BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 319—322 (1969)

The pNa Study of Sodium Alkyl Sulfates in Aqueous Solutions

Iwao SATAKE, Takashi TAHARA and Ryohei MATUURA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

(Received May 30, 1968)

The counter-ion activity coefficient of sodium alkyl sulfate with chain length from C_8 to C_{14} was determined in aqueous solutions and in the presence of added magnesium ion. The degree of association of sodium ion to the micelle (β) can be deduced from the concentration dependence of the counter-ion activity. The value of β so determined in the presence of magnesium ion was confirmed to decrease rapidly as the relative concentration of magnesium ion increases. The observed change of counter-ion activity with concentration was found to be interpreted in terms of a lameller micelle model.

The counter-ion activity coefficient in detergent solutions has recently been estimated by applying the membrane electrodes inclusive of the cation sensitive glass electrode. Botré *et al.*[1] used the membrane electrodes of both negative and positive types, and evaluated the degree of dissociation of micelles in aqueous solutions of sodium lauryl sulfate, sodium laurate and laurylamine hydrochloride. Shedlovsky *et al.*[2] used the sodium sensitive glass electrode for estimating the counter-ion activity in mixed solution of sodium alkyl sulfate with chain length from C_{10} to C_{14}. Feinstein and Rosano,[3] using the cationic glass electrode, determined the degree of dissociation of potassium and sodium carboxylate micelles at a constant cation concentration. Further, Stenius and Ekwall[4] obtained the sodium ion activity in a sodium caprylate solution by using the sodium responsive glass electrode.

Although the single-ion activity coefficient is a conventionally defined quantity in nature, the interpretation of which is subject to the same limitations as that of pH, it is of interest to estimate the counter-ion activity coefficient in detergent solutions in order to elucidate the degree of dissociation of the micelle and other related properties.

The present paper is concerned with the determination of counter-ion activities of sodium alkyl sulfates in aqueous solutions with and without added magnesium ion which is almost insensitive to the sodium glass electrode.

Experimental

In the present experiment, we used a Horiba pNa meter model N-5 with the following cell:

Na glass electrode | Detergent solution | N NH_4NO_3 |
3.33 N KCl agar bridge | Caromel electrode.

The detergents used were sodium alkyl sulfate with chain length from C_8 to C_{14}, prepared by the esterification of purified long chain alcohols.

It was rather difficult to obtain the reliable e.m.f. when the reference caromel electrode was directly immersed into the detergent solution, on account of the formation of potassium alkyl sulfate which is sparingly soluble in water at the temperature of experiment. The use of N NH_4NO_3 liquid junction, however, permits the precise determination of e.m.f. with an accuracy of ±0.005 pNa unit. The whole system was maintained at constant temperature of 25°C for C_8 to C_{12} and 35°C for C_{14} and C_{12} with added magnesium ion.

The measurement on the system of sodium dodecyl sulfate (SDS) in salt solutions was performed at a constant mole ratio (R) of $MgSO_4$ to SDS throughout a series of experiment.

The sodium sensitive glass electrode was calibrated with a sodium chloride solution of known activity.[5,6]

Results and Discussion

In Figs. 1—4, the observed values of $\log a_+$ are plotted against the logarithm of total analytical concentration (C) in mol/l of the detergent solutions. In all cases, plots of $\log a_+$ *vs.* $\log C$ are nearly linear over the concentration range below the critical micelle concentration (CMC). In this concentration range, the apparent counter-ion activity coefficient (γ_+) defined by a_+/C might be expected to be comparable with that of simple

---

[1] C. Botré, V. L. Crescenzi and A. Mele, *J. Phys. Chem.*, **63**, 650 (1959).

[2] L. Shedlovsky, C. W. Jakob and M. B. Epstein, *ibid.*, **67**, 2075 (1963).

[3] M. E. Feinstein and H. L. Rosano, *J. Colloid and Interface Sci.*, **24**, 73 (1967).

[4] P. Stenius and P. Ekwall, *Acta Chem. Scand.*, **21**, 1643 (1967).

[5] A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935).

[6] G. J. Janz and A. R. Gordon, *ibid.*, **65**, 218 (1943).

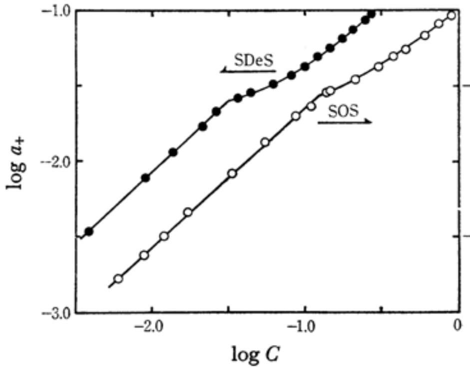

Fig. 1. The plots of log a_+ *vs.* log C for SOS and SDeS at 25°C.

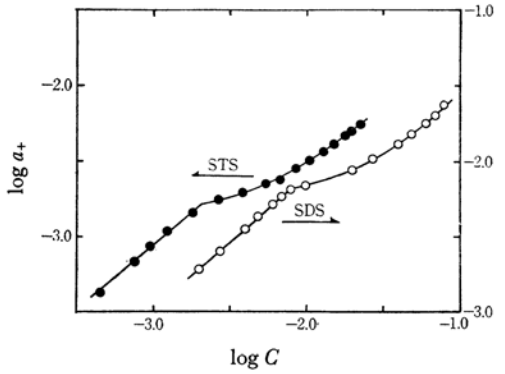

Fig. 2. The plots of log a_+ *vs.* log C for SDS at 25°C and STS at 35°C.

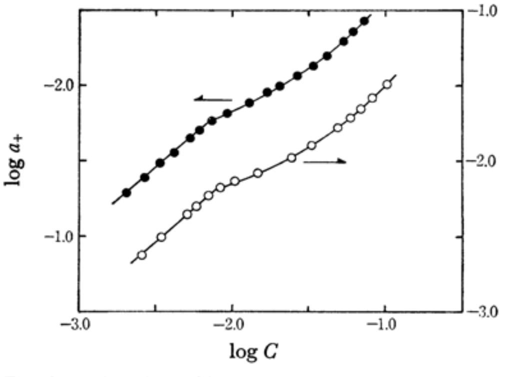

Fig. 3. The plots of log a_+ *vs.* log C for SDS at 35°C.
○: $R = 0$, ●: $R = 0.0467$

electrolyte, *e.g.* NaCl. The experimental fact is, however, not the case. The typical plot of log γ_+ *vs.* $C^{1/2}$ for sodium octyl sulfate (SOS) is given in Fig. 5 together with the value of $\gamma_\pm$ obtained for NaCl by Brown and MacInnes.⁵⁾ It will be noted that the value of γ_+ for SOS is considerably small relative to the mean activity coefficient of NaCl in an equivalent solution.

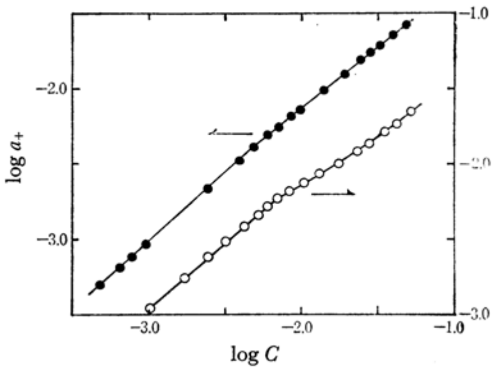

Fig. 4. The plots of log a_+ *vs.* log C for SDS at 35°C.
○: $R = 0.0957$, ●: $R = 0.299$

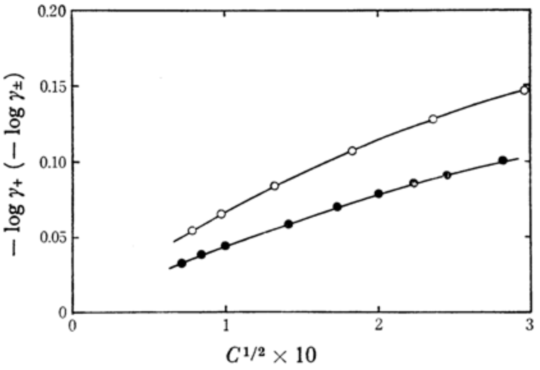

Fig. 5. The plots of $-\log\gamma_+$ *vs.* $C^{1/2}$ for SOS at 25°C.
○: SOS, ●: NaCl $(\gamma_\pm)$⁵⁾

If the Debye-Hückel theory may also be applicable to detergent solutions, the observed deviation must be ascribed either to the increased ional concentration due to the formation of polyvalent aggregates or to the existence of undissociated detergent molecules, *i. e.*, neutral ion pairs. The critical interionic distance for ion pair formation of 1–1 electrolyte is 3.57 Å in water at 25°C. It is, therefore, rather doubtful to assume the formation of neutral ion pairs with such bulky ions as octyl sulfate.

Mukerjee *et al.*⁷⁾ suggested the existence of detergent dimer on the basis of conductivity measurement for SDS. In the present case, it is difficult to account for the observed reduction of γ_+ without assuming even higher order association of detergent anions than dimer, *e. g.*, the existence of detergent pentamer. It will be, however, reasonable to assume the existence of small aggregates in the dilute concentration range below CMC, though no conclusive evidence has yet been obtained for such

---

7) P. Mukerjee, K. J. Mysels and C. I. Dulin, *J. Phys. Chem.*, **62**, 1390 (1958); P. Mukerjee, *ibid.*, **62**, 1397 (1958).

a higher aggregate as pentamer.

The deviation from linearity appearing above the CMC suggests the low degree of dissociation of the micelle. In the presence of the added magnesium ion, a break at the CMC became more obscure as the value of R, the mole ratio of $MgSO_4$ to SDS, increased and no break could be detectable above $R=0.5$. This result indicates that the fraction of sodium ion bound at the micellar surface decreases rapidly as the relative concentration of magnesium ion increases.

In general, the equilibrium distribution of counter-ion is determined by the equality of the electrochemical potential of sodium ion in bulk phase and in the micellar surface region, so that

$$\bar{\mu}_b = \bar{\mu}_s \tag{1}$$

where

$$\bar{\mu}_b = \mu_b^0 + \boldsymbol{k}T \ln a_+ + \varepsilon\psi_b \tag{2}$$

for sodium ion in bulk phase and

$$\bar{\mu}_s = \mu^0{}_s + \boldsymbol{k}T \ln C_s + \mu_s^e \tag{3}$$

for sodium ion bound at the micellar surface. Here, ψ_b is the electrical potential of the bulk phase and ε is the electronic charge. μ_s^e is the electrical part of free energy and C_s is the concentration of bound sodium ion, both at the micellar surface region. We put $\psi_b=0$ according to the common practice. It follows from Eqs. (1), (2) and (3) that

$$\ln a_+ = (\mu_s^0 - \mu_b^0)/\boldsymbol{k}T + \ln C_s + \mu_s^e/\boldsymbol{k}T. \tag{4}$$

Suppose that the micelle is lamellar and consists of m alkyl sulfate ions and $m\beta$ sodium ions bound at the micellar surface region V, giving the net charge $-m(1-\beta)\boldsymbol{\varepsilon}$. Then we have

$$C_s = 1000\, m\beta/\boldsymbol{N}V \tag{5}$$

and

$$\psi_s = -\, (\boldsymbol{k}T/\boldsymbol{\varepsilon}) \ln (2000\pi\sigma^2/D\boldsymbol{Nk}TC_b) \tag{6}$$

for the electrical potential at the outer part of Stern layer, where $\boldsymbol{N}$ is the Avogadro number, D the dielectric constant of the medium, σ the surface charge density of the micelle, and C_b the concentration of free sodium ion in the bulk solution, *i. e.*,

$$C_b = C_0 + (1-\beta)(C-C_0). \tag{7}$$

Here, C_0 is the CMC and C is the total analytical concentration of the detergent in mol/l. The expression for the electrical free energy term, μ_s^e, may be obtained by the charging process with respect to the sodium ion charge, q, at the micellar surface.

$$\mu_s^e = \int_0^\varepsilon \psi_s \, \mathrm{d}q \tag{8}$$

It follows from Eqs. (6) and (8), with substitution

$$\sigma = -\, (\boldsymbol{\varepsilon} - \beta q)/A, \tag{9}$$

that

$$\begin{aligned}\mu^e = \boldsymbol{k}T \lbrack & -\ln \{2000\pi\boldsymbol{\varepsilon}^2(1-\beta)^2/D\boldsymbol{Nk}TA^2C_b\} \\ & + 2\, \{1+(1/\beta) \ln (1-\beta)\}\rbrack.\end{aligned} \tag{10}$$

Here, A denotes the area occupied by an alkyl sulfate ion at the micellar surface. Substitution of Eqs. (5) and (10) into Eq. (4) gives

$$\begin{aligned}\ln a_+ = {} & (\mu_s^0 - \mu_b^0)/\boldsymbol{k}T + \ln \{D\boldsymbol{k}TA^2m\beta/2\pi V\boldsymbol{\varepsilon}^2(1-\beta)^2\} \\ & + 2\{1+(1/\beta) \ln (1-\beta)\} \\ & + \ln\{C_0 + (1-\beta)(C-C_0)\}.\end{aligned} \tag{11}$$

If it is assumed that the micellar parameters A, m, V and β are constant throughout the whole concentration range studied, we have

$$a_+ = \text{Const.}\{C_0 + (1-\beta)(C-C_0)\}. \tag{12}$$

From the boundary condition that $a_+ \to a_+^0$ $(=\gamma_+C_0)$ when $C \to C_0$, we obtain

$$\gamma_+ = a_+/C = \gamma_+^0\{(1-\beta) + \beta C_0/C\} \tag{13}$$

and

$$\begin{aligned}\ln \gamma_+^0 = {} & (\mu_s^0 - \mu_b^0)/\boldsymbol{k}T + \ln\{D\boldsymbol{k}TA^2m\beta/2\pi V\boldsymbol{\varepsilon}^2(1-\beta)^2\} \\ & + 2\{1+(1/\beta) \ln (1-\beta)\},\end{aligned} \tag{14}$$

where, γ_+^0 is the apparent activity coefficient of sodium ion at $C=C_0$. Using Eq. (13), we can estimate the value of β from the slope of γ_+ *vs.* C_0/C plot. It is to be noted that the equation assumed by Botré *et al.*[1)] for estimating the degree of dissociation of the micelle can be derived from the lamellar micelle model.

In the presence of added magnesium ion, we assumed that Eq. (13) may also be applicable if the relative concentration of $MgSO_4$ to SDS is small, which is the case for the present experimental condition. Under this condition, the potential determining ion of the diffuse double layer will be assumed to be the sodium ion, since the majority of the added magnesium ion will be bound at the micellar surface on account of the strong coulombic interaction with the micelle. In Fig. 6, the typical plot of γ_+ *vs.* C_0/C is given for sodium tetradecyl sulfate in water at 35°C. The linearity of the line is satisfactory over the whole concentration range studied. In the presence of added magnesium ion, however, the deviation from

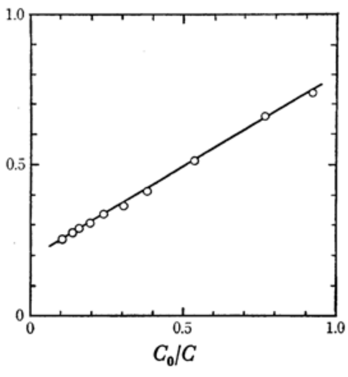

Fig. 6. The polts of γ_+ *vs.* C_0/C for STS at 35°C.

linearity is found to appear in higher concentration range above CMC. In these cases, therefore, we used the limiting slope at the CMC in the plot, γ_+ *vs.* C_0/C. The values of β are summarized in Table 1, together with those evaluated by several authors.

TABLE 1. THE VALUES OF β DETERMINED FROM pNa DATA

Detergent*	Temp. (°C)	R	CMC** (mol/l)	β	β(lit.)
SOS	25		1.27×10^{-1}	0.56	
SDeS	25		3.16×10^{-2}	0.62	0.70 2)
SDS	25		7.95×10^{-3}	0.75	0.84, 1) 0.78 2) 0.71, 8) 0.82 9)
STS	35		2.07×10^{-3}	0.76	0.87(25°C) 2)
SDS	35		8.22×10^{-3}	0.72	
SDS+$MgSO_4$	35	0.0467	7.33×10^{-3}	0.52	
SDS+$MgSO_4$	35	0.0957	6.38×10^{-3}	0.42	
SDS+$MgSO_4$	35	0.299	4.83×10^{-3}	0.18	
SDS+$MgSO_4$	35	0.510	$3.2\ \times10^{-3}$	0.14	

* SOS: Sodium octyl sulfate, SDeS: Sodium decyl sulafte, SDS: Sodium dodecyl sulfate, STS: Sodium tetradecyl sulfate.

** Determined from a break point of log a_+ *vs.* log C plot.

As is clearly shown in Table 1, the value of β increases with increasing chain length and for the same chain length it decreases with increasing temperature. Further, it is confirmed that the addition of magnesium ion to SDS gives rise to the rapid reduction of β.

Once the value of β is determined, we can estimate the specific adsorption energy $\Delta\mu^0$ $(=\mu_s^0-\mu_b^0)$ with the additional assumptions for V and A. If it is assumed here that the thickness of the Stern layer is in the order of the diameter (l) of hydrated sodium ion, the available volume for Na^+ ion in the Stern layer may be written as

$$V = mAl. \tag{15}$$

From Eqs. (14) and (15) we have

$$\begin{aligned}\Delta\mu^0/\boldsymbol{k}T &= \ln\{2\pi l\boldsymbol{\varepsilon}^2(1-\beta)^2\gamma_+^0/D\boldsymbol{k}TA\beta\}\\ &\quad -2\{1+(1/\beta)\ln(1-\beta)\}.\end{aligned} \tag{16}$$

Introducing $A=33$ Å^2 which was determined from the surface adsorption study of tritiated SDS in water,10) $l=4.6$ Å and $\gamma_+{}^0=0.815$ into Eq. (16), we obtain $\Delta\mu^0=0.85\,\boldsymbol{k}T$ for SDS at 25°C. By using the spherical micelle model, Stigter11) obtained $\Delta\mu^0=0.5\boldsymbol{k}T$ for the same detergent. The value of $\Delta\mu^0$ estimated above, however, depends on the selected values of A and l, and in fact it tends to zero as the value of A increases. Hence it will be reasonable to assume that the area obtainable by substituting $\Delta\mu^0=0$ into Eq. (16) gives the upper limit of the area per polar head of a detergent anion at the micellar surface. The values of A so determined are 77 Å^2 for SDS, 112 Å^2 for SDeS and 126 Å^2 for SOS at 25°C, respectively. These figures reflect the expanding nature of the micelle with increasing degree of dissociation of the micelle. The true areas will be smaller than these values owing to the definite positive values of $\Delta\mu^0$.

---

8) D. Stigter and K. J. Mysels, *J. Phys. Chem.*, **59**, 45 (1955).

9) J. N. Philips and K. J. Mysels, *ibid.*, **59**, 325 (1955).

10) G. J. Nilsson, *ibid.*, **61**, 1135 (1957).

11) D. Stigter, *ibid.*, **68**, 3603 (1964).