

^{139}La NMR Relaxation and Chemical Shift Studies in the Aqueous Nitrate and Chloride Solutions

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^{139}La NMR relaxations and chemical shifts in the aqueous nitrate and chloride solutions at 274–343 K were studied. The solutions in this study were $\text{La}(\text{NO}_3)_3\text{--LiNO}_3$ or --HNO_3 , and $\text{LaCl}_3\text{--LiCl}$ or --HCl systems. The dependencies of the slope for the plot of $1/T_1$ (s^{-1}) vs η/T (cP K^{-1}) on the anion concentration showed that nitrate ions form inner-sphere complexes with lanthanum in a relatively low concentration but chloride ions scarcely form below about 4.3 mol/L. In the $\text{LaCl}_3\text{--LiCl}$ systems, the quadrupole coupling constants obtained by the temperature dependencies of $1/T_1$ below about 4.3 mol/L ranged from 3.1 to 3.4 MHz, which agreed well with the value of hydrated lanthanum. In the $\text{LaCl}_3\text{--HCl}$ systems, however, the quadrupole coupling constants slightly increased with an increase in chloride ion concentration even below about 4.3 mol/L, indicating that chloride ions possibly begin to form inner-sphere complexes. Activation energies for the rotational motion of lanthanum were determined in all of the solutions by the T_1 analyses using the Arrhenius equation. The activation energies in the nitrate concentration range from 0 to 0.1 mol/L were about 14 kJ/mol and in that above 1 mol/L about 18 kJ/mol. On the basis of the quantitative analysis for the activation energies, these values were regarded as the energies for a breaking the hydrogen bond of $\text{H}_2\text{O--H}_2\text{O}$. While in the chloride ion systems, the activation energies gradually decreased above 0.6 mol/L, indicating that hydrated lanthanum ions are gradually removed from a net structure of the aqueous solution by being packed by chloride ions. Chemical shifts obtained from a series of experiments also showed that chloride ions do not form inner-sphere complexes with lanthanum below about 4.3 mol/L. Furthermore, the chloride ions induce downfield shifts and nitrate ions induce upfield relative to the value of hydrated lanthanum. It is likely that the downfield shifts in the chloride systems are due to the result of an overlapping closed-shell repulsion.

Introduction

Nuclear magnetic resonance (NMR) is a powerful technique for structural and dynamic studies in solution. In the lanthanide studies, ^{139}La is especially important from the viewpoint of giving us information about a solvated central metal. Since this nuclide is diamagnetic and has a relatively large quadrupole moment, which interacts with electron field, relaxation of ^{139}La provides the symmetry of solvated lanthanum and the distribution of anion outside the primary coordination sphere. The previous works regarding lanthanum in electrolyte solutions^{1,2} reported the ^{139}La relaxation behavior with a change in dissolved salt compositions at a constant temperature. However, we considered that measurement of relaxation time under various temperatures is better than measurement under constant temperatures in understanding the symmetry of solvated lanthanum precisely, and such measurements enable us to elucidate information regarding dynamics. Separation of lanthanides is usually performed in solution, and aqueous chloride and nitrate solutions are most frequently employed in separation methods, i.e., solvent extraction³ and ion exchange.⁴ Hence, the studies regarding these solutions are very important for understanding separation behaviors of lanthanides. In the previous studies of these solutions, the stability constants for the formation of LnCl_2^{2+} were usually determined,^{5,6} and LnCl_2^{2+} was observed in the concentrated chloride solution.⁷ The thermodynamic,⁸ spectroscopic,⁹ ultrasonic absorption,¹⁰ and NMR^{1,2} results

concluded that chloride ions form outer-sphere complexes. However, the luminescence excitation spectroscopy of Eu^{3+} ¹¹ and ^{151}Eu Mössbauer spectroscopy¹² showed evidence for formation of inner-sphere complexes. The direct structural information, obtained by the radial distribution function using X-ray and neutron diffraction methods, indicated that lanthanides in the moderate concentration of chloride ions do not form inner-sphere complexes with chloride ions^{13–18} but, in concentrated chloride solutions, form such complexes.^{17–19} Johansson et al.¹⁹ reported that, even in the relatively moderate conditions, lanthanides somewhat form inner-sphere complexes with chloride ions. As a result, chloride ions form outer-sphere complexes under the moderate conditions; however, it is uncertain if inner-sphere complexes are formed under these conditions. Accordingly, it should be discussed more. Raman studies have shown clearly that an appreciable fraction of NO_3^- ions, in the nitrate solutions, coordinate directly to lanthanide ions at low nitrate concentration.^{20,21} Additionally, the absorption spectroscopic,^{22,23} IR,²⁴ and NMR data^{1,25} clearly suggested that nitrate ions form inner-sphere complexes with lanthanides. The radial distribution functions by X-ray diffraction results also supported this and were consistent with a bidentate and symmetric²⁶ or a monodentate and asymmetric²⁷ bonding of nitrate ions in the primary coordination sphere. However, the enthalpy and entropy data were interpreted in terms of outer-sphere ion

pairs.^{28,29} Accordingly, regarding the nitrate ion systems, the interactions between lanthanides and nitrate ions in various systems have not been completely clarified yet.

In this study we measured the relaxation time of ¹³⁹La in the several solutions at 273–333 K and focused on the change in the quadrupole coupling constant with changing anion concentration. From these results, we tried to elucidate the coordination properties of the anions to lanthanum ions. Especially, we chose the solution systems which are usually used in the ion exchange and the solvent extraction of lanthanides, La(NO₃)₃–LiNO₃ or –HNO₃ and LaCl₃–LiCl₃ or –HCl systems; thus, an understanding of the behavior of lanthanum under the condition including very excess anions can be obtained. Furthermore, we determined the activation energies for the rotational motion to obtain information about the solvation of hydrated and solvated lanthanum. Additionally, we discuss the interactions between lanthanum ions and anions by the chemical shifts obtained in all of the experiments.

Theory and Experimental Conditions

Extreme Narrowing Condition. In this study, we performed a comparison of two relaxation times, T_1 and T_2 , to confirm satisfaction of the extremely narrowing condition. The T_1 values coincided with T_2 , indicating that this study is under conditions of extreme narrowing. Accordingly, we used the line widths at half-height ($W_{1/2}$) to calculate the relaxation times.

Relaxation Mechanism. Lanthanum-139 is a high-abundance (99.9%) and very sensitive nuclide for NMR. It has a relatively high quadrupole moment, $I = 7/2$, $Q = 0.22 \times 10^{-24}$ cm²; therefore, the important relaxation mechanism is nuclear quadrupole relaxation due to the interaction between electric field gradient and nucleus. Generally, for quadrupolar nuclei, an approximate expression for the line width (reciprocal of πT_1), $W_{1/2}$, is given as follows:³⁰

$$W_{1/2} = \frac{1}{\pi T_1} = \frac{3(2I+3)}{40\pi I^2(2I-1)} \left(\frac{e^2 Q q}{\hbar} \right)^2 \tau_c \quad (1)$$

where eq is the largest component of the electric field gradient at the nucleus, eQ is the quadrupole moment, and the other symbols have their usual meanings, and the usually negligible contribution of the asymmetry factor has been omitted. Lanthanum-138 is also an observable nuclide and possesses a quadrupole moment ($I = 5$, $Q = 0.49 \times 10^{-24}$ cm²). Here we compare the theoretical values of the ratios of the relaxation times of (T_1 , ¹³⁸La)/(T_1 , ¹³⁹La) to confirm the relaxation mechanism for lanthanum-139 in this study. If the main relaxation mechanism for ¹³⁹La in this study is due to quadrupole relaxation, the T_1 ratios can be theoretically determined from the spin quantum numbers, I , and quadrupole moments, Q , of ¹³⁸La and ¹³⁹La. The rotational correlation time and the electric field gradient can be canceled by taking their ratio. Figure 1 shows the values of (T_1 , ¹³⁸La)/(T_1 , ¹³⁹La) in various concentrations of lanthanum salt. The values obtained (0.47 ± 0.02 (1σ)) agreed with the theoretical value (≈ 0.47) within $\pm 0.5\%$ (1σ); the main relaxation mechanism in this study, therefore, was regarded as quadrupolar relaxation.

Correlation Time for Molecular Reorientation. We assumed that the molecular motion is described by the diffusion equation of Stokes–Einstein–Debye (SED), which describes motion of a sphere of radius r moving in a medium of viscosity

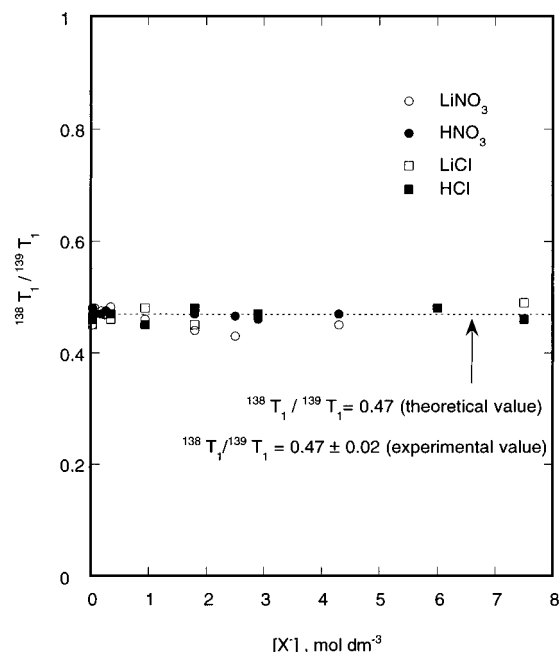


Figure 1. Comparison of the relaxation times between ¹³⁸La and ¹³⁹La NMR in aqueous nitrate and chloride solutions. X: NO₃[−]; Cl[−].

η ; the correlation time may be expressed as³¹

$$\tau_c = \frac{CV\eta}{kT} + \tau^0 \quad (2)$$

where η is the viscosity of the solution, V is the molecular volume, k is the Boltzmann constant, T is the absolute temperature, C is an experimentally determined dimensionless parameter which is concerned with the shape of the rotating molecule and hydrothermodynamic boundary conditions, and τ^0 is the zero-viscosity intercept. The τ^0 values were often found to be nearly equal to the classical free-rotor reorientational time, $\tau_F \approx (2\pi/9)(I/kT)^{1/2}$ (I being the moment of inertia).

From another point of view, the rotational correlation time is examined for the Arrhenius-type dependence on temperature. This is given by

$$\tau_c = \tau_{c,0} \exp(E_a/kT) \quad (3)$$

where E_a is the activation energy.

Experimental Section

The sample solutions were prepared by adding lithium nitrate, lithium chloride, nitric acid, and hydrochloric acid into the 0.024 mol/L of a lanthanum chloride (WAKO Pure Chemicals Industry Co.) aqueous solution. To eliminate the possible effect of hydrolysis, all of the solutions were adjusted to pH = 2 by adding hydrochloric acid. The compositions of these solutions are listed in Table 1a,b. The 0.75 mL of sample solutions were put into a 5 mm tube. The ^{139,138}La NMR spectra were measured at 275–343 K with high resolution, Varian Unity plus 400 (9.4 T) NMR. The resonance frequencies were 56.5 and 52.5 MHz for ¹³⁹La and ¹³⁸La, respectively. To measure the relaxation time, we used the inversion recovery method for longitudinal relaxation time (T_1), while for transverse relaxation time (T_2) were determined using both the line width and the Carr–Purcell–Meiboom–Gill (CPMG) methods, which were compared. The temperatures for NMR measurements were calibrated using the calibration curves from methanol and ethylene glycol ¹H NMR as usual. The viscosities were

TABLE 1: Compositions (mol/L) of the Solutions

(a) Composition of the Nitrate Solutions		
sample name	La(NO ₃) ₃	LiNO ₃ (LN- <i>n</i>) ^a or HNO ₃ (HN- <i>n</i>)
N-1	0.024	0 or 0.01
(L or H)N-2	0.024	0.012 or 0.012
(L or H)N-3	0.024	0.024 or 0.024
(L or H)N-4	0.024	0.048 or 0.048
(L or H)N-5	0.024	0.16 or 0.16
(L or H)N-6	0.024	0.24 or 0.24
(L or H)N-7	0.024	0.32 or 0.32
(L or H)N-8	0.024	0.91 or 0.91
(L or H)N-9	0.024	1.8 or 1.8
(L or H)N-10	0.024	2.5 or 2.5
(L or H)N-11	0.024	2.9 or 2.9
(L or H)N-12	0.024	4.3 or 4.3

(b) Composition of the Chloride Solutions		
sample name	LaCl ₃	LiCl (LC- <i>n</i>) ^b or HCl (HC- <i>n</i>)
C-1	0.024	0 or 0.01
(L or H)C-2	0.024	0.32 or 0.32
(L or H)C-3	0.024	0.91 or 0.91
(L or H)C-4	0.024	1.9 or 1.9
(L or H)C-5	0.024	2.9 or 2.9
(L or H)C-6	0.024	4.3 or 4.3
(L or H)C-7	0.024	6.0 or 6.0
(L or H)C-8	0.024	7.5 or 7.5

^a All of the solutions of the LiNO₃ systems (LN-2–12) contain 0.01 mol/L HNO₃ to eliminate the hydrolysis. ^b All of the solutions of the LiCl systems (LC-2–8) contain 0.01 mol/L HCl to eliminate the hydrolysis.

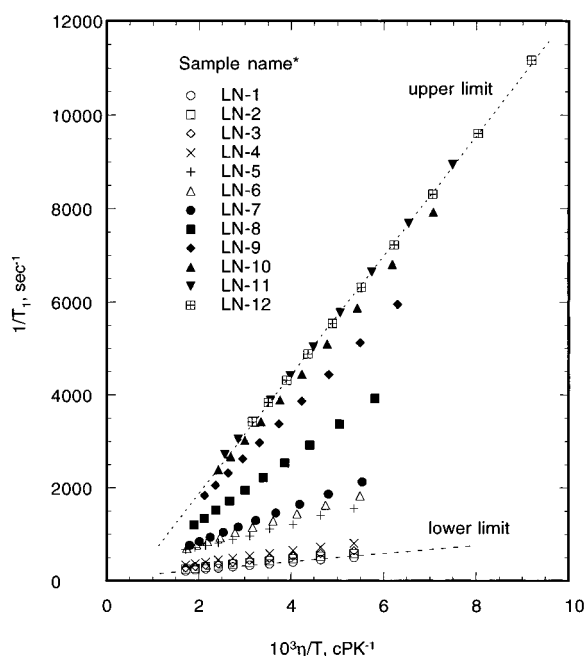


Figure 2. Plot of the reciprocal of longitudinal relaxation time of ¹³⁹La against $10^3\eta/T$ in the LiNO₃ system. *Sample names and their compositions are listed in Table 1a.

measured by using an Ostwald-type viscometer in thermostated bath in the range of 280–340 K.

Results and Discussion

Concentration and Temperature Dependence. Figure 2 shows the relationships between $10^3\eta/T$ (cP K⁻¹) and $1/T_1$ (s⁻¹) in the La(NO₃)₃ (0.024 mol/L)–LiNO₃ systems. In Figure 2, we observed good linear relationships in both nitrate ion systems, suggesting that the macroscopic viscosity corrections would adequately correct for changes in the value of the

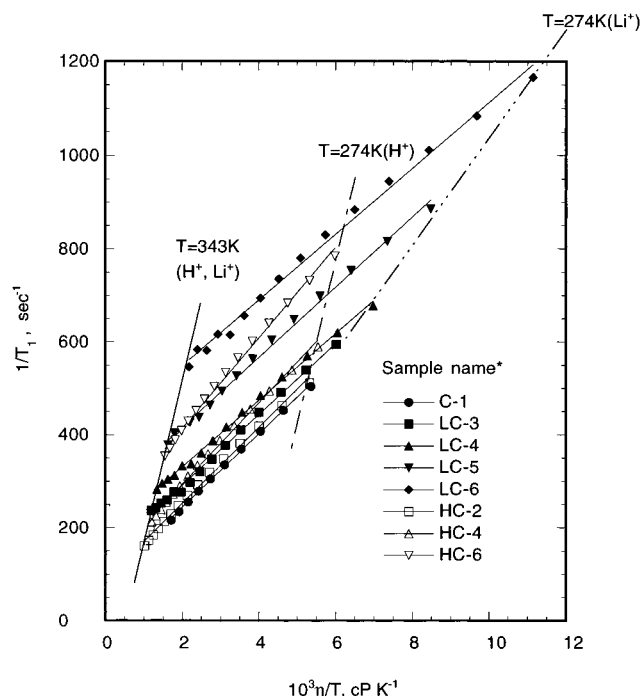


Figure 3. Plot of the reciprocal of longitudinal relaxation time of ¹³⁹La against $10^3\eta/T$ in the chloride ion system. *Sample names and their compositions are listed in Table 1b.

microscopic reorientation correlation time. These linearities indicated that coordination structures of lanthanum are not dependent on the changes in temperature. The slopes for these relationships are determined by the quadrupole coupling constants on the grounds that the relaxation times of lanthanum for these motions are expressed by eqs 1 and 2, giving us informations about changes in the configurations of ligands around lanthanum. The slope values below 0.024 mol/L (LN-3) were regarded as the values for hydrated lanthanum, since these values were approximately equal to the infinite dilution value (N-1). In the concentration range from 0.024 to 3 mol/L, the slope values increased drastically, suggesting the lanthanum ions form nitrate complexes. As mentioned previously, X-ray diffraction²⁶ and the several spectroscopic methods^{11,20,21,24,32–34} indicated that lanthanide ions form inner-sphere complexes with nitrate ions, while the thermodynamic^{28,29} and the dilatometric^{35,36} data were interpreted in terms of the formation of outer-sphere ion pairs. In this study, there is no denying completely the existence of outer-sphere ion pairs, but the inner-sphere complex is considered to be the predominant species in the nitrate solution, since the large changes in the slope in this study are not explained by outer-sphere ion pairs. In contrast, the slope value of ca. 3 mol/L (LN-11) should be the upper limit, and the slopes showed a decreasing tendency above this concentration. The formation constants indicated that LaNO₃²⁺ is the predominant complex of ca. 2 mol/L.⁶ Furthermore, LaNO₃²⁺ is regarded as an asymmetrical species. Accordingly, the slope increasing up to about 3 mol/L would be attributed to forming the asymmetrical nitrate complexes. The decreasing tendency above 3 mol/L suggests that lanthanum is forming relatively symmetrical complexes such as La(NO₃)₃²⁺ at higher concentration. As a result, it is appropriate that lanthanum would complex with one nitrate ion up to about 3 mol/L and two nitrate ions over about 3 mol/L.

Figure 3 shows the plot of $1/T_1$ (s⁻¹) vs $10^3\eta/T$ (cP K⁻¹) for LaCl₃ (0.024 mol/L)–LiCl and –HCl ion systems. In these systems, good linear correlations were also observed. These

results in both chloride ion systems suggested that the coordination structures around lanthanum did not change with changes in temperature. In the LiCl system, the approximately constant slopes for all of the concentrations (LC-3–LC-6) was a noteworthy result in contrast to the nitrate ion systems. Additionally, these slopes agreed with that of the infinite dilution value (C-1); thus, lanthanum complexes contain only water in the primary coordination sphere. Here we calculated the quadrupole coupling constant (QCC; e^2qQ/h) of lanthanum in the LiNO_3 systems. The correlation times (τ_c in eq 2) for the rotational motions are essentially accommodated by viscosity and temperature; therefore, the QCC can be calculated by the modified eq 2. On the assumption that hydrated lanthanum would be a spherical shape and has a “sticky” condition, the boundary parameter C in eq 2, is approximately equal to unity. The relaxation rate of lanthanum-139 in solutions of chloride salts are well-represented by the macroscopic viscosity.¹ The molecular volume is calculated as $2.68 \times 10^{-28} \text{ m}^3$ by the Stokes radius.^{37,38} Consequently, the QCC values are obtained as 3.1–3.4 MHz. These values agree well with Reuben's value: 3.1 MHz, which was calculated by use of τ_c obtained in LaCl_3 salts from the ^1H NMR result of hydration water.^{1,41} A significant difference between the relaxation behavior of lanthanum in the HCl and in the LiCl systems is found in Figure 3. The slopes of the hydrochloric acid solutions increased with an increase in HCl concentration beyond the slope value of hydrated lanthanum. Compared to the nitrate solution, however, the increases in slope values were very small. Thus, it seems that the coordination structures of lanthanum in the HCl system do not change drastically in the primary coordination sphere. The X-ray diffraction indicates extensive Nd, Gd–Cl inner-sphere bonding in the concentrated solutions (10 mol/L HCl solution)^{17,18} but did not indicate the La–Cl bonding in an exactly equivalent solution.¹⁴ The other structural studies by X-ray and neutron diffraction showed that the shortest Ln–Cl distances in lanthanide chloride solutions were about 4.50 Å, suggesting that chloride ions form solvent-separated ion pairs (outer-sphere complex),^{15,19,39,40} however, erbium ions somewhat form inner-sphere complexes with chloride ions even in moderate concentration ($[\text{ErCl}_3] = 0.844\text{--}2.407 \text{ mol/L}$).¹⁹ Therefore, there is a small possibility for the formation of inner-sphere complexes in the previous investigations. Accordingly, the results in the HCl system were attributed to the very small numbers of inner-sphere complexes around 4.3 mol/L (HC-6). The change in the quadrupole coupling constant (or slope) seemed to be very sensitive to a change in the condition around the metal, compared with the other methods. The reason inner-sphere complexes form only in the HCl system cannot be clearly given by this study, but the difference in the net structure of aqueous solution beyond the primary coordination sphere seemed to be important. The viscosities of lithium chloride solutions were larger than those of hydrochloric acid solutions, suggesting that hydrated lithium ions structured as a network more strongly than hydronium ion; as a result, the chloride ions in the LiCl system would hardly interact with lanthanum ions.

Activation Energy for the Rotational Motion of Complexes. The rotational correlation times are expressed by the Arrhenius-type equation as shown in eq 3. Activation energies, therefore, are calculated by the slopes in the plot of $\log(1/T_1)$ vs $1/T$ (K^{-1}). The plots showed good linearities for all samples. Figure 4 is the relationship between the concentrations of anions (NO_3^- and Cl^-) and the activation energy. The activation energies in the nitrate systems were obtained at the constant value of 14 kJ/mol in the nitrate concentration range from 0.01

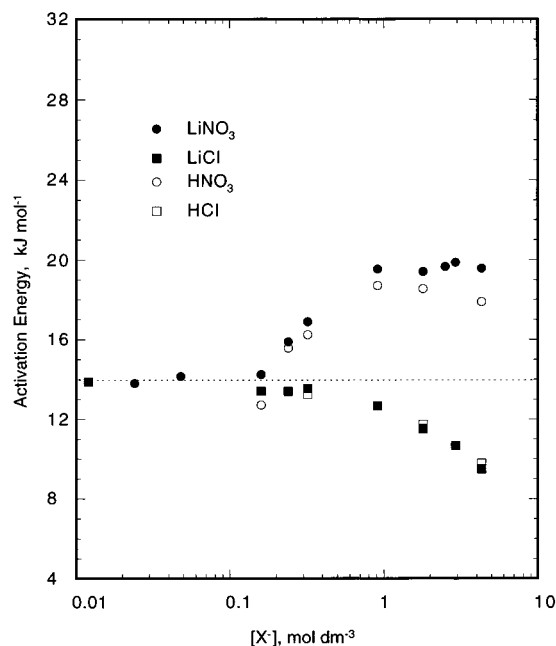


Figure 4. Activation energy of ^{139}La as a function of added anion concentration in the nitrate and chloride ion systems. X: NO_3^- ; Cl^- .

to 0.19 mol/L. These values agree well with the values in the chloride ion systems in the Cl^- concentration range from 0.01 to 0.5 mol/L. Accordingly this value was regarded as the activation energy of the hydrated lanthanum. Above 0.19 mol/L, the activation energies gradually increase and reach the equilibrium value: 18 kJ/mol in the LiNO_3 system. The increases in both the quadrupole coupling constants (the slope in Figure 3) and the activation energy were observed above 0.1 mol/L. However, the quadrupole coupling constants and the activation energies reach a maximum at about 3 and 1 mol/L, respectively (LiNO_3 and HNO_3 systems). Accordingly, the activation energy would reflect the change in the structure of the primary coordination sphere, to put it briefly, the coordination of nitrate ions to lanthanum. The previous ^1H NMR study provided us the interesting results: the activation energies of water were from 14 to 18 kJ/mol,^{42,43} which correspond to the activation energies for breaking hydrogen bonds between waters. The quantitative behaviors of the activation energies for lanthanum were analogous to those of water, suggesting that the rotational motions of hydrated lanthanum would involve breaking the hydrogen bond. As a result, the increases in the nitrate ion concentration do not directly affect an increase in activation energy but would cause an increase in the strength of the hydrogen bonds between hydration water and structured water in the secondary coordination sphere. The activation energies, therefore, possibly increase from 14 to 18 kJ/mol. Furthermore, in the nitric acid system, the activation energies gradually decreased above 1 mol/L, indicating that hydrogen bonds would gradually weaken with an increase in the nitric acid concentration in comparison with the lithium nitrate system.

On the other hand, the activation energies for the chloride ion systems above 0.3 mol/L gradually decreased. As mentioned previously, chloride ions mainly form the solvent separated ion pair with lanthanum. Therefore, in the concentrated chloride solution, most of chloride ions exist in the secondary coordination sphere, so that hydrated lanthanum would be enclosed by chloride ions. Chloride is usually regarded as a structure-breaking ion.⁴⁴ In solutions of structure-breaking salts the disrupting influence of ions on their immediate surroundings by its charge results in a net loss of structure in

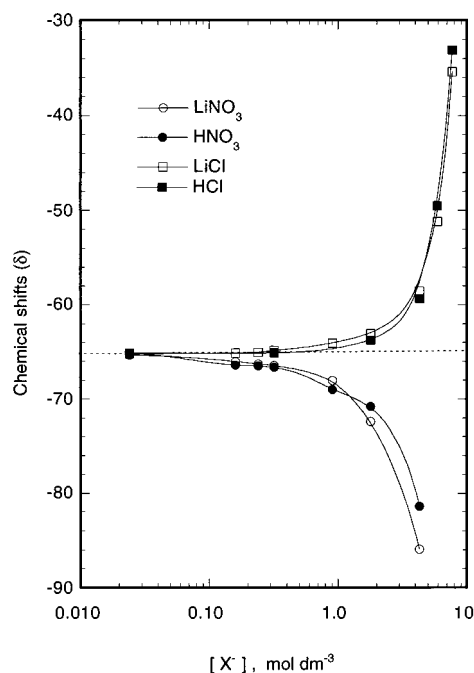


Figure 5. Chemical shift of ^{139}La as a function of added anion concentration in the nitrate and chloride ion systems. X: NO_3^- ; Cl^- .

the solution as a whole. Therefore, the decrease in the activation energy above 0.3 mol/L suggests that the lanthanum reorientation is decoupled from the surrounding structure with an increase in salt concentration.

Chemical Shifts of Lanthanum-139 NMR. In this study, the chemical shifts of lanthanum were also determined. Figure 5 shows the dependencies of the chemical shifts on the anion concentration. In the chloride ion systems, the chemical shifts of lanthanum did not change significantly below 4.3 mol/L, which approximately agrees with the results of the quadrupole coupling constants (or the slopes in Figure 3), while the chemical shifts above 4.3 mol/L drastically change to downfield. The ^{139}La chemical shift study²⁵ and the spectroscopic study for Nd^{22} reported that inner-sphere complexation occurs at higher concentrations (above 5–6 mol/L). On the other hand, in the nitrate solutions, the chemical shifts gradually changed to upfield above about 0.1 mol/L. There is a clear difference in the direction of shift between the chloride and the nitrate solution systems: downfield shifts occur in the chloride systems, and upfield shifts occur in the nitrate systems. The alkali metals (Li–Cs) NMR in the aqueous alkali halide and nitrate solutions⁴⁵ showed that halide ions produce downfield shifts and the nitrate ions give upfield shifts, suggesting that the interactions of alkali metals with halide ions are stronger than water; in contrast, those with nitrate ions are presumably weaker. Furthermore, alkali metal NMR indicates that the interactions between alkali metals and halide ions can be regarded as an overlapping closed shell between the ions, i.e., the outer p orbital of the metals and the outer s and p orbitals of neighboring ions, which is based on the Pauli principle and inner-electronic repulsion. The calculations of the quadrupole coupling constants in alkali halide molecules clearly indicated that there is little covalent bonding of charge-transfer type in these molecules.⁴⁶ Furthermore, the interactions between ions in both solid and solution systems were clearly explained by the overlap repulsive model.⁴⁷ These ideas give us a good explanation for the up- and downfield shifts of lanthanum in the nitrate and chloride solutions. Since the electron configuration of cesium ion is similar to that of lanthanum ion, and from the viewpoint of the chloride ions

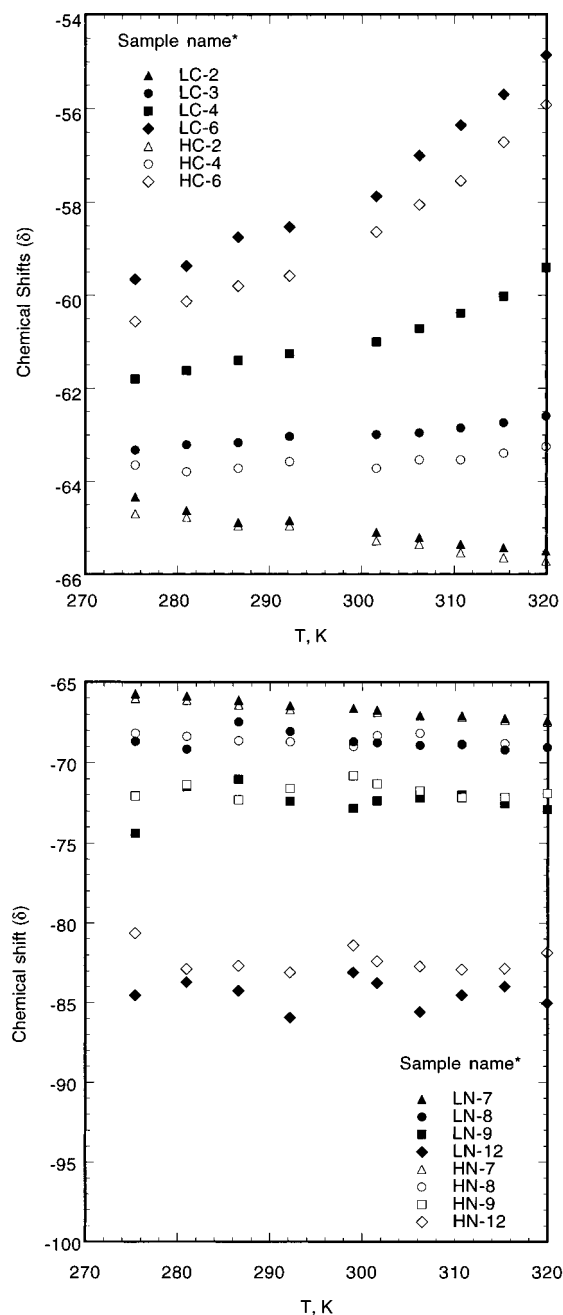


Figure 6. Chemical shift of ^{139}La as a function of temperature in the chloride ion (a, top) and nitrate ion (b, bottom) systems. *Sample names and their compositions are listed in Table 1b.

hardly forming inner-sphere complexes with lanthanum, this mechanism is considered a quite reasonable explanation. As mentioned previously, the quadrupole coupling constants of hydrated lanthanum calculated in this study are 3.1–3.4 MHz. The value even in 4.3 mol/L HCl is very small, compared with the nitrate systems; therefore, chloride ions hardly form inner-sphere complexes. Accordingly, it would be reasonable to assume that the interaction such as an overlap repulsion produce the large downfield shifts in the chloride systems. Parts a and b of Figure 6 show the ^{139}La chemical shifts as a function of temperature in the nitrate and chloride solutions. In the chloride ion systems, we found clear dependencies of chemical shifts on temperature, and the resonance above 0.91 mol/L shifts downfield with increasing temperature; and those below 0.32 mol/L shift upfield. These results also support the model, since the frequency of interaction between lanthanum and chloride

ion possibly increased with an increase in the mobility of ions, so that the closed shell overlapping occurred frequently. The L/HCl-2 are not related with this model, or rather, should be considered as an interaction with oxygen of water. In contrast, in the nitrate system, there were no dependencies on temperature in Figure 6b. This is because lanthanum would behave as a nitrate complex; in other words, the nitrate ions do not exchange on and off the lanthanum during the time frame of a lanthanum rotation. These results agree with the results where the rotational motions do not cause nitrate ions to be removed from lanthanum, as mentioned in the activation energy results.

Summary and Conclusion

^{139}La NMR relaxation times and chemical shifts in the nitrate and chloride aqueous solutions at 274–343 K were determined. We studied the coordination properties and the activation energies using a series of relaxation time analyses, and the interaction between ions by the chemical shift results.

The slopes for the plots of $1/T_1$ (s^{-1}) vs $10^3\eta/T$ (cP K^{-1}) increased with an increase in the anion concentration in the nitrate solution systems, but did not change in the chloride solution systems. Accordingly, we concluded that nitrate ions form inner-sphere complexes and chloride ions do not. Furthermore, we determined the quadrupole coupling constants of lanthanum (3.1–3.4 MHz) in the LiCl system from the temperature dependencies of reciprocal relaxation time ($1/T_1$), and these constants agreed well with the value of hydrated lanthanum. In the HCl system, however, the quadrupole coupling constants increased slightly, suggesting that chloride ions form a very small number of inner-sphere complexes around 4.3 mol/L.

Activation energies of lanthanum complexes were determined in both systems. In the nitrate ion systems, the activation energy was about 14 kJ/mol in the nitrate ion concentration range from 0 to 0.1 mol/L, and above 1 mol/L it was about 18 kJ/mol. In the range from 0.1 to 1 mol/L, the activation energies were between these values. From the quantitative analysis, these values were regarded as the energy for breaking the hydrogen bond of $\text{H}_2\text{O}-\text{H}_2\text{O}$. Furthermore, since the activation energy did not correlate with nitrate ion complexation, rotational motion does not accompany the breaking of the bond between nitrate and lanthanum ions. Therefore, lanthanum would behave as a nitrate complex. In the chloride ion systems, the activation energies were constant, 14 kJ/mol in the concentration range from 0 to 0.6 mol/L, and decreased gradually above 0.6 mol/L; lanthanum would be removed from the net structure of the solution by being packed by chloride ions.

Chemical shifts were also obtained by a series of experiments. The chemical shifts in the chloride solutions were to downfield, and those in nitrate solutions were to one upfield. From the temperature dependencies of the chemical shifts, it is likely that the downfield shifts in the chloride systems are due to the result of an overlapping closed shell repulsion between ions.

References and Notes

- (1) Reuben, J. *J. Phys. Chem.* **1975**, 79, 2154.
- (2) Nakamura, K.; Kawamura, K. *Bull. Chem. Soc. Jpn.* **1971**, 44, 330.
- (3) Yaita, T.; Tachimori, S. *Radiochim. Acta* **1996**, 73, 27.
- (4) Marcus, Y.; Abrahamer, I. *J. Inorg. Nucl. Chem.* **1961**, 22, 141.
- (5) *Gmelins Handbuch der Anorganischen Chemie*; Springer-Verlag: Berlin, 1986; Vol. D4, pp 311, 322, 325.
- (6) Sillén, L. G.; Martell, A. E. *Stability Constants*; The Chemical Society: London, 1964, Special Publication No. 17, Supplement No. 1; 1971, Special Publication No. 25.
- (7) Fukusawa, T.; Kawasui, I.; Mitsugashira, T.; Sato, A.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1982**, 55, 726.
- (8) Marcus, Y. *J. Inorg. Nucl. Chem.* **1966**, 28, 209.
- (9) Choppin, G. R.; Unrein, P. J. *J. Inorg. Nucl. Chem.* **1963**, 25, 387.
- (10) Reidler, J.; Silber, H. B. *J. Phys. Chem.* **1974**, 78, 424.
- (11) Breen, P. J.; Horrocks, W. D., Jr. *Inorg. Chem.* **1983**, 22, 536.
- (12) Greenwood, N. N.; Turner, G. E. *Inorg. Nucl. Chem. Lett.* **1971**, 7, 389.
- (13) Brady, G. W. *J. Chem. Phys.* **1960**, 33, 1079.
- (14) Smith, L. S.; Weltz, D. L. *J. Am. Chem. Soc.* **1975**, 97, 2365.
- (15) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, 70 (8), 3758.
- (16) Annis, B. K.; Hahn, R. L.; Narten, A. H. *J. Chem. Phys.* **1985**, 82 (4), 2086.
- (17) Steele, M. L.; Weltz, D. L. *J. Am. Chem. Soc.* **1976**, 98, 4424.
- (18) Steele, M. L.; Weltz, D. L. *Inorg. Chem.* **1977**, 16, 1225.
- (19) Johansson, G.; Yokoyama, H. *Inorg. Chem.* **1990**, 29, 2460.
- (20) Cheung, A. C.; Irish, D. E. *J. Inorg. Nucl. Chem.* **1981**, 43, 1383.
- (21) Kanno, H.; Hiraishi, J. *J. Phys. Chem.* **1984**, 88, 2787.
- (22) Choppin, G. R.; Henrie, D. E.; Buijs, K. *Inorg. Chem.* **1966**, 5, 1743.
- (23) Coward, N. A.; Kiser, R. W. *J. Phys. Chem.* **1966**, 70, 213.
- (24) Knoeck, J. *Anal. Chem.* **1969**, 41, 2069.
- (25) Rinaldi, P. L.; Hhan, S., A.; Choppin, G. R.; Levy, G. C. *J. Am. Chem. Soc.* **1979**, 101, 1350.
- (26) Yokoyama, H.; Johansson, G. *Acta Chem. Scand.* **1990**, 44, 567.
- (27) Caminiti, R.; Cucca, P.; D'Andrea, A. *Z. Naturforsch.* **1983**, A38, 533.
- (28) Choppin, G. R. *Pure Appl. Chem.* **1971**, 27, 23.
- (29) Choppin, G. R.; Strazik, W. F. *Inorg. Chem.* **1965**, 4, 1250.
- (30) Abragam, A. *The principle of Nuclear Magnetism*; Oxford University Press: London, 1961.
- (31) Kivelson, D.; Maddan, P. A. *Annu. Rev. Phys. Chem.* **1980**, 31, 523.
- (32) Garnsey, R.; Ebdon, D. W. *J. Am. Chem. Soc.* **1969**, 91, 50.
- (33) Reidler, J.; Silber, H. B. *J. Inorg. Nucl. Chem.* **1974**, 36, 175.
- (34) Bünzli, J. C. G.; Yersin, J. R. *Inorg. Chem.* **1979**, 18, 605.
- (35) Spiro, T. G.; Revesz, A.; Lee, J. *J. Am. Chem. Soc.* **1968**, 90, 4000.
- (36) Spedding, F. H.; Cullen, P. F.; Habenschuss, A. *J. Phys. Chem.* **1974**, 78, 1106.
- (37) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed. (revised); Butterworth: London, 1965; Chapter 11.
- (38) Stokes, R. H. In *The Structure of Electrolyte Solutions*; Hamer, W. J., Ed.; Wiley: New York, 1959; p 298.
- (39) Narten, A. H.; Hahn, R. L. *J. Phys. Chem.* **1983**, 87, 3193.
- (40) Cossy, C.; Barnes, A. C.; Endeby, J. E.; Merbach, A. E. *J. Chem. Phys.* **1989**, 90 (6), 3254.
- (41) Reuben, J. *Biochemistry* **1971**, 10, 2834.
- (42) Endom, L.; Hertz, H. G.; Thül, B.; Zeidler, M. D. *Ber. Bunsen-Ges. Phys. Chem.* **1967**, 71, 1008.
- (43) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969; Chapter 4.
- (44) John, G.; Dole, M. *J. Am. Chem. Soc.* **1929**, 51, 2950.
- (45) Deverell, C.; Richards, R. E. *Mol. Phys.* **1966**, 10, 551.
- (46) Das, T. P.; Karplus, M. *J. Chem. Phys.* **1965**, 42, 2885.
- (47) Kondo, J.; Yamashita, J. *J. Phys. Chem. Solids* **1959**, 10, 245.