The Critical Micelle Concentrations of Some Binary Mixtures Containing N, N, N, N, N, N-hexamethyl-1, 20-icosane- diyldiammonium Alkanedioate

The Critical Micelle Concentrations of Some Binary Mixtures Containing N, N, N, N′, N′, N′-hexamethyl-1, 20-icosane-diyldiammonium Alkanedioate

Iwao SATAKE, Shinji OOGA, Tamaki MAEDA, and Katumitu HAYAKAWA
(Received July 5, 1999)

Abstract

The conductometric and fluorescence probe studies were carried out for some binary mixtures containing N, N, N, N′, N′, N′-hexamethyl-1, 20-icosanediyldiammonium alkanedioate $[(CH_3)_3 {}^+N(CH_2)_{20} N^+(CH_3)_3]$ $[{}^-OOC(CH_2)_n COO^-]$ (HEA-C_n). An ideal mixing treatment of the micellar phase reproduces well the critical micelle concentration (cmc) vs. composition curves observed both for HEA-C_4 ~ HEA-C_6 and HEA-C_4 ~ HEA-C_{10} systems. However, this simplified model fails to reproduce the cmc data for HEA-C_{10} ~ dodecyltrimethylammonium chloride (DTAC) and HEA-C_{10} ~ tetradecyltrimethylammonium chloride (TTAC) systems. Although the nonideal behavior appears only at higher mole fractions of DTAC for the former system, it becomes remarkable and extends over whole composition range for the latter system. A tentative treatment based on the regular solution theory gives the interchange energies of -1.1 kT for HEA-C_{10} ~ DTAC and -3.7 kT for HEA-C_{10} ~ TTAC systems, respectively. The fluorescence measurements for these two systems suggest that the local environments around the solubilized pyrene in the mixed micelles are comparable not only to one another but to those in DTAC and TTAC micelles, regardless of the compositions.

Introduction

It has been well known that the micellar parameters of the ionic surfactant solution depend not only on the structure of the surfactant ion but on the electrical and hydrophobic characters of the counter ion. Thus, the ionic surfactant with the α, ω-type counter ion is particularly interesting, since this type of counter ion has two ionic groups at both ends of a long carbon chain which can participate in a hydrophobic interaction with the micellar interior.

Although the studies so far reported are confined mostly to the single surfactant solutions, the interesting features in their micellar properties are elucidated. In solutions of the ionic surfactants with the homologous α, ω-type counter ion, an increase in the carbon chain length (n) of the counter ion is accompanied always by a regular decrease in the critical micelle concentration (cmc) (1-5). However, the degree of counter ion binding (β) and the micelle aggregation number (m) depend significantly on the structures of both surfactant ion and counter ion head groups. For example with 1, 1′-(1, ω-alkanediyl) bispyridinium 1-tetradecanesulfonate, the value of β increases slightly with increasing n, while the value of m goes through a broad minimum around $n = 8$ ~ 10 (6). In contrast, a minimum in β appears at $n = 4$ for bis(decylammonium) dicarboxylate solutions (2). In solutions of α, ω-alkanediammonium bis(dodecyl sulfate) and bis(decyl sulfate), the values of β remain virtually constant, whereas the value of m decreases in the former system but increases in the latter system with increasing n, respectively (3, 4). In the case of

Department of Chemistry and BioScience, Faculty of Science, Kagoshima University, 1-21-35, Korimoto, Kagoshima 890-0065, Japan.

HEA-C$_n$, the value of β increases progressively with increasing n, but a shallow minimum in m appears at $n=4$ (5).

In connection with the micellar properties of the binary mixtures of these surfactants, we studied the cmc and m of the alkanediammonium bis(decyl sulfate) mixtures with $n=4$ and 6, and $n=4$ and 8 (4). In both systems, the value of m decreases rapidly with increasing mole fraction of $n=4$. A striking feature of these systems is the finding that the cmc vs. the composition curves can be well reproduced with the ideal mixing model. This fact suggests that the α, ω-type counter ions behave in the mixed micelles as if simple molecules which have little conformational freedom.

From the standpoint of the nonideality in the micellization process, the binary mixtures of HEA-C$_n$ and the conventional surfactant are particularly interesting, since their structures are considerably different from each other. With this reservation in mind, we performed the conductometric and fluorescence probe studies of some binary mixtures which consist of HEA-C$_{10}$ and the conventional cationic surfactant and of HEA-C$_n$ with different values of n.

Experimental

Materials.

The preparation and purification procedures of HEA-C$_n$ with n of 4, 6, and 10 are described elsewhere (5). Dodecyl- and tetradecyltrimethylammonium chlorides (DTAC, TTAC) were prepared by passing the aqueous solutions of the corresponding bromides (purity $>$99%, Tokyo Kasei Kogyo Co. Ltd.) through an anionic exchange column in the Cl$^-$ state, respectively. The concentrations of DTAC and TTAC stock solutions were determined by poly(vinyl chloride) membrane electrode (7). Pyrene (Aldrich Chemical Company Inc.) was passed through silica gel in a cyclohexane solution and recovered as white crystals after recrystallization from ethanol.

Measurements.

The conductivities of the mixed surfactant solutions were measured by using a Horiba Conductivity Meter ES-14. The fluorescence spectra of pyrene excited at 335 nm were recorded on a Shimazu Spectrofluorophotometer RF-5000. All measurements were conducted at 25℃.

Results and Discussion

Mixtures Consisting of HEA-C$_n$ with Different Values of n

Figure 1 shows the typical plots of the specific conductivity (κ) vs. total molar concentration (C) for binary solutions of HEA-C$_4$ and HEA-C$_6$. The break point in each curve corresponds to the cmc (C_0) at the given mole fraction (R) of HEA-C$_4$ in the mixture. Similar results were also obtained for all of the mixed systems studied. In Fig. 2 are given the C_0 vs. R curves thus determined for HEA-C$_4$ $\sim$ HEA-C$_6$ and HEA-C$_4$ $\sim$ HEA-C$_{10}$ systems. In both cases, the cmc is seen to increase monotonically with increasing R.

The micellar structures of the HEA-C$_n$ are considered to be somewhat different from those of the conventional surfactants even in single surfactant solutions. In this connection, it is important to remember that the α, ω-type surfactants with inorganic counter ions usually form loosely packed micelles (8-11) into which water molecules deeply penetrate (9, 10, 12, 13). In addition, the α, ω-type surfactant ions in the micelle are known to adopt a predominantly stretched form (11, 14, 15) while keeping a spherical shape (9, 11, 16).

Taking these into consideration, the HEA^{2+} ions which are common constituent in the present mixtures are also supposed to adopt the similar stretched conformations in the mixed micelles over whole range of R. Moreover, the bound alkanedioate counter ions on the micellar surface are expected to exclude to some extent the penetrated water molecules by extending their folded hydrocarbon chains toward the miceller interior. This in turn suggests that the mixed micelles in the present systems are more compact than the foregoing α, ω-type surfactant micelles with inorganic counter ions.

In general, the cmc of the binary surfactant mixture can be described as

$$1/C_0 = (1-R)/\gamma_1 C_1^0 + R/\gamma_2 C_2^0, \qquad (1)$$
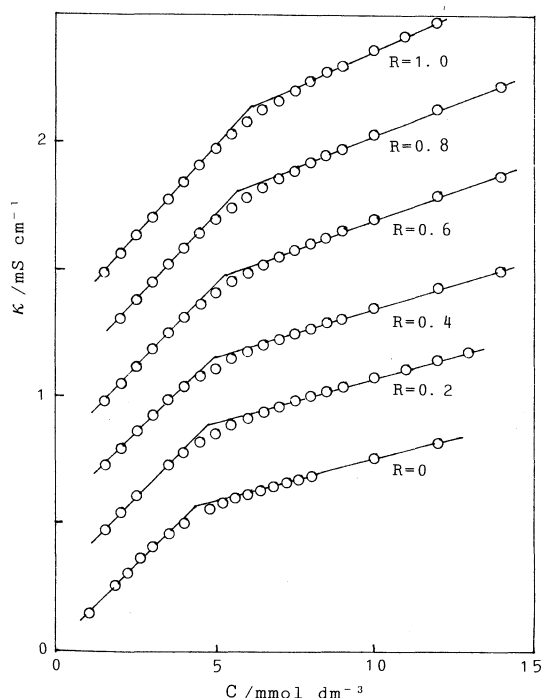
where, C_i^0 ($i=1$ or 2) refers to cmc of the single

Fig. 1. Plots of κ vs. C for mixed solutions of HEA-C$_4$ and HEA-C$_6$. The curves for $R=0.2$, 0.4, 0.6, 0.8, and 1.0 are displaced upward by 0.25, 0.5, 0.75, 1.0, and 1.25 mS cm^{-1}, respectively.

Fig. 2. Plots of C_0 vs. R for HEA-C$_n$ mixed systems.
a ; $n=4$ and 6, $C_1{}^0 =4.52$ mmol dm^{-3}, $C_2{}^0 =6.19$ mmol dm^{-3}
b ; $n=4$ and 10, $C_1{}^0 =0.77$ mmol dm^{-3}
○ ; observed. Solid lines show the calculated curves from Eq. (1) with $\gamma_1 = \gamma_2 = 1$.

surfactant solution of the i-th component and γ_i to the activity coefficient of the i-th component in the mixed micelle, respectively (16). In the present systems, i = 1 and 2 correspond to HEA-C$_6$ (or HEA-C$_{10}$) and HEA-C$_4$, respectively. The solid lines in Fig. 2 show the calculated cmc vs. R curves from Eq. 1 with an assumption of $\gamma_1 = \gamma_2 = 1$. It should be noted that the calculated curves based on an ideal mixing model agree well with the experimental data over whole range of R, in spite of the complicating micellar structures expected for the present systems. In a previous paper (4), we have reported that the cmc vs. composition curves for binary mixtures of α, ω-alkanediammonium bis(decyl sulfate)s with n =4 and 6, and $n=4$ and 8 can be reproduced well with the ideal mixing model. On the basis of this finding, we presumed that the α, ω-alkanediammonium counter ions behave in the mixed micelle as if simple molecules with little conformational freedom by extending the folded carbon chain as deeply as possible toward the micellar core. It is, therefore, highly probable that the alkanedioate counter ions in
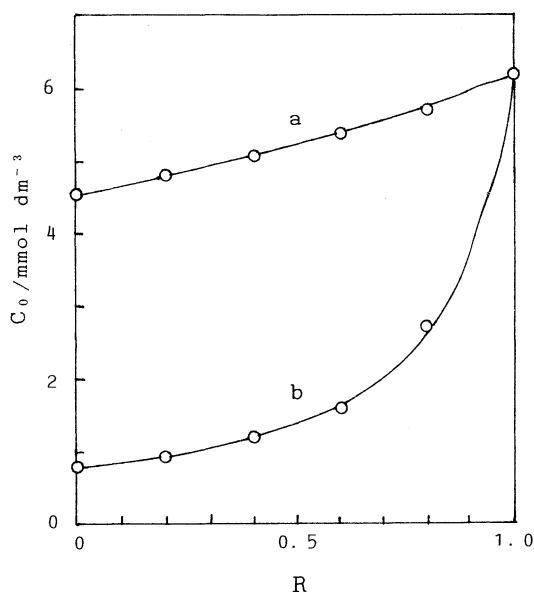
the present systems also behave as simple molecules with the similar conformational characteristics.

Mixtures Consisting of HEA-C$_{10}$ and DTAC (or TTAC)

In their study of the mixed solutions of alkyltrimethylammonium bromide of the carbon chain length p and alkane- α, ω-bis(trimethylammonium) bromide of the carbon chain length q, Zana et al. have found that the mixed micellization takes place in whole composition range for p=10 ～ q=16 and p=14 ～ q=22 systems, while in the range of the mole fraction of α, ω-type surfactant only above 0.5 for p=10 ～ q=12, p=12 ～ q=22, and p=16 ～ q=22 systems (17). The substitution of the monovalent simple counter ion by the divalent α, ω-type counter ion of longer carbon chain length is anticipated to stabilize this type of mixed micelles both through the electrostatic and hydrophobic interactions. Taking this into account, we studied the cmc's of the mixed solutions of HEA-C$_{10}$ and DTAC, and of HEA-C$_{10}$ and TTAC.

As would be expected, the mixed micellizations were observed over whole composition range in these surfactant mixtures. Figures 3 and 4 show the change in cmc with the mole fraction (R) of DTAC
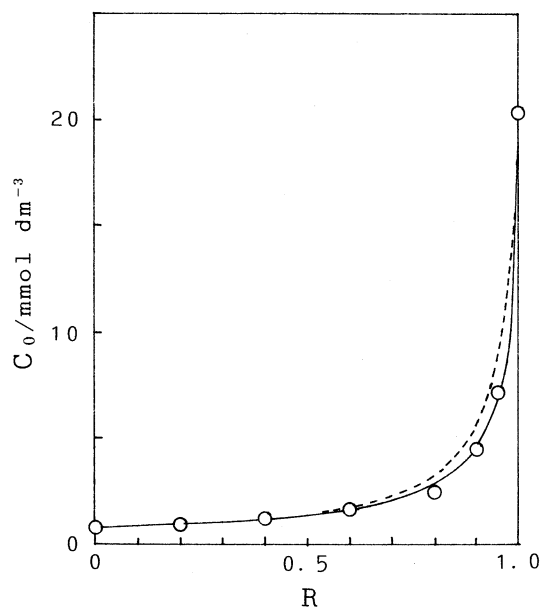

Fig. 3. Plots of C_0 vs. R for mixed solutions of HEA-C_{10} and DTAC.
$C_1{}^0 = 0.77$ mmol dm^{-3}, $C_2{}^0 = 20.3$ mmol dm^{-3},
○ ; observed
---- ; calculated curve from Eq. (1) with $\gamma_1 = \gamma_2 = 1$
―― ; calculated curve from Eqs. (1), (2), and (4) with $\omega = -1.1$ kT

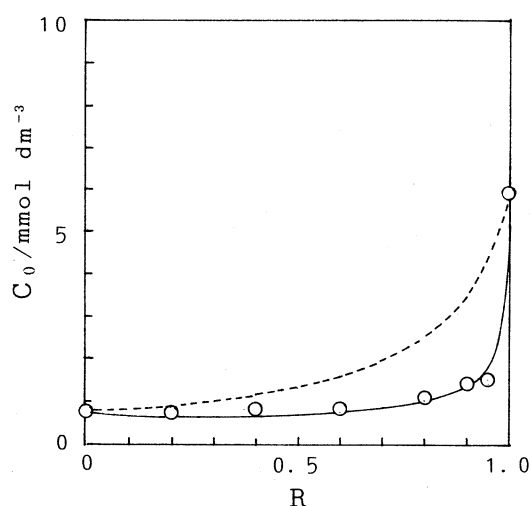Fig. 4. Plots of C_0 vs. R for mixed solutions of HEA-C_{10} and TTAC.
$C_2{}^0 = 5.95$ mmol dm^{-3}, ○ ; observed
---- ; calculated curve from Eq. (1) with $\gamma_1 = \gamma_2 = 1$
―― ; calculated curve from Eqs. (1), (2), and (4) with $\omega = -3.7$ kT

or TTAC, respectively. In these figures, the dotted lines indicate the calculated curves from Eq.(1) with $\gamma_1 = \gamma_2 = 1$.

It has been noted that the docosane- α, ω -bis(trimethylammonium) bromide and the dodecyltrimethylammonium bromide are similar to each other in their micellar parameters such as the hydrodynamic radius of the micelle, the micelle aggregation number, and the binding degree of the counter ions (18). This, in turn, implies that the α, ω -type ion corresponds roughly in micellization behavior to a monovalent conventional surfactant ion with the carbon chain length of half the α, ω -type ion. It seems, therefore, likely that the deviation from an ideal mixing behavior is, if any, rather small for HEA-C_{10} ～ DTAC system. As is clearly shown in Fig. 3, the observed cmc aggrees well with an ideal mixing curve (dotted line) up to R ～ 0.6, though the slight downward deviations appear at higher values of R. However, this is not the case for HEA-C_{10} ～ TTAC system as is shown in Fig. 4. It should be noted that an increase in the carbon chain length of the conventional surfactant ion as small as 2 introduces a remarkable nonideality into the mixed micellization process over whole range of R.

In solutions of the conventional surfactant mixtures, the regular solution theory has been known to reproduce well the cmc vs. R curves characteristic of nonideal mixing systems (16). It is, therefore, interesting to study whether a regular mixing model can be applicable or not to the present systems. According to this treatment (16), the activity coefficients in Eq. (1) are described as

$$\gamma_1 = \exp(\omega x_2{}^2/kT), \quad \gamma_2 = \exp(\omega x_1{}^2/kT), \quad (2)$$

where, x_1 and x_2 refer to the mole fractions of HEA-C_{10} and DTAC (or TTAC) in the mixed micelle, respectively. Moreover, ω represents the interchange energy defined by the number (Z) of the nearest neighbors and the interaction energy (E_{ij}) of the nearest neighbor i-j pair as

$$\omega = Z (E_{12} - E_{11}/2 - E_{22}/2). \quad (3)$$

For a given value of ω, the value of x_1 can be estimated from the following equation as a function of R.

$$x_1 [1 + C_1{}^0 R \exp \{\omega(1-2x_1)/kT\}/\{C_2{}^0(1-R)\}] = 1 \quad (4)$$

The most reliable values of ω were determined so as

to give the best fits of the experimental data. The solid lines in Figs. 3 and 4 show the theoretical cmc vs. R curves calculated from Eqs. (1), (2), and (4) with $\omega = -1.1$ kT for HEA-C_{10} ~ DTAC system and with $\omega = -3.7$ kT for HEA-C_{10} ~ TTAC system, respectively. In both systems, the agreement between observed and calculated curves is satisfactory over whole range of R. As would be expected, the magnitude of ω for HEA-C_{10} ~ DTAC system is considerably small as compared with that for HEA-C_{10} ~ TTAC system. A remarkable increase in the magnitude of ω for HEA-C_{10} ~ TTAC system will presumably be attributed to an increase in the hydrophobic interaction between both components, arising from an increase in the carbon chain length of TTAC.

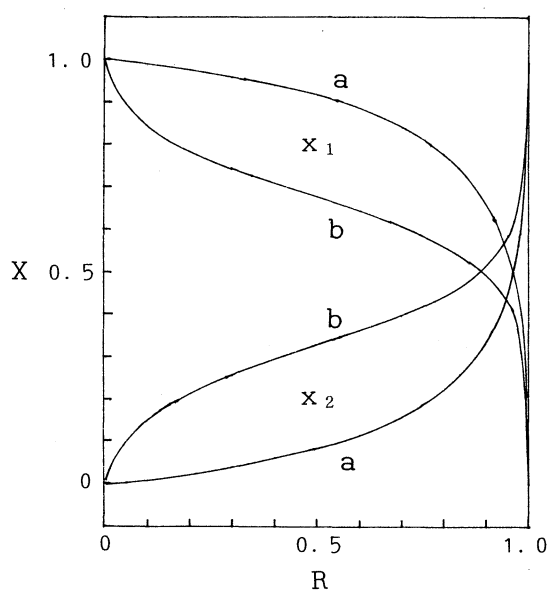Figure 5 shows the micellar composition vs. R

Fig. 5. Dependences of x_1 and x_2 in the mixed micelles on R.
a ; HEA-C_{10} ~ DTAC system, b ; HEA-C_{10} ~ TTAC system

curves calculated from Eq. (4) with the foregoing values of ω. In HEA-C_{10} ~ DTAC system, an effective increase in the mole fraction of DTAC (x_2) is seen to occur only at higher values of R. In the case of HEA-C_{10} ~ TTAC system, however, more rapid increase in the mole fraction of TTAC occurs even at lower values of R, reflecting the foregoing increase in the hydrophobic interaction in this system.

Polarity of the Micellar Interior

It is well known that the ratio of the first and third vibronic bands intensities (I_1/I_3) serves as a measure of the local polarity around the solubilized probe molecules (19). Thus, we measured the fluorescence spectra of pyrene solubilized in the mixed solutions of HEA-C_{10} ~ DTAC and HEA-C_{10} ~ TTAC as a function of R. In both systems, the value of I_1/I_3 remains virtually constant of 1.33 ~ 1.40 over whole range of R at total surfactant concentration of 10 mmol dm^{-3}. Taking into account the inherent errors in the determination of I_1/I_3, the mixed micelles in the present systems are considered to be as compact as those of DTAC and TTAC, regardless of R. This in turn suggests that the folded carbon chains of the bound decanedioate counter ions penetrate effectively into the micellar interior to give rise to the similar compact micellar structure to those of the conventional cationic surfactants.

References

1. Y. Moroi, R. Matuura, T. Kuwamura, and S. Inokuma, *J. Colloid Interface Sci.*, **113**, 225 (1986).
2. P. Li, M. Jansson, P. Bahadur, and P. Stilbs, *J. Phys. Chem.*, **93**, 6458 (1989).
3. I. Satake, T. Fukunaga, T. Maeda, Y. Soeda, and K. Hayakawa, *Bull. Chem. Soc. Jpn.*, **66**, 1618 (1993).
4. I. Satake, J. Kamikado, Y. Yasuda, T. Maeda, and K. Hayakawa, *Bull. Chem. Soc. Jpn.*, **71**, 91 (1998).
5. I. Satake, T. Morita, T. Maeda, and K. Hayakawa, *Bull. Chem. Soc. Jpn.*, **70**, 761 (1997).
6. Y. Moroi, R. Matuura, M. Tanaka, Y. Murata, Y. Aikawa, E. Furutani, T. Kuwamura, H. Takahashi, and S. Inokuma, *J. Phys. Chem.*, **94**, 842 (1990).
7. T. Maeda, M. Ikeda, M. Shibahara, T. Haruta, and I. Satake, *Bull. Chem. Soc. Jpn.*, **54**, 94 (1981).
8. S. Yiv, M. Kale, J. Lang, and R. Zana, *J. Phys. Chem.*, **80**, 2651 (1976).
9. K. Meguro, K. Ikeda, A. Otsuji, M. Taya, M. Yasuda, and K. Esumi, *J. Colloid Interface Sci.*, **118**, 372 (1987).
10. K. Ikeda, M. Yasuda, M. Ishikawa, K. Esumi, K. Meguro, W. Binana-Limbele, and R. Zana, *Colloid Polym. Sci.*, **267**, 825 (1989).
11. M. Yasuda, K. Ikeda, K. Esumi, and K. Meguro, *Bull. Chem. Soc. Jpn.*, **62**, 3648 (1989).
12. S. Yiv and R. Zana, *J. Colloid Interface Sci.*, **77**, 449 (1980).
13. K. Ikeda, K. Esumi, K. Meguro, W. Binana-Limbele, R. Zana, and B. Lindman, *J. Colloid Interface Sci.*, **130**, 290

(1989).

14. T. C. Wong, K. Ikeda, K. Meguro, O. Soderman, U. Olsson, and B. Lindman, *J. Phys. Chem.*, **93**, 4861 (1989).

15. M. Yasuda, K. Ikeda, K. Esumi, and K. Meguro, *Langmuir*, **6**, 949 (1990).

16. Y. Moroi, "Micelles," Plenum Press, New York (1992), Chap.10.

17. R. Zana, Y. Muto, K. Esumi, and K. Meguro, *J. Colloid Interface Sci.*, **123**, 502 (1988).

18. D. C. McKenzie, C. A. Bunton, D. F. Nicoli, and G. Savelli, *J. Phys. Chem.*, **91**, 5709 (1987).

19. K. Kalyanasundaram, *Chem. Soc. Rev.*, **7**, 453 (1978); J. K. Thomas, *Acc. Chem. Res.*, **10**, 133 (1977).