POLYMER SURFACTANT INTERACTIONS IN BULK AND AT THE SOLID/LIQUID INTERFACE

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ABSTRACT

Fluorescence spectroscopy is used as a means to investigate the interactions between Polyethylene Oxide (Molecular Weight 4,000 to 6,000) and Sodium Dodecyl Sulfate. The polymer was end labeled with pyrene using an esterification process and excimer formation was monitored to obtain information on the conformation of the polymer in the presence of the surfactant in bulk solution and at the alumina/water interface. Below the cmc of the surfactant there was no specific interaction between the polymer and the surfactant. Above the cmc, the micelles stretched out a coiled polymer in bulk solution. Most interestingly, when alumina with adsorbed SDS (at low adsorption density) was conditioned with Polyethylene Oxide, the polymer did not adsorb on the solid. However, at concentrations where surfactant aggregates were formed at the solid/liquid interface (hemimicelles), the polymer adsorbed in stretched form on the solid. This suggests a new way of forcing the adsorption of polymers onto solids where they otherwise may not adsorb.

INTRODUCTION

Polymeric flocculation of fine particles is a very important method for dewatering dispersed suspensions. Polymers have been used as flocculants or as dewatering aids in several systems ranging from phosphatic clays(1) to biological dispersions(2). The mechanism of adsorption of polymers and their role as flocculants is, however, not completely understood so far. Correlations between theoretical and experimental investigations(3-5) on polymer adsorption have been obtained only on model systems. However, past studies have clearly illustrated that one of the most important parameters that determines the efficiency of polymer flocculation is the conformation of the polymer at the solid-liquid interface.

Flocculation of fines using polymers has been attributed to the "bridging" of fine particles by a polymer that adsorbs with one end on one particle and with its other segments attached to the other fine particles in the system. Evidently, a polymer that attaches to one
particle with one of its segments and then protrudes into solution with its other segments most favorable for bridging flocculation to occur. This correlation between the "loop or tail" like conformation of the polymer and flocculation is intuitively acceptable, but has not been corroborated experimentally. The difficulty lies in in situ determination of the conformation of the polymer at the solid/liquid interface using spectroscopic techniques. Some of the most successful techniques in this regard are small angle neutron scattering (SANS), fluorescence spectroscopy(6,7), and attenuated total internal reflection spectroscopy (ATR). SANS is, however, an extremely elaborate and expensive technique to pursue and does not yield information on a molecular scale. On the contrary, fluorescence spectroscopy is relatively simple and has gained prominence recently as a viable alternative to examine polymer conformation in situ at the solid/liquid interface(7).

**Principles of Fluorescence Spectroscopy**

Certain molecules in their ground state $P$ when excited by light, absorb the 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 emission of light which is referred to as luminescence. Several aspects of luminescence, such as fluorescence, phosphorescence, excimer fluorescence and delayed fluorescence can be used as focal points to obtain information at the molecular level on polymer-surfactant interactions in bulk or at the solid-liquid interface(7). In the present study, we will concentrate primarily on two aspects of luminescence of a complex organic molecule pyrene: a) fluorescence and b) excimer fluorescence. Fluorescence is a radiative emission process occurring during the transition of a molecule from an excited state to the ground state. An excimer is a molecular dimer aggregate formed between an excited molecule and a molecule in the ground state. Excimer fluorescence is "red" shifted with respect to normal fluorescence. It is clear that the formation of an excimer would be a critical function of the proximity of the fluorescent moieties—in our case pyrene. Thus if two pyrene molecules are close, the probability of formation of an excimer is higher if they are far apart. The distances required for excimer formation would depend on the energy of excitation, fluorescent lifetimes, probe concentration and on the nature of the fluorescent molecule. These aspects of fluorescence are discussed in literature (8-10). A useful method of using excimer fluorescence to investigate polymer conformation is to label a polymer with a fluorescent probe such as pyrene at the ends (Figure 1a). Now if the polymer were completely stretched as shown in Figure 1b, the probes being too far apart, we would not see an excimer. On the contrary, if the polymer were coiled (Figure 1c), significant excimer fluorescence should be observed. Thus by examining the fluorescence spectrum of the polymer, either in bulk or at the solid/liquid interface we can obtain information on the conformation of the polymer. It is to be noted that excimer fluorescence can be due to both inter- and intramolecular interactions. A simple way to isolate the two is to plot the ratio of the excimer to monomer peak intensities as a function of polymer concentration. Only the intramolecular excimer ratios will be independent of polymer concentration. A more accurate method for distinguishing between inter- and intramolecular excimer formation is to carry out
Figure 1a.

PYRENE

Figure 1b.

PYRENE--PEO--PYRENE

Figure 1c.
fluorescent decay measurements as suggested by Frank et al. (11).

In the present investigation intramolecular excimer fluorescence of labeled Polyethylene Oxide (Molecular weight 6,000 to 8,000) was used to examine the interaction of this polymer with oxide minerals in the presence of different ions and surfactants. The methodology of labeling PEO has been discussed by Cuniberti and Perich (12) and labeled PEO has been widely used recently as a means of examining the interaction of this polymer with several other polymers (13-14). The effect of pyrene however, on the behavior of polyethylene oxide has not been completely studied. The inertness of pyrene as a probe of adsorbed layers that are extremely sensitive to external impurities has been proven in the alumina/sodium dodecyl sulfate system by Chandar et al. (23). In this study only PEO with attached pyrene is used. A comparison with labeled and unlabeled PEO is being pursued but based on previous results, excessive perturbation of adsorption behavior is unexpected. The concentration range of the polymer in this investigation was very low (10-20 ppm) and only intramolecular excimer fluorescence was studied. A typical fluorescence spectrum of pyrene labeled Polyethylene Oxide with the wavelengths at which monomer and excimer peaks are observed is shown in Figure 2.

![Fluorescence Spectrum](image)

**Figure 2.** Typical fluorescence spectrum of pyrene labeled polyethylene oxide

**Conformation of PEO in Bulk Solution and at the Silica Gel/Water Interface**

The fluorescence spectrum of PEO in triply distilled water and in the presence of sodium sulfate and aluminum sulfate is shown in Figure
The absence of excimer in water and the marked increase in excimer intensity in aluminum and sodium sulfate solutions clearly suggests that PEO is stretched in triply distilled water and is coiled in salt solutions. Both sodium and aluminum ions can affect the conformation of PEO due to interaction with the net negative charge ascribed to the ether oxygen in PEO. However, the higher excimer intensity in sodium sulfate solution than in aluminum sulfate (at the same polymer concentration) suggests that sodium ions are more effective in coiling PEO than aluminum. The exact mechanism of interaction between sodium sulfate and PEO is not known but evidence of this salt being used as a reagent to precipitate PEO exists in literature (16). One possibility for PEO being more coiled due to sodium than aluminum is that Na⁺ ion being smaller is more conducive to the formation of crown ethers (17) with PEO of low molecular weight. This would lead to the polymer being more coiled. The larger size of aluminum may prevent this ion from entering into the crown ether.

The fluorescence spectrum of adsorbed PEO on silica gel is shown in Figure 4. The absence of excimer shows that the polymer is stretched on the silica gel surface although at the same ionic strength it was coiled in bulk solution. Another possibility for the absence of excimer, is that the polymer adsorbs as one long tail with one end on the solid and the other end pointing into solution. In the concentration range, 10-20 ppm, and the solid-liquid ratio [0.05] studied the "tail" conformation is unlikely as we observed 100% adsorption of the polymer even at much higher polymer concentrations. As the number of adsorption sites on the solid exceed the attachment points on the polymer, the conditions for a flat conformation of the polymer are more favorable.
Figure 3b. Fluorescence spectrum of PEO in 0.5 M sodium sulfate

Figure 3c. Fluorescence spectrum of PEO in 0.5 M aluminum sulfate
Figure 4. Fluorescence spectrum of PEO in PEO adsorbed on silica gel

Figure 5. Fluorescence spectrum of PEO in SDS solution at $5 \times 10^{-5}$ M (below CNC)
PEO-SDS Interactions in Bulk Solution

Fluorescence spectroscopy can also be used to examine polymer surfactant interactions in bulk and at the solid/liquid interface. We investigated in the present study the interactions of pyrene labeled PEO with sodium dodecyl sulfate (SDS) in the presence of 0.5 M sodium sulfate. Figures 5 through 8 show the fluorescence spectra of a fixed concentration of PEO as a function of concentration of SDS at constant ionic strength. It is clear that below the critical micelle concentration of the surfactant, PEO retains its coiled conformation in bulk in the presence of the SDS monomers. Above the cmc of SDS (7 x 10^{-4}), the excimer disappears. This suggests that SDS monomers do not significantly affect the conformation of PEO but the micelles stretch out a coiled polymer. Past investigations on PEO-SDS have revealed that this surfactant and polymer interact but no information on the conformation of the polymer in the presence of the surfactant could be gleaned from them (18-20). The present investigation clearly shows that at high salt conditions a coiled polymer is almost completely stretched out in bulk solution by SDS.

PEO-SDS Interactions at the Alumina/Water Interface

Literature data on the adsorption of PEO on oxide minerals has shown that while PEO adsorbs on silica and kaolinite it does not adsorb on hematite, titania or alumina (21). This adsorption trend has also been observed with ethoxylated surfactants. In the present study also, we noticed that PEO did not adsorb on alumina. But the interaction between the SDS micelles and PEO suggested that if we form hemimicelles on alumina and then add PEO we could force the adsorption of the polymer on the solid. This was indeed the case. Alumina was conditioned with SDS at two different concentrations--5 x 10^{-5} kmol/m^3 (no hemimicelles form at this concentration), and at 5 x 10^{-3} kmol/m^3 (hemimicelles do form at this concentration). In the case where surfactant concentration was below the hemimicellar region no adsorption of PEO on alumina was found. But when hemimicelles were present, almost all the polymer adsorbed (Figures 9a,b). Most interestingly, the polymer was stretched out on the surface similar to the PEO conformation in bulk solution in the presence of micelles (Figure 10). This result can be extremely significant for forcing the adsorption of polymers onto oxides where they otherwise may not adsorb. Instead of chemically modifying the solid surface, a simple alternative is to form hemimicelles at the solid-liquid interface and then allow the polymer to adsorb.

Two-dimensional surfactant aggregates on solids are referred to as hemimicelles. The hemimicellization phenomena is prominently observed in the Alumina/SDS system. The nature, size and structure of these hemimicelles have recently been revealed using fluorescence spectroscopy (22-24).
Figure 6. Fluorescence spectrum of PEO in SDS solution at 5 x 10^{-4} M (below CMC)

Figure 7. Fluorescence spectrum of PEO in SDS solution at 5 x 10^{-3} M (above CMC)
Figure 8. Fluorescence spectrum of PEO in SDS solution at $5 \times 10^{-2}$ M (above CMC)

Figure 9a. Fluorescence spectrum of PEO: Initial concentration before adsorption on alumina
Figure 9b. Fluorescence spectrum of PEO: Final concentration after adsorption on alumina.

Figure 10. Fluorescence spectrum of PEO adsorbed on alumina.
CONCLUSIONS

Fluorescence spectroscopy is used to examine Polyethylene Oxide-Sodium dodecyl sulfate interactions in bulk and at the solid-liquid interface. Polyethylene Oxide changed its stretched conformation in bulk to coiled form in the presence of sodium and aluminum ions. The sodium ions were more effective than aluminum ions in coiling the polymer. PEO adsorbed in stretched form on the silica gel surface under high ionic strength conditions although the polymer was coiled in bulk under solution under the same conditions. Sodium dodecyl sulfate micelles caused a marked alteration of the conformation of PEO from coiled to stretched form. While the surfactant monomers had no effect on the polymer conformation, hemimicelles at the alumina/water interface influenced the adsorption of PEO on alumina significantly. While there was no adsorption of PEO on alumina below the hemimicellar region, the presence of hemimicelles led to adsorption in the stretched form of PEO.

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REFERENCES


