Inorganica Chimica Acta, *139* (1987) 147–149

Water Exchange Kinetics on Lanthanide(III) Ions: a Variable Temperature and Pressure ^{17}O NMR Study*

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Only two NMR studies of water exchange on trivalent lanthanide ions have been published [1, 2], one of which is merely an attempt to estimate the rate constants [1]. The reason is that the extreme lability of lanthanide(III) aqua ions excludes reliable measurements with low field NMR spectrometers. Reuben and Fiat [1] found lower limits varying from 2.6×10^7 s^{-1} for Tb^{3+} to 3×10^6 s^{-1} for Tm^{3+}. More recently, Southwood-Jones *et al.* [2] reported a value of 1.06×10^9 s^{-1} for Gd^{3+}. We report here a preliminary communication on the water exchange kinetics and mechanisms on the heavy lanthanide ions, studied by oxygen-17 NMR at various temperatures and pressures, on high magnetic field spectrometers.

Experimental

Lanthanide perchlorates were prepared by dissolving the appropriate oxide (Nucor) in $HClO_4$ (Merck). Resulting solutions at pH 2 were filtered and evaporated at ambient temperature under vacuum. The salts thus obtained were used to prepare solutions (typically 0.3 m in $Ln(ClO_4)_3$ and 2 m in $HClO_4$ to prevent hydrolysis) in ^{17}O enriched water (Yeda, 0.6 to 10%) (molality m: mole per kg of solvent). Solutions for variable temperature measurements were sealed in spherical glass cells and analysed from 258 to 380 K on Bruker CXP200 and WH360 spectrometers, with ^{17}O NMR frequencies of 27.1 and 48.8 MHz respectively. Variable pressure measurements were performed at 268 K from 0.1 to 250 MPa on a Bruker AM400 spectrometer at 54.3 MHz. The samples were pressurised using a homemade high pressure NMR probehead. Longitudinal relaxation rates were measured by the Inversion-Recovery method [3] and transverse relaxation rates by a modified Carr–Purcell method [4].

Results and Discussion

Swift and Connick [5] have expressed the chemical shift, $\Delta\omega$, and the transversal relaxation rate, T_2^{-1}, dependence of bulk solvent in a dilute paramagnetic system. Both parameters depend on the exchange rate constant k, equal to the inverse of the mean residence time of a solvent molecule bound to a metal ion (s and m correspond respectively to pure and bound solvent and P_m is the molar fraction of bound water):

$$T_2^{-1} - T_{2s}^{-1} = P_m k \frac{(k + T_{2m}^{-1})/T_{2m} + \Delta\omega_m^2}{(k + T_{2m}^{-1})^2 + \Delta\omega_m^2} \tag{1}$$

$$\Delta\omega = P_m \frac{\Delta\omega_m}{(k^{-1}T_{2m}^{-1} + 1)^2 + \Delta\omega_m^2/k^2} \tag{2}$$

Zimmermann and Brittin [6] expressed the longitudinal relaxation rate T_1^{-1} under analogous conditions:

$$T_1^{-1} - T_{1s}^{-1} = P_m \frac{1}{k^{-1} + T_{1m}} \tag{3}$$

For fast exchanging lanthanide systems, eqns. (1) to (3) can be greatly simplified [7], and it can be deduced that:

$$T_2^{-1} - T_1^{-1} = P_m\, \Delta\omega_m^2/k \tag{4}$$

$$\Delta\omega = P_m\, \Delta\omega_m \tag{5}$$

However, the molar fraction of bound water, P_m, depends on the coordination number (hereafter C.N.) of the metal ion. For lanthanide ions in water, it is strongly debated whether this number remains constant along the series or changes from a higher number for the early elements to a lower number for the later ones [8]. In order to clarify this point we carried out ^{17}O chemical shift measurements at various temperatures.

The variation of $\Delta\omega_m$ with T has been expressed for lanthanide solutions [9]:

$$\Delta\omega_m = \omega_0 \left[\left(\frac{2\pi g_1(g_1 - 1)J(J + 1)\mu_B}{3k_B\gamma_I T} A/h\right) + (B_2/T^2)\right] \tag{6}$$

As shown by this equation, $\Delta\omega$ as a function of $1/T$ is a quadratic curve. If a change occurs in C.N. as a function of temperature, P_m, A/h (the hyperfine coupling constant), and B_2 (a term depending on dipolar coupling between the ion and the ^{17}O nucleus) will change. This will induce a non-quadratic dependence of $\Delta\omega$ *versus* reciprocal temperature. Such behaviour has been observed by ^1H NMR in DMF solutions of Ce^{3+}, Pr^{3+} and Nd^{3+} [10].

^{17}O chemical shifts of solvent are reported in Fig. 1 for twelve aqueous lanthanide solutions. The

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*Paper presented by C.C. at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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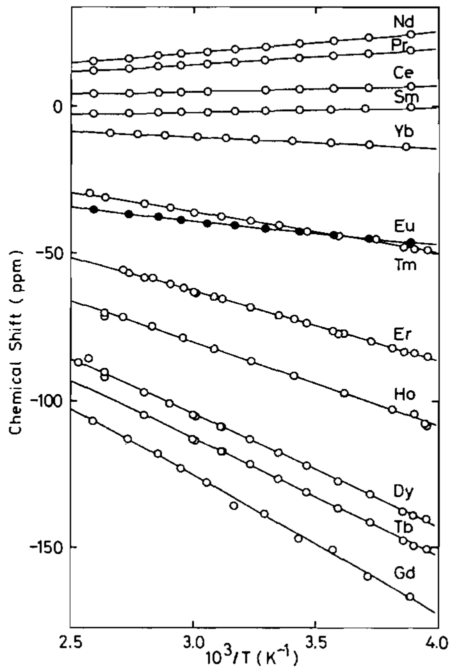

Fig. 1. ^{17}O chemical shift of water *vs.* reciprocal temperature at 4.7 T for twelve Ln^{3+} 0.3 m solutions.

absence of discontinuity in these curves suggests that the C.N. remains constant for any lanthanide aqua ion and along the whole series. Referring to Brücher *et al.* [11], who determined the hydration number in solutions of Lu^{3+}, the smallest lanthanide ion, we took a C.N. value of nine for our kinetic data treatment.

Transition state theory was used to describe the water exchange processes. In this model, the rate constant can be expressed as a function of temperature T and pressure P:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right) \qquad (7)$$

$$k = k_0 \exp\left(-\frac{\Delta V^{\ddagger}}{RT} P\right) \qquad (8)$$

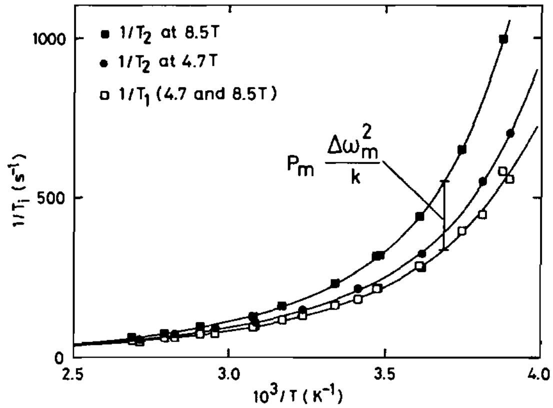

Fig. 2. An example of variable temperature relaxation results obtained in $Ho(ClO_4)_3$ 0.2994 m/$HClO_4$ 1.911 m solution. Kinetic contribution $T_2^{-1} - T_1^{-1}$ is shown.

Measurements of $\Delta\omega$, T_2^{-1} and T_1^{-1} were made at various temperatures and pressures. Differences $T_2^{-1} - T_1^{-1}$ were only significant in solutions of Tb^{3+} to Yb^{3+}, as exemplified in Fig. 2 for Ho^{3+}. Variable temperature data were treated by a multiset non-linear least-squares program, using eqns. (4) to (7). $\Delta\omega$ was shown to be independent of pressure. Relaxation data collected under pressure were treated by eqns. (4) and (8) using a constant value of $\Delta\omega_m$.

As seen in Table I, the calculated water exchange rate constants at ambient temperature are significantly larger than the estimations of Reuben and Fiat [1]. These values were evaluated from linewidth measurements made using a CW NMR spectrometer, connected to a 1.4 T magnet. Using high field magnets (4.7 to 9.3 T), enhanced kinetic contribution to the relaxation parameters can be observed. Moreover, the influence of field inhomogeneities in Ln^{3+} paramagnetic solutions were avoided by using Carr–Purcell pulse sequences on our FT spectrometers. Our kinetic results (Tb^{3+} to Yb^{3+}) complement the data of Southwood-Jones *et al.* [2] for Gd^{3+}. The rate constant decreases regularly along the series studied, following the trend in ionic radii, thus confirming the

TABLE I. Kinetic and NMR Parameters Calculated for Water Exchange on $[Ln(H_2O)_9]^{3+}$ [a]

Ln^{3+}	k^{298} (10^8 s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})	A/h (MHz)	B_2 (K^2)
Tb	4.96 ± 0.12[b]	12.08 ± 0.48	−37.9 ± 1.6	−5.7 ± 0.5	0.619 ± 0.020	11.6 ± 7.1
Dy	3.86 ± 0.09	16.57 ± 0.47	−25.0 ± 1.5	−6.0 ± 0.4	0.595 ± 0.012	21.3 ± 3.8
Ho	1.91 ± 0.03	16.36 ± 0.39	−31.5 ± 1.3	−6.6 ± 0.4	0.600 ± 0.015	5.5 ± 3.9
Er	1.18 ± 0.02	18.37 ± 0.34	−28.8 ± 1.1	−6.9 ± 0.4	0.663 ± 0.013	11.7 ± 2.2
Tm	0.81 ± 0.02	22.68 ± 0.58	−17.4 ± 1.9	−6.0 ± 0.8	0.642 ± 0.016	10.6 ± 1.5
Yb	0.41 ± 0.01	23.29 ± 0.94	−22.0 ± 3.3		0.782 ± 0.023	−0.3 ± 7.2

[a] Calculation with a C.N. of 8 increases k^{298}, A/h and B_2 by 9/8 and $\Delta S^{\ddagger}$ by 1 J K^{-1} mol^{-1}. [b] Errors given correspond to one standard deviation in the calculation procedure.

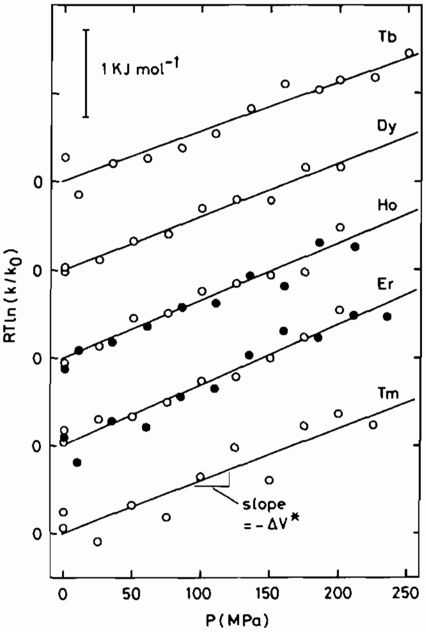

Fig. 3. Pressure dependence at 269 ± 0.5 K of water exchange rate constants on ions going from Tb^{3+} to Tm^{3+}. Ln^{3+} 0.2 m (●) and 0.3 m (○) solutions were measured at 9.3 T.

important electrostatic character of the water–metal bond.

The activation volume $\Delta V^{\ddagger}$ is known to be a good criterion for the assignment of a mechanism to solvent exchange reactions [12]. The volumes we found by variable pressure measurements on five lanthanide aqua ions are all negative and identical within experimental errors, as shown in Fig. 3. We thus conclude a similar concerted associative (I_a) mechanism for these five ions. It should be mentioned that this assignment does not depend on the C.N. of the Ln^{3+} ions. For DMF exchange, Pisaniello *et al.* [10] found a gradual I_d to D mechanistic changeover for the same ions we studied kinetically in water. This surprising difference for both solvents can be explained by steric factors: DMF is a rather large molecule compared to water and its exchange occurs preferably via a dissociative activation process.

Conclusions

Oxygen-17 NMR with high field superconductor magnets is a suitable method to determine the water exchange rates on heavy lanthanide ions. A chemical shift study on twelve lanthanide ions indicates a constant coordination number in water solutions along the whole series. Water exchange rates (5 X 10^8 s^{-1} for Tb^{3+} to 4 X 10^7 s^{-1} for Yb^{3+}) are more than one order of magnitude larger than the previous estimations by Reuben and Fiat [1]. A variable pressure study leads to the assignment of an I_a exchange mechanism on five heavy lanthanide ions.

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