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# A Reinterpretation for Ion Association at Micellar Surfaces Due to an Electrostatic Model

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**Synopsis.** Ion association at the surface of a micelle is reinterpreted by considering that counter ions are bound by an electrostatic attraction with a spherical shell which is formed by the aggregation of the polar heads of amphiphilic molecules. It was found that the degree of ion association increased slightly with the increase in the aggregation number of amphiphilic molecules.

The association of counter ions with ionic micelles[1] has been suggested in experimental investigations, and an interpretation regarding it as an electrostatic interaction has been given to this association.[2,3] The investigations instigated by this interpretation have been performed on a basis of a micelle model with a uniform surface-charge density and the thermodynamics of micelle formation. Instead of the surface-charge density, the total charges, which are obtained by summing up the charges of the polar heads of the amphiphilic molecules and counter ions near a micellar surface, are introduced in this paper. As a result, the association of counter ions with an ionic micelle can be estimated according to electrostatics.

In this paper, the distribution of the counter ions which surround an ionic micelle is represented as forming a three-layered geometrical configuration as a result of electrostatic interaction. A reinterpretaton, for which the surface-charge density of a micelle is not introduced, is given to the characteristic of ion association on the basis of this distribution of the counter ions. The three-layered geometrical configuration is formed from a spherical shell composed of the polar head group of amphiphilic molecules, a layer composed of counter ions bound to the spherical shell, and an outermost layer where the movements of ions are not restricted strongly by the electrostatic field. In this investigation, it is assumed that the force which binds the counter ions within the spherical shell composed of the polar head group is electrostatic attraction. A micellar structure which includes counter ions within such a shell has been considered.[4] This micellar structure is taken into account when Gauss' law is applied to the first integration of the Poisson equation in order to obtain an approximate solution for the nonlinear Poisson-Boltzmann equation. An analytical approximate solution for the nonlinear Poisson-Boltzmann equation for a spherical micelle was given by Evans and Ninham.[3] In this paper, the surface potential for an ionized micelle is obtained on the basis of this analytical approximate solution and Gauss' law.

The association of counter ions with a micelle is estimated on the basis of this surface potential. This result gives an ion association independent of the counter-ion concentration if the aggregation number of amphiphilic molecules is constant with the change in the counter-ion concentration. It is interesting that the property independent of the counter-ion concentration is similar to that of a polyion solution. In addition, it was found that the degree of ion association increases slightly with the increase in the aggregation number of amphiphilic molecules. Thus, the dissociation of ionic micelle decreases slightly with an increase in the counter-ion concentration.

## Model

In order to examine the association of counter ions with a micelle due to electrostatic attraction, the structure of the micellar surface should be taken into account.

It is assumed that the structure of the micellar surface is like that shown in Fig. 1. The polar heads of amphiphilic molecules in the assumed micellar model exist within a spherical surface ***D*** with a certain radius $R$, and the counter ions bound within ***D*** remain outside a spherical surface with the radius of $R-\delta R$, i.e., in a shell which has a thickness of $\delta R$. The surface potential on ***D*** is obtained by considering the micellar structure to be as is shown in Fig. 1.

The potential $\psi$ around a spherical micelle is represented for a 1-1 electrolyte by this nonlinear Poisson-Boltzmann equation:

$$\frac{d^2\psi}{dr^2}+\frac{2}{r}\cdot\frac{d\psi}{dr}=\frac{8\pi n_0 e}{\varepsilon}\sinh\left(\frac{e\psi}{kT}\right), \tag{1}$$

where $n_0$ is the bulk electrolyte concentration, $\varepsilon$ is the dielectric constant of the solvent, $e$ is the unit charge, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. The approximate solution[3] for the

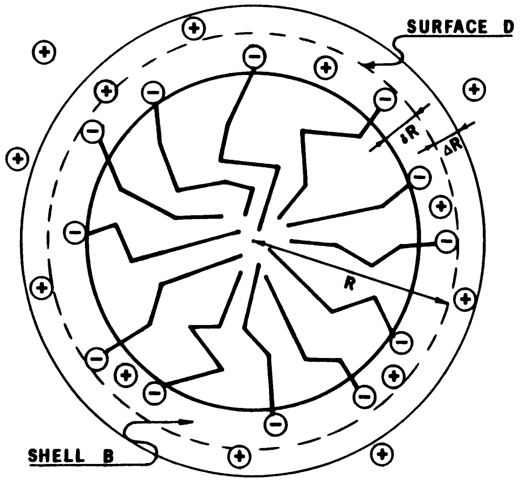

Fig. 1. Model of micelle. Polar head and counter ion are represented as (−) and (+) respectively.

surface potential $\psi_0$ on $\boldsymbol{D}$ which was obtained by Evans and Ninham from Eq. 1 is:

$$S^2 = 4\sinh^2\left(\frac{e\psi_0}{2kT}\right)\cdot\left\{1+\frac{4}{\kappa R}\cdot\frac{1}{\cosh\,(e\psi_0/2kT)+1}\right\}, \tag{2}$$

where $S \equiv -\frac{e}{\kappa kT}\cdot\left.\frac{\mathrm{d}\psi}{\mathrm{d}r}\right|_{r=R}$ and $\kappa^2 = 8\pi n_0 e^2/\varepsilon kT$.

In addition, the relation between the first and second terms on the left side of Eq. 1 for a larger $r$ is:

$$\left|\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2}\right| \gg \left|\frac{2}{r}\cdot\frac{\mathrm{d}\psi}{\mathrm{d}r}\right|,$$

as may be evaluated easily by the approximate solution of Debye-Hückel. Equation 2 is obtained by considering this relation and by integrating Eq. 1.

On the other hand, the first integration of Eq. 1 and Gauss' law lead to:

$$-\left.\frac{\mathrm{d}\psi}{\mathrm{d}r}\right|_{r=R} = \frac{Q}{\varepsilon R^2}, \tag{3}$$

where the charge $Q$ has been in this investigation to consist of two terms. One term is caused by the charge of the polar head group; the other one is caused by the charge of the counter ions, which is bound by the potential within the spherical surface $\boldsymbol{D}$. The charge $Q$ which consists of these two terms is represented as:

$$Q = -eN + \int_{R-\delta R}^{R} en_0(\exp[-e\psi/kT] - \exp[e\psi/kT])\cdot 4\pi r^2\mathrm{d}r, \tag{4}$$

where $N$ is the aggregation number of the amphiphilic molecules, assuming that the amphiphilic molecules are negatively ionized. Now, by substituting Eqs. 3 and 4 into Eq. 2, Eq. 2 is modified to the following equation:

$$\frac{e}{\varepsilon\kappa kT}\cdot\frac{1}{R^2}\cdot\{-eN + en_0\exp[-e\psi_0/kT]\cdot 4\pi R^2\cdot\delta R\}$$

$$\approx -\exp[-e\psi_0/2kT] - \frac{4}{\kappa R}, \tag{5}$$

where $e\psi_0/kT<0$ and $\exp[e\psi_0/kT] \ll 1 \ll \exp[-e\psi_0/kT]$ are taken into account, and where the integration in Eq. 4 is approximated by assuming that $\delta R$ is small. Thus, from Eq. 5 we obtain for the surface potential $\psi_0$ the following equation:

$$\exp[-e\psi_0/kT] = \left(\frac{\varepsilon\kappa kT}{8\pi e^2 n_0\delta R}\right)^2\cdot$$

$$\left[-1+\sqrt{1+\frac{16\pi e^2 n_0\delta R}{\varepsilon\kappa kT}\left(\frac{e}{\varepsilon\kappa kT}\cdot\frac{eN}{R^2}-\frac{4}{\kappa R}\right)}\right]^2. \tag{6}$$

By using Eq. 6, the association of counter ions with an ionic micelle can be estimated and the behavior of ions known.

## Results and Discussion

The number, $N_c$, of counter ions which are bound by electrostatic attraction within a spherical shell $\mathbf{B}$ is given by:

$$N_c = \int_{R-\delta R}^{R} n_0\exp[-e\psi/kT]\cdot 4\pi r^2\mathrm{d}r$$

$$\approx 4\pi R^2\delta R\cdot n_0\exp[-e\psi_0/kT].$$

Now, the degree of ion association $\beta$ for counter ions bound in $\mathbf{B}$ is represented by the ratio of $N_c$ to $N$, and, by using Eq. 6, $\beta$ is represented as:

$$\beta = \frac{\chi_0 TR}{N}\cdot\frac{R}{2\delta R}\cdot\left[-1+\sqrt{1+2\cdot\frac{\delta R}{R}\left(\frac{N}{\chi_0 TR}-4\right)}\right]^2, \tag{7}$$

where $\chi_0=\varepsilon k/e^2$. It should be noted that $n_0$ does not appear in Eq. 7. This degree of ion association $\beta$, which does not include $n_0$, suggests that if an ionic micelle is associated with more counter ions, $|\psi_0|$ will decrease more and that, as a result, the thermal dissociation of counter ions will occur more easily. On the level of approximation used to obtain Eq. 7, the number of counter ions bound within the shell $\mathbf{B}$ is entirely independent of the counter-ion concentration if the change of $N$ cannot be induced by the change in the counter-ion concentration. This result is similar to the result that Engström and Wennerström indicate for charged plates.[5] In addition, the characteristic of $\beta$ shows that the degree of ion association decreases slightly with the increase in $T$ and that it increases slightly with the increase in $N$.

Now, in order to estimate $\beta$, the radius $R$ is determined from these relations:

$$R = (\text{hydrocarbon core radius } R') + (\text{thickness of shell } \delta R)$$

and:

$$(4\pi/3)R'^3 = Nv,$$

and thus:

$$R = (3Nv/4\pi)^{1/3} + \delta R. \tag{8}$$

For $v$, we use the volume of the hydrocarbon core given by:

$$v = 27.4 + 26.9\nu\ [\text{Å}^3],$$

where $\nu$ is close to the number of carbon atoms per chain.[6] In this paper, $\nu$ is regarded as the number of carbon atoms per chain. The values of $\beta$ are shown in table 1, in which we use $\delta R$ as 3 Å[2] and the $R$ value given by Eq. 8 for lithium dodecyl sulfate (LDS) in order to calculate $\beta$.

Furthermore, another degree of ion association, $\beta'$, for counter ions bond within the spherical surface with radius $R+\Delta R$ shown in Fig. 1 is defined as:

$$\beta' = \frac{1}{N}\cdot\int_{R-\delta R}^{R} n_0\exp[-e\psi/kT]\cdot 4\pi r^2\mathrm{d}r$$

$$+\frac{1}{N}\cdot\int_{R}^{R+\Delta R} n_0\exp[-e\psi/kT]\cdot 4\pi r^2\mathrm{d}r$$

$$\approx \beta + \frac{n_0}{N}\exp[-e\psi_1/kT]\cdot 4\pi(R+\Delta R)^2\Delta R, \tag{9}$$

where $\psi_1=\psi(R+\Delta R)$ and where it is assumed that $\Delta R$ is small. In order to estimate $\psi_1$, by using Gauss' law for the spherical surface with a radius of $R+\Delta R$ on the basis of the treatment introduced in the Model, we obtain:

$$-\left.\frac{\mathrm{d}\psi}{\mathrm{d}r}\right|_{r=R+\Delta R} = \frac{-eN}{\varepsilon\,(R+\Delta R)^2}$$

$$\cdot\left\{(1-\beta) - 4\pi\Delta R(R+\Delta R)^2\frac{n_0}{N}\exp[-e\psi_1/kT]\right\},$$

Table 1. Values of $\beta$ and $\beta'$ Calculated for LDS

| $T$ <br> K | LDS <br> mol dm$^{-3}$ | LiCl[a)] <br> mol dm$^{-3}$ | $N$[b)] | $\beta$ | $\beta'$ |
|---|---|---|---|---|---|
| 308 | 0.074 | 0.0 | 57 | 0.32 | 0.43 |
| 308 | 0.074 | 0.2 | 81 | 0.37 | 0.50 |
| 308 | 0.074 | 0.4 | 92 | 0.39 | 0.52 |
| 308 | 0.074 | 1.0 | 103 | 0.40 | 0.53 |
| 308 | 0.325 | 0.0 | 79 | 0.37 | 0.49 |
| 308 | 0.598 | 0.0 | 86 | 0.38 | 0.51 |
| 308 | 0.845 | 0.0 | 93 | 0.39 | 0.52 |
| 308 | 0.985 | 0.0 | 94 | 0.39 | 0.52 |
| 308 | 1.107 | 0.0 | 96 | 0.40 | 0.53 |
| 295 | 0.294 | 0.0 | 75 | 0.37 | 0.50 |
| 310 | 0.294 | 0.0 | 71 | 0.36 | 0.47 |

a) Salt concentration in the solution of LDS. b) Data resulting from small-angle neutron-scattering data analysis for an LDS micellar system.7)

and by substituting this equation into Eq. 2 for $r=R+\Delta R$, we obtain:

$$\exp[-e\psi_1/kT] = \frac{x_0 T}{8\pi n_0 \Delta R^2} \cdot \left[-1+\sqrt{1+\frac{2\Delta R}{R+\Delta R}\cdot\left\{\frac{N(1-\beta)}{x_0 T(R+\Delta R)}-4\right\}}\right]^2. \tag{10}$$

Therefore, by substituting Eq. 10 into Eq. 9, the following formula for $\beta'$ is obtained:

$$\beta' = \beta + \frac{x_0 T(R+\Delta R)}{N}\cdot\frac{R+\Delta R}{2\Delta R}\cdot \left[-1+\sqrt{1+\frac{2\Delta R}{R+\Delta R}\left\{\frac{N(1-\beta)}{x_0 T(R+\Delta R)}-4\right\}}\right]^2. \tag{11}$$

The thickness of the shell $\Delta R$ included in Eq. 11 is:

$$\Delta R = 5.56 - \delta R\,[\text{Å}],$$

where 5.56 Å is the mean diameter of a spherical polar head of dodecyl sulfate obtained by neutron scattering for an LDS solution.7) It has been assumed here that the value of 5.56 Å corresponds to $\delta R+\Delta R$ in the micellar model shown in Fig. 1. Thus, the values of $\beta'$ obtained by Eq. 11 are shown in Table 1. These values of $\beta'$ nearly all fall in the range of 0.5—0.8, indicating generally the degree of ion association. The change in $\beta'$ with the change in the LDS concentration corresponds to the behavior of the degree of ion association obtained experimentally.7) The values of $\beta'$ in Table 1 indicate that the degree of ionic dissociation for an ionic micelle decreases slightly with the increase in the counter-ion concentration. Also, it is found that the micelles of smaller aggregation numbers have a higher degree of ionic dissociation; this is because of the characteristic of $\beta'$ depending on the change in $N$.

If dissociation occurs in a micelle, the micelle becomes less stable due to an electrostatic repulsion between the polar heads of the amphiphilic molecules. The micelles of smaller aggregation numbers are less stable because of this electrostatic repulsion. On the contrary, instability due to the electrostatic repulsion decreases with the increase in $N$, because $\beta$ values are larger for larger $N$ values. As a result, we infer that the balance point between the hydrophobic effect for aiding micellar formation and an electrostatic repulsion disturbing micellar formation exists if $N$ is larger than a certain value, although we can not discuss this balance point without the thermal influence factor.

We conclude that the characteristic of $\beta'$ agrees well with the general property of ion association with an ionic micelle, although the value of $\delta R$ has not yet been determined well enough.

## Conclusions

Pictures of a micelle with wetted outer layers surrounded by spherical polar head groups with an average diameter equal to 5.56 Å, pictures taken on the basis of neutron scattering, have been presented by Bendedouch, Chen, and Koehler.7) We have divided such a wetted outer layer into two layers consisting of two spherical shells, as is shown in Fig. 1. The values of $\beta'$ calculated by considering the two spherical shells nearly all fall in the range of 0.5—0.8, indicating generally the degree of ion association, although the value of $\delta R$ used for calculating may have some uncertainty.

In addition, it has been found that the value of $\beta'$ is independent of the counter-ion concentration, although the constancy of $N$ is required as a condition. It is also noticed that this characteristic of $\beta'$ may represent the property of a polyion solution.

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