

TABLE 2  
PARAMETERS FOR EQUATIONS (3), (4) AND (5)

Parameter	Polymer A	Polymer B	Polymer C
x	3.35	3.59	2.16
K	$1.79 \times 10^{-5}$	$5.11 \times 10^{-6}$	$2.08 \times 10^{-6}$
y	1.38	0.87	0.66
H	$1.25 \times 10^{-3}$	$2.01 \times 10^{-3}$	$2.66 \times 10^{-3}$
$M_c$	$15 \times 10^6$	$20 \times 10^6$	$7 \times 10^6$

ON THE NATURE OF INTERACTIONS BETWEEN POLYMERS  
AND SURFACTANTS IN DILUTE AQUEOUS SOLUTIONS

by

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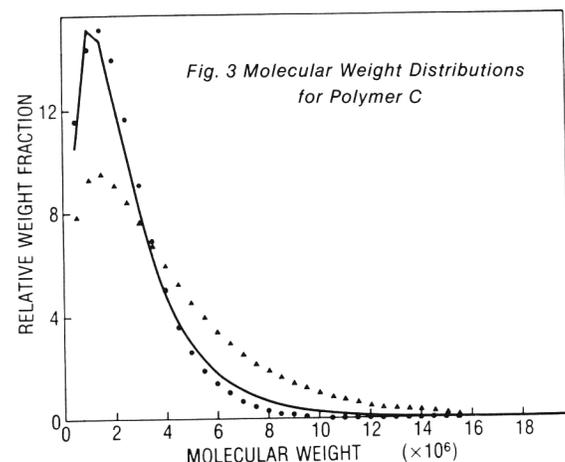
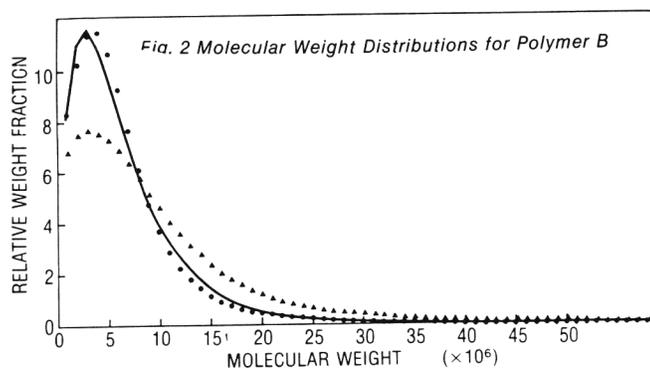
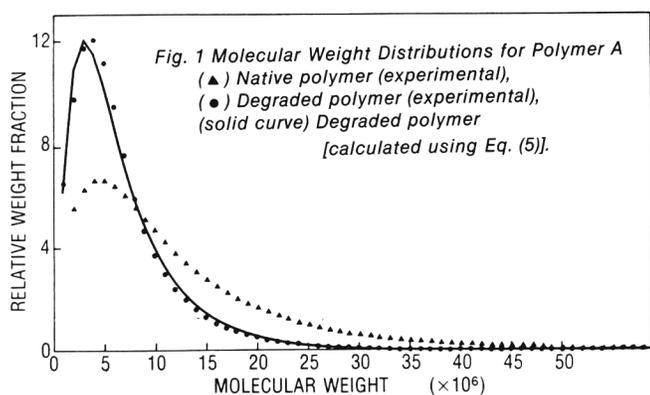
Introduction

Current attempts at enhanced oil recovery by the chemical flooding process have generated interest in the nature of interactions occurring between polymers and surfactants injected into the ground [1-4]. In the chemical flooding process, the surfactant solution is designed to yield low interfacial tensions of about  $10^{-3}$ - $10^{-4}$  dyne/cm against the formation oil. The polymer buffer is designed to provide mobility control of the injected fluids. The surfactant slugs used could be dilute or concentrated micellar solutions or microemulsions and include in addition to the surface active molecule, electrolytes and cosurfactants such as alcohols. Interactions occurring between the surfactant and the polymer molecules in these complex chemical systems can lead to phase separation and an alteration in the phase compositions from those originally designed. Consequently, the interfacial tension lowering properties of the surfactant slug and the mobility control characteristics of the polymer buffer, both may adversely be affected. Therefore, in order to develop a viable surfactant-polymer flooding process, chemical systems should be designed in which the unfavorable aspects of the polymer-surfactant interactions are minimized [1].

Very few studies have been reported in literature dealing with the problem of surfactant-polymer interactions in relation to the chemical flooding process [1-4]. The available studies concern an empirical examination of the phase behaviour of surfactant-brine-polymer-oil systems. In a few cases, the phase compositions have been measured when new phases form following the occurrence of a phase separation. However, none of these studies have attempted to identify the origin of surfactant-polymer interactions in terms of the chemical properties of the surfactant and the polymer molecules and the solution conditions.

When aqueous solutions of surfactant and polymer come into contact, the surfactant molecules can bind to the polymer molecules resulting in the formation of a polymer-surfactant complex. These complexes coexist with free surfactant molecules as well as surfactant micelles which may also be present in solution [5,6]. The interactions occurring between water, monomeric surfactant, micelles and the polymer-surfactant complex determine whether the various chemicals could remain in a single phase or whether a phase separation would occur. When oil is also present, the above interactions determine whether two or three phases would coexist and what would be their compositions.

In order to develop a quantitative thermodynamic model of phase separation in surfactant-polymer systems, with or without a coexisting oil phase, it is necessary to know the nature of the surfactant-polymer complexes and the relative proportions of these complexes and of the free and micellized surfactant. Viewing the entire system as a solution of the surfactant-polymer complex in a pseudosolvent consisting of water, electrolytes, free surfactant molecules and micelles, the methods of polymer solution thermodynamics could be used to establish the criteria for phase separation. The principal goal of this paper is to attempt at a characterization of the pseudosolvent mentioned above. For this purpose, a number of possible structural models of polymer-surfactant complexes which could appear in dilute aqueous solutions, are considered. A thermodynamic treatment is presented using which one can calculate the equilibrium concentration of surfactant monomers, micelles and polymer-surfactant complexes. The parameters appearing in the above treatment can be estimated by a consideration of the interaction forces responsible for the formation of micelles and of the



polymer-surfactant complexes. Illustrative model calculations show the existence of various critical concentrations corresponding to the onset of surfactant binding to polymer, onset of micellization, saturation of polymer with surfactant and phase separation. On the basis of the models for polymer-surfactant complexes described here, a detailed thermodynamic theory of phase separation in brine-surfactant-polymer-oil system is currently being developed. The results from these latter studies will be reported in a future paper.

#### Structure of Polymer-Surfactant Complexes

Various topologies of polymer-surfactant complexes can be visualized [5-13], 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.

No binding of surfactant to polymer (Type 1) occurs when there exists strong repulsive interaction forces between the polymer and the surfactant molecules compared to the mutual attractive interactions among the surfactant molecules. An example of such a system would be partially or totally hydrolyzed polyacrylamide polymer-anionic surfactant solutions at low ionic strengths [13]. Under these conditions, the ionic groups of the anionic polyacrylamide are dissociated. This results in strong electrostatic repulsions between the anionic groups of the polymer and the anionic polar heads of the surfactant molecule, which prevents the binding of any surfactant to the polymer.

Linear binding of single surfactant molecules along the polymer chain (Type 2) arises when the attractive binding forces between the polymer binding site and the surfactant molecule are very strong in comparison to the mutual attractions between the surfactant molecules. Such a mode of association is exhibited by ionic polymers and ionic surfactants which are oppositely charged. An example is provided by a solution of anionic polyacrylamide polymer and cationic surfactants at low ionic strengths [13]. The strong attractive electrostatic interactions between the anionic groups of the polymer and the cationic polar heads of the surfactant result in the formation of these linear structures. The polymer-surfactant complex, in this case, is very hydrophobic because of the hydrocarbonaceous exterior resulting from the binding of the surfactant to the polymer.

Intramolecular and intermolecular bridging of polymer molecules by bound surfactant molecules (Type 3) occurs, in solutions containing oppositely charged polymer and surfactant molecules, the surfactant ions being multivalent. Again, the strong electrostatic attractions between the ionic groups of the polymer and the surfactant contribute

to surfactant binding. The ability of a surfactant molecule to bind with two or more polymer binding sites gives rise to the bridgelike structure of the complex. When different binding sites of a single polymer molecule are associated with the same surfactant molecule intramolecular bridging occurs, whereas, the association of the same surfactant molecule at the binding sites of two or more polymer molecules results in intermolecular bridging.

The solubilization of a polymer molecule with a layer of bound surfactant, in the interior of surfactant micelles (Type 4) occurs in those systems where the polymer containing one layer of bound surfactant is very hydrophobic. For Type 2 systems, in which the oppositely charged ionic polymer and surfactant molecules are associated, the resulting surfactant-polymer complex is very hydrophobic. This complex can be solubilized within the hydrocarbon like interior of the surfactant micelles to form Type 4 complex structure. For example, in solutions of anionic polyacrylamide polymer and cationic surfactants, the polymer-surfactant complex of Type 2 initially forms and then precipitates out. But as the concentration of the cationic surfactant is increased the Type 2 complex is solubilized within the micelle, forming the Type 4 complex [13].

When polymer molecules are made up of hydrophobic and hydrophilic segments, its conformation in solution is characterized by partial segregation of the hydrophobic and hydrophilic segments. The surfactant molecules can find a compatible environment at the interface between these segregated microphases. In such systems, clusters of surfactant molecules along with the hydrocarbonaceous polymer segments of the microphases form a pseudomicellar structure such that the hydrocarbonaceous regions of the surfactant and the polymer segments are shielded from contact with water (Type 5). Such a structure has been suggested for swollen block copolymers made up of hydrophobic polybutadiene blocks and hydrophilic polyoxyethylene blocks [9]. However, in very dilute aqueous solutions also, it is predicted that such self-segregation would occur [5,6]. In order for the self-segregation of the two different types of segments within a single polymer molecule to occur, it is necessary that the blocks have certain minimum sizes.

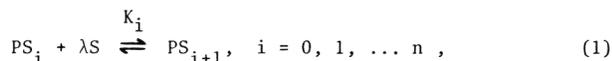
In solutions containing highly polar polymer molecules with a sufficiently flexible backbone, the polymer molecules can associate with completely formed surfactant micelles at the polar region of the micelles (Type 6). The driving force for such association is provided by the augmented shielding from water offered by the polymer to the partially exposed hydrocarbonaceous surface of the micelle. At the micelle-water interface, the polar head groups of the surfactant molecules can cover only a part of the interface between water and the hydrocarbon like interior of the micelle. Consequently, the hydrocarbon-water interfacial free energy associated with the partially exposed hydrocarbon surface of the micelle acts to destabilize the micelles. When segments of the polar polymer molecule wrap around the surface of the micelle, they provide some shielding from water to the exposed hydrocarbon surface and thereby cause a reduction in the positive interfacial free energy. This favors the formation of micelle-polymer complexes of Type 6. An example of such a polymer-surfactant complex topology has been suggested in solutions containing non-ionic polyoxyethylene polymer and anionic surfactant systems [10]. Whereas the decrease in the positive interfacial free energy favors binding, the steric interactions between the polymer segments and surfactant polar head groups, which are also present, act to oppose the formation of polymer-surfactant complexes. Indeed, one observes no binding in solutions containing non-ionic polycellulose (Dextran O-structure) polymer with a relatively inflexible backbone and anionic surfactants [13]. Also, in solutions of polyoxyethylene polymer and non-ionic polyoxyethylene type surfactants no binding is found to occur. Further, a correlation between binding of surfactant to polyoxyethylene polymer and the bulkiness of the polar head group of the anionic surfactants has also been noticed [14]. In the next section, the com-

petitive processes of surfactant binding to polymer and surfactant micellization are described using the multiple equilibria model.

#### Competitive Equilibria Of Surfactant Binding To Polymer And Micellization

A unitary description of surfactant binding to polymer is given here which is applicable to all the models of polymer-surfactant complexes considered above. Here, a single polymer molecule is assumed to have  $n$  number of binding sites available for binding by the surfactant and at each of these sites  $\lambda$  surfactant molecules are simultaneously bound. For the different types of polymer-surfactant complexes the parameters  $n$  and  $\lambda$  assume different values. For example, when the surfactant molecules bind linearly along the polymer chain (Type 2),  $n$  equals the number of ionic binding sites on the polymer and  $\lambda$  equals 1. When polymer molecules associate with completely formed micelles (Type 6),  $n$  has a value corresponding to the number of micelles associated with a single polymer molecule and  $\lambda$  is the aggregation number of these micelles.

The binding of the surfactant to the polymer can be represented using the multiple equilibria model as



where  $PS_i$  represents the polymer molecule in which  $i$  sites are filled up by bound surfactant molecules,  $S$  stands for the free surfactant molecule in solution, and  $K_i$  is the equilibrium constant for that binding step. The average number of surfactant molecules associated with each polymer molecule is given by

$$\frac{[S_b]}{[P_T]} = \frac{n\lambda K_{int} [S_f]^\lambda}{1 + K_{int} [S_f]^\lambda} \quad (2)$$

where  $[S_b]$  is the concentration of the surfactant molecules bound to the polymer,  $[P_T]$  is the total concentration of the polymer,  $[S_f]$  is the concentration of the free surfactant molecules in solution and  $K_{int}$  is the intrinsic binding constant which is the same for all the  $n$  identical binding sites.  $K_{int}$  is related to the equilibrium constant  $K_i$  of equation (1), by the expression

$$(n-i + 1) K_{int} = iK_i, \quad i = 1, \dots, n. \quad (3)$$

In addition to their binding to the polymer molecules, the surfactant molecules self-associate to form micelles in dilute aqueous solutions [5,6]. This aggregation process competes with the process of surfactant binding to the polymer, for available surfactant molecules. The micellization process can be represented by the multiple equilibria relation



where  $m$  is the aggregation number of the micelle denoted by  $S_m$ ,  $M$  is some large number representing the upper bound of aggregation and  $K'_m$  is the equilibrium constant for micellization. In general,  $K'_m$  depends upon the size  $m$  of the micelle [15-17]. One may compute the total concentration of the surfactant molecules incorporated within the micelles using the relation

$$\sum_{m=2}^M m [S_m] = \sum_{m=2}^M m K'_m [S_f]^m. \quad (5)$$

For a number of surfactants, a size distribution of micelles need not be considered because of their low polydispersity and the assumption of a single size  $m=m^*$  is adequate. The optimal micelle size  $m^*$  depends on the equilibrium constant  $K'_{m^*}$  as well as on the total surfactant concentration.

Therefore, for a given total concentration  $[S_T]$  of the surfactant, a partitioning occurs into free surfactant, polymer bound surfactant and micellized surfactant:

$$[S_T] = [S_f] + [S_b] + m^* [S_{m^*}]. \quad (6)$$

The extent of this partitioning, of course, depends on the intrinsic binding constant  $K_{int}$ , the micellization equilibrium constant  $K'_{m^*}$ , the micelle size  $m^*$ , the size  $\lambda$  of surfactant clusters bound at a polymer binding site, and the number of binding sites  $n$  per polymer molecule.

The physical factors responsible for the aggregation of surfactants as micelles have been elucidated and expressions have been developed to estimate the free energy change associated with micellization [15,17]. The physico-chemical phenomena associated with the transfer of a free surfactant molecule to a micelle are: (a) The highly structured water molecules around the hydrocarbon tail of the surfactant become free to assume more random states characterized by higher entropy. This is the essential origin of the so-called hydrophobic effect. (b) The weak water-hydrocarbon dispersion interactions of a singly dispersed surfactant are replaced by the much stronger van der Waals interactions between the hydrocarbon tails of the surfactant in the interior of the aggregates. (c) The molecular mobility of the free surfactant in solution, namely, their translational and rotational motions are substantially curtailed when the surfactant becomes part of the aggregate. (d) Part of the hydrocarbonaceous regions of the surfactant continue to remain exposed to water thus contributing to an interfacial free energy. (e) If ionic or zwitterionic polar groups are present and the ionic strength of the solution is small, then electrostatic interactions arise between the polar head groups of the surfactants constituting the aggregate [15,17]. In addition to the a priori evaluation of  $K'_{m^*}$  based on the theory of aggregation as mentioned above, one may obtain in a simpler way, a practical estimate as

$$-\left(\frac{1}{m^*}\right) RT \ln K'_{m^*} = -RT \ln \text{CMC} \quad (7)$$

where CMC is the measured critical micelle concentration in mole fraction units.

The equilibrium constant for surfactant binding at a polymer binding site could be estimated for different models of the surfactant-polymer complexes based on the interaction forces operative in each case. For the linear binding of single surfactant molecules along the polymer chain driven by ionic attractions, the binding constant accounts for the coulombic ion-ion interaction energy evaluated at a given ionic strength of the solution. Similar estimates of binding constants are made for the Type 3 complexes involving intra- and intermolecular bridging. For the Type 4 surfactant-polymer complex, the binding constant accounts for the ion-ion interaction energy associated with the one layer of bound surfactant as well as the free energy of solubilization within the surfactant micelle. For Type 5 complexes in which the clusters of surfactant molecules are oriented along the hydrophobic-hydrophilic interfaces of a self-segregated polymer, the end states of a polymer bound surfactant and one incorporated within a free micelle are very similar. Therefore, the binding constant will very closely equal the micellization equilibrium constant. When fully formed surfactant micelles are bound to the polymer molecule as in Type 6 complexes, the equilibrium constant for binding will be somewhat different from the equilibrium

constant for micellization. The difference between the two equilibrium constants accounts for the reduction in the positive interfacial free energy and the increase in the positive steric interaction energy for the polymer bound micelle compared to the free micelle in solution. Based on such estimates, one can examine the composition of surfactant-polymer solutions.

#### Surfactant Partitioning and Critical Concentrations in Surfactant-Polymer Solutions

The partitioning of the surfactant into the free surfactant, the polymer-bound surfactant and the micellized surfactant depends on the interplay between the various model parameters. Also, the experimental results show the existence of one or more critical surfactant concentrations in aqueous surfactant-polymer solutions [11-13]. In the following paragraphs, the influence of the number of binding sites  $n$ , the cluster size of the bound surfactant  $\lambda$ , the equilibrium constant  $K$ , the polymer concentration  $P_T$ , the free micellar size  $m^*$  and the free surfactant concentration  $S_f$  on the above partitioning and on various critical concentrations are discussed. One may note that,

$$K \text{ for binding} = (K_{\text{int}})^{1/\lambda} \quad (8)$$

$$K \text{ for micellization} = (K_{m^*})^{1/m^*}$$

In Figure 2, the concentrations of the polymer bound surfactant, the micellized surfactant and the total surfactant are plotted against the free surfactant concentration, assuming  $\lambda=1$ ,  $m^*=50$ ,  $P_T=10^{-7}$  mole fraction units,  $K=10^5$ . The choice of values for  $m^*$  and  $K$  are based on the typical experimental data from micellization studies and the value for  $P_T$  approximates that used in tertiary oil recovery. Three values for the number of binding sites  $n = 10, 100, 1000$  have been examined. The most important factor to note here is the value of  $\lambda$  assumed for  $\lambda$ . One may observe that for  $\lambda = 1$ , corresponding to the absence of any cooperativity in the surfactant binding to the polymer, there occurs only one critical surfactant concentration representing the onset of surfactant micellization. However, the surfactant binding to polymer takes place even at relatively low surfactant concentrations and the binding gradually reaches a maximum near the critical micelle concentration. This maximum, does not correspond to the saturation binding of the polymer. If however, we assume that  $K$  for binding is sufficiently greater than  $K$  for micellization, then the polymer can become saturated with the surfactant, without however modifying the occurrence of a single critical concentration in this system.

Figure 3 shows the influence of the surfactant cluster size  $\lambda$  on the critical behavior of the surfactant-polymer solution. As discussed above,  $\lambda = 1$  corresponds to non-cooperative surfactant binding to the polymer and the only critical concentration observed for this case is that associated with the micellization. The condition  $\lambda = 40$  corresponds to highly cooperative binding to the polymer. In this case, no surfactant binding to the polymer could occur until the free surfactant concentration  $S_f$  reaches a value of  $8 \times 10^{-6}$ . However, before this free surfactant concentration could be reached, the micellization process begins at  $S_f = 7 \times 10^{-6}$ . Therefore, one would observe only the critical surfactant concentration corresponding to the micellization in this case as well. The intermediate value of  $\lambda = 10$  corresponds to a case of weakly cooperative binding to the polymer. In this case, surfactant binding to the polymer does not begin until after  $S_f = 5 \times 10^{-6}$ . Beyond this value of the free surfactant concentration, the binding to the polymer rapidly increases. When the free surfactant concentration reaches the critical micelle concentration, micellization begins. Beyond this concentration, the sharply increasing micellized surfactant concentration

overtakes that of the polymer bound surfactant. From the plot of the total concentration against the free surfactant concentration, one may observe two transition points, one at  $S_f = 5 \times 10^{-6}$  corresponding to the onset of the surfactant binding to the polymer and the second at  $S_f = 7 \times 10^{-6}$  corresponding to the formation of micelles.

Figure 4 simulates the conditions at which surfactant binding to polymer is slightly favored over surfactant micellization:  $K = 2 \times 10^5$  for surfactant binding to the polymer and  $K = 10^5$  for surfactant micellization. The difference in the two values of  $K$  represents a standard free energy difference of about 420 cal/mole of surfactant. For  $n = 1000$ , the figure shows a highly cooperative surfactant binding to the polymer occurring at  $S_f = 4 \times 10^{-6}$ . The micellization process, for these conditions, is completely overshadowed by surfactant binding to the polymer. Only one critical surfactant concentration is therefore observed, representing the onset of the surfactant-polymer binding. For  $n = 10$ , the highly cooperative surfactant binding to the polymer begins at a critical concentration of  $S_f = 4.4 \times 10^{-6}$ . The polymer is saturated with the surfactant in all its binding sites at  $S_f = 5.6 \times 10^{-6}$ . Beyond this, the free surfactant concentration increases until it reaches the critical micelle concentration at which a sharp transition corresponding to the micellization of surfactants occurs. Under these conditions, one observes distinct critical surfactant concentrations, corresponding to the onset of the binding to the polymer, saturation of the polymer by the surfactant and the onset of micellization. One may note that the parameters influencing the critical surfactant concentrations are the size  $\lambda$  of the surfactant cluster at the polymer binding site (denoting the extent of cooperativity of the binding) and the relative difference in the values of the equilibrium constant  $K$  for binding to the polymer and for micellization. In all the cases discussed above, one may observe yet another critical concentration when the phase separation of a surfactant or polymer rich phase occurs.

#### Conclusions

Various structural descriptions of surfactant-polymer complexes which form in dilute aqueous solutions have been considered. The nature of the interaction forces between the solvent, the surfactant and the polymer molecules, as well as their stereochemical features determine which type of surfactant-polymer complexes would form. The competitive processes of surfactant binding to polymer and surfactant micellization have been modeled and illustrative calculations have been carried out to examine the equilibrium concentrations of polymer-surfactant complex, micelles and surfactant monomers for various model parameters. The calculations show that the extent of cooperativity of surfactant binding to polymer and the relative preference among the binding and micellization processes determine whether, at what concentrations and to what degree of saturation, surfactant binding to polymer would occur. The calculations also show the existence of multiple critical surfactant concentrations, which may correspond to one or more of the following events: onset of binding to polymer, onset of micellization, saturation of polymer by surfactant and phase separation. Finally, it has been suggested that knowing the relative concentrations of the free and micellized surfactant and of the polymer-surfactant complex, one can establish the properties of a pseudosolvent and thereby determine the conditions for phase separation in brine-surfactant-polymer-oil systems.

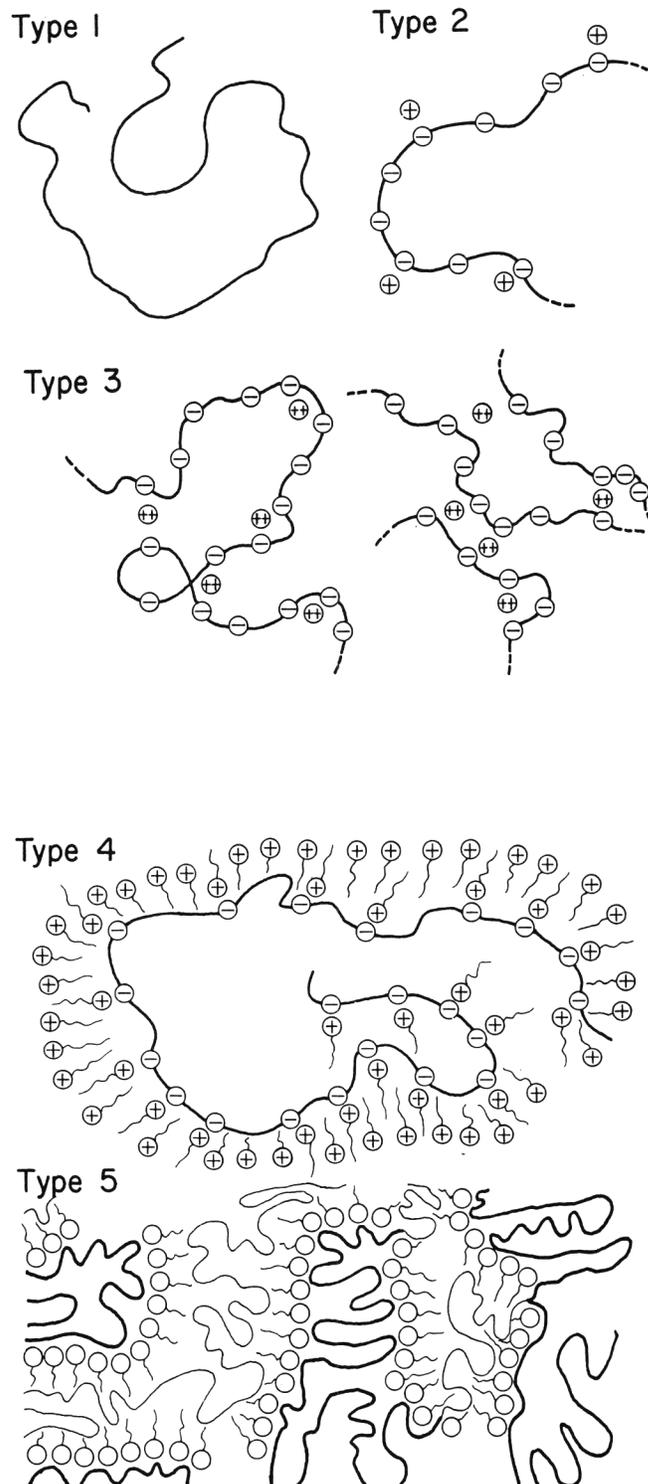
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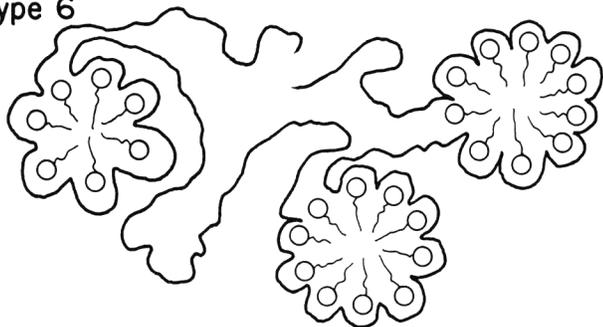
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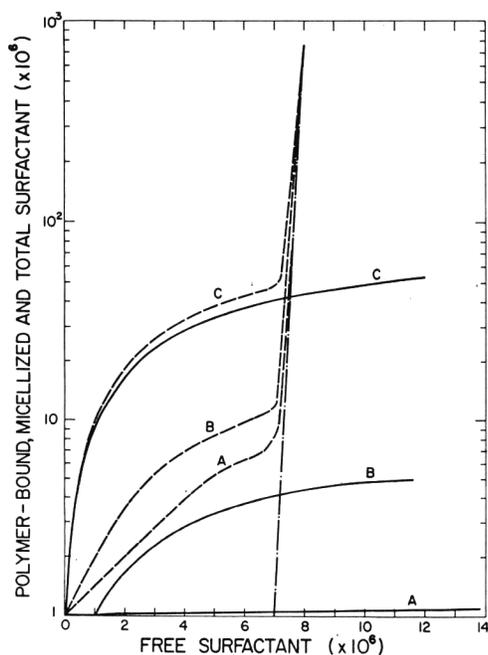
The investigation was supported by DOE contract DE-AC19-78BC20009.



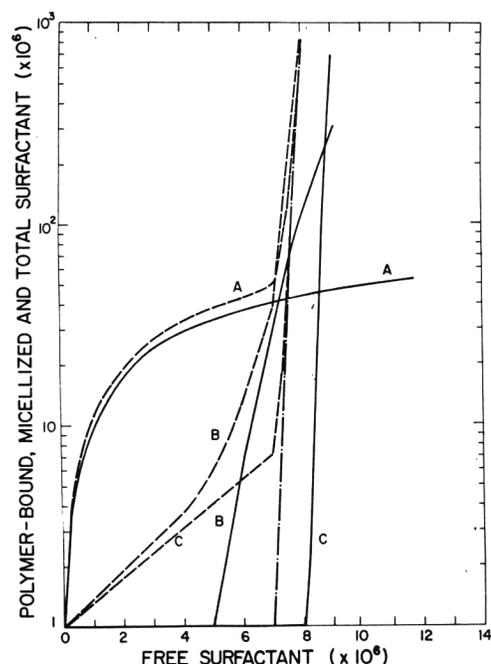
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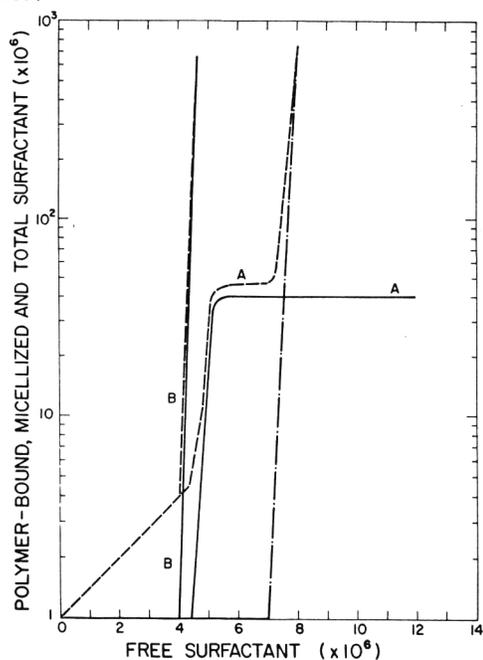
1. Schematic Descriptions of Polymer-Surfactant Complexes. The description of different types of complexes is given in the text. In the sketch for Type 5 complex, the dark lines represent hydrophilic segments and the lighter lines, the hydrophobic segments.



2. Influence of free surfactant concentration on the polymer-bound, micellized and total surfactant concentrations. The values of the model parameters used are:  $\lambda = 1$ ,  $m^* = 50$ ,  $P_T = 10^{-7}$ ,  $K$  for binding =  $10^5$ ,  $K$  for micellization =  $10^5$ . (A)  $n = 10$ , (B)  $n = 100$ , (C)  $n = 1000$ . ——— polymer bound surfactant; - - - micellized surfactant; - · - · - total surfactant. All concentrations are in mole fraction units.



3. Influence of the surfactant cluster size  $\lambda$  at the polymer binding site on the binding and the micellization behavior of the surfactant. The model parameters assume the following values:  $n = 1000$ ,  $m^* = 50$ ,  $P_T = 10^{-7}$ ,  $K$  for binding =  $10^5$ ,  $K$  for micellization =  $10^5$ . (A)  $\lambda = 1$ , (B)  $\lambda = 10$ , (C)  $\lambda = 40$ . ——— polymer-bound surfactant; - - - micellized surfactant; - · - · - total surfactant. All concentrations are in mole fraction units.



4. Influence of preferential binding equilibrium constant on the binding and the micellization behavior of the surfactant. The values of the model parameters are:  $\lambda = 40$ ,  $m^* = 50$ ,  $P_T = 10^{-7}$ ,  $K$  for binding =  $2 \times 10^5$ ,  $K$  for micellization =  $10^5$ . (A)  $n = 10$ , (B)  $n = 1000$ . ——— polymer bound surfactant; - - - micellized surfactant; - · - · - total surfactant. All concentrations are in mole fraction units.