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A Nuclear Magnetic Relaxation of ^{139}La in Ionic Aqueous Solutions

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The nuclear magnetic relaxation rates of the ^{139}La ion in aqueous solutions of halides, nitrate, sulfate, and perchlorate have been measured. The observed relaxation rates increased as the concentration of the salts increased. However, in the low concentration range, the relaxation rate divided by the relative viscosity, $\Delta\nu/\eta_r$, increased only in the cases of nitrate and sulfate, while it decreased in the cases of halides and perchlorate. It was found that the formation of inner-sphere complexes is a satisfactory explanation of the increase in the $\Delta\nu/\eta_r$ of nitrate and sulfate solutions in the low to middle concentration range. With the fact, proved by various authors, that the lanthanide ions have several coordination numbers, the decrease in the $\Delta\nu/\eta_r$ of halide and perchlorate solutions in the same concentration range can be explained in terms of the existence of an equilibrium between two hydrated species, such as:

$$La(H_2O)_9{}^{3+} \rightleftarrows La(H_2O)_8{}^{3+} + H_2O$$

and the symmetrical species, $La(H_2O)_8{}^{3+}$, contributes to the decrease in $\Delta\nu/\eta_r$. At a high nitrate concentration, after reaching the maximum value $\Delta\nu/\eta_r$ decreases, demonstrating that a symmetrical trinitrato species may be formed in the solution.

It has been shown that, in solution, lanthanide ions have no definite coordination number, being in an equilibrium between several possible coordination numbers.[1–4] The coordination numbers for the lanthanides vary through the lanthanide series, a higher coordination number is favourable for the lighter lanthanides, while a lower coordination number is favourable for the heavier lanthanides. Because ^{139}La ($I=7/2$) is diamagnetic and has a relatively large quadrupole moment (0.5×10^{-24} cm^2), which interacts with the electric field gradient, a nuclear magnetic relaxation study of ^{139}La should provide various information concerning the symmetry of the molecule and the distribution of anions outside the first coordination sphere.

Abragam[5] has derived the following relation for the relaxation of a quadrupole nucleus in solution:

$$T_1{}^{-1} = \frac{3\cdot(2I+3)}{40I^2\cdot(2I+1)}\cdot\left(1+\frac{1}{3}\xi\right)\cdot\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c \qquad (1)$$

where eQ is the nuclear quadrupole moment, where eq

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[1] L. O. Morgan and A. W. Nolle, *J. Chem. Phys.*, **31**, 365 (1959); L. O. Morgan, *ibid.*, **38**, 2788 (1963).

[2] F. H. Spedding, D. A. Csejka, and C. W. Dekock, *J. Phys. Chem.*, **70**, 2423 (1966); F. H. Spedding, M. J. Pikal, and B. O. Ayers, *ibid.*, **70**, 2430 (1966); F. H. Spedding, M. J. Pikal, and B. O. Ayers, *ibid.*, **70**, 2440 (1966); F. H. Spedding and K. C. Jones, *ibid.*, **70**, 2450 (1966).

[3] D. G. Karraker, *Inorg. Chem.*, **7**, 473 (1968).

[4] K. Nakamura, This Bulletin, **41**, 1254 (1968); K. Nakamura, *J. Inorg. Nucl. Chem.*, **31**, 455 (1969); **32**, 2265 (1970).

[5] A. Abragam, "Principles of Nuclear Magnetism," Oxford Univ. Press, London (1961), p. 314.

is the z principal component of the electric field gradient tensor, where ξ is the assymmetry parameter, and where τ_c is the correlation time for the quadrupole interaction and is given by:[6]

$$\tau_c = \frac{4\pi a^3}{3KT}\eta \tag{2}$$

assuming that the molecule can be regarded as a rigid sphere with a radium of *a*.

However, to evaluate *eq* and τ_c in ionic solutions, two different models can be used. One is that the water molecules or anions in the first coordination sphere move uncorrelatively; *i.e.*, the correlation time for the individual motion of water or an anion is shorter than the correlation time for the Brownian motion of the entire water-metal or metal-anion complex. In this case, the observed relaxation rate[7] is z (z: coordination number) times the relaxation rate for the quadrupole interaction due to the fluctuating field of one water molecule or one anion coordinated to the metal ion. Moreover, the observed relaxation rate will increase monotonously as the concentration of the salts increases. This is because of the additional electric field gradient due to ions.

However, when the mean resident time of water molecules or anions in the first coordination sphere is sufficiently longer than the correlation time for the entire complex motion, the field gradient at the metal ion will depend strongly on the symmetry of the molecule. In this case, the observed relaxation rate will not increase monotonously with the concentration increase, but will strongly depend on the kind of species existing in the solution. If the coordination fluctuates between different configurations, the observed relaxation rate will be a weighted average of the relaxation rates of different configurations.

The purpose of this paper is to obtain information on the hydration number change and the complex formation with the anion through the quadrupole interaction of ^{139}La.

Experimental

The NMR spectra were obtained with a Varian VF-16 wide-line spectrometer operating at 6.012 MHz. The magnetic fields were controlled with a "Fieldial Mark II" with a stability of 5×10^{-7}. The frequency were monitored with a Matsushita VP-437 A electronic counter. Distortion due to the finite modulation width were corrected by using different modulation widths and by extrapolating to zero amplitude. Since the observed line shape is Lorenzian, the line width (cycles/sec) is related to the relaxation time thus;

$$T_1^{-1} = \sqrt{3}\pi\Delta\nu \tag{3}$$

The relative viscosities were measured by using an Ostwald-type viscometer in a thermostat bath at 23.0±0.1°C. To check the accuracy of the method used, the relative viscosities of the $LaCl_3$ solutions were compared with the literature value[2] and found to agree within ±1%.

Reagent. The lanthanum nitrate, sulfate, perchlorate, and halide solutions were obtained by dissolving lanthanum oxide (99.95%) purchased from Michigan Chemical Corporation with these acids. All these acids were of a reagent grade and were used without further purification.

Results and Discussion

The concentration dependence of the line width can be separated into two contributions. One is the correlation time, which increases with the viscosity increase of the solution according to Eq. (2). Spedding *et al.*[2] have shown that the concentration dependence of the relative viscosity of a lanthanide chloride solution at a moderate or high concentration can be described in terms of a modification of Vand's equation in this form:

$$\ln(\eta/\eta_0) = A_3C/(1-Q''C) \tag{4}$$

where $\eta/\eta_0=\eta_r$ is the relative viscosity of the solution, where C is the molar concentration, and where A_3 and Q'' are adjustable parameters. According to Spedding, the success of Eq. (3) suggests that the major contribution of a lanthanide chloride solution at a moderate or high concentration arises from the interference of large hydrated ions with the stream of the solvent. This implies that the lanthanide ions are firmly coordinated with one row of water molecules; *i.e.*, the correlation time for the reorientational motion of the hydrated lanthanide ion is sufficiently short compared with the mean resident time of water molecules in the first coordination sphere.

Another is the change in the field gradient due to the changes in the molecular environment. These changes may involve both the change in the first hydration sphere and the change in the charge distribution around it. Figure 1 shows the concentration dependence of the ^{139}La line widths. An examination of the figure

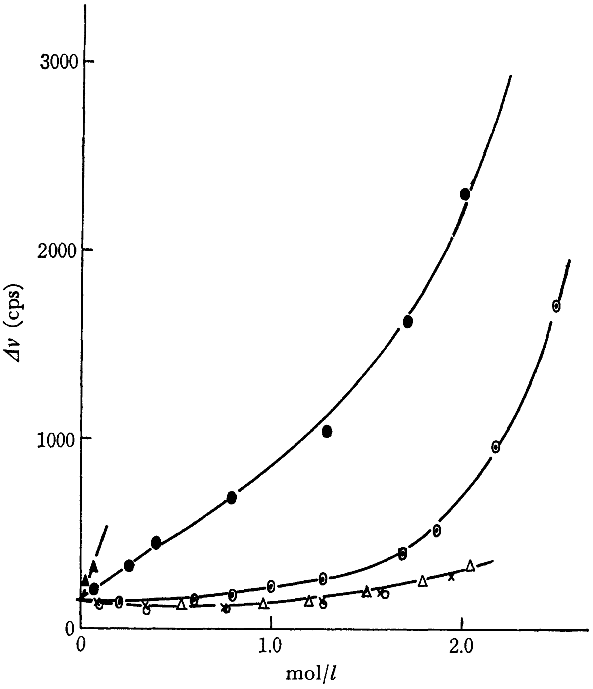

Fig. 1. The concentration dependence of ^{139}La line widths.
▲ $La_2(SO)_3$, △ $LaCl_3$, ● $La(NO_3)$, × LaBr
⊙ $La(ClO_4)_3$, ○ LaI_3

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[6] N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 697 (1948).

[7] H. G. Hertz, *Electrochem.*, **65**, 20 (1961).

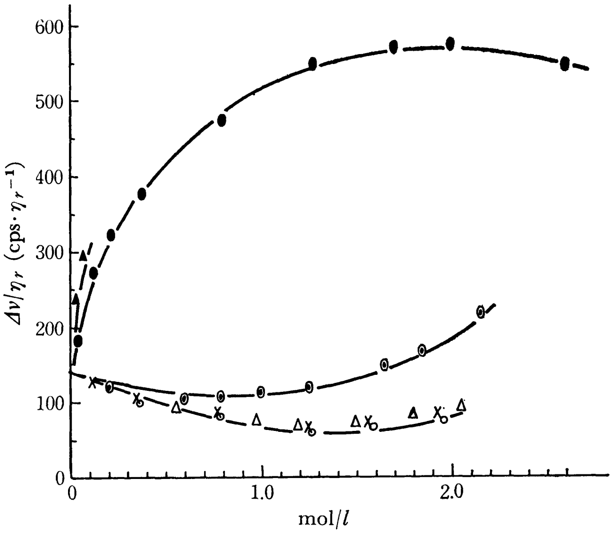

Fig. 2. The concentration dependence of ^{139}La line width/relative viscosity ($\Delta\nu/\eta_r$).
▲ $La_2(SO_4)_3$, △ $LaCl_3$, ● $La(NO_3)_3$, × $LaBr_3$
⊙ $La(ClO_4)_3$, ○ LaI_3

will show that the line widths increase with the concentration increase in the salts due to the increase in the viscosity and the change in the molecular environment. However, to ascertain the change in the molecular environment, it is necessary to divide the line width by the relative viscosity of the solution.[8] The results are shown in Fig. 2, which shows a marked difference in the concentration dependence.

Line Width at an Infinite Dilution. Since the electric field gradient at an infinite dilution is solely determined by the water molecules, the line widths at an infinite dilution are independent of as the anions, as is shown in Figs. 1 and 2. To discuss the line width at an infinite dilution, it is necessary to know the mean resident time of the coordinated water molecules, the coordination number, and the symmetry of the entire lanthanum-water complex.

As has been described previously, a relative viscosity of the $LaCl_3$ solution has shown the existence of a firmly-coordinated lanthanum ion. Recently, Reuben and Fiat[9] have calculated the water-exchange rate constants from ^{17}O NMR. Their calculated rates ranged from 2.6×10^7 to 3×10^6 sec^{-1} as the ionic-radii change from Tb to Tm. If we extraporate these rate constants to the ionic radius of La^{3+}, we obtain 2×10^9 sec^{-1}. This rate is about one-tenth of the reciprocal of the correlation time for the reorientational motion of the hydrated lanthanum ion;[10] moreover, this rate is considerably larger than the observed relaxation rates (100—1000 cps) and the chemical shift (<100 cps).[11]

The coordination numbers of hydrated lanthanide ions have been investigated by various authors. Proton NMR study[1] has shown that the coordination numbers vary in the lanthanide series, being 9 for lighter lanthanides and 6 for heavier lanthanides. On the other hand, the apparent molar volume, the heat capacity, the heat of dilution, and relative viscosity studies[2] have shown that the lanthanide ions in water exist in an equilibrium between two possible coordination numbers; *i.e.*, the coordination number of 9 is favourable for from La^{3+} to Nd^{3+}, while 8 is favourable for from Tb^{3+} to Yb^{3+}. Karraker's spectrometric study[3] of an Nd^{3+} aqueous solution supports this conclusion. He concluded that Nd^{3+} has two coordination numbers, 9 for a dilute and 8 for a concentrated aqueous solution.

The mean resident time and the existence of the two coordination numbers mentioned above indicate that the observed line width is determined by the rapid exchange condition[12] according to:

$$\Delta\nu/\eta_r = P_9\Delta\nu_9{}^0 + P_8\Delta\nu_8{}^0 \tag{5}$$

where P_9 and P_8 are the fractional populations of the species and where $\Delta\nu_9{}^0$ and $\Delta\nu_8{}^0$ are the line widths of $La(H_2O)_9{}^{3+}$ and $La(H_2O)_8{}^{3+}$ respectively at $\eta_r=1$. When 8 coordinated species is symmetrical, the observed line width will be determined only by the fraction of the 9 coordinated species by;

$$\Delta\nu/\eta_r = P_9\Delta\nu_9{}^0 \tag{6}$$

Effect of Anion Concentration. The change in $\Delta\nu/\eta_r$ due to the anion concentration increase may be interpreted in terms of the following several reasons:

1) Some kinds of the anions can replace the water molecules in the first coordination sphere of La^{3+}. This changes the symmetry of the molecule and, hence, the field gradient.

2) The activity of water decreases as the anion concentration increases. This has the effect of reducing the coordination number.

3) So far as the ions outside the first coordination sphere can be treated as point charges, fluctuations from a spherical Debye-Hückel charge distribution also contribute to the relaxation process.

Among the above three reasons, 2) and 3) do not depend strongly upon the difference in the anions of the same charge. At least, they can be considered to have similar concentration dependences. Therefore, the large difference in the concentration dependence between NO_3^- and X^- ions shown in Figs. 1 and 2 is caused primarily by 1).

Only a few studies have been made of the formation constants of lanthanum halide and nitrate. Spectrometric study[13] has shown that K_1 for $LaCl^{2+}$ is -0.2, while that for $La(NO_3)^{2+}$ is 0.26, which is smaller than that for $LaCl^{2+}$. On the other hand, ion-exchange study[14] has shown that K_1 and K_2 for La$(NO_3)^{2+}$ and $La(NO_3)_2{}^{1+}$ are 0.25 and 0.18 respectively. Depending on the experimetal method used, these values differ. However, even if we compare the formation constants derived from the same method, the large difference between the $\Delta\nu/\eta_r$ of nitrate and

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[8] R. E. Richard and B. A. Yorke, *Mol. Phys.*, **6**, 289 (1963).

[9] J. Reuben and P. Fiat, *J. Chem. Phys.*, **51**, 4918 (1969).

[10] With $a=4.0$ Å,[2] $\eta=10^{-2}$ poise, and $T=300$°K, Eq. (2) yields $\tau_c=6.8\times10^{-11}$ sec.

[11] The largest observed chemical shift in this experimental series, corresponding to that of the $La(NO_3)_3$ concentrated aqueous solution relative to the diluted aqueous solution, is about 100 cps.

[12] J. A. Pople, W. G. Shneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Chap. 10, McCraw Hill, London (1959).

[13] K. L. Mattern, UCRL-1407 (1951).

[14] R. E. Kriss and Z. A. Sheka, *Radiokhimiya*, **4**, 312 (1962).

halides can not be explained. Two probable explanations for the above discrepancy are that NO_3^- acts as a bidentate ligand15) and that halide ions can not form an inner-sphere complex.16)

If the line width of each species were known, the successive formation constants could be obtained by successive approximation and least-square fitting, using the observed line width, the total metal amount, and the anion concentration. Unfortunately, we have obtained no information about the line widths except for the line width at an infinite dilution. However, at a very low concentration where only the mononitrato complex is a dominant species, the $\Delta\nu/\eta_r$ for the mononitrato complex can be obtained by using the K_1 value (0.25) and the line width at an infinite dilution (141 cps$\cdot\eta_r^{-1}$). The calculated value for $La(NO_3)^{2+}$ is about 600 cps$\cdot\eta_r^{-1}$. It is confirmed that the highest $\Delta\nu/\eta_r$ is about 600 cps$\cdot\eta_r^{-1}$ at 1.9 M $La(NO_3)_3$ and that $\Delta\nu/\eta_r$ decreases above this concentration. Assuming that it is capable of forming an inner-sphere complex up to three NO_3^- ions, and considering the above confirmation, it may be concluded that the $\Delta\nu/\eta_r$ of $La(NO_3)_2{}^{1+}$ is above 600 cps$\cdot\eta_r^{-1}$, while that of $La(NO_3)_3$ is smaller than that of $La(NO_3)_2{}^{1+}$ due to the symmetrical configuration of the complex.

*Effect of Coordination-number Change.*17) It has been shown in coordination chemistry that perchlorate ions do not form any complexes with metal ions in the low-concentration range. The ^{17}O NMR study9)also supports this fact. As has been described previously, halide ions also form no inner-sphere complexes with lanthanide ions in the low-concentration range. Therefore, the decrease in the $\Delta\nu/\eta_r$ values of these salts can be explained in terms of the change in the hydration number of the lanthanum ion according to the following equilibrium:

$$La(H_2O)_9{}^{3+} \rightleftarrows La(H_2O)_8{}^{3+} + H_2O \tag{7}$$

The thermodynamic stability constant can be expressed as:

$$^tK_{8,9} = \frac{a_9}{a_8\cdot a_{H_2O}} = \frac{y_9}{y_8\cdot y_{H_2O}}\cdot {}^cK_{8,9} \tag{8}$$

$$\left({}^cK_{8,9} = \frac{C_9}{C_8\cdot C_{H_2O}}\right)$$

where the subscripts 9 and 8 indicate $La(H_2O)_9{}^{3+}$ and $La(H_2O)_8{}^{3+}$ species and where a, y, and C mean the activity, the molar activity coefficient, and the molar concentration respectively. The activity coefficient of H_2O in a ionic solution is measurable. However, the meaning of the activity coefficient of $La(H_2O)_9{}^{3+}$ and $La(H_2O)_8{}^{3+}$ is not known. The measured activity coefficient may be the averaged value of these two species.

If we assume that the 8 coordinated species is a symmetrical species and has a zero field gradient, the observed line width can be, from Eqs. (5) and (7), expressed as;

$$\Delta\nu = P_9\cdot\Delta\nu_9 = {}^tK_{8,9}\cdot\frac{y_8\cdot y_{H_2O}}{y_9}C_{H_2O}\Bigg/\left(1 + {}^tK_{8,9}\frac{y_8\cdot y_{H_2O}}{y_9}\cdot C_{H_2O}\right) \tag{9}$$

Figure 3 shows the calculated concentration dependence of $\Delta\nu/\eta_r$ for various values of $^cK_{8.9}$ assuming a constant activity coefficient. However, this assumption is a very rough approximation; the activity coefficient ratio, $y_8\cdot y_{H_2O}/y_9$ may strongly depend on the lanthanum salt concentration.

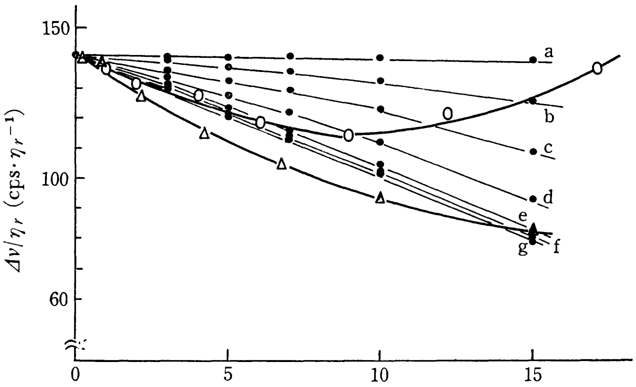

Fig. 3. The calculated concentration dependence of $\Delta\nu/\eta_r$ for various values of $^cK_{8,9}$

	$^cK_{8,9}$		$^cK_{8,9}$		$^cK_{8,9}$		$^cK_{8,9}$
a	1	c	0.03	e	0.003	g	0.0001
b	0.1	d	0.01	f	0.001		

The observed concentration dependence of $\Delta\nu/\eta_r$ for $LaCl_3$ △ and $La(ClO_4)_3$ ○ are also shown in the figure.

Figure 4 shows the concentration dependence of the fraction of $La(H_2O)_9{}^{3+}$ for various values of $^cK_{8,9}$. $\Delta\nu/\eta_r$ values calculated by using Eq. (8) are also given in the figure. The calculated $\Delta\nu/\eta_r$ values range from 140 to 25700 cps$\cdot\eta_r^{-1}$ as $^cK_{8,9}$ changes from 1 to 0.0001. However, considering the experimental facts that the highest $\Delta\nu/\eta_r$ observed in this experimental series is about 1000 cps$\cdot\eta_r^{-1}$ and that the change to 8 coordination takes place in the high-concentration range, such low formation constants as 0.01 to 0.0001 and such high formation constants as 1.0 are thought to be unlikely.

Even if we take the values of $^cK_{8,9}$ ranging from 0.1 to 0.01, as plausible constants, there are still large deviations from the observed values. However, these deviations may be compensated for if we take into account errors due to the decrease in y_{H_2O} with the concentration increase and due to the change in y_8/y_9. The differences in the kind of anions shown in Fig. 4 may come from the different dependencies of $y_8\cdot y_{H_2O}/y_9$ on the salt concentration.

Effect of an Additional Electric Field due to Ions. $\Delta\nu/\eta_r$ values for the halides and perchlorate, after reaching the minimum value, increase in the middle to high concentration range. According to Hertz,7) these increases can be explained as the result of an

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15) C. C. Addison and N. Logan, "Advance in Inorganic and Nuclear Chemistry," Vol. 6, Academic Press, New York (1964), p. 72, 136.

16) G. W. Brady, *J. Chem. Phys.*, **33**, 1079 (1960).

17) There still exists a possibility that the hydrolysis changes the line width. To check this, we measured the effect of the acid ($HClO_4$) concentration on $\Delta\nu/\eta_r$, but found no significant change other than the experimental error.

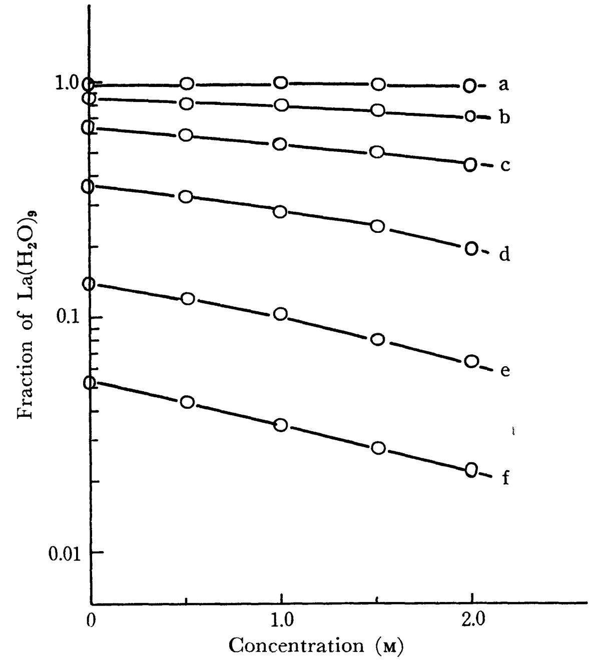

Fig. 4. The calculated concentration dependence of the fraction of La(H$_2$O)$_9$ and $\Delta\nu_9/\eta_r$ for various values of $^cK_{8,9}$.

	$^cK_{8,9}$	$\Delta\nu_9/\eta_r$ (cps$\cdot\eta_r^{-1}$)		$^cK_{8,9}$	$\Delta\nu_9/\eta_r$ (cps$\cdot\eta_r^{-1}$)
a	1	143.8	d	0.01	396.9
b	0.1	166.7	e	0.001	2,691
c	0.03	226.1	f	0.0001	25,691

additional electric field due to other ions which are spherically distributed around the central ion. He treated ions as point charges which are in a uniform distribution outside of the central ion with a radius of a. However, in strongly dissociated dilute electrolytes, the Debye-Hückel charge distribution is valid. Eisenstadt and Friedman[18] treated them by means of this distribution. In either case, such a relaxation mechanism due to the additional electric field is considered to be the same for both anions and cations. The ratio of the relaxation rate of the cation to that of the anion is, from by modifying Eqs. (31)—(36) of Ref. 7 and Eq. (5.11) of Ref. 18, approximately given by:

$$\frac{\Delta\nu^{\text{ion-ion}}_{\text{anion}}}{\Delta\nu^{\text{ion-ion}}_{\text{cation}}} = A\left(\frac{Q_{\text{anion}}}{Q_{\text{cation}}}\right)^2\left(\frac{(1-\gamma_\infty)_{\text{anion}}}{(1-\gamma_\infty)_{\text{cation}}}\right)^2 \tag{10}$$

where A is $((2I+3)/I^2(2I+1))_{\text{anion}}/((2I+3)/I^2(2I+1))_{\text{cation}}$, where $(1-\gamma_\infty)$ is the Sternheimer antishielding factor.

To understand whether the relaxation mechanism proposed by Hertz is predominant in this case for both ions, the relaxation rate for ^{79}Br in the LaBr$_3$ solution has been measured and compared with the theoretical value calculated by using Eq. (10). With the value of $eQ_{\text{La}}=0.5e\times10^{-24}$ cm^2, $eQ_{\text{Br}}=0.34e\times10^{-24}$ cm^2, $(1-\gamma_\infty)_{\text{La}}=69.0$,[19] $(1-\gamma_\infty)_{\text{Br}}=98.0$,[20] and A=9.8, the calculated value of Eq. (10) is 10.9. However, it is very hard to obtain an accurate $\Delta\nu^{\text{ion-ion}}_{\text{Br}}/\Delta\nu^{\text{ion-ion}}_{\text{La}}$ ratio experimentally, since the observed relaxation rate of ^{139}La consists of two parts:

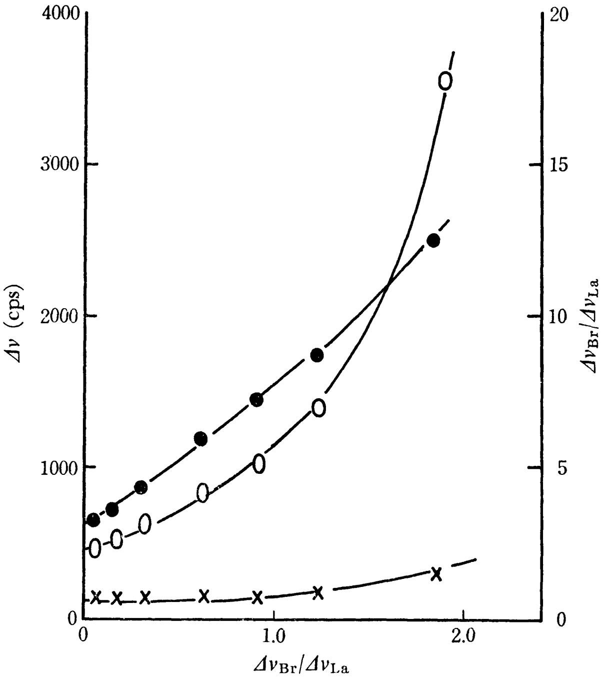

Fig. 5. The concentration dependence of ^{139}La and ^{79}Br line widths and $\Delta\nu_{\text{Br}}/\Delta\nu_{\text{La}}$.
○ ^{79}Br, × ^{139}La, ● $\Delta\nu_{\text{Br}}/\Delta\nu_{\text{La}}$

$$\Delta\nu_{\text{Br}}/\eta_r = \Delta\nu^0{}_{\text{Br}} + \Delta\nu^{\text{ion-ion}}_{\text{Br}} \tag{11}$$

$$\Delta\nu_{\text{La}}/\eta_r = P_8\Delta\nu_8{}^0 + P_9\Delta\nu_9{}^0 + \Delta\nu^{\text{ion-ion}}_{\text{La}} \tag{12}$$

where $\Delta\nu^0{}_{\text{Br}}$ is the line width of ^{79}Br at an infinite dilution. To obtain an accurate $\Delta\nu^{\text{ion-ion}}_{\text{Br}}/\Delta\nu^{\text{ion-ion}}_{\text{La}}$ ratio experimentally by using Eqs. (11) and (12), it is necessary to ascertain the value of $P_8\Delta\nu_8{}^0+P_9\Delta\nu_9{}^0$; however, this can not be obtained accurately in the present investigation.

Conclusions. Through the study of the ^{139}La relaxation times, we can draw the following conclusion: a) The line width at an infinite dilution is determined by the rapid exchange of two hydrated species; symmetrical La(H$_2$O)$_8{}^{3+}$ and unsymmetrical La(H$_2$O)$_9{}^{3+}$ are the most probable in the solution;

b) In the solutions of nitrate and sulfate, the formation of inner-sphere complexes is thought to be a main reason for the increase in $\Delta\nu/\eta_r$. This explanation is consistent with the result of ^{17}O NMR study of lanthanide aqueous solutions;[9]

c) The change in the hydration number is found to be the most probable explanation for the decrese in the $\Delta\nu/\eta_r$ of halide and perchlorate solutions, and

d) The effect of an additional electric field gradient due to anions is found to be present, but to be less effective than the other relaxation mechanisms.

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[18] M. Eisenstadt and H. Friedman, *J. Chem. Phys.*, **44**, 1407 (1966).

[19] R. E. Watson and A. J. Freeman, *Phys. Rev.*, **135**, 1209 (1964).

[20] E. G. Wikner and T. P. Dass, *ibid.*, **109**, 360 (1958).