The Micellar Properties of 1-Dodecylpyridinium Chloride as Studied by the Ion-selective Electrodes

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The surfactant ion and counterion activities of aqueous 1-dodecylpyridinium chloride with and without KCl were determined by using ion-selective electrodes. In the concentration range above the critical micelle concentration (cmc), the surfactant ion activity (a_+) was found to decrease gradually with increasing surfactant concentrations, while the reverse change was found for the counterion activity (a_-). As a result, the mean activity increased slightly but regularly with increasing concentrations. The concentration dependences of a_+ and a_- became progressively smaller as the salt concentration increased. An application of the charged phase separation model led to an apparent degree of counterion association to the micelle (β) of 0.70 regardless of the salt concentration. On the basis of these observations, the estimations were made for the concentration of monomeric surfactant ion (C_+) and the activity coefficients of counterion (γ_-) and surfactant ion (γ_+) above the cmc. The values of C_+ and γ_+ decreased appreciably, while that of γ_- increased with increasing concentrations. The value of β was also estimated from the concentration dependence of a_- and the validity of this method was discussed.

The ion-selective electrodes have widely been applied for the determination of counterion and surfactant ion activities in ionic surfactant solutions.[1-14] In most studies were used the sodium ion-sensitive glass electrodes,[2-5,7] as well as the anion-[1,6-9,14] and cation-[1,8-10,12,14] exchange membrane electrodes. In the presence of added salts, however, the liquid[11] and plastic[10,13] membrane electrodes have proved very useful because of their high selectivity for a surfactant ion over inorganic ions. It has been found that the counterion activity (a_+) in anionic surfactant solutions increases gradually with increasing surfactant concentrations through the break point at the critical micelle concentration (cmc).[1-5,7-10,12,14] According to the method advanced by Botré *et al.*,[1] an apparent degree (β) of counterion association to the micelle has been evaluated from the concentration dependence of a_+ above the cmc.[1-3,5,11] On the other hand, the surfactant ion activity (a_-) has been found to decrease monotonously with increasing surfactant concentrations above the cmc.[6-12,14] Sasaki *et al.*[7,8] and Koshinuma[9,14] have confirmed the validity of the charged phase separation model by demonstrating the constancy of $a_- a_+^{\beta}$. By ignoring the effect of micelles on the activity coefficients of monomeric ions, Sasaki *et al.*[7] and Cutler *et al.*[10] have calculated the intermicellar concentrations of counterion and surfactant ion above the cmc.

The ion-selective electrodes can also be applicable to cationic surfactant solutions, though their applications so far reported are confined mostly to anionic ones. In a previous paper,[15] we have reported that poly(vinyl chloride) membrane plasticized with bis (2-ethylhexyl) phthalate responds selectively to cationic surfactant ions, especially to 1-alkylpyridinium ion even in the presence of excess salts. The present paper is concerned with the potentiometric determination of counterion and surfactant ion activities in solution of 1-dodecylpyridinium chloride with and without added KCl.

Experimental

Materials. 1-Dodecylpyridinium chloride (DPC, Wako Pure Chemical Industry Co. Ltd.) was dissolved in hot ethanol and refluxed overnight with active carbon. After cooling the filtrate, the precipitate was purified further by repeated recrystallization from ethanol and by extraction with ether for 48 h. Potassium chloride of guaranteed grade and other chemicals of reagent grade were used without further purification.

Electromotive Force Measurements. The counterion and surfactant ion activities in DPC solutions were measured by using a chloride ion selective ceramic electrode, National IE-510103, and a poly (vinyl chloride) (PVC) membrane electrode, respectively. The following cells were constructed.

Chloride ion electrode | Sample solution (DPC, C; KCl, C_s) | 1 mol dm^{-3} NH_4NO_3 agar bridge | Reference electrode (Ag-AgCl)

Reference electrode (Ag-AgCl) | 1 mol dm^{-3} NH_4NO_3 agar bridge | Reference solution (DPC, 1×10^{-4} mol dm^{-3}) | PVC membrane | Sample solution (DPC, C; KCl, C_s) | 1 mol dm^{-3} NH_4NO_3 agar bridge | Reference electrode (Ag-AgCl)

The preparation of the PVC membrane electrode is described elsewhere.[15] The electromotive forces (EMF) of these cells were measured with an accuracy of ±0.1 mV by using a Yokogawa Universal Digital Meter Model 2502 connected to a voltage follower amplifier (input impedance$\simeq10^{13}\,\Omega$). Prior to the measurements with DPC solutions, the chloride ion electrode was calibrated with a sodium chloride solution of known activity.[16] This electrode was found to respond to the chloride ion down to 5×10^{-4} mol dm^{-3} with an ideal slope of 59.2 mV per decade change in chloride ion activity. In the case of PVC membrane electrode, the semilogarithmic plots of EMF *vs.* surfactant concentration gave a straight line with a slope of 59.1 mV in dilute concentration range below *ca.* 1×10^{-4} mol dm^{-3}. This fact suggests the Nernstian response of the PVC membrane electrode to the DPC ion.

All measurements were conducted at 25 °C. The PVC membrane was renewed after a series of experiments for a given salt concentration.

Results and Discussion

The electromotive forces (E) of the foregoing cells can be described as

$$E_+ = E_+^{*} - S\log(a_+/a_+^{*}), \tag{1}$$

$$E_- = E_-^{\circ} + S\log a_-, \tag{2}$$

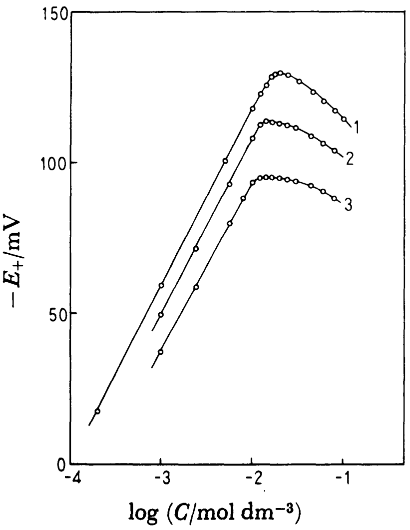

Fig. 1. The semilogarithmic plots of E_+ *vs.* C at 25 °C. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}. The curves 2 and 3 are displaced downward by 10 and 20 mV, respectively.

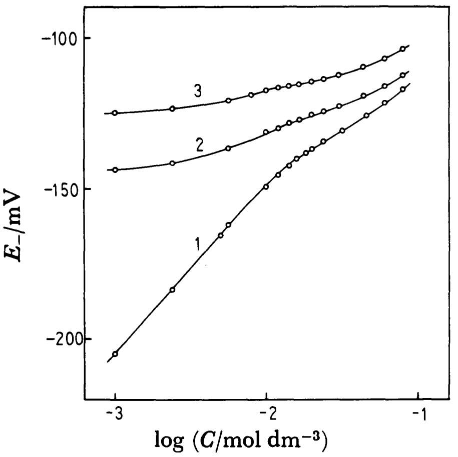

Fig. 2. The semilogarithmic plots of E_- *vs.* C at 25 °C. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}.

where E^a refers to the asymmetric potential of overall cell system, $E^{\ominus}_{\pm}$ to the standard electrode potential, S to the Nernst slope (59.2 mV at 25 °C), and superscript r to the reference solution, respectively. In Figs. 1 and 2 are plotted E_+ and E_- against the logarithm of DPC concentration (C) in the presence and absence of KCl. The break point in these figures corresponds to the cmc (C_o) at a given salt concentration (C_s). In the concentration range above the cmc, the DPC ion activity (a_+) is seen to decrease monotonously with increasing surfactant concentrations, while the reverse is found for the chloride ion activity (a_-). As would be expected, these behaviors are similar to those of surfactant ion[6-12,14] and counter-ion[1-5,7-10,12,14] activities in anionic surfactant solutions. As can be seen from Figs. 1 and 2, the addition of KCl results in a succesive decrease in the slope of E_+ or E_- *vs.* log C plots above the cmc. Figure 3 shows the concentration dependence of $E_- - E_+$ which is a measure of the mean activity ($a_\pm$). It should be noted that

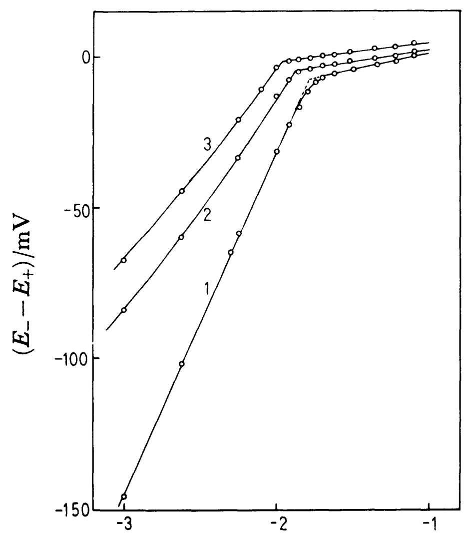

Fig. 3. The semilogarithmic plots of $E_- - E_+$ *vs.* C at 25 °C. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}.

the plot of $E_- - E_+$ *vs.* log C at higher surfactant concentrations than the cmc gives a straight line with a small but definite slope. Thus, we may write

$$\log(a_+a_-/a_+^\circ a_-^\circ) = [(E_- - E_-^\circ) - (E_+ - E_+^\circ)]/S = K_1\log(C/C_o), \tag{3}$$

where the superscript ° refers to the cmc. The values of K_1 and the cmc determined from the break points in Fig. 3 are summarized in Table 1. It can immediately be seen that an increase in salt concentration leads to a rapid decrease in K_1. In accord with the results obtained for anionic surfactant solutions,[7-10,12,14] these observations reveal that the mean activity of DPC above the cmc increases progressively with increasing surfactant concentrations unless an excess salt is added. For example in a salt free solution, the value of $a_\pm$ at 0.1 mol dm^{-3} is larger by a factor of 1.19 than that at the cmc.

In solutions of anionic surfactants such as sodium dodecyl sulfate (SDS)[7] and tetradecyl sulfate,[8] the charged phase separation model has been confirmed to hold over a wide concentration range above the cmc. According to this model, $a_+a_-^\beta$ should be constant at higher surfactant concentrations. It follows immediately from Eqs. 1 and 2 that

$$E_+/S = \beta(E_-/S) + \text{const.} \tag{4}$$

If β remains constant, therefore, the plot of E_+/S *vs.* E_-/S is anticipated to give a straight line with the slope of β. As is shown in Fig. 4, E_+/S depends in fact linearly on E_-/S in all cases studied, indicating that the charged phase separation model is also valid for DPC solution. It is worth noting that the value of β summarized in Table 1 is virtually independent of the added salt concentration.

In an attempt to estimate the intermicellar concentrations of surfactant ion and counterion in SDS solutions, Sasaki *et al.*[7] have assumed that the mean ionic molarities of these ions in a micellar solution and in a hypo-

Table 1. The potentiometric and micellar parameters of DPC solution at 25 °C

C_s/m mol dm^{-3}	C_0/m mol dm^{-3}	K_1	K_2/mV	K_3/mol^{-1} dm^3	β	β'
0	16.3	0.188	57.5	20.7	0.69	0.66
10	13.0	0.131	55.7	12.8	0.71	0.71
20	10.7	0.117	54.5	9.3	0.69	0.71

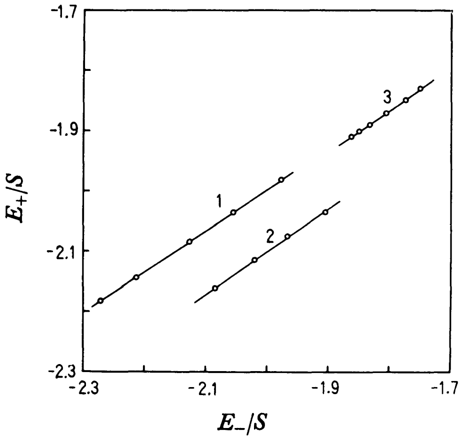

Fig. 4. Plots of E_+/S vs. E_-/S at 25 °C. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}. The curve 2 is displaced downward by 0.1.

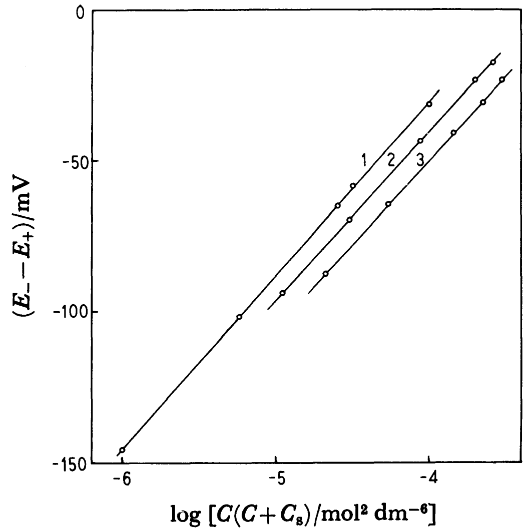

Fig. 5. Plots of $E_- - E_+$ vs. $\log[C(C+C_s)]$ in the concentration range below the cmc at 25 °C. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}. The curves 2 and 3 are displaced downward by 10 and 20 mV, respectively.

thetical solution composing only of monomeric ions are identical with each other at a given mean activity. The same assumption was also made by Cutler *et al.*[10] in their potentiometric study of SDS solutions. Their calculation suggests that the intermicellar concentration of dodecyl sulfate ion is not constant but decreases regularly as the surfactant concentration increases.[7,10] Under the same assumption, we made the tentative estimations of the intermicellar concentration of 1-dodecylpyridinium ion (C_+) and ionic activity coefficients (γ_+, γ_-) in a bulk phase. Figure 5 shows the change in $E_- - E_+$ with $\log C_{\pm}^2$ in the concentration range below the cmc, where $C_{\pm}^2$ denotes $C(C+C_s)$. Regardless of the salt concentration, the plot is found to give a straight line, *i.e.*,

$$E_- - E_+ = \text{const.} + K_2 \log C_{\pm}^2. \quad (5)$$

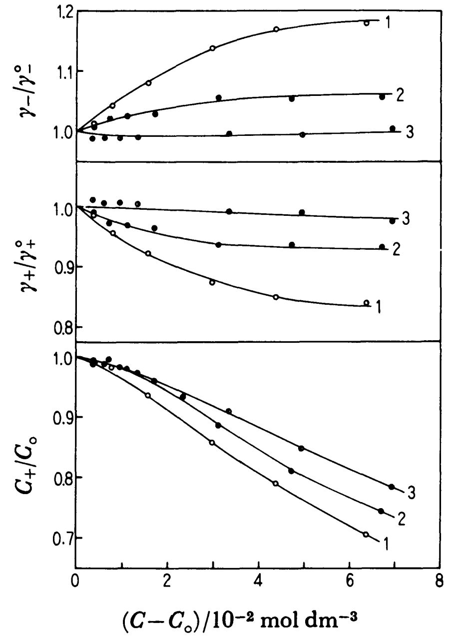

Fig. 6. The concentration dependences of C_+/C_0, γ_+/γ_+°, and γ_-/γ_-° estimated from Eqs. 6, 7, and 8. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}.

The values of K_2 are included in Table 1. Since $C_{\pm}^2$ in the micellar solution is equal to $C_+[C_+ + C_s + (1-\beta)(C-C_+)]$, Eq. 5 may be rewritten as

$$(E_- - E_-^\circ) - (E_+ - E_+^\circ) = K_2 \log[C_+\{C_+ + C_s + (1-\beta)(C-C_+)\}/C_o(C_o+C_s)]. \quad (6)$$

Equation 6 allows us to estimate the change in C_+ with the surfactant concentration above the cmc. The knowledge of γ_+ and γ_- can then be obtained by substituting the following relations into Eqs. 1 and 2.

$$a_+ = \gamma_+ C_+, \quad (7)$$

$$a_- = \gamma_-[C_+ + C_s + (1-\beta)(C-C_+)]. \quad (8)$$

The values of C_+/C_+°, γ_+/γ_+°, and γ_-/γ_-° thus calculated are plotted in Fig. 6 as a function of $C-C_o$. An important feature of Fig. 6 is a gradual decrease in C_+ with the surfactant concentration though the deviation from C_o becomes progressively smaller as the salt concentration increases. A similar behavior has also been noted for SDS solution without added salt.[7,10] Another interesting feature of Fig. 6 is a marked dependence of γ_+ and γ_- on the salt concentration. In the absence of added salt, an increase in surfactant concentration is accompanied by a decrease in the former while an anomalous increase in the latter. However, they tend eventually to level off. In the presence of 0.02 mol dm^{-3} KCl, neither γ_+ nor γ_- depends appreciably on the surfactant concentration. It is important to remember here that in the concentration range above the cmc, the total concentration of counterion in bulk phase, $C_+ + C_s + (1-\beta)(C-C_+)$, is always larger than that of coion, $C_+ + C_s$. Thus an increase in γ_-/γ_-° estimated above will be ascribed to an increase in the repulsive interaction between counterions in bulk phase compared to that at the cmc where the concentrations of counterion and coion are identical with each other.

An information about the degree of counterion association to the micelle can otherwise be obtained from the concentration dependence of counterion activity alone according to the method advanced by Botré *et al.*[1] In this treatment, it is usually assumed that the counterion activity coefficient and the concentration of monomeric surfactant ion remain constant even above the cmc.[1-3,5,11] On converting γ_- and C_+ in Eq. 8 to γ_-° and C_o respectively and denoting β in this case by β', we have

$$\begin{aligned} a_-/a_-^\circ &= \exp[2.303(E_- - E_-^\circ)/S] \\ &= 1 + (1-\beta')(C-C_o)/(C_o+C_s) \\ &= 1 + K_3(C-C_o). \end{aligned} \tag{9}$$

In all cases studied, the plot of a_-/a_-° *vs.* $C-C_o$ gives a straight line with a slope of K_3. The values of K_3 and β' are summarized in Table 1. It can immediately be seen that the difference between β' thus estimated and β is negligibly small. We must keep in mind, however, that this agreement does not necessarily support the validity of the underlying assumption of Eq. 9, since the foregoing calculations show that both C_+ and γ_- depend appreciably on the surfactant concentration. In this connection, it is important to note that a similar relation to Eq. 9 can be derived under certain conditions even if C_+ and γ_- are dependent on the surfactant concentration. An expression of the counterion activity, Eq. 8, can formally be divided into two terms; $\gamma_-(C_+ + C_s)$ and $\gamma_-(1-\beta)(C-C_+)$. If each term is linearly dependent on the surfactant concentration, *i.e.*,

$$\gamma_-(C_+ + C_s) = \gamma_-^\circ(C_o+C_s) + A\gamma_-^\circ(C-C_o) \tag{10}$$

and

$$\gamma_-(1-\beta)(C-C_+) = \gamma_-^\circ B(C-C_o), \tag{11}$$

we immediately have,

$$a_-/a_-^\circ = 1 + (A+B)(C-C_o)/(C_o+C_s). \tag{12}$$

This is exactly identical with Eq. 9 provided that the numerical value of $A+B$ is equal to $1-\beta'$. As is clearly shown in Fig. 7, indeed, the plots of the left hand sides of Eqs. 10 and 11 against the surfactant concentration give a straight line, respectively. In addition, the values of $A+B$ determined from Fig. 7 are in fair agreement with those of $1-\beta'$. Thus,the utility of Eq. 9 in determining the degree of counterion association to the micelle appears to rest on the fact that in micellar solution the counterion activity coefficient and the intermicellar concentration of the surfactant ion vary with the surfactant concentration so as to satisfy Eqs. 10 and 11.

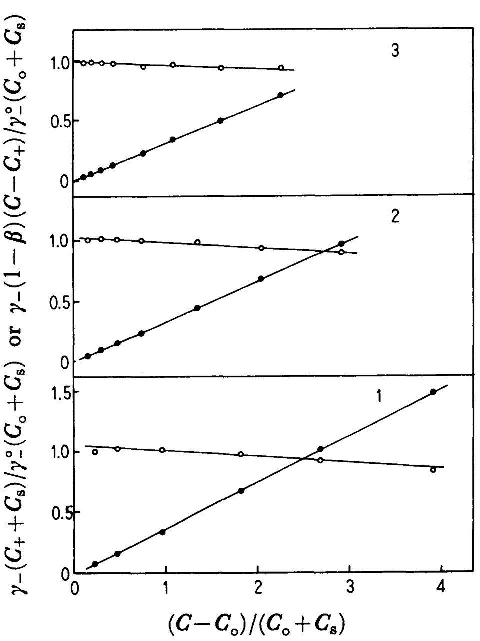

Fig. 7. The concentration dependences of the left hand sides of Eqs. 10 and 11. 1; $C_s=0$, 2; $C_s=0.01$, 3; $C_s=0.02$ mol dm^{-3}. ○; $\gamma_-(C_+ + C_s)/\gamma_-^\circ(C_o+C_s)$, ●; $\gamma_-(1-\beta)(C-C_+)/\gamma_-^\circ(C_o+C_s)$.

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References

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, *J. Phys. Chem.*, **67**, 2075 (1963).
3) M. E. Feinstein and H. L. Rosano, *J. Colloid Interface Sci.*, **24**, 73 (1967).
4) P. Stenius and P. Ekwall, *Acta Chem. Scand.*, **21**, 1643 (1967).
5) I. Satake, T. Tahara, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **42**, 319 (1969).
6) K. Kaibara, T. Nakahara, I. Satake, and R. Matuura, *Mem. Fac. Sci. Kyushu Univ. Ser. C.*, **7**, 1 (1970).
7) T. Sasaki, M. Hattori, J. Sasaki, and K. Nukina, *Bull. Chem. Soc. Jpn.*, **48**, 1397 (1975).
8) M. Koshinuma and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **48**, 2755 (1975).
9) M. Koshinuma, *Bull. Chem. Soc. Jpn.*, **52**, 1790 (1979).
10) S. G. Cutler, P. Meares, and D. G. Hall, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1758 (1978).
11) A. Yamauchi, T. Kunisaki, T. Minematsu, Y. Tomokiyo, T. Yamaguchi, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **51**, 2791 (1978).
12) E. Vikingstad, *J. Colloid Interface Sci.*, **72**, 68 (1979).
13) J. E. Newbery, *J. Colloid Interface Sci.*, **74**, 483 (1980).
14) M. Koshinuma, *Bull. Chem. Soc. Jpn.*, **54**, 3128 (1981).
15) T. Maeda, M. Ikeda, M. Shibahara, T. Haruta, and I. Satake, *Bull. Chem. Soc. Jpn.*, **54**, 94 (1981).
16) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).