The Effect of Concentration and Valency of Added Salts on the Critical Micelle Concentration of Sodium and Calcium Dodecyl Sulfates

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Introduction

In the preceding report[1], the theoretical equation for the critical micelle concentration (CMC) was derived, and it has been shown that the electrical charges of micelle forming ions play an important role in the process of micellization. In order to criticize this equation the following experiments are needed: to investigate (1) the effect of added salts on the CMC[2–5], (2) the effect of added alcohols on the CMC[6–8], (3) the CMC of soap mixtures[9–11], (4) the CMC of the surfactants which possess two or three dissociable groups at one end of their hydrocarbon chains[12], etc. As for the investigation (1), a number of papers have been published on the effect of uni-valent counterions on the CMC, and the effect of bi- or tri-valent counterions has been measured by H. Lange[3], but, so far as we know, no quantitative explanation has been published.

The present investigation was undertaken to derive the theoretical formula for the CMC values as a function of the concentration and valency of added salts and to compare it with the experimental results given by Lange[3,13].

Electrical Potential at the Charged Surface of the Micelle

If it is assumed that the surface of a micelle is plane (or at least the double layer thickness is small in comparison with the radius of curvature of micelle surface) and the charge layer on the micelle surface is homogeneous, the counterions distribute homogeneously and parallel to the micelle surface, and the electrical potential is only a function of the normal coordinate. Now the Poisson-Boltzmann equation is applied for the micelle of a plane uniformly charged surface in contact with a solution of strong electrolytes, and the following equation is obtained:

$$\Delta\phi=\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}=-\frac{4\pi}{D}\sum z_i n_i \mathrm{e}\exp(-z_i\mathrm{e}\phi/kT), \quad (1)$$

where ϕ is the electrical potential, x the coordinate normal to the surface, D the dielectric constant of the medium, e the elementary charge, z_i the valencies of the positive and negative ions, n_i the numbers of respective ions per cc. in the bulk of the solution ($n_i=C_iN/1000$, C_i mole number of ions per liter, N Avogadro number), k the Boltzmann constant and T the absolute temperature.

Considering the boundary conditions, $\phi=0$ and $\frac{\mathrm{d}\phi}{\mathrm{d}x}=0$ for $x=\infty$, we obtain;

$$\frac{1}{2}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2=\frac{4\pi kT}{D}\sum n_i\{\exp(-z_i\mathrm{e}\phi/kT)-1\}, \quad (2.1)$$

and therefore,

$$\frac{1}{2}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2_{x=0}=\frac{4\pi kT}{D}\sum n_i\{\exp(-z_i\mathrm{e}\phi_0/kT)-1\}. \quad (2.2)$$

The surface charge density, σ, may be obtained directly from the potential function. To this end we make use of the general equation[14],

$$\sigma=-\int_0^\infty\rho\mathrm{d}x=\frac{D}{4\pi}\int_0^\infty\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\mathrm{d}x=-\frac{D}{4\pi}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)_{x=0} \quad (3)$$

The latter quantity may be read from equation (2.2)

$$\left(-\frac{4\pi\sigma}{D}\right)^2=\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2_{x=0}=\frac{8\pi kT}{D}\sum n_i \{\exp(-z_i\mathrm{e}\phi_0/kT)-1\}. \quad (4)$$

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[1] K. Shinoda, *Bull. Chem. Soc. Japan*, **26**, 101 (1953).

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[13] H. Lange, a private communication.

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Equation (4) gives the electrical potential, ϕ_0, at the charged surface of the micelle.

If the micelle forming ion is anion, ϕ will be negative and $-z_i e\phi_0$ will be positive for cations, and negative for anions. As pointed out later the condition $\exp(-z_i e\phi_0/kT)\gg 1$ is satisfied[15], and the contribution of the anions and 1 in the right hand side of equation (4) can be neglected. It is apparent from (4) that the valencies or kinds of ions of the same sign as that of the long chain ions have no effect and only the valencies of ions of the opposite sign are important.

Then equation (4) gives electrical potentials in each of the following cases:

(1) for long chain salts of uni-univalent type,

1) with no added salt,

$$\phi_0=\frac{kT}{\mathrm{e}}\log\frac{2000\pi\sigma^2}{C_1DNkT}\,, \tag{5.1}$$

where

$$C_1=\mathrm{CMC}=1000\,\mathrm{n}_1/\mathrm{N}\,,$$

2) with added uni-valent cation salt,

$$\phi_0=\frac{kT}{\mathrm{e}}\log\frac{2000\pi\sigma^2}{C_1DNkT}\,, \tag{5.2}$$

where

$$C_1=\mathrm{CMC}+C_1'\,,$$

3) with added bi-valent cation salt,

$$\frac{2000\pi\sigma^2}{DNkT}=C_1\exp(\mathrm{e}\phi_0/kT)+C_2\exp(2\mathrm{e}\phi_0/kT)\,, \tag{5.3}$$

where

$$C_1=\mathrm{CMC}\,,$$

4) with added tri-valent cation salt,

$$\frac{2000\pi\sigma^2}{DNkT}=C_1\exp(\mathrm{e}\phi_0/kT)+C_3\exp(3\mathrm{e}\phi_0/kT)\,, \tag{5.4}$$

where

$$C_1=\mathrm{CMC}\,,$$

(2) for long chain salts of uni-bivalent type,

1) with no added salt,

$$\phi_0=\frac{kT}{2\mathrm{e}}\log\frac{2000\pi\sigma^2}{C_2DNkT}\,, \tag{5.5}$$

where

$$C_2=\mathrm{CMC}/2\,.$$

2) with added uni-valent cation salt,

$$\frac{2000\pi\sigma^2}{DNkT}=C_1\exp(\mathrm{e}\phi_0/kT)+C_2\exp(2\mathrm{e}\phi_0/kT)\,, \tag{5.6}$$

where

$$C_2=\mathrm{CMC}/2\,,$$

3) with added bi-valent cation salt,

$$\phi_0=\frac{kT}{2\mathrm{e}}\log\frac{2000\pi\sigma^2}{C_2DNkT}\,, \tag{5.7}$$

where

$$C_2=\mathrm{CMC}/2+C_2'\,,$$

Comparison with Experimental Observations

For a given chain length the cohesive energy contribution will be constant; however, it is clear that in the presence of added electrolytes the ions of charge opposite to that of the long chain ions have a marked influence on micelle formation by reducing the electrical repulsive forces between the head groups of the long chain ions; or, in other words, by reducing the electrical potential on the micelle surface.

Formulae (5.1)–(5.7) can be tested by the experimental data for the CMC as a function of the concentration and valency of added salts[3,13]. The CMC of long chain salts is given as[1]

$$\log\mathrm{CMC}=\log\frac{1000}{N\nu}-\frac{m\omega}{kT}+\frac{E_{el.}}{kT}-1\,, \tag{6}$$

where ν is the free volume per molecule in the micellar state, m the number of carbon atoms in hydrocarbon chain, ω the surface energy change per methylene radical, passing from the bulk of the solution into the micelle, $E_{el.}$ the electrical energy change per micelle forming ion, and would be given as $\mathrm{K}e\phi_0$.

A reasonable alternative is to assume that the dissociation degree of the micelle forming ion is not 1 but K.

Considering this alternative and combining equations (5.2), (5.7) and (6), we obtain,

$$\log\mathrm{CMC}=\log\frac{1000}{N\nu}-\frac{m\omega}{kT}+\frac{K}{Z_i}\log\frac{2000\pi K^2\sigma^2}{C_iDNkT}-1\,, \tag{7}$$

where Z_i is the valencies of respective counterions and C_i the concentrations of counterions in moles per liter.

It is expected from equation (7) that the log CMC is a linear function of log C_i and the slope of this line is K for sodium dodecyl sulfate and $K/2$ for calcium dodecyl sulfate. Comparing the experimental data measured by Lange[13] with the theoretical equation, it has been found that the slope of the plot

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[15] A. B. D. Cassie and R. C. Palmer, *Trans. Faraday Soc.*, 37, 156 (1941).

of log CMC versus log C_t is a linear function and the slope is $0.503(=K)$ for sodium dodecyl sulfate and $0.286(=K/2)$ for Calcium dodecyl sulfate, showing good agreement with the theory*.

Introducing the CMC values of sodium and calcium dodecyl sulfates into equation (7) and substituting $K=0.54$, we obtain at $T=343°\mathrm{K}$,

$$\frac{2000\pi K^2\sigma^2}{DNkT}=0.654\,.$$

This value is somewhat smaller than that expected from the values of σ**, K, D, N, k, and T, but this will be attributed to the fact that each ion contribute less charge than e to the micelle because of the accompanying counterion with the introduction of another charge.

Introducing these values into equations (5.1)−(5.7) and (6), the comparison between the theory and the experimental CMC values as a function of the concentration and valency of added salts was attained. The results are shown in Table I.

TABLE I

COMPARISON BETWEEN THE OBSERVED (BY LANGE) AND CALCULATED CMC VALUES AS A FUNCTION OF THE CONCENTRATION AND VALENCY OF ADDED SALTS AT 70°C.

Concn. of added salt in equivalent/liter	obs. CMC	calc. CMC (moles/l.)
KCl or NaCl	Sodium Dodecyl Sulfate	
0	0.0066	0.0067
0.01	0.0045	0.0045
0.02	0.00315	0.0030
0.05	0.00235	0.0023
0.1	0.0016	0.0016
0.2	0.0012	0.00115
0.5	0.00075	0.00065
$MgCl_2$ or $CaCl_2$		
0.0001	0.0060	0.0057
0.0003	0.0051	0.0048
0.0005	0.0043	0.0043
0.001	0.0039	0.0038
0.002	0.0030	0.0032
0.005	0.0022	0.0026
0.012	0.0018	0.0020
0.025	0.0015	0.0017
0.05	0.0012	0.0014
0.1	0.0010	0.0011
0.3	0.00077	0.0009
$AlCl_3$		
0.0007	0.0038	0.0024
0.001	0.0022	0.0022
0.002	0.0016	0.0014
NaCl	Calcium Dodecyl Sulfate	
0	0.0029	0.0029
0.001	0.00285	0.00285
0.004	0.0028	0.0028
0.01	0.0027	0.0027
0.02	0.0026	0.0026
0.03	0.0026	0.0024
0.05	0.0024	0.0021
0.1	0.0017	0.0015
0.2	0.00125	0.0011
0.5	0.00073	0.0006
$CaCl_2$		
0.001	0.0026	0.0028
0.005	0.00215	0.0023
0.025	0.00145	0.0016
0.1	0.00102	0.0011
0.3	0.00077	0.0008

It is apparent from Table I that the CMC values calculated using relations (5.1)−(5.7) show good agreement with the experimental ones. In the case of the large ionic radius of counterions or of the more concentrated system of counterions, the agreement between the theory and experiments is not so satisfactory.

The CMC of the Mixture of Sodium and Calcium Dodecyl Sulfates

The CMC of the mixture of sodium and calcium dodecyl sulfates can also be tested with the equation (5.3) or (5.6). In this case, however, the sum of the equivalent concentration of sodium and calcium ions is equal to the CMC, i.e., $C_1+2C_2=\mathrm{CMC}$. The comparison between the experimental and the calculated CMC values are given in Table II.

TABLE II

COMPARISON BETWEEN THE OBSERVED (BY LANGE) AND CALCULATED CMC VALUES OF MIXTURES OF SODIUM AND CALCIUM DODECYL SULFATES AT 70°C.

mole fraction of the calcium dodecyl sulfate	obs. CMC (moles/l.)	calc. CMC (moles/l.)
0	0.0066	0.0067
0.02	0.0057	0.0056
0.05	0.0053	0.0050
0.1	0.0049	0.0046
0.25	0.0040	0.0037
0.5	0.0034	0.0033
0.75	0.0031	0.0031
1	0.0029	0.0029

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* The value of K in the case of fatty acid soap is 0.56.

** δ is equal to the elementary charge divided by the cross sectional area of micelle forming ions.

Conclusion

Formulas for the electrical potentials of the micelle surface in various conditions are derived. Using these formulas, the comparison between the theory and the experiments was undertaken. From the good agreement between the theory and experiments, the CMC of sodium and calcium dodecyl sulfates as a function of the concentration and valency of added salts was explained quantitatively. The present investigation is applicable not only to the study of the micelle, but to the elucidation of the outstanding colloid chemical fact of the predominating influence of oppositely charged ions upon the electrical double layer.

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