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Estimation of the Ratio of Hidden Multivalent Ions in Nematic Lyomesophases by Using Heteronuclear NMR

Masayasu IIDA,* Yuri MIZUNO, and Yasuko MIYAGAWA
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

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An estimation of the peak areas of the ^{59}Co NMR spectra for cobalt(III) complex ions and of the ^{25}Mg spectra for magnesium aqua ions gave population ratios of their hidden ions, which are defined as too strongly interacting with nematic lyomesophases (composed of cationic or anionic surfactants) to contribute to the NMR spectra. The cobalt(III) complex ions used were $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ (en=ethylenediamine), $[Co(phen)_3]^{3+}$ (phen=1,10−phenanthroline), and $[Co(CN)_6]^{3-}$. It was revealed that appreciable amounts of multivalent ions are present as hidden ions on the lyomesophase, whose sign of charge is opposite to that of the ion in question. For such hydrophilic ions as $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(CN)_6]^{3-}$, and magnesium ions, the ions binding to the mesophases are classified into two states based on the NMR spectra: One is an outer-sphere complex (ion pair); the other is a hidden ion. In these systems the hidden ion/total ion population ratios depending on the composition of the surfactant are roughly proportional to the ion pair/total ion population ratios, which are monitored by the magnitude of the quadrupole splitting. For the phen complex, the presence of a hidden ion was observed in the range where the fraction of the anionic surfactant is high; the quadrupole splittings were also observed only in limited composition ranges.

Specific interactions between cobalt(III) complex ions and surfactants have been studied in anionic/cationic mixed nematic lyomesophase (lyotropic liquid crystal).[1,2] Information from the quadrupole splittings of the ^{59}Co NMR spectra is useful in these competition studies to determine the extent of the bindings and any specific binding-site for ions and molecules. For the analysis of the ^{59}Co NMR spectra, it is assumed that the motions of the cobalt(III) complex ions interacting with the mesophases are sufficiently rapid on the NMR time scale to contribute to the spectra, and that all of the cobalt(III) complex ions are present in the outer-sphere of the mesophases. The states of the ions interacting with the mesophases were thus classified into two categories:[3] (I) free ion (II) outer-sphere complex (with the polar group) or diffuse binding ion, where the difference between the outer-sphere complex and the diffuse binding ion is not clear from the NMR spectra. Ions or molecules in state II electrostatically interact with the anisotropic micelles, and the magnitude of the ^{59}Co quadrupole splitting is closely related to the state-II/state-I population ratio. In the present study we consider another state of the binding ions, since the signal-to-noise ratios of the ^{59}Co NMR spectra have been observed to become worse with increasing the magnitudes of the ^{59}Co quadrupolar splittings in competition studies.[1,2] The reduction can thus be attributed to the contribution of "hidden ions" which have restricted motions to a large extent due to a strong interaction with the mesophase (probably through the polar group region of the surfactant), and their ^{59}Co NMR spectra are too broad to be detected. The exchange between this state and the other states is very slow on the NMR time scale. We quantitatively interpret the reduction in the peak areas for multivalent ions, such as cobalt(III) complex ions and magnesium ions. The population ratios of the hidden ions depending on the composition of the mixed amphiphiles are related to the quadrupole splittings, whose results have been partially reported in previous papers.[1,2] The cobalt(III) complex ions used were $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(phen)_3]^{3+}$, and $[Co(CN)_6]^{3-}$. All of the cobalt(III) complex ions, except for $[Co(CN)_6]^{3-}$, were studied in both potassium dodecanoate (KDodec)/alkyltrimethylammonium bromide (alkylTMABr, i.e., tetradecyltrimethylammonium bromide (TDTMABr) or decyltrimethylammonium bromide (DTMABr)) and cesium dodecanoylalaninate (CsDDA)/TDTMABr mixed mesophase systems. $[Co(CN)_6]^{3-}$ was studied in the KDodec/alkylTMABr system, and Mg^{2+} was studied in the CsDDA/TDTMABr system.

Experimental

Materials. The cobalt(III) complexes used were $[Co(NH_3)_6]Cl_3$, $[Co(en)_3]Cl_3\cdot3H_2O$ (en=ethylenediamine), $[Co(phen)_3]Cl_3\cdot7H_2O$ (phen = 1, 10 − phenanthroline), and $K_3[Co(CN)_6]$. The preparations and the purifications of the surfactants and the cobalt(III) complexes were reported previously.[1,2,4] The magnesium ion was added as $Mg(NO_3)_2\cdot6H_2O$. Simple salts including the magnesium nitrate, used for the supporting electrolytes, were guaranteed reagents supplied from Wako Pure Chemicals.

NMR Measurements. The ^{25}Mg and ^{59}Co NMR spectra were obtained on a JEOL GX-270 FT NMR spectrometer (JEOL Ver. 1.5 program system) operating at 16.5, and 71.5 MHz, respectively. The effects of the pre-aquisition delay times on the peak areas were checked by varying them from 20 to 80 μs. At the smallest delay time the measurement may detect any rapidly decaying component of the transverse relaxation process; at the longest delay time artifacts arising from acoustic ringing are appreciably avoided. In a comparison between the two extreme cases, however, the resulting peak areas of the signals coincide with each other within 5% errors for the same samples. Most of the measurements were thus carried out in the range of 50—80 μs delay times. We always used the 90° pulse widths, that is, 15—17 μs for ^{59}Co and 35 μs for ^{25}Mg; the use of the 45° pulse width gave similar results as given by the 90° one. The NMR spectra were obtained after 12000—25000 times accumulations and the quantitative analyses were carried out using the same accumulation times as that of the reference solution. Only for the observation of the quadrupole splitting in the phen complex at $x<0.5$, 200000 times accumulations were necessary to ascertain the quadrupolar splitting of the spectra. The compositions of the mixed lyomesophases are listed in Table 1. We did not add any buffer reagents, since Mg^{2+} and $[Co(phen)_3]^{3+}$ are decomposed or hydrolyzed by the reagents. The pH values of the mesophases thus changed from 5 (TDTMABr or DTMABr system) to 9 (KDodec system) or to 8 (CsDDA system). In these pH ranges all of the cobalt (III) complexes (pH<9) and the magnesium ions (pH<8) were not decomposed or hydrolyzed.[5] As the magnesium ion precipitated with the KDodec in the composition range where this surfactant is predominantly present, it was studied only in the CsDDA/TDTMABr system. The ratios of the peak area (R_A) for the ^{25}Mg and ^{59}Co NMR spectra were calculated according to

$$R_A = \frac{A_s}{A_r} 2^{N_s - N_r}, \tag{1}$$

where A is the peak area of the plotted spectra and N is the normalization gain (according to the JEOL computer system Ver. 1.5) after the Fourier transformation of the spectra was performed. Subscripts r and s indicate the peak areas in the reference solution and those in the sample, respectively; the reference was measured in the mesophase at $x=0.0$ for the probe cations and at $x=1.0$ for $[Co(CN)_6]^{3-}$, since under these conditions it is assumed that no probe ions are present as hidden ions due to large electrostatic repulsions with the mesophases.[6] Since the population ratios of the hidden ions are related to the extent of the interaction with the mesophase, we used R_H values defined by,

$$R_H = (1 - R_A) \times 100. \tag{2}$$

Table 1. Compositions of Mixed Amphiphile 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

a) Mixed amphiphile 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.

The temperature of the sample solution was controlled to 27±0.5°C. ^{59}Co chemical shifts for the phen complex in the mesophases were measured relative to that in the simple aqueous solutions without a surfactant.

Results and Discussion

The obtained R_H values are listed in Tables 2, 3, 4, and 5. These results quantitatively show that the (complex) ions appreciably disappear due to an interaction with mesophases comprising the oppositely charged surfactants. We shall discuss the relationship between the R_H values and the quadrupole splittings.

1. The Presence of Hidden Ions. Figures 1, 2, and 3 show the R_H values for the cobalt(III) complexes (except for the phen complex) together with the normalized quadrupole splittings ($\Delta\nu_N$) as a function of x. Table 2 shows a similar result for the magnesium ion in the CsDDA/TDTMABr system; in this case no signals were detected above $x=0.5$, probably because of both the low receptivity of ^{25}Mg NMR (about 10^{-3} relative to that of ^{59}Co) and the large population ratios of the hidden ions. An anomalous change in the ^{25}Mg quadrupole splittings[7] from $x=0.0$ to 0.2 may be due to specific site bindings of Mg^{2+} to the mesophase, as has sometimes been observed for small simple ions, such as alkali and halide ions.[3,8—10]

Although the R_H values have less accuracy (they seem to have nearly 10% errors in the range where the quadrupole splitting occurs) than the values of the quadrupole splittings (having high accuracy), we can

Table 2. Effect of Replacing Tetradecyltrimethylammonium Bromide by Cesium Dodecanoyl-L-Alaninate on the ^{25}Mg NMR Spectra of the Aqua Magnesium Ions

x	$\Delta\nu_Q$/Hz	R_H/%
0.0	190	<5
0.1	20	<5
0.2	380	<5
0.3	820	12
0.4	1010	25

Table 3. Effect of Replacing Alkyltrimethylammonium Bromide (For alkyl, see Table 1) by Potassium Dodecanoate on the R_{H} Values and the Chemical Shifts for the (1) $[\mathrm{Co(NH_3)_6}]^{3+}$, (2) $[\mathrm{Co(en)_3}]^{3+}$, and (3) $[\mathrm{Co(CN)_6}]^{3-}$ Complexes

x	(1) $R_{\mathrm{H}}/\%$	(2) $R_{\mathrm{H}}/\%$	(3) $R_{\mathrm{H}}/\%$
0	—	—	45
0.1	$<5^{\mathrm{a)}}$	21	44
0.2	16	23	48
0.3	17	21	36
0.4	19	$(12)^{\mathrm{b)}}$	26
0.5	22	59	7
0.6	22	64	$<5^{\mathrm{a)}}$
0.7	24	65	<5
0.8	44	76	<5
0.9	61	84	<5
1.0	60	86	<5

a) As the estimation of the peak areas seems to contain nearly 5% errors, all the values obtained of less than 5% are expressed in the same manner. b) As this spectrum did not show a clear splitting, the apparent peak area ($R_{\mathrm{A}}=1-R_{\mathrm{H}}/100$) obtained should be significantly larger than the real value. In Fig. 2a this point is omitted.

Table 4. Effect of Replacing Tetradecyltrimethylammonium Bromide by Cesium Dodecanoyl-L-alaninate on the R_{H} Values for the (1) $[\mathrm{Co(NH_3)_6}]^{3+}$ and (2) $[\mathrm{Co(en)_3}]^{3+}$ Complexes

x	(1) $R_{\mathrm{H}}/\%$	(2) $R_{\mathrm{H}}/\%$
0	—	—
0.1	<5	7
0.2	<5	7
0.3	7	9
0.4	<5	10
0.5	7	10
0.6	<5	23
0.7	27	64
0.8	28	66
0.9	28	83
1.0	31	84

a) As the estimation of the peak areas seems to contain nearly 5% errors, all the values obtained of less than 5% are expressed in the same manner.

regard the results shown in Figs. 1, 2, and 3 as having a rough proportionality of R_{H} values to $\Delta\nu_{\mathrm{N}}$ values. In studies concerning the ion bindings from quadrupole splittings of measuring nuclei it has been assumed that the quadrupole splittings are proportional to the degree of ion-bindings as the first approximation, and that all of the ions contribute to the signals. Such an assumption seems to be reasonable when the interactions between the ions and the surfactants are purely electrostatic, and all of the ions are classified into either free ions, outer-sphere complexes (ion pairs), or diffuse-binding ions. The present results, however, clearly show the presence of another state of the ions binding to the surfactants, i.e., the hidden ions.

When probe ions containing quadrupolar nuclei strongly interact with large molecules, the transverse relaxation process for the quadrupolar nuclei sometimes show rapidly decaying components and their NMR spectra are represented as a superposition of the two Lorentzian components.[11,12] In the present study, however, such kinds of line shape were not observed. If hydrophobic molecules are dissolved into the hydrocarbon cores of the mesophase, and only weakly interact with the polar group of the surfactant, the NMR spectra of the nuclei in the probe molecule will be observable as we have reported for $[\mathrm{Co(acac)_3}]$,[2] since the motion of the hydrocarbon core is moderately rapid. We thus here regard the hidden ions as being strongly 'adsorbed' on the polar group region in the mesophase, and do not believe that all of the ions are 'absorbed' into the mesophase. The dependence of the R_{H} values on the mole fraction (x) of the surfactant would provide further details concerning the situation of ion binding to the mesophase.

2. Specific Interactions of $[\mathrm{Co(NH_3)_6}]^{3+}$, $[\mathrm{Co(en)_3}]^{3+}$, and $[\mathrm{Co(CN)_6}]^{3-}$ with Mixed Surfactants. For the ammine and en complexes (Figs. 1 and 2), the following rough trends hold regarding both the R_{H} and $\Delta\nu_{\mathrm{N}}$ values: Both of the values are larger for the en complex than for the ammine complex, and are larger in the KDodec system than in the CsDDA system. As stated previously,[1,4] the larger ^{59}Co chemical shift and the larger ^{59}Co quadrupole splitting for the $[\mathrm{Co(en)_3}]^{3+}$ due to interactions with the anions than for the $[\mathrm{Co(NH_3)_6}]^{3+}$, do not necessarily mean stronger interactions of the en complex with the anions, but that the effect of the electric field gradient on the ^{59}Co nucleus of the en complex may be larger than that of the ammine complex. Thus, the first trend mentioned above does not mean that the same kinds of interactions govern both the outer-sphere complexes and the hidden ions. Therefore, the larger R_{H} values in $[\mathrm{Co(en)_3}]^{3+}$ than in $[\mathrm{Co(NH_3)_6}]^{3+}$ suggest that the larger specific interactions with the anionic surfactants besides the electrostatic one may act for the en complex than for the ammine complex to form hidden ions. However, some cases did not follow the above two trends. For example, the R_{H} values for the en complex in the CsDDA system (Fig. 2b) are comparable to those in the KDodec system (Fig. 2a) in the x=0.7—1.0 range, while for the ammine complex the R_{H} values in the CsDDA system (Fig. 1b) are significantly smaller than in the KDodec system (Fig. 1a) for the same composition range. This result suggests the presence of specific interactions of the en complex with the surfactants, and that the interactions may be larger in the CsDDA system in spite of the smaller electric charge density of the alaninate polar group.

Since the dodecanoylalaninate mesophase is stabilized only in the presence of cesium ions, we checked the effect of the counterions (K^+ and Cs^+) on the R_{H} values. Similar results were obtained for the

Table 5. Effect of Replacing Alkyltrimethylammonium Bromide (For Alkyl, See Table 1) by Potassium Dodecanoate (a) and by Cesium Dodecanoylalaninate (b) on the R_H Values and the Chemical Shifts for the $[Co(phen)_3]^{3+}$ Complex

x	R_H/%	δ/ppm	$\Delta\nu_Q$/kHz	x	R_H/%	δ/ppm	$\Delta\nu_Q$/kHz
(a)				(b)			
0	—		<1.0	0	—	↑	<1.0
0.1	<5	from+1	<1.0	0.1	<5		<1.0
0.2	<5	to +5	<1.0	0.2	<5		<1.0
0.3	<5		<0.4	0.3	<5		<0.4
0.4	<5		<0.4	0.4	<5	±2	<0.4
0.5	<5		0	0.5	<5		0
0.6	<5		0	0.6	<5		0
0.7	8	↓	0	0.7	<5	↓	0
0.8	43	+10	0	0.8	7	−4	0
0.9	51	+25	0	0.9	18	−7	<1.0
1.0	52	+27	0	1.0	70	−5	4.1

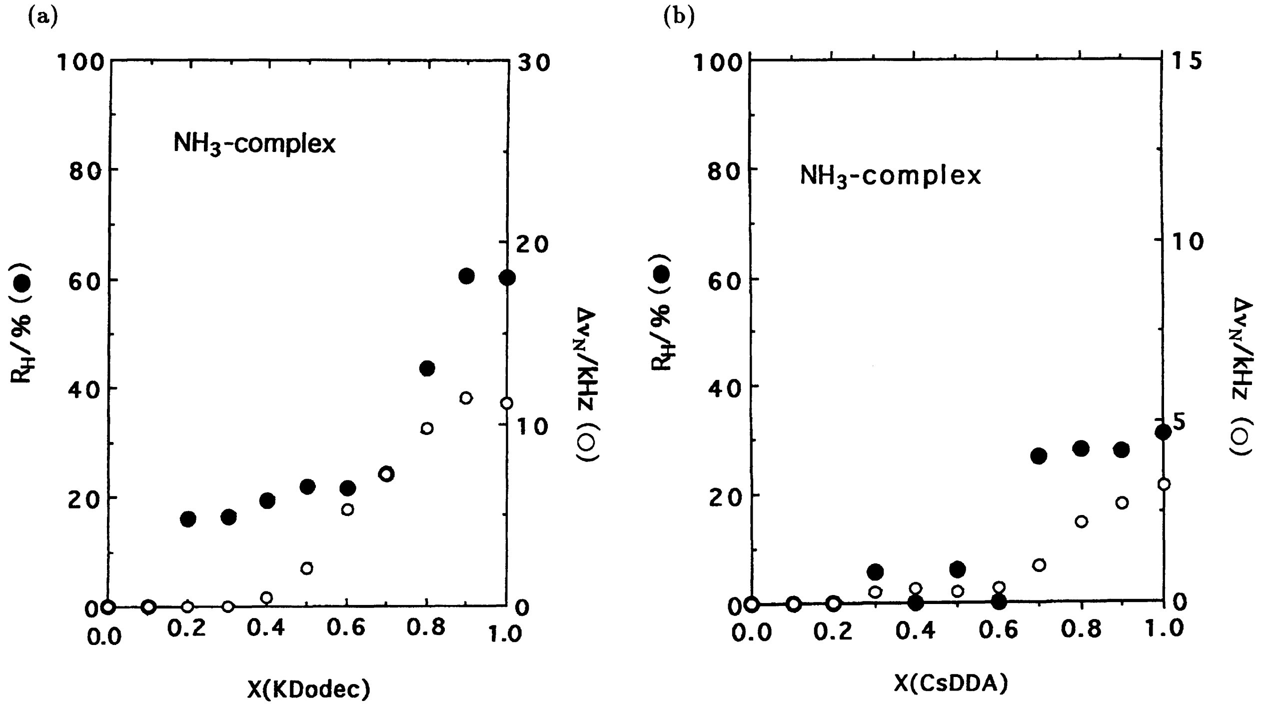

Fig. 1. Population ratios (R_H) of hidden ions and quadrupole splittings ($\Delta\nu_N$) for $[Co(NH_3)_6]^{3+}$ as a function of the mole fraction (x) of the (a) potassium dodecanoate and (b) cesium N-dodecanoyl-L-alaninate in the mixed lyomesophase system.

$[Co(en)_3]^{3+}$ complex in a system comprising KDDA (1.11 mol kg^{-1})/CsCl (0.99 mol kg^{-1})/DeOH (0.633 mol kg^{-1}), as in the above system.[13] Thus, a higher charge density of the polar group in the KDodec could be favorable for an interaction with the cationic complexes, than in the case of the CsDDA.

Furthermore, the relationship between the R_H and $\Delta\nu_N$ values is somewhat complicated in weakly interacting regions for the cobalt(III) complex cations with the dodecanoate system (Figs. 1a and 2a). The R_H values for the cobalt(III) complex cations in the KDodec systems are nearly constant over the range of x=0.2—0.6 (Fig. 1a) or 0.1—0.4 (Fig. 2a), while such an intermediately interacting region is only little detectable for the $\Delta\nu_N$ values. Such a situation did not appear regarding the R_H values for $[Co(CN)_6]^{3-}$ and Mg^{2+}. Since the surfactants interacting with the cobalt(III) complex ions are in excess (1.1x mol kg^{-1}, $x\geq0.1$) of the cobalt(III) complex ions (5—10 mmol kg^{-1}), the constancy of R_H means that there may be an intermediate step in the saturation of the ion-adsorption equilibria in interactions of the $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ complexes with the KDodec.

The other differences in the profiles between the R_H and $\Delta\nu_N$ plots are seen for cationic complexes at around the intermediate range of the composition; some discontinuous changes are seen for the R_H values, while the quadrupole splittings are more smoothly changed with

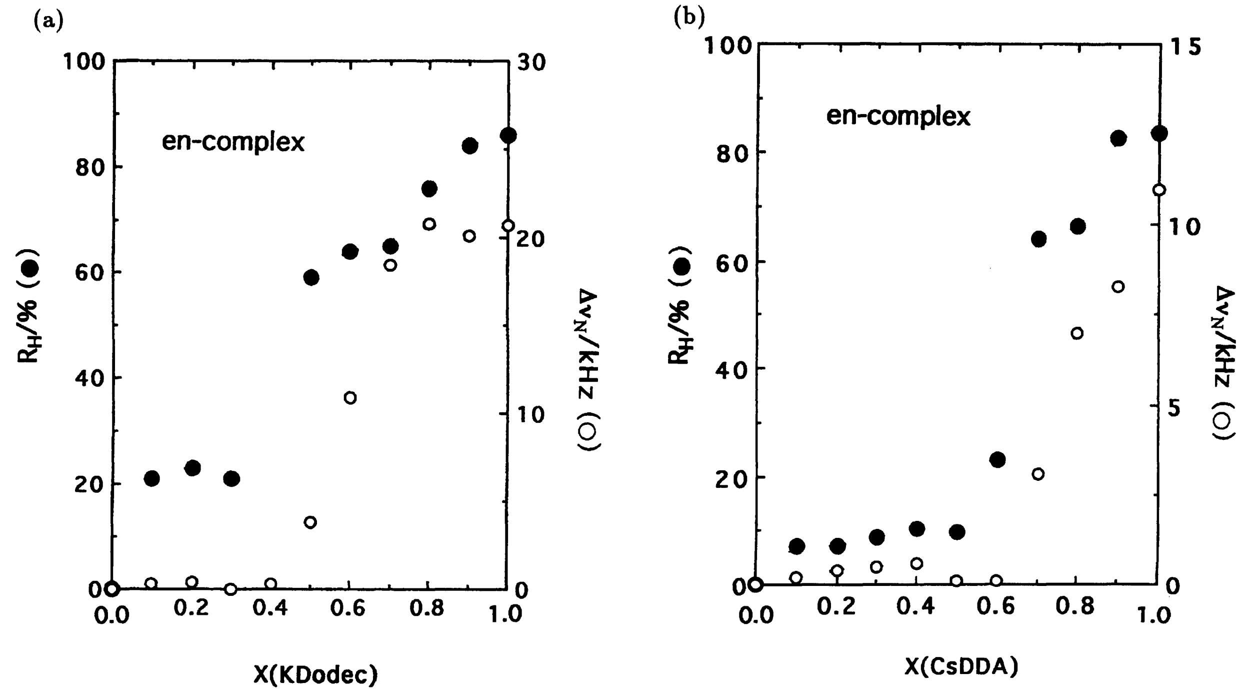

Fig. 2. Population ratios (R_H) of hidden ions and quadrupole splittings ($\Delta\nu_N$) for $[Co(en)_3]^{3+}$ as a function of the mole fraction (x) of the (a) potassium dodecanoate and (b) cesium *N*-dodecanoyl-L-alaninate in the mixed lyomesophase system.

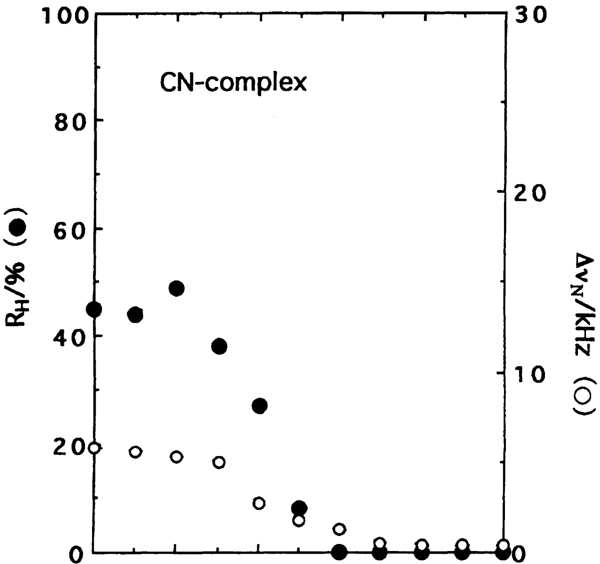

Fig. 3. Population ratios (R_H) of hidden ions and quadrupole splittings ($\Delta\nu_N$) for $[Co(CN)_6]^{3-}$ as a function of the mole fraction (x) of the potassium dodecanoate in the mixed lyomesophase system.

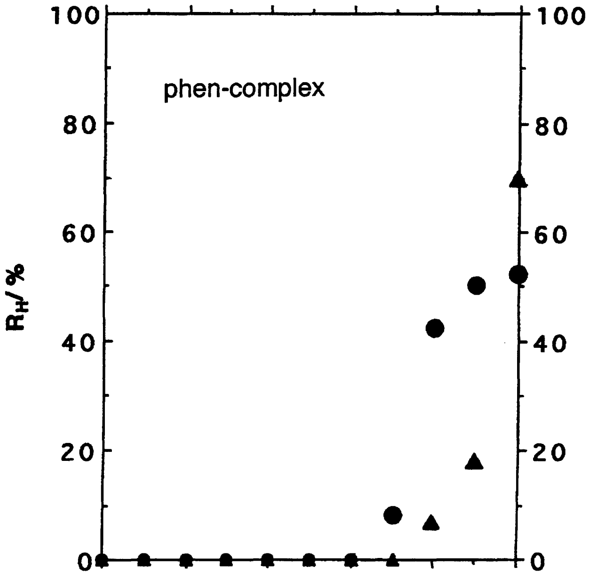

Fig. 4. Population ratios (R_H) of the hidden ions for $[Co(phen)_3]^{3+}$ as a function of the mole fraction (x) of the potassium dodecanoate (●) or of the cesium *N*-dodecanoyl-L-alaninate(▲) in the mixed lyomesophase system.

a change in the compositions (Figs. 1 and 2). This trend means that the R_H values (the extent of formation of the hidden ions) may involve more complicated interactions between the cobalt(III) complex cations and the cationic/anionic mixed surfactants than the quadrupole splittings.

3. $[Co(phen)_3]^{3+}$ Case. A remarkably poor relationship between the two parameters is seen for $[Co(phen)_3]^{3+}$; the quadrupole splitting is observed only

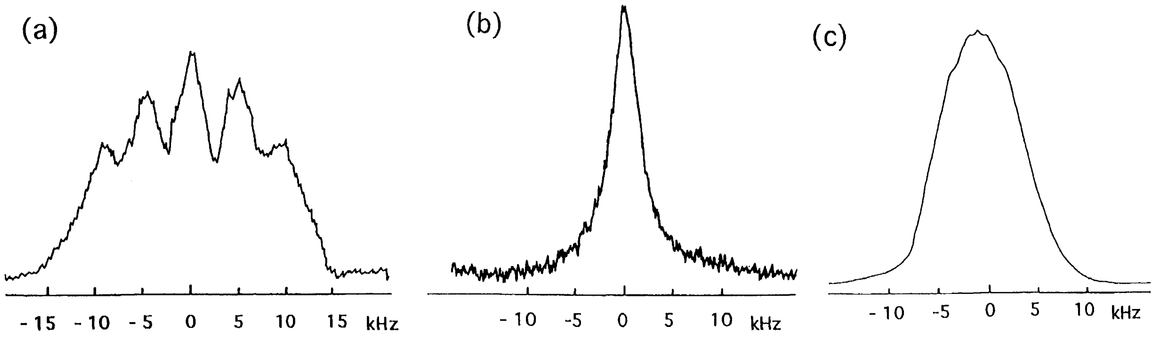

Fig. 5. ^{59}Co NMR spectra for $[\mathrm{Co(phen)_3}]^{3+}$ in (a) CsDDA mesophase ($x=1.0$, accumulation times=12000), (b) KDodec mesophase ($x=1.0$, accumulation times=12000), (c) TDTMABr mesophase ($x=0$, accumulation times=200000).

at $x=1.0$ in the CsDDA system (Fig. 5a), while the presence of hidden ions was detected over wider ranges (Table 5 and Fig. 4).

In the alkylTMABr/KDodec system, non-splitting signals in the higher x range (Fig. 5b) mean that the phen complex only slightly forms an outer-sphere complex with the polar group (little contribution of state II). It has been known that the phen complex is dissolved into hydrocarbon cores of anionic micelles in place of a direct interaction with the polar groups.[14] In order to consider the position in the mesophase for the phen complex interacting with surfactants, information from the chemical shift seems to be important.[4] A change in the chemical shift from upfield to downfield was observed above $x=0.8$ in the KDodec system (Table 5a); this downfield shift also suggests that the phen complexes which contribute to the ^{59}Co NMR spectra are present in the hydrophobic cores of the dodecanoate surfactant according to the previously proposed rule concerning the relationship between the chemical shift and the hydrophobicity in the interaction.[4] The smaller R_H values for the phen complex than the other complex cations would be due to its bulkiness. Small quadrupole splittings in the lower x range ($x<0.3$) as shown in (Fig. 5c) can be attributed to diffuse binding, whose interaction would occur through bromide counterions of the surfactant.

In the TDTMABr/CsDDA system, significant amounts of the phen complexes are present as hidden ions only above $x=0.8$; the chemical shift change was very small over all of the x ranges (Table 5b). In the higher x ranges, the chemical shift change was appreciably smaller than that in the dodecanoate system; this means that the phen complex is not very much dissolved in the hydrocarbon cores of the alaninate surfactant, even in this range, as in the dodecanoate system. That is, some of the phen complexes form ion-pairs with the polar group (upfield shift) while some of them interact with the hydrophobic cores (downfield shift);[4] a compensation of these two factors may result in small chemical shifts. It is surprising that only at $x=1.0$ in the CsDDA system is the R_H value for the phen complex significantly larger than in the KDodec system, and only at this composition can the quadrupole splitting of the $[^{59}\mathrm{Co(phen)_3}]^{3+}$ be clearly observed. The bulky phen complex (its effective ionic radius is 498 pm while that for the en complex is 362 pm)[15] may have a suitable size to form an outer-sphere complex with the alaninate polar group, whose size is larger than the dodecanoate one. This factor would also be favorable for forming a hidden ion; the interaction is effective only where the fraction of the anionic surfactant is extremely high ($x>0.8$—0.9), i.e., even small amounts (mole faction is 0.1—0.2) of the TDTMABr surfactant will block $[\mathrm{Co(phen)_3}]^{3+}$ to interact with the CsDDA. This suggests that the outer-sphere complex of the phen complex with the alaninate polar group will be stabilized through a multi-binding site with the alaninate polar group.

Conclusively, we propose further details concerning the ion-binding model in the mesophase by considering hidden ions. No quadrupole splittings for $[^{59}\mathrm{Co(phen)_3}]^{3+}$ due to an interaction with the KDodec mesophase do not always mean a small interaction of the complex ions with the mesophase.

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References

1) M. Iida and A. S. Tracey, *J. Phys. Chem.*, **95**, 7891 (1991).

2) M. Iida, Y. Miyagawa, S. Kohri, and Y. Ikemoto, *Bull. Chem. Soc. Jpn.*, **66**, 2840 (1993).

3) M. Iida and A. S. Tracey, "Structure and Dynamics of Solutions," ed by H. Ohtaki and H. Yamatera, Elsevier, Amsterdam (1992), p. 186.

4) M. Iida, Y. Miyagawa, and S. Kohri, *Bull. Chem. Soc. Jpn.*, **66**, 2398 (1993).

5) C. F. Baes, Jr., and R. E. Mesmer, "The Hydrolysis of Cations," John Wiley & Sons, New York (1976), p. 95. To check the effect of the hydrolysis of the magnesium ions on the peak areas of ^{25}Mg NMR, we measured the peak areas

for the 10 mmol dm^{-3} magnesium chloride solutions both at pH 6.5 and 8.1 (controlled by NH_4Cl–NH_3 buffer). The difference in pH was found to result in no meaningful effects on the peak areas.

6) It seems better to use a solution only dissolving the cobalt(III) complex in water as the reference. Peak areas for this alternative reference are different nearly by ±10% from those for the present reference of the same cobalt(III) complex. This difference is ambiguous and so we prefer the present reference in order to compare the peak areas in a series of the similar mesophase system. Thus the absolute R_H values may include such magnitudes of the errors.

7) Although the quadrupole splittings listed here ($\Delta\nu_Q$) and those for the phen complex (Table 5) are raw data, i.e., they are not normalized[1,2] by the ^{1}H NMR spectra of the surfactants. The difference in the definition between $\Delta\nu_N$ and $\Delta\nu_Q$ gives no effect on the present discussion.

8) A. S. Tracey and T. L. Boivin, *J. Phys. Chem.*, **88**, 1017 (1984).

9) A. S. Tracey, *Can. J. Chem.*, **62**, 2161 (1984).

10) K. Radley and A. S. Tracey, *J. Phys. Chem.*, **89**, 2657 (1985).

11) H. Monoi and H. Uedaira, *J. Magn. Reson.*, **38**, 119 (1980).

12) L. Lerner and D. A. Torchia, *J. Am. Chem. Soc.*, **108**, 4264 (1986).

13) This composition is close to that where the cesium/potassium ratio is minimum.

14) B. L. Hauenstein, Jr., W. J. Dressick, S. L. Buell, J. N. Demas, and B. A. DeGraff, *J. Am. Chem. Soc.*, **105**, 4251 (1983).

15) M. Iida, M. Iwaki, Y. Matsuno, and H. Yokoyama, *Bull. Chem. Soc. Jpn.*, **63**, 993 (1990).