^{59}Co NMR Spectroscopic Chiral Discrimination of $[Co(en)_3]^{3+}$ Enantiomers in Ionic Interacting Systems

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Formation of diastereomers of Δ- and Λ-$[Co(en)_3]^{3+}$ was investigated in aqueous chiral-electrolyte solutions using ^{59}Co NMR spectroscopy. The chiral electrolytes used were alkali salts for L- and D-tartrates, bis(μ-$(-)_{589}$-tartrato)diantimonate(III), *N*-dodecanoyl-L-(and D-)alaninate, *N*-dodecanoyl-L-threoninate, and *N*-hexadecanoyl-L-prolinate. The ^{59}Co NMR parameters for the $[Co(en)_3]^{3+}$ group were different between the enantiomers in most cases. The NMR parameters used for chiral discrimination were chemical shifts (in simple electrolyte and micellar solutions), relaxation rates (in simple electrolyte and micellar solutions), peak areas (in micellar solutions), and quadrupole splittings (in liquid crystalline solutions). The larger values of the relaxation rates suggest stronger interactions. On the other hand, the magnitude of the chemical shift change was not simply related to the extent of the interactions. For a chemical shift, the contribution of a geometrical factor seems to be dominant in systems having local anisotropy in the interaction.

^{1}H and ^{13}C NMR spectroscopies are expected to be extensively applied to chiral discrimination with the development of high-field FT-NMR spectrometers.[1] ^{59}Co NMR spectroscopy also seems to be useful for this purpose since ^{59}Co NMR parameters are sensitive to the environment around the cobalt nucleus[2,3] and ^{59}Co gives a simpler spectrum than ^{1}H and ^{13}C spectra. ^{59}Co NMR spectroscopy of intramolecular diastereomers such as $[Co(pn)_3]^{3+}$ (pn = propylenediamine) has been studied and both the chemical shift and the linewidth are largely different between the two diastereomers.[4,5] On the other hand, only slight differences in the ^{59}Co NMR parameters have been reported for the intermolecular interactions of the $[Co(en)_3]^{3+}$ enantiomers in a deoxyoligonucleotide system.[6] In our preliminary report,[7] chiral selectivity by intermolecular interactions was clearly shown in the ^{59}Co quadrupole splitting to discriminate the enantiomers of $[Co(en)_3]^{3+}$ in cholesteric liquid crystalline (anisotropic) systems composed of *N*-dodecanoyl-L-(or D-) alaninate. In the present work, we tried to see the selective interactions of the chiral (Δ- and Λ) $[Co(en)_3]^{3+}$ with chiral anions extensively and to relate the chiral selectivities to the ^{59}Co NMR parameters. The chiral anions used were L- and D-tartrates (= L- and D-tart^{2-}) (corresponds to *d*- and *l*-tart^{2-}, respectively), bis(μ-$(-)_{589}$-tartrato)diantimonate(III) (= $[Sb_2(\text{L-tart})_2]^{2-}$ (corresponds to $[Sb_2(d\text{-tart})_2]^{2-}$)), *N*-dodecanoyl-L- and D-alaninates (= L- and D-DDA^{2-}), *N*-dodecanoyl-L-threoninate (= L-DDT^{2-}), and *N*-hexadecanoyl-L-prolinate (= L-HDP^{2-}). In the former two cases, the stereospecificities in the ion pairs were monitored by measurement of ^{59}Co NMR parameters such as relaxation rates and chemical shifts. In micellar solutions, the peak areas of the ^{59}Co NMR spectra were also measured to estimate the ratio of the hidden ions[8] to the total cobalt(III) complex ions; hidden ions are defined as those too strongly adsorbed on the micelles to contribute to the ^{59}Co NMR spectra and the ratio is related to the magnitude of the interaction as well as to the above two parameters. This parameter is more convenient than other NMR parameters for monitoring the extent of the interaction, since the value includes no ambiguous physical parameters. Furthermore, as the surfactants, CsDDA and KDDT, form stable nematic lyomesophases composed of surfactant/decanol/aqueous electrolyte solutions, we measured the ^{59}Co quadrupole splittings as well as the chemical shifts and other NMR parameters for the $[Co(en)_3]^{3+}$ enantiomers in these systems.

Experimental

Materials. Crystals of Δ- and Λ-$[Co(en)_3]Cl_3\cdot H_2O$ were prepared by conversion of the corresponding iodide[9] with an ion-exchanger in the Cl^- form. The $[\alpha]_D$ values were −157.2° and +154.7° (0.1 mol dm^{-3}, aqueous solutions) for the Δ- and Λ-isomers, respectively. $Na_2[Sb_2(\text{L-tart})_2]\cdot 1.5H_2O$ was prepared by the reaction of Sb_2O_3 with sodium hydrogen L-tartrate.[10] The preparation of the alkali salts of long chain *N*-acyl amino acids followed a standard method,[11] and the salts were recrystallized twice from ethyl acetate–ethanol mixed solutions. Non-contamination of the dodecanoate or hexadecanoate was confirmed using

^{13}C NMR spectroscopy. The other surfactants were obtained from Sigma Chemical Co. and recrystallized from ethyl acetate. The other reagents were guaranteed reagents from Wako Pure Chemical Industries, Ltd.

NMR Measurements. Most of the ^{59}Co NMR spectra were measured with a JEOL GX-270 FT NMR spectrometer operating at 64.1 MHz. Only when checking the dependence of the relaxation times on the resonance frequency, did we use a JEOL GX-400 FT NMR spectrometer at 95.6 MHz. The longitudinal relaxation times (T_1) were determined by using the usual inversion-recovery method and the relaxation rates (R_1) were obtained as the reciprocal of T_1. The transverse relaxation rates (R_2) in micellar solutions were determined from the line widths ($\Delta\nu_{1/2}$) of the ^{59}Co spectra according to the relationship, $R_2=\pi\Delta\nu_{1/2}$. The temperature of the sample solution was controlled at 27±0.5 °C except for the temperature-dependency study. The concentration of $[\mathrm{Co(en)_3}]^{3+}$ was adjusted to 5×10^{-3} mol dm^{-3} in all cases. Chemical shifts were measured relative to a 5×10^{-3} mol dm^{-3} $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ solution without added salts. The component of the liquid crystalline system was basically as follows: 1.29 mol kg^{-1} of mixed anionic and cationic surfactants (CsDDA or KDDT and TDTMABr)/0.99 mol kg^{-1} CsCl aqueous solution/appropriate amounts of decanol. The details of the component are shown in Table 1 (ii) in Ref. 8.

The kinematic viscosity (ν) for 0.4 mol dm^{-3} Na$_2$(L-tart) and Na$_2$[Sb$_2$(L-tart)$_2$] solutions was measured with a Cannon–Fenske capillary viscometer at five temperatures from 27 to 65 °C. The shear viscosity (η) was obtained from the relationship $\nu=\eta/\rho$, where the density (ρ) was measured by an Ostwald-type picnometer.

Results and Discussion

Ion Pairings with L-tart^{2-} and [Sb$_2$(L-tart)$_2$]$^{2-}$. Changes in the ^{59}Co NMR parameters for the $[\mathrm{Co(en)_3}]^{3+}$ enantiomers by interactions with L-tart^{2-} and [Sb$_2$(L-tart)$_2$]$^{2-}$ ions are described in Figs. 1 and 2, respectively. The magnitudes of the changes are clearly different between the two enantiomers in all cases and are larger for the Λ-isomer than for the Δ-isomer except for the chemical shift change in the [Sb$_2$(L-tart)$_2$]$^{2-}$ systems.

Although we can in principle obtain the ion association constants for the formation of the 1 : 1 ion pairs from Figs. 1 and 2, the magnitudes of the changes in the NMR parameters over 0.1—0.5 mol dm^{-3} added salts are too large to fit reasonable association constants.[12] This deviation was especially large for the relaxation rates in the [Sb$_2$(L-tart)$_2$]$^{2-}$ systems. This larger change in the NMR parameters than the change expected from the 1 : 1 ion-pair formation could be attributed to the appreciable formation of aggregates other than the 1 : 1 ion pairs, such as triple ions (1 : 2 ion pairs). However, the relationship between which enantiomer has a larger change in the NMR parameters did not change over the anion concentration ranges studied. We therefore can discuss only which enantiomer has larger NMR parameter changes by interactions with chiral anions, that is, the difference of the NMR parameters between the two enantiomers by the interactions with chiral anions can be attributed to differences between the diastereomeric ion pairs.

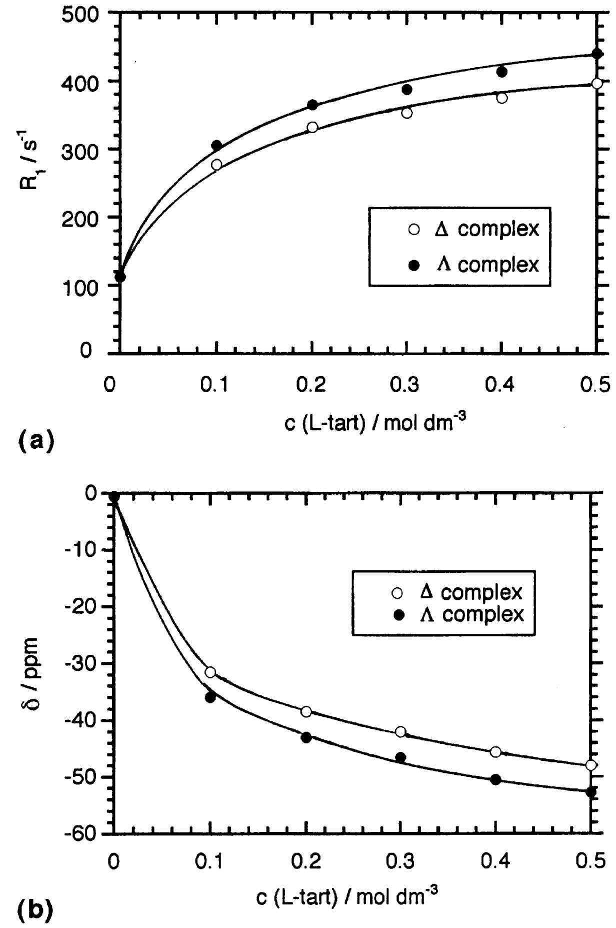

Fig. 1. Dependences of the ^{59}Co NMR (a) relaxation rates (R_1) and (b) chemical shifts (δ) for the $[\mathrm{Co(en)_3}]^{3+}$ enantiomers on the concentrations of the Na$_2$(L-tart).

As a measure for comparison between the diastereomeric ion-pairs, the relaxation rate is preferable to the chemical shift, since the former has a clearer physical meaning regarding the magnitudes of the interactions than the latter.[15] For the ^{59}Co nucleus ($I=7/2$), the relaxation is caused by the interaction of a nuclear electric quadrupole moment, *eQ*, with fluctuating electric field gradients (efg), *eq*, in the region of the nucleus. To a first approximation, the longitudinal (R_1) and transverse (R_2) relaxation rates for the $I=7/2$ nucleus can be expressed as,[16]

$$R_1=T_1^{-1}(\omega_0)=\frac{2\pi^2}{49}\chi^2(0.2J_1+0.8J_2) \tag{1}$$

$$R_2=T_2^{-1}(\omega_0)=\frac{2\pi^2}{49}\chi^2(0.3J_0+0.5J_1+0.2J_2), \tag{2}$$

where χ $(=\frac{e^2qQ}{h})$ is the quadrupole coupling constant. The J_ks are spectral densities defined as

$$J_k=\frac{\tau_C}{1+(k\omega_0\tau_C)^2} \tag{3}$$

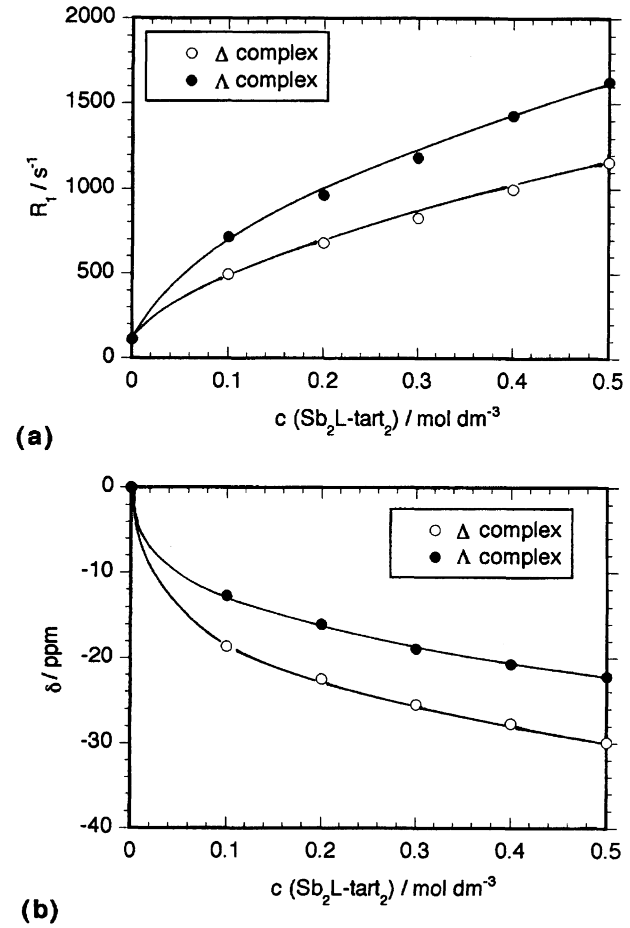

Fig. 2. Dependences of the ^{59}Co NMR (a) relaxation rates (R_1) and (b) chemical shifts (δ) for the [Co(en)$_3$]$^{3+}$ enantiomers on the concentrations of the Na$_2$[Sb$_2$(L-tart)].

where ω_0 is the nuclear precession frequency and τ_C is the reorientational correlation time at the quadrupolar nucleus of interest. If $1/\tau_C$ is much larger than ω_0, both the relaxation rates, R_1 and R_2, are equivalent and independent of the frequency, ω_0 (extreme narrowing condition).

When we measured the ^{59}Co R_1 values for the Λ-isomer in 0.4 mol dm^{-3} solutions of L-tart^{2-} and [Sb$_2$(L-tart)$_2$]$^{2-}$ at 95.6 MHz, the values nearly coincided (within a few percent error) with those measured at 64.1 MHz. Therefore, the motion of [Co(en)$_3$]$^{3+}$ is under an extreme narrowing condition and R_1 can be written as $2\pi^2\chi^2\tau_C/49$ for the results in Figs. 1(a) and 2(a). In the above parameters, the value of τ_C increases with increasing ionic interactions. Although the effective χ value decreases only by formation of specific ion-pairs with some oxyanions such as sulfate and phosphate ions,[17,18] it remains almost constant or increases slightly (a few %) for [Co(en)$_3$]$^{3+}$ by the interaction with carboxylate or other multivalent ions.[18] From this viewpoint, the results in Figs. 1(a) and 2(a) show that the Λ-isomer interacts more strongly with both L-tart^{2-} and [Sb$_2$(L-tart)$_2$]$^{2-}$ than the Δ-isomer does and the difference in the NMR parameters between the enantiomers is larger in the presence of [Sb$_2$(L-tart)$_2$]$^{2-}$ than in the presence of L-tart^{2-}. These two trends in the selectivity are consistent with the previous results studied by circular dichroism and by chromatography.[13] The results in Table 1 also show that the Δ–D interaction is almost the same as the Λ–L interaction and the Λ–D interaction is almost the same as the Δ–L interaction.

As the correlation time, τ_C, generally follows the Arrhenius relationship, and the other parameters in Eq. 1 can be assumed to be nearly constant with varying temperatures, we measured the relaxation rates at five temperatures (27—65 °C) for each enantiomer in the presence and absence of 0.4 mol dm^{-3} L-tart^{2-} or [Sb$_2$(L-tart)$_2$]$^{2-}$.[19] The apparent activation energies obtained from the slopes of the log R_1 vs. T^{-1} plots are 13.5±0.6 kJ mol^{-1} in the absence of the added salts, 18.8±0.6 kJ mol^{-1} in the 0.4 mol dm^{-3} L-tart^{2-} system, and 26.2±0.5 kJ mol^{-1} in the 0.4 mol dm^{-3} [Sb$_2$(L-tart)$_2$]$^{2-}$ system; no difference was detected between the two enantiomers. As the correlation time (τ_C) is proportional to the viscosity (Stokes–Einstein–Debye equation), we also measured the activation energies for the viscosities under the same conditions to separate the contribution of the ion–water interaction from the correlation time. Although the viscosity increases in the order pure water<Na$_2$(L-tart) solution<Na$_2$[Sb$_2$(L-tart)$_2$] solution, the activation energies obtained are 15.4±0.6 kJ mol^{-1} in water, 15.2±0.6 kJ mol^{-1} in 0.4 mol dm^{-3} Na$_2$(L-tart) solution, and 15.6±0.6 kJ mol^{-1} in 0.4 mol dm^{-3} Na$_2$[Sb$_2$(L-tart)$_2$] solution. Therefore, the activation energies for the ^{59}Co relaxation rates depend on the extent of the interaction, that is, the interaction increases in the order no added salts<L-tart^{2-} system<[Sb$_2$(L-tart)$_2$]$^{2-}$ system. The larger activation energy in the Na$_2$[Sb$_2$(L-tart)$_2$] system than that in the Na$_2$(L-tart) system corresponds to the larger chiral discrimination ability of the former reagent. However, almost the same activation energies for the two enantiomers would seem to show a lack of differences in their interactions with the anions. As the maximum error (0.6 kJ mol^{-1}) in the estimation of the activation energies

Table 1. ^{59}Co NMR Chemical Shifts (δ) and Longitudinal Relaxation Rates (R_1) for Δ- and Λ-Isomers of the [Co(en)$_3$]$^{3+}$ in the Presence of D- and L-tart^{2-} Anions

	L-tart^{2-}		D-tart^{2-}	
[tart^{2-}]/mol dm^{-3}	Δ-Isomer	Λ-Isomer	Δ-Isomer	Λ-Isomer
(i) δ/ppm				
0.2	−38.1	−42.6	−42.8	−38.3
0.4	−45.2	−50.1	−49.8	−45.0
(ii) R_1/s^{-1}				
0.2	330	361	353	324
0.4	370	407	410	372

appears as the fluctuation of 27% of the relaxation rates (according to the relation, $\exp(600/8.3\times300)=1.27$), a difference within 27% in the relaxation rates is not able to be discriminated. This is the case for the 0.4 mol dm^{-3} $\mathrm{Na_2(L\text{-}tart)}$ system, while the difference of the relaxation rates between the enantiomers in the 0.4 mol dm^{-3} $\mathrm{Na_2[Sb_2(L\text{-}tart)_2]}$ system is larger than this value. Therefore, we concluded that the difference in the activation energies between the diastereomers is not significant even when it is expected to be detected.

A change in the chemical shift which also generally monitors the extent of the ionic interaction gave somewhat complicated results. Although the change in the chemical shift was in the order Δ-isomer$<\Lambda$-isomer in the $\mathrm{L\text{-}tart^{2-}}$ system, and this order is the same as that obtained for the relaxation rate, the order is reversed in the $\mathrm{[Sb_2(L\text{-}tart)_2]^{2-}}$ system. This irregularity seems to be a curious result. But it suggests that the ion pairing in the latter system has larger microscopic anisotropy than that in the former system and that the process of ion pairing may induce magnetic anisotropy by virtue of the electrostatic perturbation of the crystal field about the otherwise spherical complex.[21] Therefore, one possible explanation for this result is the effect of the magnetic anisotropy on the chemical shift. In this case, the chemical shift is described to be proportional to the order parameter, $S=(3\cos^2\theta_\mathrm{i}-1)/2$ where θ_i is the angle between the local director of the electric field gradient (efg) from the anion and the axis of molecular reorientation of the complex ion. In fact, this effect has been reported for chemical shifts in stereoselective ion-pairings[21,22] and hydration in colloidal systems.[23—27] If the θ_i value in the Δ–L ion pair is smaller than that in the Λ–L pair, the change in the chemical shift can become larger in the former case than in the latter system by overcoming the smaller interaction. On the other hand, the relaxation rate is insensitive to the order parameter when the reorientational motion of the ion in question is fast.[23] Therefore, if the difference in the configuration between the two diastereomeric ion pairs significantly affects the order parameters, such factors can break the simple relationship between the extent of the interaction and the magnitude of the chemical shift, while it would not break this relationship for the relaxation rate.

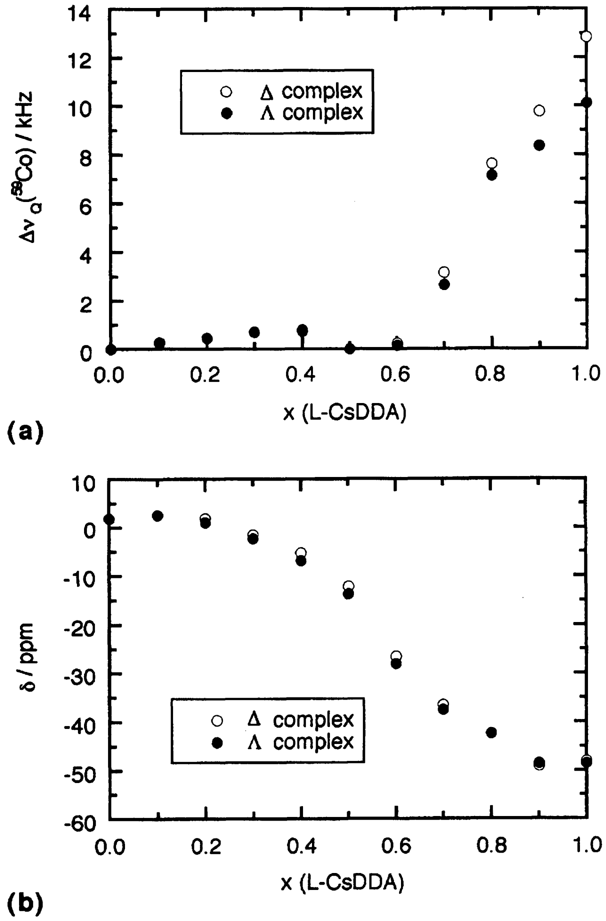

Fig. 3. ^{59}Co quadrupole splittings (a) and chemical shifts (b) of Δ- and Λ-$\mathrm{[Co(en)_3]^{3+}}$ in the mixed TDTMABr/L-CsDDA liquid crystalline system as a function of the mole fraction (x) of L-CsDDA.

In Liquid Crystalline and Micellar Solutions. ^{59}Co NMR quadrupole splitting was observed in liquid crystalline systems composed of cesium *N*-dodecanoyl-L-alaninate (CsDDA)/tetradecyltrimethylammonium bromide (TDTMABr) mixed surfactant and potassium *N*-dodecanoyl-L-threoninate (KDDT)/tetradecyltrimethylammonium bromide (TDTMABr) mixed surfactant systems. The results are described in Figs. 3 and 4 together with those for the chemical shifts. The results in the two liquid crystalline systems are very similar to each other, that is, the $\Delta\nu_\mathrm{Q}$ value for the Δ-isomer is significantly larger than that for the Λ-isomer while the difference in the chemical shift is very small. The difference in $\Delta\nu_\mathrm{Q}$ between the two enantiomers is almost the same in the two systems. This trend is different from that previously reported for D- and L-alanines.[28] In that case, alanine molecules align more extensively in the threoninate liquid crystalline system than in the alaninate system since the former amphiphile has two chiral centers. The difference between the alanine molecule and the $\mathrm{[Co(en)_3]^{3+}}$ ion may be due to the more flexible structure of the former molecule than the latter complex ion, that is, the effect of the two chiral centers of the threoninate head group on the chiral discrimination would be larger in the interaction with the more flexible linear molecules. It is characteristic of liquid crystalline systems that quadrupole splitting is a more sensitive distinguisher of the chiral interaction with the surfactant head group than chemical shifts. Both quadrupole splitting and chemical shifts are represented by a second-rank tensor and they are linearly related as a first approximation.[29] However, this relationship does not hold in lyotropic liquid crystalline systems as previously reported by us.[30] Table 2 also shows that the Λ–D interaction is the same as the Δ–L one and that the Δ–D

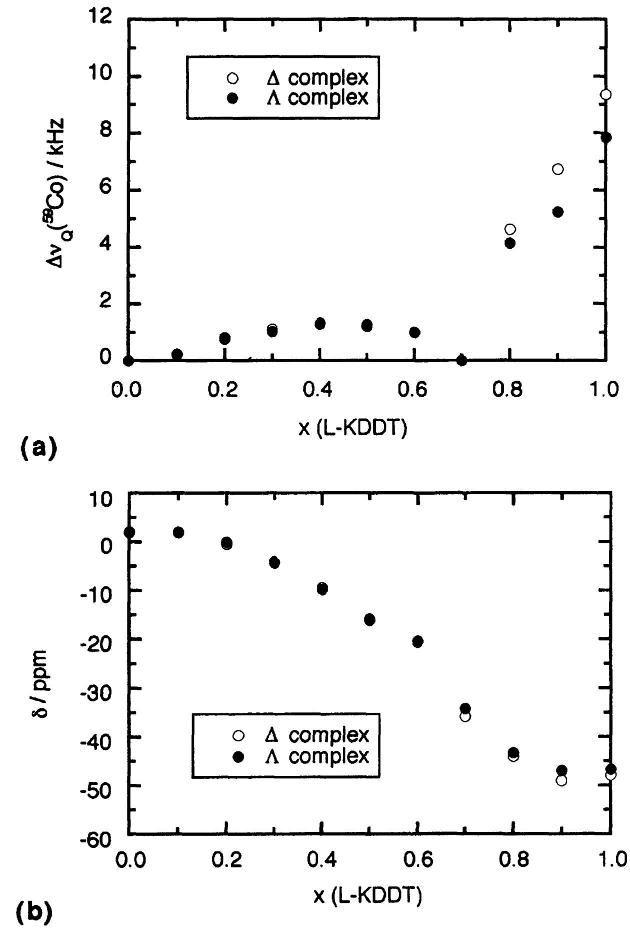

Fig. 4. ^{59}Co quadrupole splittings (a) and chemical shifts (b) of Δ- and Λ-[Co(en)$_3$]$^{3+}$ in the mixed TDTMABr/L-KDDT liquid crystalline system as a function of the mole fraction (x) of L-KDDT.

Table 2. Quadrupole Splittings ($\Delta\nu_Q$/kHz) of ^{59}Co NMR Spectra for Optical Isomers of [Co(en)$_3$]Cl$_3$ in the Liquid Crystals Composed of Cs-DDA (1.29 mol/kg)

	Δ-Isomer	Λ-Isomer	Racemic
L-CsDDA	12.6	10.7	11.4
D-CsDDA	10.8	12.6	11.7
DL-CsDDA	11.2	11.2	11.2

interaction is the same as the Λ–L one. Quadrupole splitting is more clearly defined than chemical shifts in counterion binding,[31] and thus it is convenient to use this parameter in the following discussions. The differences in the $\Delta\nu_Q$ values can be attributed to those of the microscopic binding parameters, i.e. the products of the two factors, the extent of the binding ($p_b\chi_b$, where p_b is the fraction of the binding ions and χ_b is the quadrupole coupling constant for the binding ions), and the order parameter (S_b) for the binding ion, since $\Delta\nu_Q$ can be expressed as,[32]

$$\Delta\nu_Q \propto p_b\chi_b S_b = p_b(e^2q_bQ/h)(3\cos^2\theta_i - 1)/2, \qquad (4)$$

where q_b is the electric field gradient at the nucleus of the binding ion, Q is the nuclear electric quadrupole moment, and θ_i is the angle between the liquid crystal axis (director) and the electric field gradient from the polar group at site i. Figure 5 is a model of the interaction between [Co(en)$_3$]$^{3+}$ and the head group of the dodecanoylalaninate on the basis of a previous paper[33] where the cobalt(III) complexes bind simultaneously to the two head groups.

A lower sensitivity of the chiral discrimination in the liquid crystalline system (as shown in the chemical shift) was also observed in the relaxation rate and the ratio of the hidden ions than for the quadrupole splitting: The longitudinal relaxation rates in the L-CsDDA system were 1724 s^{-1} for the Δ-isomer and 1701 s^{-1} for the Λ-isomer, and the proportions of the hidden ions were 84±2% for both the ions. For these parameters, the differences between the enantiomers do not seem to be significant in the liquid crystalline system. Only the difference in the quadrupole splitting is significant and this difference is mainly attributed to that of the configuration of the cobalt(III) complex ion binding to the liquid crystals, since the quadrupole splitting is especially sensitive to the configuration of the ion-binding.[32—34] Thus we consider that the contribution of the geometric factor (θ_i) in the configuration of the ion-binding to the quadrupole splitting may be larger than the extent of the binding in the present system. As a smaller θ_i makes quadrupole splitting larger, θ_i may be smaller in the Δ–L and Λ–D pairs than those in the Δ–D and Λ–L pairs. Chiral discrimination by the other NMR parameters is, on the other hand, possible in isotropic micellar solutions as will be described below. The lower sensitivities of the NMR parameters in liquid crystalline systems than in other systems may be due to the presence of the cosurfactant (decanol) in the liquid crystalline solutions. That is, the electric charge density at the

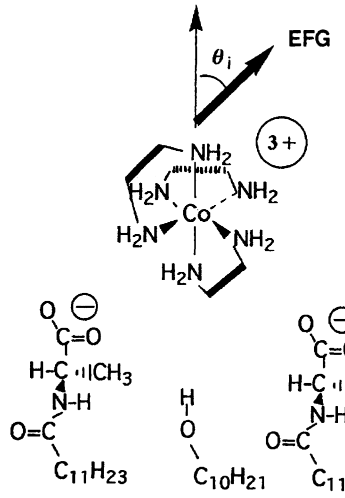

Fig. 5. Schematic representation for the interaction between [Co(en)$_3$]$^{3+}$ and the alaninate head group in the liquid crystalline system.

Table 3. ^{59}Co NMR Chemical Shifts (δ), Longitudinal Relaxation Rates (R_1), Transverse Relaxation Rates (R_2) (in Parentheses), and Percentages of the Hidden Ions (R_H) for Δ- and Λ-Isomers of the $[Co(en)_3]^{3+}$ in the Presence of Chiral Surfactants[a)]

	δ/ppm		R_1/s^{-1} (R_2/s^{-1})		R_H/%	
	Δ-Isomer	Λ-Isomer	Δ-Isomer	Λ-Isomer	Δ-Isomer	Λ-Isomer
[L-KDDA]/mol dm^{-3}						
0.05	−45.4	−40.8	1590	1850		
			(2980)	(3420)		
0.1	−45.8	−40.2				
0.2	−46.1	−40.6	1560	1900	10	11
			(2950)	(3410)		
			1406$^{b)}$	1703$^{b)}$		
1.0	−49.9	−43.6	1680	1930		
			(2980)	(3440)		
[L-KDDT]/mol dm^{-3}						
0.05	−43.6	−40.6	1780	1680		
			(2940)	(2660)		
0.1	−44.1	−40.5				
0.2	−44.1	−40.9	1754	1670	7	6
			(2860)	(2550)		
			1582$^{b)}$	1486$^{b)}$		
1.0	−48.2	−44.6	1855	1727		
			(2990)	(2640)		
[L-KHDP]/mol dm^{-3}						
0.05	−48.3	−40.4	1870	2750		
			(3700)	(5840)		
0.1	−49.1	−39.8				
0.2	−49.6	−39.8	1880	2790	12	32
			(3940)	(5960)		
			1660$^{b)}$	2251$^{b)}$		
1.0	−53.5	−44.3	1965	2720		
			(3930)	(6910)		

a) CMC for all the surfactants are around 0.01 mol dm^{-3}. b) These values were measured at 95.6 MHz. All the other relaxation rates were measured at 64.1 MHz.

water–surfactant interface should be diluted with appreciable decanol/surfactant molar ratios (20%(x=0.9 in Figs. 3 and 4)—45%(x=1.0)). This view is supported by the measurements of the alaninate micellar solutions which have the same composition as the liquid crystalline solutions but without decanol, where the change in the chemical shift was different between the Δ- (−48 ppm) and Λ-isomer (−43 ppm). The relative chemical shift change is similar to that observed in dilute micellar solutions as shown in Table 3, where the change in the chemical shift is larger for the Δ–L pair than for the Λ–L pair, as seen in the $[Sb_2(\text{L-tart})_2]^{2-}$ solution. It is interesting that this order, Δ–L pair > Λ–L pair, is the same as that for quadrupole splittings ($\Delta\nu_Q$) in liquid crystalline systems. In these cases, microscopically anisotropic interactions can change the order parameter (i.e. the geometric factor, θ_i). However, quadrupole splitting may be more sensitive to the geometry of the interaction than other NMR parameters and therefore in liquid crystalline systems only the former parameter could discriminate the diastereomeric interactions.

In isotropic micellar solutions, on the other hand, NMR parameters such as relaxation rates, chemical shifts, and percentages of the hidden ions were in most cases different between the two enantiomers as listed in Table 3. In these systems, the following three features are remarkable. First, all the relaxation rates depend on the resonance frequency while the relative magnitudes of the relaxation rates are the same compared between the two enantiomers of the en complex at the two frequencies. Secondly, the differences in the NMR parameters between the two enantiomers are the largest in the KHDP micellar systems. Thirdly, in the KDDT micellar solution, the relaxation rate for the Δ–L pair is slightly larger than that for the Λ–L pair contrary to the relative magnitudes of the relaxation rates in all the other systems. The second feature indicates that the sterically rigid structure of the head group can discriminate the enantiomers of the $[Co(en)_3]^{3+}$ complex ions as observed in the $[Sb_2(\text{L-tart})_2]^{2-}$ ion-pairing system. As the extreme narrowing condition is not fulfilled here, we obtained the R_2 values from the linewidths of

Table 4. Estimated Correlation Times for Δ- and Λ-Isomers of the $[Co(en)_3]^{3+}$ in the Chiral Surfactant Systems

	$10^{10}\tau_C/s^{-1}$	
	Δ-Isomer	Λ-Isomer
[L-KDDA]/mol dm^{-3}		
0.2	4.3	4.5
[L-KDDT]/mol dm^{-3}		
0.2	4.3	4.6
[L-KHDP]/mol dm^{-3}		
0.2	4.8	7.0

the spectra and the results are listed in parentheses in Table 3. Although the absolute values of R_2 are appreciably larger than those of R_1, the relative magnitudes of the former values compared between the two enantiomers are very similar to those for the latter values. That is, both the relaxation rates are larger for the Λ-isomer than for the Δ-isomer in the KDDA and KHDP systems, while they are slightly larger for the Δ-isomer than for the Λ-isomer in the L-KDDT system.

For the R_2 values, the contribution of the slower motion of the species tends to be more effective than that for the R_1 values. In such a case, the relationship between the two relaxation rates expressed by Eqs. 1 and 2 does not simply hold. The results are listed in Table 4. If the slower component of the relaxation rate is effective, it would be proportional to the square of the order parameter,[23—27] while the chemical shift is proportional to the order parameter as stated above. Wennerström et al. have proposed a global treatment denoted as the 'two-step model'.[23] This model is applicable for ^{13}C relaxations in spherical-micellar solutions which are formed below around 1 mol dm^{-3} surfactant concentration. According to this model, the spectral density function (Eq. 3) is expressed as:

$$J(\omega_0) = \frac{S_b^2\tau_s}{1+(\omega_0\tau_s)^2} + \frac{(1-S_b^2)\tau_f}{1+(\omega_0\tau_f)^2}, \qquad (5)$$

where τ_s and τ_f are the correlation times associated with the slow and fast motions and S_b is the order parameter defined in Eq. 4. The correlation times were assumed to fall in the ranges of $10^{-9}<\tau_s<10^{-7}$ s and $10^{-12}<\tau_f<10^{-11}$ s. However, if the extreme narrowing condition does not hold as in the present case and the slow-motion state does not significantly contribute to the relaxation rate, the second term will govern the relaxation rate. On the basis of this assumption, we considered only the second term in Eq. 5. As we obtained the R_1 values at the 2 resonance frequencies, the R_1 (at 64.1 MHz)/R_1 (at 95.6 MHz) ratio gives τ_C values at 0.2 mol dm^{-3} surfactant concentration by considering Eq. 1 and the second term of Eq. 5. These results are also listed in Table 4. The values obtained lie in the range of the intermediate value between the τ_f and τ_s ranges described above. Therefore, in the present system the contribution of τ_s may be negligible while the extreme narrowing condition does not hold. Although the difference in the τ_C values between the Δ-isomer and the Λ-isomer is small except for the L-KHDP system, it seems reasonable to consider that the motion of the Λ–L pair is more restricted than that of the Δ–L pair as seen in the L-tart^{2-} and $[Sb_2(\text{L-tart})_2]^{2-}$ systems.[35]

The percentage of ions adsorbed on the micelle (R_H) is important here since this value may directly monitor the extent of the interaction with micellar and liquid crystalline systems (having no ambiguous physical parameters).[8] As the R_H value is larger for the Λ–L pair than for the Δ–L pair in the KHDP micellar solutions, the interaction in the Λ–L pair is stronger than that in the Δ–L pair. In the other systems, the differences between the enantiomers should be within experimental errors since the R_H value contains larger errors than the other NMR parameters. This result suggests that the larger size of the L-KHDP head group enhances the discrimination of the $[Co(en)_3]^{3+}$ ions on the micelles. This viewpoint also supports the larger difference in the correlation times between the two enantiomers for the L-KHDP system than the other systems as shown in Table 4.

In the KDDT system, it is somewhat difficult to determine which factor inverts the relative magnitude of the relaxation rates compared to the other systems. If the difference in the τ_C values between the two enantiomers in Table 4 is significant, the relationship that the Λ–L pair interaction is stronger than that of the Δ–L pair also holds in this system. In this case, the larger R_1 value for the Δ–L pair may come from the contribution of the order parameter, S_b in Eq. 5, that is, the Δ–L diastereomer has a larger θ_i value than the Λ–L pair. As the threoninate head group has two chiral centers, the effect of the geometric factor on the relaxation rate may be significant and may complicate the relationship between the R_1 and τ_C values. If only the fast motion expressed in the second term of Eq. 5 is effective and the order parameter (S_b) has a negative sign, the effect of this factor on the relaxation rate is the same trend as that on the chemical shift compared to the two enantiomers.

In conclusion, ^{59}Co NMR parameters are sensitive to the interactions of $[Co(en)_3]^{3+}$ enantiomers with chiral anions. A comparison between the two enantiomers shows that the larger relaxation rate means the stronger diastereomeric interaction except in L-KDDT micellar solutions. On the other hand, for the chemical shift, the order parameters from local anisotropic interactions may complicate the relationship with the extent of the interaction. In most cases, the ^{59}Co NMR parameters obtained do not contradict the selectivity that the Λ–L and Δ–D interactions are stronger than the Λ–D and Δ–L interactions, as has been shown by other methodologies.

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