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THERMODYNAMICS OF SURFACTANT–POLYMER INTERACTIONS IN DILUTE AQUEOUS SOLUTIONS

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A thermodynamic model for surfactant binding to polymers in dilute aqueous solutions is presented. It assumes that the intramolecular contacts between the polar and the non-polar polymer segments resemble the macroscopic hydrocarbon–water interface, where preferential accumulation of surfactant occurs. The model also considers the competitive surfactant micellization.

1. Introduction

Current efforts towards tertiary oil recovery by surfactant–polymer flooding process has generated interest in the nature and the extent of surfactant binding to polymer molecules in dilute aqueous solutions [1]. Whereas the literature on the protein–surfactant interactions is extensive [2], there exists no model for an a priori characterization of solutions containing surfactants and synthetic macromolecules. In previous papers [3,4] we have developed a thermodynamic model for surfactant aggregation in dilute aqueous solutions. Considering that the driving force for the formation of micellar aggregates as well as for the binding of surfactant to the polymer (in the absence of strong ionic interactions) are essentially the same, namely, the hydrophobic interactions, I suggest here a plausible model that describes the surfactant binding to the polymer in dilute aqueous solutions.

In this model, the polymer molecules of interest are considered to be composed of hydrocarbonaceous segments and polar segments. For a given polymer conformation in solution (as determined by the interactions involving the segments and the solvent), a definite number of contacts between the polar and the non-polar segments get generated. These contacts between the dissimilar segments resemble on a molecular scale, the macroscopic hydrocarbon–polar medium interface.

Therefore, they may be viewed as the probable locations of surfactant binding. Clusters of surfactant molecules bind at these contacts to form pseudomicelles in such a way that the hydrocarbonaceous segments of the polymer as well as the hydrocarbon tail of the surfactant both are effectively shielded from unfavorable contacts with water.

Here, the number of dissimilar segment interfaces is computed from available models for the conformation of polymer molecules in solution [5–7]. Surfactant binding to polymer at these interfaces as well as the competitive surfactant micellization are simultaneously described using the size distribution model developed earlier [3,4] for micellization. The micellization theory [3,4,8] also provides estimates for the equilibrium constants associated with surfactant binding to the polymer.

2. Binding sites on the polymer molecule

In this model, the polymer molecules are considered to exist as isolated molecules because of the very dilute solution conditions. For an isolated AB type co-polymer molecule in solution, Pouchly et al. [6,7] have examined the extent of segregation of subchains A and B. We consider that the approach of Pouchly et al. can be used to describe any macromolecule in which distinct hydrocarbonaceous (A) and polar (B) segments can be identified.

Let us consider a polymer molecule with N_A and N_B segments of type A and B respectively. The segment densities when referred to the same volume δV are $\rho_A(\bar{\gamma}_A)$ and $\rho_B(\bar{\gamma}_B)$, where $\bar{\gamma}_A$ and $\bar{\gamma}_B$ are the distances from the center of gravity of the polymer coil to the segments A and B. Considering the total volume V, the probability of simultaneous occurrence of A and B at any region, given $\bar{\gamma}_{AB} = \bar{\gamma}_A - \bar{\gamma}_B$ is

$$p_{AB}(\bar{\gamma}_{AB}) = \int_V [\rho_A(\bar{\gamma}_A)/N_A] \, [\rho_B(\bar{\gamma}_B)/N_B] \, dV. \qquad (1)$$

The number of intramolecular contacts n_{AB} between the A and the B segments is proportional to $p_{AB}(\bar{\gamma}_{AB})$. If $\mathcal{P}(\bar{\gamma}_{AB})$ is the probability of occurrence of a polymer conformation in which the A and the B segments are separated by $\bar{\gamma}_{AB}$, then taking into account all the polymer conformations, one obtains [6] for n_{AB}:

$$n_{AB} = \beta \int_V [p_{AB}(\bar{\gamma}_{AB})] \, \mathcal{P}(\bar{\gamma}_{AB}) \, d\bar{\gamma}_{AB}, \qquad (2)$$

where β is a proportionality constant. Similarly, for the A–A contacts and the B–B contacts, one can write [6]

$$n_{AA} = \int_V \tfrac{1}{2}\beta [\rho_A(\bar{\gamma}_A)]^2 \, d\bar{\gamma}_A,$$

$$n_{BB} = \int_V \tfrac{1}{2}\beta [\rho_B(\bar{\gamma}_B)]^2 \, d\bar{\gamma}_B, \qquad (3)$$

where the factor $\tfrac{1}{2}$ accounts for the duplicate counting of the segments and the proportionality constant β is assumed to be the same for all types of contacts.

Using the expressions developed by Flory and coworkers [9,10] for the segment densities ρ and the probability $\mathcal{P}$, one can determine [6] the numbers of various types of pairwise contacts involving segments A and B

$$n_{AB} = \beta(N_A + N_B)^{1/2} [x(1 - x)]$$

$$\times \{\tfrac{4}{27}\pi[xl_A^2\alpha_A^2 + (1 - x)l_B^2\alpha_B^2]\}^{3/2}$$

$$+ J_{AB}(N_A + N_B)^{1/2}x(1 - x)\}^{-1}, \qquad (4)$$

$$n_{AA} = \beta(N_A + N_B)^{1/2}(2\pi x)^{1/2}/\tfrac{4}{27}\pi l_A^3\alpha_A^3, \qquad (5)$$

$$n_{BB} = \beta(N_A + N_B)^{1/2}[2\pi(1 - x)]^{1/2}/\tfrac{4}{27}\pi l_B^3\alpha_B^3. \qquad (6)$$

In the above equations, l denotes the segment lengths, α the linear expansion coefficients, x is the fraction $N_A/(N_A + N_B)$ of the A type segmenets, and

$$J_{AB} = (v_A v_B/v_S)(1 - \chi_{SA} - \chi_{SB} + \chi_{AB}), \qquad (7)$$

where v refers to molecular volumes, χ to the Flory–Huggins interaction energy parameters, and the subscript S to the solvent. The proportionality constant β can be determined using an approximate normalization condition

$$n_{AB} + 2(n_{AA} + n_{BB}) = N_A + N_B. \qquad (8)$$

The n_{AB} contacts between the A and the B segments are not uniformly distributed, but probably occur as clusters of contacts. If one assumes that a cluster of δ contacts constitutes a surfactant binding site on the polymer, then the total number of surfactant binding sites n available per polymer molecule is n_{AB}/δ.

3. Competitive micellization and binding to polymer

The surfactant molecules added to the aqueous solution containing the polymer can (a) bind to a polymer binding site in the form of a cluster of λ surfactant molecules to form a pseudomicelle, or (b) self-associate to form micellar aggregates in solution. Therefore, at equilibrium, the aqueous solution consists of singly dispersed surfactant molecules and micellar aggregates of all possible sizes in addition to the surfactant-bound polymer molecules with different degrees of saturation. We assume that the different types of particles in solution can be viewed as distinct chemical species each characterized by its own standard chemical potential. The total free energy G of the aqueous solution is then given by

$$G = N_S\mu_S^0 + N_1\mu_1^0 + \sum_{g=2}^{\infty} N_g\mu_g^0 + N_p\mu_p^0 + \sum_{j=1}^{n} N_{pj}\mu_{pj}^0$$

$$+ kT\left[N_S \ln X_S + N_1 \ln X_1 + \sum_{g=2}^{\infty} N_g \ln X_g\right.$$

$$\left. + N_p \ln X_p + \sum_{j=1}^{n} N_{pj} \ln X_{pj}\right], \qquad (9)$$

where N represents the number of different types of

particles, μ^0 their standard chemical potential in dilute aqueous solution, X their mole fractions and subscripts 1, g, p and pj refer to the singly dispersed surfactant, micellar aggregates of aggregation number g, free polymer molecules and surfactant-bound polymer with j sites filled, respectively.

The equilibrium state is determined by the minimization of the total free energy G subject to the mass conservation constraints on the total number of surfactant molecules N_T and the total number of polymer molecules N_{PT}

$$N_1 + \sum_{g=2}^{\infty} gN_g + \sum_{j=1}^{n} jN_{pj} = N_T, \tag{10}$$

$$N_p + \sum_{j=1}^{n} N_{pj} = N_{PT}. \tag{11}$$

Corresponding to the equilibrium condition, one obtains the micellar size distribution as

$$X_g = X_1^g \exp[-(\mu_g^0 - g\mu_1^0)/kT], \tag{12}$$

and the concentration of the surfactant-bound polymers as

$$X_{pj} = X_p X_1^{Nj} \exp[-(\mu_{pj}^0 - \mu_p^0 - Nj\mu_1^0)/kT]. \tag{13}$$

In eq. (9) for the total free energy G, the expression used for the entropy of mixing is the ideal one in which the size differences amongst the pseudochemical species constituting the solution are not taken into account. Another limiting expression is the Flory–Huggins type expression in which the mole fractions are replaced by volume fractions though this may not be sufficiently satisfactory in very dilute solutions.

The above equations show that the size distribution of the micellar aggregates is determined by the free surfactant concentration as well as the standard free energy difference between the micellized and the free surfactant. The extent of binding of the surfactant to the polymer depends both on the free surfactant and the free polymer concentrations as well as on the standard free energy difference between the surfactant-bound polymer in solution and the free surfactant plus the free polymer in solution.

4. Free energies of micellization and binding to polymer

Explicit expressions have been developed [3,4] for the micellization free energies which include contributions from (a) structural changes in water, (b) van der Waals interactions between the hydrocarbon tails of the surfactants, (c) reduction in the translational and the rotational freedoms of motion of the surfactants on aggregation, (d) hydrocarbon–water interfacial free energy at the incompletely shielded micelle–aqueous medium interface, and (e) interactions between the polar groups at the micellar surface. Using these expressions one could obtain [3,4] the most probable micelle size g^* and the corresponding standard free energy difference $(\mu_{g^*}^0 - g^*\mu_1^0)/g^*$. Since the environment of a surfactant molecule at the polymer binding site (as part of the pseudomicelle) is considered to be very similar to that in the most probable surfactant micelle, the standard free energy difference per surfactant molecule associated with micellization and surfactant binding to polymer are likely to be comparable. Hence,

$$(\mu_{g^*}^0 - g^*\mu_1^0)/g^* = (\mu_{pj}^0 - \mu_p^0 - Nj\mu_1^0)/Nj. \tag{14}$$

Using the expressions developed so far, one could compute the extent of surfactant binding to polymer and of surfactant micellization, given the chemistry of the polymer and the surfactant molecules, their concentrations in solutions, and other solution conditions such as ionic strength and temperature.

5. Model predictions

The model suggests that the number of interfaces between the hydrophobic (A) and the polar (B) type segments increases as the composition of the polymer is changed from either pure A or pure B to one containing comparable amounts of A and B. This is shown in fig. 1 for different values of segment A–segment B and segment A (or B)–solvent interaction energy parameters. As a result, the extent of surfactant binding to polymer increases with increasing hydrophobicity of the polymers and reaches a maximum for a polymer containing about equal numbers of the hydrophobic and hydrophilic segments. Experimental results are, indeed, in agreement with the above predictions [11]. In systems containing anionic surfactants, a suggested order of increasing surfactant binding is polyvinyl al-
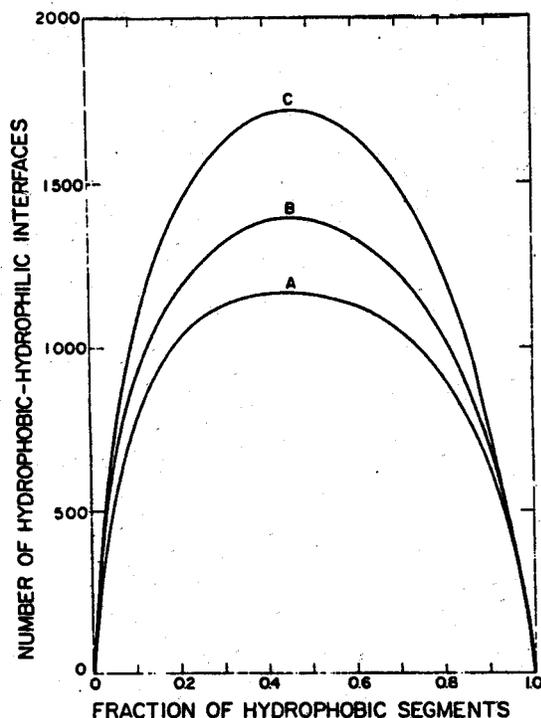
Fig. 1. Dependence of the number of hydrophobic–hydrophilic interfaces on the fraction of the hydrophobic segments in the polymer. The calculations are carried out for $v_S = 30\ \text{A}^3$, $N = 10000$, $v_A = 10^3\ v_S$, $v_B = 10^3\ v_S$, $l_A = l_B = 1000$ A. The model parameters for the three curves are as follows: (A) $x_{SA} = 0.15$, $x_{SB} = 0.15$, $x_{AB} = 0.5$; (B) $x_{SA} = 0.15$, $x_{SB} = 0.15$, $x_{AB} = 0$; (C) $x_{SA} = 0.45$, $x_{SB} = 0.45$, $x_{AB} = 0$.

Fig. 2. Influence of the surfactant cluster size λ at the polymer binding site on the binding and the micellization behavior of the surfactant. The model parameters assume the following values: $n = 1000$, $g^* = 50$, $\Sigma\ X_{pj} = 10^{-7}$, 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.

cohol, polyethylene glycol, methyl cellulose, polyvinyl acetate, polypropylene glycol and polyvinyl pyrrolidone [11]. This ordering is also consistent with that of increasing hydrophobicity of the polymers. Further, it has been found [11] that sodium dodecyl sulfate binds in increasing quantities to polyvinyl alcohol—polyvinyl acetate co-polymer, as the degree of saponification and hence of the co-polymer hydrophobicity is increased.

The model predicts the occurrence of either one or two critical surfactant concentrations corresponding to the onset of surfactant binding to the polymer and/or surfactant micellization. The existence of these critical concentrations depends on the relative influence of the number of binding sites n, the cluster size λ of the surfactant pseudomicelles at the polymer binding sites, the standard free energy differences associated with surfactant binding to the polymer and that associated with
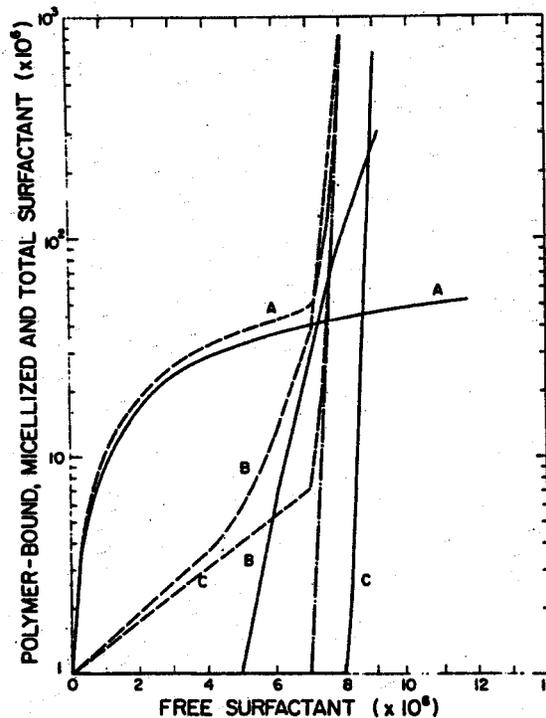
surfactant micellization. In fig. 2, the calculated concentrations of the polymer-bound, micellized and total surfactant are plotted against the free surfactant concentration for $n = 1000$, $\Sigma\ X_{pj} = 10^{-7}$ and $\lambda = 1, 10, 40$. For simplicity, micelles are considered to be monodispersed with an aggregation number $g^* = 50$. The standard free energy change per surfactant molecule associated with micellization and that for binding to the polymer are considered equal and a physically reasonable value of about -7 kcal/mole (or, a corresponding equilibrium constant $K = 10^5$) is used in the calculations [3,4,8].

The value $\lambda = 1$ corresponds to non-cooperative surfactant binding to the polymer. For this case, the surfactant binding process begins at very low surfactant concentrations and proceeds continuously. The only critical concentration observed is that associated with

micellization. For $\lambda = 40$, the cluster size of the surfactant in the pseudomicelle is almost comparable to the size of the surfactant micelle in solution. The binding process is highly cooperative but for the parameter chosen here, micellization overshadows binding to the polymer and only one critical concentration corresponding to micellization is observed. The value of $\lambda = 10$ represents a case of moderately cooperative binding. In this case one observes that no surfactant binding to polymer occurs at low concentrations of surfactant. A first critical point is observed at which surfactant binding to the polymer begins, which proceeds rapidly as the surfactant concentration is increased. When the free surfactant concentration reaches the critical micelle concentration, a second critical point is observed corresponding to the onset of micellization which subsequently overtakes the surfactant binding to the polymer. Available experimental data also identify either one or two critical concentrations in surfactant—polymer solutions [11–13].

The model suggests a possible way based on stereo-chemical rearrangements of the polymer segments for reducing the surfactant binding to the polymer while retaining the polymer characteristics required for the tertiary oil recovery application. For example, keeping the overall chemical composition of the polymer invariant, one can decrease the segment lengths l_A and l_B, while increasing the number of segments, N_A and N_B. This would result in an increase in the number of segmental interfaces n_{AB}. Generally, such a change will give rise to an increase in surfactant binding to the polymer. However, if the segment lengths are decreased below certain critical values, then due to steric requirements, effective hydrophobic bonding of the hydrocarbonaceous regions of the polymer as well as the surfactant in the pseudomicelles is not realized. In terms of the model parameters, this would mean, that the standard free energy difference associated with surfactant binding to the polymer becomes less favorable than that for micellization. Therefore, the micellization process will overshadow surfactant binding to the polymer, thus reducing, if not eliminating the binding process. This suggestion is currently being investigated.

6. Conclusions

A thermodynamic model is suggested here to predict the extent of surfactant binding onto the polymers in dilute aqueous solutions. In this model the intramolecular contacts between the hydrophobic and the polar segments of the polymer are treated as the analogs of the macroscopic hydrocarbon—polar medium interfaces and hence as the preferential locations for surfactant binding. The competitive surfactant micellization process is also considered. Because of the similarity of the thermodynamic driving forces and of the end states of the surfactant in the two processes, the standard free energy change per surfactant molecule associated with the two processes are assumed to be equal. The predictions of the model are in qualitative accord with the available experimental data. Work is underway towards verifying the quantitative predictions of the model.

References

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