Electron Relaxation Rates of Lanthanide Aquo-cations

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Measurements of the proton relaxation rates of lanthanide(III) aquo-ion solutions show that the correlation times, which govern the proton relaxation times in these solutions, are very short (*ca.* 10^{-13} s), and are predominantly due to the electron-spin relaxation times of the cations. The variations in the relaxation rates for different Ln^{III} ions are discussed in terms of modulation of the different ligand-field splittings. The temperature dependence of the relaxation rates has also been studied and a relationship to the magnitude of ligand-field splittings of the different Ln^{III} ions is discussed.

In a previous paper [1] we established that the interactions between the nuclear and electron spins which cause proton relaxation in some lanthanide(III), Ln^{III}, complexes are isotropic. We have also developed a method by which we could calculate the hydration numbers of lanthanide(III) complexes.[1] The method required a study of the relaxation time of a nucleus in a known position in a rigid organic ligand, L, in addition to the study of the relaxation times of the protons of water molecules, all in the complex $[ML_n(OH_2)_m]$. In aquo-ions of Ln^{III} there is no ligand, L, and other methods must be used. The relaxation rate of the bulk water is a function of the hydration number of the aquo-ion, x_0, the *total* magnetic moment, μ, and the distance, r, of the water protons from the paramagnetic centre. Since the magnetic moments of the lanthanide(III) aquated ions and complexes are known, the relaxation enhancements are expected to be a function of two unknowns; the electron correlation time, τ_e, and the hydration number, x_0. Knowledge of the electron correlation time would then make it possible to evaluate the hydration number of the aquo-ions.

Earlier work [2] using line widths to measure ^{17}O-relaxation enhancements of solvent water was complicated by the fact that ^{17}O line widths are a sum of contributions from contact and pseudocontact interactions and it was therefore almost impossible to get accurate values for the electron correlation times. In this paper we will use the proton relaxation times of complexes containing different lanthanide(III) ions, which suffer much reduced contact interaction, to determine the electron-spin relaxation times of these ions. We shall then discuss their hydration.

EXPERIMENTAL

Lanthanide(III) perchlorate solutions were prepared as described earlier.[3] Five aqueous solutions, pH range 3—4, covering the range of molalities of 0.01—0.05 of lanthanide(III) perchlorate (Ln = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, or Yb) were prepared using microburettes. Aqueous methanol (0.5% v/v) rather than water itself was used to prevent droplet formation in the n.m.r. tube at the higher temperatures. The measurement of longitudinal relaxation times, T_1, were made at different temperatures, 5—57 °C, using a Bruker Minispec 20 spectrometer with an attached Grant Instrument type FH 15 temperature regulator. Measurements of the longitudinal and transverse, T_t, relaxation times of the samples were made using a Newport 2.7 MHz spectrometer operated at 24 ± 1 °C. Two other solutions of each lanthanide(III) salt were prepared in D_2O and their T_1 values were measured at 24 ± 1 °C using a Bruker HX90 spectrometer operated in the Fourier-transform mode.

RESULTS

The enhancement of relaxation rates of diamagnetic solvent protons in the presence of paramagnetic lanthanide(III) ions is a result of strong local fields produced by the presence of unpaired electron(s). The molal longitudinal and transverse relaxation rate enhancements m.l.r.e. and m.t.r.e. are given by (1) where W is the molal concentration

$$\text{m.r.e.} = \frac{x_0}{W}\left(\frac{1}{T_M} - \frac{1}{T_W}\right) \qquad (1)$$

of water, $1/T_M$ is the corresponding relaxation rate of nuclei (spin ½) in the presence of the paramagnetic ion, and $1/T_W$ is the water relaxation rate in the absence of ions.

TABLE 1

Molar relaxation enhancements (m.r.e./kg mol^{-1} s^{-1}) of water protons in the presence of different lanthanide ions at a variety of temperatures and measured at 20 MHz

Ce	θ_c/°C	8.5	15.2	26.2	34.7	45.6	56.7
	m.l.r.e.	9.2	9.0	8.4	8.1	7.7	7.4
Pr	θ_c/°C	8.0	15.6	25.0	35.2	45.0	56.2
	m.l.r.e.	10.2	10.2	10.1	10.2	10.1	10.2
Nd	θ_c/°C	9.5	15.0	26.2	34.7	45.6	56.7
	m.l.r.e.	25.0	24.3	22.8	21.8	20.6	19.9
Sm	θ_c/°C	8.9	15.3	25.1	34.9	45.2	55.3
	m.l.r.e.	2.0	1.8	1.8	1.7	1.7	1.7
Eu	θ_c/°C	8.5	15.2	25.3	35.0	46.0	55.0
	m.l.r.e.	1.7	1.7	1.6	1.7	1.6	1.6
Tb	θ_c/°C	10.0		26.0	36.0	45.1	57.3
	m.l.r.e.	327.9		320.2	317.4	312.2	309.0
Dy	θ_c/°C	9.4	15.0	26.0	36.0	45.0	57.2
	m.l.r.e.	594.2	588.0	575.5	563.2	554.2	543.1
Ho	θ_c/°C	10.0	15.0	26.0	36.0	45.0	57.2
	m.l.r.e.	384.8	379.2	375.8	368.7	367.3	361.7
Er	θ_c/°C	7.2	14.3	25.8	35.6	45.6	55.7
	m.l.r.e.	427.7	413.8	396.0	385.1	369.1	358.3
Tm	θ_c/°C	7.0	14.3	26.0	35.6	45.6	55.6
	m.l.r.e.	486.0	452.0	408.0	381.2	351.5	326.0
Yb	θ_c/°C	10.0	15.0	26.0	36.0	45.3	57.2
	m.l.r.e.	58.3	56.4	52.8	50.3	48.1	45.1
H_2O	θ_c/°C	9.5	19.0	23.0	36.5	45.0	55.0
	$1/T_1$(s^{-1})	0.56	0.44	0.40	0.27	0.24	0.20

The results of the measurements of the molal longitudinal relaxation enhancements of various lanthanide(III) ions at different temperatures are given in Table 1. Each value is calculated from measurements of $1/T_1$ on five solutions of different molality, plotted against concentration, and subjected to a least-squares analysis to obtain the gradient. Measurements of diamagnetic lanthanum(III) solutions over the same ranges of concentration and temperature gave values of relaxation times similar to those of pure water (air saturated). Studies of solutions of neodymium(III) and erbium(III) ions in slightly more concentrated perchloric acid, pH *ca.* 1.5, showed no change in their relaxation rates from those at pH = 3—4. We conclude that there are no polynuclear or hydroxo-species in lanthanide(III) solutions in this range of pH. The results, Table 1, show that in general for each lanthanide(III) ion a decrease in the relaxation enhancement occurs with increase of temperature but that the solutions of Pr^{III} and Eu^{III} have a constant relaxation enhancement over the range of temperature studied. Our observations, Table 1, are very different from those reported by Conger and Selwood in 1952.[4] At that time lanthanide salts were of doubtful purity. However, Bock [5] reported a value of $1/T_1$ of 9.9 s^{-1} for 0.018 mol dm^{-3} $DyCl_3$ solution at room temperature, which is in good agreement with the value 10.3 s^{-1} calculated from the results in the present study for the same concentration.

Measurements of T_1 and T_t of the solutions at 2.7 MHz are listed in Table 2. T_t values were obtained using the Carr–Purcell pulse sequence. Table 2 also includes the results of T_1 measurements using the Bruker HX90 spectrometer applying a 180–τ–90° pulse sequence. It is clear from Table 2 that the enhancements (m.l.r.e. and m.t.r.e. separately) measured at various frequencies, 2.7, 20, and 90 MHz, are the same within experimental error. Table 2 also shows that the longitudinal and transverse enhancements are the same, also within experimental error. These observations differ from those found in the study of gadolinium(III) solutions [6] which exhibited marked variation of the enhancements with frequency. The cause of this difference lies in the difference in the electron correlation time, τ_s, which is very short and governs the relaxation rates in all the different lanthanide(III) solutions, except for those of Gd^{III} for which the correlation time is that of rotation since its electron correlation time is much longer.[6]

TABLE 2

The frequency dependence of molar relaxation enhancements (kg mol^{-1} s^{-1}) at 20 °C

Metal ion	m.l.r.e. (90 MHz)	m.l.r.e. (20 MHz)	m.l.r.e. (2.7 MHz)	m.t.r.e. (2.7 MHz)
Ce	9.4 ± 0.5	8.5 ± 0.2	8.6 ± 0.2	9.0 ± 0.4
Pr	11.3 ± 0.5	10.5 ± 0.2	10.4 ± 0.2	11.2 ± 0.4
Nd	24.3 ± 1.0	23.2 ± 0.5	22.9 ± 0.5	24.0 ± 1.0
Sm		1.8 ± 0.2		
Eu	1.6 ± 0.2	1.6 ± 0.2	1.6 ± 0.2	1.6 ± 0.2
Tb	324.0 ± 10.0	319.0 ± 10.0	329.0 ± 10.0	340.0 ± 10.0
Dy	592.0 ± 10.0	569.0 ± 10.0	573.0 ± 10.0	586.0 ± 10.0
Ho	396.0 ± 10.0	376.0 ± 10.0	391.0 ± 10.0	401.0 ± 10.0
Er	415.0 ± 10.0	398.0 ± 10.0	406.0 ± 10.0	419.0 ± 10.0
Tm	404.0 ± 10.0	413.0 ± 10.0	406.0 ± 10.0	417.0 ± 10.0
Yb	53.0 ± 2.0	53.0 ± 2.0	53.5 ± 2.0	54.5 ± 20

DISCUSSION

For isotropic interaction between the electron and nuclear spins the appropriate equations [7,8] for $1/T_{1M}$ and $1/T_{tM}$ are (2) and (3) respectively. Here, r is the distance from the nucleus to the paramagnetic centre, τ_c is the correlation time which characterizes the dipolar (first term in each equation) interaction, τ_e is the correlation time which characterizes the scalar interaction, and A is the hyperfine coupling constant. The other symbols are conventional.

The correlation times in these equations are defined as $1/\tau_c = 1/\tau_s + 1/\tau_M + 1/\tau_R$ and $1/\tau_e = 1/\tau_s + 1/\tau_M$ where τ_M is the lifetime of a nucleus in the bound site,

$$\frac{1}{T_{1M}} = \frac{2}{15}\left[\frac{\gamma_I^2 g^2 J(J+1)\beta^2}{r^6}\right]\left(\frac{3\tau_c}{1+\omega_I^2\tau_c^2}+\frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right) + \frac{2}{3}J(J+1)\left(\frac{A}{\hbar}\right)^2\left(\frac{\tau_e}{1+\omega_s^2\tau^2_e}\right) \quad (2)$$

$$\frac{1}{T_{tM}} = \frac{1}{15}\left[\frac{\gamma_I^2 g^2 J(J+1)\beta^2}{r^6}\right]\left(4\tau_c + \frac{3\tau_c}{1+\omega_I^2\tau^2_c} + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right) + \frac{1}{3}J(J+1)\left(\frac{A}{\hbar}\right)^2\left(\frac{\tau_e}{1+\omega_s^2\tau_c^2}+\tau_e\right) \quad (3)$$

τ_R is the rotational correlation time of the bound paramagnetic ion, and τ_s is the electron-spin relaxation time. In the lanthanide(III) ions in solution, except Gd^{III}, the observed correlation time must be τ_s since it is close to 10^{-13} s (see below) which is much shorter than the exchange or rotational correlation times. Thus $1/\tau_s = 1/\tau_e \gg 1/\tau_R \gg 1/\tau_M$ and consequently $\omega_I^2\tau_e^2 \ll \omega_s^2\tau_e^2 \ll 1$. The expressions $(1 + \omega_I^2\tau_c^2)$ and $(1 + \omega_s^2\tau_c^2)$ are then equal to one.

Assuming that the value of -3.5×10^4 Hz for the hyperfine coupling constant, A, is invariant along the lanthanum series,[9] the magnitudes of the scalar terms were found to be less than 0.2% of the dipolar terms. Thus the Solomon–Bloembergen equations reduce to (4).

$$\frac{1}{T_{1M}} = \frac{1}{T_{tM}} = \frac{20}{15}\left(\frac{\gamma_I^2\mu^2\beta^2}{r^6}\right)\cdot\tau_s \quad (4)$$

This equation accords with the observations recorded in Table 2, in that the molal relaxation enhancements m.l.r.e. and m.t.r.e. are equal and both are frequency independent.

Table 3 lists values of the distances from Ln^{III} to bound water protons used in subsequent calculations. The values were calculated from the data of Shannon and Prewitt [10] for crystalline lanthanide(III) compounds with a co-ordination number of eight. This is the only complete series of values available.

TABLE 3

Distances from lanthanide ions (ref. 10) to water protons in crystals of eight-co-ordinate lanthanide(III) compounds

Metal ion	r/Å	Metal ion	r/Å
Ce	3.214	Tb	3.120
Pr	3.208	Dy	3.111
Nd	3.199	Ho	3.101
Sm	3.166	Er	3.083
Eu	3.150	Tm	3.072
Gd	3.140	Yb	3.065

Figure 1 shows the electron-spin relaxation time of the different lanthanide(III) ions at 24 ± 1 °C, calculated from equations (1) and (4) assuming the hydration number is nine, as is suspected, and constant along the series, and without taking into account any outersphere contribution to the total enhancement, since it must be small. It is to be noted from Figure 1 that the electron correlation times in the second half of the series are longer than those of the first half, while the thulium(III) ion shows the longest correlation time.

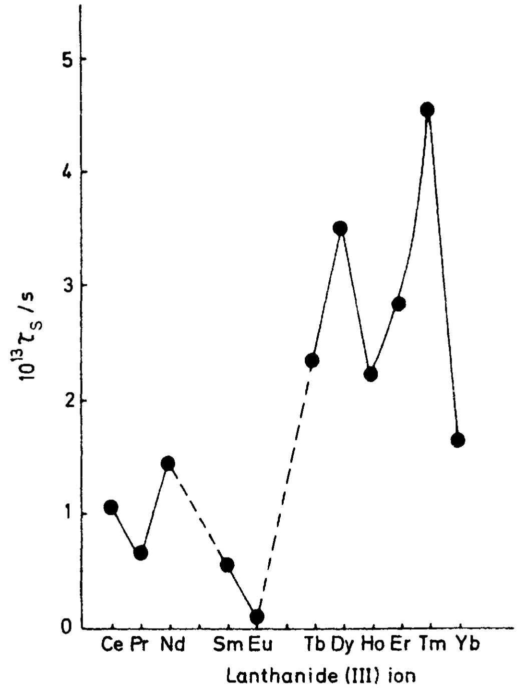

FIGURE 1 Electron-spin relaxation times of Ln^{III} aquo-ions at 21 ± 1 °C

As mentioned before there is a general decrease in the relaxation rates with increasing temperature. This is due to the temperature dependence of the electron spin correlation time, τ_s, which can be expressed by equation

$$\tau_s = \tau_s^{\circ} e^{-\Delta E^{\ddagger}/RT} \qquad (5)$$

(5) where $\Delta E^{\ddagger}$ is the activation energy for the process controlling τ_s. Table 4 gives the values of $\Delta E^{\ddagger}$, calculated from a least-squares treatment of the changes of the relaxation rate with temperature using equation (5). This table shows that the activation energies of the electron-spin relaxation time are very small and of the order of 1—6 kJ mol^{-1}. Granot and Fiat [11] measured the line width ($1/\pi T_t$) of dysprosium(III) solutions from 20 to 92 °C. The values of ($1/T_t$) obtained are very similar to those of ($1/T_1$) obtained in the present study. Granot and Fiat [11] obtained a value of 1.34 kJ mol^{-1} for the activation energy of the Dy^{III} relaxation rate which is in excellent agreement with that, 1.38 kJ mol^{-1}, obtained in the present study.

TABLE 4

Activation energies, $\Delta E^{\ddagger}$/kJ mol^{-1}, of the proton relaxation enhancements of water due to different lanthanide(III) ions

Ce	3.58	Dy	1.38
Pr	0.00	Ho	0.97
Nd	3.86	Er	2.75
Sm	2.39	Tm	6.22
Eu	0.00	Yb	4.19
Tb	0.98		

The activation energy of the electron-spin relaxation times follows the order $Tm^{III} > Yb^{III} > Ce^{III} > Sm^{III} > Dy^{III} > Ho^{III} \simeq Tb^{III}$. Relaxation rates of Pr^{III} and Eu^{III} are temperature independent as far as can be measured. We observe that the value of $\Delta E^{\ddagger}$ for Tm^{III} is rather different from that for the other ions much as the electron-spin relaxation time, τ_s, of this ion was larger than expected at room temperature.

All the above correlation times are very short and are considered to be brought about by modulation of the crystal field by molecular vibration of the water molecules in the first co-ordination sphere of the complex.[12] Using such modulation Zaripov [13] calculated the electron correlation times for cerium(III) and praseodynium(III) ions to be of the order of 10^{-13}—10^{-14} s. This is the same order of magnitude as the values obtained in the present study. The observation (Table 4) that the water relaxation rates in the presence of Pr^{III} and Eu^{III} are temperature independent and yet must be a function of hydration number, x_0, then indicates that these ions exist in solution with a constant hydration number, independent of temperature, and the most likely conclusion is that x_0 is a fixed whole number for Pr^{III} and Eu^{III}. We must next explain the differences in activation energies of the relaxation times of the other lanthanide(III) aquo-ions. Apart from the possibility that hydration numbers can change with temperature we must also examine the temperature dependence of the electronic states. For most of the lanthanide(III) aquo-ions all ligand-field levels are approximately equally occupied at room temperature as the splitting is small relative to kT. Figure 2 shows the crystal-field energy levels [14] of the ground states of the crystalline $LnCl_3 \cdot 6H_2O$. The highest overall splitting is found in the thulium(III) salt and here they are greater than kT. The highest activation

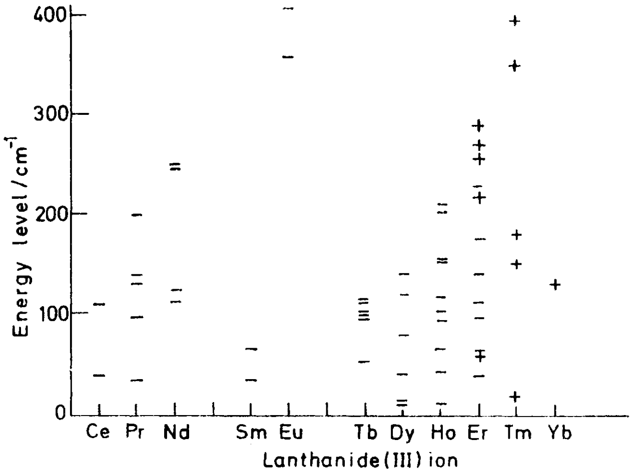

FIGURE 2 Crystal-field energy levels (ref. 14) of Ln^{III} ions. Data for the lighter lanthanides (—) relate to $LaCl_3 \cdot 6H_2O$ lattices, whereas those for the heavier lanthanides (+) relate to $YCl_3 \cdot 6H_2O$ lattices

energy $\Delta E^{\ddagger}$ in Table 4 is also found for Tm^{III}. This suggests that the temperature dependence of τ_s may be due to the changing occupation of the crystal-field levels with temperature and not to a change in hydration. The values of the activation energies for Er^{III} and Nd^{III} are next largest to that of Tm^{III} and their energy-level splitting is also somewhat greater than kT.

While studying the properties of lanthanide(III) ions as shift reagents we have noted anomalies associated with, in particular, thulium(III) and erbium(III) ions, see ref. 1. In a recent paper we observed that the internal motion of the dipicolinate ion, L, in $[Tm^{III}L_3]$, and to a lesser degree in the $[Er^{III}L_3]$ complex, was much slower than that in other $[Ln^{III}L_3]$ complexes.[1,3] In this paper we have observed a higher activation energy, $\Delta E^{\ddagger}$, of the relaxation rate of protons in the complexes of Tm^{III} and Eu^{III} in the series of $[Ln^{III}(OH_2)_n]$ ions. In turn this means that the relaxation enhancement of water protons by thulium(III) ions and, to a lesser degree, by erbium(III) ions, is too large at the lower temperatures relative to its susceptibility. We inferred that this was due to a large τ_s. It is likely that a common cause of these anomalies of Tm^{III} and Er^{III} lies in the ligand-field splitting energies of these ions in some complexes. We shall consider these problems in more detail in a future paper.

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