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A ^{59}Co NMR Study of the Interactions of Some Cobalt(III) Complexes in Nematic Lyomesophases

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^{59}Co NMR spectroscopy was used to study the interactions of cationic or neutral octahedral cobalt(III) complexes such as $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ (en=ethylenediamine), $[Co(NO_2)(NH_3)_5]^{2+}$, and $[Co(acac)_3]$ (acac=acetylacetonato) with surfactants in their nematic liquid crystalline solutions. The specific interactions of the complexes with the surfactants were studied in a replacement of one surfactant by another that had a different polar group. The extent of the binding of these complexes was monitored through the ^{59}Co quadrupole splittings. The relationship between the extent of the binding and the magnitude of the quadrupole splitting did not hold when comparing the three cationic complexes. A comparison between the potassium dodecanoate (KDodec)/tetradecyl (or decyl)trimethylammonium bromide (TDTMABr or DTMABr) and the cesium *N*-dodecanoyl-L-alaninate (CsDDA)/tetradecyltrimethylammonium bromide (TDTMABr) mixed surfactant systems in the interaction with $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ complexes showed that these complexes bind to the alaninate polar group through a weakly interacting site in the range of the intermediate composition of the mixed surfactants; such a kind of the binding was negligible or smaller in the dodecanoate system. $[Co(acac)_3]$ complex was solubilized to liquid crystals and the interactions with the surfactant depended on their polar groups in spite of the electric neutrality of the complex.

Nematic lyotropic liquid crystals (nematic lyomesophases) provide an advantage for the NMR spectroscopic investigation of the interactions between simple ions or molecules with surfactants since they spontaneously align in the magnetic field of the NMR spectrometer.[1—3] The interactions of metal complexes with surfactants, on the other hand, have attracted much attention to elucidate the mechanism of useful catalytic function of organized molecular aggregates in the reactions of various metal complexes.[4] From these viewpoints it seems to be significant to study the interactions between metal complexes and surfactants in nematic liquid crystals by using NMR spectroscopy. In a previous study,[5] one of us studied specific interactions of cobalt(III) complexes such as $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ with various kinds of surfactants by an observation of ^{59}Co quadrupole splittings ($\Delta\nu_Q$) in a nematic lyotropic liquid crystalline system prepared from a mixed surfactants/1-decanol/electrolyte/water system; this procedure is called here a replacement study. Such a system has an advantageous property in that it allows the two kinds of surfactants to be mixed in various proportions while maintaining the other components, i.e., electrolytes and water, in constant mole proportions to the total surfactant. In this study, we used cobalt(III) complexes such as $[Co(NO_2)(NH_3)_5]^{2+}$, $[Co(en)_3]^{3+}$, and $[Co(acac)_3]$ as well as $[Co(NH_3)_6]^{3+}$ to see specific interactions with surfactants by the replacement study. The effects of the ligands and the charge numbers of the metal complexes on the interactions were monitored by the ^{59}Co quadrupole splittings. The interactions of the cationic complex ions in the dodecanoylalaninate system are also compared with those in a dodecanoate one.

The quadrupole splittings ($\Delta\nu_Q$) for the probe ions or molecules interacting with liquid crystals can be expressed as

$$\Delta\nu_Q = \frac{3}{4I(2I-1)}\left(3\cos^2\theta - 1\right)P_b S_b \chi_b, \qquad (1)$$

where θ is the angle between the liquid crystal axis (director) and the magnetic field, P_b the fraction of the binding ions, S_b the order parameter, and χ_b the quadrupole coupling constant for the binding ions. χ_b is further expressed as $e^2 q_b Q/h$ where q_b is the electric field gradient at the nucleus of the binding ion and Q is the nuclear electric quadrupole moment. We showed in a previous paper,[6] that the width ($\Delta\nu_{1/2}$) at half-height of the envelope of the proton spectra that are dipolar coupled to each other for the hydrocarbon chain is proportional to the ($3\cos^2\theta-1$) term from comparison between similar surfactant systems. Actually, normalized $\Delta\nu_N$ values are defined to monitor the binding of the cobalt(III) complex to the surfactants as follows.[5,6]

$$\Delta\nu_N = \frac{\Delta\nu_{1/2}(\text{mean})}{\Delta\nu_{1/2}}\Delta\nu_Q \propto P_b \chi_b S_b, \qquad (2)$$

where $\Delta\nu_{1/2}$(mean) is the average of the $\Delta\nu_{1/2}$ values over all the composition ranges of the mixed surfactants. Among these three parameters of P_b, χ_b, and S_b, the contribution of the S_b factor has provided unique insight into the sites of ions especially for the alkaline or the halide ions,[2,7,8] while the product of P_b and χ_b reflects the extent of the ion binding and usually governs the $\Delta\nu_N$ value.[2] When looking the specific interactions from the profile for $\Delta\nu_N$ values depending on the composition, it seems more convenient for us to express the normalized quadrupole splitting as

$$\Delta\nu_N = \sum_i^n P_i \Delta\nu_i, \qquad (3)$$

where P_i is the proportion of ions in each site and $\Delta\nu_i$ is the quadrupole splitting for that site. On the other hand, when comparing between the cobalt(III) complexes in the extent of their interactions with the same surfactant system, we take the ratio $\Delta\nu_Q/\Delta\nu_{1/2}$ since the $P_b\chi_bS_b$ values can be directly compared each other under the same conditions.

Experimental

Materials. Potassium dodecanoate was prepared from dodecanoic acid by neutralization with potassium hydroxide followed by recrystallization from ethanol (95%) several times. Decylammonium bromide[9] and cesium *N*-dodecanoyl-L-alaninate[10] were prepared by standard methods. Tetradecyltrimethylammonium and decyltrimethylammonium bromides were obtained from the Sigma Co. and the Tokyo Kasei Co., respectively. They were recrystallized twice from their ethyl acetate–ethanol solutions. The cobalt(III) complexes, $[Co(NH_3)_6]Cl_3$,[11] $[Co(NO_2)(NH_3)_5]Cl_2$,[12] $[Co(en)_3]Cl_3\cdot3H_2O$,[13] and $[Co(acac)_3]$,[14] were also prepared according to standard procedures. The simple salts used for the control of the ionic strength were guaranteed reagents of Wako Pure Chemical Industries, Ltd. The 1-decanol was supplied by Tokyo Kasei Co. Ltd. and once distilled.

Compositions of the Amphiphilic Nematic Liquid Crystalline Solutions. The lyotropic mesophases used in this study had basically the following components: surfactants/electrolyte solutions of 5% deuterated H_2O containing 5—10 mmol kg^{-1} cobalt(III) complexes/1-decanol. The mixed surfactant systems used are potassium dodecanoate (KDodec)/tetradecyl (or decyl) trimethylammonium bromide (generally simplified as alkylTMABr below), cesium *N*-dodecanoyl-L-alaninate (CsDDA)/tetradecyltrimethylammonium bromide (TDTMABr), and decylammonium bromide (DABr)/TDTMABr. The alkylTMABr used was TDTMABr, except in a few cases where decyltrimethylammonium bromide (DTMABr) was used instead. The detailed compositions other than the cobalt(III) complexes are listed in Table 1. The cobalt(III) complexes were added to each liquid crystalline solution before NMR measurements. The pHs for the system containing the KDodec or the CsDDA were adjusted to 10.0—11.0 by using ethylenediamine/HBr (for the KDodec) or HCl (for the CsDDA) buffer reagents. To confirm the absence of the interference by the buffer reagents, we also measured the ^{59}Co quadrupole splittings for the $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ complexes in the KDodec/alkylTMABr and in the CsDDA/TDTMABr mixed surfactant systems over x (mole fraction of the anionic surfactant) = 0.0—1.0 range without buffer reagents. In these cases the pHs for the alkylTMABr/KDodec or CsDDA mixed systems were changed from 5 to 9 by replacing the alkyltrimethylammonium by the anionic surfactants. However, no significant differences were observed for the quadrupole splittings between in the presence and in the absence of the buffer reagents. As both the KDodec and CsDDA are the salts of weak acids, the measurements at pH 11.5—11.8 were also done to see the effects of the protonated surfactants for both the $[Co(NH_3)_6]^{3+}$ (only in the alaninate system) and the $[Co(en)_3]^{3+}$ complexes which are fairly stable even in alkaline regions. In this case, we used buffer solutions containing higher amounts of ethylenediamine.

Table 1. Compositions of Mixed Surfactant Systems[a)]

(i) Alkyltrimethylammonium Bromide (TDTMABr, DTMABr) –Potassium Dodecanoate (KDodec) [b)]

x	TDTMABr/mg	DTMABr/mg	KDodec/mg	DeOH/mg
0.0	420		0	65
0.1	379		31	44
0.2	338		59	25
0.3	295		89	9
0.4		210	120	40
0.5		175	149	19
0.6		141	180	9
0.7		105	208	13
0.8	85		239	25
0.9	43		268	48
1.0	0		299	79

(ii) Tetradecyltrimethylammonium Bromide–Cesium Dodecanoyl-L-Alaninate (CsDDA) [c)]

x	TDTMABr/mg	CsDDA/mg	DeOH/mg
0.0	373	0	66
0.1	336	44	52
0.2	299	89	41
0.3	262	133	33
0.4	225	178	23
0.5	187	226	18
0.6	148	270	16
0.7	111	315	26
0.8	74	359	53
0.9	37	403	81
1.0	0	448	100

(iii) Tetradecyltrimethylammonium Bromide (TDTMABr) –Decylammonium Bromide (DABr) [d)]

x	TDTMABr/mg	DABr/mg	KBr/mg	DeOH/mg
0.0	560	0	58	83
0.1	504	37	58	82
0.2	472	78	61	78
0.3	436	123	66	72
0.4	395	174	68	65
0.5	350	231	75	60
0.6	300	296	81	61
0.7	258	397	97	54
0.8	187	492	105	49
0.9	102	604	116	43
1.0	0	738	130	9

a) Mixed surfactant systems were prepared for the respective cobalt(III) complexes and the scattering of each weight was at most 3 mg. The stock solutions are b) 0.50 mol kg^{-1} KBr, c) 0.99 mol kg^{-1} CsCl, d) 0.01 mol kg^{-1} pyridine–0.02 mol kg^{-1} HBr of 5% deuterated H_2O.

NMR Measurements. The ^{1}H, ^{2}H, and ^{59}Co NMR spectra were obtained on a JEOL GX-270 FT NMR spectrometer operating at 270.0, 41.5, and 64.1 MHz, respectively. The temperature of the sample solution was controlled at 27±0.5°C.

After the NMR measurement, the pH of the sample solution was measured with an Orion Research model 701A Ion

Analyzer.

Results and Discussion

1. $[Co(NO_2)(NH_3)_5]^{2+}$ and $[Co(en)_3]^{3+}$ Complexes in KDodec/AlkylTMABr System.

The normalized quadrupolar splittings ($\Delta\nu_N$) of the ^{59}Co NMR spectra defined above are shown in Fig. 1 and Table 2 for the $[Co(NO_2)(NH_3)_5]^{2+}$ and in Fig. 2-(b) and Table 3(b) for the $[Co(en)_3]^{3+}$ complex in mixed KDodec/alkylTMABr system.[15] As the quadrupole splitting is usually proportional to the extent of the ion binding, they showed appreciable interactions with the oppositely charged polar group. The result for the $[Co(NH_3)_6]^{3+}$ complex, which has already been studied, is reproduced in Fig. 3(b).[5] The $\Delta\nu_N$ vs. x plots roughly agree with each other and the electrostatic interactions seem to govern their profiles. When comparing the three cationic complexes, however, we can find some significant differences between them. One of the difference is the magnitude of the quadrupole splitting in the KDodec system (x=1.0); the values decrease in the order, $[Co(NO_2)(NH_3)_5]^{2+}$ ($\Delta\nu_Q/\Delta\nu_{1/2}$= 5.71) > $[Co(en)_3]^{3+}$ (2.89) > $[Co(NH_3)_6]^{3+}$ (1.64). From the electrostatic viewpoint, the magnitude of the interaction should be in the order $[Co(NH_3)_6]^{3+}$ > $[Co(en)_3]^{3+}$ > $[Co(NO_2)(NH_3)_5]^{2+}$ by considering their ion-association constants with sulfate ions.[16] One possible factor of this quite reverse order would be the electric field gradient (eq_b or χ_b in Eq. 1), that is, the q_b value will be the largest for the pentaamminenitro complex and the smallest for the hexaammine complex.

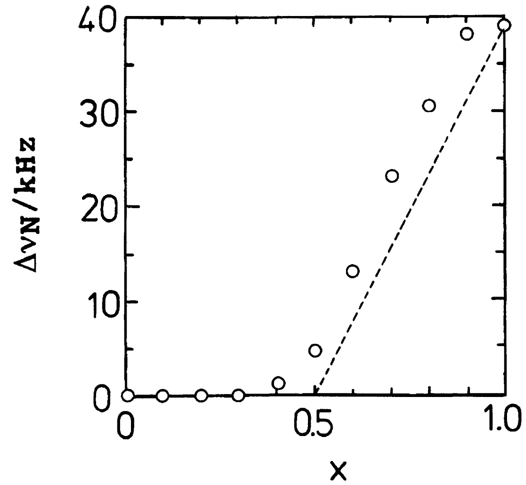

Fig. 1. Cobalt-59 quadrupole splittings ($\Delta\nu_N$) for $[Co(NO_2)(NH_3)_5]^{2+}$ as a function of the mole fraction (x) of the KDodec in the mixed KDodec/alkylTMABr mesophase system. (For compositions, see Table 1-(i)). The data were taken from Table 2.

Table 2. ^{59}Co NMR Quadrupole Splittings ($\Delta\nu_Q$) and Their Normalized Values ($\Delta\nu_N$) for $[Co(NO_2)(NH_3)_5]^{2+}$ and Half-Widths ($\Delta\nu_{1/2}$) of the Enveloped ^{1}H Spectra for the Alkyl Chains of the Surfactants, as a Function of Mole Fraction (x) of Potassium Dodecanoate in Total Surfactant.

	^{59}Co		^{1}H
x	$\Delta\nu_Q$/kHz	$\Delta\nu_N$/kHz	$\Delta\nu_{1/2}$//kHz
0	0	0	6.2
0.1	0	0	6.1
0.2	0	0	6.5
0.3	0	0	6.6
0.4	1.1	1.2	6.0
0.5	5.2	4.6	7.7
0.6	15.2	13.2	7.8
0.7	24.8	23.0	7.3
0.8	30.7	30.2	6.9
0.9	37.7	38.2	6.7
1.0	39.2	39.1	6.8

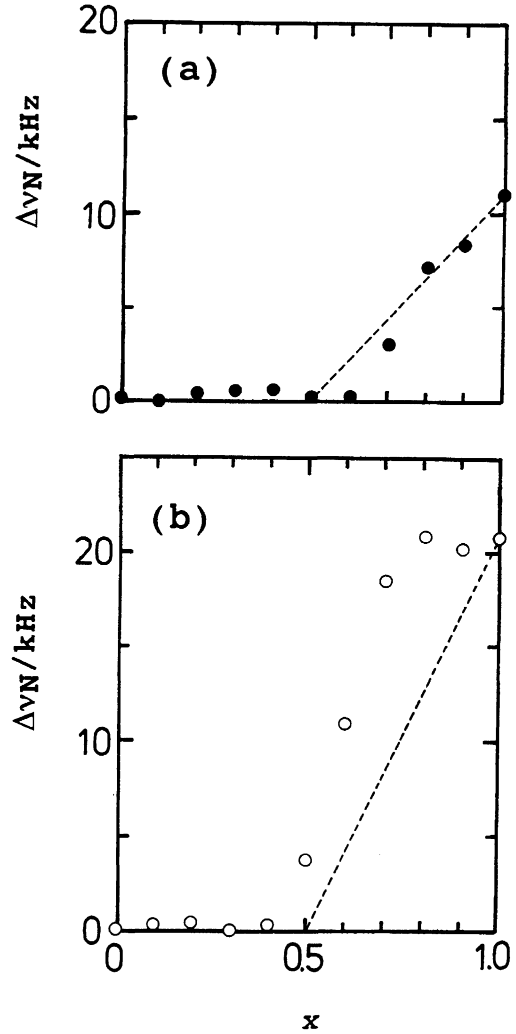

Fig. 2. Cobalt-59 quadrupole splittings ($\Delta\nu_N$) for $[Co(en)_3]^{3+}$ as a function of the mole fraction (x) of (a) CsDDA in the mixed CsDDA/TDTMABr mesophase system as compared with (b) the corresponding KDodec system. The data were taken from Table 3.

For both the complexes, $\Delta\nu_N$ vs. x plots can be roughly simplified as in the following relationship by

Table 3. ^{59}Co NMR Quadrupole Splittings ($\Delta\nu_Q$) and Their Normalized Values ($\Delta\nu_N$) for [Co(en)$_3$]$^{3+}$, Corresponding Values for ^{2}H of Deuterated Water, and Half-Widths ($\Delta\nu_{1/2}$) of the Enveloped ^{1}H Spectra for the Alkyl Chains of the Surfactants, as a Function of Mole Fraction (x) of Cesium Dodecanoyl-L-Alaninate (a) and of Potassium Dodecanoate (b) in Total Surfactant.

(a)	^{59}Co		^{2}H		^{1}H	pH
x	$\Delta\nu_Q$/kHz	$\Delta\nu_N$/kHz	$\Delta\nu_Q$/Hz	$\Delta\nu_N$/Hz	$\Delta\nu_{1/2}$/kHz	
0.0	0	0	3	3	7.0	10.0
0.1	0.2	0.2	9	10	6.5	10.1
0.2	0.3	0.4	15	17	6.4	10.2
0.3	0.4	0.5	22	24	6.7	10.2
0.4	0.5	0.6	32	36	6.7	10.2
0.5	<0.2	<0.2	47	54	6.5	10.2
0.6	<0.2	<0.2	63	75	6.3	10.2
0.7	2.7	3.1	92	107	6.4	10.2
0.8	6.7	7.0	141	148	7.1	10.3
0.9	8.3	8.3	176	175	7.5	10.2
1.0	10.9	11.0	221	223	7.4	10.5
1.0	12.1	11.9	236	232	7.6	11.6

(b)	^{59}Co		^{2}H		^{1}H	pH
x	$\Delta\nu_Q$/kHz	$\Delta\nu_N$/kHz	$\Delta\nu_Q$/Hz	$\Delta\nu_N$/Hz	$\Delta\nu_{1/2}$/kHz	
0	0	0	12	13	6.6	10.9
0.1	0.3	0.3	11	13	6.5	10.7
0.2	0.4	0.4	16	17	6.6	10.7
0.3	<0.1	<0.1	19	20	6.9	10.8
0.4	0.3	0.3	22	22	6.9	11.0
0.5	4.1	3.8	49	44	7.8	11.0
0.6	11.7	10.9	103	94	7.7	11.0
0.7	18.5	18.4	143	143	7.0	10.5
0.8	19.8	20.8	144	149	6.8	10.8
0.9	20.2	20.1	205	200	7.2	11.0
1.0	20.8	20.7	214	208	7.3	11.2
1.0	22.8	21.0			7.6	11.8

using Eq. 3.

$$x = 1.0 \rightarrow 0.5$$
$$\Delta\nu_N = \Delta\nu_I(2x-1)$$
$$x < 0.4$$
$$\Delta\nu_N \approx 0 \qquad (4)$$

where $\Delta\nu_I$ is the quadrupole splitting by the interaction with the potassium dodecanoate. Equation 4 means that the cobalt(III) complexes bind simultaneously to two carboxylate polar groups according to the three site model[7,8] and the complexes are released from the polar groups with a replacement of one of the two carboxylates by the cationic surfactant. The broken lines in Figs. 1, 2, and 3 are given by putting $\Delta\nu_I$=12 kHz for the hexaammine, 21 kHz for the en, and 39 kHz for the pentaamminenitro complexes in Eq. 4. Significant deviations of the experimental results from the broken lines were seen for all the complexes; especially, it is characteristic that the quadrupole splittings are almost constant above x=0.8 for the en complex and above x=0.9 for both the ammine complexes. As the concentration of the complex (5—10×10^{-3} mol kg^{-1}) is much less than that of the total surfactant (1.25 mol kg^{-1}), the constancy of $\Delta\nu_N$ above x=0.9 or 0.8 does not mean an occupation of the binding site by the complexes; it seems better to consider that the complex ion interacts with the carboxyl polar group so strongly that this ion pair is destroyed only after a significant proportion (mole fraction is 0.2 or 0.3) of the anionic polar group is replaced by the cationic polar group. Such a model of the formation of the inhomogeneous ion-pair was proposed for Al(OH)$_4^-$ interacting with the KDodec/alkylTMABr mixed system.[17] Upper deviations of the experimental values from the broken lines over the x=0.4—0.7 range also suggest the stronger interactions of the complex ions with the two carboxylate polar groups than

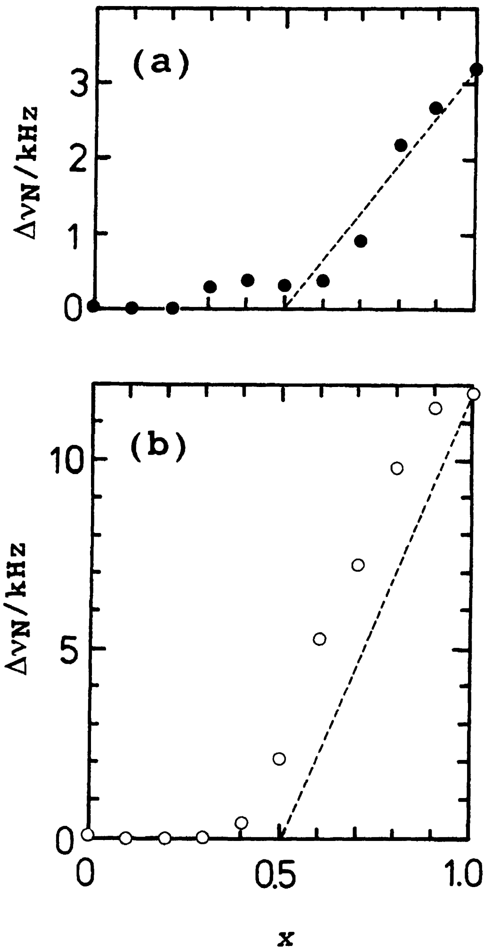

Fig. 3. Cobalt-59 quadrupole splittings ($\Delta\nu_N$) for [Co(NH$_3$)$_6$]$^{3+}$ as a function of the mole fraction (x) of alaninate in (a) the mixed CsDDA/TDTMABr mesophase system as compared with (b) the corresponding KDodec system. The data for CsDDA were taken from Table 4 and those for KDodec were from Table 1 in Ref. 5, respectively.

expected from the simple model.

2. $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ Complexes in the CsDDA/TDTMABr System as Compared with Those in the KDodec/AlkylTMABr System. A similar study using the *N*-dodecanoyl-L-alaninate in place of the dodecanoate gave $\Delta\nu_N$ vs. x plots somewhat different in profile from the dodecanoate system, (Figs. 2(a) and 3(a) and Tables 3(a) and 4) while the quadrupole splitting of ^2H of water molecules (Table 3(a) and (b)) indicates that the extent in the hydration is nearly identical in both the systems. The results in Figs. 2(a) and 3(a) can be fitted to Eq. 3. The broken lines in Figs. 2(a) and 3(a) were also drawn from the same model as described in the dodecanoate system (Eq. 4), by taking $\Delta\nu_I=3.2$ kHz for the hexaammine complex and 11 kHz for the en complex. Both Figs. 2(a) and 3(a) show that the experimental results are closer to the simple model than in the case of the dodecanoate systems above $x=0.5$, while a weakly interacting region is more clearly present in the range of $x=0.3$—0.6 (for the hexaammine complex) or 0.2—0.6 (for the ethylenediamine complex). Although the added electrolytes to stabilize the liquid crystal phase will slightly affect the ionic interaction of the cobalt(III) complexes with the surfactants, the difference between the two systems can be basically attributed to the different polar groups interacting with the cobalt(III) complex.[18]

The smaller $\Delta\nu_I$ values and the better fitting to the simple model in the CsDDA system than in the KDodec system show smaller interactions of the complexes with the alaninate polar groups, probably due to a dispersion of the charge density in this polar group. In spite of the smaller quadrupole splittings of the complexes by the interactions with the alaninate polar group than those with the dodecanoate polar group, the larger quadrupole splittings were observed in the lower x regions. (Tables 2, 3, and 4 and Table 1 in Ref. 5) Below $x=0.4$ the coexistence of the CsDDA with a larger polar group than that of the KDodec will be more favorable for the cationic cobalt(III) complexes to interact with the liquid crystal phase, since the alaninate polar group is placed outside the micelles in the mixed surfactant systems according to the sketch by Marcondes Helene and Figueiredo Neto.[19] As has been shown in previous studies,[3,7,8] the sign of the quadrupole splitting (governed by that of the S_b parameter in Eq. 2) in a weakly interacting system is sometimes negative and in such a case the probe ions are intervening between the polar groups. Only relative signs can be measured experimentally; for this purpose, dependency of the quadrupole splittings on temperature or on composition is generally used.[3] In both the hexaammine and en complexes we observed that the quadrupole splitting at $x=0.7$ increases with an increase in temperature from 20 to 50 °C while it slightly decreases both at $x=0.1$ and 0.4 in the same temperature range. These temperature dependences were not so remarkable as those seen for the ^{39}K ion in the oleate system, where the sign of the quadrupole splitting is decided to be negative since its temperature dependence has a minimum of a zero point.[3] However, in this study the contrast of the temperature dependence of the quadrupole splitting at $x=0.7$ (the sign should be positive) to those at the other x values suggest the quadrupole splitting in the latter case has a negative sign. The presence of the minimum at $x=0.5$—0.6 for the en complex also supports this view. If the quadrupole splittings in the weakly interacting range have negative signs, the interaction is a specific site binding rather than a diffuse binding.

Although the first protonation constant of the D,L-alaninate is around $\log K_1=9.9$,[20] a change in pH from 9 to 11.5 had little effect on the NMR data. (See the Experimental Section and Tables 3 and 4)

Table 4. ^{59}Co NMR Quadrupole Splittings ($\Delta\nu_Q$) and Their Normalized Values ($\Delta\nu_N$) for $[Co(NH_3)_6]^{3+}$ as a Function of Mole Fraction (x) of Cesium Dodecanoyl-L-Alaninate in Total Surfactant

x	$\Delta\nu_Q$/kHz	$\Delta\nu_N$/kHz
0.0	0	0
0.1	0	0
0.2	0	0
0.3	0.3	0.3
0.4	0.4	0.4
0.5	0.3	0.3
0.6	0.4	0.4
0.7	0.9	1.0
0.8	2.5	2.2
0.9	3.2	2.7
1.0	3.3	3.2
1.0[a]	3.2	3.2

a) pH 11.5.

3. $Co(acac)_3$ Complex. This complex was solubilized into this nematic liquid crystalline solutions and had ^{59}Co NMR spectra with quadrupole splittings. The splitting spectra clearly came from the complex present in the hydrophobic alkylchain side (oily side) of the amphiphilic aggregates. The magnitude of the quadrupole splitting was changed by the composition of the surfactants; the results are listed in Table 5. These results indicate that although the complex should be present in the oily side of the mixed surfactant micelles the interactions with the surfactants are affected by the polar group. The quadrupole splittings were thus observed through weak (anisotropic) interactions between the neutral complex and the charged polar group.

In the mixed KDodec/alkylTMABr system, the $\Delta\nu_N$ value plotted as a function of the surfactant compositions had a minimum (Fig. 4(i)) indicating that even the interaction of neutral complex with the liquid crystal phase depends on the ionic polar group. The presence of the minimum will be due to the apparently

Table 5. ^{59}Co NMR Quadrupole Splittings ($\Delta\nu_Q$) and Their Normalized Values ($\Delta\nu_N$) for [Co(acac)$_3$] and Half-Width ($\Delta\nu_{1/2}$) of the Enveloped ^{1}H spectra for the Alkyl Chains of the Surfactants as a Function of Mole Fraction (x) of Potassium Dodecanoate (a) and Decylammonium Bromide (b) in Total Surfactant

(a)	^{59}Co		^{1}H
x	$\Delta\nu_Q$/kHz	$\Delta\nu_N$/kHz	$\Delta\nu_{1/2}$/kHz
0	5.5	5.9	6.2
0.1	4.7	5.5	5.7
0.2	4.4	4.8	6.2
0.3	4.2	4.6	6.1
0.4	4.1	3.8	7.2
0.5	4.8	4.2	7.7
0.6	6.1	5.1	8.0
0.7	5.7	5.9	6.5
0.8	7.0	6.7	7.0
0.9	6.6	6.6	6.7
1.0	6.7	7.0	6.4

(b)	^{59}Co		^{1}H
x	$\Delta\nu_Q$/kHz	$\Delta\nu_N$/kHz	$\Delta\nu_{1/2}$/kHz
0	6.6	6.1	6.8
0.1	6.6	5.9	7.0
0.2	6.2	5.4	7.2
0.3	5.1	4.8	6.6
0.4	3.4	3.5	6.1
0.5	3.0	3.4	5.5
0.6	3.3	3.4	6.0
0.7	3.2	3.2	6.2
0.8	3.5	3.5	6.2
0.9	3.4	3.7	5.7
1.0	3.3	3.7	5.5

neutral surface of the liquid crystals in this composition range where the two opposite charges on the polar groups compensated for each other and the interaction of the polar groups with the neutral complex should be the smallest.

In the system shown in Fig. 4(ii) larger quadrupole splitting is observed in the TDTMABr system than in the DABr system. As all the quadrupole splittings for the ions and water molecules hitherto studied[5,21] have larger values in the decylammonium system than in the tetradecyltrimethylammonium system, this result for the ^{59}Co of Co(acac)$_3$ is the first case having an opposite trend. This specificity in this system is probably a consequence of hydrophobic attraction between the acetylacetonato complex and the trimethylammonium polar group. Such an appearance of the quadrupole splitting even in a non-electrostatic system has already been reported for ^{23}Na spectra in a nonaqueous liquid crystal in which the sodium ion is complexed by the cryptand C222.[22] Our result, however, showed that the interaction of the non-charged complex with the ionic polar group of the surfactants depends on the kind of the polar group.

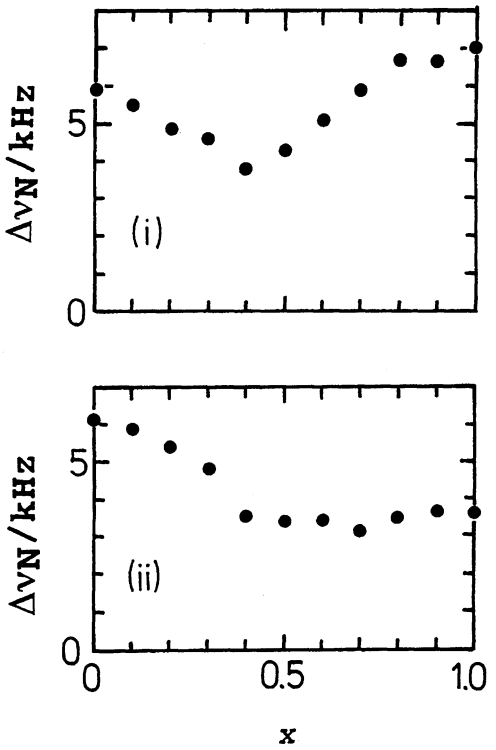

Fig. 4. Cobalt-59 quadrupole splittings ($\Delta\nu_N$) for Co(acac)$_3$ as a function of the mole fraction (x) of (i) KDodec in the mixed KDodec/alkylTMABr mesophase system and (ii) DABr in the mixed DABr/TDTMABr. The data were taken from Table 5. (For compositions of the mixed systems, see Table 1).

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15) Although we used here $\Delta\nu_N$ in place of $\Delta\nu_Q$, the discussions for all the results on the quadrupole splittings are almost the same as those by using the raw data of $\Delta\nu_Q$. (See Tables 2, 3, 4, and 5)

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18) In the alaninate system, as the cesium ion is necessary to stabilize the liquid crystal phase, we added CsCl (0.99 mol kg^{-1}) as a supporting electrolyte and furthermore used the cesium ion as the counterion of the dodecanoylalaninate. A partial displacement of the cesium ions by the potassium ions is also possible to keep the liquid crystal phase. We therefore checked the effects of the potassium ion by using KDDA in place of the CsDDA. At $x=1.0$, $\Delta\nu_N$ value of the $[^{59}Co(en)_3]^{3+}$ in KDDA system ($[K^+]=1.25$ mol kg^{-1} and $[Cs^+]=0.99$ mol kg^{-1}) almost agreed with that in the CsDDA system ($[Cs^+]=2.25$ mol kg^{-1}). This result indicates that the difference between the potassium ion and the cesium ion has little effect on the ^{59}Co quadrupole splittings.

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