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Multinuclear NMR Studies on Micellar Formation of Aqueous [Co(*N*-octyl- or *N*-dodecylethylenediamine)(3,7-Diazanonane-1,9,-diamine)]$^{3+}$ Solutions

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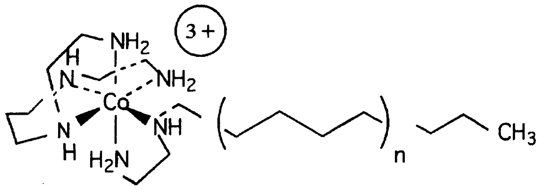
The aggregation of [Co(R-en)(2,3,2-tet)]X_3 (R-en = *N*-octyl- or *N*-dodecylethylenediamine, 2,3,2-tet = 3,7-diazanonane-1,9-diamine, and X = Cl or ClO_4) in water was investigated by ^{59}Co, ^{35}Cl, $^{35}ClO_4$, $^{2}H_2O$, and ^{1}H NMR measurements. NMR parameters, such as the relaxation rates and linewidths for the ^{59}Co and ^{35}Cl nuclei, were appreciably changed by micellar formation. We determined the CMC (critical micelle concentration) values (0.12 mol kg^{-1} for the octyl complex perchlorate, 0.008 mol kg^{-1} for the dodecyl perchlorate, and 0.010 mol kg^{-1} for its chloride) by measuring the NMR relaxations. The obtained CMC values are much larger than those previously reported on these surfactants, and are comparable to those of monovalent surfactants having the same alkyl-chain length. The aggregation of [Co(dod-en)(2,3,2-tet)]X_3 (X = Cl or ClO_4) in aqueous solution was also measured using vapor-pressure osmometry; the result supports the formation of ion aggregates at the CMCs, which was determined by NMR measurements. The ^{35}Cl NMR measurements indicate that the interaction of the chloride counter ion with the dodecyl complex ion was appreciably larger than that with the dodecyltrimethylammonium ion at concentrations even below CMC. The effect of the trivalent positive charge of the cobalt(III) surfactant on the CMC value may be attenuated by the large size of the head group. A characteristic downfield shift of the ^{59}Co resonance was observed due to the formation of micelles.

NMR spectroscopy provides useful information from a microscopic point of view concerning the process of micellization in complicated systems.[1,2] The presence of multivalent ions is especially effective in this process, and studies of multivalent-ion binding using multinuclear NMR have been performed in many systems.[3,4] On the other hand, the number of multivalent surfactants is much less than that of monovalent surfactants, and the detailed mechanisms of their micellizations have not been well studied. It a previous study,[5] one of the present authors (M.I.) and his co-workers have prepared [Co(oct-dhpta)]$^-$ and [Co(dod-dhpta)]$^-$ (oct-dhpta = 1, 3-diamino-2-(octanoyloxy)-propane-*N*,*N*,*N*′,*N*′-tetraacetate ion, dod-dhpta = 1,3-diamino-2-(dodecanoyloxy) propane-*N*,*N*,*N*′,*N*-tetraacetate ion), and studied their ^{59}Co NMR spectroscopies on the micellization of their aqueous solutions. That was the first study on the physical properties of aqueous cobalt(III) surfactant solutions using ^{59}Co NMR spectroscopy, which was useful for following the aggregation process, owing to its high receptivity and sensitivity to environmental changes.[6,7] The cobalt(III) complex is regarded as being a unique head group, since its charge number, size, and hydrophobic and hydrophilic characters can be systematically designed. Recently, [Co(R-en)(2,3,2-tet)]X_3 (R = *N*-octyl or *N*-dodecyl and X = Cl or ClO_4) surfactants (Fig. 1) have been synthesized by Yashiro et al.[8] This complex is a novel type of surfactant with a trivalent positive charge, which can be conveniently used to observe the electrostatic effect on the aggregation process; however, the physical properties of its aqueous solutions have not been studied in detail. Our basic strategy is to use the center nucleus of the headgroup as a probe in NMR measurements.



Co-alkyl-en
n = 1 : octyl
n = 2 : dodecyl

Fig. 1. Schematic representation of [Co(R-en)(2,3,2-tet)]$^{3+}$ molecule. (R = *N*-octyl ($n = 1$) or *N*-dodecyl ($n = 2$)).

In the present study we measured ^{59}Co and ^{1}H NMR concerning the head group of the [Co(R-en)(2,3,2,-tet)]X_3 surfactant, ^{35}Cl NMR for the counter ions, and ^{2}H NMR for the solvent water. The CMCs for the present systems were previously measured using the Wilhelmy method.[8] The reported values, 2.0×10^{-4} mol dm^{-3} (perchlorate) for the octyl complex and 3.3×10^{-5} mol dm^{-3} (perchlorate) or 1.14×10^{-3} mol dm^{-3} (chloride) for the dodecyl complex, are extraordinarily low for the length of the alkyl chains. These results indicate that the electric charge of the head group is appreciably effective on the CMCs, against the general rule.[9] However, in the present ^{59}Co and ^{35}Cl NMR studies we concluded that the CMCs of these aqueous cobalt(III) surfactant solutions are much larger than the reported values, and are comparable to those of solutions of other surfactants having the same alkyl chains. The measurements of ^{59}Co and ^{35}Cl NMR provide us with useful information concerning microscopic aspects of micellar formation. The aggregation was also followed using the vapor-pressure depression for the dodecyl complexes (chloride and perchlorate).

Experimental

N-octylethylenediamine (oct-en),[10] *N*-dodecylethylenediamine (dod-en),[10] and [CoCl$_2$(2,3,2-tet)](ClO$_4$) (Co(tet))[11] were prepared by literature methods. The preparations of [Co(oct-en)(2,3,2-tet)](ClO$_4$)$_3$ and [Co(dod-en)(2,3,2-tet)]X$_3$ (X = Cl or ClO$_4$) were performed by a slight modification of Yashiro's method.[8] That is, Co(tet) (5 mmol) and R-en (10 mmol) were dissolved in DMSO (50 mL) and stirred for 5 h. After 100 mL of water was added, a white precipitate was removed by filtration. The mixtures of the complexes were separated using an SP-Sephadex C-25 column (Na$^+$ form) according to a method described in Ref. 8; the eluent was then repeatedly desalted by gel-permeation chromatography (Sephadex G-15). The final crystals were obtained by recrystallization from a minimum amount of warm ethyl acetate. The chloride complex was prepared by a conversion of the perchlorate with a Cl$^-$-form ion-exchanger. The purity of the cobalt(III) surfactants was identified by the elemental analyses and ^{13}C NMR spectra.[12] Anal. [Co(oct-en)(2,3,2-tet)](ClO$_4$)$_3$. Found: C, 29.47; H, 6.42; N, 11.72%. Calcd for $C_{17}H_{44}N_6O_{12}Cl_3Co$: C, 29.59; H, 6.38; N, 12.18%. [Co(dod-en)(2,3,2-tet)](ClO$_4$)$_3$. Found: C, 34.25; H, 7.21; N, 10.96%. Calcd for $C_{21}H_{52}N_6O_{12}Cl_3Co$: C, 33.81; H, 7.03; N, 11.27%. A preparation of [Co(en)$_3$]Cl$_3$·3H$_2$O was followed by a literature method.[13] Dodecyltrimethylammonium chloride (DTMACl) was obtained by a conversion of the corresponding bromide (from Tokyo Kasei Co.) with a Cl$^-$ ion-exchanger. The sodium dodecyl sulfate used was a guaranteed reagent of Wako Pure Chemical Industries, Ltd.

The ^{59}Co, ^{35}Cl, ^{2}H, and ^{1}H NMR spectra were obtained on a JEOL GX-270 FT NMR spectrometer operating at 64.6, 26.5, 41.5, and 270.2 MHz, respectively. The ^{1}H NMR spectra were measured in 99.5% D$_2$O and the ^{2}H NMR spectra were measured in 5% D$_2$O solutions. The ^{59}Co NMR spectra for aqueous 5 mmol kg^{-1} solutions of the octyl and dodecyl derivatives were found at −573 ppm and −571 ppm from aqueous 5 mmol kg^{-1} solutions of [^{59}Co(NH$_3$)$_6$]$^{3+}$, respectively. The ^{59}Co linewidths are 2.9 kHz for both surfactants of 5 mmol kg^{-1} solutions. The longitudinal relaxation rates were obtained by an inversion-recovery method, using the pulse sequence (−180°-*t*-90° pulse-T)$_n$. For T_1 measurements, 8—10 different pulse intervals (*t*) were used with a waiting time (*T*) of more than 8T_1. Here, we used the longitudinal relaxation rates (R_1) defined as $R_1 = 1/T_1$. When T_1 could not be exactly obtained, the linewidth ($\Delta\nu_{1/2}$) was used as a measure of the transverse relaxation rate (R_2) according to the relationship $R_2 = \pi\cdot\Delta\nu_{1/2}$. All of the NMR measurements were performed at 27 °C.

The depression of the vapor pressure for the aqueous dodecyl surfactant solution was measured with a Knauer Vapor Pressure Osmometer at 37 °C. In this method, the magnitude of the vapor-pressure depression is proportional to the difference in the temperature (ΔT) between a water-wetted thermistor and a solution-wetted thermistor. We can thus write

$$\Delta T = k\left\{\left(\frac{m'}{M_1}\right)+Bm'^2+Cm'^3+\cdots\right\}, \qquad (1)$$

where *k* is a constant depending on the solvent and the apparatus used, M_1 is the molecular weight of the solute, m' is the solute concentration in g kg^{-1} unit, and *B* and *C* are the virial coefficients. At a lower concentration the ΔT vs. m' plot is almost linear, and the slope gives the molecular weight (M_1). At a higher concentration, the second and third terms may significantly contribute to the ΔT values. If a drastic change, such as micellar formation, occurs in the solute–solute interactions, the plot may be curved at the critical concentration. At first we estimated the molecular weights of the surfactants from a plot of the vapor pressure vs. concentration, which is expressed in the solute weight/solvent weight ratio. In this procedure we used NaCl solutions for the calibration.

Results and Discussion

^{59}Co NMR Studies. Figure 2 shows the change in the linewidths ($\Delta\nu_{1/2}$) or the longitudinal relaxation rates (R_1) as functions of the cobalt(III) surfactant concentrations for the octyl and dodecyl complexes. In Fig. 2(a), we compare the R_1 and R_2 values using the relationship $R_2 = \pi\Delta\nu_{1/2}$. It is characteristic that both R_1 and R_2 start to steeply increase at specified concentrations (around 0.12 mol kg^{-1} for the octyl derivative and 0.01 mol kg^{-1} for the dodecyl ones). In the present study, we regarded a drastic increase in the relaxation rate as indicating the formation of ion aggregates, such as micelles, as follows.

Figure 2(a) shows that in the lower concentration ranges the R_2 values (8.5×10^3 s^{-1}) are around 10% larger than the corresponding R_1 values. This difference may be due to the contribution of the ^{59}Co scalar coupling to ^{14}N ($R_{2\mathrm{sc}}$), which greatly affects the R_2 value for highly symmetric amine complexes, such as [Co(NH$_3$)$_6$]$^{3+}$ and [Co(en)$_3$]$^{3+}$.[14] However, the difference in the present system is appreciably smaller compared to the above two cases; although the ^{59}Co relaxation mechanism is often complicated, we can consider that the present ^{59}Co relaxations are mainly governed by the quadrupolar mechanism.

As a first approximation, the relaxation rates (R_1 and R_2) for the quadrupolar nuclei ($I > 1/2$) can be expressed as[15—17]

$$R_1 = \frac{1}{T_1} = \frac{3\pi^2 2I+3}{10I^2(2I-1)}\left\{\frac{e^2qQ}{h}\right\}^2 (0.2J_1 + 0.8J_2) \qquad (2)$$

and

$$R_2 = \frac{1}{T_2} = \frac{3\pi^2 2I+3}{10I^2(2I-1)}\left\{\frac{e^2qQ}{h}\right\}^2 (0.3J_0 + 0.5J_1 + 0.2J_2), \qquad (3)$$

where e^2qQ/h is the quadrupole coupling constant and J_k are the spectral densities. In colloidal systems the spectral density function should be expressed on the basis of the "two-step model" as[18]

$$J_k(\omega_0) = (1-A)\tau_f + \frac{A\tau_S}{1+(k\omega_0\tau_S)^2}, \qquad (4)$$

where τ_S and τ_f are the correlation times associated with the slow and fast motions, and *A* is the square of the order parameter. For a free ion, *A* is zero and is around 0.2 for the nucleus of the head group in spherical micelles, while it changes along with a change in the micellar shape. For the

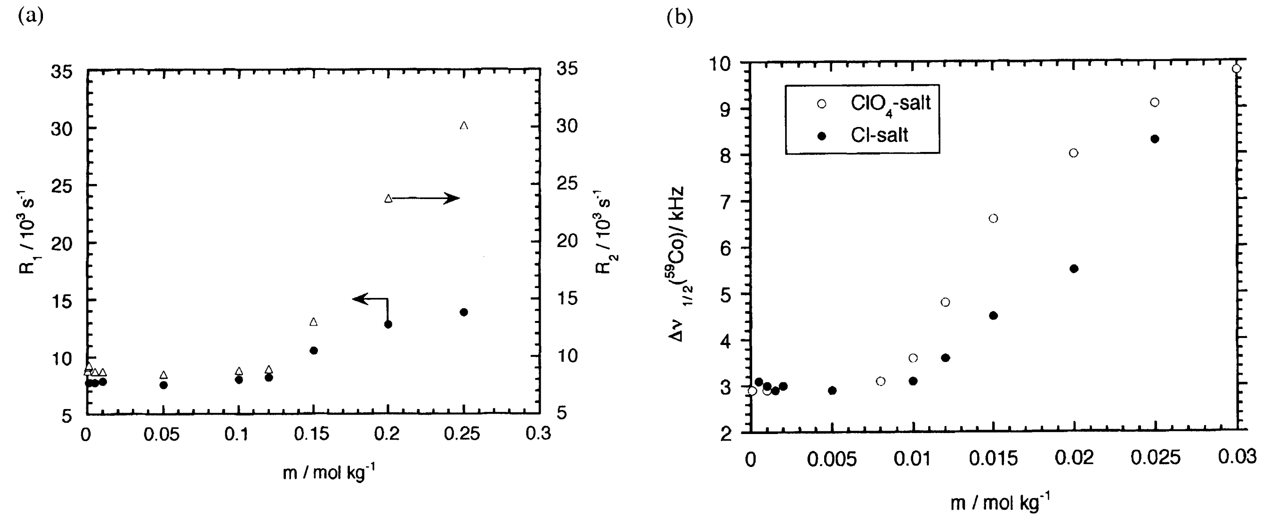


Fig. 2. (a) ^{59}Co longitudinal (R_1) and transverse relaxation rates (R_2) for [Co(oct-en)(2,3,2-tet)](ClO$_4$)$_3$ in aqueous solutions as a function of the cobalt(III) complex concentration. (b) ^{59}Co linewidths for [Co(dod-en)(2,3,2-tet)]X$_3$ (X=ClO$_4$ (○) and Cl (●)) in aqueous solutions as functions of the cobalt(III) complex concentrations.

nucleus of the counter ion, the A value depends on the binding site at the micelles. However, τ_S is much larger (around two orders of magnitudes) than τ_f, and, therefore, the J_i value (or the relaxation rate) may steeply increase with the formation of micelles. In the region where the surfactant concentration is not well beyond the critical concentration, Eq. 4 may be applicable and $\omega_0\tau_S$($\omega_0{}^{-1}$ is 2.5×10^{-9} s for ^{59}Co nucleus and 6.5×10^{-9} for ^{35}Cl nucleus) will not be much larger than unity ("near extreme narrowing" condition). Under this condition, although the linear proportionality between τ_S and the spectral density function does not hold, the relaxation rate may steeply increase along with the formation of aggregates, such as micelles. On the other hand, except for special cases,[19,20] the eq values for ^{59}Co and ^{35}Cl nuclei increase,[19,21] or remain nearly constant with an increase in the interaction. Therefore, in the process of micellization, where motional restrictions and ionic interactions of solutes drastically change, we can regard an increase in the relaxation rates as the formation of ion aggregates.[22]

Furthermore, on the basis of the two-state model, the relaxation rates ($R_i = R_1$ or R_2) in the interacting system for the 'free' and 'bound' states can be expressed as

$$R_i = p_F R_{iF} + p_B R_{iB}, \tag{5}$$

where p_F and p_B are the relative populations of the two states. Since R_{iB} is larger than R_{iF}, the increase in the relaxation rates with an increase in the concentration suggests an increase in the fraction of the bound cobalt(III) surfactant.

Since the linewidths at concentrations below and above the previously reported CMC (the values are written in the Introduction Section) are almost constant for the respective systems, aggregation would not occur around those concentrations. As will be confirmed later, the actual critical points are the concentrations at which the ^{59}Co relaxation rates steeply increase.

The difference between the perchlorate and the chloride is significant for the dodecyl complex (Fig. 2(b)): The critical concentration is slightly lower for the perchlorate than for the chloride, and the perchlorate aggregates to a greater extent below 0.025 mol kg^{-1}. Above 0.025 mol kg^{-1}, on the contrary, the aggregation of the chloride proceeds extensively and the ^{59}Co spectrum of the chloride was too broad to be observed at 0.03 mol kg^{-1} (For the perchlorate complex, the ^{59}Co spectrum disappeared above 0.05 mol kg^{-1}.) The ^{35}Cl relaxation rate also steeply increases above 0.025 mol kg^{-1}, as will be shown later. (Fig. 5(b)). The difference between the perchlorate and chloride salts is discussed later along with the results of the counter-ion relaxations.

Although the magnitude of the ^{59}Co chemical-shift change is slight, the profile is characteristic of micellar formation. Figure 3 shows the change in the ^{59}Co chemical shifts as functions of the [Co(oct-en)(2,3,2-tet)]$^{3+}$ (a) and [Co(dod-en)(2,3,2-tet)]$^{3+}$ (b) concentrations. The chemical shifts were measured relative to those for 0.2 mmol kg^{-1} solutions. The result for the anionic [Co(oct-dhpta)]$^-$ complex is also shown for a comparison in Fig. 3(a). (In a previous paper for [Co-(alkyl-dhpta)]$^-$,[5] the ^{59}Co chemical shift results were not reported.) In the lower concentration range, the ^{59}Co signals of the cationic complexes shift slightly upfield, while those of the anionic complex shift downfield. This trend follows the general rule concerning the ^{59}Co chemical shift changes due to the ion-pairings of cationic and anionic complexes with hydrophilic counter ions.[19,23,25] For the cationic complex, the signal starts to shift downfield at around the critical concentrations deduced from the ^{59}Co relaxations. (0.12 mol kg^{-1} for [Co(oct-en)(2,3,2-tet)]$^{3+}$ and 0.01 mol kg^{-1} for [Co(dod-en)(2,3,2-tet)]$^{3+}$) For the anionic [Co(oct-dhpta)]$^-$ complex, on the other hand, the change occurs in the opposite direction. The break point (0.05 mol kg^{-1}) for [Co(oct-dhpta)]$^-$ also nearly coincides with the CMC of the previously reported value.

It is characteristic that the chemical shifts tend to fall downfield due to the micellization for the cationic cobalt(III) sur-

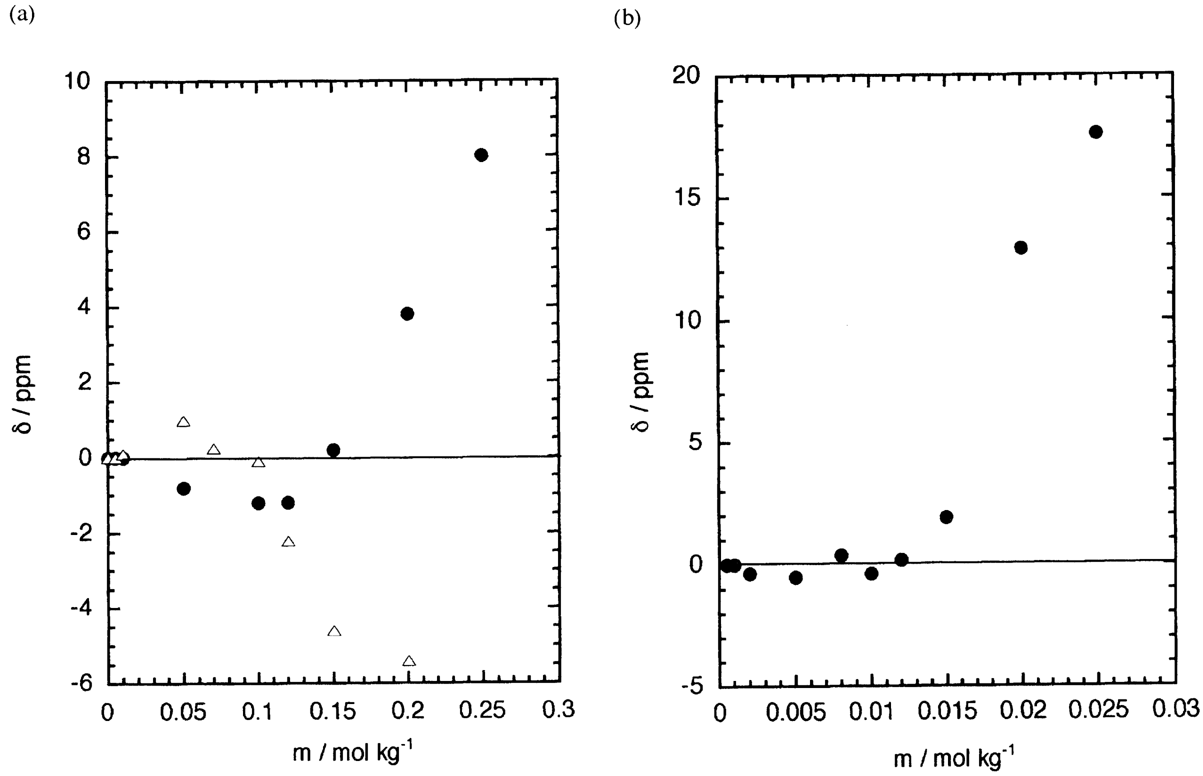


Fig. 3. (a) ^{59}Co chemical shifts for (I) [Co(oct-en)(2,3,2-tet)](ClO$_4$)$_3$ (●) and (II) Na[Co(oct-dhpta)] (△) in aqueous solutions as functions of the cobalt(III) complex concentrations. (b) ^{59}Co chemical shifts for [Co(dod-en)(2,3,2-tet)](ClO$_4$)$_3$ in aqueous solutions as a function of the cobalt(III) complex concentration.

factants. The ^{59}Co chemical shift for [Co(en)$_3$]$^{3+}$ has been related to the donor number of solvents by Mayer.[24] In the case of the en complex, the upfield shift is explained as an increase in the hydrogen bond between the amine protons of the ligands and the solvent molecules. On the basis of this principle, the downfield shift in the present system suggests that the interaction between the amine protons in the ligands and the water molecules decreases upon micellization. For the anionic [Co(oct-dhpta)]$^-$, the upfield shift upon micellization should be due to the negative charge of the head group; also, dehydration around the cobalt(III) headgroup may occur similarly to the cationic complex case, since a similar trend has been shown by Delville et al. for the [^{59}Co(CN)$_6$]$^{3-}$ system interacting with various hydrophobic cations.[25]

^{35}Cl, ^{1}H, and ^{2}H$_2$O NMR Changes in the Aggregation Process. Since the cobalt(III) surfactant is tripositive, counterions are extensively bound to the head group, and their NMR behavior also seems to be a good probe for monitoring the aggregation process of the cobalt(III) surfactant.[26] The ^{35}Cl$^-$ and ^{35}ClO$_4^-$ (I=3/2) relaxation rates may be governed by the quadrupolar mechanism (Eqs. 2 and 3) more completely than the ^{59}Co relaxation,[27] and the relaxation rate is considered to be sensitive to ionic interactions. The longitudinal relaxation rates for the counter ions of the octyl and dodecyl complexes are depicted in Figs. 4 (a) and (b), respectively. These results also show that the relaxation rates steeply increase above the critical concentrations, which almost coincide with those observed in the ^{59}Co linewidths. We can recognize that the true CMCs for [Co(alkyl-en)(2,3,2-tet)]$^{3+}$ are defined as the concentrations at which the ^{59}Co relaxation rates start to increase, as shown in Fig. 2.[28]

In the dodecyl complex (b), the difference between the chloride and perchlorate ions is remarkable. The ^{35}Cl$^-$ relaxation rate (26 s^{-1} for the hydrated 'free' chloride ion) increases more steeply with an increase in the complex concentration and, above 0.03 mol kg^{-1}, the ^{35}Cl$^-$ spectrum was too broad to be observed. Although the ^{35}ClO$_4^-$ relaxation rate (4.0 s^{-1} for the hydrated 'free' perchlorate ion) also increases, the concentration dependence is smaller. (In Fig. 4(a) the ordinate scale for the ^{35}ClO$_4^-$ relaxations is taken to be 6.5(=26/4) times as large as that for the ^{35}Cl$^-$ ordinate for convenience of comparison.) Considering the result of the ^{59}Co relaxations for both the chloride and perchlorate salts (Fig. 2(b)), we compared the Cl$^-$ and ClO$_4^-$ effects on the aggregation.

Since the ^{59}Co spectra disappeared at higher concentrations in both dodecyl complex salts, the aggregation process can be deduced from the ^{35}ClO$_4^-$ NMR. The maximum (around 0.1 mol kg^{-1}) in Fig. 4(a) indicates the saturation of counter-ion binding; above this concentration the micellar structures may be somewhat changed along with an increase in the concentration, since the change in the micellar shape also affects the extent of counter-ion binding.[29] The stronger binding of the chloride ion than the perchlorate ion to the cobalt(III) surfactant could be due to the smaller ionic radius of the former ion, which is consistent with the order of the

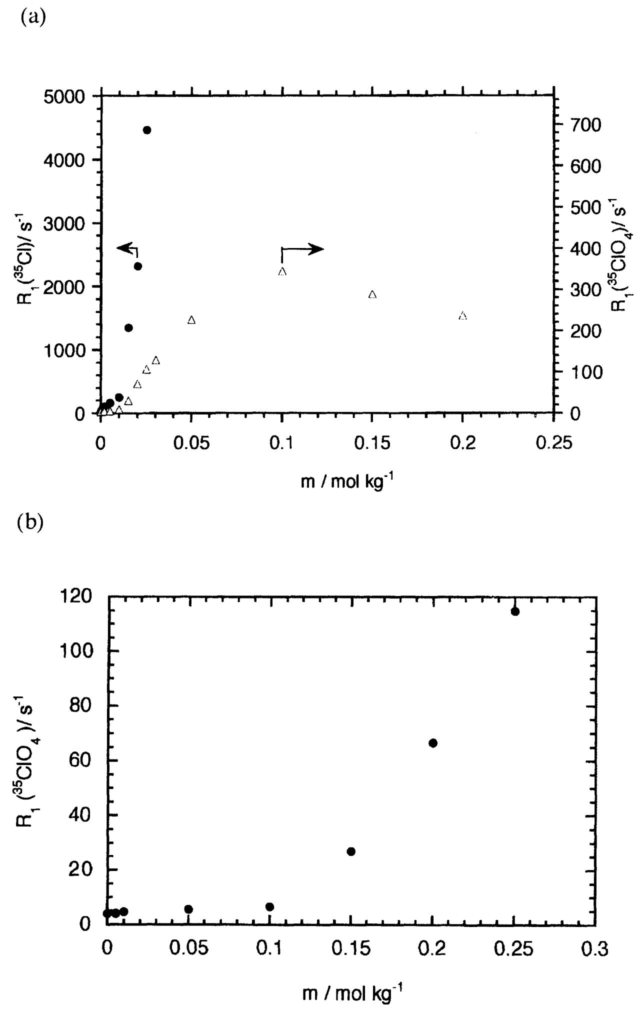


Fig. 4. (a) $^{35}Cl^-$ (●) and $^{35}ClO_4^-$ (△) longitudinal relaxation rates (R_l) for [Co(dod-en)(2,3,2-tet)]X_3 (X=Cl or ClO_4) in aqueous solutions as a function of the solute molality. (b) $^{35}ClO_4^-$ longitudinal relaxation rates (R_l) for [Co(oct-en)(2,3,2-tet)]$(ClO_4)_3$ in aqueous solutions as a function of the cobalt(III) surfactant molality.

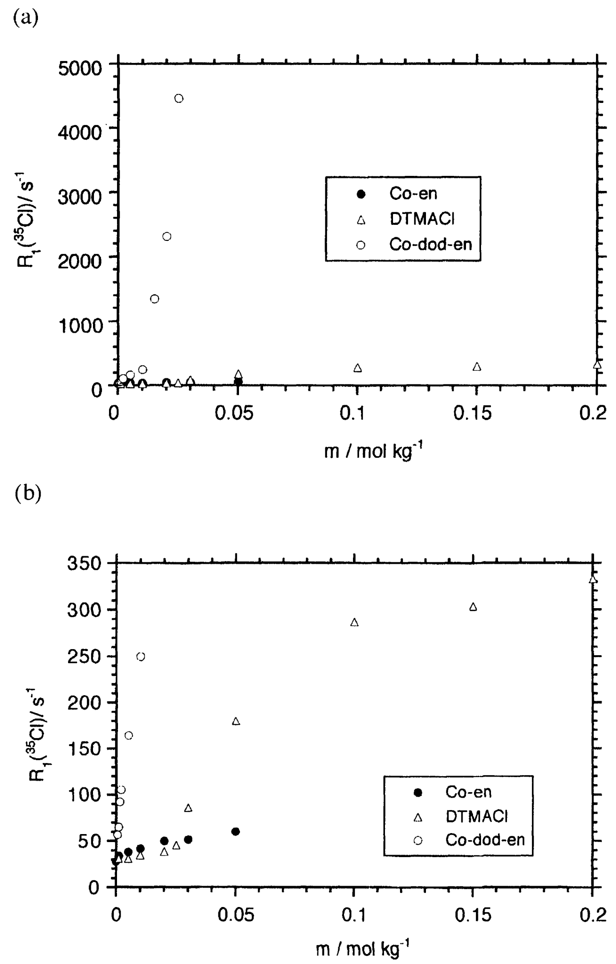


Fig. 5. (a) $^{35}Cl^-$ longitudinal relaxation rates (R_l) for [Co(dod-en)(2,3,2-tet)]Cl_3 (○) in aqueous solutions compared to the dodecyltrimethylammonium chloride (△) and [Co(en)$_3$]Cl_3 (●) systems as functions of the solute concentrations. (b) Enlarged the ordinate of (a).

lyotropic series. However, as shown in the ^{59}Co relaxations, at lower concentrations the presence of the perchlorate ion would be advantageous to form micelles of the cobalt(III) surfactant than the chloride ion. In other words, it is possible that the interaction of the chloride ion with the surfactant inhibits micellar formation, while this ion may be more effective for micellar growth than the perchlorate ion.

It is significant to consider the interactions of the chloride counter ions based on a comparison between the cobalt(III) surfactant and other cations. Figure 5 shows the $^{35}Cl^-$ relaxations for [Co(dod-en)(2,3,2-tet)]Cl_3 together with those for dodecyltrimethylammonium chloride (DTMACl) and [Co(en)$_3$]Cl_3. Since R_l can be assumed to be proportional to the extent in the interaction of the chloride ion, the chloride ion should interact with the cobalt(III) surfactant appreciably more than with the other cations, even below CMC (Fig. 5(a)). It is characteristic (Fig. 5(b)) that the R_l value is slightly larger in the [Co(en)$_3$]$^{3+}$ system than in the DTMA system at lower concentrations, while the relationship is reversed at higher concentrations (above 0.03 mol kg^{-1}). In the lower concentration range, the chloride ion interacts with [Co(en)$_3$]$^{3+}$ more strongly than with the DTMA cation at the 1 : 1 molecular level, due to the difference in the charge number. On the other hand, DTMA forms micelles above CMC (0.02 mol kg^{-1}), and the effective charge of the DTMA cation should be larger than [Co(en)$_3$]$^{3+}$ in this concentration range. The appreciably larger interaction of the chloride ion is seen more in the [Co(dod-en)(2,3,2-tet)]$^{3+}$ system than in the other two systems. Taking into account the charge number, the larger effect in the dod-en complex than in the en complex blow CMC seems to be specific. This effect of the cobalt(III) surfactant on the $^{35}Cl^-$ relaxations may be due to the larger motional restriction of the chloride ion by the cobalt(III) surfactant cation. This specific interaction of the chloride ion with the cobalt(III) surfactant is not detected by either ^{59}Co NMR or vapor-pressure osmometry. It is possible that the larger motional restriction of the chloride ion due to the cobalt(III) surfactant than due to the en complex is because of the slower motion of the former cation if the extent of the interaction is the same below cmc. However, the ^{1}H NMR chemical shift for $[Co(dod\text{-}en)(2,3,2\text{-}tet)]^{3+}$ compared to $[Co(en)_3]^{3+}$ also slightly shows a similar effect as observed in the case of $^{35}Cl^-$ relaxations (Fig. 6). We can consider here that in a simple ionic interacting system the extent of the ^{1}H chemical shift change reflects the extent of the interaction. In this figure, therefore, the (axial) methylene protons (3a) in the ethylenediamine moiety[30] of the dod-en complex should be more affected by the interaction with the chloride ions than those in the dodecyl chains (3b, 3c) and in the en complex(2). Therefore, there is a larger interaction between the head group of the trivalent positive surfactant and the chloride ion, compared to the en complex. One possible explanation for the specific interaction in the former complex is that the hydrophilic region of the cobalt(III) headgroup is more limited by the hydrophobic alkyl chain, and thus the counter-ion binding occurs at selective sites in the head group than in the en complex. It is noticeable that this specific interaction can be detected by NMR measurements, and, furthermore, that $^{35}Cl^-$ relaxation is more sensitive and drastically changeable due to ionic interactions. Since $^{35}Cl^-$ relaxation is affected by both the correlation times (τ_C) and the electric-field gradients, this parameter seems to be more sensitive to monitoring the counter-ion binding to the complex cation.

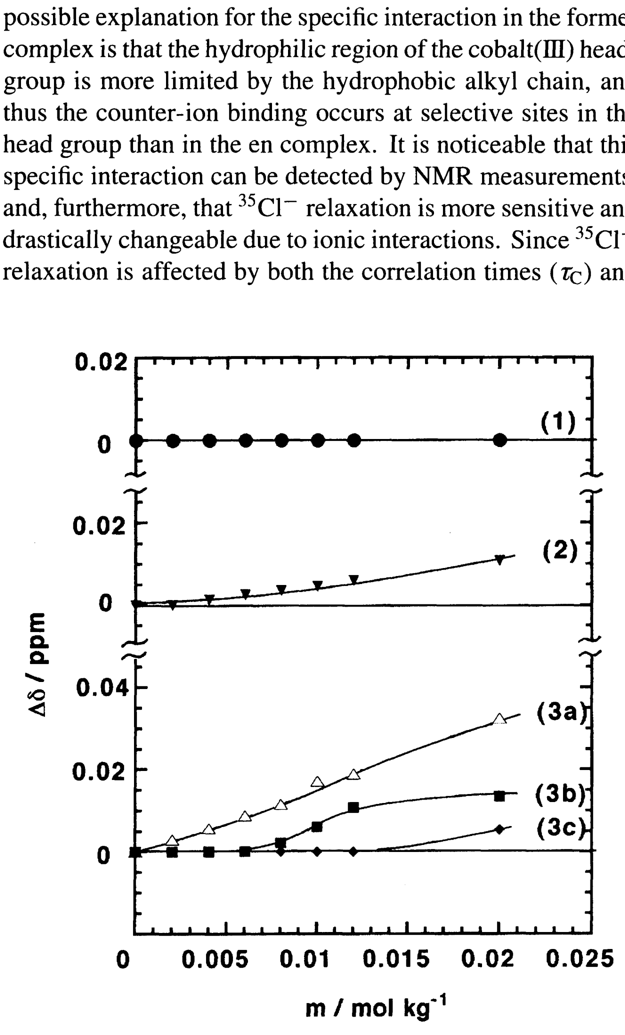


Fig. 6. ^{1}H chemical shift changes ($\Delta\delta$) for the ligands of the complex ions and trace H_2O as a function of the complex concentrations. The lines are drawn as an aid to the eye. (1) trace H_2O. (2) axial methylene protons of $[Co(en)_3]Cl_3$. (3) $[Co(dod\text{-}en)(2,3,2\text{-}tet)]Cl_3$. (a) axial methylene protons of the en and 2,3,2-tet ligands, (b) methylene group protons of the dodecyl chain, (c) terminal methyl protons of the dodecyl chain. The chemical shifts were compared to that of the methyl protons of acetone (7 mmol dm^{-3}) and their values extrapolated to zero concentration are as follows. (1) 2.5511 ppm, (2) 0.5684 ppm, (3a) 0.3298 ppm, (3b) −0.9452 ppm, (3c) −1.3672 ppm.

The $^{2}H_2O$ relaxation was not so greatly affected by the aggregation as expected from the fact that water molecules exist in a large excess of the surfactant ions. We show the result for the dodecyl complex in Fig. 7. The slight increase in the relaxation rate means that the ratio of the binding water to the bulk water increases upon micellization. This trend has been observed in many surfactant systems,[1,31] and the break point corresponds to cmc.

Vapor-Pressure Osmometry (VPO) of Aqueous [Co(dod-en)(2,3,2-tet)]$^{3+}$ Solutions. The vapor-pressure depression of aqueous solutions also offers significant information concerning aggregations. In this measurement, we used $[Co(dod\text{-}en)(2,3,2\text{-}tet)]Cl_3$. and $[Co(dod\text{-}en)(2,3,2\text{-}tet)](ClO_4)_3$, compared to SDS and DTMACl. At first, we measured the molecular weights of these four surfactants below 0.01 mol kg^{-1} according to the method described in the experimental section. The obtained molecular weights almost agree (within 5% errors) with the calculated ones, assuming that SDS and DTMACl are 1-1 electrolytes, and that the cobalt(III) surfactants are 1-3 electrolytes. Figure 8 shows a plot of the vapor-pressure depression vs. the surfactant concentrations for the aqueous $[Co(dod\text{-}en)(2,3,2\text{-}tet)]Cl_3$ and $[Co(dod\text{-}en)(2,3,2\text{-}tet)](ClO_4)_3$ solutions (b) compared with the cases of SDS and DTMACl (a). The break points for the SDS and DTMACl systems correspond to the well-known cmc values, and those for the cobalt(III) surfactant salts also agree with the cmcs determined by the present NMR measurements. The agreement of the molecular weights below cmc means that specific counter-ion binding is not detected from the macroscopic viewpoint in this concentration range. The Z value defined as the (slope 1)/(slope 2) ratio (where 1 and 2 mean below and above the critical point, respectively) is the apparent aggregation number of micelles.[32] The larger Z value for SDS (8.7) than that for DTMACl (2.5) is consistent with the larger aggregation number of SDS (around 80) than that of DTMACl (around 60).[9] However, the relative value of the slope (2) is strongly correlated to the extent of

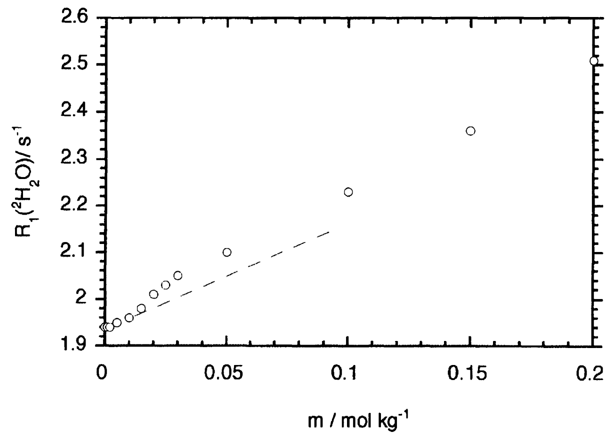


Fig. 7. $^{2}H_2O$ longitudinal relaxation rates (R_1) as a function of $[Co(dod\text{-}en)(2,3,2\text{-}tet)](ClO_4)_3$ molality.

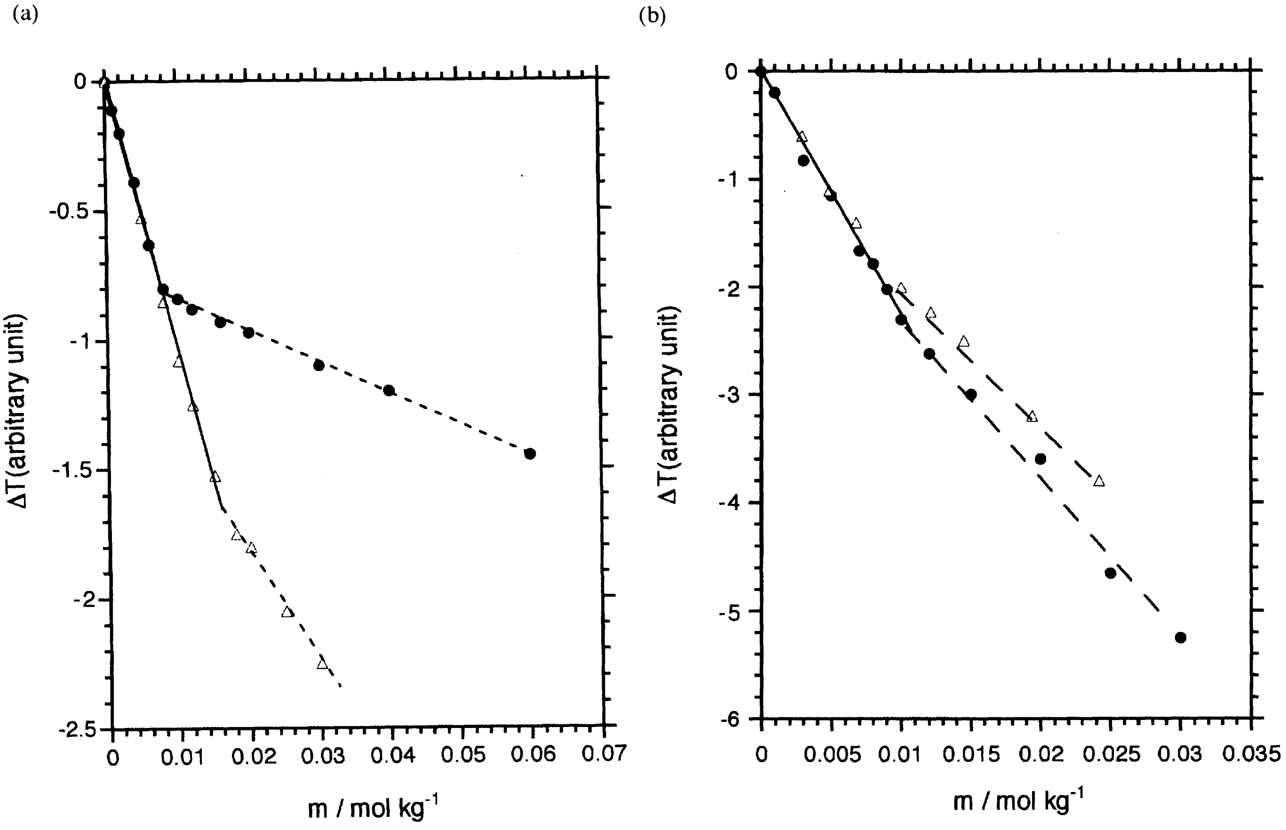


Fig. 8. Depression of the vapor pressure for aqueous surfactant solutions. All the data were measured in the same sensitivity setting. (a) SDS (●) and DTMACl (△). (b) [Co(dod-en)(2,3,2-tet)]Cl_3 (●) and [Co(dod-en)(2,3,2-tet)]$(ClO_4)_3$ (△).

Table 1. Critical Micelle Concentrations of Some Octyl and Dodecyl Surfactants in Aqueous Media

Compound	Temp/°C	cmc/mol dm^{-3}	Reference
$C_8H_{17}SO_3Na$	40	0.16	9
$C_8H_{17}SO_4Na$	40	0.14	9
$C_8H_{17}N(CH_3)_3Cl$	25	0.18	9
[Co(oct-en)(2,3,2-tet)]$(ClO_4)_3$	27	0.12[a]	This study
Na[Co(oct-dhpta)]	27	0.07	5
$C_{12}H_{25}SO_4Na$	25	0.008	9
[$C_{12}H_{25}$Pr]Cl	25	0.017	9
$C_{12}H_{25}N(CH_3)_3Cl$	25	0.015	9
[Co(dod-en)(2,3,2-tet)]Cl_3	27	0.010[a]	This study
[Co(dod-en)(2,3,2-tet)]$(ClO_4)_3$	27	0.008[a]	This study
Na[Co(dod-dhpta)]	27	0.002	5

a) These values are in mol kg^{-1} units.

the counter-ion binding in the micelles, and the Z value is not very closely related to the aggregation number of micelles, as shown in the case of nonionic surfactants.[32] Although the slight change in the slope for the Co-(dod-en) complex (Z is around 1.6-1.8 for both salts) suggests a small aggregation number of the micelles, a detailed interpretation of the Z value is difficult in the present systems, since the counter-ion binding is strong in ionic micellar systems.

Since the molecular weights could be exactly estimated below cmc, any aggregation is negligible in this concentration range; this seems to be in conflict with that of the ^{35}Cl relaxations and the ^{1}H NMR chemical shifts for the cobalt(III) surfactants. We therefore recognize that the interaction between the chloride ion and the surfactant below cmcs is insensitive to a change in the vapor-pressure depression, while it is sensitive to the NMR parameters. It can be roughly said that the cmc values obtained from the vapor-pressure depression are consistent with those from NMR studies; the latter method is more sensitive to ion aggregations.

The finally confirmed cmc values obtained for the present cobalt(III) surfactant solutions are listed in Table 1 together with those for surfactants having dodecyl and octyl chains. This table shows that the effect of the head group charge on the cmc value can not be explicitly seen in the present cobalt(III) surfactants. The smaller cmc values for [Co(alkyl-dhpta)]$^-$ are noticeable. The molecular feature of this surfactant which is distinguishable from the other monovalent surfactants is the size of the head group. The larger size of the head group results in a lowering of the effective charge density. Since nonionic surfactants have much lower cmcs than do ionic surfactants containing equivalent hydrophobic groups,9) a lower electric-charge density may give smaller cmc values of the surfactants. The charge density of the cobalt(III) complex head group is also reduced due to the large size of the head group. As can be seen in the ^{35}Cl relaxations, the counter ions interact with the head group extensively in a trivalent positive surfactant system based on microscopic viewpoint, and this interaction may also attenuate the effect of the head group charge on micellization. Although counter-ion binding of the trivalent positive surfactant was not detected in the vapor-pressure depression, this effect is significant in an NMR study. The ^{35}Cl relaxation studies suggest that the chloride ion interacts with the cobalt(III) surfactant more strongly than does the perchlorate ion, whereas the cmc of the perchlorate is slightly smaller than that of the chloride. In this comparison, a smaller net charge of the head group due to the larger ion-binding is not effective concerning the micellization.

In conclusion, the cmc values of the trivalent positive cobalt(III) surfactants are not appreciably different from those of those surfactants having equivalent alkyl chains. The remarkable feature of the present surfactants is the strong interaction of the chloride counter ions. The effect of the trivalency of the head group on the aggregation may be attenuated by the counter-ion interaction and the large size of the head group.

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