figure 4.3.8. Schematic picture for the coiling and stretching effect of NP-15 on PAA presented in Figure 4.3.7.
4.3.4. Summary

1. NMR measurements: NP15 interacts with PAA through hydrogen bonding. The PEO tail of NP15 molecules forms hydrogen bonding with PAA. The NP-15 aggregates possess a looser structure in the presence of PAA.

2. Fluorescence labeling technique: The hydrogen bonding between PAA and NP15 induces a conformational change of PAA. By manipulating the amount of NP15, PAA coiling index (thus solution viscosity) can be controlled. It was found that monomer of NP15 can coil up PAA while NP15 micelles can stretch up PAA chains. Since the interaction is mainly through hydrogen bonding, the interaction becomes stronger as the pH decreases. When pH
is higher than 5, NP15 micelles could not interact with PAA strongly. It is either its monomer in solution or individual molecules in the micelles that interact with PAA without any co-operative effect in this case.

3. In alumina suspension, for the case when PAA is added first, both the optimum flocculation and the maximum PAA coiling index match CMC values of NP15 (tentative explanation is that NP15 monomers collapse PAA loops and tails which are restored when NP15 micelles form); when NP15 is added first, both the optimum flocculation and minimum of coiling index fall around CMC of NP15. The latter addition mode is more complex than the former and understanding of the mechanisms will require further detailed studies.
4.4. Role of Sequential addition of Polyacrylic Acid (PAA) and Sodium Dodecyl Sulfate (SDS) mixtures and their conformation in Dispersion/Flocculation of Alumina

4.4.1. Introduction

Since both polymers and surfactants adsorb on solids in certain operations, it is useful to determine the effect each has on the adsorption properties of the other. Most studies in the past have focused on systems where there are interactions between the polymer and the surfactant with very little work on co-adsorption of non-interacting polymers and surfactants. In one of the rare examples of the latter, Gebhardt and Fuerstenau\textsuperscript{107}, while confirming the absence of any interaction between Polyacrylic amide (PAAm) and sodium dodecanesulfonate (SDSO\textsubscript{3}) in solution, demonstrated that pre-adsorbed PAAm on hematite had no effect on either the adsorption of SDSO\textsubscript{3} (except at high concentrations of the latter) or on its electrophoretic mobility. On the other hand, Hollander\textsuperscript{108} determined that each ingredient in a PAAm/dodecyl benzyl sulfonate (DDBS) system had a depressing effect on the adsorption of the other on kaolinite. Such an effect was found also by Moudgil and Somasundaran\textsuperscript{109} for the adsorption of the SDSO\textsubscript{3}/PAAm pair on hematite. Some attempt has been made to explain the adsorption in the above studies based on data for some bulk properties. There is however no direct, systematic measurement of the microscopic properties involved in such interactions. The aim of this work is to correlate the bulk properties with microscopic properties for illustrating mechanisms behind the interfacial processes in the systems.

The model system chosen for this study is that of polyacrylic acid (PAA) and sodium dodecyl sulfate (SDS) in an aqueous suspension of alumina. Both PAA and SDS are anionic
in nature and they will therefore adsorb on positively charged alumina mainly by
electrostatic attraction. The adsorption behaviors of both PAA and SDS as well as the effects
of their adsorption on alumina suspension stability have been well studied, however no data
is found on their role in determining alumina stability for the case where PAA and SDS co-
exist.

4.4.2. Effect of addition mode

Results obtained for different sequences of additions of sodium dodecyl sulfate (SDS)
and polyacrylic acid (PAA) are given in Figure 4.4.1 and it can be seen that the stability of
alumina suspension is very much dependent on the addition sequence. When SDS is added
to the suspension before PAA (SDS/PAA mode), the turbidity changes markedly as a
function of the added SDS concentration; whereas when PAA is added first (PAA/SDS
mode), there is very little dependence on the SDS additions. When the three curves
corresponding to SDS/PAA mode, PAA/SDS mode and SDS alone are compared, it can be
seen that the SDS/PAA curve lies between those for PAA/SDS mode and for SDS alone, the
suspension stability being similar to that for adding SDS alone at high SDS concentrations
and approaching that for PAA/SDS mode at low SDS concentrations.
Figure 4.4.1. Turbidity of alumina suspension for SDS/PAA addition mode, PAA/SDS addition mode, and addition of only SDS.

In order to elucidate the molecular mechanisms behind the above flocculation/dispersion behavior, polymer conformation was measured under different addition sequences using pyrene labeled PAA (py-PAA) as the fluorescence probe. It can be seen from Figure 4.4.2 that polymer becomes more stretched when it adsorbs on alumina surface from the solution. Furthermore, when SDS is added first, PAA coiling index is found to increase continuously with SDS dosage and this corresponds to a similar decrease in system turbidity as shown in Figure 4.4.1. In contrast, for the case where PAA is added first, SDS has no effect on either the system turbidity or the PAA conformation at all SDS dosages.
Figure 4.4.2. PAA coiling index at alumina/water interface under the SDS/PAA and PAA/SDS addition modes as well as in solution in the presence of SDS.

On the basis of the above measurements of suspension turbidity and polymer coiling index, it is proposed that when SDS is added first, the pre-adsorbed surfactant causes "blocking" of the adsorption of the PAA added later, resulting in a smaller fraction of the polymer trains and thus a higher coiling index. However, when PAA is added first, SDS does not "block" adsorption of PAA which could be either due to masking of the polymer chains or due to prevention of SDS adsorption. Since a measure of the adsorption density of SDS in the presence of pre-adsorbed PAA (Figure 4.4.3) shows SDS adsorption not to be affected by PAA, it can be concluded that when PAA is added first, the subsequent adsorption of SDS does not affect PAA conformation. Because adsorbed SDS is very likely masked by the
dangling polymer chains, the suspension stability is not affected also. A schematic representation of the adsorbed states for both addition modes are given in Figure 4.4.4.

![Graph showing adsorption isotherm of SDS on alumina in the presence of pre-adsorbed PAA](image)

*Figure 4.4.3. Adsorption isotherm of SDS on alumina in the presence of pre-adsorbed PAA*
4.4.3. Effect of amount of pre-adsorbed polyacrylic acid (PAA)

Being masked by the PAA chains, SDS species have essentially no effect on the behavior of the whole system. When PAA concentration is decreased, at some point it can not be expected to be able to mask SDS completely and SDS will then begin to play a role. Figure 4.4.5 shows the turbidity of alumina suspension for PAA alone and PAA/SDS addition mode with SDS concentration kept constant.
Figure 4.4.5. Turbidity of alumina suspension as a function of PAA concentration in the absence and presence of SDS (PAA/SDS mode).

It can be seen from this figure that the optimum flocculation concentration of PAA when used alone is around 0.5 ppm. This is also the minimum concentration required to mask SDS molecules completely. The two curves in Figure 4.4.5 overlap when PAA concentration is above this concentration and deviate significantly from each other at PAA concentration below 0.5 ppm, i.e., SDS starts to have an effect on the system when PAA concentration is less than 0.5 ppm. When PAA concentration is very low, there are not enough chains available to mask SDS; on the other hand, at very high PAA concentrations, a significant fraction of adsorption sites on alumina are pre-occupied by the polymer and thus SDS adsorption density is reduced (Figure 4.4.6). When PAA concentration is higher than 350 ppm, there is no adsorption of SDS.
4.4.4. Stirring time

Since PAA adsorption is irreversible while SDS adsorption is readily reversible, given enough stirring time during the flocculation process, addition sequence should not be expected to make any difference, i.e., both the PAA coiling index and the suspension turbidity for SDS/PAA addition sequence should approach those for PAA/SDS sequence. It can be seen from Figure 4.4.7(a) that it takes about 30 minutes of stirring for the system to reach equilibrium with SDS/PAA sequence. During this process, the SDS adsorption density is found to remain constant (Figure 4.4.7(b)), indicating re-distribution of SDS instead of it being replaced, i.e., PAA relaxes and reoriented while SDS redistribute on alumina surface to comply with the polymer relaxation/reorientation.

Figure 4.4.6. SDS adsorption density on alumina as a function of pre-adsorbed PAA.
4.4.5. Effect of time interval between additions of PAA and SDS

Although SDS does comply with PAA relaxation as stirring proceeds, when SDS and PAA are added to alumina suspension at the same time, the system turbidity is more similar to that for SDS added alone (Figure 4.4.8). This suggests that SDS adsorbs more rapidly and
reversibly on alumina than the polymer. It can also be seen from Figure 4.4.8 that the flocculation/dispersion behavior of alumina suspension is very sensitive to the addition sequence of the two species. When flocculation time is of a few minutes, the species added first is always playing a dominating role, no matter how small the time interval between the two additions.

![Graph](image)

Figure 4.4.8. The effect of time interval between SDS and PAA additions on alumina stability.
4.4.6. Kinetics of SDS adsorption in the presence and absence of PAA

Finally, it was observed that the SDS adsorption is facilitated by the presence of small amounts of PAA (Figure 4.4.9). It is suggested that trace amounts of pre-adsorbed PAA can prevent flocculation caused by the SDS at certain SDS concentrations. This in turn can also prevent any retardation of adsorption due to inaccessibility of polymer into interior of flocs if they form.

Figure 4.4.9. The kinetics of SDS adsorption is enhanced by the presence of small amounts of pre-adsorbed PAA
4.4.7. Summary:

1. Effect of a pair of non-interacting polymer and surfactant on the adsorption of each other and on flocculation can be marked depending particularly on the addition sequence.

2. When SDS, the surfactant, was added first, the conformation of the polymer, PAA, and the suspension stability were found to vary with SDS dosages. A desired stability level can thus be obtained by manipulating SDS concentration. When PAA is added first, the SDS molecules adsorbed subsequently are masked by the polymer and make contribution neither to the PAA conformation nor to the suspension stability. For example, for the system studied, SDS adsorption density is not hampered by pre-adsorbed PAA as long as PAA concentration is not very high (<50ppm). Also, when PAA concentration is less than 0.5 ppm (which was also the optimal flocculation concentration) SDS was no longer masked by PAA; under these conditions, SDS had a measurable effect on the system behavior.

3. Time of reagentizing had a significant effect on both the adsorption and flocculation. If the flocculation time is on the order of a few minutes, the species added first plays a predominant role independent of time interval between the two addition. When flocculation time was long, PAA showed a governing role. PAA adsorption is irreversible while SDS adsorption is readily reversible. Both PAA coiling index and system turbidity for the SDS/PAA addition sequence approached those for the PAA/SDS addition sequence. In the former addition sequence, SDS is considered to redistribute itself to comply with PAA adsorption and its conformation.

4. A small amount of pre-adsorbed PAA can retard flocculation caused by SDS of certain concentrations and thereby accelerate the adsorption of SDS on alumina.
4.5. NMR Study of Water in Flocs

4.5.1. Introduction

Polymer/surfactant adsorption can lead to colloidal stability or particle flocculation, both of which are of importance in many industrial processes. Floc structure is one of the most important features of particle flocculation and this involves floc size, density and strength\textsuperscript{110, 111, 112, 113, 114, 115}. Spectroscopic techniques to investigate floc structure have been mainly limited to small angle neutron scattering (SANS)\textsuperscript{116, 117, 118} and CAT scan\textsuperscript{119}. SANS is based on the assumption that the observed interference pattern of the scattered radiation is determined by the distribution of separations between particle centers in the flocs\textsuperscript{6}. CAT is a special X-ray instrument that can produce three-dimensional images of an object.

Although designed for medical purposes, the CAT has been effectively utilized to study sedimentation and flocculation systems\textsuperscript{10}. In addition to SANS and CAT scan, computer simulation has also been used to characterize floc structure\textsuperscript{120, 121, 122, 123, 124}. The purpose of this work is to show the potential of using proton NMR to study water in flocs, and thereby obtain information on floc structure by analysis of NMR line shapes, intensities, and signal positions.

Proton NMR of water has been applied extensively to the study of solid-solute interactions such as water-glass\textsuperscript{125, 126 127}, water-clay\textsuperscript{128, 129}, protein solution\textsuperscript{130}, biological tissues\textsuperscript{131}, water-hydrated alumina\textsuperscript{132}, and water-silica powder\textsuperscript{133}. A marked decrease of the proton longitudinal and transverse relaxation times $T_1$ and $T_2$, as well as an increase in the $T_1/T_2$ ratio, has been observed compared to the values for pure or "bulk" water. The results were interpreted in terms of layers of water molecules with restricted mobility in the vicinity
of an interface. Water molecules are dynamically exchanged between an environment in which they relax slowly (free-water phase) and one in which they relax rapidly (bound water phase at or near the interface). Under conditions of rapid exchange on the NMR time scale, a single relaxation rate is observed and is the weighted average of the individual rate for each environment\textsuperscript{134}. Accordingly, the signal on the spectrum is broader for a higher ratio of bound to free water.

When the exchange of molecules between sites corresponding to different resonances is slow on the NMR time scale, multiple peaks can be observed. Two signals were reported for ion-exchange resin-water\textsuperscript{135} and silica-water systems\textsuperscript{136}. One signal was attributed to bulk water, while the other signal corresponds to water inside the resin or silica pores. Similar phenomena were observed for protein-water\textsuperscript{137},\textsuperscript{138} and carbosil-water\textsuperscript{139} systems, as well as a series of gels and macroreticular ion-exchange resins in water\textsuperscript{140},\textsuperscript{141}.

The difference of the chemical shift of the water signals has been discussed in terms of number of hydrogen bonding for oxide particles (silica systems) and ion-hydration effect (resins). However, this concept was challenged when multiple signals were found for systems without either donor-acceptor interactions or ion-hydration effect. The chemical shift difference for water signals was proposed to result from the contact of water with solids\textsuperscript{142}. It was also found that signals with different chemical shift values resulted when different pore sizes were employed.

In our investigation of alumina and zeolite flocs, the "H-bonding giving rise to the shift" was shown to be inadequate to explain the observations. When alumina and zeolites were studied in this investigation, in addition to the signal due to bulk water, an extra
downfield shifted signal was also observed. This second signal could not be adequately accounted for using the hydrogen-bonding theory, and hence it is attributed to the Bulk Magnetic Susceptibility (BMS)\textsuperscript{143,144} effect. The basic idea in the BMS theory is that a water molecule inside and outside a compartment will possess two different chemical shift values. This effect was found to be important in \textit{in vivo} NMR imaging study of biological tissues\textsuperscript{33,34} and may be useful for explaining what was observed in this study. According to BMS theory, the downfield shift results from water trapped in small compartments: pores in the particles or micro-channels within the flocs depending on what kind of particles are used.

4.5.2. NMR spectra of native flocs

With many of the samples investigated, separate resonances for the water protons were observed for alumina-water and zeolite-water systems, indicating a slow exchange of molecules between the sites corresponding to these resonances on the NMR time scale. These separate signals were attributed to water in micro-channels (trapped water) and macro-channels (bulk water) of the flocs as shown in Figure 4.5.1. In the case of highly porous zeolite, the porous internal surface within individual particles forms micro-channels in which the water is adsorbed; while for alumina, the micro-channels exist within the alumina aggregates formed by numerous primary alumina particles. In contrast to previous NMR reports on colloidal systems described above, our research involves \textit{in situ} study of natural flocs where the solid-liquid ratio is not quantitatively manipulated. It was proposed\textsuperscript{145} that two processes of water removal can occur with time: relatively fast expulsion of water in the macro-channels (bulk water removal) and relatively slow expulsion of water from within the
flocs (trapped water removal). The former is an inter-floc process while the latter is a intra-floc one (Figure 4.5.1). Therefore, when ratios of different water signals are examined, the values are for different settling times of the flocs because water is extruded as the floc densifies. Only flocs settled for the same time can be compared with each other. The time effect for zeolite-water system is shown in Figure 4.5.2, where the peak for trapped water increases with time as the zeolite floc settles and densifies due to bulk water expulsion.

Figure 4.5.1. Schematic representation of intra-floc water and inter-floc water as well as their expulsion processes.
Figure 4.5.2. The time effect on NMR peak ratio.

Common flocculants are of three types: salt, polymer, and surfactant. Salt and small polymer molecules are expected to induce flocculation mainly by charge neutralization, which produces very compact and dense flocs. In contrast, bridging is considered to be the mechanism for large polymer induced flocculation, and the resulting flocs are much bigger and less dense than those produced by salt or small polymers. Surfactants are less commonly used as flocculants. Surfactants induce flocculation by imparting hydrophobicity to the particles when the surfactant species orients with its hydrocarbon moiety towards the aqueous phase. Examples of the proton NMR of a compact and a loose floc system are shown in Figure 4.5.3. Since the fraction of trapped water is related to the floc density, loose flocs produced by the addition of small amounts of PAA contain an amount of trapped water that is so small that only one bulk water peak is observed; on the other hand, addition of
appropriate amounts of SDS enhances the floc packing density.

Figure 4.5.3. Flocs produced by three kinds of flocculants: salt, polymer and surfactant.

For fixed time scale, the particle size can be expected to affect the packing. Figure 4.5.4 shows the NMR spectra for a zeolite-water system for particles varying in size by a factor of 10 (The zeolite samples were synthesized by Wei Li in Prof. Turro’s group). It can be seen that the peak ratio of the trapped water to bulk water increases with decreasing particle size, indicating a denser packing of smaller particles and a greater fraction of trapped water for two ZSM-5 zeolites differing in particle size but not in pore size or polarity. The three kinds of zeolite particles possess the same internal pore size and pore structure, thus, in agreement with BMS theory, result in the same frequency shift for the trapped water. It is important to note that the composition of the 100µ silicalite particles (Si:Al>1000) is
- different from those of the other two (Si:Al=80:20). Nevertheless, the NMR signal for water shows the same down-field shift for all of the zeolite samples. This again indicates compartmental effect instead of donor-acceptor interaction with the particle surface.

\[ \text{100}\mu \text{ Silicalite.} \]

\[ \text{20}\mu \text{ ZSM-5 (Si:Al = 80:20)} \]

\[ \text{10}\mu \text{ ZSM-5 (Si:Al = 80:20)} \]

\[ \text{Chemical Shift (ppm)} \]

Figure 4.5.4. Particle size effect for zeolite in water.

Packing density can be changed also with temperature. This effect can be seen from an examination of Figure 4.5.5. For hydrophilic alumina particles, the trapped-water peak decreases markedly with an increase in temperature, which means that the packing is less
dense at higher temperature. For 10μ zeolite (Si:Al=80:20) which is much less hydrophilic than alumina, however, the temperature effect is quite different. The trapped water peak, instead of decreasing without changing its original resonance frequency, moves towards the bulk water peak as temperature is increased. This difference is associated with the fact that water molecules is expelled from the small hydrophobic pores as temperature is raised, and/or exchange between water inside and outside the pores begins to take place.

![Diagram showing temperature effect for alumina and zeolite flocs.](image)

**Figure 4.5.5.** Temperature effect for alumina and zeolite flocs.
4.5.3. Surfactant induced flocs:

The adsorption of sodium dodecyl sulfate (SDS) on alumina has been well studied, with an adsorption isotherm which can be divided into 4 regions\(^{147}\) (Figure 4.5.6). The surfactant adsorbs non-cooperatively and electrostatically as individual ions in region I and associate into soloids (hemimicelles) in region II of the isotherm. In the soloids, the surfactants are oriented with their charged headgroups toward the solid surface, while the hydrocarbon chains protrude into the aqueous phase, thus forming hydrophobic patches on the surface. Further adsorption results in an increasing number of surfactant aggregates, with surfactant molecules adsorbing with an opposite orientation once the surface is neutralized by the oppositely charged surfactant. Finally, in the plateau region, region IV, the adsorption layer possesses the structure of a bilayer with the adsorbed surfactant presenting the external surface with a changed structure.

![Figure 4.5.6. SDS induced flocs at different SDS concentrations (left: NMR spectra; upper right: adsorption isotherm; lower right: flocculation results).](image-url)
Figure 4.5.6 shows the water signals measured for alumina flocs with different coverages of SDS. The flocculation data could be correlated with the NMR spectra. The SDS coverage is illustrated by indicating its position on the corresponding adsorption isotherm. As described above, the hydrophobicity of alumina increases with SDS adsorption in adsorption regions I and II and starts to decrease from region III until it reaches a constant value in region IV where adsorption is saturated. Therefore, particles in sample c are most hydrophobic and have the strongest tendency for flocculation (Figure 6). Accordingly, the separation between the two peaks varies and shows a clear trend. The separation for sample c is the largest and decreases towards the two ends of the adsorption isotherm. This peak separation change indicates a change of the compartmental structure in the flocs. A more downfield shifted peak denotes a better screened and smaller compartments for trapped water. As the compartmental structure becomes bigger and more open, the two peaks start to approach each other.

The more hydrophobic the particles are, the stronger can be their tendency to aggregate in water. However, it is interesting to note from the NMR spectra that flocs resulted from the more hydrophobic particles have a slightly higher ratio of free/trapped water, which is also in agreement with their higher specific sediment volume (Figure 4.5.6). In other words, although better flocculation can be achieved with more hydrophobic particles, less overall packing density is achieved. This is attributed to the stronger attraction between hydrophobic particles causing a larger viscous force working against the gravitational driving force of better packing of flocs. Inter-floc water (bulk water) expulsion is therefore retarded after flocs settle down.
4.5.4. Polymer flocculated particles

Polymers are the commonly used flocculants. We have studied dual polymer flocculation with the system Percol-polyacrylic acid (PAA)-alumina\textsuperscript{148}. For this study, 5 ppm of the cationic polymer (Percol) and 5 ppm of the anionic polymer (PAA) were used to produce very good flocculation. In this system, PAA is first adsorbed on alumina and served as the anchor for Percol which bridges the particles together.

NMR spectra were taken at different times after the flocculation. As shown in Figure 4.5.7, due to the loose structure of polymer-bridging induced flocs, the ratio of trap to bulk water signal is much smaller than that for particles with adsorbed surfactant and bare particles. The amount of trapped water becomes smaller with time and eventually disappears, with the signal for bulk water staying the same. The disappearance of the trapped water suggests intra-floc water expulsion accompanying with polymer rearrangement. This phenomenon occurs more readily with polymer-induced loose flocs where the bulk water removal is hindered by the presence of the polymer.

4.5.5. Conclusion

The feasibility of using conventional proton NMR spectroscopy for studying floc structure and floc sedimentation is demonstrated. It provides a quick and straightforward method to follow the inter-floc and intra-floc water expulsion processes and to examine the floc packing and structure. Some new information was gained on surfactant and polymer induced flocs.
Figure 4.5.7. Time effect for dual polymer induced flocs.
4.6. Computer simulation for flocculation of particles with surface heterogeneity

4.6.1. Introduction

One of the principal, long-term goals of colloid science has been to understand the mechanisms of flocculation and the structure and kinetics of aggregate formation. The emphasis of much computational work in the past has been toward developing an understanding of the nature and origin of the structures that result. Considerable progress has been made using Monte Carlo techniques to simulate kinetics of growth processes. A universal feature of the models appears to be the self-similar fractal nature of the clusters that are formed. The models investigated can be divided into two major classes. In what has become known as diffusion-limited aggregation (DLA)\textsuperscript{149,150}, the growth of aggregates takes place by collisions of an individual particle with a growing aggregate. The individual particles diffuse independently and become part of the aggregate whenever a collision occurs. The second model, commonly known as cluster-cluster aggregation, takes into account the possibility that clusters themselves can diffuse and stick together to form a larger aggregate.

In its original version\textsuperscript{151,152}, the cluster-cluster model starts with a collection of equal-sized individual spherical particles randomly placed in a box. These particles are then allowed to undergo diffusion simulated by a pure random walk. When two particles come into contact, they irreversibly stick together to form a rigid dimer which is also able to diffuse within the box. The mechanism can be replicated until a single large aggregate remains alone in the box.

A number of extensions have been made over the years based on the original version
of cluster-cluster aggregation\textsuperscript{153,154,155,156,157,158,159,160}. However, in all previous studies, the particles are taken as points or spheres with uniform surface properties, which is not realistically the case in most flocculation practices. For example, in patch model of flocculation, the particle surface is composed of positive and negative patches. It is the heterogeneous surface that is the essence of the patch flocculation. Thus, a more realistic model would be one which employs spheres with non-uniform surfaces in the computer simulation. This would not only help one to study the flocculation induced by patch adsorption of polymer, but also surfactant induced flocculation and any other systems involving surface heterogeneity.

The novel approach created for the purpose of surface heterogeneity involves the following steps:

1. Generate a cluster of randomly distributed particles in a box (5000 if not otherwise noted).

2. Generate unique surface properties for the surface of each individual particle – for example, after dividing each sphere into 20 pieces of equal size, make positive label for 5 patches and negative labels for the rest 15 patches. The distribution of the 5 positive patches is random for all the particles. In this case, we will have particles with a surface coverage of 25\% (i.e., polymer occupies 25\% the particle surface as in the case of patch model) and the polymer size will be 1/20 of the sphere periphery.

3. In each iteration, all the particles/aggregates undergo random walks, with the step size decreasing with the aggregate size represented by the number of particles in the aggregate.
4. Whenever the centers of any two particles are equal or smaller than the particle diameter, irreversible aggregation takes place. Particles in one aggregate will move together in the rest simulation process.

5. The average number of aggregates can be recorded as a function of number of step size (which is an indication of time) for the study of flocculation kinetics. Floc structure can be studied when all the 5000 particles form a single aggregate.

To define the size and structure of the final flocs, radius of gyration \((R_g)\) and anisotropy ratio \((A)\) are used\(^{161}\).

The anisotropy \(A\) can be quantitatively investigated by diagonalizing the tensor of the radii of gyration:

\[
(R_{ab})^2 = \sum_{i,j} (r_{ia} - r_{ja})(r_{ib} - r_{jb})/N^2 \quad (4.2)
\]

where \(a\) and \(b\) refer to the coordinates and \(i\) and \(j\) to the particles in the aggregate.

The usual radius of gyration (squared) is simply the trace of the tensor:

\[
R^2 = \sum_a (R_{aa})^2 \quad (4.3)
\]

Using the hierarchical procedure in two dimensions, the tensor is diagonalized, and the ratio of the larger to lower eigenvalues \((R_1)^2\) and \((R_2)^2\) is designated as anisotropy ratio \(A\).

\[
A = \frac{\langle (R_1)^2 \rangle}{\langle (R_2)^2 \rangle} \quad (4.4)
\]
This approach provides a simple way to study different parameters involved in flocculation of particles with surface heterogeneity.

4.6.2. Surface Coverage

Our initial results show that as polymer coverage increases, the kinetics of flocculation are enhanced (Figure 4.6.1). As can be seen from the figure, this enhancement in kinetics is more obvious when the surface coverage is low. At higher surface coverages, in the range of 25%–50% coverage, the enhancement is quite insignificant.

Figure 4.6.1. Kinetics of flocculation as a function of polymer surface coverage (the inserted figure shows the kinetics for the first 100 steps)
Taking flocculation rates for particles with 50% surface coverage to be 100% at different stages of flocculation, the above figure (4.6.1) can be represented in another way where difference of flocculation rate for particles with different surface coverages can be more easily seen (Figure 4.6.2). It is well known that flocculation rate results from both collision rate and collision efficiency. The former increases with the number of aggregates and therefore decays with step number, whereas the latter could be taken as more or less constant along the flocculation process, with a higher constant value for particles with higher surface coverage. Therefore, particles with a lower surface coverage starts with a lower flocculation rate (as determined by its surface coverage), which decays more slowly compared with those for particles of a higher surface coverage. This accounts for the smaller difference between particles with different surface coverages with increasing step numbers, as shown in Figure 4.6.2.

Figure 4.6.2. Relative flocculation rates for particles with different surface coverage.
It is interesting to note that the final flocs as shown in Figure 4.6.3, vary with polymer surface coverage. Although a higher surface coverage results in quicker/better flocculation, the resulting floc has a looser structure. This is probably because as the collision efficiency decreases with a lower surface coverage, particles/aggregates have a better chance to explore the core of other aggregates, instead of being captured on the periphery of aggregates.

![Diagram of floc structure](image)

(a) 5%  
(b) 15%  
(c) 25%

Figure 4.6.3. Examples of floc structure for particles with polymer surface coverages of 5%, 15% and 25%.

The radii of gyration ($R_g$) were calculated to quantify the size of floc as a function of surface coverage. The result is shown in Figure 4.6.4. Each point is an average of 10 floc sizes and the standard deviation are plotted as error bars. The increase in floc size can be seen from this figure as the surface coverage increases to 25%. When surface coverage is higher than 25%, however, a plateau value is reached and the flocs stop growing in size. It is to be noted that this plateau value is about 1/4 of that when collision efficiency is considered 100% as in the case of homogeneous surfaces.
Figure 4.6.4. Relative floc size as a function of surface coverage (compared with floc size where collision efficiency is 100%)

The anisotropy ratio (A) was attempted here to quantify the shape/anisotropy of the flocs. Due to the large fluctuation of this value, no conclusion can be firmly drawn. It can only be observed that in general, there seems to be an increase in isotropy as surface coverage/collision efficiency increases.
Figure 4.6.5. Anisotropy ratio (A) as a function of surface coverage (compared with those for 100% collision efficiency and ideal spheres)

4.2.3. Patch Size

Patch size, in the case of polymer-induced patch flocculation, is related to polymer size. Since collision efficiency is determined by patch ratio/surface coverage instead of the size of individual patches, it is expected that patch size should not make any difference in modeling patch flocculation. However, from Figure 4.6.6, an increase in flocculation rate with smaller patch size can be seen. In the initial stage when collision rate is a dominant factor, the curves diverge more with step number (Inserted part of Figure 4.6.6), suggesting a bigger difference in collision efficiency with step numbers.
Figure 4.6.6 Effect of patch size on flocculation kinetics (patch ratio is kept at 25% while patch size equals to 1/4, 1/20 or 1/40 of the particle periphery respectively)

This puzzle can be solved by examining the patch ratio for aggregate. It can be seen, from a geometric point of view, that patch ratio for aggregate is not the same as that for individual particle. Once an aggregate is formed, there is a large area of surface unavailable for further collision (Figure 4.6.7). The patch ratio in the hidden area, x, is different from that of the individual particle, y. Only when the particle surface is divided into a large number of patches, x will approach y. The difference between x and y is larger with bigger patch size.
The relationship between collision efficiency and patch size for particles with 25% coverage is derived to be:

\[ E = 0.236 - 0.1275x - 0.25x^2 \]

Apparently, the collision efficiency (E) decreases with patch ratio of the aggregate (x).

Figure 4.6.7. Schematic representation of hidden area of aggregates which is not available for further collision.
3. Addition mode

In the above tests, each particle possesses the same degree of surface coverage, denoting an ideal mixing. Since non-ideal mixing is the real case in most applications, it is of importance to study the effect of addition mode.

As can be imagined, when polymer is injected from the center of a slurry container and not mixed properly, the particle surface coverage will vary as a function of its distance to the location of polymer addition, i.e. container center: particles near the center of the container will likely have a higher surface coverage while the ones in the corners will have a lower coverage.

In the first piece of test for non-ideal mixing, the container is divided into 3 regions defined by 3 squares of different sizes but the same center. The area ratio is 1:1:2. Particles are evenly distributed in these 3 regions. In the case of ideal mixing, particles in all the regions possess a 25% polymer coverage. Two cases of non-ideal mixing were created with the total amount of positive patch kept equal to that for the case of ideal mixing. In one case of non-ideal mixing, 15%, 25% and 45% are the surface coverages for outer, intermediate, and inner regions respectively. In the other case, 5%, 25% and 65% are the surface coverages, representing a larger uneven mixing.

Comparison between the ideal mixing and the non-ideal mixing cases shows that kinetics of flocculation is retarded for non-ideal mixing while there seems to be not much difference observed for the final floc structure (Figures 4.6.8&4.6.9)

It can be concluded that ideal mixing is preferred in order to achieve rapid flocculation.
Figure 4.6.8. Mixing effect on flocculation kinetics

Figure 4.6.9. Mixing effect on floc structure
4.6.5. Summary

The above results manifest the feasibility of the novel approach to study flocculation of particles with heterogeneous surfaces. Some conclusions can be drawn from these initial results:

1. Effect of patch ratio

Flocculation rate -- Particles with a higher ratio always have a higher flocculation rate. The difference is maximum at the initial stage when flocculation is dominated by collision efficiency; with increase in time, collision rate becomes more important and the difference in flocculation rate continues to decrease.

Floc size -- Floc size increases with patch ratio and reaches a plateau region when patch ratio is in the range of 25% to 50%. Flocs produced from particles with surface heterogeneity are much smaller compared to those with surface homogeneity where collision rate is considered to be 100%.

Floc shape -- It is likely that bigger flocs produced from higher patch ratio has a lower anisotropy value, i.e., they are more isotropic in shape.

2. Effect of patch size

At a constant patch ratio, smaller patch is preferred. This conclusion can be reached from both a geometrical calculation and a computer simulation. It has to be noted that floc strength and thus floc breaking is not taken into account.

3. Effect of mixing

An even distribution of patches is preferred for rapid flocculation.

Much remains to be studied regarding the aspects mentioned above: surface coverage,
patch size and addition mode. Some other aspects such as solid loading effect can also be conveniently studied. In addition, it will be challenging to explore floc breaking as a function of individual floc strength.
Chapter 5. Summary and Conclusions

Polymers and surfactants play very important roles in colloidal stability (floculation or dispersion) in almost every industry. However, there is a lack of deep understanding of the field due to the complexity of the systems involved. Apparently, there is a need for both a systematic study on different systems and a more powerful multi-pronged approach to enhance the problem-solving capabilities. It is therefore attempted in this study to make a parallel investigation on some interesting systems and on some novel methods as the tools for the study. A summary of the results and the conclusions drawn are presented below:

Surfactant adsorption on mineral oxides

It was confirmed from the case study - adsorption of trimethylammonium bromides on negatively charged alumina - that the type of the adsorption isotherm and the adsorption mechanism for ionic surfactants depend on the type of substrate used. The four region model proposed in the 60's is still proven to be valid for metal oxides with a constant potential. It was shown from ESR measurements that the surfactant layer becomes more viscous as the adsorption density increases. An increase in viscosity of the surfactant layer with surfactant chain length was also observed. Solloid aggregation numbers along the adsorption isotherms were obtained with time-resolved fluorescence. In addition to bigger solloids at higher adsorption density with a trend as predicted by the four region model, the aggregation number also increases with surfactant chain length. Furthermore, it is suggested that although the substrate may decide the type of adsorption isotherm, the shape of the isotherm
within one type is dominated by solloid nature as influenced by many factors such as the type of surfactant, the substrate and the solution conditions.

**Dual polymer flocculation**

Flocculation of alumina can be markedly enhanced by choosing an appropriate pair of oppositely charged polymers: polyacrylic acid (PAA) and cationic copolymer (Percol). PAA chosen in this study produces primary flocs and also serves as anchors for the adsorption of the second polymer. Charge neutralization and bridging are found to co-exist in the formation of primary flocs. Bigger primary flocs can be formed with larger PAA, resulting in a decreased optimum dosage of the second polymer required. A wider molecular distribution of PAA M.W. can also widen the optimum dosage range of Percol and is hence preferred. With the second polymer, bigger flocs form with the larger polymer, and increase in charge density reduces the optimum polymer dosage. This can be explained using patch model. From the polymer conformation study, it was found that increase in the concentration of one of the two polymers makes the other polymer more stretched. Finally, it was found that sequential addition is a better mode than co-addition, i.e., polymer complexation should occur after the adsorption of the first polymer, since polymer adsorption is essentially irreversible. In this mode, a maximum amount of the second polymer is available for complexation coupled with bridging.
Suspension in the presence of polymer and an interacting surfactant

Using polyacrylic acid (PAA), non-ionic ethoxylated surfactant (NP-15), and alumina suspension as the model system, interaction between the polymer and the surfactant as well as its effect on the suspension stability were studied. It was shown from the NMR data that PEO segments of NP-15, including the PEO tail, form hydrogen bonding with PAA. The NP-15 aggregates in the presence of PAA have a looser structure compared to that in the absence of PAA. The hydrogen bonding between these two species induces a conformational change of PAA. By manipulating the amount of NP15, PAA coiling index can be controlled. It was found that monomer of NP15 can coil up PAA while NP15 micelles can stretch PAA chains. Since the interaction is mainly through H-bonding, the interaction is greater at lower pH values. When pH is higher than 5, the interaction between NP15 micelle and PAA is negligible. In the presence of alumina suspension, when PAA is added first, both the optimum flocculation and the maximum of PAA coiling index match with CMC of NP15. The tentative explanation is that NP15 monomers collapse PAA loops and tails which are restored when NP15 micelles form.

Suspension in the presence of polymer and a non-interacting surfactant

Effect of a pair of non-interacting polymer and surfactant on the adsorption of each other and on flocculation of adsorbent can be marked depending particularly on the addition sequence.

When SDS, the surfactant, was added first, the conformation of the polymer, PAA, and the suspension stability were found to vary with SDS dosages. A desired stability level
can thus be obtained by manipulating SDS concentration. When PAA is added first, the SDS molecules adsorbed subsequently are masked by the polymer and make contribution neither to the PAA conformation nor to the suspension stability. For example, for the system studied, SDS adsorption density is not hampered by pre-adsorbed PAA as long as PAA concentration is not very high (<50ppm). Also, when PAA concentration is less than 0.5 ppm (which was also the optimal flocculation concentration) SDS was no longer masked by PAA; under these conditions, SDS had a measurable effect on the system behavior.

Time of reagentizing had a significant effect on both the adsorption and flocculation. If the flocculation time is on the order of a few minutes, the species added first plays a predominant role independent of time interval between the two addition. When flocculation time was long, PAA showed a governing role. PAA adsorption is irreversible while SDS adsorption is readily reversible. Both PAA coil index and system turbidity for the SDS/PAA addition sequence approached those for the PAA/SDS addition sequence. In the former addition sequence, SDS is considered to redistribute itself to comply with PAA adsorption and its conformation.

A small amount of pre-adsorbed PAA can retard flocculation caused by SDS of certain concentrations and thereby accelerate the adsorption of SDS on alumina.

**NMR study on floc structure**

The feasibility of using conventional proton NMR spectroscopy for studying floc structure and floc sedimentation is demonstrated. Since water at different locations shows NMR signals of different chemical shifts, it provides a quick and straightforward method to
follow the inter-floc and intra-floc water expulsion processes and to examine the floc packing and structure. A higher packing density usually results in a higher ratio of intra- to inter-water signal. A bigger and more open compartmental structure correlates with peaks with bigger separation. For polymer-induced loose flocs, intra-floc water repulsion is more readily observed since the bulk water expulsion is hindered by the presence of the polymer.

**Computer simulation for flocculation of particles with surface heterogeneity**

A computer program was created to study flocculation of particles with heterogeneous surfaces. It was found that particles with a higher patch ratio flocculate at a higher rate. The difference in flocculation rate is maximum at the initial stage when flocculation is dominated by collision efficiency; with increase in time, collision rate becomes the governing factor and the difference in flocculation rate continues to decrease. Floc size grows with patch ratio and reaches a plateau value when patch ratio is in the range of 25%-50%. Flocs produced from particles with surface heterogeneity are much smaller compared with those with surface homogeneity where collision rate is considered to be 100%. It is likely that bigger flocs produced from higher patch ratio has a lower anisotropy value, i.e., they are more isotropic in shape. At a constant patch ratio, smaller patch size is preferred for rapid flocculation, when floc strength and thus floc breaking is not taken into account. Finally, an even distribution of patch ratio, resulting from a good mixing, is preferred for faster flocculation.
Chapter 6. Suggestions for Future Work

The present study has provided more information on some important systems and indicated feasibility of some new approaches for the study in this field. Based on the results obtained, the following problems are identified for further study:

**Systematic study on complicated systems:**

Several different combinations of 2 flocculants were studied in this work, including a polymer in the presence of an interacting polymer, an interacting surfactant, and a non-interacting surfactant. It would be useful to list all the possible combinations in a table and fill the blank ones with studies on model systems (e.g., "two non-interacting polymer" is identified as an unstudied combination). The table could be made even bigger by considering salts of different charges as another important flocculant or extend the combination to 3 or even more components. As multi-component systems are important for many industries, this kind of systematic work will provide a very basic and helpful guide.

**Novel approaches**

The novel approaches of this work, applications of conventional NMR and computer simulation in flocculation/dispersion, have not yet been widely applied to different systems yet. Therefore, a lot more could be done in the future.

For computer simulation, there are a lot more aspects can be studied by utilizing the current program created. For example, the present study involves effective collision upon
contact of two patches of opposite charges. For some cases such as hemimicelle adsorbed particles, flocculation happens when patches of similar nature get into contact (i.e., hydrophobic patches occupies by surfactants). This could be conveniently studied by a slight modification of the current program. Effect of solid loading can be studied even without any modification of the computer program. In addition, a much more challenging work, which also requires more intelligence in the programming work, is to study the patch effect as well as the floc-breaking/floc-strength at the same time. It has to be noted that computer simulation simulates a very ideal system: there might be quite a difference between what appears on the screen and what happens in the real suspensions.

A multi-pronged approach

Different approaches have been attempted for studying flocculation and dispersion over the years: conventional measurements of the bulk properties, recently-adapted spectroscopic methods for molecular level understanding, novel applications of NMR which does not require any spin label or probe, or computer simulation. It would be important to study model systems with all the possible approaches at the same time, to identify the strength and weakness of each.
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Appendix A

C programming program (used for computer simulation for flocculation)

#include <stdio.h>
#include <math.h>
#include <sys/time.h>

int npnt=5000; /* number of particle */
int MAXPATCH=20; /* number of patches */
int POSPATCH=1; /* positive patches */
int MAXSTEP=2;
float RADIUS=0.001;
int STEPSIZE=10; /* how many time of radius */
int AGGTOTAL;
float pi;
struct particle{
    float cx;
    float cy;
    int patchcharge[40];
} PAR;

struct particle pars[5000];

struct point { int parnum: struct point *next;} POINT;

struct point *aggregate[5000];

int aggrnum[5000];

float xmin[5000], xmax[5000], ymin[5000], ymax[5000];

int checkstick(int par1, int par2)
{
    float cx1, cx2, cy1, cy2;
    float dist, angle;
    int patchnum1, patchnum2;
    int ret;

    pi=3.1415926536;
    ret=0;

    cx1=pars[par1].cx; cx2=pars[par2].cx;
cy1=pars[par1].cy; cy2=pars[par2].cy;

dist= sqrt((cx2-cx1)*(cx2-cx1)+(cy2-cy1)*(cy2-cy1));
if (dist<= 2*RADIUS)
{
    if (dist<0.00001) ret=1;
    else
    {
        angle= acos((cx2-cx1)/dist);
        if (cy2<cy1) angle= 2*pi- angle;

        patchnum1=angle/(2*pi/MAXPATCH);
        if (angle<pi)
            patchnum2=(angle+pi)/(2*pi/MAXPATCH);
        else
            patchnum2=(angle-pi)/(2*pi/MAXPATCH);

        if (pars[par1].patchcharge[patchnum1] != pars[par2].patchcharge[patchnum2])
            ret=1;
    }
}
return(ret);

printinterme(int step)
{
    int i;
    FILE *fl;
    struct point *header;
    int histo[5001];
    char fname[10];

    for (i=1;i<=npnt;i++) histo[i]=0;
    for (i=0; i<npnt;i++)
    {
        if (aggnnum[i]>0) histo[aggnnum[i]]++;
    }
sprintf(fname,"histo%d.yyy",step);
fl=fopen(fname,"w");
fprintf(fl,"Average %d\n", AGGTOTAL);
for (i=1;i<=npnt;i++)
    fprintf(fl,"%d\n",histo[i]);
fclose(fl);
sprintf(fname,"%d_%yy",step);
fl=fopen(fname,"w");
    for (i=0;i<npnt;i++) fprintf(fl, "%f \n",pars[i].cx);
fclose(fl);
sprintf(fname, "y%d_{yyy}" ,step);

fl=fopen(fname,"w");
    for (i=0;i<npnt;i++) fprintf(fl, "%f\n", pars[i].cy);
fclose(fl);
}

printresult()
{
    int i,j;
    FILE *fl;
    struct point *header;
    int histo[5001];
    int totalagg;
    float radgy, ani;
    float rxx,rry,rrxy;
    float eigen1, eigen2;

    rxx=0.0; ryy=0.0,rrxy=0.0;
    for (i=0;i<npnt;i++)
        for (j=i+1;j<npnt;j++)
            {
                rxx=rxx+((pars[j].cx-pars[i].cx)*(pars[j].cx-pars[i].cx));
                ryy=rry+((pars[j].cy-pars[i].cy)*(pars[j].cy-pars[i].cy));
                rxy=rrxy+((pars[j].cx-pars[i].cx)*(pars[j].cy-pars[i].cy));
            }
    rxx=rxx/npnt; ryy=rry/npnt; rxy=rrxy/npnt;

    radgy=sqrt( rxx+rry);
    eigen1=(rxx+rry)+sqrt((rxx-rry)*(rxx-rry)+4*rxy*rxy);
    eigen2=(rxx+rry)-sqrt((rxx-rry)*(rxx-rry)+4*rxy*rxy);
    ani=eigen1/eigen2;
}
/*  totalagg=0;
  for (i=1; i<=npnt;i++) histo[i]=0;
  for (i=0;i<npt;i++)
    if (aggnum[i]>0)
      histo[aggnum[i]]++;
    totalagg++;
  }

  fl=fopen("histo.yyy", "w");
  printf( "Average %f \n", npnt/(totalagg*1.0));
  for (i=1;i<=npnt; i++)
    fprintf(fl,"%d\n", histo[i]);
  fclose(fl);
  fl=fopen("hx.yyy", "w");
  for (i=1;i<=npnt;i++) fprintf(fl,"%d\n",i);
  fclose(fl);
*/

fl=fopen("x.yyy","w");
  for (i=0;i<npt;i++) fprintf(fl, "%f \n".pars[i].cx);
  fclose(fl);
  fl=fopen("y.yyy","w");
  for (i=0;i<npt;i++) fprintf(fl, "%f\n".pars[i].cy);
  fclose(fl);

fl=fopen("aggrlist","w");
  fprintf(fl,"rad of gyr: %fn", radgyr);
  fprintf(fl,"anisotropy: %fn", ani);
  for (i=0;i<npt;i++)
    {
      header=aggregate[i];
      while (header!=NULL)
        {
          fprintf(fl,"%dn", header->parnum);
          header= header->next;
        }
    }
fclose(f1);
}

main()
{  float done, pi;
  int i, j;
  int patchl, step;
  float angle, dx, dy;
  struct point *header, *headeri, *headerj;
  int current, par1, par2, stick;

  FILE *d;
  /*  d=fopen("../matlab/ml.m","w");
   */
  /* This file store the data for matlab. Matlab will draw the graph of the
   convex hull. */

  pi=3.1415926536;
  /*  printf("input # of particles\n");
   scanf("%i",&npnt);
   */
  done=1.0; for (i=1; i<=15; i++) done=done*2.0; done--;

  AGGTOTAL=npnt;
  srand(10);

  for (i=0; i<npnt; i++)
  {
    pars[i].cx=rand()/done; pars[i].cy=rand()/done;

    for (j=0; j<MAXPATCH; j++) pars[i].patchcharge[j]=0;
    j=0;
    while (j<POSPATCH)
    {
      patchl=rand()%MAXPATCH;
      if (pars[i].patchcharge[patchl]==0)
      {
        pars[i].patchcharge[patchl]=1; j++;
      }
    }

    aggregate[i]=(struct point *)malloc(sizeof(POINT));
aggregate[i]->parnum=i; aggregate[i]->next=NULL;
agnum[i]=1;

xmin[i]=pars[i].cx; xmax[i]=pars[i].cx;
ymin[i]=pars[i].cy; ymax[i]=pars[i].cy;
}
step=0;
while (AGGTOTAL>1)
{
    /* step++;
       if (step%10==0 & & step <100)
           printinterme(step);
       if (step%100==0)
           printinterme(step);
       printf("step # %d\n",step);
    */
    for (i=0;i<nptr;i++)
    {
        if (agnum[i]>0)
        {
            angle=2*pi*(rand()/done);
            /* dx=(RADIUS*STEPSIZE)*cos(angle)/pow(agnum[i]*1.0,1.0/2.0);
                dy=(RADIUS*STEPSIZE)*sin(angle)/pow(agnum[i]*1.0, 1.0/2.0);
            */
            dx=(RADIUS*STEPSIZE)*cos(angle);
            dy=(RADIUS*STEPSIZE)*sin(angle);
            if (((xmax[i]+dx <=1.0) & & (xmin[i]+dx >=0.0)
                & & (ymax[i]+dy <=1.0) & & (ymin[i]+dy >=0.0))
            {
                xmax[i]=xmax[i]+dx:
                xmin[i]=xmin[i]+dx;
                ymax[i]=ymax[i]+dy;
                ymin[i]=ymin[i]+dy;
                header=aggregate[i];
                while (header!=NULL)
                {
                    current=header->parnum;
                    pars[current].cx = pars[current].cx +dx;
                    if (pars[current].cx<0)
                        pars[current].cx=0;
                    header=header->next;
                }
            }
if (pars[current].cx>1)
    pars[current].cx=1;
pars[current].cy= pars[current].cy + dy;
if (pars[current].cy<0)
    pars[current].cy=0;
if (pars[current].cy>1)
    pars[current].cy=1;

header= header->next:
}
}
}

for (i=0;i<npnt;i++)
{
    if (aggnum[i]>0)
    {
        for (j=i+1 ; j<npnt; j++)
        {
            if (aggnum[j]>0)
            {
                if (((xmax[i]>xmax[j]) && (xmin[i]<xmax[j]) +
                    2*RADIUS) || ((xmax[j] > xmax[i])
                    && (xmin[j] < xmax[i]+ 2*RADIUS))
                && (((ymax[i]>ymax[j]) && (ymin[i] < ymax[j])
                    + 2*RADIUS) || ((ymax[j]>ymax[i])
                    && (ymin[j] < ymax[i]+2*RADIUS))))
                {
                    stick=0;
                    headeri=aggregate[i];
                    while (stick==0 && headeri!= NULL)
                    {
                        par1 = headeri->parnum;
                        /*
                         printf("%d\n",par1); */
                        headerj=aggregate[j];
                        while (stick==0 && headerj!=NULL)
                        {
                            par2=headerj->parnum;
                            /*
                             printf("%d\n",par2); */
                            stick= checkstick(par1,par2);
                            if (stick==0) headerj=headerj->next;
                        }
                    }
                }
            }
        }
    }
if (stick==0) header=header->next;
}

if (stick==1)
{ AGGTOTAL--;  
  header= aggregate[i];
while (header->next != NULL) header=header->next;
  header->next= aggregate[j];
  aggregate[j]=NULL;
  aggnum[i]=aggnum[i]+aggnum[j];
  aggnum[j]=0;

  if (xmax[i]<xmax[j]) xmax[i]=xmax[j];
  if (xmin[i]>xmin[j]) xmin[i]=xmin[j];
  if (ymax[i]<ymax[j]) ymax[i]=ymax[j];
  if (ymin[i]>ymin[j]) ymin[i]=ymin[j];
}

}

printresult();
}
Appendix B
Deuterium NMR study for solloid dynamics

Relaxation time $t_1$ and $t_2$ were measured for SDS soloids (deuterium located nearest to the SDS head-group) on alumina at different pHs and salt concentrations. It can be see from the data listed in the table that changing pH has a much bigger effect in immobilizing solloid than increasing the salt concentration. This work is not furthered due to the low sensitivity thus a extremely long time involved in the acquisition.

<table>
<thead>
<tr>
<th>pH</th>
<th>salt</th>
<th>Adsorption density ($10^4$mol/m$^2$)</th>
<th>$t_1$(ms)</th>
<th>$t_2$(μm)</th>
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<td>6.5</td>
<td>27.5 122</td>
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<tr>
<td>System 2</td>
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<td>0.1</td>
<td>7.5</td>
<td>18 35</td>
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<td>0.5</td>
<td>7.3</td>
<td>25 68</td>
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Appendix C
Data for Figures

Figure 4.1.1

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<td>4.92E-2 1.83E-6</td>
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<tr>
<td>1.93E-2 3.43E-6</td>
<td>3.29E-2 2.27E-6</td>
<td>3.36E-2 1.64E-6</td>
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<tr>
<td>2.48E-4 3.16E-6</td>
<td>6.78E-3 2.70E-6</td>
<td>2.33E-2 1.29E-6</td>
</tr>
<tr>
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<td>1.75E-2 1.67E-6</td>
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<tr>
<td>1.16E-4 2.53E-7</td>
<td>3.77E-3 2.26E-6</td>
<td>1.43E-2 1.25E-6</td>
</tr>
<tr>
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Figure 4.1.2

|        | 1.56E-6 2.26E-9 | 1.56E-6 1.70E+0 |
|        | 1.31E-5 7.69E-9 | 3.29E-5 2.17E+1 |
| 3.29E-5 1.07E-8 | 1.07E-4 4.20E+1 |
| 9.16E-5 2.02E-8 | 1.29E-4 1.67E+1 |
| 1.07E-4 9.34E-8 | 2.48E-4 1.70E-0 |
| 9.82E-5 1.50E-7 | 1.93E-2 7.70E+0 |
| 1.29E-4 2.44E-7 |        |
| 1.20E-4 7.48E-7 |        |
| 2.48E-4 3.16E-6 |        |
| 1.93E-2 3.43E-6 |        |
| 3.08E-5 1.20E-8 |        |
| 8.55E-5 2.39E-8 |        |
| 1.12E-4 8.92E-8 |        |

Figure 4.1.3.

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</tr>
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<tr>
<td>2.48E-4 3.16E-6</td>
<td>3.02E-4 1.56E-1</td>
</tr>
<tr>
<td>1.20E-4 7.48E-7</td>
<td>9.20E-5 2.37E-0</td>
</tr>
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</tr>
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<td>1.29E-4 2.44E-7</td>
<td>1.03E-5 2.27E-0</td>
</tr>
<tr>
<td>9.82E-5 1.50E-7</td>
<td></td>
</tr>
<tr>
<td>1.07E-4 9.34E-8</td>
<td></td>
</tr>
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<td>1.56E-3 1.55E-1</td>
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### Figure 4.2.1.

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### Figure 4.2.2.

| 1      | 356   | 17   |
| 2      | 211   | 3    |
| 3      | 143   | 17   |
| 4      | 106   | 2    |
| 5      | 82    | 2    |
| 6      | 60    | 2    |
| 7      | 51    | 2    |
| 8      | 44    | 2    |
| 9      | 119   | 2    |

### Figure 4.2.3.

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<tr>
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</table>

|             |             | 2             |
|             |             | 3             |
|             | 50          | 94             |
|             | 60          | 137            |
|             | 70          | 154            |
|             | 80          | 251            |
|             | 100         | 367            |
### Figure 4.2.4.

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### Figure 4.2.5.

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**Figure 4.2.7.**

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**Figure 4.2.8.**

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<th>Solid/Liquid interface (co-addition)</th>
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**Figure 4.3.2.**

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**Figure 4.3.3**

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### Figure 4.3.4.

- **1.00E-7:** 5.91E-1 8.00E-3 4.37E+0
- **7.20E-7:** 6.22E-1 3.62E-3 4.28E+0
- **2.17E-6:** 6.11E-1 9.51E-4 4.26E+0
- **7.09E-6:** 6.37E-1 6.95E-4 4.22E+0
- **2.13E-5:** 6.69E-1 3.37E-4 4.06E+0
- **6.23E-5:** 6.14E-1 1.09E-4 4.01E+0
- **6.91E-4:** 2.21E-1 7.11E-5 4.02E+0
- **6.00E-3:** 1.88E-1 3.31E-5 4.02E+0
- **6.33E-5:** 6.59E-1 9.73E-6 4.00E+0
- **3.37E-4:** 2.47E-1 5.53E-6 4.00E+0
- **6.82E-4:** 2.09E-1 1.00E-7 4.00E+0
- **1.35E-3:** 2.00E-1

### Figure 4.3.5.

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### Figure 4.3.6.

- **3.4:** 0.361
- **3.8:** 0.371
- **4.55:** 0.245
- **5.7:** -0.053
- **7.1:** -0.104
- **10.2:** -0.061

### Figure 4.3.7.

- **1.00E-6:** 396 0.11
- **3.00E-6:** 371 0.16
- **1.00E-5:** 266 0.49
- **3.75E-5:** 258 0.55
- **3.00E-4:** 412 0.56
- **1.00E-4:** 160 0.587
- **3.00E-4:** 332 0.51
- **1.00E-3:** 496 0.36

### Figure 4.3.9.

- **1.00E-6:** 613
- **3.00E-6:** 595 0.55
- **1.00E-5:** 430 0.48
- **3.75E-5:** 140 0.37
- **1.00E-4:** 218 0.54
- **3.00E-4:** 445 0.55
- **3.75E-5:** 144
- **1.00E-6:** 739
- **1.00E-4:** 160
- **3.00E-4:** 536
- **1.00E-7:** 605
- **1.00E-5:** 498
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### Figure 4.4.7

(a) | time | turbidity | coiling index |
---|---|---|---|
    | 3  | 480   | 0.38       |
    | 5  | 495   | 0.39       |
    | 11 | 504   | 0.36       |
    | 15 | 682   | 0.37       |
    | 30 | 990   | 0.33       |
    | 80 | 1003  | 0.32       |

(b) | time | turbidity | coiling index |
---|---|---|---|
    | 3  | 480   | 9.43E-7     |
    | 5  | 495   | 8.57E-7     |
    | 11 | 504   | 9.37E-7     |
    | 15 | 682   | 9.21E-7     |
    | 30 | 990   | 9.83E-7     |
    | 80 | 1003  |             |

### Figure 4.4.8

| time | value |
---|---|
    | -180 | 133           |
    | -120 | 105           |
    | -30  | 167           |
    | 0    | 212           |
    | 10   | 740           |
    | 30   | 735           |
    | 60   | 741           |
    | 180  | 834           |
    | 180  | 710           |

### Figure 4.4.9

| kinetics | With PAA | Without PAA |
---|---|---|
    | 1  | 8.57E-7 | 5.14E-7     |
    | 2  | 1.17E-7 | 8.57E-7     |
    | 5  | 1.23E-6 | 1.23E-6     |
    | 8  | 1.22E-6 | 5.14E-6     |
    | 10 | 1.21E-6 |             |
    | 20 | 1.30E-6 |             |
    | 40 | 1.20E-6 |             |
    | 5  | 8.54E-7 |             |
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