NUMERICAL CALCULATION OF THE ELECTROSTATIC POTENTIAL AROUND AN IONIC MICELLE WITH COUNTER ION BINDING

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A numerical solution of the nonlinear Poisson-Boltzmann equation (PBE) is presented for a system of spherical micelles with counterion binding. The approach investigates the following effects on ion-micelle interactions, (i) total surface charge, (ii) competitions of different counter ions on micellar surfaces and (iii) surface potential determination. The theory is applied to interpret the ion activities in micellar solution as measured by ion-selective electrodes.

In recent years, physical chemists and biochemists have become more interested in the interactions and reactions that take place at charged surfaces in solution, for instance, on ionic micelles, microemulsions, vesicles and membranes.

In these systems, it is very important to understand the interaction of the micellar surface and its counterions, that is, the distribution of ions around the charged surface. This is necessary to understand phenomena such as micelle catalyzed chemical reactions[1], the stability of colloids[2] and the free energy of charged surface systems[3].

Among the experimental techniques used in investigating counterion-charged surface interactions, the simplest one may be the measurement of the thermodynamic activities of the counterion by the ion-selective electrode method[4]. In this technique, one measures the decrease of ion activity due to its strong adsorption on the charged surface. Usually, the electrode responds only to the activity of a selected ion following the Nerst law over several decades of ion concentration.

For micellar solutions, the problem can often be simplified to point-like charges interacting with a spherical macroion. The adsorption can be divided into surface (Stern layer) adsorption and electric double layer adsorption[5]. Therefore, a detailed knowledge of the ion distribution in the vicinity of charged surfaces is necessary for a complete understanding of the processes involved.

In this paper, our interest is on a mixed-electrolyte system, an ionic micelle and a simple electrolyte. There are at least two kinds of counterion exchanges on the micellar surface. The surface potential is determined by both kinds of ions.

In principle, the measured ion activity of a certain ion reflects its adsorption both on the Stern layer and on the electric double layer. For the double layer, the relation between the electric field $\vec{E}$ and the distribution of the charge ρ is described by the Poisson equation

$$\vec{\nabla}\cdot(D\epsilon_0\vec{E})=\rho \qquad (1)$$

where $\vec{E}$ is given by

$$\vec{E}=-\vec{\nabla}\phi \qquad (2)$$

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D is the dielectric constant, ϵ_0 is the vacumn permittivity, and ϕ is the electric potential.

With a Boltzman distribution of charges, we have the Poisson-Boltzmann equation

$$\nabla^2\phi(r) = -\frac{1}{D\epsilon_0}\Sigma_\alpha eZ_\alpha C_\alpha \exp\left[-\frac{eZ_\alpha\phi(r)}{k_BT}\right] \quad (3)$$

where k_B is the Boltzmann constant and C_α is the concentration of the αth ion.

Evidently, there are no exact analytical solutions for Poisson-Boltzmann equation for spherical system. The purpose of this paper is to devise a numerical procedure for the solution of the Poisson-Boltzmann equation. The approach will answer the following questions: (i) What is the effect of the total surface charge on the adsorption behavior? (ii) What is the effect of the competition between different counterions on the micellar surface? (iii) How is surface potential to be determined? With these aims, we emphasize the coulombic interaction and the chemical exchange on the surface. The short-range potentials[6], hydration forces[7] and the compressibility of the solvent[8], are neglected.

Previously, Bentz[9] had considered an approximate closed-form solution to PBE with cation binding, their method, however, is limitted to larger spheres (radii$<10\kappa^{-1}$). Frahm and Diekmann[10] also considered a numerical approach to a modified PBE which is suitable to micellar systems. Our approach is similar to that of Frahm and Diehmann, however we wish to study more explicitly the influence on the surface potential of mixed electrolytes in competition in the Stern layer. In this initial study, we have neglected the field dependence of the dielectric constant. This will be the subject of later work.

THEORY

We will consider our micelle as a sphere of radius a consisting of g surfactant molecules. The solution consists of simple ions with concentrations C_α. Thus the Debye screening constant κ is

$$\kappa^2 = \frac{e^2}{D\epsilon_0 k_BT}\Sigma_\alpha Z_\alpha^2 C_\alpha \quad (4)$$

where Z_α is the charge of the αth species.

In terms of the reduced variables

$$\mu = \kappa R - \kappa a \quad (5a)$$

$$\Phi(\mu) = e\phi/k_BT, \quad (5b)$$

the Poisson-Boltzmann equation can be written as

$$\frac{d^2\Phi}{d\mu^2} + \frac{2}{(\mu+\kappa a)}\frac{d\Phi}{d\mu}$$
$$= -\frac{e^2}{\kappa^2 D\epsilon_0 k_BT}\Sigma_\alpha Z_\alpha C_\alpha e^{-Z_\alpha\Phi}$$
$$= -\frac{1}{2I}\Sigma_\alpha Z_\alpha C_\alpha e^{-Z_\alpha\Phi} \quad (6)$$

with I as the ionic strength

$$I = \frac{1}{2}\Sigma_\alpha Z_\alpha^2 C_\alpha. \quad (7)$$

The boundary condition of the PBE will be determined by the surface charge:

$$\left.\left(\frac{d\phi}{dr}\right)\right|_{r=a} = -\frac{\sigma}{D\epsilon_0}, \quad \phi(r=a)=\phi_0$$

or

$$\left.\left(\frac{d\Phi}{d\mu}\right)\right|_{\mu=0} = -\frac{\sigma e}{\kappa k_BTD\epsilon_0}, \quad \Phi(\mu=0)=\Phi_0 \quad (8)$$

where σ is the surface charge density

$$\sigma = \frac{q}{4\pi a^2}$$

determined by the degree of counterion binding. The assymptotic value of $\phi(r)$ is of course zero,

$$\lim_{r\to\infty}\phi(r) = 0. \quad (9)$$

Let us consider a solution of surfactant $M_a P$ with concentration C_a and an added strong electrolyte $M_b Q$ with concentration C_b. $M_a P$ forms micelles of g aggregates at critical micelle concentration (CMC), C_M. Let the degree of dissociation of M_a

at the micellar surface be α, and β be the number of M_b ions adsorbed per micelle, including both the Stern layer and the double layer. Then one has

$$[M_a] = C_M + \alpha(C_a - C_M) \qquad (10a)$$

$$[P] = C_M \qquad (10b)$$

assuming that the monomer concetration of $M_a P$ is constant beyond the CMC. One also has

$$\begin{rcases} [M_b]_0 = C_b \\ [Q] = C_b \end{rcases} \qquad (11)$$

$$[\text{micelle}] = (C_a - C_M)/g \qquad (12)$$

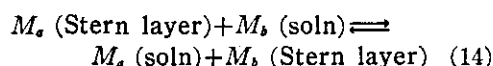where $[M_b]_0$ represents the "unperturbed" concention of M_b if no adsorption of ions on micelle occurs.

Now β is related to the experimentally measured concentration of M_b, $[M_b]$, through an electrode responding to M_b only by

$$\beta = \frac{[M_b]_0 - [M_b]}{[\text{micelle}]} = \frac{\{C_b - [M_b]\}g}{C_a - C_M}. \qquad (13)$$

From Eqs. (10), (11), (12), α and β can, in principle, be calculated after the ion concentrations (activities) $[M_a]$ and $[M_b]$ are measured using the approapriate selective electrodes.

The next step, then, is to relate α and β to the surface potential ϕ_0. The problem is to relate the percentage of β in the double layer and the Stern layer. Let the percentage of adsorbed M_b in the Stern layer be α_b, the percentage in double layer will then be $1 - \alpha_b$.

We consider a simple exchange mechanism

$$M_a \text{ (Stern layer)} + M_b \text{ (soln)} \rightleftharpoons$$
$$M_a \text{ (soln)} + M_b \text{ (Stern layer)} \quad (14)$$

That is, a one-to-one replacement is postulated. Then Eq. (10a) should be revised as

$$[M_a] = C_M + \alpha(C_a - C_M) + \alpha_b\{C_b - [M_b]\}. \quad (15)$$

The last term is the part driven out from the micelle surface. Also, the concentra-

tion of free M_b ion in solution C_b' should be

$$C_b' = C_b - \alpha_b\{C_b - [M_b]\}$$
$$= C_b(1 - \alpha_b) + \alpha_b M_b. \qquad (16)$$

The surface charge and surface charge density of micelle will be given by Z_m and σ, respectivel,

$$Z_m = -(\alpha g - \alpha_b \beta) \qquad (17a)$$

$$\sigma = Z_m/4\pi a^2. \qquad (17b)$$

With Eqs. (15), (16), (17), one can start to solve the Poisson-Boltzmann equation and calculate the surface potential. This potential should be related to α, β and α_b. In the next section, we will give a short discussion of the numerical procedure.

NUMERICAL PROCEDURE

In our solution of the PBE, the surface potential appears, at first, to be an adjustable parameter. One guesses Φ_0 initially and then solves the initial value problem to "shoot" the boundary condition $\Phi(\infty) = 0$. If the estimated Φ_0 is not right, then we again iterate from $r = a$ until $\Phi(r \to \infty) = 0$. For an initial guess, we use the zeroth order approximation

$$\Phi(0) = 2 \sinh^{-1}\left[-\frac{1}{2}\left(\frac{d\Phi}{d\mu}\right)_{\mu=0} \right] \qquad (18)$$

for a flat surface.

The numerical quadrature we used is the 4th Runge-Kutta-Nyström method preceding in equidistant steps. The solution is judged to be good if the potential decreases to 0.1% of its initial value without go-away behavior. The accuracy of the procedure has been checked in two examples. We tested the pocedure on the Debye-Hückel formula and on a linearized Poisson-Boltzmann equation. We also tested it against a known analytical solution of the PBE for a flat surface. The deviations of $\phi(r)$ are less than 0.01% and for $\phi'(r)$ less than 1%.

One important part of our procedure

is to test that electric neutrality is maintained. The total charge surrounding the micelle should be equal and opposite in sign to the charge on the micelle. That is,

$$\int_a^\infty 4\pi r^2 \left\{ \sum_\alpha Z_\alpha C_\alpha e^{-\frac{e Z_\alpha \phi(r)}{k_B T}} \right\} dr = -Z_m \quad (19)$$

or

$$\frac{4\pi}{\kappa^3} \int_0^\infty (\mu + \kappa a)^2 \sum_\alpha Z_\alpha C_\alpha \exp(-Z_\alpha \phi(\mu)) d\mu = -Z_m . \quad (20)$$

The electric neutrality condition is generally satisfied within 0.6% error.

All the calculations in this paper are done on an Apple II microcomputer. Programs are available upon request.

RESULTS AND DISCUSSIONS

First, we consider a simple model system of pure micelle formed from $M_a P$ with no salt added. In this model calculation, the aggregation number is 70, the degree of dissociation $\alpha = 0.10$, and $a = 15$Å. We calculated two cases of ionic strength, 0.01 M and 0.001 M. A typical potential versus distance curve is shown in Fig. 1. The calculated surface potentials are
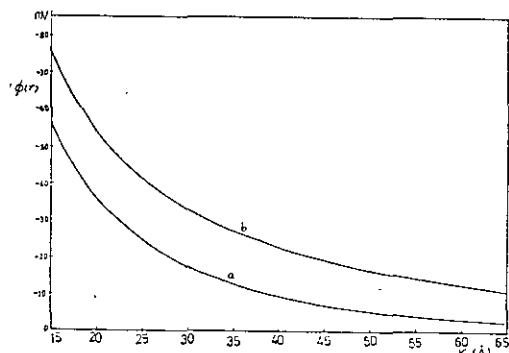
Fig. 1. Potential versus distance a for model micelle system of simple $M_a P$ with no $M_b Q$ added.
$g = 70$, $\alpha = 0.10$, $a = 15$Å
Ionic strength: (a) $I = 0.01 M$
(b) $I = 0.001 M$

$-56.95\, mV$ and $-75.58\, mV$, respectively. Many repeated calculations indicate that our method is applicable for surface potentials within the range $\pm 100\, mV$. As expected the absolute value of the surface potential decreases as the ionic strength increases. We will not go into more detail since this has been amply discussed before.[2]

We want now to consider the cation binding problem when a second salt is added. For this, we consider the simple model discussed in section 2. To make it more realistic, we use the experimental data reported by Su, Chen and Mou[1]. They measured copper ion concentration in the presence of sodium dodecylsulfate micelles. For the system considered, $[M_b]_0 = 5 \times 10^{-4}\, M$ and $C_M = 2.4 \times 10^{-3}\, M$. For the three cases considered, the measured copper concentrations are (a) $C_a = 0.015\, M$, $[M_b] = 2 \times 10^{-6}\, M$; (b) $C_a = 0.01\, M$, $[M_b] = 8.17 \times 10^{-6}\, M$; (c) $C_a = 0.001\, M$, $[M_b] = 6 \times 10^{-7}\, M$. These give (a) $\beta = 2.4$, (b) $\beta = 3.6$, (c) $\beta = 5.4$ respectively. To proceed, we made an assumption that the aggregation number $g = 70$. This number is arbitrary, but in the correct range as estimated from other similar systems[11]. The value of α is the most uncertain. From similar studies for pure SDS, we set the $\alpha = 20\%$. We chose a higher value of α than in Fig. 1 because of the presence of M_b replacing M_a. We note that this is only a model calculation, a complete predication needs a whole set of data that is not yet available in the literature. We then proceeded to calculate the surface potential as a function of α_b. The results are reported in Fig. 2. As one can see, the absolute value of surface potential decreases as Stern layer binding becomes stronger ($\alpha_b \to 1$). The decrease is more effective when micelle concentration is lower (curve c). At $\alpha_b = 0$, the $\phi(a)$ are slightly different due to the different ionic strengths considered in a, b, and c. This indicates that the stability of the micelle against coagulation is probably lower at lower surfactant concentrations when salts are added. For some cations,
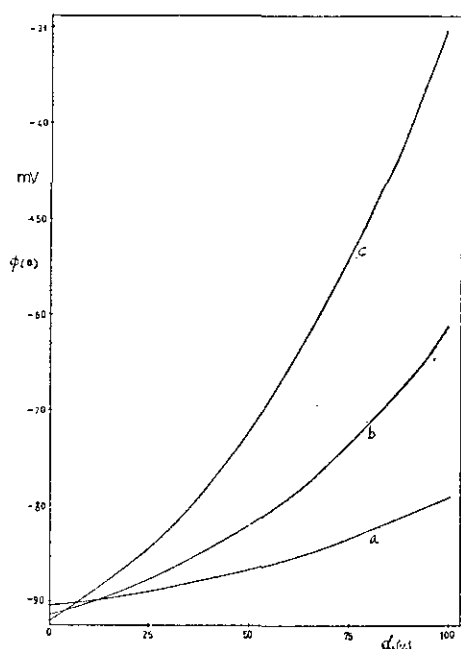
Fig. 2.   Surface potential of $\phi(a)$ versus α_b at several β values. $[M_bP]_0=5\times10^{-4}$ M $C_M=2.4\times10^{-3}\,M$, $g=70$, $\alpha=0.20$, $a=15$Å
Cases
(a) $C_a=0.015\,M$, $[M_b]=2\times10^{-6}\,M$
(b) $C_a=0.01\,M$, $[M_b]=8.17\times10^{-6}\,M$
(c) $C_a=0.001\,M$, $[M_b]=6\times10^{-3}\,M$

a colloid precipitation would even occur.

Up to now, we have not been able to determine the surface potential unambiguously since α_b is usually unknown. α_b cannot be determined solely from ion activities measured with electrodes because the measured effect includes both types of bindings, Stern layer and double layer. To give a complete description one needs to know the total binding of both ions on the micellar surface. This information is not easy to obtain. A promising technique to obtain this information is to measure the fluorescence quenching of a solubilized fluorophore by surface ions[12].

To conclude, we have attempted an explanation of ion-micelle interaction based on a chemical exchange model on the micelle surface and a Poisson-Boltzmann equation outside the micelle. We can relate the degree of dissociation and

counterion activities to the surface potential of the micelle by developing a numcerical procedure to solve the PBE. The final results indicate what kinds of experimental data are necessary for a complete understanding of the whole ion-micelle interaction behavior. We have used this method to give a partial explanation of the experimental results of Su et al.[4]. Further work to give more quantitative explanations will be necessary in future developments.

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