

THE MICELLAR PROPERTIES OF
DODECYLTRIMETHYLAMMONIUM ALKANESULFONATES IN
AQUEOUS SOLUTIONS

著者	SATAKE Iwao, IDE Kazutoshi, FUKUNAGA Tomoko, MAEDA Tamaki, HAYAKAWA Katumitu
journal or publication title	鹿児島大学理学部紀要. 数学・物理学・化学
volume	24
page range	61-69
別言語のタイトル	ドデシルトリメチルアンモニウム-アルカンスルホン酸塩水溶液中におけるミセル物性
URL	http://hdl.handle.net/10232/00004003

THE MICELLAR PROPERTIES OF DODECYLTRIMETHYLAMMONIUM ALKANESULFONATES IN AQUEOUS SOLUTIONS

By

Iwao SATAKE, Kazutoshi IDE, Tomoko FUKUNAGA,
Tamaki MAEDA and Katumitsu HAYAKAWA

(Received September 3, 1991)

Abstract

The potentiometric and fluorescence probe techniques were applied for the determination of the micellar parameters of dodecyltrimethylammonium alkanesulfonates with chain length from 1 to 6 in aqueous solutions. The critical micelle concentration was found to decrease regularly with increasing counterion chain length, while the reverse changes were found for the degree of counterion binding to the micelle and the micelle aggregation number. The solubilizing properties of these surfactant solutions were also studied. These surfactants are supposed to form a mixed micelle in which the hydrocarbon tail of the counterion participates in the hydrophobic interaction with the micellar core.

Introduction

A number of papers have been concerned with the micellar properties of ionic surfactants with organic counterions (1-23). In these surfactant solutions, an additional hydrophobic interaction between micelle core and hydrophobic moiety of counterion plays an important role in determining the micellar properties such as critical micelle concentration (CMC), micelle aggregation number (m), and the degree of counterion binding to the micelle (β). For example with ionic surfactants with homologous series counterions, an increase in the counterion chain length is always accompanied by a regular decrease in CMC (1-5), while a regular increase in β (1, 2, 5, 6), and m (5). Similar characteristic behaviors are also noted for the mixed solutions of anionic and cationic surfactants (7-9), as well as for the ionic surfactants with tetraalkylammonium counterions (10-12). In the case of aromatic counterions, such micellar parameters as CMC, m , and β depend significantly on the substituent position (13-20). A typical example is decyltrimethylammonium bromide in excess sodium hydroxybenzoate solutions, in which CMC and m of ortho isomer are quite

* Department of Chemistry, Faculty of Science, Kagoshima University, Kagoshima 890, Japan.

different from those of metha and para isomers (16).

These studies shed light on the importance of the structure and hydrophobicity of organic counterion in the micellization process of ionic surfactants. So far as we now, however, little is known about the ionic activities in solutions of ionic surfactants with organic counterions. In this paper, we studied the micellar properties of dodecyltrimethylammonium alkanesulfonates with hydrocarbon chain length (n) from 1 to 6, with special attention to the concentration dependences of surfactant ion and counterion activities.

Experimental

Materials. The stock solutions of dodecyltrimethylammonium alkanesulfonates (DTAC $_n$ S) were prepared by titrating dodecyltrimethylammonium hydroxide (DTA OH) with the corresponding alkanesulfonic acid (HC $_n$ S). DTA OH and HC $_n$ S were prepared by passing the aqueous solutions of DTABr (Tokyo Kasei Kogyo Co., Ltd., guaranteed grade) and NaC $_n$ S (Tokyo Kasei Kogyo Co., Ltd., extra pure grade) through an anion-exchange column (Amberlite IRA-400) in the OH $^-$ state and a cation-exchange column (Amberlite IR-120B) in the H $^+$ state, respectively. Pyrene (purity >98%, Wako Pure Chemical Industries Co., Ltd.) was passed through silica gel in cyclohexane solution and recovered as white crystals.

Electromotive Force Measurements. The surfactant ion activities in DTAC $_n$ S solutions were measured potentiometrically by using the following nitrobenzene liquid membrane electrode.

Reference electrode (Ag-AgCl)|1 mol dm $^{-3}$ NH $_4$ Cl agar bridge|Reference solution (DTABr, 1 mmol dm $^{-3}$)|Nitrobenzene (DTADS, 5 mmol dm $^{-3}$)|Sample solution|1 mol dm $^{-3}$ NH $_4$ Cl agar bridge|Reference electrode (Ag-AgCl)

Here, DTADS denotes dodecyltrimethylammonium dodecylsulfate which was prepared by mixing aqueous solutions of DTABr and NaDS, and recrystallized twice from acetone. The experimental setup of the cell is described elsewhere (24).

The following cell based on the anion-exchange membrane (Tokuyama Soda Co., Ltd., Neosepta AVS-4T) was used for the determinations of counterion activities.

Reference electrode (Ag-AgCl)|1 mol dm $^{-3}$ NH $_4$ Cl agar bridge|Reference solution (DTAC $_n$ S, 1 mmol dm $^{-3}$)|Anion-exchange membrane|Sample solution|1 mol dm $^{-3}$ NH $_4$ Cl agar bridge|Reference electrode (Ag-AgCl)

Prior to the measurements with DTAC $_n$ S solutions, the anion-exchange membrane was soaked in 1 mol dm $^{-3}$ NaC $_n$ S solution for a week.

The electromotive forces of these cells were measured with an accuracy of ± 0.1 mV by using a Corning Digital 112 pH Research Meter. The electromotive forces of these cells can be described as

$$E_i = E_i^\circ + S_i \log a_i, \quad i = + \text{ or } - \quad (1)$$

where E_i° refers to the standard electromotive force, a_i to the ionic activity of component i , and S_i to the observed slope of E_i vs. $\log a_i$ plot, respectively. The estimation of the

surfactant ion and counterion activity coefficients requires a knowledge of the respective ionic radius in solution. According to Shinoda and Soda (25), the partial molal volume per methylene group of singly dispersed surfactant ion is the order of $15 \text{ cm}^3 \text{ mol}^{-1}$. The use of this value together with the volumes of ionic head groups (26) permits the tentative estimation of the radii of DTA^+ and C_nS^- . The ionic radii so determined are 0.26, 0.29, 0.31, 0.33, 0.35, and 0.36 nm for C_nS^- with $n=1$ to 6, and 0.44 nm for DTA^+ , respectively. In solutions of DTAC_nS , the semilogarithmic plot of E_+ vs. a_+ gave a straight line down to *ca.* $1 \times 10^{-4} \text{ mol dm}^{-3}$ with a slope (S_+) of -60.0 mV for $n=1$, -59.6 mV for $n=2$, -59.5 mV for $n=3$, and -59.1 mV for $n=4$, respectively. An excellent agreement between the observed slopes and an ideal Nernst slope (59.2 mV at 25°C) suggests that the nitrobenzene liquid membrane is completely permselective to dodecyltrimethylammonium ion. The semilogarithmic plot of E_- vs. a_- also gave a straight line down to *ca.* $1 \times 10^{-3} \text{ mol dm}^{-3}$ with a slope (S_-) of 56.7, 56.3, 56.6, 55.8, 56.0, and 56.2 mV for $n=1$ to 6, respectively. Although observed slopes are somewhat smaller than the ideal Nernst slope, we can still estimate the counterion activity (a_-) from Eq. 1, since these slopes are reproducible on replicate measurements.

Fluorescence Decay Measurements. Fluorescence decay curves were measured by using the time-resolved fluorescence spectrometer (NAES-1100, Horiba Ltd.). Pyrene was solubilized in DTAC_nS solutions by sonicating the mixture for 30 min in such a way that the average number of pyrene molecules per micelle is less than 1. Prior to the measurements, all of the sample solutions were thoroughly deoxygenated 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 solubilized pyrene was determined spectrophotometrically at 337 nm ($\epsilon=48400$).

Solubilization Measurements. The solubilization of toluene in ETAC_nS solutions was determined spectrophotometrically at 261.5 nm.

All measurements were conducted at 25°C .

Results and Discussion

In Figs. 1 and 2 are shown the plots of E_+ and E_- vs. the logarithm of DTAC_nS concentration (C), respectively. The break point in these figures corresponds to the CMC (C_o) at a given counterion chain length (n). In analogy with a variety of ionic surfactants with inorganic counterions (27 and references therein), an increase in the surfactant concentration above CMC causes a monotonous decrease in the surfactant ion activity (a_+), while the reverse change in the counterion activity (a_-). As is clearly shown in Fig. 2, however, an increase in n results in a successive decrease not only in C_o but in the slope of E_- vs. $\log C$ plots above the CMC. Figure 3 shows the typical plots of a_- vs. C constructed from Fig. 2 for DTAC_6S . The counterion activity is seen to increase linearly with increasing concentration through a break point which corresponds to C_o . Similar results are also obtained for all of the surfactants studied. The values of C_o thus

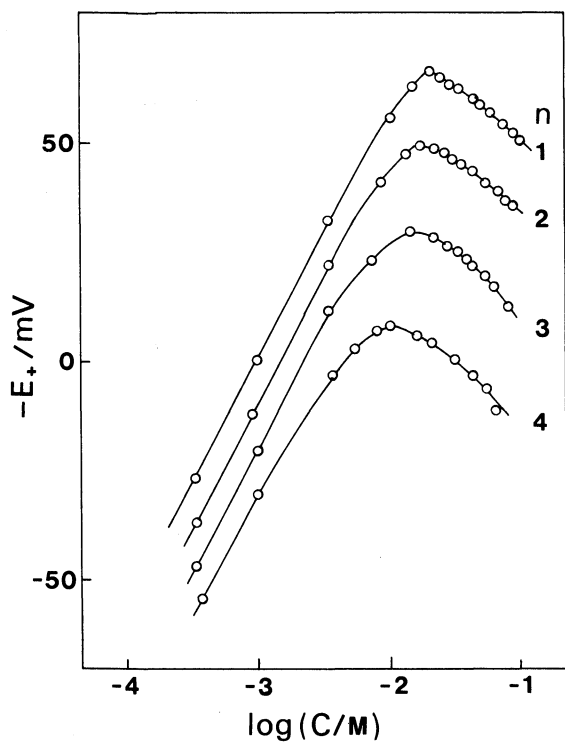


Fig. 1 The semilogarithmic plots of E_+ vs. C for DTAC_nS with $n=1$ to 4. The curves for $n=2, 3,$ and 4 are displaced downward by 10, 20, and 30 mV, respectively.

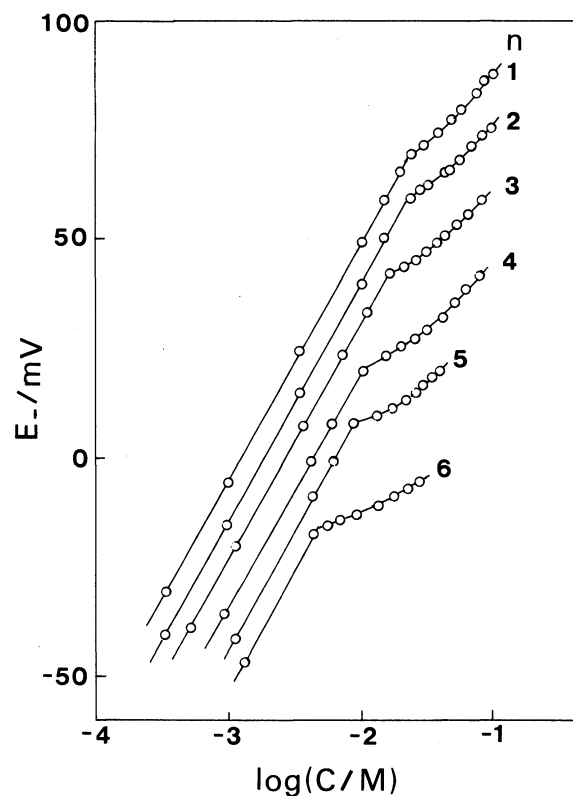


Fig. 2 The semilogarithmic plots of E_- vs. C for DTAC_nS with $n=1$ to 6. The curves for $n=2, 3, 4, 5,$ and 6 are displaced downward by 10, 20, 30, 40, and 50 mV, respectively.

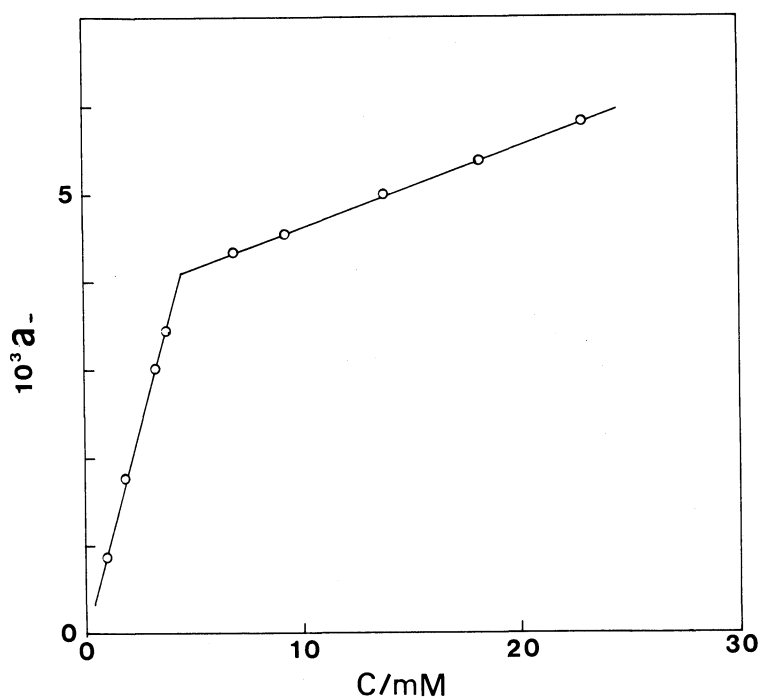


Fig. 3 The typical plot of a_- vs. C for DTAC_6S .

Table 1. The Micellar Parameters of DTAC_nS

Surfactant	$\frac{C_0}{\text{mmol dm}^{-3}}$	β	m	$\frac{S}{\text{mol/mol surfactant}}$
$n=1$	22.9	0.68*	65	0.41
$n=2$	20.8	0.72*	67	0.48
$n=3$	14.7	0.76*	69	0.60
$n=4$	11.6	0.80*	74	0.87
$n=5$	7.2	0.84**	84	2.03
$n=6$	4.5	0.90**	205	2.53

*: The average of the values estimated from Eqs. 2 and 3.

** : The value estimated from Eq. 3.

determined are summarized in the second column of Table 1 and plotted in Fig. 5 against n . As would be expected, the C_0 vs. n profile resembles the results obtained for similar ionic surfactants with homologous series counterions (1–5, 7–9). The observed decrease in C_0 suggests that the dodecyltrimethylammonium ions aggregate with alkanesulfonate ions to give rise to a mixed micelle in which the hydrocarbon chain of the latter extends toward the micellar core.

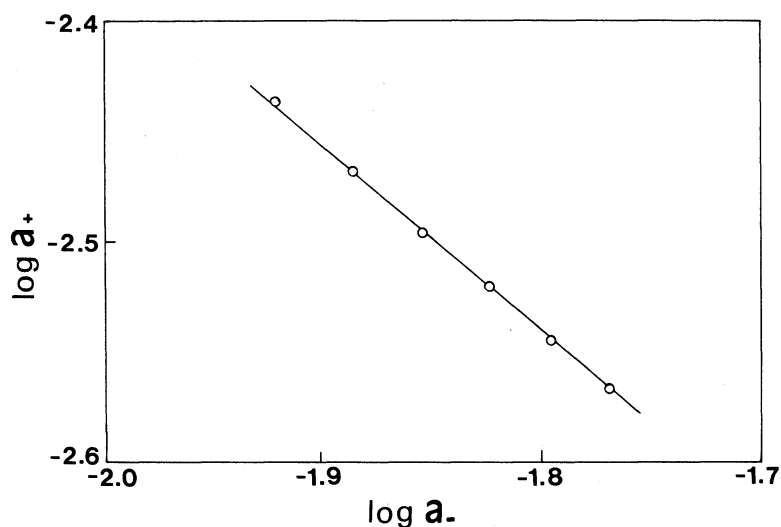
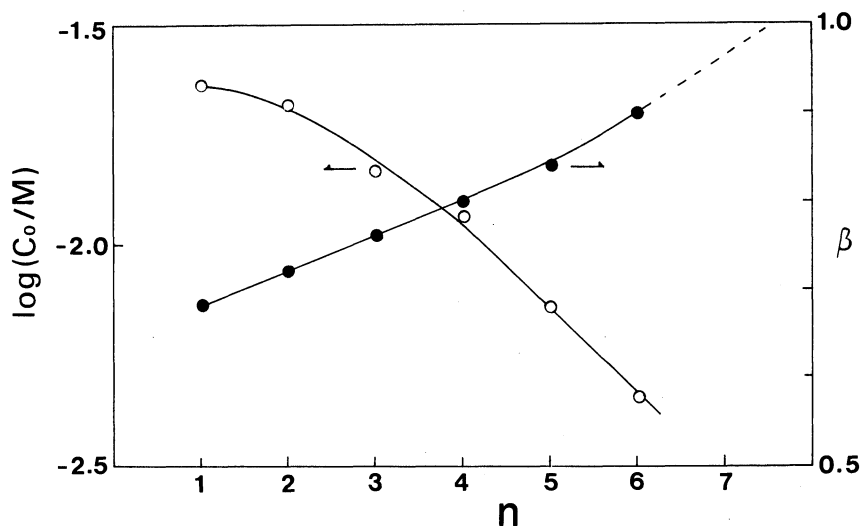
An increase in n should necessarily be accompanied by a regular increase in β , since the hydrophobic interaction increases with increasing counterion chain length. In fact, the conductometric determinations of β for alkylammonium and alkyltrimethylammonium dodecylsulfates (1) and dodecyltrimethylammonium alkanates (5) revealed that the value of β increases monotonically as n increases. Similar behaviors were also obtained by NMR self-diffusion measurements for decylammonium alkanates (2, 6). In the present systems, we estimated the value of β from a_- vs. C plots shown in Fig. 3 according to the method first advanced by Botré *et al.* (28) and later extended by Maeda and Satake (27) to include the concentration dependences of counterion activity coefficient and the concentration of monomeric surfactant ion above CMC. According to this treatment, the value of β can be described as

$$a_-/a_-^0 = 1 + (1 - \beta)(C - C_0). \quad (2)$$

Here, a_-^0 refers to the counterion activity at the CMC. An information about β can otherwise be obtained by the charged phase separation model (29) written as $a_+ a_-^\beta = \text{constant} = K$ or

$$\log a_+ = -\beta \log a_- + \log K. \quad (3)$$

Thus, $\log a_+$ vs. $\log a_-$ plot is expected to give a straight line with the slope of $-\beta$ provided that this model is also applicable to the present systems. The typical example for DTAC₄S is shown in Fig. 4. Similar results are obtained for all of the systems studied. These observations imply that the charged phase separation model is valid for solutions of ionic surfactants not only with inorganic counterions but with organic counterions which lead to the mixed micelle formation. The values of β thus determined are summarized in the third

Fig. 4 The typical plot of $\log a_+$ vs. $\log a_-$ for DTAC₄S.Fig. 5 The changes in C_0 and β with counterion chain length, n . \circ : C_0 . \bullet : β .

column of Table 1 and plotted against n in Fig. 5. It is interesting to note that the value of β increases monotonically with increasing counterion chain length and tends eventually to unity at $n=7\sim 8$. This in turn suggests that the mixed micelle with $n=7\sim 8$ behaves virtually as a nonionic micelle composing apparently of 1:1 ionic complex unless precipitation occurs.

We can now estimate the transfer free energy per methylene group (ω) of counterion from bulk to micellar phase. By taking into account the fact that the transfer free energy of a homologous series hydrocarbon is a linear function of the chain length (30), the standard free energy change associated with the micellization process of DTA⁺ and C_nS⁻ can be written as $\Delta\mu^0 + \beta n\omega$, where $\Delta\mu^0$ denotes the transfer free energy of DTA⁺. On ignoring the activity coefficients, we immediately have

$$(1 + \beta) \ln (C_o/55.5) = (\Delta\mu^o + \beta n \omega) / kT. \quad (4)$$

This equation implies that $(1 + \beta) \ln (C_o/55.5)$ is linearly dependent on βn , since $\Delta\mu^o$ is constant in the present systems. The resulting plot shown in Fig. 6 gives in fact a straight line above $n=4$. It should be noted that the estimated value of ω of -1.2 kT is comparable to that of -1.1 kT for ionic surfactants with inorganic counterions (31). The decrease in slope at shorter chain length indicates that the contribution of the first two or three methylene groups of alkanesulfonate ion to the hydrophobic interaction with micellar core is much smaller than that of the rest of the hydrocarbon chain.

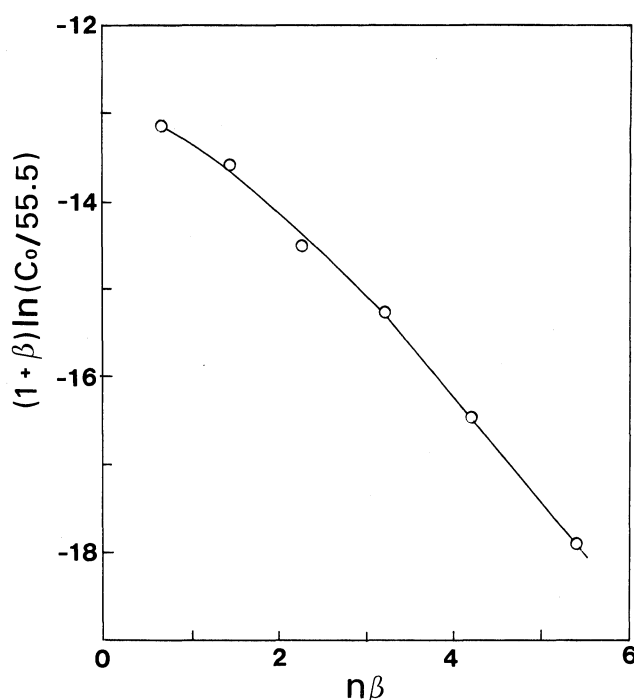


Fig. 6 The plot of $(1 + \beta) \ln (C_o/55.5)$ vs. $n\beta$.

In their study of the micellar properties of dodecyltrimethylammonium alkanates, Brady *et al.* (5) reported the regular increase in the micelle aggregation number (m) with counterion chain length. A similar increase in m was also noted by Anacker and Underwood (7) for decyltrimethylammonium bromide in 0.5 mol dm^{-3} sodium alkanates. In this connection, we determined the counterion chain length dependence of m by fluorescence probe technique. In Fig. 7 is shown the typical fluorescence decay curve of pyrene solubilized in DTAC₃S solution at $C=50 \text{ mmol dm}^{-3}$. This type of decay curve has been known to be described by the following equation based on the Poisson distribution of the probe molecules in micelles (32).

$$I = I_o \exp [R \{ \exp (-k_E t) - 1 \} - k_1 t] \quad (5)$$

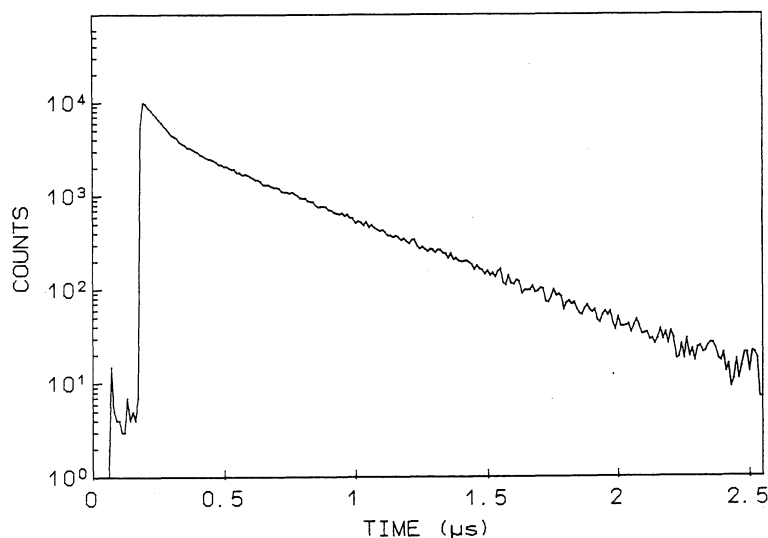


Fig. 7 The typical fluorescence decay curve of solubilized pyrene in DTAC₃S solution at $C=50$ mmol dm⁻³.

Here, 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.*, $R=[\text{pyrene}]/[\text{micelle}]$, respectively. The values of I_0 , R , k_E , and k_1 were determined by the nonlinear least squares treatment based on modified Marquardt method. The value of m can then be evaluated from the following relation.

$$m=R(C-C_0)/[\text{pyrene}]. \quad (6)$$

It must be kept in mind, however, that the value of m calculated from Eq. 6 for the present systems represents the number of dodecyltrimethylammonium ions per micelle. The results are summarized in the fourth column of Table 1. The value of m was virtually independent of the surfactant concentration regardless of the counterion chain length. It is seen that the value of m increases regularly with increasing n upto $n=5$ and rises abruptly to 205 at $n=6$. A drastic increase in m at $n=6$ will be ascribed to an increase in β . In such a system as $\beta=0.90$, the electrostatic free energy term of micelle formation is expected to be small enough to facilitate the micellar growth.

Zhao and Li studied the solubilization of *n*-octane and *n*-octanol by polyoxyethylenated cationic-anionic surfactants (23). In equimolar mixed surfactant solutions ($C_8H_{17}\cdot C_6H_4\cdot (OC_2H_4)_{9,8}\cdot SO_4Na \sim C_pH_{2p+1}NC_5H_5Br$), they found that the solubilization of octane increases regularly from 1.31 for $p=8$ to 2.58 mol/mol surfactant for $p=16$. This is also the case for the present systems. The last column of Table 1 shows the solubilization of toluene (S) in mol/mol micelle forming surfactant in DTAC_{*n*}S solutions. In conformity with the result obtained by Zhao and Li, the value of S increases rapidly with increasing counterion chain length. Apart from the detailed structural consideration of solubilized

micelle, an abrupt increase in S at $n=5\sim 6$ will be attributed to an increase in the overall hydrophobic moiety of the mixed micelle arising from the increase both in m and β . The change in micellar shape presumably play an important role in determining the value of S , especially at higher counterion chain length.

References

1. A. Packter and M. Donbrow, *J. Pharm. Pharmacol.*, **15**, 317 (1963).
2. M. Jansson and B. Jönsson, *J. Phys. Chem.*, **93**, 1451 (1989).
3. H. Hoffmann, H. Nüsslein and W. Ulbricht, "Micellization, Solubilization, and Microemulsions", Ed. by K. L. Mittal, Vol. 1, P 263 (1977), Plenum Press, New York and London.
4. S. Kaneshina, O. Shibata, M. Nakamura and M. Tanaka, *Colloids and Surfaces*, **6**, 73 (1983).
5. J. E. Brady, D. F. Evans, G. G. Warr, F. Grieser and B. W. Ninham, *J. Phys. Chem.*, **90**, 1853 (1986).
6. M. Jansson and P. Stilbs, *J. Phys. Chem.*, **91**, 113 (1987).
7. E. W. Anacker and A. L. Underwood, *J. Phys. Chem.*, **85**, 2463 (1981).
8. M. Almgren and S. Swarup, *J. Phys. Chem.*, **87**, 876 (1983).
9. Z.-J. Yu and G.-X. Zhao, *J. Colloid Interf. Sci.*, **130**, 414 (1989).
10. P. Mukerjee, K. J. Mysels and P. Kapauan, *J. Phys. Chem.*, **71**, 4166 (1967).
11. K. M. Kale and R. Zana, *J. Colloid Interf. Sci.*, **61**, 312 (1977).
12. T. Inoue, M. Ikeuchi, T. Kuroda and R. Shimozawa, *Bull. Chem. Soc. Jpn.*, **54**, 2613 (1981).
13. S. Gravsholt, *J. Colloid Interf. Sci.*, **57**, 575 (1976).
14. F. M. Menger, D. Y. Williams, A. L. Underwood and E. W. Anacker, *J. Colloid Interf. Sci.*, **90**, 546 (1982).
15. A. L. Underwood and E. W. Anacker, *J. Phys. Chem.*, **88**, 2390 (1984).
16. A. L. Underwood and E. W. Anacker, *J. Colloid Interf. Sci.*, **106**, 86 (1985).
17. A. L. Underwood and E. W. Anacker, *J. Colloid Interf. Sci.*, **117**, 296 (1987).
18. C. Gamboa, H. Rios and L. Sepulveda, *J. Phys. Chem.*, **93**, 5540 (1989).
19. A. B. Rezvani, A. L. Underwood and E. W. Anacker, *J. Colloid Interf. Sci.*, **142**, 294 (1991).
20. S. J. Bachofer, U. Simonis and T. A. Nowicki, *J. Phys. Chem.*, **95**, 480 (1991).
21. K. L. Stellner, J. C. Amante, J. F. Scamehorn and J. H. Harwell, *J. Colloid Interf. Sci.*, **123**, 186 (1988).
22. T. Kato, M. Iwai and T. Seimiya, *J. Colloid Interf. Sci.*, **130**, 439 (1989).
23. G. Zhao and X. Li, *J. Colloid Interf. Sci.*, **144**, 185 (1991).
24. I. Satake, S. Noda and T. Maeda, *Bull. Chem. Soc. Jpn.*, **56**, 2581 (1983).
25. K. Shinoda and T. Soda, *J. Phys. Chem.*, **67**, 2072 (1963).
26. J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).
27. T. Maeda and I. Satake, *Bull. Chem. Soc. Jpn.*, **57**, 2396 (1984).
28. C. Botré, V. L. Crescenzi and A. Male, *J. Phys. Chem.*, **63**, 650 (1959).
29. T. Sasaki, M. Hattori, J. Sasaki and K. Nukina, *Bull. Chem. Soc. Jpn.*, **48**, 1397 (1975); M. Koshinuma and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **48**, 2755 (1975).
30. C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd Ed., John Wiley & Sons, New York (1980), Chap. 2.
31. K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants", Academic Press, New York (1963), Chap. 1.
32. S. S. Atik, M. Nam and L. A. Singer, *Chem. Phys. Lett.*, **67**, 75 (1979).