MICRODOMAINS IN POLYMER SOLUTIONS

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VISCOMETRIC INVESTIGATION OF COMPLEXES BETWEEN POLYETHYLENEOXIDE AND SURFACTANT MICELLES

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ABSTRACT

Nonionic polymers in aqueous solutions may associate with surfactant micelles to form polymer-micelle complexes. In this work, the polymer-micelle association is examined by viscometrically monitoring the conformational changes induced in the polymer. Polyethylene oxide with a flexible backbone and dextran with a rigid backbone have been examined in solutions of anionic, cationic, and nonionic surfactants. It is found that no polymer-micelle association takes place in case of dextran. For polyethylene oxide, the extent of polymer-micelle association is large for anionic micelles and small for cationic micelles. It decreases with increasing bulkiness of the surfactant head group. We conclude that the physical factors governing the polyethylene oxide-micelle association are (i) the extent of augmented shielding from water provided by the polymer segments to the hydrocarbon core of the micelles and (ii) the steric and electrostatic interactions between the polymer segments and the surfactant head group at the micellar surface. For these reasons, polymer-micelle complex formation is not favored if the polymers have rigid backbones, if the surfactants have bulky head groups, or if the polarity of the surfactant head group is similar to that of the polymer.

INTRODUCTION

The interactions between surfactant molecules and synthetic polymers in aqueous solutions are of interest for many chemical, pharmaceutical, mineral processing and petroleum engineering applications. The mutual presence of polymer and surfactant molecules alter the rheological properties of solutions, adsorption characteristics at the solid-liquid interfaces, stability of colloidal dispersions, the solubilization capacities in water for sparingly soluble molecules, and liquid-liquid interfacial tensions.[1,2] The ability of the surfactant and the polymer molecules to influence the above solution and interfacial characteristics is controlled by the state of their occurrence in aqueous solutions. Generally, the aqueous solution is composed not only of singly dispersed surfactant and polymer molecules but also of surfactant aggregates such as micelles or vesicles as well as intermolecular complexes between the polymer and the surfactant.

Various topologies of polymer-surfactant complexes can be visualized,[3] depending on the nature of the interaction forces operative between the solvent, the surfactant and the polymer and also based on their stereochemical features. One may consider the following structures (Figure 1):

Type 1 - No surfactant is bound to the polymer and the latter remains as free polymer in solution.

Type 2 - Single surfactant molecules are bound linearly along the length of the polymer molecules.

Type 3 - A single surfactant molecule binds at more than one binding site of a single polymer molecule, giving rise to intramolecular bridging. Alternatively, a single surfactant molecule binds to more than one polymer molecule giving rise to intermolecular bridging.

Type 4 - The polymer molecule along with a layer of surfactant molecules bound on it is solubilized in the interior of a surfactant micelle.

Type 5 - Clusters of polymer segments and surfactant molecules associate to form pseudomicelles such that the hydrocarbonaceous regions of the polymer segments and of the surfactant are shielded from having contact with water.

Type 6 - Pure surfactant micelles associate with the polymer molecule in such a way that the polymer segments partially penetrate and wrap around the polar head group region of the surfactant micelles. A single polymer molecule can associate in this manner with one or more surfactant micelles depending on the polymer and micellar properties.

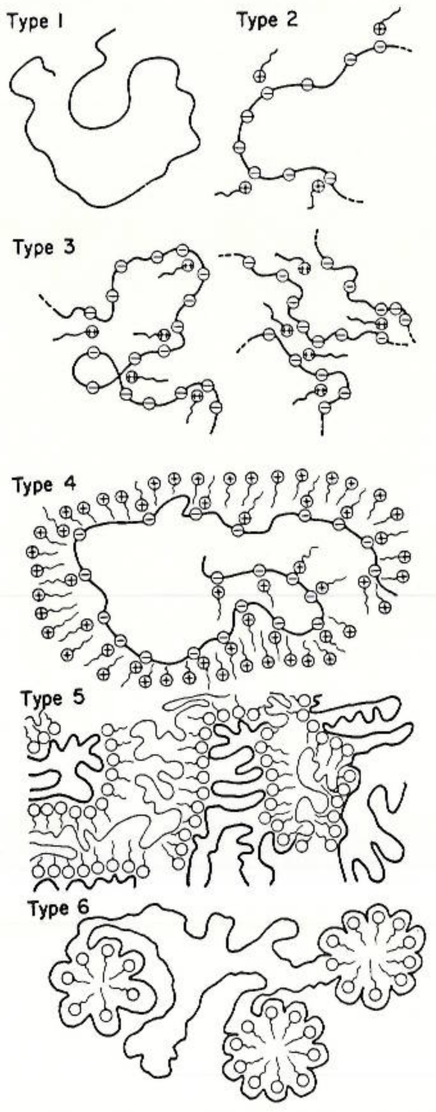

Figure 1. Schematic representations of polymer-surfactant complexes described in the text. In the block copolymer-surfactant complex (Type 5), the dark lines represent the polar blocks of the polymer molecule whereas the lighter lines represent the non-polar blocks.

Of the above, two types of complexes are considered to form in solutions of nonionic polymers. One type (Type 5) occurs in block copolymers consisting of polar and nonpolar blocks. In this case, the polymer molecule assumes a conformation in solution characterized by self-segregation of polar and nonpolar blocks. The surfactant molecules locate themselves at the interfaces between these segregated regions. A quantitative description of such a block copoloymer-surfactant complex has been developed in our earlier paper.[4,5]

The other type of complex (Type 6) is visualized as consisting of the polymer molecule wrapped around spherical surfactant micelles with the polymer segments partially penetrating the polar head group region of the micelles. Indirect clue to its formation is provided by studies which show that the binding of some surfactants to nonionic polymers occurs only above a critical concentration of the surfactant.[6-11] The existence of such a critical binding concentration implies that binding is a cooperative process and must involve a cluster of surfactant molecules. Recent studies based on nmr and neutron scattering measurements[12,13] have given further evidence to the topology of such a complex.

The principal goal of this paper is to examine the physical forces responsible for this latter type of polymer-surfactant micelle association. Since the formation of a polymer-micelle complex gives rise to gross conformational changes in the polymer molecule, a measurement of the solution viscosity provides the simplest means for monitoring polymer-micelle association. Here, the viscosity data on solutions containing polymer and surfactant of different molecular structures are used to explore the nature of polymer-micelle complex formation.

EXPERIMENTAL RESULTS

The viscosities of polymer-surfactant solutions as well as those of the surfactant and of the polymer alone have been measured at 25°C using a Cannon-Fenske capillary viscometer. Two high molecular weight nonionic polymers and anionic, cationic and nonionic surfactants have been used in this study (Table I).

The relative viscosity of the polyethylene oxide-surfactant solution, $\eta_{rel} = \eta(\text{PEO + surfactant})/\eta\ (\text{PEO})$, is plotted in Figure 2 as a function of the surfactant concentration for different surfactants. For anionic SDS, η_{rel} remains invariant at 1 up to a concentration of 4×10^{-3} M, indicating absence of any association. Beyond 4×10^{-3} M SDS, the relative viscosity shows a large increase up to about 2.6×10^{-2} M SDS. This can be attributed to the association of SDS micelles with the PEO segments and the resulting expansion of the PEO molecules. Beyond 2.6 $\times 10^{-2}$ M SDS, a reduction in the relative viscosity is observed. This is because, when saturation binding of SDS to PEO is reached (say at 2.6

Table I

POLYMERS AND SURFACTANTS EVALUATED

Polyethylene Oxide, PEO (Union Carbide)

Nonionic Polymer with a Flexible Backbone.

M. Wt. 5×10^6.

Dextran, DEX (Pharmacia Fine Chemicals)

Nonionic Polymer with Rigid Backbone. M. Wt. 2×10^6.

Sodium Dodecyl Sulfate, SDS (Pfaltz and Bauer)

Anionic Surfactant, Eq. Wt. 288, $a_p = 17\text{Å}^2$, CMC=8×10^{-3}M.

Sodium Dodecyl Benzene Sulfonate, SDBS (Alcolac)

Anionic Surfactant, Eq. Wt. 348, $a_p = 17\text{Å}^2$, CMC=1.72×10^{-3}M.

8-Phenyl Hexadecane Benzene Sulfonate, UT-1 (University of Texas at Austin)

Anionic Surfactant, Eq. Wt. 404, $a_p = 17\text{Å}^2$, CMC=9.6×10^{-4}M.

Has two alkyl chains per surfactant.

Dodecyl Amine Hydrochloride, DAC (Eastman Kodak)

Cationic Surfactant, Eq. Wt. 222, $a_p = 12\text{Å}^2$, CMC=1.4×10^{-2}M.

Didodecyl Dimethyl Ammonium Bromide, DDAB (Eastman Kodak)

Cationic Surfactant, Eq. Wt. 463, $a_p = 17\text{Å}^2$, CMC=6×10^{-5}M.

Has two alkyl chains per surfactant.

Ethyl Hexadecyl Dimethyl Ammonium Bromide, EHD (Eastman Kodak)

Cationic Surfactant, Eq. Wt. 378, $a_p = 35\text{Å}^2$, CMC=8×10^{-4}M.

Isooctyl Phenoxy Polyoxyethanol, Triton X-100 (Rohm and Haas)

Nonionic Surfactant, Eq. Wt. 648, $a_p = 42\text{Å}^2$, CMC=1.6×10^{-4}M.

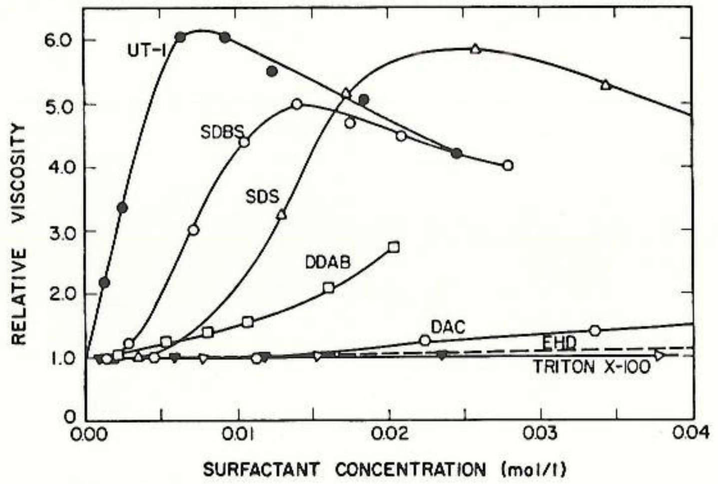

Figure 2. Influence of various types of surfactants on the relative viscosity of the solutions containing 1000 ppm polyethylene oxide-surfactant micelle complexes.

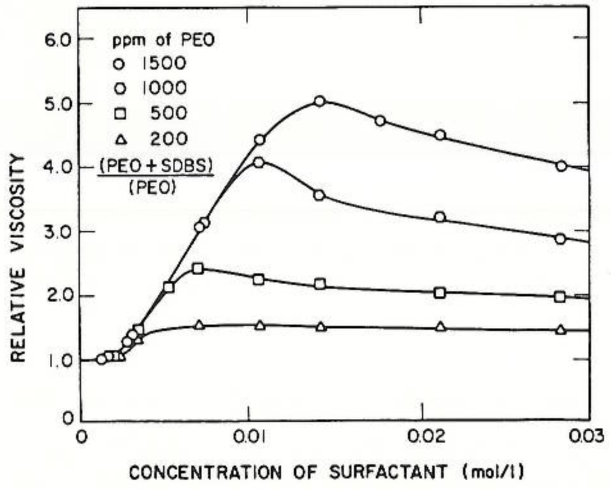

Figure 3. Influence of polymer concentrations on the relative viscosity of solutions containing polyethylene oxide and anionic sodium dodecyl benzene sulfonate micelles.

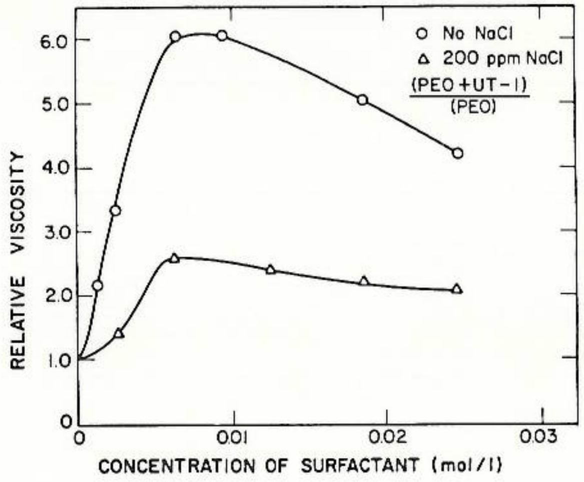

Figure 4. Influence of electrolyte NaCl concentration on the relative viscosity of solutions containing 1000 ppm polyethylene oxide and 8-phenyl hexadecane benzene sulfonate micelles. The polyelectrolyte type behavior of the polymer-micelle complex can be noted.

x 10^{-2} M SDS), further addition of SDS results in an increase in the concentration of singly dispersed SDS molecules and of free SDS micelles unattached to the polymer. This gives rise to an increase in the ionic strength of the solution and a consequent reduction in η_{rel}, as is expected for polyelectrolyte solutions.[14] The behavior of the other anionic surfactants SDBS (Figure 3) and UT-1 (Figure 4) in solutions containing PEO is very similar to that of the PEO + SDS solution. As is to be expected, the critical binding concentrations and the concentrations corresponding to saturation binding of the surfactant are however different from those of SDS. In contrast to the behavior of these anionic surfactants, all the cationic surfactants display relative viscosities close to one implying low degrees of binding to the PEO, with EHD demonstrating virtually no binding. Also remarkable is the relative viscosity of unity and hence the complete absence of binding shown by the nonionic surfactant Triton X-100.

Figure 5 shows the viscosity ratio of the Dextran-surfactant solution, $\eta_{ratio} = \eta_{(dextran + surfactant)}/\eta_{(dextran)} \times \eta_{(surfactant)}$, for solutions containing SDBS and EHD. The data show that no binding occurs in case of both anionic SDBS and cationic EHD with nonionic dextran polymer. The absence of any surfactant binding is also confirmed by surface tension measurements (Figure 6) which show that the surface tensions of SDBS and SDS solutions in the absence of and in the presence of dextran are identical.

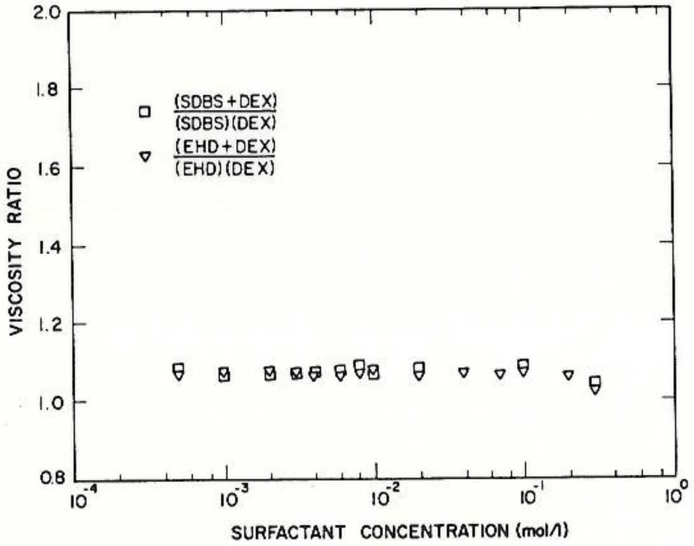

Figure 5. Viscosity ratios of solutions containing (a) non-ionic dextran polymer and anionic sodium dodecyl benzene sulfonate micelles and (b) dextran polymer with cationic ethyl hexadecyl dimethyl ammonium bromide micelles. The polymer concentration is 1000 ppm in both cases.

In Figure 7, the relative viscosity of SDS + PEO solutions are plotted as a function of the concentration of n-butanol and Triton X-100 which are used as additives. Both the additives form mixed micelles with SDS and the composition of the mixed micelles changes as the concentration of the additives is altered. When no additives are present the PEO + SDS solution is at a SDS concentration of 2.6 x 10^{-2} M corresonding to saturation binding of SDS to PEO. As the concentration of the additives is increased, η_{rel} decreases indicating a decrease in polymer-micelle association. The viscosity data show that the nonionic surfactant is very effective in causing a decrease in polymer-micelle association. These viscometric results are interpreted in the following section in terms of the binding and competitive micellization processes.

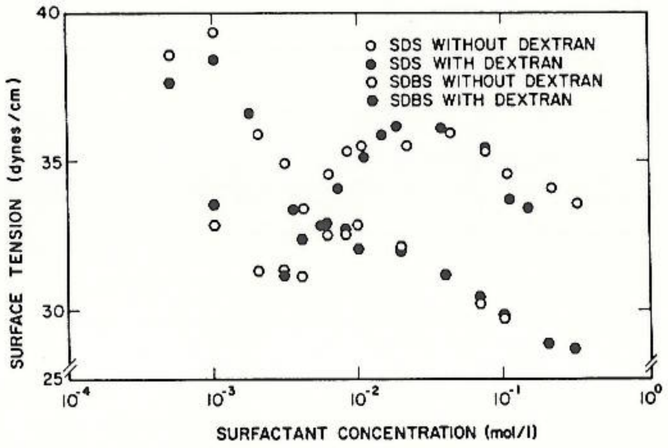

Figure 6. Surface tension of (a) solutions containing 1000 ppm polyethylene oxide and SDS on SDBS micelles and (b) solutions containing SDS on SDBS micelles but in the absence of any polymer.

THERMODYNAMICS OF POLYMER-MICELLE ASSOCIATION

The physical picture of the polymer-surfactant micelle complex described earlier suggests that the following factors are relevant to the association process: (i) the penetration of polymer segments in the polar head group region of the micelles augments the shielding from water of the hydrocarbon core of the micelle, (ii) the crowding of the polymer segments along with the surfactant head groups at the micelle surface increases mutual steric repulsions, and (iii) the dipoles of the polymer segments electrostatically interact with the surfactant head groups at the micellar surface. Further, since the micelles associating with the polymer are quite similar to the free micelles, the formation of the polymer-micelle complex is also influenced by factors determining surfactant micellization.

For an aqueous solution containing free micelles of size M and polymer-micelle complexes in which n micelles of size λ are associated with each polymer molecule, the total mole fraction of the surfactant (S_T) is given[3-5] by

$$[S_T] = [S_f] + \frac{n\lambda K_b\,[S_f]^{\lambda}P_T}{1 + K_b\,[S_f]^{\lambda}} + M\,K_m[S_f]^M \qquad (1)$$

where S_f is the mole fraction of the singly dispersed surfactant, P_T is the total mole fraction of the polymer, K_b is the intrinsic binding constant for the polymer-micelle complexation, and K_m is the equilibrium constant for micellization. In eq. (1), the three terms on the right hand side represent the singly dispersed surfactant, polymer bound surfactant and surfactant in free micelles, respectively. The critical binding concentration is approximately equal to $(K_b)^{-1/\lambda}$ and the critical micelle concentration (CMC) is close to $(K_m)^{-1/M}$. However, if polymer-micelle association occurs in a given solution then the formation of free micelles takes place at a surfactant concentration much beyond the usual CMC. The relative magnitudes of K_b, K_m, λ and M determine whether or not polymer-micelle complex formation occurs and what is the composition of the various species present in solution.

Taking into account the physical factors relevant to polymer-micelle association, the binding and micellization equilibrium constants can be related:

$$(-RT\ \ln K_b{}^{1/\lambda}) - (-RT\ \ln K_m^{1/M}) = \Delta G^o_{\substack{\text{inter-}\\\text{facial}}} + \Delta G^o_{\text{steric}} + \Delta G^o_{\substack{\text{electro-}\\\text{static}}} \qquad (2)$$

where $\Delta G^o{}_{\text{interfacial}}$ is the free energy contribution due to the augmented shielding of the hydrocarbon core of the micelles by polymer segments, $\Delta G^o{}_{\text{steric}}$ is the contribution representing steric repulsions between polymer segments and surfactant head groups and $\Delta G^o{}_{\text{electrostatic}}$ accounts for the electrostatic interactions between the polymer dipoles and surfactant head groups.

In the case of dextran polymer, the rigidity of its backbone does not permit the polymer segments to penetrate the polar head group region of the micelles. As a result, the various free energy contributions in eq. (2) are all practically zero and $K_b{}^{1/\lambda} = K_m{}^{1/M}$. Assuming $\lambda = M$, from eq. (1) we note that as long as $nP_T << 1$, for all values of S_f, the formation of free micelles is favored compared to that of the polymer-micelle complex. For 1000 ppm dextran of a molecular weight of 2 million, $P_T \approx 10^{-8}$ and $n \approx 10$ to 10^3. Therefore, no association of surfactant micelle to the polymer can occur as is indicated by the viscometric and surface tension data. This behavior is expected for all polymers which because of their relative rigidity cannot penetrate into and thus modify the nature of the head group region of the micelles.

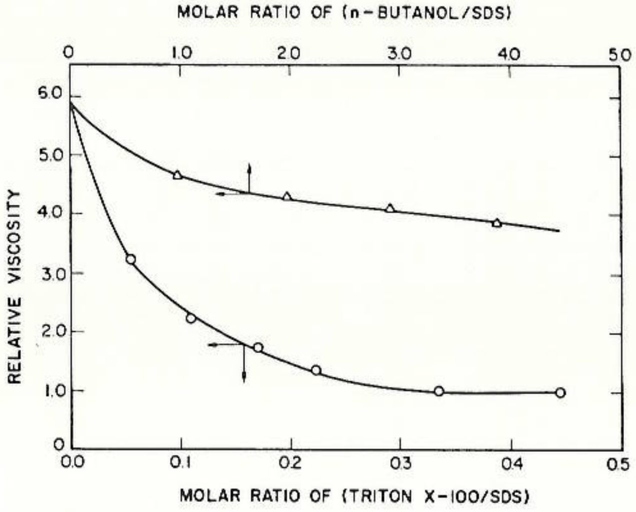

Figure 7. Relative viscosity of solutions containing 1000 ppm polyethylene oxide and 2.6×10^{-2} M sodium dodecyl sulfate as a function of the amounts of n-butanol and Triton X-100 added to the solution.

In contrast, because of the flexible nature of polyethylene oxide, the polymer segments can penetrate the polar surface of the micelles and modify the nature of that interface. Assuming that polymer segments shield about 10 Å^2 (per surfactant molecule) of the hydrocarbon core area of the micelle from water, $\Delta G^o_{\text{interfacial}}$ is approximately -1.2 RT, taking the hydrocarbon water interfacial tension to be 50 dynes/cm. $\Delta G^o{}_{\text{steric}}$ can be estimated in a manner similar to that used in our micellization model.[15]

$$\Delta G^o{}_{\text{steric}} = -\ RT\ \ln[(a - a_p - a_{pol})/(a - a_p)], \qquad (3)$$

where a is the surface area per molecule of the hydrocarbon core of the micelle, a_p is the cross-sectional area of the polar head group of the surfactant, and a_{pol} is the projected area of the polymer segments at the micellar interface per surfactant molecule. The area $(a - a_p)$ is a measure of the freedom of movement of head groups at the micelle surface in the absence of polymer segments and $(a - a_p - a_{pol})$ is the corresponding quantity when the polymer segments are present. For a = 66 Å^2 corresponding to the largest spherical micelle and assuming a_{pol} = 10 Å^2, $\Delta G^o_{\text{steric}}$ is about 0.20 RT for a_p = 10 Å^2, 0.35 RT for a_p = 30 Å^2 and 1 RT for a_p = 50 Å^2. The electrostatic contribution can be estimated by treating the electron deficient oxygen atom of the ether linkage in PEO as free ions which modify the electrostatic repulsion between the surfactant head groups. $\Delta G^{o}_{electrostatic}$ is therefore the difference in the electrostatic repulsions between surfactant head groups[15] at the micellar surface when PEO is present and when it is absent. By this approximation, PEO of molecular weight 5×10^{6} at 1000 ppm is equivalent to about 0.05 M electrolyte, and the corresponding $\Delta G^{o}_{electrostatic}$ is -0.12 RT for SDS. This contribution is favorable to polymer-micelle association. For cationic surfactants interacting with PEO, $\Delta G^{o}_{electrostatic}$ is +ve and hence is unfavorable to polymer-micelle association.

The approximate estimates for the free energy contributions show that as the size of the polar head group of the surfactant increases, the steric repulsion increases. Consequently both K_b and the extent of polymer-micelle complexation would decrease. Further the electrostatic contribution is favorable to the association of anionic micelles and unfavorable to that of cationic micelles. This explains the viscometric data of PEO in the presence of various surfactants shown in Figure 2. When mixed micelles of SDS + Triton X-100 form, the number of Triton molecules per micelle increases as the ratio of Triton X-100 to SDS is increased. As a result, because of the bulky head group of Triton X-100, the extent of PEO-mixed micelle association sharply decreases as shown by the viscosity data of Figure 7. All the above estimates are obtained, for the illustrative purposes of this paper, based on $a_{pol} = 10$ Å^{2}. However, a better estimate of this projected area may be possible from a consideration of the atomic dimenisons and bond movements of the PEO segments and the surfactant head groups. Nevertheless, the qualitative conclusions of this paper remain valid for modified estimates for a_{pol}, as well.

CONCLUSION

The formation of polymer-micelle complexes is governed by (i) the extent of augmented shielding provided by polymer segments to the hydrocarbon core of the micelles, and (ii) the steric and electrostatic interactions between the polymer segments and the surfactant head groups at the micellar surface. For these reasons, polymer-micelle complex formation is not favored if the polymers have rigid backbones, if the surfactants have bulky head groups or if the polarity of the surfactant head group is similar to that of the polymer.

REFERENCES

1. M. M. Breuer and I. D. Robb, Chemistry and Industry, 13, 531 (1972).
2. I. D. Robb in "Anionic Surfactants - Physical Chemistry of Surfactant Action," (Ed., E. H. Lucassen Reynders), Marcel Dekker, New York (1981).
3. R. Nagarajan, Polymer Preprints, 22, No. 2, 33 (1981).
4. R. Nagarajan, Chemical Physics Letters, 76, 282 (1980).
5. R. Nagarajan and M. P. Harold, in "Solution Behavior of Surfactants," (Eds., K. L. Mittal and E. J. Fendler), Plenum Press, New York (1982). V. 2.
6. S. Saito, J. Colloid Interface Sci., 24, 227 (1967).
7. M. L. Fishman and F. R. Eirich, J. Phys. Chem., 75, 3135 (1971).
8. M. J. Schwuger, J. Colloid Interface Sci., 43, 491 (1973).
9. M. L. Smith and N. Muller, J. Colloid Interface Sci., 52, 507 (1975).
10. T. Gilanyi and E. Wolfram, Proc. Int. Conf. Colloid Surf. Sci., V. 1 (1975), p. 633.
11. M. N. Jones, J. Colloid Interface Sci., 23, 36 (1967).
12. B. Cabane, J. Phys. Chem., 81, 1639 (1977).
13. B. Cabane, in "Solution Behavior of Surfactants," (Eds., K. L. Mittal and E. J. Fendler), Plenum Press, New York (1982). V. 1.
14. F. Oosawa, Polyelectrolytes, Marcel Dekker, New York (1971).
15. R. Nagarajan and E. Ruckenstein, J. Colloid Interface Sci., 71, 580 (1979).