The Micellar Properties of Dodecyltrimethylammonium Chloride as Studied by Ion-Selective Electrodes and Fluorescence Probe Technique

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The activities of the surfactant ion, counter ion, and co-ion in micellar solutions of dodecyltrimethylammonium chloride (DTAC) in the presence of NaCl were determined by using ion-selective electrodes. An application of the charged phase separation model gave an apparent degree of counter ion association to the micelle of 0.68 regardless of the salt concentration. A tentative estimation of the intermicellar concentrations of surfactant ion and counter ion was made on the basis of an assumption that the activity coefficients of the monomeric surfactant ion and co-ion were identical with each other. In the concentration range above the critical micelle concentration (cmc), the intermicellar concentration of the surfactant ion decreased gradually with increasing surfactant concentration, whereas the reverse was found for that of counter ion. Similar behaviors were also found for the activity coefficients of these ions. However, an increase in salt concentration caused a successive decrease in the concentration dependences of intermicellar concentrations as well as activity coefficients. Measurements were also made with the fluorescence decay curves of micelle-solubilized pyrene. An analysis based on the knowledge of the intermicellar concentration of surfactant ion estimated above revealed that the micelle aggregation number of DTAC remained virtually constant over wide concentration range above the cmc.

The use of the ion-selective electrodes gives valuable informations about the micellar properties of ionic surfactant solutions such as an apparent degree (β) of counter ion association to the micelle and the intermicellar concentrations of surfactant ion (C_1) and counter ion (C_2). In the concentration range above the critical micelle concentration (cmc), an increase in surfactant concentration has been found to accompany always a monotonous decrease in surfactant ion activity (a_1)[1-11] while a linear increase in counter ion activity (a_2).[2-4,6,7,9-17] It has also been noted by Sasaki et al.[2] and Koshinuma[3] that $a_1a_2^\beta$ remains constant in accordance with a charged phase separation model. This fact provides a simple method for the determination of β. However the estimations of C_1 and C_2 require a knowledge of the activity coefficients of surfactant ion and counter ion in the presence of polyvalent micellar ions. In this connection, Sasaki et al.[2] and Cutler et al.[4] have ignored the effect of micellar ions on the activity coefficients of monomeric ions in their calculations of C_1 and C_2 in sodium dodecyl sulfate solution. The same procedure was also applied for the potentiometric study of 1-dodecylpyridinium chloride solution with and without added salt.[11]

In this paper is described an attempt to estimate C_1 and C_2 from activity data of surfactant ion, counter ion, and co-ion in solution of dodecyltrimethylammonium chloride with added salt. On the basis of a knowledge of C_1, we also determined the concentration dependence of the micelle aggregation number from the fluorescence decay curves of micelle-solubilized pyrene.

Experimental

Materials. Dodecyltrimethylammonium chloride (DTAC) was prepared by passing the aqueous solution of the corresponding bromide (purity>99%, Tokyo Kasei Kogyo Co., Ltd.) through an anion-exchange column (Organo, IRA-400) in the Cl^- state. The concentration of DTAC was determined by drying aliquots of the stock solution over phosphorus pentaoxide in vacuo at 110 °C. Pyrene (purity>98%, Wako Pure Chemical Industries Co., Ltd.) was passed through silica gel in cyclohexane solution and recovered as white crystals. The purified pyrene gave the value of 1.8—1.9 for the ratio I_1/I_3 of the intensities of the first and the third vibronic peaks of the fluorescence spectrum in aqueous solution.

Electromotive Force Measurements. The counter ion and co-ion activities in DTAC solutions were measured potentiometrically by using a National chloride ion selective ceramic electrode IE-510103 and a HORIBA sodium ion selective glass electrode 1512A-06T, respectively. The following cell was constructed for the measurement of the surfactant ion activity.

> Reference electrode (Ag–AgCl)| Reference solution (DTAC, 1 mmol dm^{-3})|PVC membrane|Sample solution (DTAC; C, NaCl; 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.[18] The electromotive forces (emf) of these cells were measured at 25 °C to a precision of ±0.1 mV with a Yokogawa Universal Digital Meter Model 2502 connected to a voltage follower amplifier (input impedance=$10^{15}\ \Omega$). Prior to the measurements with DTAC solutions, the chloride ion and sodium ion electrodes were calibrated with a sodium chloride solution of known activity.[19] The semilogarithmic plot of emf vs. NaCl concentration gave a straight line down to ca. 5×10^{-4} mol dm^{-3} with a slope of 59.2 mV for the chloride ion electrode and 57.5 mV for the sodium ion electrode, respectively.

Fluorescence Decay Measurements. Fluorescence decay curves were measured by using the time-resolved fluorescence spectrophotometer (NAES-1100, HORIBA,Ltd.) at

25 °C. Pyrene was solubilized in DTAC stock solution (0.22 mol dm^{-3}) by sonicating the mixture for 30 min. All of the sample solutions were thoroughly deoxygenated before measurements by repeated freeze-pump-thaw cycles. Pyrene was excited at 337 nm and its emission was monitored through the filters (TOSHIBA, V-V40 monochrofilter and UV-35 cut-off filter). After fluorescence decay measurements, the concentration of pyrene was determined spectrophotometrically at 337 nm.

All measurements were conducted at constant salt concentrations (C_S).

Results and Discussion

The electromotive forces of the foregoing cells can be described as

$$E_i = E_i^{\ominus} + S_i \log a_i, \quad i = 1, 2, \text{ and } 3 \qquad (1)$$

where $E_i^{\ominus}$ refers to the standard electromotive force, a_i to the ion activity of component i, S_i to the observed slope of E_i vs. log a_i plot, and subscript 1, 2, and 3 to the surfactant ion, counter ion, and co-ion, respectively. If we denote the values at the cmc by superscript °, we immediately have

$$a_i/a_i^{\circ} = \exp\,[2.303(E_i - E_i^{\circ})/S_i]. \qquad (2)$$

In Figs. 1, 2, and 3 are shown the plots of E_1, E_2, and E_3 vs. the logarithm of DTAC concentration (C) at various NaCl concentrations (C_S), respectively. In consistent with previous results for 1-dodecylpyridinium chloride solutions,[11] an increase in DTAC concentration causes a monotonous decrease in a_1 but an increase in a_2 in the concentration range above the cmc. It should also be noted that the concentration dependences of a_1 and a_2 tend to decrease regularly with increasing salt concentrations. Similar salt effects are also noted for surfactant ion[5] and counter ion[16] activities in anionic surfactant solutions. The values of cmc (C_O) determined from the break points in Figs. 1 and 2 are summarized in Table 1. At higher surfactant concentrations, the value of E_3 is seen to decrease slightly but regularly with increasing concentrations, though the rate of decrease becomes progressively smaller as the salt concentration increases. The observed decrease in E_3 can reasonably be ascribed to the decrease in the activity coefficient (γ_3) of Na^+ ion, since the concentration of which is kept constant under our experimental conditions. These results allow us to estimate not only the degree (β) of counter ion association to the micelle but the activity coefficients and intermicellar concentrations of surfactant ion and counter ion respectively.

According to the charged phase separation model which has been confirmed to hold both in anionic[2-4,6,9,10] and cationic[9,11] surfactant solutions, $a_1 a_2^{\beta}$ should be constant in the concentration range above

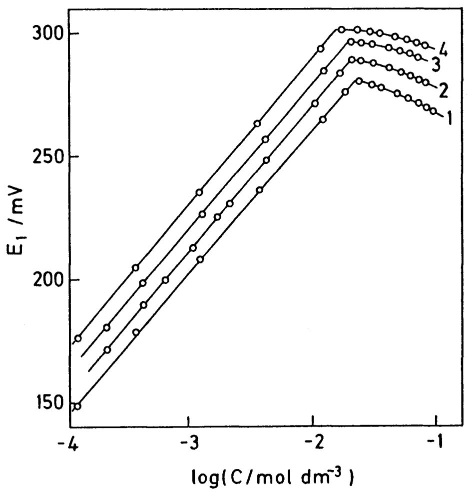

Fig. 1. The semilogarithmic plots of E_1 vs. C at 25 °C. The curves 2, 3, and 4 are displaced upward by 10, 20, and 30 mV, respectively. C_S/mmol dm^{-3}: 1; 0.5, 2; 5, 3; 10, 4; 20. The data for C_S=0 and 0.5 mmol dm^{-3} agree with each other within an experimental error.

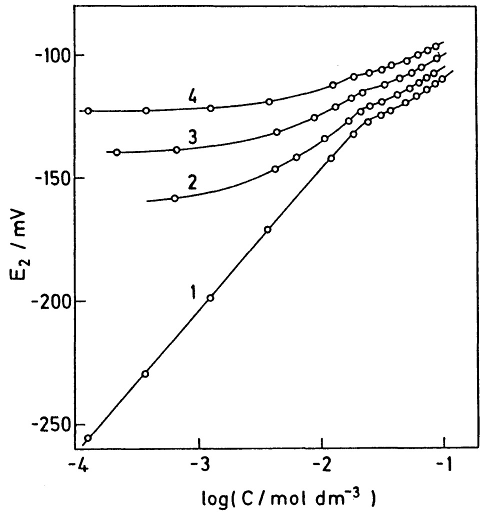

Fig. 2. The semilogarithmic plots of E_2 vs. C at 25 °C. C_S/mmol dm^{-3}: 1; 0, 2; 5, 3; 10, 4; 20.

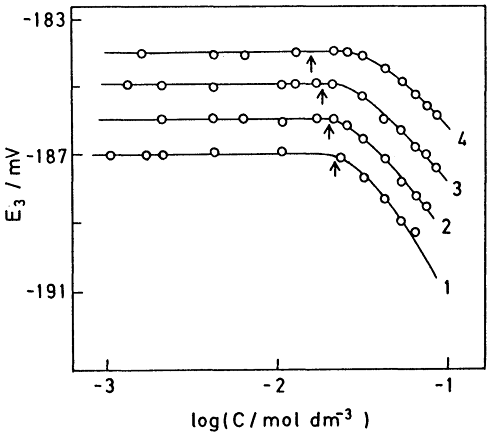

Fig. 3. The semilogarithmic plots of E_3 vs. C at 25 °C. The curves 2, 3, and 4 are displaced upward by 59, 72, and 92 mV, respectively. The arrow indicates the cmc determined from the break points in Figs. 1 and 2. C_S/mmol dm^{-3}: 1; 0.5, 2; 5, 3; 10, 4; 20.

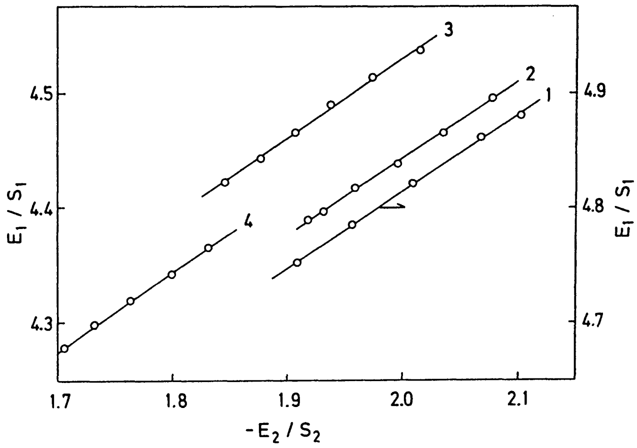

Fig. 4. Plots of E_1/S_1 vs. E_2/S_2 at varying salt concentrations. C_S/mmol dm^{-3}: 1; 0, 2; 5, 3; 10, 4; 20.

the cmc. It follows immediately from Eq. 1 that

$$E_1/S_1 = \text{const.} - \beta \cdot E_2/S_2. \qquad (3)$$

As is shown in Fig. 4, a plot of E_1/S_1 against E_2/S_2 gives in fact a straight line regardless of the salt concentration. It should be noted that the value of β summarized in Table 1 is little affected by the salt concentration. A similar constancy in β was also found for 1-dodecylpyridinium chloride solutions with added salt.[11]

The estimation of the intermicellar concentration (C_1) of surfactant ion from a_1 data requires a knowledge of the activity coefficient (γ_1) which is experimentally rather difficult to determine. In this connection, it seems reasonable to assume that the activity coefficients of surfactant ion and co-ion in the bulk phase are nearly identical with each other, since the only difference between them lies in their ionic sizes. At a constant salt concentration, which is the case for the present experiment, this assumption leads immediately to

$$\gamma_1/\gamma_1^\circ \simeq \gamma_3/\gamma_3^\circ = a_3/a_3^\circ \qquad (4)$$

$$C_1/C_1^\circ = C_1/C_o \simeq a_1 a_3^\circ / a_1^\circ a_3. \qquad (5)$$

These equations enable us to estimate the concentration dependences of γ_1 and C_1 from the electromotive force data. The knowledge of the intermicellar concentration (C_2) and the activity coefficient (γ_2) of the counter ion can then be obtained by substituting the values of β and C_1 estimated above into the following relations.

$$C_2/C_2^\circ = C_2/(C_S + C_o) = [C_1 + C_S + (1-\beta)(C - C_1)]/(C_S + C_o) \qquad (6)$$

$$\gamma_2/\gamma_2^\circ = a_2 C_2^\circ / a_2^\circ C_2 \qquad (7)$$

The estimated values of γ_1, C_1, γ_2, and C_2 relative to those at the cmc are plotted in Figs. 5 and 6 as a function of $C - C_o$. At a given salt concentration, γ_1 and C_1 decrease monotonously with increasing surfactant concentrations, whereas the reverse change is found for γ_2 and C_2. An increase in salt concentration tends to depress the variations in γ_1, C_1, and γ_2 with surfactant concentration.

Table 1. The Values of C_o and β at Varying Salt Concentrations

C_S/mmol dm^{-3}	C_o/mmol dm^{-3}	β
0	22.4	0.68
5	20.4	0.67
10	18.8	0.69
20	16.2	0.68

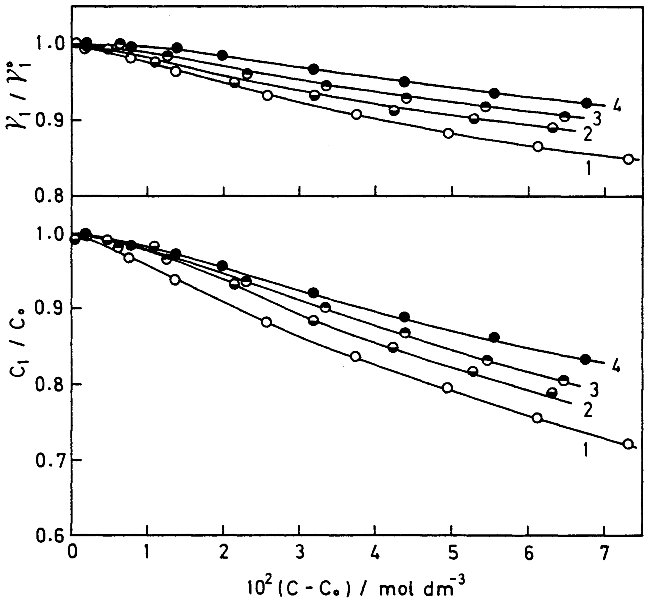

Fig. 5. The concentration dependences of γ_1/γ_1° and C_1/C_o estimated from Eqs.4 and 5. C_S/mmol dm^{-3}: 1; 0.5, 2; 5, 3; 10, 4; 20.

An attempt to estimate these parameters was made by Sasaki et al.,[2] Cutler et al.,[4] and Koshinuma[6,10] on the basis of the assumption that the mean ionic molarity of surfactant ion and counter ion in a micellar solution is identical with that in a hypothetical solution composing only of monomeric ions at a given mean activity. In solution of sodium dodecyl sulfate,[2,4] the value of C_1 thus calculated was found to have a tendency to decrease monotonously with surfactant concentration. According to the same assumption, we[11] also estimated the concentration dependences of γ_1, C_1, and γ_2 in solutions of 1-dodecylpyridinium chloride with and without added salt, and obtained the similar curves to those shown in Figs. 5 and 6. Unfortunately, however, an application of the above treatment to the present system leads to somewhat larger variations in these parameters with surfactant concentration. In their electrostatic approach based on the cell model, Gunnarsson et al.[20] made the numerical calculations of not only surfactant ion and counter ion activities but the intermicellar concentration of surfactant ion. It should be noted that their result for C_1 in sodium

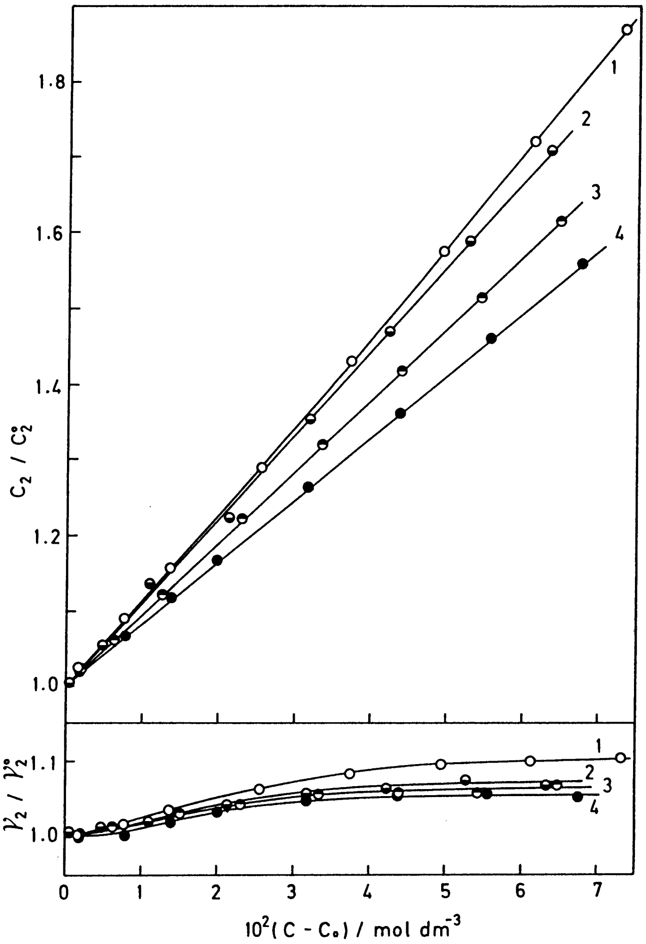

Fig. 6. The concentration dependences of C_2/C_2° and γ_2/γ_2° estimated from Eqs. 6 and 7. C_S/mmol dm^{-3}: 1; 0, 2; 5, 3; 10, 4; 20.

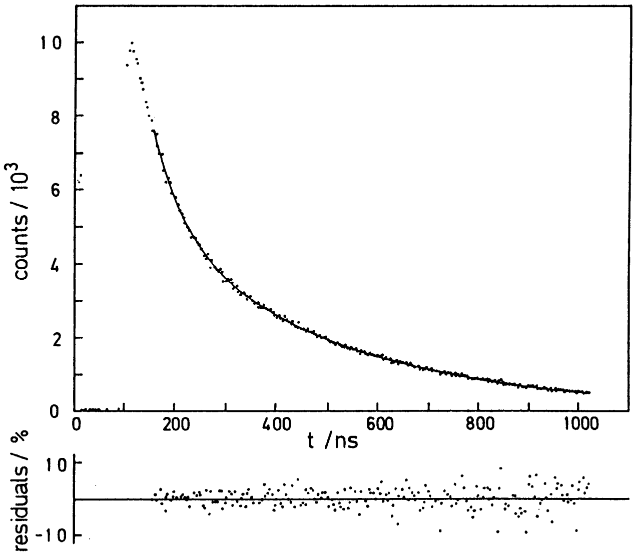

Fig. 7. The typical fluorescence decay curve and residuals at 25 °C. C=41.8 mmol dm^{-3}, C_S= 0.5 mmol dm^{-3}, [pyrene]=0.252 mmol dm^{-3}. Solid line: nonlinear least-squares fit.

Table 2. The Micelle Aggregation Number of DTAC at C_S=0.5 mmol dm^{-3}

C/mmol dm^{-3}	n	n'
35.2	62	56
41.8	61	55
48.4	63	57
52.8	61	55
59.4	62	56
72.6	63	57
220.0	—	63

dodecyl sulfate solution without added salt agree qualitatively well with the present results given in Fig. 5.

In order to demonstrate the utility of C_1 data, we determined the micelle aggregation number (n) of DTAC by fluorescence probe technique under the same experimental conditions as those for the activity measurements. Figure 7 shows the typical fluorescence decay curve of the micelle-solubilized pyrene at C_S=0.5 mmol dm^{-3} and C=41.8 mmol dm^{-3}. It has been well-known that this type of decay curve is described by the following equation based on the Poisson distribution of the pyrene molecules in micelles.[21)]

$$I = I_0 \exp[R\{\exp(-k_E t) - 1\} - k_1 t] \qquad (8)$$

where, I and I_0 are the fluorescence intensities at time t and zero, k_E and k_1 are the first-order rate constants for the intramicellar excimer formation and decay processes, and R is the number of fluorescence probe per micelle, i.e., R=[Pyrene]/[micelle], respectively. The values of I_0, R, k_E, and k_1 were evaluated from the observed decay curves by using the nonlinear least squares treatment based on modified Marquardt method.[22)] According to the definition of R, we immediately have

$$n = R(C - C_1)/[\text{Pyrene}]. \qquad (9)$$

The use of Eq. 9 together with C_1 data shown in Fig. 5 permits the precise determination of the micelle aggregation number. The values of n thus determined at C_S=0.5 mmol dm^{-3} are summarized in the second column of Table 2. It is worth noting that the value of n remains essentially constant over wide concentration range above the cmc. In conventional estimations of n based on the fluorescence probe technique,[23–28)] C_1 in Eq. 9 has always been replaced by the cmc, C_0. Such a calculation is valid only at higher surfactant concentrations where C_1 can safely be ignored as compared to C. In the concentration range near the cmc, however, it must be kept in mind that the use of C_0 instead of C_1 tends to underestimate the value of n. For the sake of comparison, the micelle aggregation number, n', calculated from Eq. 9 with C_1=C_0 is also given in Table 2. As would be anticipated, an appreciable difference is found between n and n' in the concentration range up to ca. 7×10^{-2} mol dm^{-3}. At sufficiently high surfactant concentrations, however, the value of n' agrees well with the constant value of *n* at lower concentrations. These observations seem not only to reveal the importance of the knowledge of C_1 in the determination of micelle aggregation number by fluorescence probe technique, but to support the validity of the potentiometric method for estimating C_1 in ionic surfactant solution.

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