CHARACTERIZATION OF SURFACTANT AND POLYMER AGGREGATES AT THE CERAMIC SOLID - SOLUTION INTERFACE USING IN-SITU SPECTROSCOPIC TECHNIQUES

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INTRODUCTION

There has been an increasing awareness recently of the value of applying the principles of surface and colloid science to ceramics processing. Colloidal processing techniques offer greater control over mixing and packing density variations as compared to dry powder routes. Particles in a colloidal suspension can be dispersed through particle-particle repulsive forces resulting from electrostatic interaction, steric hindrance, or a combination of both. Such particle-particle repulsion helps assure both the breakup of the soft agglomerates held together by van der Waal's forces and the formation of well-dispersed suspensions, even in multi-phase systems. Colloidal suspensions may be effectively used to eliminate unwanted flaw origins, such as hard agglomerates and particles larger than a certain size. It has thus become the major objective of ceramic processing engineers to achieve a better control of the state of the dispersion of the powder processed and of the consequent suspension stability. There has been considerable work done recently on techniques to control the stability of a dispersion through judicious adsorption of polymers and surfactants. Most of these are based on an empirical approach primarily due to lack of suitable techniques to monitor the processes in-situ and on a molecular scale. Extensive work has been done on understanding the physico-chemical interactions that govern the formation of adsorption layers using methods involving determination of adsorption isotherms, zeta potential, hydrophobicity and heat of adsorption. While these methods provide useful information on a mechanistic level, the importance of structure of the adsorbed layers in controlling the interfacial properties has
been noted recently. For example, in addition to the extent of surfactant adsorption on particles, the orientation of the adsorbed surfactant molecule will indeed influence their flotation. Similarly, conformation of the polymeric species play a major role in the flocculation/dispersion of colloidal particles and information on the micro and nanostructure of the adsorbed layers can help to manipulate the system behavior.

Spectroscopic techniques are suitable for generating information on a molecular scale at the solid-liquid interface without disturbing the equilibrium. Spectroscopy requires the presence of intrinsic or extrinsic probes. Spectroscopic methods based on luminescence emission and paramagnetic resonance require an appropriate spectroscopically sensitive label whereas techniques like nuclear magnetic resonance (NMR), infra-red (IR) and Raman utilize the inherent nuclear spin and vibrational modes. When using an externally added probe, care should be taken to ensure that the probe itself is inert and does not perturb the equilibrium and dynamics of the process. Recently, research in this laboratory has been directed towards developing spectroscopic techniques (fluorescence spectroscopy, electron spin resonance spectroscopy (ESR), and time resolved Raman spectroscopy) for examining the adsorbed layers at the solid-liquid interface in-situ. The use of these techniques is based on the fact that the spectral responses of the probes are highly environment dependent and as such serve to characterize the environment in which they reside. Various probes used in these studies are depicted in figure 1.

Figure 1: Various probes used in the spectroscopic studies
Principles of the different techniques and the information obtained from them are discussed in the following sections.

**PRINCIPLES OF IN-SITU SPECTROSCOPIC TECHNIQUES**

**Fluorescence Spectroscopy**

Certain organic molecules in their ground state \( P \) when excited by light, absorb incident light energy and reach an electronically excited state \( P^* \). The transition of the molecule from the excited state \( P^* \) to the ground state \( P \) is accompanied by the emission of light which is referred to as luminescence. Complex organic molecules that are commonly used as luminescence probes typically absorb energy in the spectral range 250 to 650 nm which corresponds to transitions with energy changes of 2-5 eV. Several features of luminescence, such as fluorescence, phosphorescence, excimer fluorescence and delayed fluorescence can be used as tools to obtain information at the molecular level on polymers and surfactants in the bulk and at the solid-liquid interface. The luminescence experiment essentially involves measurement of changes in the emission properties of a probe or its photochemical intermediates in order to determine the nature and rates of photophysical and photochemical processes in the system. In this respect, fluorescence is the most widely used technique. Fluorescence responses are sensitive to changes in the microenvironment around the probe so that a luminescence probe in different microenvironments will display experimentally distinct luminescence properties characteristic of each microenvironment. The fluorescent probe utilized here is pyrene. A typical emission spectrum of pyrene is shown in Figure 2.

The excimer formation tendency of pyrene is widely exploited for analysis of aggregation and conformational studies. An excimer is a dimer formed between an excited molecule and a molecule in the ground state. The photophysics of pyrene monomer (eq. 1) and excimer formation (eq. 2) can be represented as follows:

\[
P + h\nu \rightarrow P^* \rightarrow P + h\nu'
\]

(1)

\[
P + P^* \rightarrow (PP)_{excimer}^* \rightarrow P + P + h\nu''
\]

(2)
Excimer fluorescence in pyrene is observed as a broad spectral band centered around 480 nm that is red shifted with respect to the monomer emission. The excimer complex is formed only when the aromatic rings approach each other within 0.4-0.5 nm\(^8\).

The extent of excimer formation will depend upon a number of factors, viz., number of probes in the system and the viscosity of the environment in which the probe resides. In a fragmented media such as surfactant micelles or surfactant aggregates at the solid-liquid interface, the distribution of the probe molecules throughout the system as well as aggregate size will affect the observed decay profiles\(^9\). In micellar media it is generally assumed that the probes are distributed among the micelles according to Poisson statistics. It has been shown that such assumptions are valid. Based on this and on the photophysics of pyrene fluorescence, the decay in fluorescence intensity with time is given by:

\[
I_t = I_0 \exp \left[ -k_m \cdot t - n (1 - \exp \{k_e \cdot t\}) \right]
\]  

where \(n\) is the average number of probes per aggregate, \(k_m\) is the rate constant of decay of an excited pyrene monomer, and \(k_e\) is the excimer formation-dissociation rate constant. At long times, the fluorescence decay profiles represent the decay due to monomeric emission in the absence of
excimer formation. Therefore equation 3 reduces to:

$$\ln \left[ \frac{I}{I_0} \right] = -n - k_o \cdot t$$

and extrapolation to \( t=0 \) gives \( n \), the average number of probe in each aggregate. For micellar systems (or for that matter, any hydrophobic aggregate), \( n \) is defined as:

$$n = \frac{[P]}{[Agg]} = \frac{[P] \cdot N}{C_o - CMC}$$

where, \([P]\) is the probe concentration and \( C_o \) is the total surfactant concentration. For surfactant aggregates at the solid-liquid interface, instead of the critical micellization concentration (CMC) the equilibrium or residual concentration can be used.

Another application of excimer fluorescence of pyrene is in determining polymer conformation. Pyrene can be randomly attached onto a polymer chain ensuring that the amount of pyrene is low so that it does not affect the polymer dissolution characteristics significantly. Since the pyrene is covalently bonded to the polymer chain, excimer formation will depend upon the conformation of the polymer. Depending upon the solution conditions, if the polymer is coiled we would detect significant excimer formation. If on the other hand the polymer were stretched or extended then the probability of two pyrene molecules coming close to one another would be low and subsequently excimer formation would be low. The ratio of excimer and monomer intensities would then provide a measure of the conformation of the polymer. A high value of this ratio would indicate a coiled polymer and a low value would indicate a stretched polymer. The ratio can therefore be termed as the *coiling index*. It must be noted here that excimer formation would be a true indicator of polymer conformation only if the excimer formation were intramolecular. Intermolecular excimer formation can be avoided by maintaining dilute solutions of the labeled polymer. If concentrated solutions need to be studied a mixture of labeled and unlabeled polymers should be used. A simple test to differentiate between inter- and
intramolecular excimer formation is to determine the value of the coiling index as a function of polymer concentration. If the excimer formation is intramolecular then the ratio would not be affected by polymer concentration, however if it were intermolecular it would increase with increase in polymer concentration.

Electron Spin Resonance Spectroscopy\textsuperscript{11}

Electron Spin Resonance (ESR) is a form of spectroscopy that is well suited to the study of molecular structure and dynamics. It is a technique dependent on transitions between spin levels of molecular unpaired (paramagnetic) electrons in an external magnetic field in the form of absorption of microwave radiation. The intrinsic angular momentum of a free electron splits in an external magnetic field and undergoes hyperfine splitting upon the influence of secondary magnetic moments of neighboring nuclei. The range of applications of ESR can be extended by spin labeling methods where stable free radicals are incorporated into systems of interest so as to characterize their dynamic and physical properties. The nitroxide radical is commonly used in spin labeling. In this study, doxyl stearic acid (stearic acid labeled with a nitroxide bearing moiety) was chosen as the probe owing to the fact that this structure resembles the dodecylsulfate molecules to some extent. The anionic functionality and long alkyl chain should enable the probes to coadsorb with the sodium dodecylsulfate. A typical spectrum of a doxyl stearic acid is shown in figure 3.

![Figure 3: ESR spectrum of nitroxyl radical labeled stearic acid](image)

Several pieces of information can be obtained from the ESR response of these type of probes\textsuperscript{12}:

1. Polarity of the probe environment: this can be used to reveal the location of the probe.
2. Viscosity/structural ordering of the probe environment: hindrance in the rotational motion of the probe induces line broadening of the spectrum which can be used to access the fluidity of the probe environment.
3. State of aggregation of the probe molecules: when two probe molecules interact, the resulting spectrum is characteristic of a phenomenon called spin-spin relaxation. This feature can be exploited to describe the state of aggregation of molecules at the solid-liquid interface.

Resonance Raman Spectroscopy\textsuperscript{13}

Raman spectroscopy gives information on the vibrational energy levels of molecules. The frequency shifts and the intensity changes of the Raman lines of the probe molecule can be utilized to characterize the environment of the probe. Raman spectroscopy is highly suitable for use in an aqueous environment compared to IR, due to the near transparency of the former and the ease with which the whole vibrational region of interest can be covered. While vibrational frequencies of molecules in the bound state should be different from that in the free state, they are also susceptible to changes in the symmetry properties of the environment. Very few definitive studies exist in the literature on the Raman spectroscopy of surfactants in solution. Raman investigations of surfactant adsorbates are reported as surface-enhanced Raman studies at the ceramic solid-solution interface.

The Raman probe used by us was tris (2,2' - bipyridine) ruthenium (II) chloride - Ru(bpy)\textsubscript{3}\textsuperscript{2+}. The third harmonic of a Nd-YAG laser was the excitation source (pulse energy, 5 mJ; pulse width, 6 ns; wavelength; 354.5 nm). The spectrum of the probe was calculated using published spectra in literature. Figure 4 depicts the ground, excited and emitted state absorption spectra of the ruthenium complex. Figure 5 shows the ground state and excited state spectra of Ru(bpy)\textsubscript{3}\textsuperscript{2+} in water. The excited state consists of 14 lines, two sets of 7 lines each corresponding to the ground and excited state transitions. All these transitions are known to originate from the excited state species. They are assigned roughly to the various symmetric stretching vibrations of the C-N and C-C bonds of the bipyridine ring.

Infra-Red Spectroscopy

Infrared (IR) spectroscopy is concerned with light of wavelength ranging from 2000 to 5 x 10\textsuperscript{7} nm. When infrared radiation is incident on an organic molecule, it is absorbed and converted to energy of molecular vibration. Molecular bonds between atoms are constantly undergoing stretching and bending motions at frequencies which depend upon the masses of the atoms involved and the type of chemical bond joining the atoms.
Figure 4: Absorption (A) and emission (C) spectra of Ru(bpy)$_3^{2+}$ and the excited state transient absorption spectrum (B) of Ru(bpy)$_3^{2+}$

Figure 5: Raman spectra of ground and excited state Ru(bpy)$_3^{2+}$

Since the frequencies of the various vibrations of the molecule correspond to those of IR radiation, absorption of the radiation occurs, producing an increase in the amplitude of the molecular vibrational modes. No irreversible change in the molecule results because the energy gained by the molecule in the form of light is soon lost in the form of heat. By plotting the ratio of light passing through the sample, $I$, to the intensity of light striking the sample, $I_0$, versus the frequency of the radiation, an IR spectrum is obtained. Instead of using incident radiation frequency, it is customary to use wavenumbers (units of cm$^{-1}$) which is the frequency, $\nu$, divided by the velocity of light, $c$, expressed in cm/sec. In Fourier Transform Infrared (FTIR) spectroscopy, which is more commonly used, the signal intensity measured at the detector is the cosine fourier transform of a wavenumber dependent spectral intensity. For additional information, there exist a host of excellent references in literature$^{14}$. In practical applications, FTIR has been developed for solid and liquid samples. Depending on the absorption spectra, the mode of interaction between the adsorbate and adsorbent can be inferred. There are several variants of this technique such as diffuse reflectance infrared Fourier transform (DRIFT) and attenuated total reflectance (ATR) which have been designed for use with different kinds of samples.
CHARACTERIZATION OF ADSORBED SURFACTANT LAYERS

Surfactant Aggregation at the Solid-Liquid Interface: Effect on Dispersion Stability

It was realized in the early fifties that alkyl compounds could be used to improve the colloidal stability of carbon black-hydrocarbon suspensions without affecting the system's electrostastics, and that the stability can be optimized by judicious choice of chain length\textsuperscript{15}. Subsequently, research conducted by one of the authors indicated similar behavior for anionic surfactants - oxide minerals in aqueous as well as nonaqueous media.\textsuperscript{16,17,18} A model mineral/surfactant system studied in aqueous media was alumina/sodium dodecylsulfate. A typical adsorption isotherm for this system is shown in Figure 6. This isotherm is characterized by four distinct regions\textsuperscript{19}: Region I, dominated by electrostatic adsorption; region II, marked by a sharp rise in the adsorption caused by surfactant aggregation on the particles; region III, characterized by a decreasing slope even though surfactant adsorption continues to increase and region IV, representing maximum surface coverage and marked by micelle formation in the bulk.

![Figure 6: Adsorption isotherm of sodium dodecylsulfate (SDS) on alumina. Surfactant aggregation numbers determined at various adsorption densities are shown along the isotherm](image)

The concept of surfactant aggregation at the solid-liquid interface has been employed by several authors, to account for the sharp changes in interfacial properties such as the amount adsorbed, hydrophobicity and zeta potential observed above a critical surfactant concentration. This process was

Characterization Techniques for the Solid-Solution Interface 205
termed hemimicellization by analogy to micellization. Lateral aggregation, for example, among adsorbed dodecylsulfate species on alumina has been shown to result in drastic increase in the adsorption density, settling rate as well as the electrophoretic mobility20 (figure 7). The hemimicellar aggregates that form in region II were viewed as two-dimensional monolayered structures with the tails extended towards the solution side. The molecular structure of the adsorbed layer itself has been the subject of often controversial speculation. Spectroscopic probing using fluorescence, ESR and Raman methods were designed to yield information on the microstructure of the adsorbed layer.

Figure 7: Changes in interfacial properties of alumina as a result of sodium dodecylsulfate adsorption

Fluorescence Studies of Surfactant Aggregation at the Alumina-water Interface

Fluorescence emission of pyrene in micellar solutions can be used to obtain information on the aggregation number of surfactants. For this the decay kinetics of the monomer and excimer emissions of pyrene at different concentration levels are determined and a kinetic analysis based on the relations connecting the decay rates of the monomer and excimer is carried
out from the decay profiles of pyrene in the sodium dodecylsulfate (SDS) layers adsorbed on alumina at different adsorption densities. It was confirmed first that the micromolar concentrations of pyrene used in our experiments did not affect the adsorption of SDS on alumina. The aggregation numbers thus obtained are marked on the adsorption isotherm in figure 6. The aggregates in region II appear to be relatively of uniform size, but in region III there is a marked increase in the aggregate size. These results give an idea of the evolution and structure of the adsorbed layer. Region II and above seem to be characterized by surfactant aggregates of limited size. Since the surface is not totally covered, there are enough positive sites available for SDS and adsorption occurs mainly by increasing the number of aggregates rather than the size of each aggregate. The transition from region II to III corresponds to the iso-electric point of alumina and adsorption in this region occurs through the growth of the existing aggregates. A schematic representation of the evolution of the adsorbed layer is provided in figure 8.

Figure 8: Schematic representation of the growth of sodium dodecylsulfate aggregates at the alumina-water interface

Electron Spin Resonance Studies of Surfactant Adsorption and Aggregation

Stable free radical nitroxide spin probes were chosen for our ESR studies. They were the three isomeric 5-, 12- and 16- doxyl stearic acids (5-D, 12-D, 16-D). These spin labels were coadsorbed individually on alumina along with the main adsorbate, sodium dodecylsulfate (SDS), and the regions of the adsorption isotherm were studied. The responses of 16-D along the adsorption isotherm are shown in figure 9. The broad spectrum obtained at
low adsorption densities is characteristic of the spin-spin relaxation occurring when two nitroxides interact with each other (spectrum A). As the adsorption of the dodecylsulfate among the probe increases and its aggregates form, probe-probe interactions decrease and a sharper anisotropic spectrum is obtained (spectrum C) which indicates greater mobility of the probe. The spectra of 16-D was compared with the spectra of the probe in ethanol-glycerol mixtures of known viscosities and a microviscosity of 120-165 cP was estimated for the SDS aggregates.

![Figure 9](image)

**Figure 9:** ESR spectra of 16-doxyl stearic acid in sodium dodecylsulfate - alumina slurries along various regions of the adsorption isotherm

Figure 10 compares the spectra of the 5-, 12- and 16- doxyl stearic acid obtained in SDS hemimicelles with those in ethanol/glycerol mixtures and it is evident that the nitroxide closer to the surface is more immobile than the one farthest from it. This implies that the chain segments near the surface are tightly packed while those near the end of the chain are considerably more disordered. Thus ESR spectroscopy with nitroxide spin probes is demonstrated here to be an adept method for probing the microstructure of adsorbed layers.
ESR response of the three probes (5, 12 & 16-doxyl stearic acid) in sodium dodecylsulfate hemimicelles adsorbed on alumina and in ethanol/glycerol mixtures. From left to right, the probe describes an environment increasingly closer to the alumina surface.

Figure 10: Time Resolved Resonance Raman Studies

The Raman spectra of the probe in sodium dodecylsulfate aggregates at the alumina-water interface corresponding to different regions along the adsorption isotherm are shown in figure 11. The spectra obtained in regions I and II remain similar to that obtained in aqueous spectrum. The spectra in regions III and IV show variation in intensity and frequency, indicating a definite trend in the magnitude of the changes. The shift in frequencies and variation in intensities of some of the Raman lines for various regions of the isotherm almost trace the shape of the isotherm when plotted as a function of residual concentration. This suggests that the sensitivity of the Raman probe to changes in the hemimicellar environment can be exploited to obtain information on the structure of adsorbed layers.

ESR IN NON-AQUEOUS MEDIA

The traditional medium for the processing of ceramic powders has been water but in some recent developments, organic media have been preferred to eliminate some of the defects arising in aqueous media. For instance, ceramics of current interest such as nitrides and carbides, which tend to develop oxide surfaces when processed in water are better processed in nonaqueous media. Nonaqueous liquids are used also when drying is a particular problem such as in casting electronic substrates. They are also favored when the dispersion of the powder material requires use of processing...
Steric stabilization has been considered recently as a major mechanism in non-aqueous dispersions. The mechanisms governing the steric stabilization are rather well understood, especially when using macromolecular additives. However, the choice of stabilizer for a particular system has been empirical. Recently we have used spectroscopic techniques to investigate the conformation of molecules at the solid-liquid interface and its role in determining the efficiency of interfacial phenomena such as

Figure 11: Resonance Raman spectra of Ru(bpy)$_3^{2+}$ on alumina slurry, and along various regions of the sodium dodecylsulfate/alumina adsorption isotherm.
aggregation/dispersion of colloidal suspensions in non-aqueous media.\textsuperscript{24,25} In non-aqueous media, line broadening due to spin-spin relaxation, that was observed in aqueous media, was not detected in experiments performed with 5, 12 and 16-D stearic acids adsorbed on alumina in cyclohexane. This is direct evidence for the fact that in non-polar media, surfactant molecules do not interact laterally as in the case of aqueous solutions where surfactant hemimicelles are formed at the alumina-water interface.

On the other hand, when the probe is coadsorbed with Aerosol OT, the stearic acid molecules show significant changes in their ESR line shape as indicated in figure 12. At low surface coverage, interactions between the probe and the alumina surface leads to a "frozen" spectrum due to slow rotation of the molecules. When Aerosol OT is added, its adsorption induces sufficient surface pressure to push the nitroxide away from the surface in the case of 12 and 16-D stearic acid, allowing the molecules to dangle out in a stretched conformation.

![Figure 12](image)

Figure 12: ESR spectra obtained with 5- and 16-doxyl stearic acids adsorbed at the alumina/cyclohexane interface in the presence of various amounts of Aerosol OT.

In figure 13 changes in the ESR response of 12-doxyl stearic acid are shown as a function of Aerosol OT adsorption density. It is to be noted that using changes in the ESR signal intensity at a given position on the ESR
spectrum, it is possible to follow the kinetics of surfactant adsorption nearly instantaneously and continuously, an experiment not easily performed by any technique.

Figure 13: Adsorption isotherm of Aerosol OT on alumina in cyclohexane and corresponding ESR spectra obtained using 12-doxyl stearic acid as a probe

As can be seen from figure 14, among other changes in the spectrum, a third peak appears and progressively increases in intensity as the surfactant adsorption is increased. This peak corresponds to the highly mobile population of probe molecules dangling in solution by the coadsorption of surfactant around them. It was arbitrarily selected as an indicator of surfactant adsorption since it changes significantly during surfactant adsorption. The overall adsorption phenomenon is relatively fast and 80% of the total adsorption was complete within the first 10 minutes after surfactant addition.

The above results illustrate the wide range of information ESR can provide a ceramic chemist and their relevance to fundamental investigations of colloidal dispersions in non-aqueous media: it offers an unique means to study surfactant adsorption at interfaces and allows quantitative measurement of the packing density of adsorbed layers, a critical parameter for steric stabilization. For most of the above mentioned applications, ESR spectroscopy does have some inherent disadvantages that we tried to minimize. The probes used reflect the properties of the environment in which
it resides, but it also perturbs to a certain extent as can be seen from figure 9. Another limitation of this technique is that it can be used only for systems that have extremely low concentrations of free radicals and other paramagnetic impurities. Presence of transition metal ions such as Fe, Cu and Ti either as soluble species or in the mineral itself limits the use of this technique. Finally, extreme caution must be exercised while obtaining quantitative information from the spectra because the ESR signal intensity does not depend only on the probe concentration in the system, but it also varies according to the location of the sample in the spectrometer cavity, the presence of impurities in the cavity and sample.

![Graph](image)

**Figure 14:** Intensity of the ESR peak (indicated by the dotted line on the spectra in insets) as a function of surface coverage from the adsorption isotherm data

**Infra-red Spectroscopy at the Solid-Liquid Interface**

In separation of francolite from dolomite by flotation using potassium oleate as the collector, it was observed that selective separation expected from single mineral tests could not be achieved when using a mixture of the minerals. This was attributed to the non-selective precipitation of calcium and magnesium oleate species on the mineral surfaces, thereby altering their interfacial properties. The surface chemical characteristics of oleate precipitates were examined using FTIR/ATR spectroscopy. At low oleate concentrations, there was individual oleate molecule adsorption on the mineral surface without any precipitation; as the oleate concentration was further increased, surface precipitation of Ca and Mg oleates occurred...
inducing hydrophobicity on the mineral surfaces; at high oleate concentrations, interaction with the dissolved mineral species caused bulk precipitation, leading to a loss of flotation selectivity and resulted in high reagent consumption.

ROLE OF POLYMER CONFORMATION IN COLLOIDAL STABILITY

Dispersion or flocculation of suspended particles is determined by macromolecular adsorption both in terms of the amount adsorbed and the configuration of the adsorbed species. Even though it has been recognized that configuration of polymers at the interfaces can lead to either flocculation or dispersion, it has never been established as to what type of conformation (stretched versus coiled or flat versus dangled) is optimal for the above or as to how one can manipulate a system to achieve the optimum configuration. This lack of knowledge has been essentially due to the non-existence of reliable in-situ techniques with which one can determine conformation and orientation of species adsorbed on solids in liquids. Techniques such as gel permeation chromatography, light scattering and viscosity can give information on the average conformation of the polymer in the bulk but are incapable of doing so at the solid-liquid interface. Recently we have developed a multi-pronged approach involving simultaneous measurements of dispersion/flocculation responses and configuration of adsorbed polymer species using luminescence spectroscopy of pyrene-labeled polyacrylic acid.

Dispersion/flocculation of alumina suspensions by polyacrylic acid was studied and the effect of polymer conformation on the suspension stability was determined. The conformation of the polymer at the solid/liquid interface was monitored as a function of pH. At low pH (~4) the adsorbed polymer was found to be coiled while at high pH (~8), it was stretched. The conformational state of the polymer in solution was same as that adsorbed on alumina.

In our efforts to manipulate the polymer conformation at the solid/liquid interface for dispersion control, it was discovered that if the polymer is adsorbed first at low pH, and then the pH raised, excellent solid-liquid separation is obtained (Figure 15a). On the other hand, if the polymer was adsorbed on alumina at pH 10 and then decreased to 4, the flocculation responses were not as significant as those obtained in figure 15 but were as bad as those found under fixed pH conditions (figure 15b). Comparing this to the system under fixed pH conditions (Figure 16) it can be concluded that a change in adsorbed polymer conformation from coiled to slightly extended will result in best settling results. A schematic representation of the conformational changes of the polymer is shown in

214 Characterization Techniques for the Solid-Solution Interface
Starting from pH 4, the coiled polymer in solution (uncharged polymer) adsorbs and remains in the same coiled conformation on the positively charged alumina surface (17a). When the pH is raised to the intermediate neutral range (~5-7), ionization of PAA generates some negative charges on the polymer, and causes the polymer chain to expand.

Figure 17 a-f. Starting from pH 4, the coiled polymer in solution (uncharged polymer) adsorbs and remains in the same coiled conformation on the positively charged alumina surface (17a). When the pH is raised to the intermediate neutral range (~5-7), ionization of PAA generates some negative charges on the polymer, and causes the polymer chain to expand.

Flocculation properties of alumina with 20 ppm PAA as a function of final pH under changing pH conditions with the initial pH of 4 (a) and 10 (b).

Flocculation of aqueous alumina suspensions with 20 ppm PAA.
The alumina is still positively charged and the polymer will adsorb due to electrostatic attraction (17b). Raising the pH above the point of zero charge of alumina (pH 8.5), the solid particles become negatively charged similar to the polymer and under these conditions, electrostatic repulsion would cause the polymer to be displaced away from the particles and "dangle" from the particle into the aqueous phase (17c). In contrast, when the suspension is first treated with PAA at pH 10, the polymer is probably weakly adsorbed on the surface through hydrogen bonding (17d). Reducing the pH to below the pzc of alumina, the charge on the particles becomes positive and increases attraction with the polymer. This may result in the PAA adsorbing in a flat conformation to maximize the contact between the polymer and mineral (17e). Further reduction in the pH to the region where PAA is neutral does not alter the conformation of the adsorbed polymer (17f). The conformation in figure 17b and c is most suited to flocculation hence the observed performance when the pH of the adsorbed polymer is raised from 4 to 10. On the other hand, the conformation in figure 17 e and f is least suited for flocculation hence there is no increase in flocculation when the pH is lowered from 10 to 4.

![Figure 17](image)

**Figure 17:** Schematic representation of variation in polymer conformation at the alumina-solution interface under changing pH conditions

**POTENTIAL OF NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY**

Fluorescence and ESR spectroscopy require the use of external probes: such probing has demonstrated its usefulness in providing information unobtainable by other means but, no matter what precautions are taken, there will always be a question on the extent to which the probe perturbs its environment. This is why non invasive techniques are preferred when
available. NMR is a spectroscopic technique that has this non-invasive quality. Recent advances in NMR instrumentation has made it possible to study various reagents, at very dilute concentrations and even at the solid-liquid interface. In some exploratory work, we have established that this can be used to study adsorbed layers at the solid-liquid interface, both in aqueous and non-aqueous media. Even though there was reagent in the supernatant proper set-up of the parameters can eliminate interference from signals in bulk solution so that only the adsorbed layer is probed. It will not be long before this technique will be applied to more in-depth studies at the solid-solution interface and take research in interfacial technology to an entirely new level.

SUMMARY

Structural characterization studies are of immense help for understanding the nature of the adsorbed layers and thus to provide a better opportunity for manipulating and controlling interfacial properties for such diverse applications as ceramic processing, magnetic tape manufacturing, liquid inks, paints, cosmetics and oil recovery from tar sand. This article summarizes some of the recent results obtained in this laboratory on the in-situ characterization of adsorbed layers at the ceramic solid-solution interface in aqueous as well as nonaqueous solutions using fluorescence spectroscopy, electron spin resonance spectroscopy and resonance raman spectroscopy. The approach used here can be used for better prediction of suspension behaviors and offers new techniques to assess steric stabilization. Control of colloidal stability by in-situ manipulation of adsorbed polymer conformation has been clearly demonstrated.

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