Theory of Surfactant Aggregation in Water/Ethylene Glycol Mixed Solvents

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The aggregation behavior of surfactants in mixed solvents composed of water and ethylene glycol is predicted using an extension to our theory of aqueous surfactant solutions. The extension accounts for the dependence of (i) the surfactant tail transfer free energy, (ii) the aggregate core-solvent interfacial free energy, and (iii) the headgroup interaction free energy on the composition of the mixed solvent. As the proportion of ethylene glycol in the mixed solvent increases, the model predicts an increase in the critical micelle concentration (cmc), a decrease in the average aggregate size, an increase in the aggregate polydispersity, and a stronger dependence of the average aggregation number on the total surfactant concentration. The model reveals that (a) large values for cmc originate primarily from the smaller magnitude of the surfactant tail transfer free energy in the mixed solvent, (b) the aggregation numbers are small mainly because of the smaller magnitude of the hydrocarbon-mixed solvent interfacial tension, and (c) neither the cmc nor the aggregate size are greatly affected by the lower dielectric constant of the mixed solvent. The predicted aggregation characteristics of cetyl pyridinium bromide, cetyl trimethylammonium bromide, and sodium dodecyl sulfate at various compositions of the mixed solvent are presented for illustrative purposes and are compared with available measurements.

Introduction

The self-assembly of surfactants in polar organic solvents such as formamide, N,N-dimethyl formamide, dimethyl sulfoxide, dimethyl acetamide, N-methyl acetamide, glycerol, and ethylene glycol, and in some aqueous−organic mixed solvents has been investigated experimentally to explore how the solvent characteristics influence aggregation. Among these solvents, one of the most widely studied[1−12] is ethylene glycol. Both inter- and intramolecular hydrogen bonds are formed in ethylene glycol, although not as strong as those formed in water. With use of mixtures of water and ethylene glycol as solvents, the aggregation behavior of some surfactants including Aerosol OT,[7] cetyl pyridinium bromide,[8,10] cetyl trimethylammonium bromide,[9] tetradecyl trimethylammonium bromide,[11] sodium dodecyl sulfate,[9] and octyl and nonyl phenyl polyoxyethylene ethers[12] have been investigated experimentally. However, no commensurate effort has been made to develop and apply theoretical models to predict the aggregation behavior of surfactants in polar organic solvents and in aqueous−organic mixed solvents.

In a recent article,[13] we showed that quantitative predictions of the aggregation behavior of surfactants in ethylene glycol can be obtained by adapting our theory of micellization in water[14] to polar organic solvents. In this article, we extend the theory to binary mixtures of water and ethylene glycol. Illustrative predictions of the critical micelle concentration (cmc), the average aggregation numbers, and the aggregate size polydispersity are obtained for cetyl pyridinium bromide (CPBr), cetyl trimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS). The predicted cmc values are compared with available experimental data.

Thermodynamics of Micellization

The thermodynamic relations describing the aggregation behavior of surfactants in solutions are by now well established.[15] The equilibrium size distribution of aggregates can be calculated from

$$X_g = X_1{}^g \exp - \left(\frac{\mu_g^o - g\,\mu_1^o}{kT} \right) = X_1{}^g \exp - \left(\frac{g\,\Delta\mu_g^o}{kT} \right) \qquad (1)$$

where X_1 and X_g are the mole fractions of the singly dispersed surfactant molecules and aggregates of size g, and μ_1^o and μ_g^o are their standard chemical potentials, defined as those corresponding to infinitely dilute solution conditions. The factor $\Delta\mu_g^o$ represents the difference in the standard chemical potential between a surfactant molecule

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Table 1. Geometrical Properties of Aggregates

spherical micelles (radius $R_S \leq l_S$)

$$V_g = \frac{4\pi R_S^3}{3} = g v_S \qquad A_g = 4\pi R_S^2 = ga$$

$$A_{g\delta} = 4\pi(R_S + \delta)^2 = ga_\delta$$

$$P = \frac{V_g}{A_g R_S} = \frac{v_S}{a R_S} = \frac{1}{3}$$

globular micelles (semiminor axis $R_S = l_S$,
semimajor axis $b \leq 3l_S$, eccentricity E)

$$V_g = \frac{4\pi R_S^2 b}{3} = g v_S$$

$$A_g = 2\pi R_S^2 \left[1 + \frac{\sin^{-1} E}{E(1 - E^2)^{1/2}} \right] = ga, \quad E = \left[1 - \left(\frac{R_S}{b} \right)^2 \right]^{1/2}$$

$$A_{g\delta} = 2\pi(R_S + \delta)^2 \left[1 + \frac{\sin^{-1} E_\delta}{E_\delta(1 - E_\delta^2)^{1/2}} \right] = ga_\delta$$

$$E_\delta = \left[1 - \left(\frac{R_S + \delta}{b + \delta} \right)^2 \right]^{1/2}$$

$$P = \frac{V_g}{A_g R_S} = \frac{v_S}{a R_S}, \quad \frac{1}{3} \leq P \leq 0.406, \quad R_{eq} = \left(\frac{3V_g}{4\pi} \right)^{1/3}$$

in an aggregate of size g and a singly dispersed surfactant molecule in the solvent. To calculate X_g, an explicit expression for $\Delta\mu_g^0$ as a function of the size and shape of micelles is needed.

Small micelles are spherical. When the aggregation number g exceeds the value corresponding to the largest spherical micelle (i.e., the radius of the sphere equals the extended length of the surfactant tail), nonspherical globular or rodlike micelles form. Our calculations show that only small micelles form for the systems and conditions considered, and hence, we limit our discussion to spherical and globular micelles. The average geometrical characteristics of globular micelles are represented using the prolate ellipsoidal shape.[14] Table 1 provides a summary of equations to calculate the volume of the hydrophobic core of the aggregate (V_g), the total surface area of the core (A_g), the total surface area at a distance δ from the core surface ($A_{g\delta}$), and a packing parameter P, as functions of the aggregation number g. The areas per surfactant molecule a ($=A_g/g$) and a_δ ($=A_{g\delta}/g$), decrease with increasing aggregation number g. The aggregation number g along with the surfactant tail volume v_S and the extended tail length l_S, completely describes all the geometrical properties of aggregates. For hydrocarbon surfactants, v_S and l_S can be calculated (at T K) from the group contributions of the methylene and methyl groups:

$$v(CH_3) = 54.6 + 0.124 \, (T - 298) \, \text{Å}^3,$$
$$l(CH_3) = 2.765 \, \text{Å}$$

$$v(CH_2) = 26.9 + 0.0146 \, (T - 298) \, \text{Å}^3,$$
$$l(CH_2) = 1.265 \, \text{Å} \quad (2)$$

Free Energy of Micellization in Mixed Solvents

Various contributions to $\Delta\mu_g^0$ have been identified previously[14] by considering the changes experienced by a surfactant molecule when it is transferred from the solvent to an aggregate of size g. These contributions account for the following factors: (i) the surfactant tail is removed from contact with the solvent and transferred to the hydrophobic core of the micelle ($\Delta\mu_g^0$)$_{tr}$, (ii) the surfactant tail inside the micelle has a conformation different from that in a pure hydrocarbon liquid because of the molecular packing requirements inside the micelle ($\Delta\mu_g^0$)$_{def}$, (iii) the formation of the micelle creates an interface allowing for contact between the hydrophobic core and the solvent ($\Delta\mu_g^0$)$_{int}$, (iv) the headgroups of surfactants at the micelle surface exhibit steric repulsions ($\Delta\mu_g^0$)$_{ste}$, and (v) the headgroups, if they are ionic or zwitterionic, also exhibit electrostatic repulsions, ($\Delta\mu_g^0$)$_{ionic}$ or ($\Delta\mu_g^0$)$_{dipole}$. Expressions for each of these free-energy contributions, applicable to ethylene glycol−water mixtures, are given below. More detailed discussion concerning the origin of each of the expressions can be found in ref 14.

Transfer of the Surfactant Tail. The transfer free energy from the mixed solvent depends on the transfer free energies from pure water and pure ethylene glycol and also on the nature of interactions between the two solvents. Applying the Flory−Huggins equation to the mixed solvent, one gets:[16]

$$\left(\frac{\Delta\mu_g^0}{kT} \right)_{tr,mix} = \varphi_W \left(\frac{\Delta\mu_g^0}{kT} \right)_{tr,W} + \varphi_{EG} \left(\frac{\Delta\mu_g^0}{kT} \right)_{tr,EG} - \varphi_W \ln \frac{V_W}{V} - \varphi_{EG} \ln \frac{V_{EG}}{V} + \chi_{WEG} \, \varphi_W \, \varphi_{EG} \quad (3)$$

where subscripts W and EG refer to water and ethylene glycol, φ_W and φ_{EG} are their volume fractions in the mixture, V is the molar volume of the mixed solvent ($V = X_W V_W + X_{EG} V_{EG}$) calculated from the molar volumes V_W and V_{EG} and mole fractions X_W and X_{EG} of the two components, and χ_{WEG} is the Flory interaction parameter between water and ethylene glycol.

Expressions for the transfer free energy from water have been developed previously using experimental solubility data for hydrocarbons in water. The group contributions of methyl and methylene groups to the transfer free energy are given[14] by the expressions:

$$\left(\frac{\Delta\mu_g^0}{kT} \right)_{tr,W} = 5.85 \ln T + \frac{896}{T} - 36.15 - 0.0056 \, T \text{ for } CH_2$$

$$\left(\frac{\Delta\mu_g^0}{kT} \right)_{tr,W} = 3.38 \ln T + \frac{4064}{T} - 44.13 + 0.02595 \, T \text{ for } CH_3 \quad (4)$$

Expressions for the transfer free energy from ethylene glycol have been developed[13] using the infinite dilution activity coefficient data for paraffinic hydrocarbons in ethylene glycol[17] available at four temperatures ranging between 298 K and 363 K. The group contributions to the transfer free energy from ethylene glycol, of methyl and

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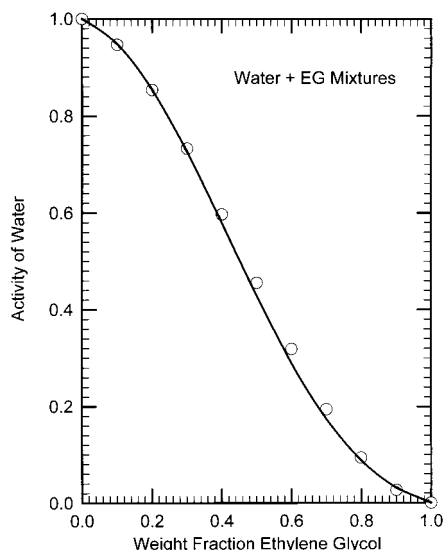(17) Pierotti, G. J.; Deal, C. H.; Derr, E. L. *Ind. Eng. Chem.* **1959**, *51*, 95.

Figure 1. Activity of water vs weight fraction of ethylene glycol in the solvent mixture at 25 °C. The points are activities calculated using the UNIFAC group contribution approach. The line shows the fitting of calculated activity data by the Flory−Huggins model (eq 6) for a water−ethylene glycol interaction parameter of $\chi_{WEG} = -2.3$.

methylene groups, are given[13] by:

$$\frac{(\Delta\mu_g^0)_{tr,EG}}{kT} = 0.149 \ln T - \frac{720}{T} - 0.0021 \, T \text{ for CH}_2$$

$$\frac{(\Delta\mu_g^0)_{tr,EG}}{kT} = 0.307 \ln T - \frac{428}{T} - 0.003083 \, T \text{ for CH}_3 \tag{5}$$

The Flory interaction parameter χ_{WEG} is obtained by fitting the activity data for water−ethylene glycol mixtures to the Flory−Huggins equation. In the absence of adequate experimental data, we calculate the activity of water (a_W) in the solvent mixture as a function of composition using the UNIFAC group contribution method[18] and fit these data to the expression given by the Flory−Huggins model:

$$\ln a_W = \ln(1 - \varphi_{EG}) + \left(1 - \frac{1}{N_{EG}}\right)\varphi_{EG} + \chi_{WEG}\varphi_{EG}^2 \tag{6}$$

Here, N_{EG} is the ratio of the molar volume of ethylene glycol to that of water and has the value of 3.1 at 298 K, for which all the computations have been performed. An estimate of $\chi_{WEG} = -2.3$ for the Flory interaction parameter fits the activity data well as indicated by Figure 1. The negative value for the interaction parameter signifies stronger water−ethylene glycol attractive interactions compared to the average of water−water and ethylene glycol−ethylene glycol interactions.

The transfer free energy strongly influences the cmc, but does not play a direct role in determining the equilibrium size of the micelles formed, because it does not depend on the aggregate size g. However, in the ionic surfactants, the cmc determines the ionic strength, and thereby influences the free-energy contribution from ionic headgroup interactions (discussed below). This latter contribution depends on the aggregate size, and conse-

quently, the transfer free energy plays an indirect role in influencing the equilibrium size of ionic surfactant aggregates.

Deformation of the Surfactant Tail. The surfactant tail has to assume a conformation inside the micelle consistent with the maintenance of liquidlike density in the core while keeping that end of the tail connected to the headgroup at the micelle−solvent interface. This molecular packing requirement can be satisfied only by allowing a variation of chain deformation along its length. The following expression for the free-energy contribution due to this factor was developed in our earlier work[14] by adapting the approach used for polymers with a large number of segments:

$$\frac{(\Delta\mu_g^0)_{def}}{kT} = \left(\frac{9P\pi^2}{80}\right)\left(\frac{R_S^2}{N_S L^2}\right) \tag{7}$$

where P is the packing parameter dependent on the aggregate shape as defined in Table 1, L is the size of a segment taken equal to 4.6 Å (corresponding to 3.6 methylene groups), N_S ($=l_S/L$) is the number of segments in the surfactant tail.

Formation of Aggregate Core−Solvent Interface. On aggregation, an interface is formed between the micelle and the surrounding solvent medium. Because the headgroup−solvent interaction at the interface is not different from the headgroup−solvent interaction of a singly dispersed surfactant molecule, it makes no new contribution. However, at the interface, there is residual contact between a part of the hydrophobic core and the solvent. The free energy due to this hydrocarbon core−solvent contact can be calculated[14] from:

$$\frac{(\Delta\mu_g^0)_{int}}{kT} = \left|\frac{\sigma_{agg}}{kT}\right|(a - a_o) \tag{8}$$

where σ_{agg} is the interfacial tension between a hydrocarbon liquid (representing the micelle core) and the solvent mixture, a_o is the area per molecule shielded from contact with the solvent because of the presence of the headgroup, and $(a - a_o)$ is the residual hydrocarbon−solvent contact area per molecule. If the headgroup has a cross-sectional area a_p larger than the cross-sectional area v_S/l_S, (also equal to L^2) of the tail, then a_o is equal to L^2. If a_p is smaller than L^2, then the headgroup does not shield the entire tail cross-section, and the shielded area a_o is equal to a_p.

The interfacial tension σ_{agg} between the mixed solvent and a hydrocarbon liquid is estimated on the basis of the Prigogine theory,[19] which recognizes that the surface composition should determine the interfacial tension and that it must be different from the bulk composition, in solutions. The surface composition is calculated via the relation

$$\ln\left[\frac{(\varphi_{EG}^S/\varphi_{EG})^{1/N_{EG}}}{(1 - \varphi_{EG}^S)/(1 - \varphi_{EG})}\right] = \frac{(\sigma_{SW} - \sigma_{SEG})}{kT}v_W^{2/3} +$$
$$\frac{3}{4}\chi_{WEG}[(1 - \varphi_{EG}) - \varphi_{EG}] - \frac{1}{2}\chi_{WEG}[(1 - \varphi_{EG}^S) - \varphi_{EG}^S] \tag{9}$$

where the superscript S refers to the surface, σ_{SW} is the surfactant tail−water interfacial tension, and σ_{SEG} is the

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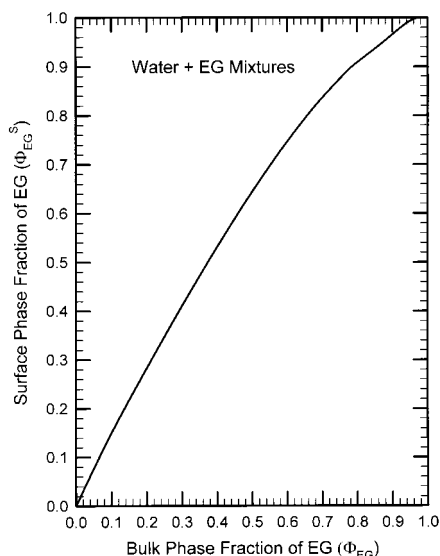
Figure 2. The composition of the ethylene glycol−water system in contact with the surface of the hydrophobic micelle core as a function of the composition of the bulk solvent mixture. The surface composition is calculated using the Prigogine theory as discussed in the text.

surfactant tail−ethylene glycol interfacial tension. Once the surface composition φ_{EG}^{S} is known, the interfacial tension σ_{agg} is calculated from

$$\left(\frac{\sigma_{agg} - \sigma_{SW}}{kT}\right) v_W^{2/3} = \ln\left(\frac{1 - \varphi_{EG}^{S}}{1 - \varphi_{EG}}\right) +$$
$$\left(\frac{N_{EG} - 1}{N_{EG}}\right)(\varphi_{EG}^{S} - \varphi_{EG}) + \chi_{WEG}\left[\frac{1}{2}(\varphi_{EG}^{S})^2 - \frac{3}{4}(\varphi_{EG})^2\right] \tag{10}$$

The interfacial tensions of the two pure solvents against a hydrocarbon liquid, σ_{SEG} and σ_{SW}, are related to pure component surface tensions via the relations:

$$\sigma_{SEG} = \sigma_S + \sigma_{EG} - 2\psi_{SEG}(\sigma_S\sigma_{EG})^{1/2}, \ \psi_{SEG} = 0.78$$

$$\sigma_{SW} = \sigma_S + \sigma_W - 2\psi_{SW}(\sigma_S\sigma_W)^{1/2}, \ \psi_{SW} = 0.55 \tag{11}$$

where ψ_{SEG} and ψ_{SW} are constants whose values have been estimated from knowledge[13,14,20] of all the tensions appearing in eq 11. The surface tensions σ_S of the surfactant tail (of molecular weight, M), σ_{EG} of ethylene glycol, and σ_W of water can be calculated (in units of dyn/cm or mN/m) from the relations:[13,14,21]

$$\sigma_S = 35.0 - 325 \, M^{-2/3} - 0.098 \, (T - 298)$$

$$\sigma_{EG} = 48.5 - 0.1(T - 298) \tag{12}$$

$$\sigma_W = 72 - 0.16(T - 298)$$

The competition between the surface and the bulk for ethylene glycol is determined by the relative magnitudes of the ethylene glycol−hydrocarbon and water−hydrocarbon interfacial tensions and by the water−ethylene glycol interactions. The fact that the ethylene glycol−hydrocarbon interfacial tension is lower than the water−

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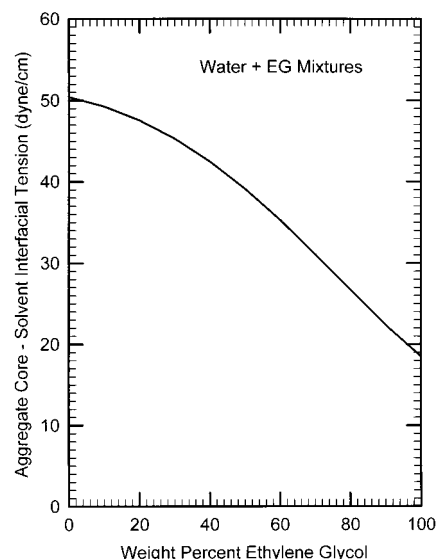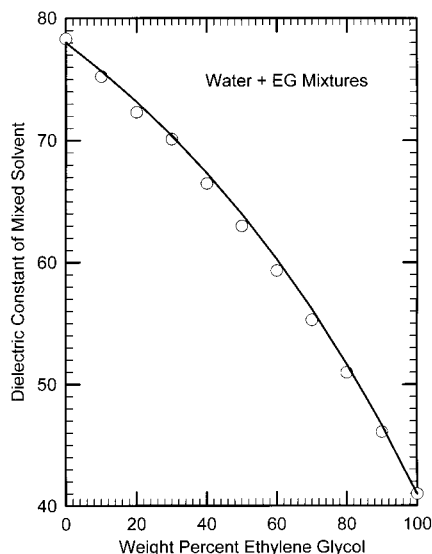(21) Panzer, J. *J. Colloid Interface Sci.* **1973**, *44*, 142.

Figure 3. The interfacial tension between the solvent mixture and the hydrophobic micelle core as a function of the composition of the bulk solvent mixture. The interfacial tension is calculated using the Prigogine theory as discussed in the text.

hydrocarbon interfacial tension should favor the surface being enriched in ethylene glycol. The fact that strong attractive interactions exist between water and ethylene glycol in the bulk (as represented by the negative value for χ_{WEG}) should counteract such surface enrichment. The surface composition predicted by the Prigogine theory as a function of the bulk composition of the mixed solvent is shown in Figure 2 and the resulting interfacial tension is plotted in Figure 3. The calculated results from Prigogine theory show that the two effects discussed above mutually compensate one another, which results in the surface composition being not dramatically different from the bulk composition and σ_{agg} being practically equal to the composition average of the pure component interfacial tensions.

Headgroup Steric Interactions. The crowding of surfactant headgroups at the micelle surface leads to steric repulsions. The corresponding free-energy contribution is calculated from a simple model based on excluded hard core areas of the headgroups, in analogy with the excluded volume effect appearing in the van der Waals equation of state:[14]

$$\frac{(\Delta\mu_g^0)_{ste}}{kT} = -\ln|1 - \frac{a_p}{a}| \tag{13}$$

Headgroup Ionic Interactions. For ionic surfactants, one has to consider the electrostatic interactions between the charged headgroups located at the aggregate surface. These interactions are calculated[14] using approximate analytical solutions to the Poisson−Boltzmann equation:

$$\frac{(\Delta\mu_g^0)_{ionic}}{kT} = 2\left[\ln\left(\frac{S}{2} + \left[1 + \left(\frac{S}{2}\right)^2\right]^{1/2}\right)\right] - \frac{2}{S}\left(\left[1 + \left(\frac{S}{2}\right)^2\right]^{1/2} - 1\right) - \frac{4}{\kappa S(R_S + \delta)} \ln\left(\frac{1}{2} + \frac{1}{2}\left[1 + \left(\frac{S}{2}\right)^2\right]^{1/2}\right) \tag{14}$$

where

$$S = \frac{4\pi e^2}{\epsilon_{mix}\kappa a_\delta kT}, \ \kappa = \left(\frac{8\pi n_o e^2}{\epsilon_{mix} kT}\right)^{1/2}, \ n_o = \frac{(C_1 + C_{add})N_{Av}}{1000} \tag{15}$$

Figure 4. Dielectric constant of water−ethylene glycol mixed solvent as a function of the mole fraction of ethylene glycol, at 25 °C. The points are experimental data from ref 22, whereas the line is calculated using pure solvent properties and the correlation given by eq 16.

Here, e is the electronic charge (4.8×10^{-10} esu), ϵ_{mix} is the dielectric constant of the mixed solvent, δ is the distance from the hydrophobic core surface to the surface where the center of the counterion is located, κ is the reciprocal Debye length, n_0 is the number of counterions per cm^3 of the solution, C_1 is the molar concentration of the singly dispersed surfactant molecules, C_{add} is the molar concentration of the uni-univalent salt added to the solution, and N_{Av} is the Avogadro's number. For prolate ellipsoids, the radius R_s is replaced with the equivalent radius R_{eq} (defined in Table 1).

The dielectric constant ϵ_{mix} is available from experimental measurements for various compositions of the water−ethylene glycol mixture and at various temperatures from 273 K to 353 K.[22] We have correlated the dielectric constant of the mixture to that of the pure components by the composition-dependent relation

$$\ln \epsilon_{mix} = X_W \ln \epsilon_W + X_{EG} \ln \epsilon_{EG} - 0.30 X_W X_{EG} \qquad (16)$$

where no explicit dependence of temperature appears, although the relation is accurate throughout the entire temperature range of 273 K to 353 K. The quality of the correlation above can be seen from Figure 4 where the experimental and correlated dielectric constants for the solvent mixture are shown at 298 K. The dielectric constants of water and ethylene glycol appearing in the equation above are given by[13,14,23]

$$\epsilon_W = 87.74 \exp[-0.0046(T - 273)]$$

$$\epsilon_{EG} = 46.6 \exp[-0.00516(T - 273)] \qquad (17)$$

Headgroup Dipole Interactions. For zwitterionic surfactants, one has to consider the electrostatic interactions among the dipoles of the headgroups located at the aggregate surface. This interaction free energy is estimated by considering that the poles of the dipoles generate an electrical capacitor and the distance between the planes

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of the capacitor is equal to the dipole length d in the zwitterionic headgroup. Consequently, one gets for spherical micelles[14] the expression

$$\frac{(\Delta \mu_g^0)_{dipole}}{kT} = \frac{2\pi e^2 R_S}{\epsilon_{mix} a_\delta kT}\left[\frac{d}{R_S + \delta + d}\right] \qquad (18)$$

where δ is the distance from the core surface to the place where the dipole is located. For prolate ellipsoids, the same equation is used but with the radius of the spherical core R_S replaced with the equivalent radius R_{eq} of the ellipsoidal core.

Molecular Constants for Surfactants. To perform size-distribution calculations only a single molecular constant (a_p) is needed for nonionic surfactants, two molecular constants (a_p and δ) are needed for ionic surfactants, and three constants (a_p, d, and δ) are needed for zwitterionic surfactants. The area a_p is a hard-core area of the headgroup. It is estimated from knowledge of the bond lengths, bond angles, and atomic volumes using a molecular model of the headgroup. The dipole length d of the dipolar headgroup and the distance δ from the core surface at which it is located are also estimated from knowledge of the bond lengths and bond angles. The distance δ from the core surface at which the center of the counterion center is located an ionic headgroup is also determined using knowledge of bond lengths and bond angles. Once these constants are estimated using molecular structural information on the headgroup, they are used to predict the behavior of surfactants of various tail lengths in a variety of calculations such as those pertaining to cmc, micelle size, temperature effects, electrolyte effects, solvent effects, sphere-to-rod transition, mixed micelles, solubilization, etc.[14] The molecular constants are thus not fitting parameters, because a very wide range of solution properties for a homologous family of surfactants have to be predicted using the same molecular constant.

The surfactants selected for the predictive calculations are the three most recently studied in water−ethylene glycol mixtures: cetyl pyridinium bromide (CPBr), cetyl trimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS). For the pyridinium bromide headgroup, we estimate $a_p = 34$ Å^2 and $\delta = 2.2$ Å, for the trimethylammonium bromide headgroup, $a_p = 54$ Å^2 and $\delta = 3.45$ Å and for the sodium sulfate headgroup, $a_p = 17$ Å^2 and $\delta = 5.45$ Å.[13,14] As mentioned above, these molecular constants previously have been used to perform a wide range of calculations involving these surfactants. For example, the two molecular constants $a_p = 17$ Å^2 and $\delta = 5.45$ Å for the sodium sulfate headgroup have been used to calculate the cmc and micelle size of sodium alkyl sulfates (from C$_8$ to C$_{16}$), how they change with ionic strength, the dependence of the sphere-to-rod transition parameter as a function of the alkyl chain length, temperature and ionic strength, the cmc of mixtures of alkyl sulfates, composition of these mixed micelles, cmcs of mixtures of SDS with a nonionic surfactant, the extent of solubilization of hydrocarbons in SDS micelles, the cmc and micelle size of SDS in the presence of solubilized hydrocarbons, etc.[14]

Computational Approach. The free-energy expressions are introduced in eq 1 where X_1 and g are the independent variables and X_g is the dependent variable. We calculate the size distribution X_g as a function of g for a specified value of the monomer concentration X_1. The total surfactant concentration X_{tot} is then calculated to be ($X_1 + \Sigma g X_g$) in mole fraction units, where the summation extends over all values of g. The surfactant concentrations

expressed as molar concentrations C and mole fractions X in this article are interrelated via the conversion relation

$$C = \frac{1000}{V_{\text{surf}} + (1 - X)/X[V_{\text{EG}}X_{\text{EG}} + V_{\text{W}}X_{\text{W}}]} \quad (19)$$

where V_{surf} is the molar volume of the surfactant. The molecular volume of the surfactant is obtained by adding the headgroup volume (approximately 200 Å^3 for pyridinium bromide, 190 Å^3 for trimethylammonium bromide, and 60 Å^3 for sodium sulfate) and the tail volume (calculated using eq 2). The molar volume of ethylene glycol is taken to be 56 cm^3/mol whereas the molar volume of water is 18 cm^3/mol.

From the calculated size distribution (X_g vs g), the true weight-average and the number-average aggregation numbers (g_w and g_n), the apparent weight-average and the apparent number-average aggregation numbers ($g_{w,\text{app}}$ and $g_{n,\text{app}}$) can be calculated based on the definitions

$$g_w = \frac{\sum g^2 X_g}{\sum g X_g}, \; g_n = \frac{\sum g X_g}{\sum X_g}$$

$$g_{w,\text{app}} = \frac{X_1 + \sum g^2 X_g}{X_1 + \sum g X_g}, \; g_{n,\text{app}} = \frac{X_1 + \sum g X_g}{X_1 + \sum X_g} \quad (20)$$

where the summations extend to all values of $g > 1$. The polydispersity in the aggregate size is given by the ratio (g_w/g_n), known as the polydispersity index.

The cmc usually is defined as the surfactant concentration at which an experimentally measured solution property displays a sharp transition in behavior. Because of this operational definition, the cmc usually depends on the type of experimental measurement being made. For example, surface tension depends largely on the concentration of the monomeric surfactant as the total surfactant concentration is altered. Consequently, a sharp transition in the plot of X_1 (or C_1) against the total concentration $X_{\text{tot}} = X_1 + \sum g X_g$ (or C_{tot}) can be used to determine the cmc. Properties such as osmotic pressure, vapor pressure, and freezing point depression depend on the total number of distinct species present in the solution. Therefore, the cmc measured using such techniques can be determined from a plot of the apparent number-average aggregation number $g_{n,\text{app}}$ versus the total surfactant concentration. The solubilization of dyes which is a common technique for determining the cmc depends on the concentration of surfactant present in the aggregated form. The cmc measured by the dye solubilization technique can thus be determined by plotting $\sum g X_g$ against the total surfactant concentration. In using light scattering to determine the cmc, the scattering intensity is dependent on the average mass of the species in solution. Thus, in this case, the cmc can be determined from a plot of the apparent weight-average aggregation number $g_{w,\text{app}}$ versus the total surfactant concentration. In addition to the approaches discussed above, other methods can also be listed for the experimental measurement and/or calculation of the cmc. In this article, the cmc is estimated by plotting X_1, $\sum g X_g$, $g_{w,\text{app}}$, or $g_{n,\text{app}}$ against the total surfactant concentration and identifying the concentration at which a sharp transition in the plotted variable is observed. The computations have been performed for many mixed solvent compositions. As limiting compositions of the mixed solvent system, the aggregation behavior in water and in ethylene glycol are also computed for the three surfactants.

Comments on Model Parameters, Their Variability and Consequences for Predicted Results. In developing the quantitative free-energy model, we have either directly estimated model parameters or used models to estimate some parameters. First are the molecular constants such as the volume and length of surfactant tail and volume of headgroup, the constants a_p, δ, and d associated with the headgroup (depending on the headgroup type), and molar volumes of water and ethylene glycol. We have already commented on the three constants a_p, δ, and d associated with the headgroup and all the other constants are accurately known from experimental density data. Concerning the second kind of molecular parameters, for calculating the transfer free energy in the mixed solvent, we have used the Flory theory. Errors in the estimated transfer free energy will affect the magnitude of the calculated cmc but not the aggregation number. For calculating the interfacial tension between the micelle core and the mixed solvent, we have used the Prigogine theory. Errors in the estimated interfacial tension will affect both the predicted cmc and the micelle aggregation number. In both the Flory model and the Prigogine model, we have used the water−ethylene glycol interaction parameter estimated from the UNIFAC group contribution method. A change in value of this parameter will thus affect both the transfer free energy and the interfacial tension, and thereby affect the calculated results. Finally, for the dielectric constant of the solvent mixture, we have used available experimental data correlated by an empirical equation. In our view, whenever direct experimental information on any of the model parameters is available, it is best to use it for the calculations. However, in the absence of such data, the best estimates are made using available models such as those of Flory and Prigogine and the UNIFAC method. The advantage of the present theory is that it is predictive. Therefore, no attempt will be made to view any of the model parameters as adjustable constants. As discussed below, the experimental determination of the cmc in systems containing a large amount of ethylene glycol in the solvent mixture is not as accurate as in water, especially when the surfactant tail length decreases. This factor should be kept in mind; it would be necessary to compare experimental results from many independent sources to validate and develop the present theory.

Results and Discussion

Critical Micelle Concentration of CPBr. The four different ways of determining the cmc discussed above are used to estimate the theoretical cmc of CPBr in mixed solvents. The calculated values of X_1, $\sum g X_g$, $g_{n,\text{app}}$, and $g_{w,\text{app}}$ are plotted as functions of the total surfactant concentration $X_{\text{tot}} = X_1 + \sum g X_g$, in Figures 5 to 8 for ethylene glycol composition in the mixed solvent of 0 wt % (pure water), 40 wt %, 80 wt %, and 100 wt % (pure ethylene glycol), respectively. The plots in Figure 5 for water show sharp transitions in behavior indicating a clearly identifiable cmc of the surfactant. Similar sharp transitions in the shapes of the plotted properties can be observed for both the 40 and 80 wt % ethylene glycol solutions, although the sharpness of the transition for the 80 wt % solution is not as pronounced as for the 0 and 40 wt % ethylene glycol systems. Figure 8 for pure ethylene glycol shows markedly differing behavior in that it is very difficult to observe a sharp transition in most of the plotted properties as the total surfactant concentration is increased. Although, all the curves in Figure 8 reflect the presence of aggregates, the physical properties (represented by the computed variables) change only gradually
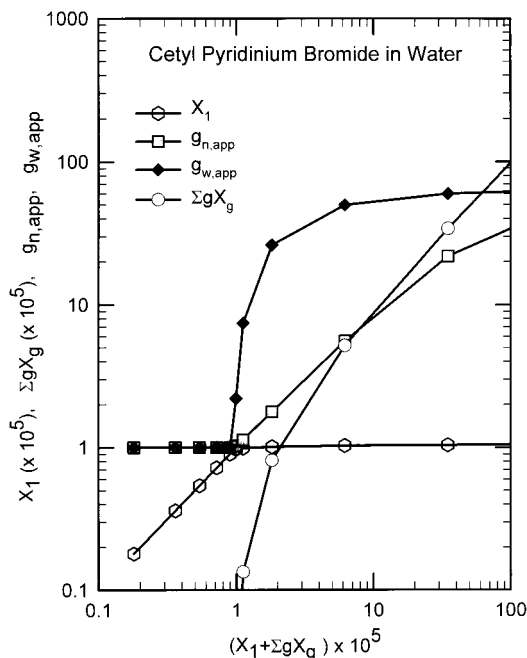
Figure 5. Calculated size-dependent variables for cetyl pyridinium bromide solutions in water as a function of the total surfactant concentration. All concentrations are expressed in mole fraction units. See text for the definitions of the apparent aggregation numbers.
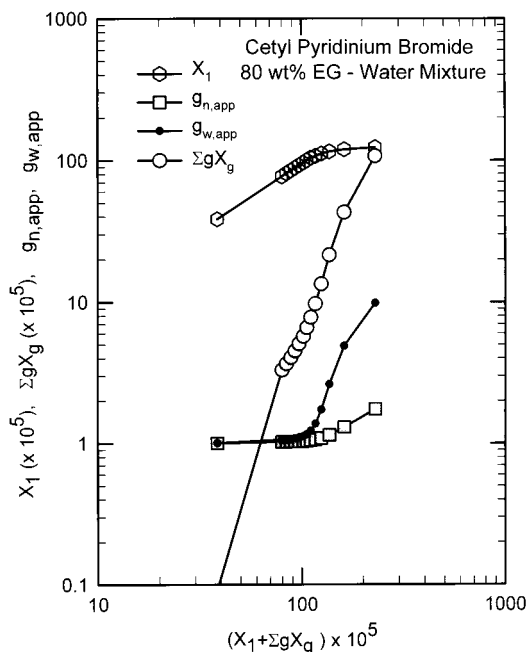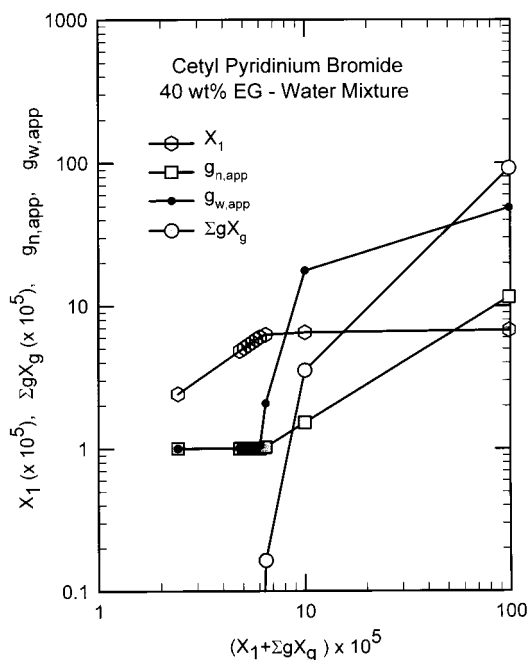

Figure 7. Calculated size-dependent variables for cetyl pyridinium bromide solutions in the water−ethylene glycol mixed solvent containing 80 wt % ethylene glycol as a function of the total surfactant concentration. The lines refer to the same size-dependent variables as in Figure 5.

Figure 6. Calculated size-dependent variables for cetyl pyridinium bromide solutions in the water−ethylene glycol mixed solvent containing 40 wt % ethylene glycol as a function of the total surfactant concentration. The lines refer to the same size-dependent variables as in Figure 5.
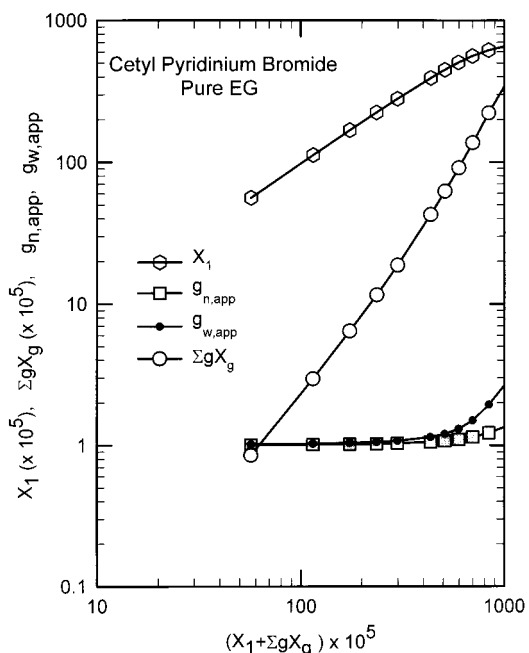

Figure 8. Calculated size-dependent variables for cetyl pyridinium bromide solutions in ethylene glycol as a function of the total surfactant concentration. The lines refer to the same size-dependent variables as in Figure 5.

over a wide range of surfactant concentrations. To identify a single concentration in this range as the cmc becomes difficult and there is considerable ambiguity in the determinations made. The cmc values determined by the different approaches for aqueous solutions from Figure 5 are quite close to one another, whereas there is appreciable variation among the estimates of cmc in ethylene glycol from Figure 8.[13] The cmc values estimated from a plot of X_1 vs X_{tot}, are presented in Figure 9 as a function of the amount of ethylene glycol in the mixed solvent. Also shown

for comparison are available experimental data based on electromotive force (emf),[10] conductivity,[8] and surface tension[8] measurements.

Micelle Size and Polydispersity of CPBr. The calculated weight average aggregation numbers and the index of polydispersity are plotted in Figure 10 as a function of the ethylene glycol content in the mixed solvent. The calculated results correspond to a total surfactant concentration of 0.2 M. The average aggregation number of the micelle decreases significantly as the amount of ethylene glycol is increased. This is accompanied by a
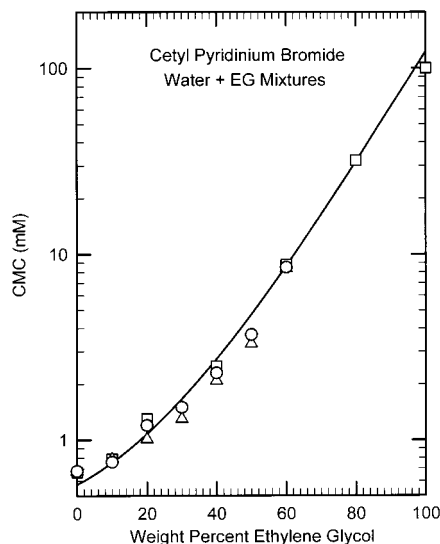
Figure 9. Critical micelle concentration of cetyl pyridinium bromide as a function of the composition of the mixed solvent system. The experimental data indicated by squares are from emf measurements,[10] circles from conductivity measurements,[8] and triangles from surface tension measurements.[8]
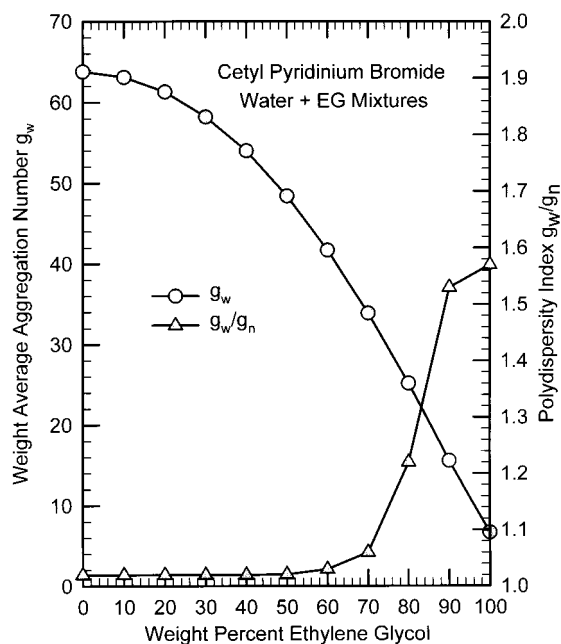

Figure 10. True weight-average aggregation number and the polydispersity index of cetyl pyridinium bromide aggregates as a function of the composition of the mixed solvent, at a total surfactant concentration of 0.2 M.

Figure 11. Dependence of the weight-average aggregation number of cetyl pyridinium bromide micelles in the water–ethylene glycol mixed solvent as a function of the total surfactant concentration. Results for the solvent systems containing 0, 40, 80, and 100 wt % ethylene glycol are presented.

Figure 12. Critical micelle concentration of cetyl trimethylammonium bromide as a function of the composition of the mixed solvent. The experimental data[9] are from conductance measurements.

simultaneous increase in the aggregate polydispersity index. In pure ethylene glycol, the solution contains mainly small oligomers resulting in an average aggregation number of about 6. The calculated average aggregation numbers are shown as functions of the total surfactant concentration in Figure 11 for the four solvent compositions. Even at very large surfactant concentrations, the aggregation numbers are small in the mixed solvents compared with the typical behavior in water (where aggregation numbers of about 60 can be observed). Further, as the ethylene glycol content in the mixed solvent is increased, the dependence of the average aggregation number on the total surfactant concentration becomes stronger. This is anticipated for polydispersed aggregates, as shown by general thermodynamic considerations.[14]
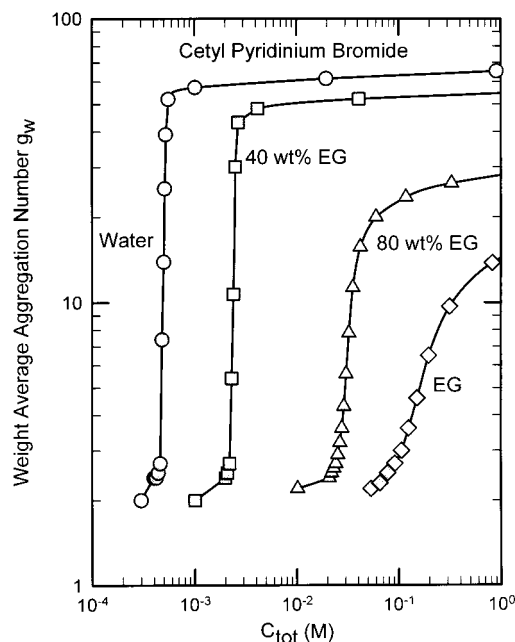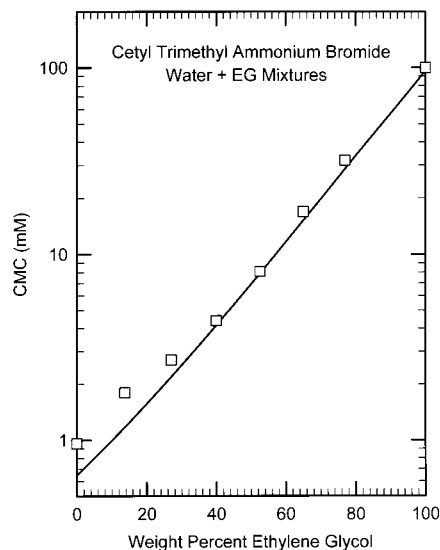
Aggregation Behavior of CTAB. The cmc of CTAB calculated from the plot of X_1 versus X_{tot}, are shown in Figure 12 along with experimental data based on conductance measurements.[9] For CTAB in water, experimental cmc values in the range 0.7 to 1 mM have been reported based on different measurement techniques,[24] and one may therefore anticipate even larger variations in the mixed solvents. The difference between the calculated and measured cmcs in Figure 12 for all solvent compositions lies within this range of experimental uncertainty. The predicted weight-average aggregation number of CTAB is shown in Figure 13, as a function of

(24) Van Os, N. M.; Haak, J. R.; Rupert, L. A. M. *Physicochemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*; Elsevier: Amsterdam, 1993.
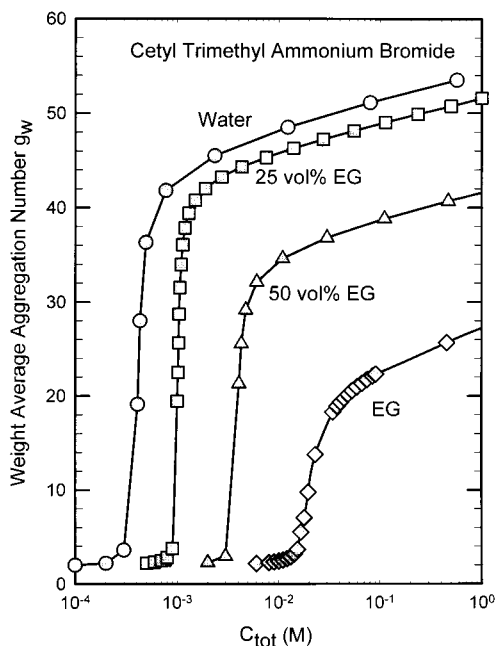
Figure 13. Dependence of the weight-average aggregation number of cetyl trimethylammonium bromide micelles in water−ethylene glycol mixed solvent as a function of the total surfactant concentration. Results for the solvent systems containing 0, 25 50, and 75 vol% ethylene glycol are presented.
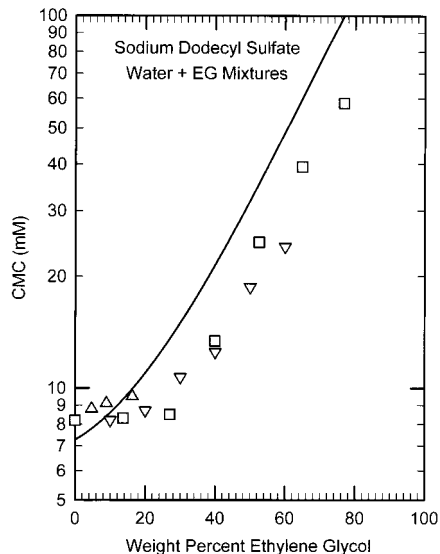

Figure 14. Critical micelle concentration of sodium dodecyl sulfate as a function of the composition of the mixed solvent. The experimental data based on conductance measurements are from ref 9 (squares), ref 25 (triangles), and ref 26 (inverted triangles).

the total surfactant concentration, for four solvent compositions (0, 25, 50 and 75 vol% ethylene glycol). The results are qualitatively similar to those presented above for CPBr.

Aggregation Behavior of SDS. The cmc of SDS calculated from the plot of X_1 versus X_{tot}, are shown in Figure 14 along with experimental data based on conductance measurements.[9,25,26] The predicted aggregation numbers of the SDS aggregates are smaller than those of CPBr and CTAB, at comparable solution conditions, because of the shorter tail length of SDS. Indeed, in pure
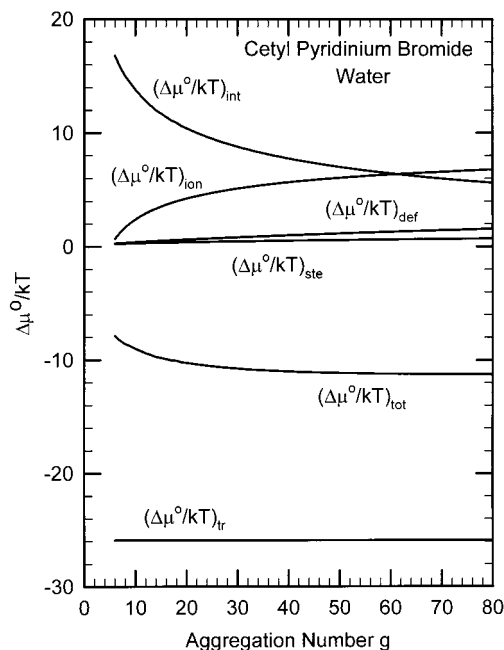
(25) Lee, D. J.; Huang, W. H. *Colloid Polym. Sci.* **1996**, *274*, 160.
(26) Gracie, K.; Turner, D.; Palepu, R. *Can. J. Chem.* **1996**, *74*, 1616.

Figure 15. Contributions to the standard free-energy change associated with aggregation of cetyl pyridinium bromide in water as a function of the aggregation number. See text for a discussion of the various contributions.

ethylene glycol, only dimers, trimers and tetramers of SDS are indicated even at very high surfactant concentrations. In Figure 14, we observe relatively large deviations between calculated cmc and that measured by conductance, at higher ethylene glycol concentrations in the mixed solvent. An obvious explanation is that because of the small size of the SDS aggregates in mixed solvents (compared with the CPBr and CTAB), the identification of a sharp transition in the measured property (which is the basis of the experimental cmc) becomes ambiguous as the amount of ethylene glycol in the mixed solvent increases. Even in water, where the aggregates are larger and a sharper transition in the measured properties is possible, a range of cmc values between 7 and 8.4 mM has been reported.[24] The change in slope of the conductance curve which is used for the experimental identification of the cmc becomes increasingly difficult to observe clearly when the ethylene glycol content in the solvent mixture is large. We speculate that the cmc determined by conductance is systematically lower than the calculated cmc because of the different way by which the presence of small aggregates influences conductivity from the way they influence the X_1 versus X_{tot} relation (which is the basis for theoretical predictions).

Influence of Solvent on Aggregation Characteristics. The contrasting aggregation behavior of surfactants in water and in water−ethylene glycol mixed solvents can be understood quantitatively on the basis of the differences in the properties of the two solvent systems. These differences are responsible for important variations in the free-energy contributions to micelle formation in the two solvent systems. The free-energy curves calculated for CPBr are shown in Figure 15 for water and Figure 16 for ethylene glycol.

The three solvent-dependent free-energy contributions show major differences between their values in water and those in ethylene glycol. The first is the surfactant tail transfer free energy which accounts for the solvophobic effect. The magnitude of the transfer free energy is considerably smaller in ethylene glycol than in water. This
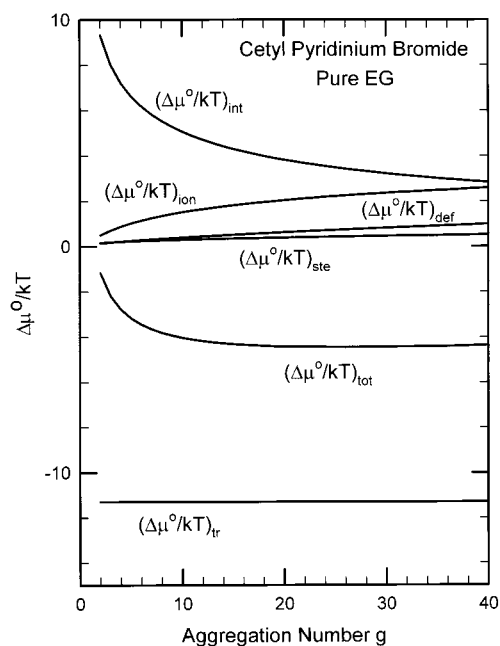
Figure 16. Contributions to the standard free-energy change associated with aggregation of cetyl pyridinium bromide in ethylene glycol as a function of the aggregation number. See text for a discussion of the various contributions.

results in the larger magnitude of the cmc in ethylene glycol compared with that in water and an increase in the cmc as the fraction of ethylene glycol in the solvent mixture is increased.

The second solvent-dependent free-energy contribution is that associated with the formation of the aggregate core-solvent interface. The interfacial free energy is smaller in the ethylene glycol solutions than in water because of the considerably smaller ethylene glycol–hydrocarbon interfacial tension compared with the water–hydrocarbon interfacial tension (see Figure 3). This is primarily responsible for the smaller aggregation numbers of the equilibrium aggregates formed in ethylene glycol solutions. Further, the lower hydrocarbon–ethylene glycol interfacial tension causes the cmc to decrease, whereas the larger area per molecule (associated with small aggregation numbers) causes the cmc to increase. The competition between these two factors can cause an increase or a decrease in the cmc in ethylene glycol solutions compared with that in water. However, the dependence of cmc on this free-energy contribution is always much weaker when compared with the dependence of the cmc on the tail transfer free energy. Therefore, one always observes an increase in cmc with increasing ethylene glycol content in the solvent mixture.

The third solvent-dependent contribution is associated with the electrostatic headgroup interactions. The dielectric constant of ethylene glycol is lower than that of water. This should lead to an increase in the magnitude of ionic interaction energy in ethylene glycol solutions compared with aqueous solutions. But the calculated free-energy values show that this is not the case, and the ionic interactions in the low dielectric constant medium are indeed smaller and not larger than those in water. This is because the concentration of the singly dispersed surfactant (X_1) at which the aggregates become possible is much larger in ethylene glycol and the mixed solvents than in water; consequently, the ionic strength is substantially higher in mixed solvents than in water. The decrease in ionic headgroup repulsions due to higher ionic strength more than compensates for the increase in ionic headgroup repulsions due to the lower dielectric constant of ethylene glycol. The net effect is a decrease in the ionic headgroup interaction energy in mixed solvents compared with in water. Thus, these interactions contribute to a reduction in the cmc in the mixed solvents. However, the influence of these interactions on the cmc is negligible when compared with the influence of the tail transfer free energy. Hence, the observed cmc always increases with increasing amounts of ethylene glycol in the mixed solvent. Concerning the micelle size, one may expect that the decrease in the ionic repulsions in ethylene glycol and in mixed solvents compared with in water will result in larger aggregation numbers. But this effect is more than compensated by the decrease in the interfacial energy in ethylene glycol and mixed solvents compared with water, which causes the aggregation numbers to become much smaller.

Conclusions

The aggregation behavior of surfactants in water–ethylene glycol mixed solvents is investigated theoretically on the basis of a simple extension to our model of micelle formation in aqueous solutions. The free energy of micellization includes three solvent-dependent contributions. Expressions for these free-energy contributions have been developed as a function of the composition of the mixed solvent. With use of these free-energy expressions, the cmc, the size distribution of aggregates, their average aggregation numbers, and polydispersity have been calculated for cetyl pyridinium bromide, cetyl trimethylammonium bromide, and sodium dodecyl sulfate for various compositions of the mixed solvent. The calculated results show that the cmc increases, the average aggregation number of the micelle decreases, and the polydispersity increases as the amount of ethylene glycol in the solvent mixture is increased. The large magnitude of the cmc originates primarily from the small magnitude of the tail transfer free energy from ethylene glycol compared with that from water. The small equilibrium aggregation numbers are a result of the low ethylene glycol–hydrocarbon interfacial tension compared with the water–hydrocarbon interfacial tension. Although the dielectric constant of ethylene glycol is smaller than that of water, the ionic interactions at the micelle surface decrease rather than increase in the mixed solvents, because of the higher monomer concentrations (typified by the larger cmcs) which give rise to higher ionic strengths. However, despite the larger ionic strengths and weaker ionic headgroup repulsions, the equilibrium aggregation numbers are small because of the dominating influence of the interfacial energy contribution.