

VISCOMETRIC INVESTIGATION OF COMPLEXES BETWEEN  
POLYETHYLENEOXIDE AND SURFACTANT MICELLES

by  
R. Nagarajan and B. Kalpakci  
Department of Chemical Engineering  
The Pennsylvania State University  
University Park, PA 16802

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 [1,2]. The ability of the surfactant and the polymer molecules to influence various solution and interfacial characteristics is controlled by the state of their occurrence in aqueous solutions. We have recently summarized six possible types of intermolecular complexes between the polymer and the surfactant [3]. Of these, two types of complexes are considered to form in solutions of nonionic polymers (Figure 1). One type occurs in block copolymers consisting of polar and nonpolar blocks. A quantitative description of such a block copolymer-surfactant complex has been developed in our earlier paper [4,5]. The other type of complex 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.

Experimental Results

The relative viscosity of the polyethylene oxide-surfactant solution is plotted in Figure 2 as a function of the surfactant concentration for different surfactants. For anionic SDS,  $\eta_{rel}$  remains invariant at 1 up to a concentration of  $4 \times 10^{-3}$  M, indicating absence of any association. Beyond  $4 \times 10^{-3}$  M SDS, the relative viscosity shows a large increase which 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  $2.6 \times 10^{-2}$  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  $\eta_{rel}$ , as is expected for polyelectrolyte solutions [14]. The behavior of the other anionic surfactants SDBS and UT-1 in solutions containing PEO are very similar to that of the PEO + SDS solution. In contrast, all the cationic surfactants display low degrees of binding to the PEO, with EHD demonstrating virtually no binding. Also remarkable is the complete absence of binding shown by the nonionic surfactant Triton X-100. In the case of dextran polymer, the relative viscosity of the Dextran-surfactant solution for solutions containing SDBS and EHD remains 1 showing that no binding occurs. The absence of any surfactant binding is also confirmed by surface tension measurements.

Thermodynamics of Polymer-Micelle Association

For an aqueous solution containing free micelles of size M and polymer-micelle complexes in which n micelles of size  $\lambda$

are associated with each polymer molecule, the total mole fraction of the surfactant ( $S_T$ ) is given [3-5] by

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

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  $K_b^{-1}$  and the critical micelle concentration is close to  $K_m^{-1}$ . 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 CMC. The relative magnitudes of  $K_b$ ,  $K_m$ ,  $\lambda$  and M determine whether or not polymer-micelle complex formation occurs and what is the composition of the various species present in solution.

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.

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

$$(-RT \ln K_b) - (-RT \ln K_m) = \Delta G_{inter-facial}^o + \Delta G_{steric}^o + \Delta G_{electro-static}^o \quad (2)$$

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 zero and  $K_b = K_m$ . Assuming  $\lambda = M$ , from eq. (1) we note that as long as  $nP_T \ll 1$ , 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 molecular weight 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.

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  $10\text{\AA}^2$  (per surfactant molecule) of the hydrocarbon core area of the micelle from water,  $\Delta G_{interfacial}^o$  is approximately  $-1.2$  RT, taking the hydrocarbon-water interfacial tension to be 50 dynes/cm.  $\Delta G_{steric}^o$  can be estimated in a manner similar to that used in our micellization model [15].

$$\Delta G_{steric}^o = -RT \ln[(a_o - a_p - a_{po1}) / (a_o - a_p)], \quad (3)$$

where  $a_o$  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  $a_{po1}$  is the projected area of the polymer segments at the micellar interface per surfactant molecule. The area  $(a_o - a_p)$  is a measure of the freedom of movement of head groups at the micelle surface in the absence of polymer segments and  $(a_o - a_p - a_{po1})$  is the corresponding quantity when the polymer segments are present. For  $a_o = 66\text{\AA}^2$  corresponding to the largest spherical micelle and assuming  $a_{po1} = 10\text{\AA}^2$ ,  $\Delta G_{steric}^o$  is about 0.20 RT for

$a_p = 10\text{\AA}^2$ ,  $0.35\text{ RT}$  for  $a_p = 30\text{\AA}^2$  and  $1\text{ RT}$  for  $a_p = 50\text{\AA}^2$ . An upper bound of 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.  $\Delta G_{\text{electrostatic}}^{\circ}$  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  $5 \times 10^6$  at 1000 ppm is equivalent to about 0.05 M electrolyte, and the corresponding  $\Delta G_{\text{electrostatic}}^{\circ}$  is  $-0.12/\text{RT}$  for SDS. This contribution is favorable to polymer-micelle association. For cationic surfactants interacting with PEO,  $\Delta G_{\text{electrostatic}}^{\circ}$  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. All the above estimates are obtained, for the illustrative purposes of this paper, based on  $a_{\text{pol}} = 10\text{\AA}^2$ . However, a better estimate of this projected area may be possible from a consideration of the atomic dimensions and bond movements of the PEO segments and the surfactant head groups.

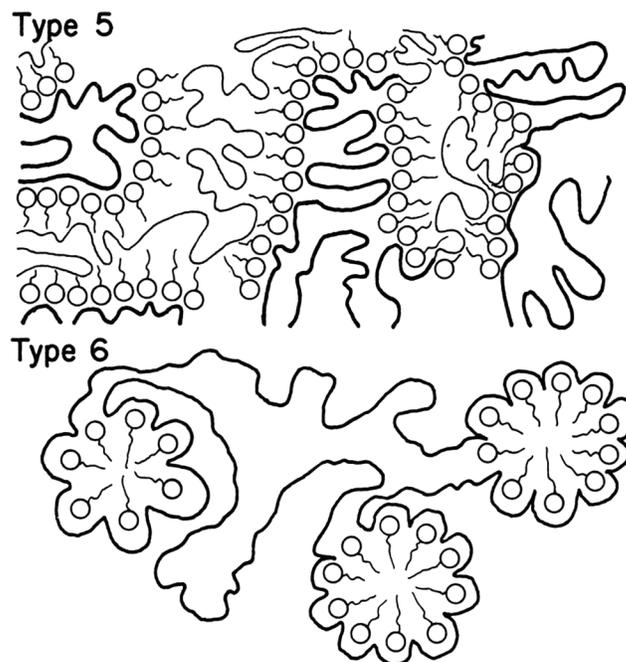
#### Conclusion

The formation of nonionic polymer surfactant 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, little or no complex formation occurs either if the polymers have rigid backbones, or if the surfactants have bulky head groups or if the polarity of the surfactant head group is similar to that of the polymer.

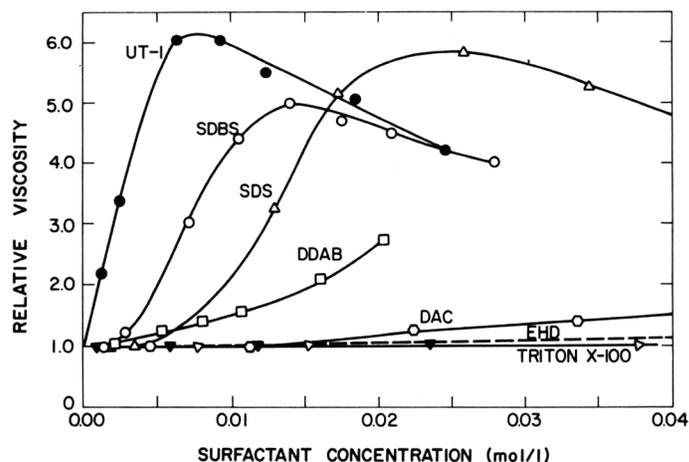
#### References

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 (in press).
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 (1976).
12. B. Cabane, *J. Phys. Chem.*, **81**, 1639 (1977).
13. B. Cabane, paper presented at the International Symposium on Solution Behavior of Surfactants, Clarkson, USA (1980).
14. F. Oosawa, *Polyelectrolytes*, Marcel Dekker, New York (1971).
15. R. Nagarajan and E. Ruckenstein, *J. Colloid Interface Sci.*, **71**, 580 (1979).

Polyethylene Oxide (PEO), Dextran (DEX), Sodium Dodecyl Sulfate (SDS), Sodium Dodecyl Benzene Sulfonate (SDBS), 8-Phenyl Hexadecane Benzene Sulfonate (UT-1), Dodecyl Amine Hydrochloride (DAC), Didodecyl Dimethyl Ammonium Bromide (DDAB), Ethyl Hexadecyl Dimethyl Ammonium Bromide (EHD), Isooctyl Phenoxy Polyoxyethanol (Triton X-100).



1. Schematic descriptions of nonionic polymer-surfactant complexes. 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. Type 6 is the visualization of a complex between surfactant micelles and a polymer molecule.



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