Estimation of the Ionic Distribution in a Reverse Micelle: Effect of Ionic Size

Jyh-Ping Hsu* and Ji-Ming Jiang

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617

Shiojenn Tseng

Department of Mathematics, Tamkang University, Tamsui, Taipei, Taiwan 25137

Received: April 15, 2003; In Final Form: September 5, 2003

The effect of ionic size on both the degree of dissociation of the surfactant shell of a spherical reverse micelle and the spatial distribution of ionic species inside is examined on the basis of a modified Poisson−Boltzmann equation and a local ideal mixing rule. The dissociation of surfactant molecules is the consequence of the competition between the entropic effect of counterions in the aqueous core, the osmotic effect of the surfactants on the micelle shell, and the effect of electrical interactions. We show that the ion distribution close to the surfactant shell can be altered remarkably, and the saturation adsorption concentration varies with dissociation conditions. The free energy associated with the dissociation of surfactant molecules is studied taking the steric effect of ionic species into account. The presence of a neutral particle in a reverse micelle is found to have a negative effect on the degree of dissociation of the surfactant shell.

1. Introduction

At concentrations above the critical micelle concentration, aqueous solutions that are immiscible in organic liquid can form monodispersed droplets in the organic phase through addition of appropriate surfactants.[1,2] A water-in-oil microemulsion system, for example, comprises aqueous droplets in an oily continuum, stabilized by a layer of amphiphiles at the droplet interface. Under appropriate conditions, the droplets, called reverse micelles, are spherical and nanosized. Owing to its potential usage in various areas such as pharmaceuticals, lubrication, preparation of nanosized particles, and separation processes,[3−7] to name a few, such a thermodynamically stable system has drawn the attention of researchers of various fields. Previous analyses include studies on the structure transition, the phase behavior, and the microstructure of reverse micelles.[8−13] In water-in-oil microemulsions, stable aqueous droplets can be obtained through the introduction of surfactants, which form the outer layer of a reverse micelle. It is known that the properties of a microemulsion system correlate closely with the polar interiors of reverse micelles,[14−19] and the dissociation of surfactants plays a key role. This feature is widely used to extract metals from an aqueous solution and to prepare nanosized particles. In biotechnology, the hydrophilic enzymes solubilized in the aqueous core of a reverse micelle can provide a new pathway for enzyme-catalyzed reactions. According to Tsao et al.,[20] the solubilization of the entities inside a reverse micelle has a significant influence on its polar interior.[20] Garcia-Rio et al.[21] indicated that the addition of electrolytes in the aqueous phase has the effect of hindering the electrical percolation of a microemulsion.

A microemulsion system can exhibit many interesting and important behaviors, such as clustering and electrical percolation. Although experimental studies suggest that these behaviors relate closely to the electrical interactions involved,[22,23] relevant mechanisms are still not well-understood, and theoretical descriptions are rather limited. Most of the theoretical studies on the electrical interaction in a reverse micelle system are based on the classic Poisson−Boltzmann equation.[20,24−26] This approach has the limitations in describing the adsorption of ions to a highly charged surface and the steric effect arising from the finite ion size. Apparently, if a reverse micelle is small, the steric effect due to the size of dissociated ions becomes essential. Both the electrical potential and the distribution of ions inside can be changed abruptly near the inner surface of a reverse micelle. On the basis of a primitive model, Tsao et al.[20] proposed a rough criterion of $R/a \leq 40$ for the significance of the steric effect through Monte Carlo simulation. Various attempts have been made to modify the classic Poisson−Boltzmann equation so that the finite size of ionic species can be taken into account.[27−31] Usually, this can be accomplished by excluding the ions from the Stern layer next to a charged surface. Borukhov et al.,[32] for example, proposed a modified Poisson−Boltzmann equation for the description of the adsorption of large ions to a charged monolayer. Their analysis was based on a mean-field approach with the lattice-gas formalism, and its applicability was justified to be satisfactory. Bratko[33] studied spatial correlations among the ions confined in the aqueous core of inverted micelles in a microemulsion by theories going beyond the simplest versions of the Poisson−Boltzmann approximation, which, like the treatment of Outhwaite,[34] incorporates ion size effects on a rigorous basis.

The spatial variation of the ionic concentration inside a reverse micelle depends largely upon the charged conditions on the surfactant layer enclosing it. The thermodynamic properties and the stability of a microemulsion system are also closely related to these conditions. In this study, the problem considered by Tsao et al.[20] is reanalyzed. The charged conditions of the surfactant layer of a reverse micelle are investigated through a free energy formalism, which is based on a locally ideal mixing assumption. Resorting to a modified Poisson−Boltzmann equation, which takes the finite size of ionic species into account, the degree of dissociation of surfactant molecules on the

* To whom correspondence should be addressed. Fax: 886-2-23623040. E-mail: jphsu@ccms.ntu.edu.tw.

Ionic Surfactant S

$\oplus$ Counterions

$\longrightarrow \ominus$ Surfactant ions

$\longrightarrow \bullet$ Neutral Surfactants
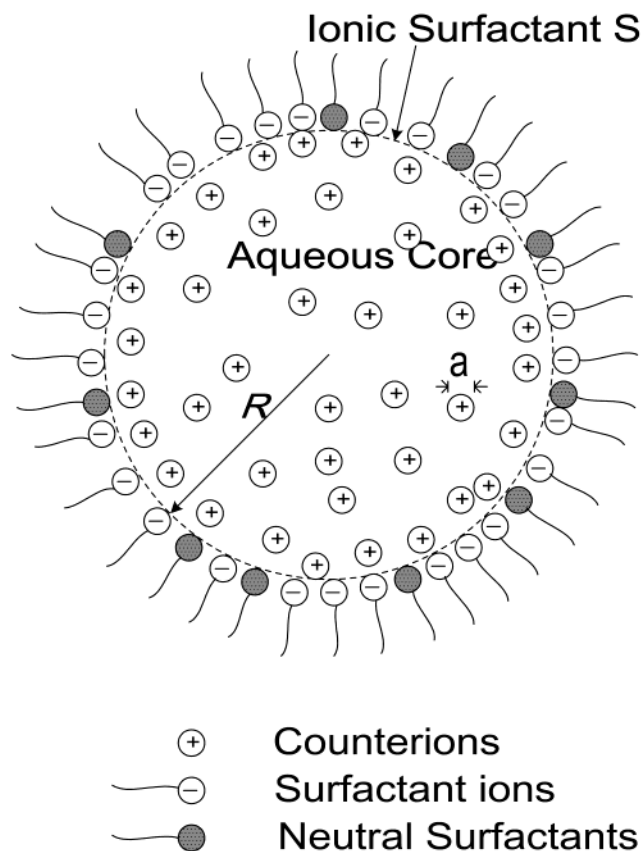
Figure 1. Schematic representation of the system, where a spherical reverse micelle comprises an aqueous core of radius R and a surfactant shell, and a is the diameter of counterions.

surfactant shell of a spherical reverse micelle is evaluated. The influence of the presence of a soluble, nanosized particle in a reverse micelle on the dissociation of surfactant molecules is also discussed.

2. Modeling

The system under consideration is illustrated in Figure 1, where a spherical reverse micelle comprises an aqueous core of radius R and a surfactant shell. We assume that the counterions in the aqueous core mainly come from the dissociation of the surfactant layer. We assume that the dissociation of surfactant molecule SC through the reaction

$$SC_{(s)} \leftrightarrow S^{Z-}_{(s)} + C^{Z+}_{(aq)} \qquad (1)$$
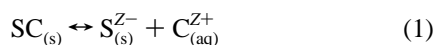
yields charged species S^{Z-} on the surfactant shell (s), and the counterion C^{Z+} is released to the aqueous core. For simplicity, we assume that the dissociation of surfactant will not change the microstructure of a reverse micelle. Also, all the possible quantum effects are assumed to be negligible. Suppose that the surfactant ion S^{Z-} and the associated neutral species SC form a regular solution thermodynamically, that is, the entropy of mixing can be evaluated on the basis of a locally ideal mixing assumption.[35] Let γ be the effective interaction energy of a surfactant molecule referring to the hydrophilic headgroup repulsion. The chemical potential of SC, μ_{SC}, can be expressed as

$$\mu_{SC} = \mu^{\circ}_{SC} + k_B T \ln X_{SC} + \gamma(1 - X_{SC})^2 \qquad (2)$$

where k_B is the Boltzmann constant, T is the absolute temper-

ature, and X_{SC} is the mole fraction of SC on the surfactant shell. If we let X_S be the surface mole fraction of S^{Z-}, then

$$\mu_S = \mu^{\circ}_S + k_B T \ln X_S + \gamma(1 - X_S)^2 - ze\psi_S \qquad (3)$$

where μ_S is the chemical potential of S, z is the valence of the counterions, e is the elementary charge, and ψ_S stands for the electrical potential on the surfactant shell. Note that μ°_i accounts for the chemical potential of species i when its mole fraction is unity in a regular solution. In the aqueous core, the mixture of counterions and water molecules is also assumed to obey the random mixing rule. The chemical potential of the counterions, μ_C, can be expressed as

$$\mu_C = \bar{\mu}^{\circ}_C + k_B T \ln Y_C(r) + ze\psi(r) \cong$$
$$\mu^{\circ}_C + k_B T \ln c(r) + ze\psi(r) \quad (4)$$

where μ°_C is the chemical potential of the counterions in the aqueous phase and $\bar{\mu}^{\circ}_C$ is the chemical potential of the counterions in a vacuum. Since $Y_C \ll 1$, as is usually the case, the mole fraction of counterions, $Y_C(r)$, can be approximated by the corresponding concentration, $c(r)$. The extent of the dissociation reaction of the surfactant molecules, η, is defined as

$$\eta \equiv \int_\Omega [c(r) - c^E(r)] \, d\Omega \qquad (5)$$

where Ω is the volume of the system and the superscript E denotes the equilibrium property. The degree of dissociation of surfactant molecules and the distribution of counterions in the aqueous core can be derived by minimizing the total free energy of a reverse micelle, f_T. The variation of f_T with respect to η, $c(r)$, and ψ yields respectively the dissociation equilibrium condition, the Boltzmann distribution of counterions, and the Poisson–Boltzmann equation for the system under consideration.[36] Applying the equilibrium dissociation condition to a surfactant shell yields

$$\frac{\delta f_T}{\delta \eta} = \mu_S + \mu_C - \mu_{SC} = 0 \qquad (6)$$

Substituting eqs 2–4 into this expression gives

$$\frac{c_S X_S}{1 - X_S} \exp\left(\frac{\gamma}{k_B T}(1 - 2X_S)\right) = K_d \qquad (7)$$

where c_S is the concentration of counterions on the surfactant shell. Note that c_S is bounded by $1/a^3$, which occurs at the closest packing of counterions. The intrinsic equilibrium constant K_d, which depends on both T and P, is defined as

$$K_d \equiv \exp\left(\frac{\mu^{\circ}_{SC} - \mu^{\circ}_s - \mu^{\circ}_c}{k_B T}\right) \qquad (8)$$

Due to the approximation employed in eq 4, K_d has the units $1/L^3$. Its value can be evaluated from the equilibrium constant associated with the dissociation of ionic surfactant through NMR spectroscopy or fluorescence probes. It can be shown that if the headgroup repulsion energy is much less than the thermal energy, eq 7 can be rewritten as

$$X_S = \frac{1}{1+\lambda}\Bigg[1 + \frac{\lambda(1-\lambda)}{(1+\lambda)^3}\frac{\gamma}{k_B T} + \frac{\lambda(1-\lambda)(\lambda^4 + 2\lambda^2 + 6\lambda - 1)}{2(1+\lambda)^6}\left(\frac{\gamma}{k_B T}\right)^2 + O\left(\frac{\gamma}{k_B T}\right)^3\Bigg] \quad (9)$$

where $\lambda = c_S/K_d$ represents the scaled adsorption concentration of counterions. It can be shown that $0 \leq X_S \leq 1$. If $\gamma = 0$, eq 9 reduces to the mass action model for the dissociation reaction occurring on the surfactant shell. The right-hand side of eq 9 converges rapidly when the number of terms increases, and using the first few terms is sufficient.

Because the ionic species in the aqueous core of a reverse micelle come from those dissociated from the surfactant molecules, the spatial variation of the electrical potential can be described by, in terms of the terminology of Borukhov et al.,[32]

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\left(\frac{c_0 ze}{\epsilon}\right)\frac{\exp(-ze\beta\psi)}{1 - \phi + \phi\exp(-ze\beta\psi)},$$
$$0 \leq r \leq R \quad (10)$$

and the spatial variation of the concentration of counterions is

$$c(r) = \frac{c_0\exp(-ze\beta\psi)}{1 - \phi + \phi\exp(-ze\beta\psi)} \quad (11)$$

In these expressions $\beta = (k_BT)^{-1}$, ϵ is the relative permittivity, and $\phi = a^3c_0$ is the volume fraction of counterions at an arbitrary reference point r' in the aqueous solution with $\psi(r') = 0$ and $c(r') = c_0$. It should be pointed out that because only the linear term in the packing effect correction is considered, eqs 10 and 11 are limited to low packing fractions, and our analysis may overestimate the net effect at higher values of ϕ. In general, a rigorous excluded volume calculation in a hard sphere fluid needs to account for multiple exclusions prevalent at high concentrations. The symmetric nature of the present problem suggests that $r' = 0$ can be chosen, for simplicity. Note that, because they may be influenced by the surface charge density on the surfactant shell, both c_S and c_0 cannot be determined a priori. In general, c_0 needs to be evaluated simultaneously with eq 10. The surface charge density σ' on the surfactant shell that specifies the ionized surfactant headgroups can be expressed as

$$\sigma' = -ze\rho X_S \quad (12)$$

where ρ denotes the total surface density of SC and S^{z-} on the surfactant shell. Note that, to calculate the degree of dissociation of surfactant from eq 9, the relation between c_0 and σ' has to be determined.

For convenience, we define the scaled radial distance $x = r/R$, and the scaled electrical potential $y = ze\beta\psi$. In terms of these variables, eqs 10 and 11 become respectively

$$\frac{1}{x^2}\frac{d}{dx}\left(x^2\frac{dy}{dx}\right) = -(\kappa R)^2\frac{\exp(-y)}{1 - \phi + \phi\exp(-y)} \quad (13)$$

and

$$\frac{c(x)}{c_0} = \frac{\exp(-y)}{1 - \phi + \phi\exp(-y)} \quad (14)$$

where $\kappa = (z^2e^2c_0/\epsilon k_BT)^{1/2}$ is the reciprocal Debye length. The boundary conditions associated with eq 13 include

$$\frac{dy}{dx} = 0, \quad x = 0 \quad (15)$$

$$\frac{dy}{dx} = -\sigma, \quad x = 1 \quad (16)$$

where σ is the scaled surface charge density defined by $\sigma = -(zeR\sigma'/\epsilon k_BT)$. Note that σ is positive because σ' and z have different signs. For a simpler treatment, we set $y(x=0) = 0$; that is, the electrical potential at the center of the system is chosen as the reference level. For illustration, we consider the case in which all the counterions are monovalent and the headgroup repulsion is negligible, that is, $z = 1$ and $\gamma = 0$.

The c_0-X_S relation can be determined numerically through a shooting scheme. For a given $X_S = X_S^f \leq 1$ and a set of $\{\rho, R, a, K_d\}$, σ is calculated. If $\sigma > 1$ (high charge density), an initial guess for c_0, $c_0^{(1)}$, is chosen as $c_0^{(1)} = \frac{1}{50}(\sigma'^2/\epsilon k_BT)$. On the other hand, if $\sigma \leq 1$, the value $c_0^{(1)} = -(3\sigma'/zeR)$, which is based on the Debye–Huckel result, is adopted. Substituting $c_0^{(1)}$ and σ into eqs 13, 15, and 16 yields the initial value of y, $y^{(1)}$, which is then used to evaluate the initial value of c_S, $c_S^{(1)}$, from eq 14. The initial value of X_S, $X_S^{(1)}$, is calculated by eq 9 and $c_S^{(1)}$. Define $\Delta_k = X_S^{(k)} - X_S^f$. If $\Delta_1 < 0$, another value of c_0, $c_0^{(2)}$, with $c_0^{(2)} > c_0^{(1)}$ is assumed. On the other hand, if $\Delta_1 > 0$, a $c_0^{(2)}$ with $c_0^{(2)} < c_0^{(1)}$ is chosen. The above procedure is repeated until Δ_k is smaller than a prespecified small value. The c_0-X_S relation is obtained after the previous steps are performed.

Suppose that the total free energy associated with a reverse micelle can be approximated by

$$f_T \approx N(\mu_{SC}^{\circ} + \mu^d) + N_W\mu_W^{\circ} \quad (17)$$

where the subscript W represents a water molecule and N and N_W are respectively the total number of surfactant molecules on the surfactant shell and the total number of water molecules in the aqueous phase. The chemical potential arising from the dissociation of surfactant, μ^d, can be expressed as[20]

$$\frac{\mu^d}{k_BT} = \ln(1 - X_S) - X_S + \frac{y_S}{2}X_S - 2\pi\frac{c_0R}{\rho}\int_0^1 y\exp(-y)x^2\,dx \quad (18)$$

where $y_S = y(x=1)$. This expression indicates that the contribution to μ^d comprises three parts: the entropic effect, the effect of osmotic pressure arising from ionized surfactant, and the electrostatic effect. Note that if $X_S = 0$, c_0 vanishes, and $\mu^d = 0$.

The present analysis is also applicable to the case when a particle is present in the aqueous core of a reverse micelle. This occurs, for example, when the extraction of metal or proteins is conducted in a microemulsion system. Let us consider the case where a spherical particle with a scaled radius x_p is located at the center of a reverse micelle. The surface of the particle is free of charge and regarded as the electrical reference point. In this case, the boundary condition expressed in eq 15 becomes

$$\frac{dy}{dx} = 0 \quad \text{and} \quad y = 0, \quad x = x_p \quad (19)$$
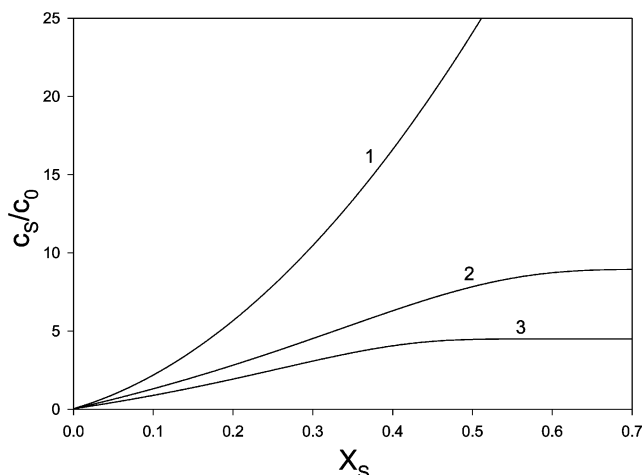
The effect of the dissolution and the size of the particle on the degree of dissociation of surfactant molecules can be examined by solving eq 13 subject to eqs 16 and 19.

3. Results and Discussions

Parametric studies including the relative magnitudes of ionic species, the dissociation constant of the surfactant, and the size of a soluble particle are conducted to simulate the behaviors of a reverse micelle under various conditions. Figure 2 shows the variations of the scaled spatial distribution of counterions, $c(x)/c_0$, for various ionic sizes. This figure reveals that $c(x)/c_0$ reaches
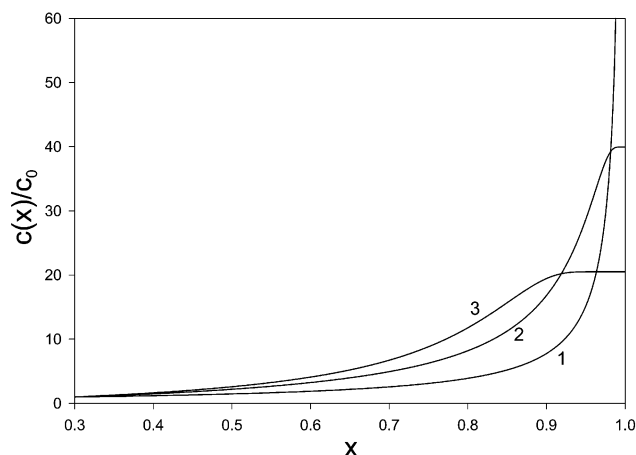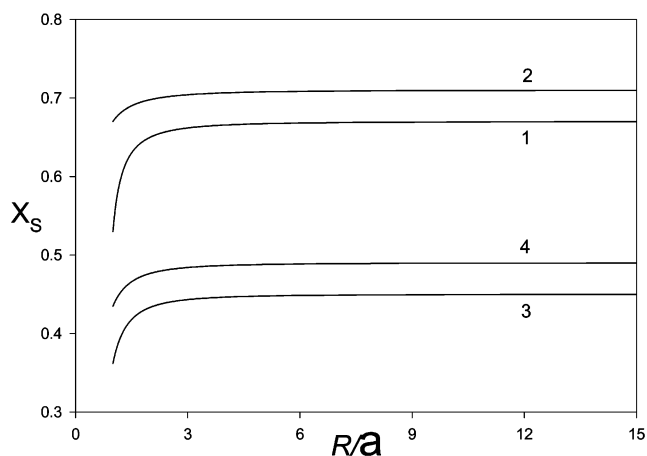
Figure 2. Variation of $c(x)/c_0$ as a function of x for different ion sizes: curve 1, $a = 0$ nm; curve 2, $a = 0.5$ nm; curve 3, $a = 1$ nm. Parameters used are as follows: $\rho = 1$ nm^{-2}, $R = 15$ nm, $K_d = 5$ nm^{-3}.

Figure 4. Variation of X_S as a function of R/a for different K_d for the case when $\rho = 1$ nm^{-2}. $K_d = 5$ nm^{-3} for curves 1 and 2, and $K_d = 1$ nm^{-3} for curves 3 and 4, respectively. $a = 0.5$ nm for curves 1 and 3, and $a = 0.7$ nm for curves 2 and 4.
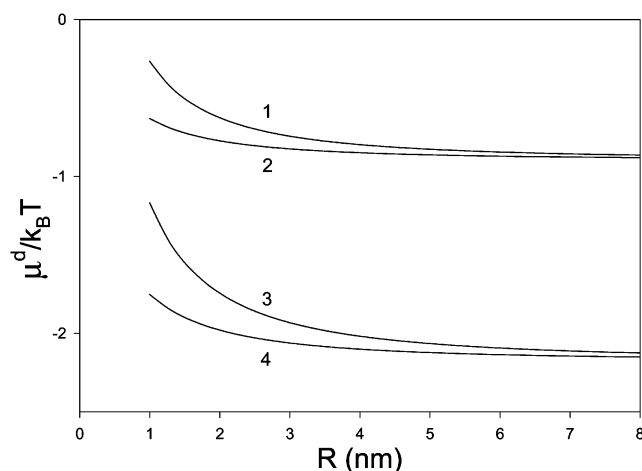

Figure 3. Variation of c_S/c_0 as a function of the degree of dissociation X_S for different ionic sizes. Parameters used are $\rho = 1$ nm^{-2} and $R = 15$ nm: curve 1, $a = 0$ nm; curve 2, $a = 0.5$ nm; curve 3, $a = 1$ nm.


Figure 5. Variation of the free energy per surfactant molecule due to dissociation as a function of R at different ionic size for the case when $\rho = 2$ nm^{-2}. $K_d = 1$ nm^{-3} for curves 1 and 2, and $K_d = 10$ nm^{-3} for curves 3 and 4, respectively. $a = 0$ nm for curves 1 and 3, and $a = 0.3$ nm for curves 2 and 4.

a maximum on the surfactant shell ($x = 1$). For the case where the size of counterions is neglected, $c(x)/c_0$ increases rapidly as $x \rightarrow 1$. On the other hand, if the size of the counterions is considered, $c(x)/c_0$ levels off as $x \rightarrow 1$, and the larger the size of the counterions, the smaller the $c(x=1)/c_0$, which is expected, since the concentration of counterions at $x = 1$ is proportional to the number of its closest packing near the surfactant shell. Since for a fixed dissociation constant, K_d, the degree of dissociation of surfactant molecules decreases with the increase in c_S, Figure 2 implies that the charge density on the surfactant shell is a function of the size of the counterions. Under the conditions of Figure 2, X_S is 0.519, 0.641, and 0.775 when the diameters of the counterions are 0, 0.5, and 1 nm, respectively. Note that neglecting the size of the counterions will underestimate the charge density on the surfactant shell.

The variations of the scaled concentration of counterions on the surfactant shell c_S/c_0 as a function of the degree of dissociation, X_S, for various ionic sizes are illustrated in Figure 3. As can be seen in this figure, the effect of ionic size on c_S/c_0 is prominent; the larger the X_S, or the larger the size of the counterions, the greater the deviation in c_S/c_0 if the size of the counterions is neglected. For the case $a \neq 0$, as X_S increases, c_S/c_0 approaches a saturated value, which arises from the fact

that the dissociation of surfactant molecules reaches thermodynamic equilibrium.

Figure 4 illustrates the variations of the degree of dissociation of surfactant, X_S, as a function of the scaled reverse micelle size R/a for various combinations of K_d and a. This figure suggests that the increase in the size of a reverse micelle has the effect of raising the degree of dissociation of surfactants, which is expected because the larger the R/a, the more the space available for the dissociated counterions. Note that X_S reaches the equilibrium value when R/a exceeds about 3. Figure 4 also shows that, for a fixed counterion size, a larger K_d leads to a higher degree of dissociation of surfactant molecules and that, for a fixed K_d, the larger the counterions, the greater the degree of dissociation. The latter can be explained by the fact that, for a fixed K_d, the larger the counterions, the lower the value of c_S and, therefore, the higher the degree of dissociation, as predicted by the mass action model.

The effect of the size of a reverse micelle R on the scaled chemical potential of a surfactant molecule, μ^d/k_BT, which arises from its dissociation is presented in Figure 5. This figure shows that, for a fixed size of a reverse micelle, μ^d/k_BT is small if the dissociation constant is large or the counterion is large. The latter implies that the steric effect of counterions is positive to

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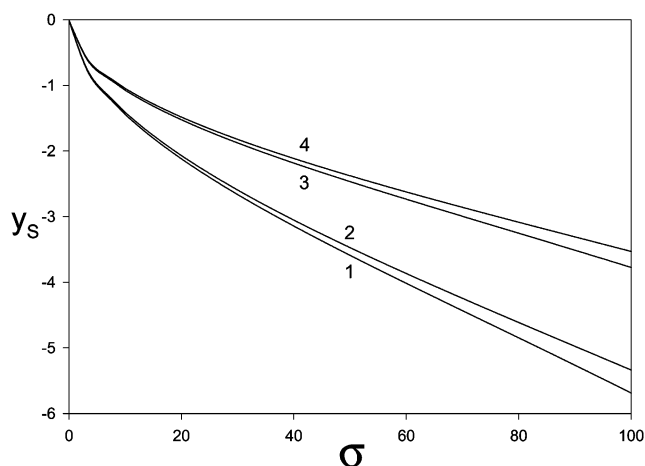
Figure 6. Variation of the surface potential y_S as a function of the surface charge density σ at different x_p for the case when $\rho = 2$ nm^{-2} and $R = 10$ nm. $x_p = 0.6$ for curves 1 and 2, and $x_p = 0.8$ for curves 3 and 4, respectively. $a = 0$ nm for curves 1 and 3, and $a = 0.3$ nm for curves 2 and 4.
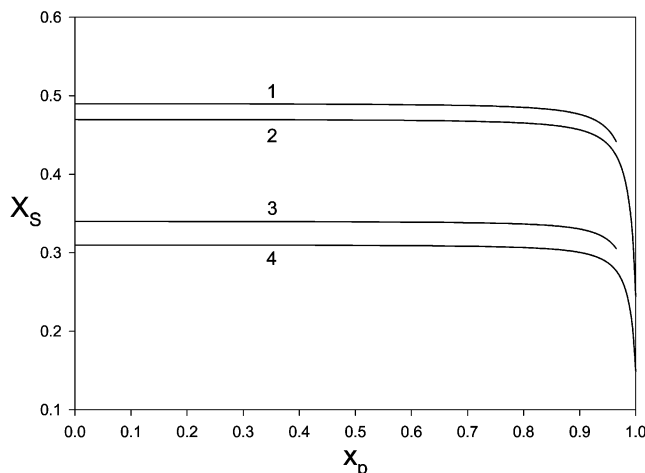
Figure 7. Variation of X_S as a function of the scaled size x_p of a particle for the case when $\rho = 2$ nm^{-2} and $R = 10$ nm. $K_d = 2$ nm^{-3} for curves 1 and 2, and $K_d = 0.5$ nm^{-3} for curves 3 and 4, respectively. $a = 0.3$ nm for curves 1 and 3, and $a = 0$ nm for curves 2 and 4.

the decrease of μ^d/k_BT. It becomes insignificant, however, if R/a exceeds about 25. For fixed dissociation constant and counterion size, μ^d/k_BT decreases with the increase of R. This is because, under the conditions assumed, X_S increases with the increase in R, as shown in Figure 4, but μ^d/k_BT decreases with the increase in X_S when the electrical potential is low.

The effect of the presence of an uncharged particle in a reverse micelle on the charged conditions of its surfactant shell is illustrated in Figure 6, where the scaled electrical potential on the surfactant shell, y_S, as a function of the corresponding scaled surface charge density σ is illustrated. Figure 6 reveals that $|y_S|$ increases monotonically with the increase in σ. For a given σ, $|y_S|$ decreases with both the increase in the size of the particle, x_p, and the increase in the size of the counterions, a. Note that because the volume of the particle is proportional to x_p^3, for a given σ, the average concentration of counterions increases and the level of the surface potential decreases with the increase in x_p. The variations of the degree of dissociation of surfactant molecules, X_S, as a function of the scaled particle size, x_p, at different K_d values are illustrated in Figure 7. This figure reveals that the influence of x_p on X_S is important when x_p exceeds about 0.8. In general, X_S decreases with the increase

in x_p, and as in the discussion of Figure 2, neglecting the size of counterions will underestimate X_S. The latter becomes insignificant, however, as $x_p \rightarrow 1$. That is, the dissociation of surfactant molecules is hindered by the presence of the particle, and the steric effect of counterions is unimportant if the size of the particle is comparable to that of the reverse micelle.

In the present study, factors such as ion−surfactant shell and ion−ion interactions are neglected; that is, we focus mainly on the effect of the size of ions. Also, because the thermal Brownian motion of the particle in the aqueous core can affect the structure of a reverse micelle, the position of the particle may be shifted due to a change in the temperature. As a result, the dipole moment effect may come into play.[24] However, the contributions from the phase of low dielectric constant can be ignored compared with that of the aqueous phase, and our analysis remains valid.

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