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The Micellar Properties of α,ω-Alkanediammonium Bis(dodecyl sulfate) in Aqueous Solutions

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The micellar properties of α,ω-alkanediammonium bis(dodecyl sulfate) with hydrocarbon chain length (n) from 3 to 6 were studied by conductivity, surfactant ion activity, and fluorescence quenching measurements. The critical micelle concentration (CMC) decreases gradually with increasing n in such a way that ln CMC vs. n plot gives a straight line above $n=3$. The binding degree of counterion head group to the micelle remains virtually constant of 0.95 regardless of n studied. The estimated value of -0.36 kT for the transfer free energy per methylene group of counterion from aqueous to micellar environments suggests that the hydrocarbon part of the counterion participates in the weak hydrophobic interaction with micellar core. Although the micelle aggregation number is always larger than those of bivalent metal dodecyl sulfates, it tends to decrease as n increases.

A number of papers have been concerned with the colloid chemical properties of α,ω-type amphiphiles which have two ionic groups separated by a long hydrocarbon chain of varying chain length. These amphiphiles are found to assume a wicket-like conformation in which two ionic groups are anchored at the air–water interface.[1—7] In addition, their micellar solutions are characterized by a lowering in the Krafft Point,[8] an increase in the critical micelle concentration (CMC),[1,2,5,8—12] and a decrease in the micelle aggregation number (m)[4—6,13—16] as compared with those of usual univalent ionic surfactants of equal hydrocarbon chain length.

In view of their characteristic structures, α,ω-type amphiphilic ions are also interesting molecules for elucidating the effects of the charge spacing as well as the hydrophobicity of the intervening hydrocarbon chain of the counterion on the micellar properties of ionic surfactant solutions. In this connection, Moroi et al.[17—20] made the systematic studies on the micellar properties of 1,1′-(1,ω-alkanediyl)bispyridinium 1-tetradecanesulfonate ($R_nP^{2+}(R_{14}SO_3^-)_2$) with counterion chain length (n) from 2 to 14. They have found that the CMC remains virtually constant up to $n=6$, but decreases regularly with further increase in n.[17,18] They have also noted that the binding degree of counterion head group (β) increases monotonically with increasing n, while m goes through a minimum around $n=10$.[19] In the case of decylammonium dicarboxylate surfactants ($R_nC^{2-}(R_{10}NH_3^+)_2$), however, it has been found that the value of CMC decreases almost linearly with increasing n and a minimum in β appears at $n=4$.[21] Studies were also made for the micellar properties of the mixed solutions of sodium dodecyl sulfate (SDS) and *N*,*N*′-(1,12 dodecanediyl)bis(triethylammonium bromide).[22]

In this paper, we present the micellar properties of α,ω-alkanediammonium bis(dodecyl sulfate) with n from 3 to 6 studied by conductivity, surfactant ion activity, and fluorescence quenching measurements.

Experimental

Materials. The α,ω-alkanediamine dihydrochlorides with n from 3 to 6 ($R_nA^{2+}Cl^-{}_2$, Tokyo Kasei Kogyo Co., Ltd.) were decolorized by refluxing their solutions with activated charcoal powder. Sodium dodecyl sulfate (Nacalai Tesque, Inc.) was purified by repeated recrystallization from ethanol and by extraction with ether for 8 h. Pyrene (Nacalai Tesque, Inc.) was passed through silica gel in cyclohexane solution and recovered as white crystals after the recrystallization from ethanol. Tris(2,2′-bipyridine)-ruthenium(II) dichloride (Ru(bpy)₃, Sigma Chemical Co.) and 9-methylanthracene (9-MeA, Wako Pure Chemical Industries Ltd.) were used without further purifications.

The α,ω-alkanediammonium bis(dodecyl sulfate) ($R_nA^{2+}(R_{12}SO_4^-)_2$) with $n=3$, 4, and 6 were prepared by cooling the mixed solution of SDS and a large excess of corresponding $R_nA^{2+}Cl^-{}_2$. The resulting precipitates were recrystallized twice from $R_nA^{2+}Cl^-{}_2$ solution, then from water, and finally dried in vacuo over phosphorus pentaoxide. An alternate method was applied to the preparation of $R_5A^{2+}(R_{12}SO_4^-)_2$, since its solubility in water was comparatively high. A large excess of barium dodecyl sulfate was heated with stirring in solution of $R_5A^{2+}SO_4^{2-}$ which had been prepared by passing the aqueous solution of $R_5A^{2+}Cl^-{}_2$ through an anion-exchange column (Organo, IRA-400) in the SO_4^{2-} state. The filtrate was again stirred with barium dodecyl sulfate under heating. After filtration, the concentration of $R_5A^{2+}(R_{12}SO_4^-)_2$ stock solution was determined potentiometrically by using surfactant ion selective membrane electrode.

Method. The conductivities of $R_nA^{2+}(R_{12}SO_4^-)_2$ solutions were measured by using TOA Electronics conductivity meter, model CM-50AT.

The surfactant ion activities in $R_nA^{2+}(R_{12}SO_4^-)_2$ solutions were measured potentiometrically by using the following cell. The poly(vinyl chloride) (PVC) membrane consists of 20% PVC and 80% tri-*p*-tolyl phosphate by weight and contains about 0.5 mmol dm^{-3} dioctadecyldimethylammonium dodecyl sulfate as an ionic carrier.

Reference electrode (Ag-AgCl) | 1 mol dm^{-3} KCl Agar bridge | Reference solution (SDS, 1 mmol dm^{-3}) | PVC membrane | Sample solution ($R_nA^{2+}(R_{12}SO_4^-)_2$, c) | 1 mol dm^{-3} KCl Agar bridge | Reference electrode (Ag–AgCl)

The electromotive force (E) of the cell was measured by using Toko pH meter, model TP-1000, with an accuracy of ±0.1 mV.

The fluorescence spectra of pyrene and Ru(bpy)$_3$ excited at 337 and 455 nm respectively were recorded on Shimadzu Spectrofluorophotometer RF-5000. Pyrene was solubilized in $R_nA^{2+}(R_{12}SO_4{}^-)_2$ solutions by sonicating the mixtures for 15 min in such a way that the average number of pyrene molecules per micelle is less than 0.5. The same sonication technique was also applied to the solubilization of 9-MeA in $R_nA^{2+}(R_{12}SO_4{}^-)_2$ solutions containing Ru(bpy)$_3$. The concentration of 9-MeA was determined spectrophotometrically at 388 nm (ε=7500). The concentration of Ru(bpy)$_3$ was adjusted to the order of 10^{-7} mol dm^{-3} so as to depress the number of solubilized Ru(bpy)$_3$ molecules in a micelle below unity.

All measurements were conducted at 35 °C.

Results and Discussion

Figure 1 shows the plots of conductivity (κ) vs. the molar concentration (c) of $R_nA^{2+}(R_{12}SO_4{}^-)_2$ with n from 3 to 6. The critical micelle concentrations (c_0) determined from the break points in this figure are summarized in Table 1. The observed gradual decrease in c_0 with n suggests that the hydrophobic interaction between the hydrocarbon part of the counterion and the micellar core appreciably contributes to the stabilization of $R_nA^{2+}(R_{12}SO_4{}^-)_2$ micelle. It is also worth noting that the slope of κ vs. c curve above CMC is extremely small regardless of n. This in turn suggests that the binding degree of counterion head group to the micelle (β) is close to unity, since the ratio of the slopes of κ vs. c curves below and above CMC approximately corresponds to $1-\beta$.[4,5,11,16,23,24] The values of β thus estimated from Fig. 1 are given in Table 1. It can immediately be seen that α,ω-alkanediammonium counterions condense effectively on the micellar surface resulting in a virtual neutralization of the micellar charge.

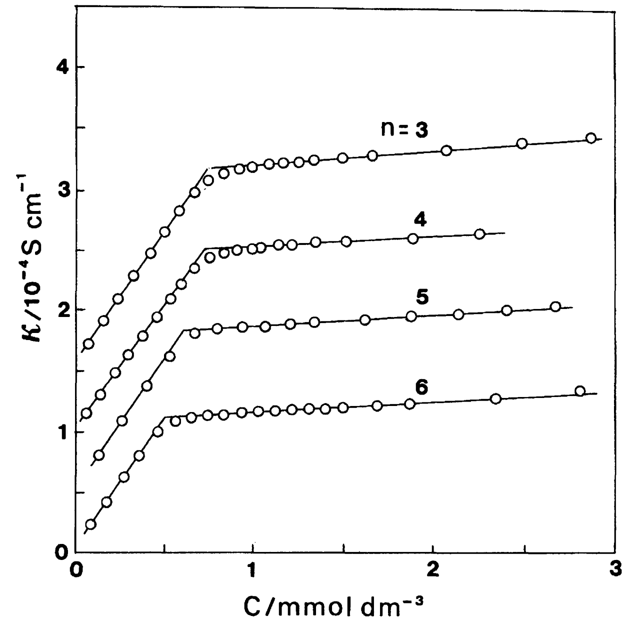

Fig. 1. Plots of κ vs. c. The curves for n=3, 4, and 5 are displaced upward by 150, 100, and 50 µS cm^{-1}, respectively.

Table 1. The Micellar Parameters of $R_nA^{2+}(R_{12}SO_4{}^-)_2$ Solutions

n	CMC/mmol dm^{-3}	β	m
3	0.74	0.95	232
4	0.70	0.95	247
5	0.63	0.96	172
6	0.56	0.96	162

The concentration dependence of dodecyl sulfate ion activities reflects well the above situation. Figure 2 shows the semilogarithmic plots of E of the foregoing cell vs. the molar concentration (c) of $R_nA^{2+}(R_{12}SO_4{}^-)_2$ with n=4 and 6. The values of CMC determined from the break points in Fig. 2 agree well with those from conductivity data. In the concentration range below CMC, the linear relations with a slope (S) of 60.6 mV for n=4 and 60.0 mV for n=6 were found to hold down to 1×10^{-5} mol dm^{-3}. The observed values of S are in good agreement with an ideal Nernst slope of 61.1 mV at 35 °C, suggesting almost ideal response of the membrane electrode to dodecyl sulfate ion. In both cases, the value of E remains virtually constant over wide concentration range above the CMC. This in turn means that dodecyl sulfate ion activity (a_-) remains constant in this concentration range, since the value of E can be described as E=const.+S log a_-. These behaviors are in marked contrast to the usual 1–1 type ionic surfactant solutions in which E vs. log c plots are always concave to the log c axis because of an appreciable degree of counterion dissociation of the micelle.[25] According to the phase separation treatment of the micelle formation, $a_-a_{2+}{}^{\beta/2}$ should be constant above CMC. Here a_{2+} refers to the counterion activity. Thus the observed constancy in a_-

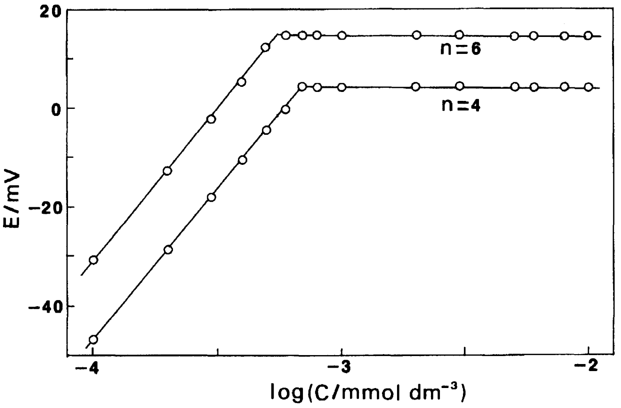

Fig. 2. The semilogarithmic plots of E vs. c. The curve for n=6 is displaced upward by 10 mV.

above CMC implies that β is close to unity above CMC since $a_{2+} \approx c_0 + (1-\beta)(c-c_0)$ so far as we neglect the activity coefficient of the counterion.

It should be noted that the observed values of CMC and β for the present system depend somewhat differently on n from those for $R_nC^{2-}(R_{10}NH_3^+)_2$ and $R_nP^{2+}(R_{14}SO_3^-)_2$ systems. In the former case,[21] it has been found that the CMC decreases almost linearly with increasing n up to 6, while the value of β has a broad minimum of 0.75 around n=4. In the latter case, however, the CMC has been found to decrease only above n=6,[17] in spite of the monotonous increase in β from 0.82 for n=2 to 0.98 for n=14.[19]

In Fig. 3 is shown the plot of ln c_0 vs. n. A linear relationship observed above n=3 allows us to estimate the free energy change ($\Delta\mu^0$) for transferring one methylene group of counterion from an aqueous medium to micellar phase, since the slope of the straight line corresponds to $\Delta\mu^0/(1+2/\beta)$ kT.[17] Although the estimated value of $\Delta\mu^0$ of -0.36 kT is considerably smaller than that of -1.1 kT for usual ionic surfactants with inorganic counterions,[26] the hydrocarbon part of the R_nA^{2+} counterion with $n \geqq 4$ is supposed to participate in the weak hydrophobic interaction with the micellar core.

It is well-known that the ratio of the intensities of the first and third vibronic bands of the pyrene fluorescence spectrum (I_1/I_3) reflects the polarity of the microenvironment around the probe molecule.[27] In order to check the effect of α,ω-type counterion on the local polarity of the ionic micelle, we measured this ratio as the function of $R_nA^{2+}(R_{12}SO_4^-)_2$ concentration. The results are shown in Fig. 4. In all cases, I_1/I_3 remains constant of 1.08—1.11 in the concentration range above CMC. Taking into account the fact that these values agree well with that of 1.09—1.17 for SDS micelle, the α,ω-type counterions seems to play a minor role in determining the local polarity of the micelle even if they participate in the hydrophobic interaction with the micellar core.

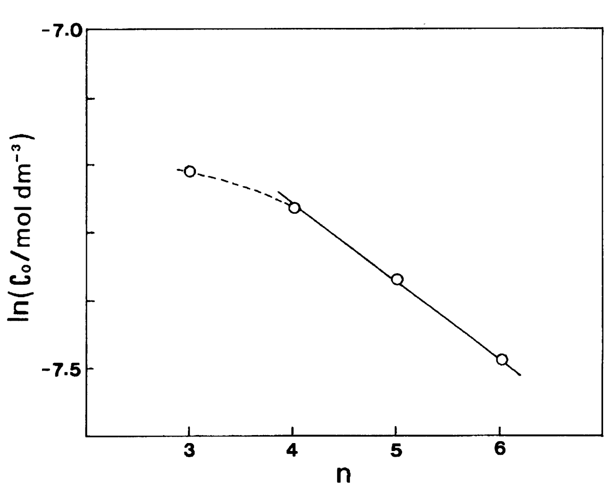

Fig. 3. The plot of ln (c_0/mol dm^{-3}) vs. n.

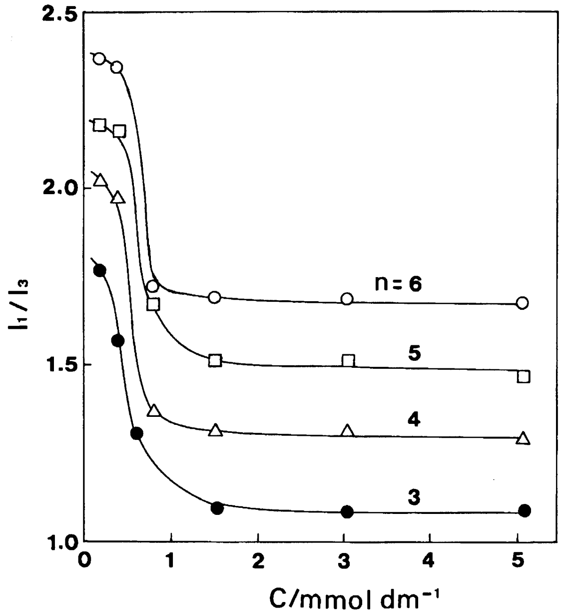

Fig. 4. The concentration dependences of I_1/I_3. The curves for n=4, 5, and 6 are displaced upward by 0.2, 0.4, and 0.6, respectively.

The fluorescence probe technique also provides an information about the micelle aggregation number (m). It has been well-known that the fluorescence intensity of the probe in the presence of the quencher can be described by the following equation based on the Poisson distribution of the quencher molecules in micelles.[28]

$$\ln (I_0/I_q) = mc_q/2(c-c_0) \tag{1}$$

Here, I_q and I_0 refer to the fluorescence intensity of the probe with and without quencher and c_q to the concentration of the quencher, respectively. In the present experiments, we followed the fluorescence intensity of Ru(bpy)$_3$ at 602 nm as a function of 9-MeA concentration. Figure 5 shows ln (I_0/I_q) vs. c_q plots at a given $R_nA^{2+}(R_{12}SO_4^-)_2$ concentration. It must be kept in mind that the value of m estimated from the slope of the straight line in Fig. 5 represents the number of dodecyl sulfate ions per micelle. The values of m thus determined are given in Table 1. In all cases, the concentration dependence of m was virtually undetected. It should be noted that the values of m for $R_nA^{2+}(R_{12}SO_4^-)_2$ are much larger than those of SDS (65, present experiment) and bivalent metal dodecyl sulfates[29] (m=85—103). Moreover, the value of m tends to decrease with increasing n. A similar behavior is noted for $R_nP^{2+}(R_{14}SO_3^-)_2$,[19] although the magnitude of m is quite different from the present system. In that case, the value of m is found to vary with n from 74 for n=2 to 67 for n=14 through a broad minimum of 33 around n=10.

An interesting comparison may be made among the micellar parameters of $R_nA^{2+}(R_{12}SO_4^-)_2$, R_nP^{2+}

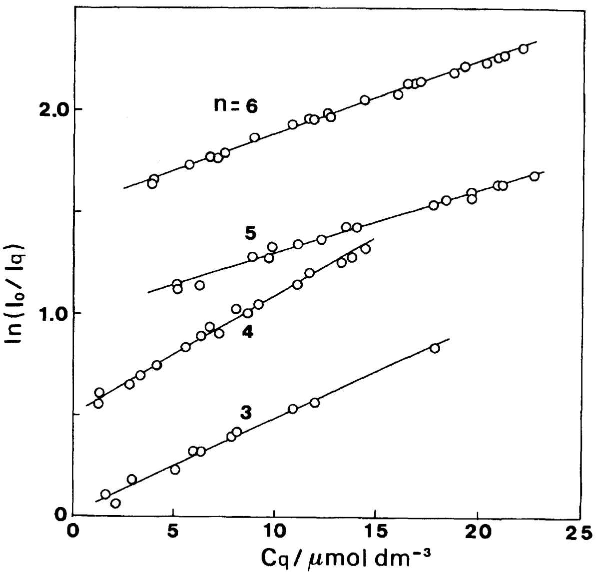

Fig. 5. Plots of ln (I_0/I_q) vs. c_q. [$R_nA^{2+}(R_{12}SO_4^-)_2$] /mmol dm^{-3}=3.2 ($n$=3), 2.9 ($n$=4), 3.0 ($n$=5), and 3.0 ($n$=6). The curves for n=4, 5, and 6 are displaced upward by 0.5, 1.0, and 1.5, respectively.

$(R_{14}SO_3^-)_2$, and $R_nC^{2-}(R_{10}NH_3^+)_2$. For example with $n=6$, the values of CMC, β, and m are 0.56 mM, 0.95, and 162 for $R_nA^{2+}(R_{12}SO_4^-)_2$, 0.19 mM, 0.88, and 34 for $R_nP^{2+}(R_{14}SO_3^-)_2$,[17,19] and 9.5 mM, 0.83 for $R_nC^{2-}(R_{10}NH_3^+)_2$,[21] respectively. Unfortunately, the value of m has not been determined for the last system. It is true that the micellar parameters of ionic surfactants depend not only on the surfactant ion chain length but on the structures of both surfactant ion and counterion head groups,[26] but those for three systems described above differ unexpectedly from one another. It is thus probable that a slight difference in the structures of surfactant ion and counterion head groups are remarkably amplified on the micellar parameters of ionic surfactants with α,ω-type counterion.

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