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The Adsorption of Dodecyldimethylammonium Chloride on Aqueous Surfaces of Concentrated NaCl Solutions

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Surface tension of aqueous NaCl solutions of dodecyldimethylammonium chloride has been measured at high NaCl concentrations. Surface excesses of surfactant cation, Na^+ and Cl^- are derived by means of the Gibbs adsorption isotherm from the derivatives of surface tension with respect to surfactant concentration and NaCl concentration. The rational mean activity coefficients of surfactant and NaCl are both approximated by a common expression satisfying the Brönsted principle for mixed electrolytes but including the ionic strength as a variable. Saturated value of surface excess of surfactant cation remains constant at low NaCl concentrations up to 0.10 M, while it increases as the NaCl concentration exceeds 0.50 M. The adsorption of Na^+ is negative at low NaCl concentrations, but it increases rapidly and is positive above 0.50 M NaCl. Surfactant and NaCl are subject to the strong salting-out effect when the NaCl concentration is higher than 0.50 M. The Corrin-Harkins plot of the critical micelle concentration at high NaCl concentrations deviates from the straight line.

Recently[1,2] we have developed a general method for applying the Gibbs adsorption isotherm to aqueous solutions of electrolytes and elucidated implication of the Gibbs convention for the dividing surface and distinction of chemical species from components in the multicomponent system. The method enables us to derive the surface excesses of surfactant ion, coion and counterion from surface tension data, when it is applied to aqueous solutions containing an ionic surfactant and a simple salt, having a common counterion, but without forming any micelle yet.

In a previous paper[3] we have published some results of surface tension measurements on aqueous NaCl solutions of dodecyldimethylammonium chloride and derived the surface excesses of surfactant cation (D^+), Na^+, and Cl^- by means of the Gibbs adsorption isotherm. The previous work was restricted to the region of NaCl concentrations less than 0.50 M, and the mean activity coefficients of surfactant and NaCl were both approximated by the limiting expression of the Debye-Hückel equation. Then we obtained a strongly positive adsorption of surfactant cation at the saturation. However, we also found a small positive adsorption for Na^+ or coion, which would not necessarily be reasonable in the presence of dilute NaCl, because coions should be repelled from the surface dominantly occupied by surfactant cations.

In the present work we will extend the surface tension measurements on the same solutions up to the region of higher NaCl concentrations and examine how the surface excesses of ions are influenced by the salting-out effect. In this paper we will present the experimental results obtained in the present work and also include the previous data together. We will develop a treatment based on more exact expressions for the mean activity coefficients of electrolytes and apply it to obtain surface excesses of surfactant cation, Na^+ and Cl^-.

Experimental

Dodecyldimethylammonium chloride was prepared from *N*,*N*-dimethyldodecylamine by passing dry HCl gas, as previously described.[3] Commercial dimethyldodecylamine was purchased from Tokyo Kasei Kogyo Co., Inc., and purified by fractional distillation.

Surface tension of aqueous solutions was determined at 25±0.01 °C by means of the drop weight method, in the same way as previously performed.[3]

Results

Figure 1 shows the relation of surface tension, γ, with logarithm of molar concentration of surfactant, $\log C$, at different NaCl concentrations, C_s. Surface tension decreases with increasing surfactant concentration and also with increasing NaCl concentration. At concentrations higher than the critical micelle concentration, C_0, surface tension always remains constant. The lowering of surface tension is formally represented by

$$-\mathrm{d}\gamma = RT\{\Gamma_2'\mathrm{d}\ln C + \Gamma_3'\mathrm{d}\ln C_s\} \tag{1}$$

where R is the gas constant and T is the temperature. The apparent surface excesses are defined by

$$\Gamma_2' = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ln C}\right)_{C_s} \tag{2}$$

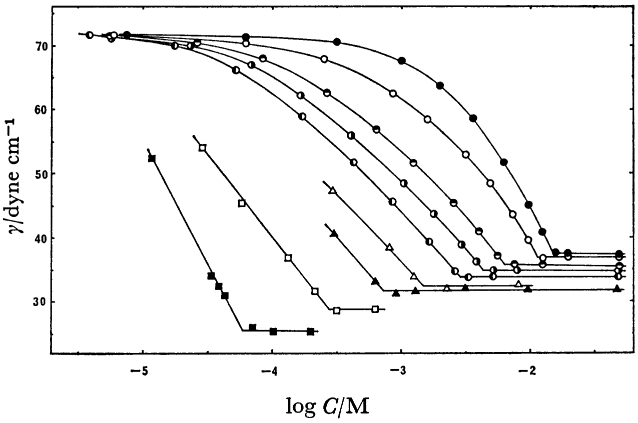

Fig. 1. Variation of surface tension with logarithm of surfactant concentration at different NaCl concentrations.

C_s (M): ●; 0, ○; 0.01, ◓; 0.05, ◑; 0.10, ◐; 0.20, △; 0.50, ▲; 0.94, □; 2.00, ■; 4.00.

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† 1 M=1 mol dm^{-3}, 1 dyne cm^{-1}=1 mN m^{-1}.

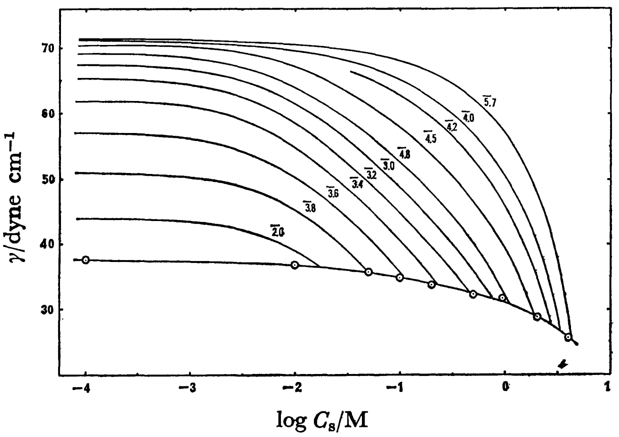

Fig. 2. Variation of surface tension with logarithm of NaCl concentration at different surfactant concentrations. Values of log C are given for the curves obtained by interpolation. ○, Constant surface tension at a given NaCl concentration, obtained at surfactant concentrations higher than the critical micelle concentration.

Table 1. Critical micelle concentration, apparent surface excess and surface tension associated with aqueous NaCl solutions of dodecyldimethylammonium chloride

C_s (M)	C_0 (10^{-3} M)	Γ_2' at C_0 (10^{-10} mol cm^{-2})	γ at C_0 (dyne cm^{-1})
0	14.7	7.66	37.6
10^{-4}	14.6	6.90	37.6
0.01	11.4	6.34	36.9
0.05	6.27	4.64	35.8
0.10	4.29	4.39	34.8
0.20	2.84	4.13	33.9
0.50	1.48	4.02	32.4
0.94	0.725	4.03	31.8
2.00	0.276	4.52	28.8
4.00	0.059	6.74	25.6

$$\Gamma_3' = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_s}\right)_C . \tag{3}$$

As can be seen in Fig. 1, it is clear that $\Gamma_2'=0$ for $C>C_0$.

In Fig. 2 surface tension is plotted against log C_s at different surfactant concentrations. The lowest curve gives dependence of the constant surface tension on NaCl concentration, the constancy being observed at concentrations higher than the critical micelle concentration.

Table 1 summarizes related numerical data derived from Figs. 1 and 2, together with those previously obtained. With increasing NaCl concentration, the value of Γ_2' decreases in the range of NaCl concentrations up to 0.50 M, and then it increases rapidly at higher NaCl concentrations. In addition, the constant value of surface tension observed above C_0 is lowered with increasing NaCl concentration. The critical micelle concentration decreases with increasing NaCl concentration.

Discussion

The Gibbs Adsorption Isotherm. We will be mainly concerned with the adsorption of ions in the region of concentrations lower than the critical micelle concentration. It was shown[1] that the Gibbs adsorption isotherm for aqueous solutions containing DCl (dodecyldimethylammonium chloride) and NaCl can be expressed by either

$$-\mathrm{d}\gamma = \Gamma_{D^+}\mathrm{d}\mu_{D^+} + \Gamma_{Na^+}\mathrm{d}\mu_{Na^+} + \Gamma_{Cl^-}\mathrm{d}\mu_{Cl^-} \tag{4}$$

or

$$-\mathrm{d}\gamma = \Gamma_{D^+}\mathrm{d}\mu_{DCl} + \Gamma_{Na^+}\mathrm{d}\mu_{NaCl} \tag{5}$$

provided that no micelle is formed yet. Here Γ_i is the surface excess of species or component, i, and μ_i is its chemical potential. Equation 4 is subject to an electroneutrality condition

$$\Gamma_{D^+} + \Gamma_{Na^+} = \Gamma_{Cl^-} \tag{6}$$

while Eq. 5 is free from such a subsidiary condition.

The chemical potentials of DCl and NaCl are given by

$$\mu_{DCl} = \mu^\circ_{DCl} + RT\ln y_\pm^2 C_{D^+}C_{Cl^-} \tag{7}$$

$$\mu_{NaCl} = \mu^\circ_{NaCl} + RT\ln y_{s\pm}^2 C_{Na^+}C_{Cl^-} \tag{8}$$

where the superfix ° means the standard states assigned to 1 M DCl and 1 M NaCl, respectively, in the ideal state, and $y_\pm$ and $y_{s\pm}$ are the mean activity coefficients of DCl and NaCl. The molar concentrations of ions are expressed by

$$C_{D^+} = C,\ C_{Na^+} = C_s,\ \text{and}\ C_{Cl^-} = C + C_s. \tag{9}$$

The molar mean activity coefficients of DCl and NaCl, $y_\pm$ and $y_{s\pm}$, can be related to their rational mean activity coefficients, $f_\pm$ and $f_{s\pm}$, by[5a)]

$$\frac{y_\pm}{f_\pm} = \frac{y_{s\pm}}{f_{s\pm}} = \frac{\rho_w}{\rho - \frac{M-2M_w}{1000}C - \frac{M_s-2M_w}{1000}C_s} \tag{10}$$

where M_w, M, and M_s are the molecular weights of water, DCl, and NaCl, respectively, and ρ_w and ρ are the densities of water and the solution respectively.

It will be demonstrated below that the rational mean activity coefficients of DCl and NaCl can be approximately represented by an identical expression as a function of ionic strength, $C+C_s$. Then we have identities and introduce abbreviations as follows:

$$\eta = \left(\frac{\partial \ln y_\pm^2}{\partial C}\right)_{C_s} = \left(\frac{\partial \ln y_{s\pm}^2}{\partial C}\right)_{C_s} \tag{11}$$

$$\eta_s = \left(\frac{\partial \ln y_\pm^2}{\partial C_s}\right)_C = \left(\frac{\partial \ln y_{s\pm}^2}{\partial C_s}\right)_C \tag{12}$$

Introducing these approximations we arrive at the expression of Gibbs adsorption isotherm in the form of Eq. 1, in which the apparent surface excesses are given by

$$\Gamma_2' = \left(1+\frac{C}{C+C_s}+\eta C\right)\Gamma_{D^+} + \left(\frac{C}{C+C_s}+\eta C\right)\Gamma_{Na^+} \tag{13}$$

$$\Gamma_3' = \left(\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma_{D^+} + \left(1+\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma_{Na^+}. \tag{14}$$

By solving Eqs. 13 and 14 we obtain the surface excesses of D^+ and Na^+, and also, together with Eq. 6 we have the surface excess of Cl^-.

$$\Gamma_{D^+} = \frac{1}{2+\eta C+\eta_s C_s}\left\{\left(1+\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma_2' - \left(\frac{C}{C+C_s}+\eta C\right)\Gamma_3'\right\} \tag{15}$$

$$\Gamma_{Na^+} = \frac{1}{2+\eta C+\eta_s C_s}\left\{-\left(\frac{C_s}{C+C_s}+\eta_s C_s\right)\Gamma_2' + \left(1+\frac{C}{C+C_s}+\eta C\right)\Gamma_3'\right\}, \tag{16}$$

and

$$\Gamma_{Cl^-} = \frac{1}{2+\eta C+\eta_s C_s}(\Gamma_2'+\Gamma_3'). \tag{17}$$

It can be readily seen from Eq. 15 that

$$\Gamma_{D^+} = \Gamma_2' \tag{18}$$

provided that C_s is very high or much higher than C. That is, the value of Γ_{D^+} is independent of the choice of activity coefficients of DCl and NaCl, if the NaCl concentration is sufficiently high.

The Mean Activity Coefficients and Their Derivatives. The molar mean activity coefficients of DCl and NaCl are related to their rational mean activity coefficients by means of Eq. 10. We will derive the approximate forms of rational mean activity coefficients of DCl and NaCl in their mixed solutions as follows.

According to Brönsted's principle of specific interaction of ions,[4,5d] the rational mean activity coefficients can be written

$$\log f_{\pm} = -\frac{P\sqrt{C+C_s}}{1+Qa\sqrt{C+C_s}} + BC + B_{Cl^-}C_s \tag{19}$$

$$\log f_{s\pm} = -\frac{P\sqrt{C+C_s}}{1+Qa\sqrt{C+C_s}} + B_sC_s + B_{Cl^-}C \tag{20}$$

where the constants, P and Q, of the Debye-Hückel electrostatic term are determined by temperature and dielectric constant, and the ionic radius, a, serves as an adjustable parameter.[5b] The salting-out constants, B and B_s, are characteristic of DCl and NaCl, respectively, and the specific ion interaction constant, B_{Cl^-}, represents the averaged specific interaction of Cl^- with D^+ and Na^+. Our experimental range covers 0—10^{-2} M for C and 0—4.00 M for C_s.

In a recent work Cutler, Meares, and Hall[6] measured the activity coefficients of sodium dodecyl sulfate in NaCl solutions and found that the mean activity coefficient obeys the Debye-Hückel equation of Guggenheim type, that is, P=0.5115 and Qa=1.000 in Eq. 19, when the NaCl concentration is in the range of 0—0.2 M and the surfactant concentration is lower than the critical micelle concentration. This means that an ionic surfactant behaves like a simple salt such as NaCl unless micelles are formed. Then we may anticipate that the activity coefficient of dilute surfactant obeys Eq. 19, in which the salting-out term is negligibly small.

Robinson and Stokes[5c] published following values of parameters in Eq. 20 which fit well the observed values of $\log f_{s\pm}$ for NaCl solutions up to 2.00 M at 25 °C.

$$P = 0.5115, \quad Qa = 1.316, \quad B_s = 0.055 \tag{21}$$

In Eq. 19 we will also be able to use the identical value of Qa, because of thermodynamic requirement and of small contribution of the ionic-size term. In addition, since the value of C is small, it will not introduce serious errors even if we put $B=B_s$.

We have scarce information about the value of B_{Cl^-}. The result of Cutler *et al.*[6] suggests that the last term of Eq. 19 is negligibly small when C_s is lower than 0.2 M. We may expect that the value of B_{Cl^-} is not very large. Then the last term of Eq. 20 would have a small magnitude as compared to the other two terms: if C_s is as low as 0.01 M, the term will be negligible in comparison with the former, and if C_s is higher, the term will be much smaller than the salting-out term. Considering such a small contribution of this term and also the principle of ionic strength, we may include it in a single term without serious errors by putting $B_{Cl^-}=B$.

In this approximation we have a common expression for the molar mean activity coefficients of DCl and NaCl:

$$\log f_{\pm} = \log f_{s\pm} = -\frac{P\sqrt{C+C_s}}{1+Qa\sqrt{C+C_s}} + B_s(C+C_s) \tag{22}$$

together with Eqs. 21. Then we obtain

$$\eta = \eta_0 + \frac{2\left[\left(\frac{\partial\rho}{\partial C}\right)_{C_s} - \frac{M-2M_w}{1000}\right]}{\rho - \frac{M-2M_w}{1000}C - \frac{M_s-2M_w}{1000}C_s} \tag{23}$$

$$\eta_s = \eta_0 + \frac{2\left[\left(\frac{\partial\rho}{\partial C_s}\right)_{C} - \frac{M_s-2M_w}{1000}\right]}{\rho - \frac{M-2M_w}{1000}C - \frac{M_s-2M_w}{1000}C_s} \tag{24}$$

where

$$\eta_0 = -\frac{2.303P}{(1+Qa\sqrt{C+C_s})^2\sqrt{C+C_s}} + 4.606B_s. \tag{25}$$

For actual calculations of ρ and $(\partial\rho/\partial C_s)_C$ we may use the literature values of density of NaCl solutions.[7] The density of aqueous electrolyte solutions can be represented by a quadratic form of molal concentration, m_s, up to 4.00 M, which is equivalent to write

$$\frac{C_s}{m_s} = \rho_w - \alpha m_s \tag{26}$$

where α is a constant. For NaCl solutions at 25 °C, ρ_w=0.9970 g cm^{-3} and α=0.0183. It is found alternatively that

$$\rho = \rho_w + 0.00387\sqrt{C_s} + 0.0362C_s. \tag{27}$$

For the calculation of $(\partial\rho/\partial C)_{C_s}$, which is given by

$$\left(\frac{\partial\rho}{\partial C}\right)_{C_s} = \frac{M(1-\bar{v}\rho_0)}{1000} \tag{28}$$

at low C values, we have used the value of partial specific volume of DCl, $\bar{v}$, in water, 1.06,[8] where ρ_0 is the density of water or NaCl solutions.

Surface Excesses of Ions. Figure 3 shows the surface excesses of D^+, Na^+, and Cl^- as functions of surfactant concentration. It is seen in Fig. 3 (a)

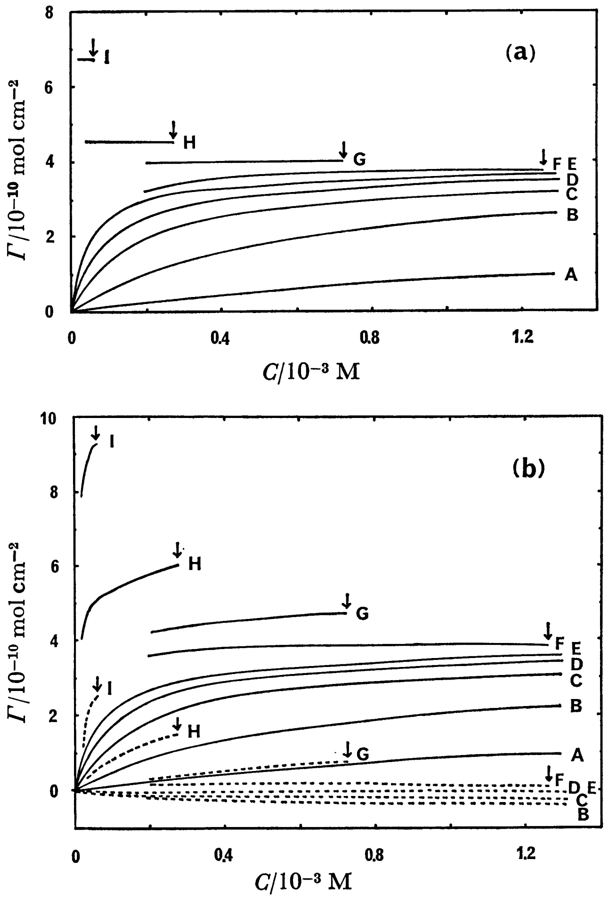

Fig. 3. Adsorption isotherms of ions on aqueous surfaces of different NaCl concentrations. (a) Γ_{D^+} *vs.* C; (b) Γ_{Na^+} (----) and Γ_{Cl^-} (——) *vs.* *C*. Arrows indicate the location of critical micelle concentrations. C_s (M): A; 0, B; 0.01, C; 0.05, D; 0.10, E; 0.20, F; 0.50, G; 0.94, H; 2.00, I; 4.00.

that the value of Γ_{D^+} increases more rapidly and reaches the saturated value at a lower concentration, as the NaCl concentration is higher. This is caused by the electrostatic shielding effect of added NaCl on the charged layer of adsorbed surfactant. When the NaCl concentration exceeds 0.20 M, the value of Γ_{D^+} has already reached the saturated value and is constant at the concentration range in concern. Table 2 gives the saturated values of Γ_{D^+} at different NaCl concentrations, which are obtained as the values of Γ_{D^+} at the critical micelle concentration. Figure 4 shows the saturated value of Γ_{D^+} as a function of NaCl concentration. With increasing NaCl concentration, the saturated adsorption of surfactant cation is at first almost constant and then slightly decreases. When the NaCl concentration exceeds 0.50 M, the adsorption increases at higher NaCl concentrations. This increase in adsorption must be ascribed to the salting-out effect of NaCl. The observed behavior of saturated adsorption of dodecyldimethylammonium ion is different from that of dodecyl sulfate ion, since it was reported for aqueous solutions of sodium dodecyl sulfate[9–11] that the adsorption of dodecyl sulfate ion is strongly promoted by the addition of NaCl up to 0.1 M. The difference in adsorption behavior between these surfactants must be elucidated in future work.

Table 2. Surface excesses of surfactant cation, Na^+ and Cl^- at the critical micelle concentration

C_s (M)	Γ_{D^+} at C_0 (10^{-10} mol cm^{-2})	Γ_{Na^+} at C_0 (10^{-10} mol cm^{-2})	Γ_{Cl^-} at C_0 (10^{-10} mol cm^{-2})
0	4.13[a]	—	4.13[a]
0.01	4.27	−0.36	3.91
0.05	4.26	−0.23	4.03
0.10	4.25	−0.16	4.09
0.20	4.08	−0.01	4.07
0.50	4.01	0.09	4.10
0.94	4.03	0.67	4.70
2.00	4.52	1.49	6.01
4.00	6.74	2.51	9.25

a) These values were calculated by using the limiting expression of Debye-Hückel equation for the mean activity coefficient of surfactant.

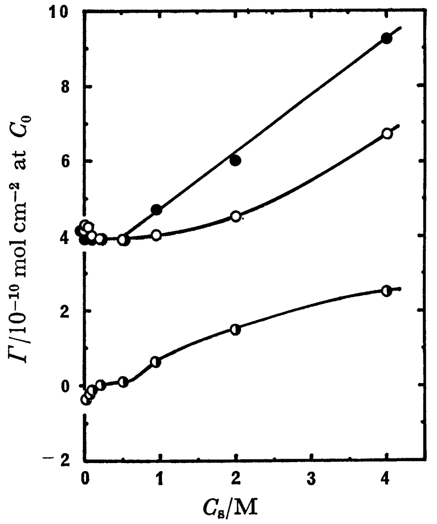

Fig. 4. Surface excesses of ions at the critical micelle concentration plotted against NaCl concentration. ○; Γ_{D^+}, ◑; Γ_{Na^+}, ●; Γ_{Cl^-}.

It is seen in Fig. 3 (b) that the adsorption of Na^+ and Cl^- is still increasing without reaching their saturation even at the critical micelle concentration, if the NaCl concentration is higher than 0.50 M. Values of Γ_{Na^+} and Γ_{Cl^-} at the critical micelle concentration are also listed in Table 2, and they are plotted as functions of NaCl concentration in Fig. 4. Previously,[3] the value of Γ_{Na^+} was calculated at low NaCl concentrations, by assuming the limiting expression of Debye-Hückel equation for activity coefficients, and it was found to be positive. In the present treatment assuming a more exact equation for the activity coefficients, the value of Γ_{Na^+} at the critical micelle concentration is negative at low NaCl concentrations, and then it turns to be positive at NaCl concentrations higher than 0.10 M. The negative adsorption of coion, Na^+, at low NaCl concentrations seems to be more reasonable. The initial negative adsorption of Na^+ decreases with increasing NaCl concentration, which numerically comes from the contribution of the effect

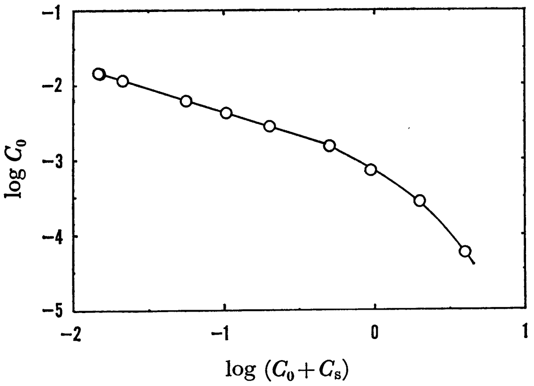

Fig. 5. The Corrin-Harkins plot. Relation of logarithm of critical micelle concentration with logarithm of chloride ion concentration.

of ionic size represented by the term, Qa, in Eq. 22. In the Gouy theory of diffuse double layer an increase in negative adsorption of coion should occur when the NaCl concentration increases. The marked increase in positive adsorption of Na^+ observed at NaCl concentrations higher than 0.50 M is caused by the salting-out term, B_s, of Eq. 22.

In the above treatment we have made some simplification to express the two rational activity coefficients in the common form, Eq. 22. In Eq. 19 we could also set $B=B_{Cl^-}=0$, as was found by Cutler *et al.*,[6] but this would not be applicable for the region of higher NaCl concentrations. If we assume $B=B_{Cl^-}=0$, however, Eq. 16 leads to much larger values of Γ_{Na^+} at higher NaCl concentrations. We may then conclude that the approximate form of activity coefficients, Eq. 22, is effective in the Gibbs adsorption isotherm for mixed solutions of an ionic surfactant and a simple salt, as far as the surfactant does not form micelles.

The Corrin-Harkins Relation. Previously[3] we have demonstrated that the Corrin-Harkins plot of the critical micelle concentration is linear up to 0.20 M NaCl. As can be seen in Fig. 5, however, such a linear relation no longer holds between logarithm of critical micelle concentration and logarithm of ionic strength, when the plot is extended to higher NaCl concentrations. It seems likely that the linear Corrin-Harkins relation is closely connected with the electrostatic shielding effect of simple salt but is disrupted by the other effects such as counterion binding and salting-out.

In a current paper[12] we are reporting the same results on the critical micelle concentration determined by light scattering. According to the results of light-scattering measurement, the Corrin-Harkins plot is linear as far as the spherical micelles are formed, but it deviates from the straight line when the rod-like micelles become more stable. It is inferred that the sphere-rod transition of ionic micelles would be caused by the difference in electrostatic effect of added salt, or, more directly, in the degree of counterion binding.

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