The Micellar Parameters of α,ω-Alkanediammonium Bis(decyl sulfate) Solutions and Their Mixtures

Iwao Satake,* Junichiro Kamikado, Youji Yasuda, Tamaki Maeda, and Katumitu Hayakawa

Department of Chemistry, Faculty of Science, Kagoshima University, Korimoto, Kagoshima 890

(Received July 24, 1997)

Conductometric and fluorescence probe investigations were carried in order to elucidate the micellar parameters of α,ω-alkanediammonium bis(decyl sulfate) with carbon-chain lengths (n) from 4 to 8 and their mixtures. In single surfactant systems, an increase in n was accompanied by a regular decrease in the critical micelle concentration (cmc) and a rapid increase in the micelle aggregation number (m), while the binding degree of the counter ion head group remained virtually constant at 0.90. The transfer free energy per methylene group of the counter ion from aqueous to micellar environments varied with increasing n from -0.35 kT to -0.68 kT. This fact suggests that the hydrocarbon chain of the counter ion, even with $n=4$, can participate in the weak hydrophobic interaction with the micellar interior. In mixed solutions of $n=4$ and 6, and $n=4$ and 8, the cmc vs. y (mole fraction of $n=4$) curves can be well interpreted in terms of the ideal mixing model. In both systems, the value of m gradually increases with increasing y. The fluorescence probe experiments indicate that the local environment around the solubilized pyrene in the mixed micelle resembles one another, regardless of y.

In recent years, the characteristic micellar properties have been reported for ionic surfactants consisting of the conventional monovalent surfactant ion and the α,ω-type divalent counter ion.[1—6] In these surfactant solutions, the hydrophobicity of the intervening carbon chain of the counter ion plays an important role in determining the micellar parameters, such as the critical micelle concentration (cmc), micelle aggregation number (m), and binding degree (β) of the counter ion head group. In their study of the micellar properties of 1,1′-(α,ω-alkanediyl)bispyridinium 1-tetradecanesulfonate ($R_nPy_2(TS)_2$) with the counter ion chain length (n) from 2 to 14, Moroi et al.[1] have found that the cmc remains virtually constant up to $n=6$, but decreases regularly with increasing n in such a way that log cmc vs. n plot gives a straight line above $n\geqq 8$. They have also found that the value of m goes through a minimum around $n=8$—10, while the value of β gradually increases along with an increase in n.[3] Based on the thermodynamic[1] and NMR[4] analyses, the counter ions with $n\geqq 8$ can participate effectively in a hydrophobic interaction with the micellar interior by directing its folded carbon chain toward the micellar core. A similar study was also performed by Li et al.[5] for bis(decylammonium) dicarboxylates ($R_nCa_2(DeA)_2$) with n from 1 to 6. In this case, however, the cmc was found to decrease linearly with increasing n over the whole range of studied n. Moreover, a broad minimum in a β vs. n plot was found to appear at $n=3$—4. In a previous paper,[6] we reported on the micellar parameters of α,ω-alkanediammonium bis(dodecyl sulfate) ($R_nAm_2(DS)_2$) with n from 3 to 6. In this system, log cmc vs. n plot gives the straight line above $n\geqq 4$ and the value of m decreases rapidly with increasing n through a maximum at $n=4$. In addition, the value of β remains virtually constant of 0.95 in contrast to $R_nPy_2(TS)_2$ and $R_nCa_2(DeA)_2$ systems.

These findings reveal that the micellar parameters of this type of ionic surfactant depend not only on the charge spacing of the counter ion, but strongly on the structures of both the surfactant ion and the counter ion head groups. So far as we know, however, little is known about the effect of the surfactant ion chain length on the micellar parameters of this type of ionic surfactant. In this paper, we report on conductometric and fluorescence probe investigations of the micellizations of α,ω-alkanediammonium bis(decyl sulfate) ($R_nAm_2(DeS)_2$) with $n=4$, 6, and 8, and their mixtures.

Experimental

Materials. Sodium decyl sulfate (SDeS) was prepared by the esterification of 1-decanol (Tokyo Kasei Kogyo Co., Ltd.) and purified first by repeated recrystallization from 1-butanol, and then from ethanol. It was then converted to $Ba(DeS)_2$ by mixing aqueous solutions of SDeS and $BaCl_2$. Stock solutions of $R_nAm_2(DeS)_2$ with $n=4$, 6, and 8 were prepared by stirring a large excess of $Ba(DeS)_2$ in a warm solution of $R_nAm_2SO_4$ which had been prepared by the neutralization of α,ω-alkanediamine ($n=4$, 6 from Tokyo Kasei Kogyo Co., Ltd. and $n=8$ from Aldrich Chemical Company, Inc.). The concentration of the stock solution was determined by passing aliquots of a $R_nAm_2(DeS)_2$ solution through a cation-exchange column in the H^+ state, and titrating the resulting HDeS solution with NaOH. The amount of $Ba(DeS)_2$, which is the principal impurity in the stock solutions, was confirmed by atomic-absorption spectrometry to be less than 0.5 mole per cent of $R_nAm_2(DeS)_2$. The Krafft ranges visually estimated for these surfactants were 16.0 °C for $n=4$, 10.3 °C for $n=6$, and 16.5 °C for $n=8$, respectively.

Pyrene and 3,4-dimethylbenzophenone (DMBP) (both from Aldrich Chemical Company, Inc.) were used without further purifications.

Measurements. The conductivities of the surfactant solutions were measured by using a Horiba Conductivity Meter ES-14. The fluorescence spectrum of pyrene excited at 337 nm was recorded on a Shimadzu Spectrofluorophotometer RF-5000. Pyrene was solubilized in surfactant solutions by sonicating the mixtures for 10 min and standing overnight.

All measurements were conducted at 35 °C.

Results and Discussion

Single Surfactant System. The values of cmc (C_0) estimated from the break points in the $\varkappa$ vs. C plots in Fig. 1 are summarized in Table 1. As would be expected from the results reported previously for the $R_nA_m(DS)_2$system,[6] an increase in n from 4 to 8 is accompanied by a regular decrease in the cmc of $R_nAm_2(DeS)_2$. This fact also suggests that the hydrophobic interaction of the hydrocarbon moiety of the counter ion with the micellar interior increases regularly with increasing n. By taking into consideration that the cmc of the divalent metal decyl sulfates are of the order of 5 mmol dm^{-3},[7] this type of hydrophobic interaction is considered to take place even for the R_nAm_2 counter ion with $n=4$.

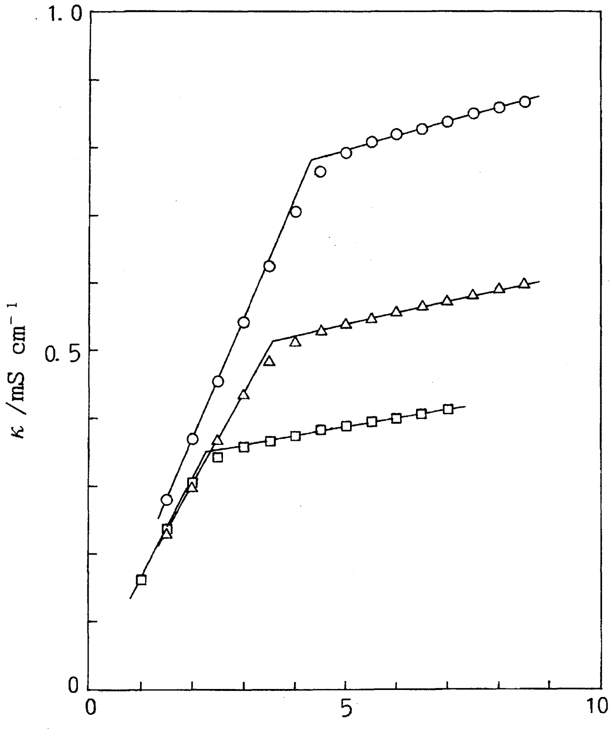

Fig. 1. Plots of $\varkappa$ vs. C for $R_nAm_2(DeS)_2$ solutions. ○; $n=4$, △; $n=6$, □; $n=8$.

The conductivity data permit us to estimate the binding degree (β) of the counter ion head group, since the ratio of the slopes of $\varkappa$ vs. C plots below and above cmc gives approximately $1-\beta$.[8—13] The values of the thus-determined β are 0.89 for n=4 and 6, and 0.91 for n=8, respectively. By taking into account the error inherent in the estimation of β, the observed value of β for the present system should be regarded as being constant at least up to n=8. In a previous paper,[6] we reported the same constancy of β for $R_nAm_2(DS)_2$ system. It is, however, important to note that quite different behaviors have been observed for the $R_nPy_2(TS)_2$[3] and $R_nCa_2(DeA)_2$[5] systems. In the former system, the value of β increases monotonically with increasing n up to 14, while in the latter system, it shows a minimum at $n=4$. In all systems, the value of β is expected to increase along with an increase in the foregoing hydrophobic interaction between the counter ion and the micellar interior. However, this is not the case for the $R_nAm_2(DeS)_2$ and $R_nCa_2(DeA)_2$[5] systems. Moreover, β vs. n and cmc vs. n relationships for these systems are considerably different from each other, in spite of their structural resemblance. This fact together with the results for the $R_nPy_2(TS)_2$ system reflect the importance of the structures, possibly the hydrated radii, of both the counter ion and the surfactant ion head groups in determining the n dependences of the micellar parameters of this type of ionic surfactant. In analogy with conventional homologous-series surfactants, such as sodium alkyl sulfates,[14] the observed value of β for $R_nA_m(DeS)_2$ is slightly smaller than that of 0.95 for $R_nAm_2(DS)_2$.

We can now estimate the free energy change ($\Delta\mu^0$) for transferring one methylene group of the counter ion from an aqueous environment to micellar environment on the basis of the following equation[1]

$$\Delta\mu^0 = -(1+2/\beta)RT(\Delta\ln C_0/\Delta n). \qquad (1)$$

The substitution of the data for n=4 and 6, and n=6 and 8 into Eq. 1 gives $\Delta\mu^0$ of -0.35 RT and -0.68 RT, respectively. A comparison of the resulting $\Delta\mu^0$ with that of -1.1 RT for the usual ionic surfactants with inorganic counter ions[15] also supports that the weak hydrophobic interaction between the R_nAm_2 ion and the micellar interior takes place, even with

Table 1. The Micellar Parameters of $R_nAm_2(DeS)_2$ Mixed Systems

	$n=4$—6				$n=4$—8		
	C_0				C_0		
y	mmol dm^{-3}	m	I_1/I_3	y	mmol dm^{-3}	m	I_1/I_3
0 (n=6)	3.55	145	1.16	0 (n=8)	2.22	181	1.11
0.2	3.65	137	1.16	0.2	2.53	167	1.12
0.4	3.80	131	1.16	0.4	2.77	151	1.12
0.6	3.93	130	1.15	0.6	3.11	145	1.12
0.8	4.14	127	1.17	0.8	3.60	144	1.15
1.0 (n=4)	4.30	115	1.19				

n=4. In view of the subsequent increase in the magnitude of $\Delta\mu^0$, the folded carbon chain of the counter ion with $n>8$ is supposed to effectively participate in this type of hydrophobic interaction with $\Delta\mu^0$, which is comparable to that for the usual surfactant ion. In fact, Moroi et al.[1] have obtained $\Delta\mu^0$ of $-1.2\,RT$ for $R_nPy_2(TS)_2$ with $n \geqq 8$.

In order to evaluate the polarity of the micellar interior, we measured the fluorescence spectra of pyrene solubilized in $R_nAm_2(DeS)_2$ solutions, since the ratio of the first and third vibronic bands intensities (I_1/I_3) gives a measure of the local polarity around the probe molecule.[16] The thus-obtained values of I_1/I_3 at 10 mmol dm^{-3} are given in Table 1. It should be noted that the value of I_1/I_3 is virtually independent of n and comparable to that of 1.12 for SDeS micelle. This in turn suggests that the $R_nAm_2(DeS)_2$ micelle is as compact as that of the SDeS micelle in spite of the penetration of the folded carbon chain of the α,ω-type counter ion into the micellar core.

The fluorescence quenching technique based on the following equation permits us to estimate the value of m[17]

$$\ln(I_0/I_q) = mC_q/2(C - C_0). \tag{2}$$

Here, I_0 and I_q refer to the fluorescence intensities of pyrene with and without a quencher (DMBP), and C_q to the concentration of the quencher, respectively. Figure 2 shows typical plots of $\ln(I_0/I_q)$ vs. C_q for n=4, 6, and 8 at C=10 mmol dm^{-3}. The results are given in Table 1. In a previous paper,[6] we reported that the value of m for the $R_nAm_2(DS)_2$ system decreases regularly from 247 at n=4 to 162 at n=6. A similar decrease in m with n has also been noted for the $R_nPy_2(TS)_2$ system up to n=8.[3] In contrast to these systems, the observed value of m for the present system is seen to increase rapidly with increasing n. It should be noted that the decrease in the carbon chain length of the surfactant ion as small as 2 bring about the reverse change in the n dependence of m, though the origin of this anomalous behavior remains unclear at the present stage.

Mixed Surfactant System. In view of the flexibility of the hydrocarbon chain of the α,ω-type counter ion, it is interesting to study the micellar parameters of the mixed surfactants with different counter ion chain lengths. In Fig. 3 are shown the changes in the cmc of the mixed solutions of n=4 and 6, and n=4 and 8 with the mole fraction (y) of n=4 in the mixture. In both systems, the cmc increases monotonically with increasing y in a similar manner as the conventional anionic surfactant mixtures with inorganic counter ions.[15] In mixed micelles, the binding degree of the respective counter ion should necessarily depend on y. In the present systems, however, it seems to be reasonable to assume that the overall binding degree of two kinds of counter ions remains approximately constant over whole range of y, since the value of β for a single surfactant system is virtually independent of n. With this simplification, the cmc (C_0) of the mixed system can be described by the following equation[18]

$$1/C_0 = y/\gamma_1 C_1^0 + (1-y)/\gamma_2 C_2^0. \tag{3}$$

Here, γ_1 and γ_2 refer to the activity coefficients for n=4 and n=6 or 8 in the mixed micelle, and C_1^0 and C_2^0 to the respective cmc in the single surfactant solutions. The solid lines in Fig. 3 show the calculated cmc curves from Eq. 3 with an additional assumption of ideal mixing of two components ($\gamma_1=\gamma_2\simeq 1$). The fact that the calculated curves well reproduce the experimental data supports the validity of the underlying assumptions. Thus, the R_nAm_2 counter ions seem to behave in the mixed micelle as if simple molecules in which their flexible carbon chain has little conformational freedom. With this reservation in mind, the separated ionic

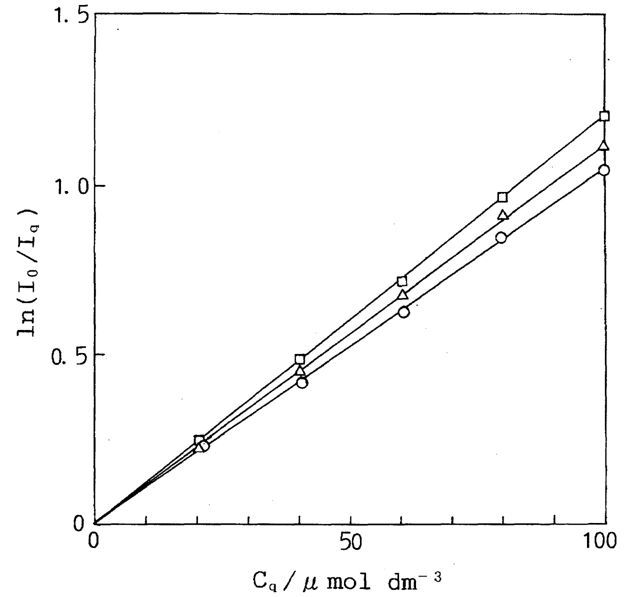

Fig. 2. Plots of $\ln(I_0/I_q)$ vs. C_q for $R_nAm_2(DeS)_2$ solutions at 10 mmol dm^{-3}. [Pyrene]=2 μmol dm^{-3} ○; n=4, Δ; n=6, □; n=8.

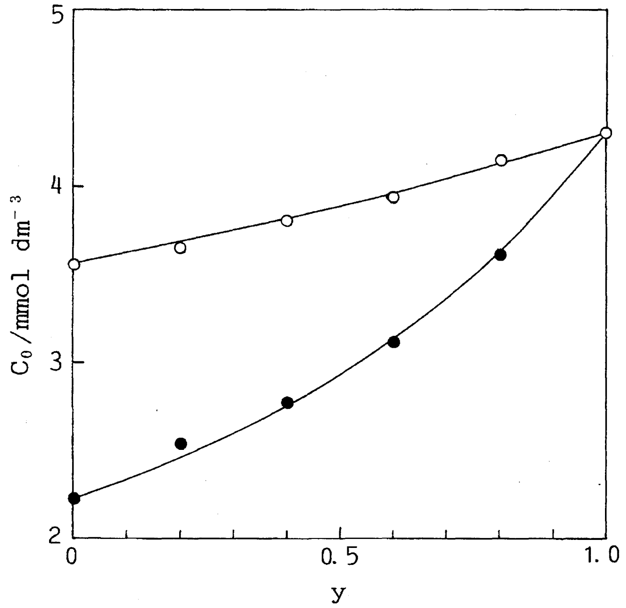

Fig. 3. Plots of C_0 vs. y for $R_nAm_2(DeS)_2$ mixed systems. ○; n=4 and 6, ●; n=4 and 8. Solid lines show the calculated curves from Eq. 3.

head groups of the R_nAm_2 ion are supposed to be located side by side, or at least close, to each other at the micellar surface so that the folded carbon chain may extend as deeply as possible toward the micellar core.

The changes in m and I_1/I_3 with y are summarized in Table 1. It can be immediately seen that the values of I_1/I_3 for both mixed systems are similar to one another, regardless of y. This fact suggests that the change in the relative composition of the R_nAm_2 counter ions with different carbon chain length in the mixed micelle little affects the local polarity or the packing state around the solubilized pyrene.

In both systems, a decrease in y is necessarily accompanied by an increase in the overall hydrophobic interaction between the counter ions and micellar interior because of an increase in the relative composition of the counter ion with a longer chain length. Thus, the value of m is anticipated to increase with decreasing y. This is indeed the case for the present systems. In both cases, the value of m is seen to gradually increase as y decreases, though a narrow plateau tends to appear at y=0.4—0.6 for the n=4—6 system and y=0.6—0.8 for the n=4—8 system, respectively.

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