

## Binding of Sodium Dodecyl Sulfate to Polyethylene Oxide at the Silica-Water Interface

The effect of preadsorbed polyethylene oxide (PEO) on silica on the subsequent adsorption of sodium dodecyl sulfate (SDS) on the silica was investigated in this study. Even though SDS does not normally adsorb on the similarly charged silica, it is shown that anionic SDS can be made to adsorb on it in the presence of preadsorbed PEO. The role of polymer molecular weight and the mode of addition of SDS were also investigated. The amount of SDS bound to PEO preadsorbed on silica was not affected by the polymer molecular weight. Interestingly, adsorption of SDS determined from its mixtures with PEO in solution is lower than that found on preadsorbed PEO on silica. It is also shown that interactions between PEO and SDS at the silica-water interface are stronger than the interactions between them in bulk solution. © 1992 Academic Press, Inc.

### INTRODUCTION

Interactions between polymers and surfactants have been the subject of past investigations because of the enormous potential offered by the resultant complexes in applications such as those of enhanced oil recovery, flotation, flocculation, and colloidal stability. Advantages of using polymer and surfactants in conjunction have been demonstrated in the areas of flotation (1, 2), flocculation (3), and colloidal stability (4). Despite the importance of the solid-liquid interface in each of the above applications, the behavior of the polymer-surfactant complex at the solid-liquid interface has not received much attention. The effect of interacting pairs of polymers and surfactants on the adsorption of each other has been studied with respect to enhancement as well as suppression of such adsorption (5-8). It has been found that the interacting polymer-surfactant pairs generally enhance the adsorption of each other on several adsorbents. In addition, we have shown that preadsorption of sodium dodecyl sulfate on alumina can force subsequent adsorption of polyethylene oxide onto the substrate where it normally does not adsorb (9, 10). In the present study, interactions between polyethylene oxide and sodium dodecyl sulfate were studied at the silica-water interface. The aim was to investigate the effects of polymer-surfactant interactions on the adsorption characteristics of the polymer and the surfactant. The effects of polymer molecular weight and the mode of addition of the SDS were also determined.

### EXPERIMENTAL

#### Materials

Spherosil XOB15 silica from Rhone Poulenc, France, was used as received. The particle size range was specified to be from 40 to 100  $\mu\text{m}$  with a mean pore size of 1200 Å. The specific surface area measured by nitrogen BET adsorption was 25  $\text{m}^2/\text{g}$ . Polyethylene glycol of weight

average molecular weight of 4948 (polydispersity index 1.03) was purchased from Scientific Polymer Products, New York. In addition, polyethylene oxide of weight average molecular weight of 23,000 (polydispersity index 1.08) from Polymer Laboratories, Inc., UK, and sodium dodecyl sulfate (>99% purity) from ICN Pharmaceuticals were used as received. Triply distilled water was used for all experiments.

#### Methods

For polymer adsorption tests, 0.4 g of silica was conditioned in 5 ml of triply distilled water for 2 h. After this initial conditioning, 5 ml of polymer solution of the desired concentration was added and the slurry conditioned for 4 h. Polymer adsorption was complete in 2 h and there was no further change during conditioning for 2 to 12 h. Polymer residual concentration was measured using a Rosemount Analytical's Dohrmann DC-90 total organic carbon analyzer.

For studying the adsorption of sodium dodecyl sulfate on silica in the presence of preadsorbed polymer, polymer adsorption was first conducted as described above. The desired amount of a concentrated SDS stock solution was then added to the suspension and conditioned further for 12 h. The solids were separated by centrifugation and the supernatant was analyzed for SDS concentration using a two-phase titration technique (11).

Surface tension was determined using a Fisher du Nouy ring tensiometer.

All experiments were carried out at room temperature ( $23 \pm 2^\circ\text{C}$ ) and at natural pH (6.5 to 7.0).

### RESULTS AND DISCUSSION

The adsorption isotherms of polyethylene oxide of two different molecular weights on silica are shown in Fig. 1. The adsorption is characteristic of the high affinity type

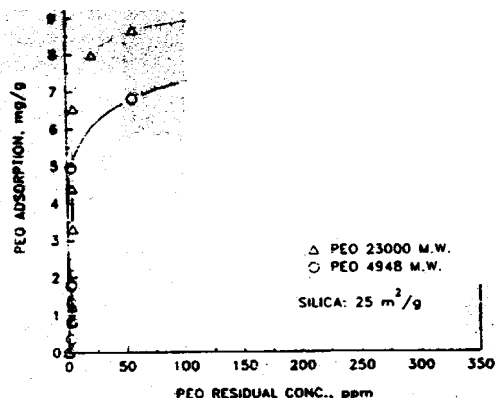


FIG. 1. Adsorption isotherms of polyethylene oxide of two molecular weights on silica.

and the higher molecular weight PEO adsorbs to a greater extent than the lower molecular weight polymer. The adsorption mechanism of polyethylene oxide on silica is well established in the literature and is said to be hydrogen bonding between the ether oxygen of the polymer and the surface silanol groups (10). As expected, sodium dodecyl sulfate did not adsorb on silica by itself (Fig. 2) since under the test conditions both the mineral and the surfactant are negatively charged (pzc of silica  $\approx 2$ ) (10). Similar results have been obtained earlier for the adsorption of dodecyl benzenesulfonate on silica (12). In the present investigation, different amounts of sodium dodecyl sulfate were contacted with silica pretreated with a fixed amount of polyethylene oxide. The polymer concentration chosen was such that there was no residual polymer left in solution, thus avoiding any interference from interactions between PEO and SDS in bulk solution. The adsorption of SDS on silica in the presence of preadsorbed PEO is shown in Fig. 2. Interestingly, the anionic surfactant which did not adsorb on silica by itself does so to a considerable extent in the presence of preadsorbed polyethylene oxide. The isotherm obtained could be considered to be the binding isotherm of SDS on PEO and is similar to that obtained using dialysis experiments (13). The mechanism of interaction between sodium dodecyl sulfate and polyethylene oxide at the silica surface could be similar to that in bulk-solution association between the ether oxygen of the polymer and the head group of the surfactant.

The binding of the surfactant to the polymer occurs above a certain concentration and within a narrow concentration range. Saturation adsorption is reached near the critical micellization concentration of the surfactant. The saturation adsorption of SDS is  $6.1 \times 10^{-5}$  moles per gram of silica. Considering that there is 4 mg/g of preadsorbed PEO, the adsorption of SDS corresponds to 0.671 mol SDS per mol of ethylene oxide. This is higher than the ratios reported in the literature for bulk interactions

between PEO and SDS (0.4142 by Shirahama (13) and 0.38 by Francois *et al.* (14)). A probable reason for this could be that interaction between PEO and SDS is stronger at the solid-liquid interface than that in bulk solution. A similar observation has been made for polyvinyl pyrrolidone-sodium dodecyl sulfate interactions at the titania-water interface (5). The shape of the binding isotherm of sodium dodecyl sulfate on polyethylene oxide is similar to the adsorption of surfactants on oxide minerals and the sharp increase in the adsorption above a certain surfactant concentration may be attributable to strong interaction between the hydrocarbon chains of the surfactant (15). Using spectroscopic techniques, it has been shown that the surfactant aggregates (or hemi-micelles) formed at the solid-liquid interface are more tightly packed than surfactant micelles (16). Similarly, SDS bound to PEO at the solid-liquid interface could be more tightly packed than the SDS bound to PEO in bulk solution, accounting for the high binding ratio of SDS to PEO.

For the same preadsorbed polymer density, there is no effect of the polymer molecular weight (Fig. 2). It has been reported in the literature that, above a PEO molecular weight of 4000, interactions between PEO and SDS in bulk solution are largely independent of the molecular weight (17). Similarly, at the interface there is no effect of PEO molecular weight on the binding of SDS to PEO. Conformation of the polymer can play a significant role in determining the interactions between polymer and surfactant, but in the present case the difference in molecular weights of the polymers studied is apparently not high enough to cause any significant change in the conformation. Since PEO adsorbs strongly on silica both of the polymers can be expected to adsorb in the stretched form (18) with no significant change in the conformation of the adsorbed polymers.

In the above case the polymer was preadsorbed on silica and then the surfactant was brought into contact with the system. In contrast to this, adsorption from mixtures of

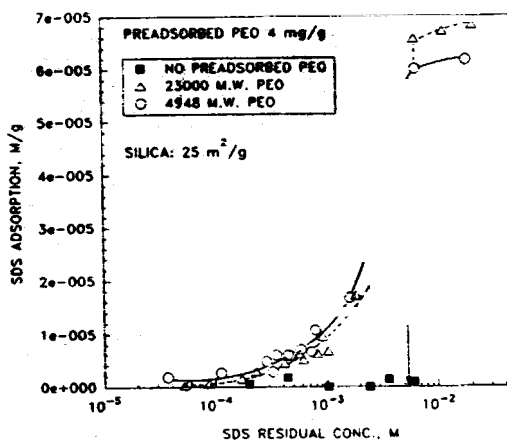


FIG. 2. Adsorption of sodium dodecyl sulfate on silica pretreated with polyethylene oxide.

PEO and SDS was also determined and the results obtained are shown in Fig. 3. Adsorption from mixtures is consistently lower than the binding of SDS to preadsorbed PEO. Results obtained for interactions between PEO and SDS in bulk solution under similar conditions are shown in Fig. 4. The surfactant concentration at which PEO-SDS interactions commence is  $\approx 1.5 \times 10^{-3} M$ . This is close to the concentration at which the sodium dodecyl sulfate adsorbs on silica when the adsorption is from mixtures. Adsorption of SDS on preadsorbed PEO begins at SDS concentrations as low as  $2 \times 10^{-4} M$ . The SDS concentration at which PEO-SDS interactions begin to interact at the solid-liquid interface is lower than that in bulk solution. This supports earlier results that interactions between PEO and SDS are stronger at the solid-liquid interface than in bulk solution. It is possible that the PEO and the SDS interact in solution and then the complex adsorbs at the silica-water interface. It is also possible that the PEO-SDS complex in bulk exists in equilibrium with the complex formed at the silica-water interface.

#### SUMMARY

Interactions between polyethylene oxide and sodium dodecyl sulfate were studied at the silica-water interface. It was observed that SDS, which does not otherwise interact with silica, does adsorb onto it in significant amounts in the presence of preadsorbed PEO. The binding isotherm of SDS on PEO at the solid-liquid interface was similar in shape to that for the bulk solution reported in the literature using dialysis experiments as their foundation. Saturation adsorption is obtained over a narrow concentration range just below the critical micelle concentration of the surfactant. Also, the binding of SDS to PEO at the solid-liquid interface is larger than the binding in bulk

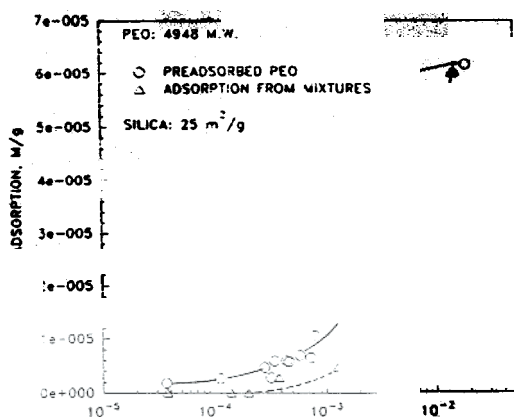


FIG. 3. Adsorption of sodium dodecyl sulfate on silica from mixtures of polyethylene oxide and sodium dodecyl sulfate.

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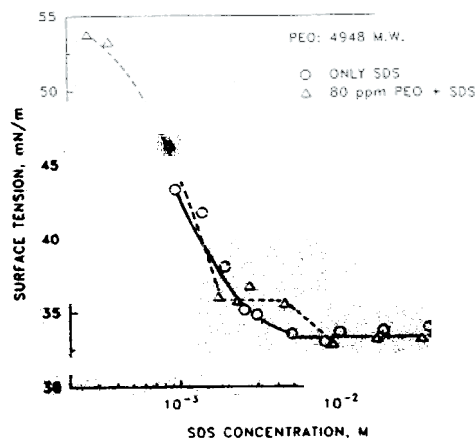


FIG. 4. Interactions between polyethylene oxide and sodium dodecyl sulfate in bulk solution as detected by surface tension measurements.

solution. A binding ratio of 0.67 mol SDS per mol of ethylene oxide on silica was obtained versus 0.38–0.41 for the binding in bulk solution. There was no measurable effect of molecular weight of the PEO on the amount of SDS extracted from the solution onto the silica-water interface. Adsorption of sodium dodecyl sulfate took place also from a premixed solution of PEO and SDS, but in lesser amounts than when PEO was preadsorbed. It is demonstrated that polymer-surfactant interactions can be used to force adsorption of the surfactant onto a surface where it normally does not adsorb.

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