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NMR Studies on the Aggregation of Mononuclear and Dinuclear Cobalt(III) Amphiphilic Complexes Having Alkyl Chains

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The aggregation of novel type cobalt(III) surfactants, such as $[Co(en)_2\{NH_2(CH_2)_2S(1\text{-}C_nH_{2n+1})\}]^{3+}$ (n = 6, 8, and 12) and $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_mS(CH_2)_2NH_2\}Co(en)_2]^{6+}$ (m = 8 and 12), was studied in water using multinuclear NMR spectroscopies, ^{1}H NMR self-diffusions, and ^{1}H NMR chemical shifts. The ^{59}Co linewidths of the surfactants were useful to monitor the premicellar and micellar formation. It was revealed that the tripositive mononuclear surfactants have comparable cmc (critical micelle concentration) values to those for the usual monovalent surfactants having the same alkyl chains. The ^{35}Cl longitudinal relaxation rates for the counterions were useful to monitor the two kinds of ionic interactions, i.e., those with the surfactant monomers and with the micelles. We determined the cmcs for the premicellar formation in the hexyl mononuclear and octyl dinuclear complex systems. The determination of this kind of cmc has become possible by using such highly charged complexes as the cystam complex and by measurements of the ^{59}Co linewidths and of the ^{35}Cl longitudinal relaxation rates. The self-diffusion coefficient for the surfactants revealed that the aggregation behavior is similar in comparison between the hexyl mononuclear and octyl dinuclear complexes or between the octyl mononuclear and dodecyl dinuclear complexes.

Surfactant metal complexes are expected to provide a wide range of interesting phenomena on the aggregation behavior in solutions due to a variety of their charge numbers, sizes, and the extent of hydrophobicity and of hydrophilicity by a combination of central metals and ligands.[1] However, their physical properties in solutions have not been extensively studied.[2—6] In the studies so far performed, novel characters of surfactant metal complexes have been revealed, and the results should provide significant information on surfactant solution chemistry. One of the present authors (K.Y.) previously reported syntheses of cobalt(III) surfactants of $[Co(en)_2\{NH_2(CH_2)_2S(1\text{-}C_nH_{2n+1})\}]^{3+}$ (n = 8, 10, and 12) and $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_mS(CH_2)_2NH_2\}Co(en)_2]^{6+}$ (m = 8 and 10).[7,8] They are abbreviated here as a cystam ($NH_2(CH_2)_2S$ = cystamine) complex. These compounds are especially novel-type amphiphiles due to their highly positive charge or the α,ω-type surfactant (for the latter). However, there have been no studies on the physical properties of their aqueous solutions; we report here studies on self-associations of the mononuclear (n = 6, 8, and 12) and dinuclear (m = 8 and 12) complexes using NMR spectroscopies, such as ^{59}Co and ^{35}Cl relaxations, ^{1}H PGSE (pulsed field gradient spin-echo) self-diffusions, and ^{1}H chemical shifts. We determined the cmcs and compared the results with the other surfactants hitherto studied. Although a higher charged headgroup is considered to be less favorable to micellization from an electrostatic viewpoint,[9] neutralization of the surfactant charge by the counterions seems to be advantageous to micellization, and cmc for the surfactant was consequently close to that for the monovalent surfactant having the same alkyl chains.[5] In previous studies,[4,5] one of the present authors (M. I.) measured the ^{59}Co linewidths and ^{35}Cl relaxation rates for aqueous cobalt(III) surfactant solutions, and revealed that these values provide useful information on the cmcs and ionic interactions in micellization. The NMR methodology is favorably utilized for novel surfactants to understand the relationship between the aggregation process and the ionic interactions, since this method can give microscopic information concerning both surfactants and counterions by using smaller amounts of samples compared to the conventional methods, such as electric conductivities and viscosities.

One of the present purposes is to correlate the multivalency of the surfactants with the counterion-bindings in the micellization using NMR spectroscopies. The ^{35}Cl relaxations will give useful information on the two kinds of chloride ion bindings, i.e., ionic interactions with free surfactants and with their aggregates. The ^{59}Co linewidth of the surfactant headgroup showed a clear criterion for premicellar formation. ^{1}H PGSE self-diffusion studies for the surfactants and solvent water also gave information on the aggregation processes of cobalt(III) surfactants. The obtained cmc values were compared with the usual surfactants having the same alkyl chains to understand the effects of the headgroups on the aggregation behavior. The other aim of the present study is to understand the unique aggregation processes of the dinuclear

(α,ω-type) highly-charged complexes. The aggregation of the dinuclear dodecyl and octyl complexes will be discussed in comparison with appropriate mononuclear complexes.

Materials and Methods.

Materials. The cobalt(III) complexes, $[Co(en)_2\{NH_2(CH_2)_2S\text{-}(1\text{-}C_nH_{2n+1})\}]Cl_3$ (n = 6, 8, and 12) and $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_mS(CH_2)_2NH_2\}Co(en)_2]Cl_6$ (m = 8 and 12), were prepared according to a previously reported method for the latter of m = 8.[7] In purifying complexes, however, we modified the previous method as follows. For the mononuclear complexes, after *N*,*N*-dimethyl formamide (DMF) of the reaction solvent and unreacted bromoalkane were extracted into diethyl ether, the resulting dark red oil was dissolved in methanol, adsorbed on an LH-20 column, and eluted with methanol. The first crop of orange solution was evaporated to dryness in a rotary evaporator, a small amount of water was added, and sodium perchlorate was added to crystallize the perchlorate. The chloride was obtained by conversion of the perchlorate with an ion-exchanger in the Cl^- form. For the dinuclear complex, although removal of the sodium chloride used for the eluting agent in the SP-Sephadex C-25 chromatography was somewhat difficult, we completely removed it by the following method. Most amounts of NaCl contained in the eluates were removed by repeated crystallization from water with the addition of ethanol. A dinuclear complex containing trace NaCl was extracted into small amounts of dimethyl sulfoxide, and the chloride of the complex was crystallized out with an addition of ethanol.

We used mixtures of *rac*- and *meso*-isomers of the dinuclear complexes, since the differences in the physical properties among these isomers would be negligible for the purpose of the present studies. The purities of crystals were confirmed using CHN elemental analyses[10] and ^{59}Co NMR spectra. The Karl–Fischer titration and CHN elemental analyses evidenced that of all the complexes include some amounts of water in the crystals, as shown in the note 10.

NMR Measurements. ***T_1* and Line-Width Measurements.** Most of the ^{59}Co and ^{35}Cl NMR spectra were obtained on a JEOL JNM GX-270 FT NMR spectrometer operating at 64 and 26 MHz, respectively. The longitudinal relaxation time (T_1) for the ^{35}Cl nucleus or ^{59}Co nucleus was obtained by the inversion-recovery method using the pulse sequence of (-180° pulse-τ-90° pulse-T-)$_n$. For measurements of T_1, ten different pulse intervals (τ) were used with a waiting time (T) of more than $6T_1$. In order to check the dependence of T_1 on the observation frequencies, we also measured the ^{35}Cl T_1 values for the dodecyl complexes on a JEOL FX-90 spectrometer operating at 8.8 MHz, since the surfactants having the longest alkyl chains will form the largest aggregates, and therefore have the largest possibility for the relaxation times to be out of the extreme narrowing condition. The linewidths ($\Delta\nu_{1/2}$) of the ^{59}Co spectra were correlated with their T_2 values as follows:

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2}. \tag{1}$$

The T_1 values were determined within 5% errors and the linewidths were within 0.1 kHz errors. For the same reason as ^{35}Cl T_1, we also measured the ^{59}Co linewidths for the dinuclear complex at 21 MHz and compared the results with those measured at 64 MHz. In the present study, we discuss the relaxations using the R_1 ($= T_1^{-1}$) or $\Delta\nu_{1/2} \propto R_2$ ($= T_2^{-1}$) values.

Self-Diffusion Studies. The self-diffusion coefficients were measured by the NMR FT-PGSE (Fourier Transform Pulsed-Gradient Spin-Echo) technique.[11] The measurements were performed on a JEOL FX-90 spectrometer operating at 90 MHz for protons. The spectrometer was equipped with an apparatus that produced a field gradient in the range 0.3—1.0 T m^{-1}. The solvent used was 99.9% deuterium oxide. For the water, the change in the intensity of the ^{1}HDO signal was followed. For the surfactants, the intensity of their methylene ^{1}H signals of alkyl chains was followed. The accuracy of the measured diffusion coefficients is estimated to be better than ±5%.

^{1}H NMR Chemical Shifts. We followed a slight ^{1}H NMR chemical shift change for the hexyl mononuclear complex as a typical case. The measurements were performed on a JEOL JNM GX-270 spectrometer operating at 270 MHz. The ^{1}H NMR signals used were terminal methyl protons and methylene protons of alkyl chains and axial methylene protons of the ethylenediamine moiety for the hexyl mononuclear complex. We call them peaks 1, 2, and 3, respectively. The chemical shifts were compared to that of the water proton, since our previous result showed that the water protons and additive acetone protons are almost unchanged by interactions with the cobalt(III) surfactants.[5] The samples were dissolved in 99.9% D_2O.

All of the NMR measurements were performed at 27 °C. The temperature was controlled within ±0.5 °C by a JEOL GVT2 temperature control unit.

Results and Discussion

Aggregation of Mononuclear and Dinuclear Complexes in Aqueous Solutions Monitored by ^{59}Co Linewidths and ^{35}Cl Longitudinal Relaxation Rates. The relaxation rates (or linewidths) of the solutes and solvents tend to increase with an increase of the solute concentrations. In order to precisely discuss the relaxations in aggregate systems, we firstly checked dependence of the relaxation rates on the observation frequencies.[12] The measurements were performed for the dodecyl mononuclear and dinuclear complexes, where the ^{35}Cl relaxation rates or the motional restrictions of chloride ions by the surfactants should be the largest. As a consequence, we confirmed that concerning both the ^{59}Co linewidths and the ^{35}Cl relaxation rates the values observed at two frequencies agree within 5% error; that is, the extreme narrowing would hold in all of the present systems. Furthermore, we confirmed that the ^{59}Co transverse relaxation rates are governed by the quadrupolar relaxations by measurements of the longitudinal relaxation times (T_1) in comparison with the linewidths for the 0.1 mol kg^{-1} hexyl mononuclear complex.[13] We can thus express the ^{59}Co linewidths as follows:

$$\pi\Delta\nu_{1/2} = 1/T_2 = R_{2Q} = \frac{2\pi^2}{49}\left(\frac{eQ}{h}\right)^2\left(eq(\mathrm{M})\right)^2\tau_{c\perp}(\mathrm{M}), \tag{2}$$

where eQ is the quadrupolar moment of the ^{59}Co nucleus, eq(M) the electric field gradient along the principal axis at the nuclear site, and τ_c(M) the rotational correlation time for the complex. As we previously revealed, an increase in the ^{59}Co relaxation rates with an increase in the interactions of cobalt(III) complexes in micellar systems can be ascribed to increases in both eq and τ_c.[15] The other previous results show that the ^{59}Co relaxation rate in $[Co(en)_3]^{3+}$ is negligibly affected by Cl^-;[16,17] in the present systems; the effect will be further less because of the larger size of the complexes. We can thus consider that the increase in the ^{59}Co linewidths would occur by self-associations of the complex. In discussing ^{59}Co spectrum broadening, the following pseudophase or two-state model is applicable as a first approximation:[18]

$$R_i = p_F R_{iF} + p_M R_{iM}, \tag{3}$$

where p_F and p_M are the fractions of the 'free' and 'micellar' states, respectively, for the surfactant molecules ($p_F+p_M = 1$). Because R_{iM} ($i = 1$ or 2) is larger than R_{iF}, the increase in the relaxation rates with an increase in the concentration can be ascribed to an increase in the micellar fractions (p_M).

The ^{35}Cl longitudinal relaxation rates, which were also nearly independent on the observation frequencies, can be similarly expressed as

$$R_1 = \frac{1}{T_1} = \frac{2\pi^2}{5}\left(\frac{eQ}{h}\right)^2 \left(eq(\mathrm{Cl})\right)^2 \tau_c(\mathrm{Cl}), \tag{4}$$

where eQ is the quadrupolar moment of the ^{35}Cl nucleus, eq(Cl) the electric field gradient, and τ_c(Cl) the reorientational correlation time for the fluctuating electric-field gradients at the position of the Cl nucleus. In Eq. 4, both eq(Cl) and τ_c(Cl) would increase with an increase in the interactions between the chloride ion and the cobalt(III) surfactant. We can consider that the ^{35}Cl longitudinal relaxation rate is a sensitive probe for monitoring the extent of the interaction with the surfactants and that of the motional restriction by the binding to the surfactants.

1. Mononuclear Hexyl, Octyl, and Dodecyl Cystam Complexes. The ^{59}Co linewidth vs. cobalt(III) complex concentration plots shown in Figs. 1(a) and 2 for the dodecyl and octyl mononuclear complexes have break points at 0.02 and 0.3 mol kg^{-1}, respectively. The ^{35}Cl relaxation rates in the same system (Figs. 1(b) and 2) also show similar break points at nearly the same concentration, which will therefore correspond to cmc. In the dodecyl complex system (Fig. 1(a)), the ^{59}Co linewidth shows the simplest profile which can be understood from Eq. 3: at concentrations below cmc, only the monomer contributes to the linewidth while above cmc the extent of interaction with the micelles increases with an increase in the surfactant concentrations. On the other hand, for the octyl complex (Fig. 2), we can see that the ^{59}Co linewidth slightly increases with an increase in the concentration, even below cmc. It is possible that this trend is due to the formation of premicelles.

In the hexyl cystam complex, both the ^{59}Co linewidths and ^{35}Cl relaxation rates (Fig. 3(a)) steadily increase at concentrations above 0.2 mol kg^{-1} with an increase in the concentration, and then above 0.5 mol kg^{-1} they showed slightly upward deviations from the linear relationship. Such an upward deviation is generally observed for the counterion relaxations in the micellizations, since the counterions bound to the higher aggregates are more motionally restricted than those bound to the free surfactant. We can see another characteristic feature that in the lower concentration ranges the relaxation rates steeply increase. This feature is clearly seen,

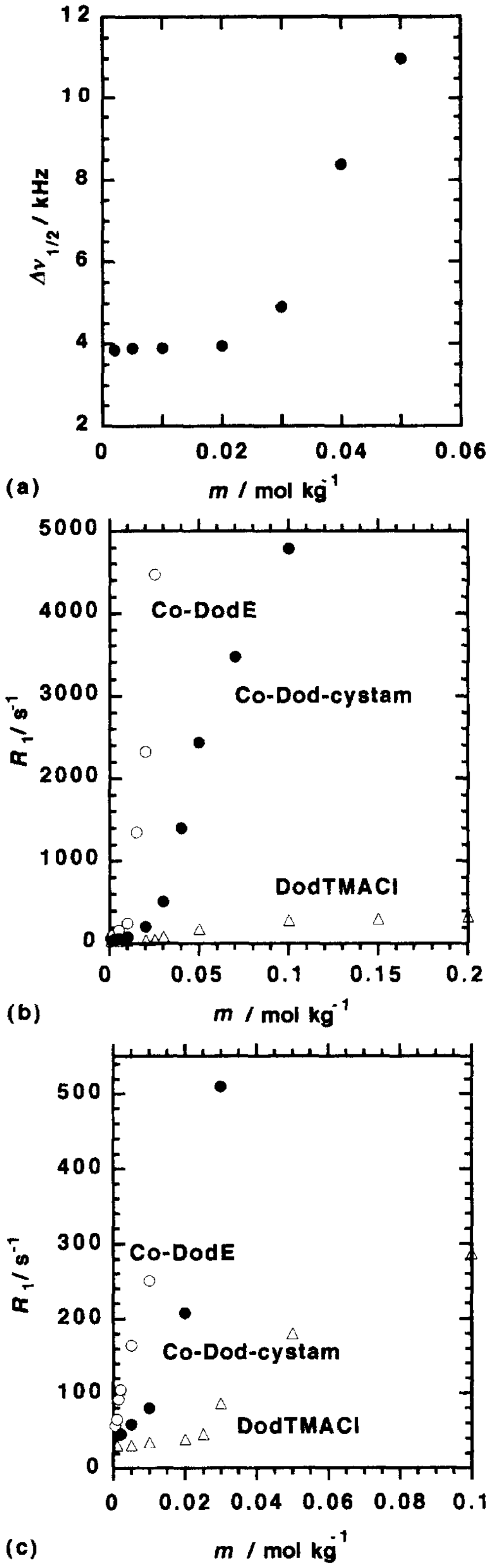

Fig. 1. (a) ^{59}Co NMR linewidths ($\Delta\nu_{1/2}$(^{59}Co)) for the dodecyl mononuclear complex as a function of the complex concentrations. (b) ^{35}Cl longitudinal relaxation rates in the aqueous dodecyl cystam complex (abbreviated as Co-Dod-cystam) compared to [Co(DodE)(2,3,2-*tet*)]Cl$_3$ (as Co-DodE) and to dodecyltrimethylammonium chloride (as DodTMACl). (c) Enlarged the ordinate of (b) in the lower concentration ranges.

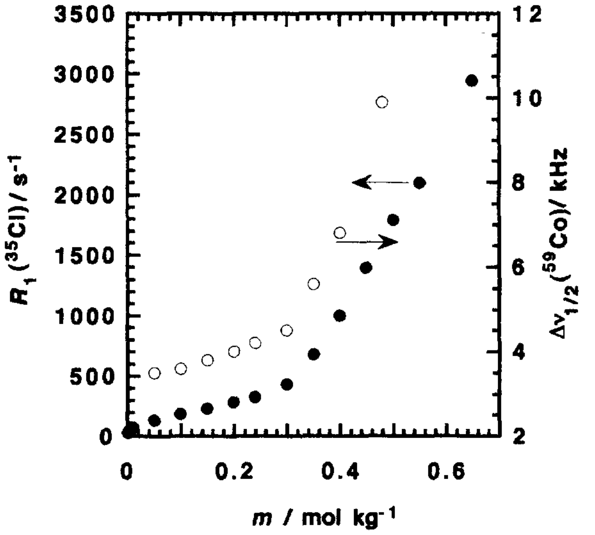

Fig. 2. ^{59}Co NMR linewidths ($\Delta\nu_{1/2}(^{59}Co)$) (○) and ^{35}Cl longitudinal relaxation rates ($R_1(^{35}Cl)$) (●) for the octyl mononuclear complex as a function of the complex concentrations.

except for the dodecyl complex, and is described for the hexyl mononuclear complex as a typical case. (Fig. 3(b); the ^{35}Cl relaxation rate at $m = 0$ was determined from that in the 0.01 mol kg^{-1} NaCl solution, where the ionic interactions of the chloride ion with the sodium ion will be negligible.) This stage of steep increase in the relaxation rates can be attributed to the interactions of chloride ions with the cobalt(III) surfactant monomer, as has been reported by our group for $[Co(en)_3]Cl_3$.[5] After this steep increase, the ^{59}Co linewidth starts to increase. A similar profile was seen in the octyl dinuclear complex system, as shown below (Fig. 5).

Here, we try to interpret the steep increase in the ^{35}Cl relaxations from the ion-pair formation equilibrium between the chloride ions and the tripositive hexyl mononuclear complex as a typical case. For the overall relaxation rates, a similar relationship as Eq. 3 can be written, i.e.,

$$R_1 = R_{1f}p_f + R_{1b}p_b, \tag{5}$$

where R_{1f} is the relaxation rate for 0.01 mol kg^{-1} NaCl (corresponding to the intercept in Fig. 3(b)) and R_{1b} that for the ion-pair; p_f and p_b are the fractions of free and bound Cl$^-$, respectively. The ion-pair formation constant (K_{IP}) for the tripositive cobalt(III) complex chloride is expressed as

$$K_{IP} = \frac{x}{(c_t - x)(3c_t - x)}, \tag{6}$$

where x is the concentration of ion-pairs and c_t the total concentration of the cobalt(III) complex. Concerning p_f and p_b, the following relationship is also to be considered: $p_f + p_b = 1$ and $p_b = x/3c_t$. In order to estimate the extent of the ion-pair formation, we used the following Debye–Hückel equation for the concentration dependence of K_{IP}:

$$\log K_{IP}(\mu) = \log K_{IP}(\mu = 0) - \frac{6 \times 0.5\sqrt{\mu}}{1 + 0.3a\sqrt{\mu}}, \tag{7}$$

where μ is ionic strength and a (in Å) the closest distance of approach of ions.

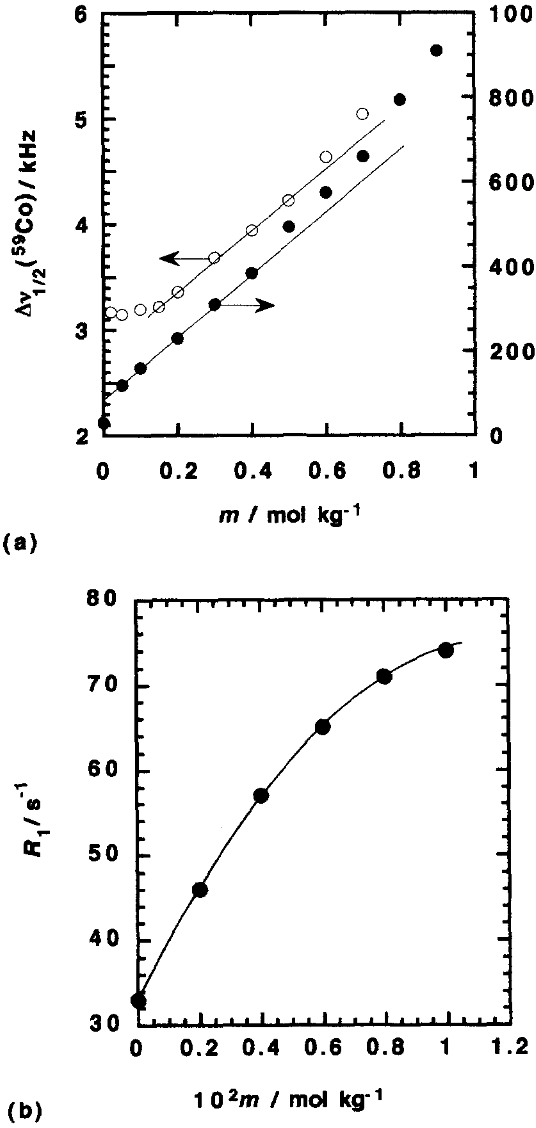

Fig. 3. (a) ^{59}Co NMR linewidths ($\Delta\nu_{1/2}(^{59}Co)$) (○) and ^{35}Cl longitudinal relaxation rates ($R_1(^{35}Cl)$) (●) in the aqueous hexyl mononuclear complex solutions. (b) Expanded the ordinate of $R_1(^{35}Cl)$ in the lower concentration ranges. The line in (b) is the calculated one using $R_{1b} = 900$ s^{-1} and K_{IP} ($\mu = 0$) = 20 mol^{-1} kg (see text).

From Eqs. 5, 6, and 7, we can determine the two parameters, K_{IP} ($\mu = 0$) and R_{1b}, so as to fit the experimental results in Fig. 3(b); in Eq. 7 we take 6 Å (= 0.6 nm) as the a value, whose estimation error does not significantly affect the result. According to the Fuoss theory, K_{IP} ($\mu = 0$) is estimated to be 18 mol^{-1} kg.[19] If we take 900 s^{-1} and 20 mol^{-1} kg as R_{1b} and K_{IP} ($\mu = 0$), respectively, the calculated relaxation rates well explain the experimental results, as shown in Fig. 3(b). This calculation satisfactorily fits the experimental results up to 0.1 mol kg^{-1} where the hexyl complex may still be present as monomers deduced from the ^{59}Co linewidths (Fig. 3(a)). This calculation says that about 36% of the cobalt(III) complex is ion paired with the chloride ion at 0.1 mol kg^{-1}. The optimized values of K_{IP} ($\mu = 0$) and R_{1b} mean that a specific interaction between the chloride ion and the cobalt(III) complex is not detected, but that the ion-pairing of the chloride ion with the complex ion appreciably affects the ^{35}Cl relaxation parameters (as a product of $\{eq(\mathrm{Cl})\}^2$ and $\tau_c(\mathrm{Cl})$ in Eq. 4).

The ^{1}H NMR chemical shift may also provide useful information on the interactions in the cystam complex. Figure 4 shows the changes in the chemical shifts for the hexyl complex with an increase in the complex concentration. There is a different trend in the changes in comparing between the peak positions in the alkyl chains and those in the ethylenediamine parts. It can be seen that for the methylene protons (peak #3) in the ethylenediamine the chemical shift shows a maximum at 0.20 mol kg^{-1}, which nearly agrees with the break point for the ^{59}Co line widths, and then the ^{1}H spectrum shifts to upfield. Below this concentration, the ^{35}Cl relaxation rates show that the interaction of the headgroups with the chloride ions proceeds and the strong electrostatic repulsion between the positively charged headgroups would be gradually reduced. Above this concentration, the reduction of the headgroup-repulsion will facilitate the self-association. The ^{59}Co linewidth and ^{1}H chemical shift of peaks #1 and #2 are insensitive to the neutralization of the headgroups, but are more sensitive to self-association. On the other hand, the ^{35}Cl relaxation rate and ^{1}H chemical shift of peak #3 are sensitive to both interactions and are changed accompanying with a change in the interaction modes. We can thus understand that the premicelles may start to be formed at 0.15—0.20 mol kg^{-1}.

In order to see the relationship between the ion-pairing and micellization, we show ^{35}Cl relaxation vs. concentration plots for the dodecyl cystam complex in comparison with the other dodecyl surfactant system (Fig. 1(b)). The results for the 2,3,2-*tet* complex (= (3.7-diazanonane-1,9-diamine)(*N*-dodecylethylenediamine)cobalt(III) chloride, abbreviated as Co-DodE complex) and dodecyltrimethylammonium chloride (DodTMACl), were taken from Ref. 5. The appreciably larger effects of the positive charge of the cobalt(III) surfactants on the counterion relaxations are seen compared to the univalent DodTMA cation. Because the sizes and molecular weights of the cystam complex are similar to those of the 2,3,2-*tet* complex, the ^{35}Cl relaxation rate is a good probe to monitor the extent of the chloride ion-interactions in comparing between the two complexes below cmc (Fig. 1(c), enlarged coordinate of (b)). The degree of motional restriction of the counterions is significantly larger in the 2,3,2-*tet* complex system than in the cystam one. This result is reasonable, since the former complex has more N–H protons, and is therefore more favorable to form hydrogen bondings with the chloride ion, as shown in a previous study.[5]

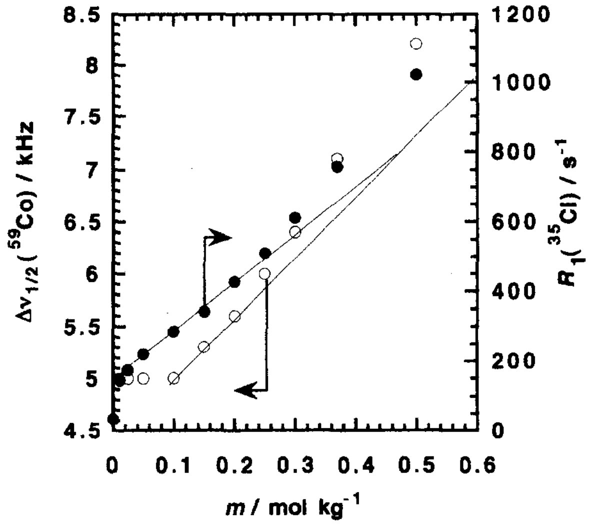

Fig. 5. ^{59}Co NMR linewidths ($\Delta\nu_{1/2}(^{59}\mathrm{Co})$) (○) and ^{35}Cl longitudinal relaxation rates ($R_1(^{35}\mathrm{Cl})$) (●) in the aqueous octyl dinuclear complex solutions. The lines are drawn as an aid to the eye.

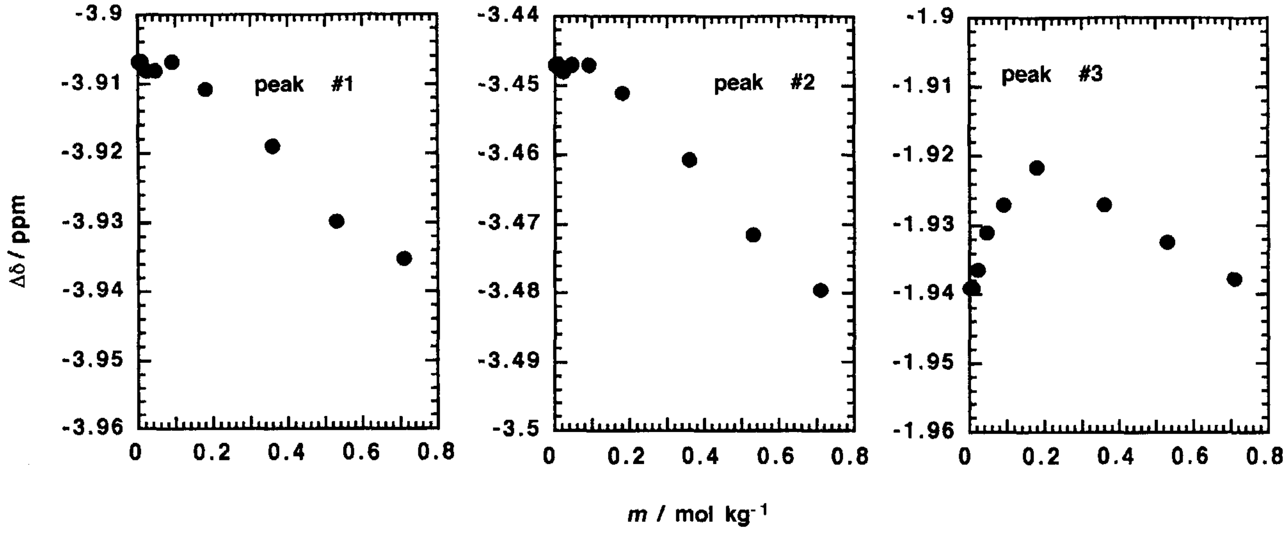

Fig. 4. ^{1}H chemical shift changes ($\Delta\delta$) for the ligand of hexyl mononuclear complex (●) as a function of the complex concentrations. peak #1 is terminal methyl protons of the alkyl chains. peak #2 is methylene group protons of the hexyl chains. peak #3 is axial methylene protons of the ethylenediamine ligands. The chemical shifts were compared to that of trace (around 0.1%) H_2O.

We determined the cmcs for the cobalt(III) surfactants from the concentration dependence of the ^{59}Co NMR linewidths; the results are listed in Table 1 together with the values for the other surfactants. An increase in the electric charge of the headgroup should increase the cmc values due to the electrostatic repulsions.[9] However, the cmcs listed in Table 1 show that the tripositive surfactants have comparable cmc values to those for the usual univalent surfactants. One possibility of the similar cmc values is ascribed to a reduction of the electrostatic repulsion by the counterion bindings.[5] Therefore, the larger cmc values for the octyl and dodecyl cystam complexes than for the corresponding 2,3,2-*tet* complex would probably be due to the smaller degree of the counterion bindings in the former complex. A simple calculation for the mononuclear hexyl complex described above suggests that the extent of the counterion bindings would not be so large as the net positive charge is reduced to unity. The headgroup sizes should thus also be effective on micellar formation, since the larger size of the headgroup would reduce the electrostatic repulsions between the headgroups.

2. Dinuclear Octyl and Dodecyl Cystam Complexes Compared to the Mononuclear Hexyl and Octyl Complexes. The result of the ^{59}Co NMR linewidths for the octyl dinuclear complex showed that slight self-association starts at around 0.10 mol kg^{-1}, while a critical point is not clearly detected (Fig. 5). This result suggests that lower aggregates, like premicelles, are formed prior to the normal micelles. However, we can see slight upward deviations from the linear relationships above 0.25 mol kg^{-1} both in the ^{59}Co linewidth and ^{35}Cl relaxation-rate plots, whose profiles are similar to those for the hexyl mononuclear complex. Therefore, this break point can be recognized as the critical point for the higher micelles. On the other hand, higher aggregates, like normal micelles, would be more clearly formed in the dodecyl dinuclear complex (Fig. 6(a)). In this system, cmc for the premicelle is not clear, and may be present below 0.1 mol kg^{-1}, since the ^{59}Co linewidth gradually increases below 0.1 mol kg^{-1}. It is noticed that there is a trend that the dependence of cmcs on the alkyl chain length of the α,ω-type surfactants is smaller than that for the normal surfactant.[23] This trend seems to appear more remarkably in the present system, i.e., the cmc for the dinuclear octyl complex is almost the same (0.25 mol kg^{-1}) as that for the dinuclear dodecyl complex, whereas the break points in the ^{59}Co linewidth is clearer in the dodecyl complex than in the octyl complex.

In order to directly compare the extent of the aggregations between the mononuclear and dinuclear complexes, the diffusion coefficients may be more useful,[24] as discussed below.

Aggregations of Mononuclear and Dinuclear Complexes Studied by Self-Diffusions for the Complex Surfactants. Figure 7 shows the self-diffusion coefficients for the surfactants and solvent water as functions of the surfactant concentrations. In order to see the relative change in the diffusion coefficients in comparison between the surfactant and water, we express the ordinate by logarithm scales. The concentration dependence of the diffusion coefficients for ions is in principle described by the Onsager equation.[20] Although the diffusion coefficients for the surfactant complexes would be affected by both the counterion bindings and self-associations, the former effect becomes relatively small when the surfactant size is large enough compared to the counterion one. Here, we estimate the interactions with

Table 1. Critical Micellar Concentrations for the Aqueous Cobalt(III) Cystam Complex Solutions Compared to the Surfactants Having the Same Alkyl Chains

	cmc/mol kg^{-1}	T/°C	References
(1) Hexyl surfactants			
Cystam complex	(0.5)[b]	27	This work
NaHexanesulfonate	(0.5)[b]	27	21
NaHexylsulfate	(1.0)[b,c]		18
(2) Octyl surfactants			
Cystam complex	0.30	27	This work
[Co(OE)(2,3,2-*tet*)](ClO$_4$)$_3$[a]	0.12	27	5
NaOctanesulfonate	0.16[c]	40	22
NaOctylsulfate	0.14[c]	25	22
OTMABr[a]	0.14[c]	25	22
(3) Dodecyl surfactants			
Cystam complex	0.020	27	This work
[Co(DodE)(2,3,2-*tet*)]Cl$_3$[a]	0.010	27	5
NaDodecanesulfonate	0.012[c]	25	22
NaDodecylsulfate	0.008[c]	25	22
DodTMACl	0.020[c]	25	22
(4) Dinuclear complexes			
Octyl cystam complex	(0.25)[b]	27	This work
Dodecyl cystam complex	0.25	27	This work

a) OE = Octylethylenediamine. DodE = Dodecylethylenediamine. OTMABr = Octyltrimethylammonium bromide. b) These values are not clearly defined. c) The unit is in mol dm^{-3}.

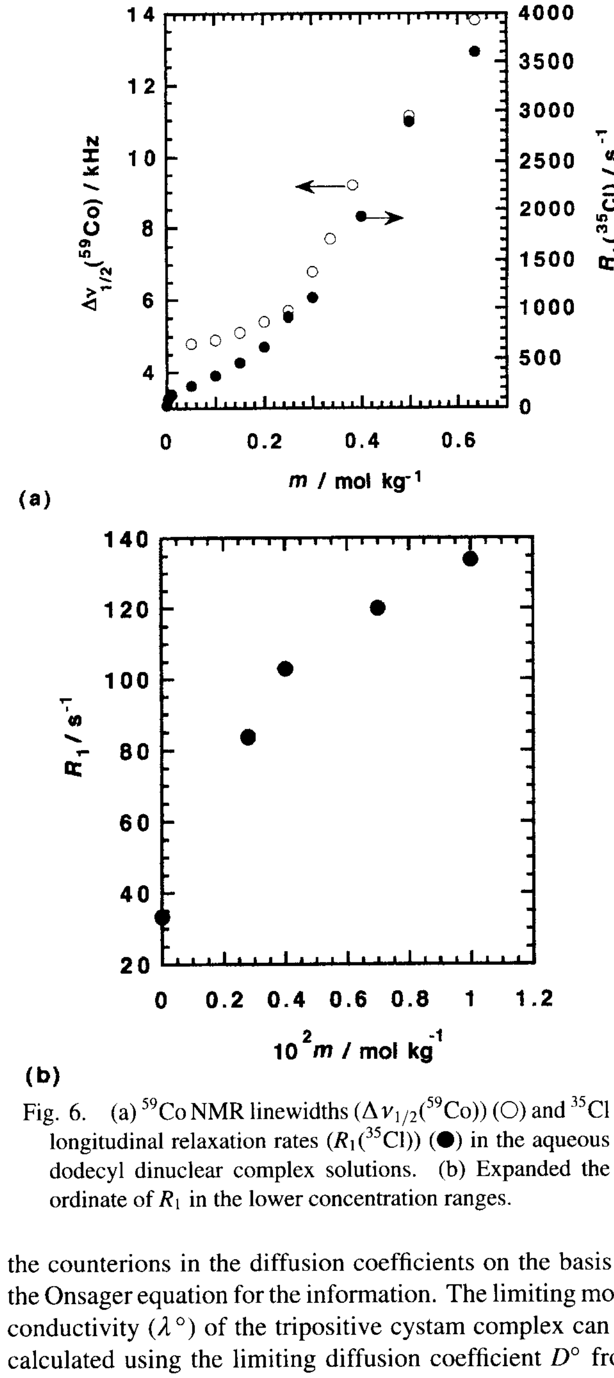

Fig. 6. (a) ^{59}Co NMR linewidths ($\Delta\nu_{1/2}(^{59}\mathrm{Co})$) (○) and ^{35}Cl longitudinal relaxation rates ($R_1(^{35}\mathrm{Cl})$) (●) in the aqueous dodecyl dinuclear complex solutions. (b) Expanded the ordinate of R_1 in the lower concentration ranges.

the counterions in the diffusion coefficients on the basis of the Onsager equation for the information. The limiting molar conductivity (λ°) of the tripositive cystam complex can be calculated using the limiting diffusion coefficient D° from the Nernst equation:[20,25]

$$D^\circ = 2.68 \times 10^{-7}\lambda^\circ \qquad \text{at } 27\ ^\circ\text{C}. \tag{8}$$

If we assume that the tripositive cobalt(III) surfactants behave as univalent cations by the counterion-bindings in the present concentration ranges, the Onsager equation for the hexyl and octyl cystam complexes (where D° is 4.0×10^{-10} m^2 s^{-1}) is

$$D = D^\circ(1 - 0.262\sqrt{c}), \tag{9}$$

where the limiting molar conductivity for the chloride ion is 0.00795 S m^2 mol^{-1}. In Figs. 7(a) and 7(b), the straight lines are calculated by Eq. 9. The deviations from the straight lines would be mainly governed by the self-associations; the result suggests that the hexyl and octyl cystam complexes would significantly aggregate, as discussed above.

As the surfactant size increases and the dehydration occurs upon micellization, the differences in the diffusion coefficients between the surfactants and water significantly increase above cmc.[24] The slight break points appear in Fig. 7(a)—(e) and their concentrations almost agree with those obtained from the relaxation methods, although those in the diffusion coefficients are less clear compared to those in the ^{59}Co and ^{35}Cl relaxations. The extent of changes in the slope at this critical concentration becomes larger with an increase in the alkyl-chain lengths. In the dodecyl mononuclear complex (Fig. 7(c)), the formation of micelles is most clearly indicated and the diffusion coefficients can also be expressed on the basis of the two-state model.

In the hexyl mononuclear (Fig. 7(a)) and octyl dinuclear complex (Fig. 7(d)) systems, there are no clear break points but the differences in the diffusion coefficients between the surfactant and water tend to increase at higher concentrations. The increase in such differences would mean the formation of aggregates, and is larger in the longer-chained systems.

As the ^{59}Co linewidth of the surfactant monomer significantly depends on the molecular symmetry around the cobalt nucleus, it is not appropriate to directly compare the absolute ^{59}Co linewidths between the complexes to see the aggregation processes. On the other hand, the diffusion coefficient seems to be more convenient to compare the extent of the aggregations between the analogous molecules for the following reasons. This observable has a clearer physical meaning than a relaxation rate; furthermore, a decrease in the diffusion coefficient for the solute by a concentration change would be mainly governed by the solute size if the solute in problem is large enough compared to the counter ions.[26] We thus compare the diffusion coefficients for the hexyl and octyl mononuclear complexes with those for the dinuclear octyl and dodecyl complexes, respectively, as follows.

The results for water and the surfactants show similar profiles in comparison with the octyl mononuclear and dodecyl dinuclear complexes (Figs. 7(b) and 7(e)). Although the diffusion coefficient of the surfactant at infinite dilution is significantly larger in the former complex, probably due to the smaller size, the coefficient (6.9×10^{-11} m^2 s^{-1}) for the octyl mononuclear complex at 1.0 mol kg^{-1} is close to that of the dodecyl dinuclear complex at 0.6 mol kg^{-1} (6.7×10^{-11} m^2 s^{-1}). The micellar shape composed of the octyl mononuclear complexes will be similar to that of the dodecyl dinuclear complex, since the latter surfactant would aggregate through their alkyl chains.

In the octyl dinuclear complex, Fig. 7(d) shows a good linearity and the plot has no clear break point, that is, the diffusion coefficient is less sensitive to the aggregations compared to the ^{59}Co linewidth and ^{35}Cl longitudinal relaxation rate. The profile in Fig. 7(d) is similar to that for the hexyl mononuclear complex. (Fig. 7(a)) The slope of $\log D$ vs. m plot in the octyl dinuclear complex (-0.72) is nearly twice that in the hexyl mononuclear complex (-0.33). This relationship also suggests an analogy in the aggregation in

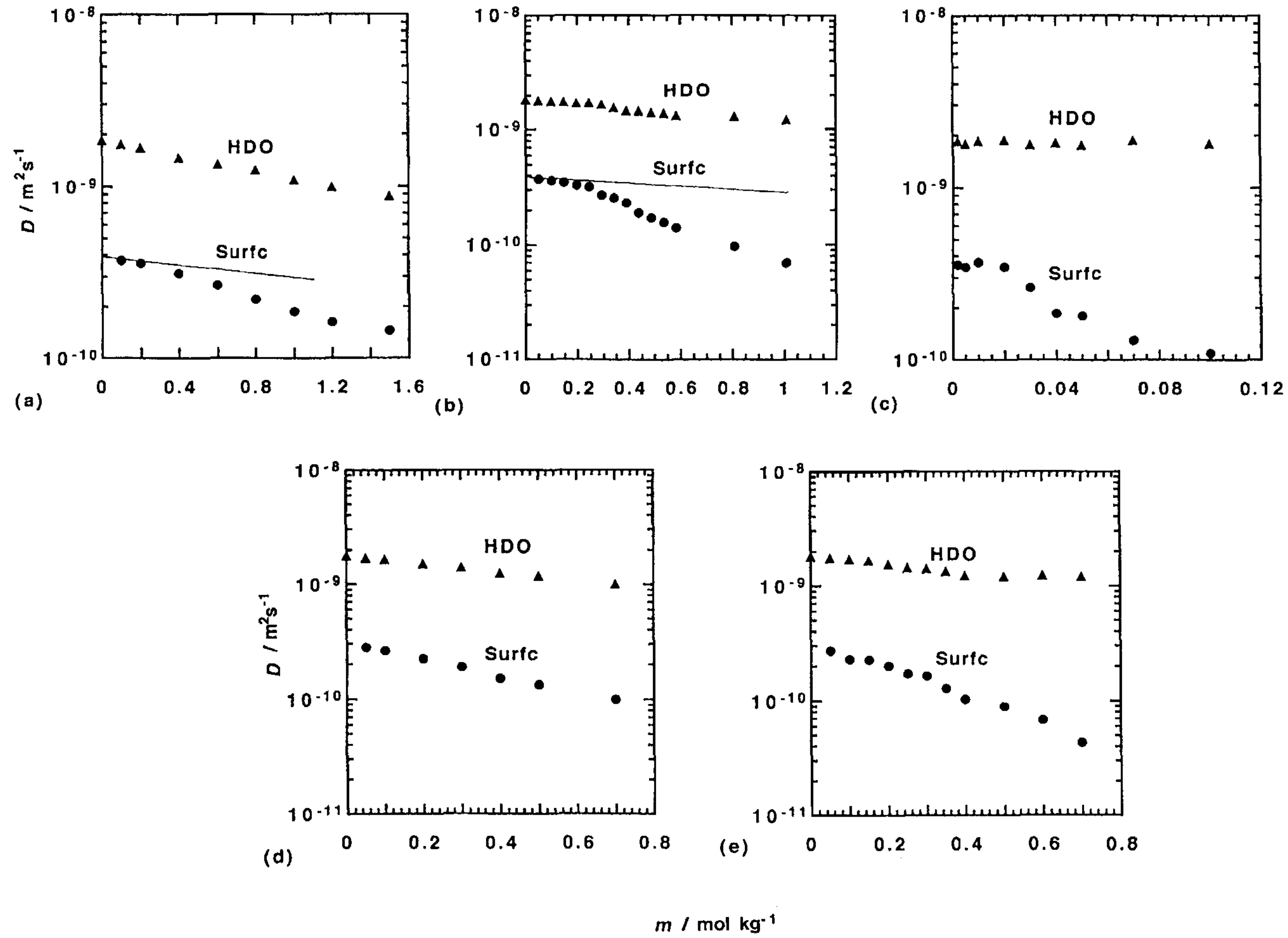

Fig. 7. Self-diffusion coefficients for the water (HDO) and the surfactant (Surfc) as a function of the surfactant concentrations in the aqueous (a) hexyl cystam, (b) octyl cystam, (c) dodecyl cystam, (d) octyl dinuclear, and (e) dodecyl dinuclear complexes. The lines are calculated on the basis of the Onsager's equation for the mononuclear complexes.

comparing between the two systems if the concentration is considered to be the headgroup unit.

In conclusion, the ^{59}Co linewidth was useful to monitor the micellar and premicellar formation, while the ^{35}Cl longitudinal relaxation rate showed two kinds of ionic interactions, i.e., the counterion bindings to the surfactant monomers and to the aggregates. It is characteristic that in the hexyl mononuclear and octyl dinuclear complex systems the ^{59}Co linewidths suggest the presence of critical points for the premicelles. The ^{59}Co linewidth and ^{35}Cl longitudinal relaxation rate are useful to monitor the aggregation process in the present systems where the surfactants are highly charged and the premicelles are formed. The extent of the self-aggregation of dinuclear dodecyl and octyl complexes is analogous to that of the octyl and hexyl mononuclear complexes, respectively, by considering the structures of the complexes in the headgroup unit.

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13 There is a possibility that the transverse relaxation is significantly affected by mechanisms other than the quadrupolar one.[14] In order to check this point, we also measured the ^{59}Co T_1 for the 0.1 mol kg^{-1} hexyl mononuclear complex over the temperature range 27—52 °C and compared the results with the T_2 values (calculated from the ^{59}Co linewidths) under the same conditions. The result is as follows: T_1 and T_2 are 112 and 103 μs, respectively, at 27 °C, and both R_1 and R_2 follow the Arrhenius relationship with their apparent activation energies of 16 ± 1 kJ mol^{-1}. These results clearly show that the present ^{59}Co relaxations are governed by the quadrupolar mechanism.

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$$K_{\mathrm{IP}}\,(\mu=0)=\frac{4\pi N_{\mathrm{A}}a^3e^{\mathrm{b}}}{3000},$$

where N_{A} is Avogadro's number, b ($=3e^2/4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 kTa$ for 3 : 1 electrolyte) is Bjerrum parameter. If we take 6 Å as the a value, we can obtain $K_{\mathrm{IP}}\,(\mu=0)=18$.

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