The Micellar Properties of Ionic Surfactants Consisting of the α,ω-Type Surfactant Ion and the Same Type Counter Ion

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The micellar properties of N, N, N, N', N', N'-hexamethyl-1, 20-icosanediyldiammonium, or the corresponding di(1-pyridinium)alkanedioates $^{-}OOC(CH_2)_nCOO^{-}$ ($n = 2$—10), were studied by conductivity and pyrene fluorescence measurements. In both systems, the critical micelle concentration (cmc) varied little up to $n = 4$, but decreased rapidly with a further increase in n. The binding degree (β) of the alkanedioate counter ion was virtually independent of the type of surfactant ion head group and gradually increased from 0.69 at $n = 2$ to 0.91 at $n = 10$. The observed n dependences of cmc and β were similar to those of the conventional ionic surfactants with an α,ω-type counter ion, indicating the importance of the hydrophobic interaction between the hydrocarbon part of the counter ion and the micellar core. On the basis of a phase-separation model, the transfer free energy per methylene group of the counter ion from aqueous-to-micellar environments was estimated to be about -1.0 RT. The fluorescence measurements suggest that the surface layer of the micelle becomes progressively loose as n decreases. The micelle aggregation numbers of the bis (trimethylammonium) salts are of the order of 50.

It is well known that the α,ω-type surfactant ions show considerably different micellar properties than those of the conventional monovalent surfactant ions.[1—17] The presence of separated charges at both ends of a long carbon chain leads not only to increases in the critical micelle concentration (cmc)[1—6,13,14] and the free energy of micelle formation,[1,3,14] but also to a decrease in the micelle aggregation number,[6,9—12,15,16] as compared with those of the corresponding monovalent surfactant ion. They usually form loosely packed micelles[4,6,10,13] into which water molecules deeply penetrate.[5,6,9,10] It is also noted that the α,ω-type surfactant ions adopt a predominantly stretched form[13,15,16] in the micelle while maintaining a spherical shape.[6,11,13]

Studies were also made for the ionic surfactants which consist of a conventional monovalent surfactant ion and an α,ω-type counter ion.[18—23] For a given surfactant ion, an increase in the carbon chain length (n) of the counter ion is always accompanied by a regular decrease in cmc.[18,20,22,23] Thus, the carbon chain of the counter ion with a longer length is considered to fold and participate in a hydrophobic interaction with the micellar core.[18,20,21,23] Although the binding degree (β) of the counter ion head group remains constant for the α,ω-alkanediammonium ion,[23] that for the alkanedioate ion goes through the minimum at $n = 4$.[22]

In view of these findings, an ionic surfactant consisting of an α,ω-type surfactant ion and the same type counter ion is anticipated to show a similar behavior in n dependences of cmc and β to the conventional ionic surfactant with an α,ω-type counter ion, while in the packing state of the micellar interior to an α,ω-type surfactant with an inorganic counter ion. So far as we know, however, little is known about the micellar properties of this type of surfactant. In order to clarify the combined effect of the charge separations of both the surfactant ion and the counter ion on the micellar properties of the ionic surfactant solutions, we carried out conductometric and pyrene fluorescence studies of the micellar properties of N, N, N, N', N', N'-hexamethyl-1, 20-icosanediyldiammonium or di (1-pyridinium) alkanedioates with varying carbon chain length.

Experimental

Materials. 1, 20-Icosanediyldi (1-pyridinium) alkanedioate ($Py^{+}C_{20}H_{40}Py^{+}$) $^{-}OOC(CH_2)_nCOO^{-}$, abbr. $C_{20}Py_2$-C_n, and N, N, N, N', N', N'-hexamethyl-1, 20-icosanediyldiammonium alkanedioate $[(H_3C)_3N^{+}(CH_2)_{20}N^{+}(CH_3)_3]$ $^{-}OOC(CH_2)_nCOO^{-}$, abbr. $C_{20}Me_6$-C_n, with counter ion chain lengths n of 2, 4, 6, 8, and 10 were synthesized from 1, 20-dibromoicosane, abbr. $C_{20}Br_2$, and alkanedioic acids $HOOC(CH_2)_nCOOH$, abbr. $C_n(COOH)_2$, according to the following procedures.

The 11-bromoundecanoic acid (Tokyo Kasei Kogyo Co. Ltd.) was converted to $C_{20}Br_2$ by Kolbe′s electrolysis in methanol after neutralization with a 0.1 molar amount of NaH relative to the acid. The product was repeatedly recrystallized from methanol until a thin-layer chromatographical test gave one spot of $C_{20}Br_2$. It was then converted to the pyridinium bromide ($C_{20}Py_2Br_2$) by refluxing in pyridine at 60 °C. The crude product was decolorized overnight in methanol with activated charcoal powder. After removing methanol under reduced pressure, the product was purified by recrystallization from an acetone–ethanol mixture. The hexamethyldiammonium dibromide ($C_{20}Me_6Br_2$) was prepared by refluxing $C_{20}Br_2$ with an ethanol solution of excess trimethylamine at 70 °C. The product was recrystallized twice from an ethanol–acetone mixture and further purified by ether extraction for 24 h.

Stock solutions of $C_{20}Py_2$-C_n and $C_{20}Me_6$-C_n were prepared, respectively, by neutralizing $C_n(COOH)_2$ (Tokyo Kasei Kogyo Co. Ltd.) with $C_{20}Py_2(OH)_2$ and $C_{20}Me_6(OH)_2$ solutions, which had been prepared by passing aqueous solutions of $C_{20}Py_2Br_2$ and $C_{20}Me_6Br_2$ through an anionic exchange column (Bio-Rad Laboratories AG1-X4) in the OH^- state. For the sake of a comparison, the corresponding surfactants with $SO_4{}^{2-}$ counter ion were also prepared.

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 surfactant solutions were measured by using a Horiba Conductivity Meter ES-14.

The fluorescence spectra of pyrene excited at 337 nm were recorded on a Shimadzu Spectrofluorophotometer RF-5000. The fluorescence-decay curves were measured using a Horiba time-resolved fluorescence spectrometer NAES-1100. Pyrene was solubilized in surfactant solutions by sonicating the mixtures for 10 min and standing for 12 h. Prior to the measurements, the sample solutions were thoroughly deoxygenated by repeated freeze-pump-thaw cycles. The concentration of solubilized pyrene was determined spectrophotometrically at 337 nm both before and after each fluorescence decay measurement.

All of the measurements were conducted at 25 °C.

Results and Discussion

1. Critical Micelle Concentration. Figures 1 and 2 show the conductivity data of $C_{20}Me_6$-C_n and $C_{20}Py_2$-C_n solutions, respectively. For the sake of a comparison, the data for sulfate counter ion systems are also shown in these figures. The values of cmc, determined from the break points in Figs. 1 and 2, are summarized in Table 1. In solutions of the conventional monovalent surfactants, the cmc of alkylpyridinium salt is well known to be slightly smaller than that of the corresponding alkyltrimethylammonium salt.[24] This is also the case for the present systems, as is clearly shown in Table 1. It is important to note here that the observed cmc of 6.70 mmol dm^{-3} for $C_{20}Me_6$-SO_4 is unexpectedly close to that of 8.2 mmol dm^{-3} for $C_{20}Me_6$-Br.[13,16] This is in marked contrast to the conventional ionic surfactant solutions in which an increase in the counter ion valency is always accompanied by a drastic decrease in the cmc. For example, with divalent metal dodecyl sulfates,[25] their cmc (ca. 1.2 mmol dm^{-3}) are much smaller than that (ca. 8 mmol dm^{-3}) of sodium dodecyl sulfate (SDS). It has been reported that the surface layer of the $C_{20}Me_6$-Br micelle has a loosely packed structure.[13] It is therefore likely that the foregoing small difference between the values of cmc for bromide and the sulfate counter ions results from a decrease in the surface-charge density, which necessarily leads to a decrease in the electrical free energy term relative to the overall free energy change of micelle formation.

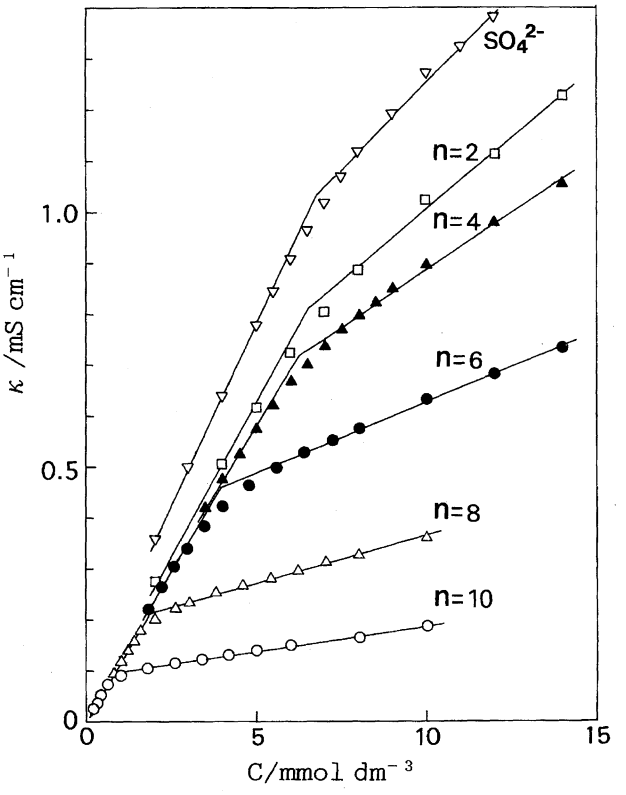

Fig. 1. Plots of κ vs. C for $C_{20}Me_6$-C_n solutions.

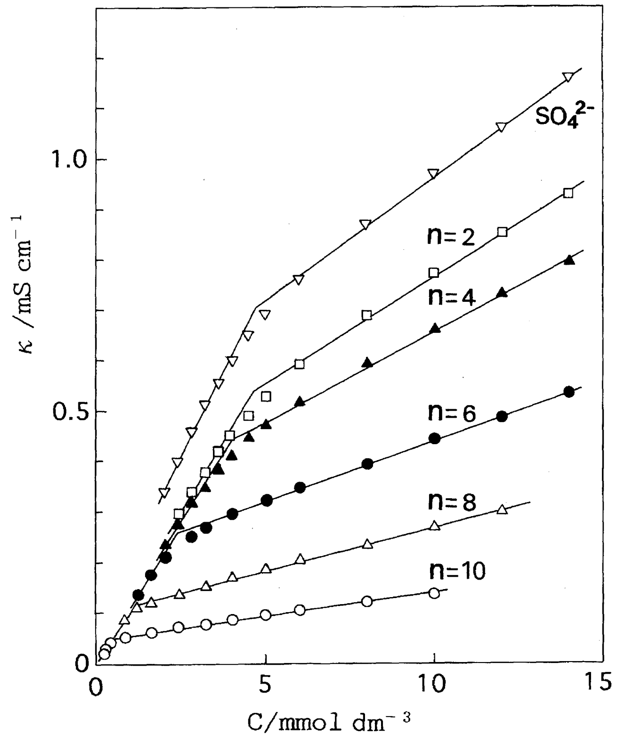

Fig. 2. Plots of κ vs. C for $C_{20}Py_2$-C_n solutions.

In both systems, the observed values of cmc for the sulfate, succinate (n=2), and adipate (n=4) counter ions are similar to one another. This fact suggests that the coulombic interaction of the counter ion with the micellar surface remains virtually unchanged, at least up to charge separation of the order of 4 methylene groups, since one or two methylene groups adjacent to the ionic head group are known to make little or no contribution to the hydrophobic interaction.[26]

The most striking feature of Table 1 is the rapid decrease in the cmc above $n=4$. Similar behaviors were also observed for ionic surfactants consisting of a monovalent surfactant ion and an α,ω-type counter ion.[18,22,23] A regular decrease in the cmc was found to occur at $n=6$ for α,ω-alkanediyldi

Table 1. The Micellar Parameters of $C_{20}Me_6$-C_n and $C_{20}Py_2$-C_n Solutions

Counter ion	cmc/mmol dm^{-3}		β		I_1/I_3	m
	$C_{20}Me_6$-C_n	$C_{20}Py_2$-C_n	$C_{20}Me_6$-C_n	$C_{20}Py_2$-C_n	$C_{20}Me_6$-C_n	$C_{20}Me_6$-C_n
SO_4^{2-}	6.70	4.70	0.73	0.71	1.60	51
$n=2$	6.35	4.66	0.69	0.68	1.63	46
4	6.19	4.04	0.71	0.71	1.60	44
6	3.88	2.43	0.79	0.78	1.55	47
8	1.91	1.19	0.85	0.84	1.48	51
10	0.77	0.44	0.92	0.90	1.41	59
					1.37 (DTAC)	

(1-pyridinium) bis (1-tetradecanesulfonate),[18] $n=4$ for α,ω-alkanediammonium bis (dodecyl sulfate),[23] and $n=1$ for decylammonium alkanedioate,[22] respectively. These characteristic behaviors were interpreted in terms of a successive increase with n in the hydrophobic interaction between the micellar core and the folded hydrocarbon chain of the α,ω-type counter ion.[18,23] The same type of hydrophobic interaction also seems to be responsible for the observed regular decrease in the cmc with n in the present systems.

2. Binding Degree of Counter Ion. It should be noted that the slope of the $\varkappa$ vs. surfactant concentration (c) plot above the cmc decreases regularly with increasing n. This in turn implies that the binding degree (β) of the ionic group of the alkanedioate counter ion increases regularly as n increases, since the ratio of the slopes of $\varkappa$ vs. C plots below and above cmc is known to give approximately $1-\beta$.[5,12,13,16,27] The estimated values of β from conductivity data are shown in the third column of Table 1. As would be expected, the value of β increases monotonically from 0.68—0.69 at $n=2$ to 0.90—0.92 at $n=10$, suggesting the importance of the foregoing hydrophobic interaction other than the electrostatic one in the stabilization of the counter ion at the micellar surface. As far as the value of β is concerned, the difference in the head group structure of the surfactant ion appears to play a minor role.

3. Transfer Free Energy per Methylene Group of Counter Ion. Knowledge concerning cmc and β allows us to estimate the transfer free energy per methylene group (ω) of the carbon chain of the counter ion from bulk to micellar phases. By taking into account the fact that the transfer free energy of a homologous series hydrocarbon is linearly dependent on the chain length,[26] the standard free energy change of micelle formation can be written as $\Delta\mu^0+\beta n'\omega$, where $\Delta\mu^0$ refers to the transfer free energy of the surfactant ion and n' to the effective chain length of the counter ion hydrocarbon moiety which can participate in the hydrophobic interaction with the micellar core. By ignoring the activity coefficients, and denoting the cmc by C_0, it immediately follows from the charged phase-separation model[28] that

$$(1+\beta)\ln C_0 = (\Delta\mu^0 + \omega\beta n')/RT. \quad (1)$$

As already mentioned, one or two methylene groups adjacent to the ionic head group make little or no contribution to the hydrophobic interaction. With this reservation in mind, we made tentative estimations of ω by substituting $n'=n-2$ and $n-4$. The resulting plots for $n'=n-2$ are shown in Fig. 3. In both systems, a linear relationship is seen to hold only above $n=6$. This, in turn, suggests that at least 6 methylene groups are required for the onset of an effective hydrophobic interaction between the hydrocarbon part of the α,ω-type counter ion and the micellar core. The values of ω were estimated to be -0.92 RT for $C_{20}Me_6$-C_n and -1.02 RT for $C_{20}Py_2$-C_n from the slopes of the straight lines above $n=6$ in Fig. 3. The use of $n'=n-4$ gives similar values of ω, i.e., -0.99 RT for the former and -1.04 RT for the latter, respectively. It is worth nothing that the thus-determined values of ω are comparable to those of -1.1 RT for the conventional ionic surfactants with inorganic counter ions.[29]

4. Polarity of Micellar Interior and Micelle Aggregation Number. It is well known that the ratio of the first and third vibronic band intensities (I_1/I_3) of the pyrene fluorescence spectrum gives a measure of the local polarity of the hydrocarbon moiety near to the head group where the probe molecules are solubilized.[30] The forth column of Table 1 gives the observed values of I_1/I_3 for $C_{20}Me_6$-SO_4 and $C_{20}Me_6$-C_n at 15 mmol dm^{-3}, together with that for dodecyltrimethylammonium chloride (DTAC). Although

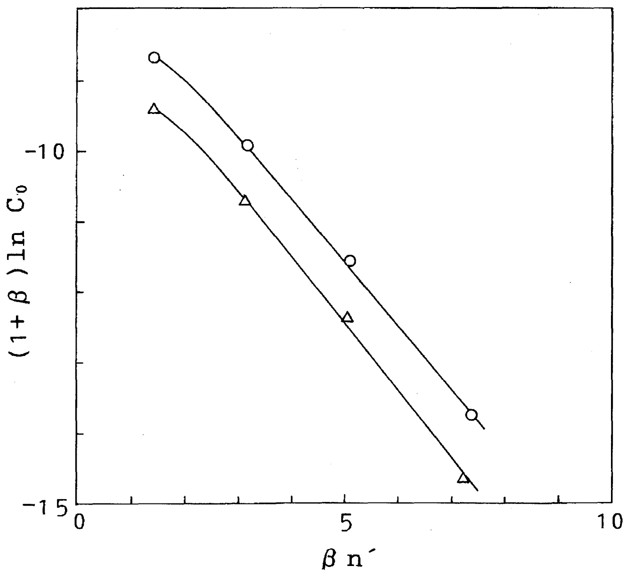

Fig. 3. Plots of $(1+\beta)\ln C_0$ vs. $\beta n'$ for $C_{20}Me_6$-C_n and $C_{20}Py_2$-C_n solutions. ○; $C_{20}Me_6$-C_n, △; $C_{20}Py_2$-C_n.

the value of I_1/I_3 for n=10 is as small as that for DTAC, it gradually increases with decreasing n, and eventually tends to 1.63 at n=2. This, in turn, suggests that the local polarity around the solubilized pyrene molecules also gradually increases with decreasing n. By taking into account the location of the solubilized probe molecules in the micelle, the surface layer of the $C_{20}Me_6$-C_n micelle is expected to become progressively loose as n decreases, presumably as a result of the penetration of water molecules. A similar loosely packed structure is also expected for the surface layer of the $C_{20}Me_6$-SO_4 micelle, since the value of I_1/I_3 is comparable to those for n=2 and 4. This result seems to support the foregoing presumption concerning the cmc of the $C_{20}Me_6$-SO_4.

The fluorescence technique also provides information about the micelle aggregation number (m). Figure 4 shows the typical fluorescence decay curve of the pyrene solubilized in the $C_{20}Me_6$-C_{10} micelle at 20 mmol dm^{-3}. The values of m, calculated from the equation derived by Atik et al.,[31] are given in the last column of Table 1. It is interesting to note that the value of m for the sulfate counter ion is more than twice as large as that for the corresponding Br^- counter ion (m=19),[13] in spite of the resemblance in their cmc. This is in marked contrast to the relationship between the cmc and m for conventional ionic surfactants, where the substitution of a monovalent counter ion by a divalent one results in a remarkable increase in m and a decrease in the cmc.[25] In solutions of $C_{20}Me_6$-C_n, the value of m remains virtually constant up to n=6, but tends to increase slightly with a further increase in n. This behavior can presumably be attributed to an increase in the foregoing hydrophobic interaction between the counter ion and the micellar core. In their NMR study of N, N, N, N', N', N'-hexaethyl-1, 20-icosanediyldiammonium dibromide, Wong et al.[15] pointed out that the α,ω-type surfactant ion adopts a predominantly stretched form in a spherical micelle. It is therefore probable that the $C_{20}Me_2{}^{2+}$ ions in the present systems also adopt a similar stretched conformation in the micelle, though we lack experimental evidence about the micellar structures at the present stage.

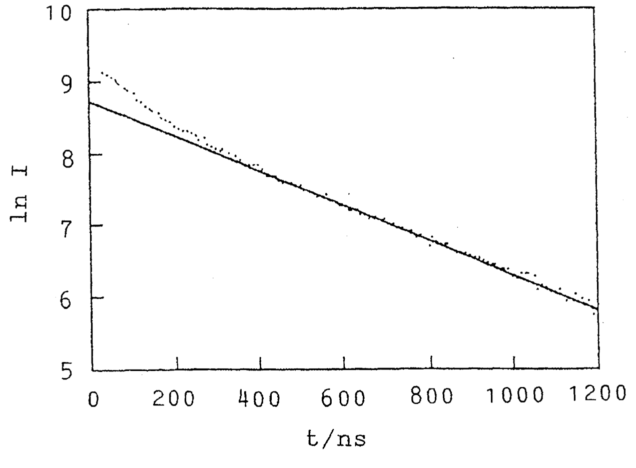

Fig. 4. The typical fluorescence decay curve of the solubilized pyrene in $C_{20}Me_6$-C_{10} solution at 20 mmol dm^{-3}. [Pyrene]=250 μmol dm^{-3}.

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