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^{2}H and ^{139}La NMR Spectroscopy in Aqueous Solutions at Geochemical Pressures

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Abstract: *Nuclear spin relaxation rates of ^2H and ^{139}La in $LaCl_3 + {}^2H_2O$ and $La(ClO_4)_3 + {}^2H_2O$ solutions were determined as a function of pressure in order to demonstrate a new NMR probe designed for solution spectroscopy at geochemical pressures. The ^2H longitudinal relaxation rates (T_1) vary linearly to 1.6 GPa, consistent with previous work at lower pressures. The ^{139}La T_1 values vary both with solution chemistry and pressure, but converge with pressure, suggesting that the combined effects of increased viscosity and enhanced rates of ligand exchange control relaxation. This simple NMR probe design allows experiments on aqueous solutions to pressures corresponding roughly to those at the base of the Earth's continental crust.*

Geochemists invest much energy in models of aqueous solutions at elevated temperatures and pressures. A common model was recently extended to 1200 °C and 6.0 GPa[1] and predictions are now possible over such an extraordinary range of temperatures and pressures that experimental verification is difficult. This fact led us to design a simple NMR probe that allows experiments on solutions to 2.0 GPa.[2] Although there is a long history of high-pressure NMR in solution chemistry,[3] the pressures are usually limited to 0.5 GPa or less, with a few pioneering exceptions.[4]

Here we show that the design can reproduce previous results at lower pressures (< 0.5 GPa) and we extend them to nearly 2.0 GPa. We choose $LaCl_3$ and $La(ClO_4)_3$ electrolytes in ^2H_2O because the Jonas group[5] previously measured ^{2}H T_1 values on similar solutions, as well as viscosities, up to 0.5 GPa. Furthermore, these 1:3 electrolytes have a considerable freezing-point depression, which allows us to achieve gigapascal pressures at ambient temperatures.

We observe T_1 values for ^{2}H in $LaCl_3 + {}^2H_2O$ solutions to decrease nearly linearly with pressures up to 1.6 GPa (Figure 1). Results for 4.5 M $LaCl_3$ solutions are shown in Figure 1 a and a full set of ^{2}H T_1 measurements as a function of solution composition is shown in Figure 1 b. The data overlay those of Lee et al.[5] at P smaller than 0.5 GPa and exhibit the same variation with pressure. In most experiments, ^{2}H T_1 values initially rise, as was observed in previous work. The rise is attributed to electrolyte-induced solvent structuring[6,17] and values reach a maximum value at approximately 0.1–0.2 GPa.[3d,e,7] In the solutions with varying electrolyte concentrations, the T_1 values decrease as pressures increase above 0.2 GPa (Figure 1 b) undoubtedly reflecting increases in the solution viscosities, as was originally interpreted by Lee

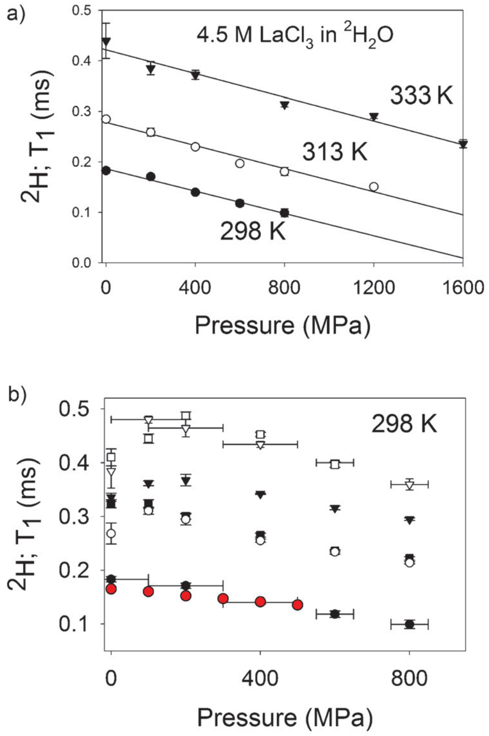

Figure 1. a) T_1 values from ^{2}H NMR spectra as a function of pressure of 4.5 M $LaCl_3 + {}^2H_2O$ solutions. The lines are linear regressions. The T_1 values as a function of solution composition at 298 K are shown in (b). The solid circles (●) are 4.5 M $LaCl_3$ and the red symbols (●) identify data of Lee et al. (1974).[5] The $LaCl_3 + {}^2H_2O$ solutions are: ○ = 1.0 M, ▼ = 0.5 M, ▽ = 0.1 M, and the $La(ClO_4)_3 + {}^2H_2O$ solutions are: ■ = 1.0 M and □ = 0.1 M. Uncertainties in pressure are ±100 MPa at 400 MPa or less and 50 MPa at pressures higher than 400 MPa. They are shown only for the 0.1 M and 4.5 M $LaCl_3$ data to avoid clutter and are assigned as the 95 % prediction interval from repeated external calibrations (see the Supporting Information).

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et al.,[5] albeit over a smaller pressure range. Save possibly for the 4.5 M $LaCl_3$ solutions, only a fraction of the ^2H were held in solvation spheres of La^{III}.

The T_1 values for ^{139}La, however, differ considerably with concentration under ambient conditions and the values also vary much more with pressure than T_1 values for ^2H in these same solutions (Figure 2). The differences in ^{139}La T_1 values diminish with pressure until the values for all solutions converge to near 0.25 ms near $P \gtrsim 1.2$ GPa, which also is close to the T_1 values observed for the most concentrated solutions (Figure 2). As expected, acidification had little effect on the measured ^{139}La T_1 values, indicating that the results are not strongly influenced by the hydrolysis of La^{III} ($pK_1 = 8.5$[8]). The ^{139}La T_1 value for an acidic solution of 1.0 M $LaCl_3$ at pD = 2.6, is 1.02 ± 0.03 ms virtually identical to the unacidified sample (pD = 5.45; $T_1 = 1.04 \pm 0.03$ ms).

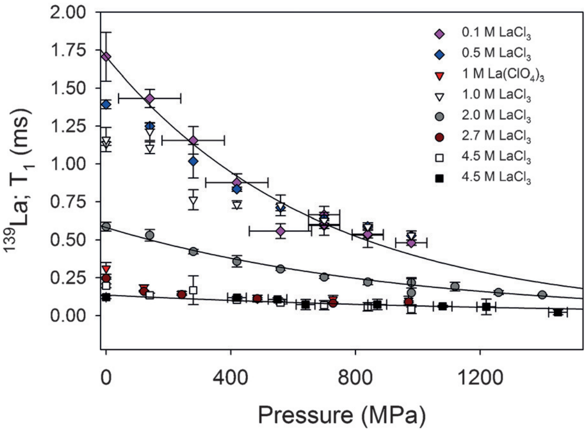

Figure 2. Rates of longitudinal relaxation (T_1) for ^{139}La at 298 K in $LaCl_3 + {}^2H_2O$ and $La(ClO_4)_3 + {}^2H_2O$ solutions. Uncertainties in T_1 correspond to the estimated standard deviation of five replicate measurements. Uncertainties in pressure are usually ±100 MPa at 400 MPa or less and 50 MPa at pressures higher than 400 MPa; they are shown only for the 0.1 M $LaCl_3$ data to avoid clutter. An exception is the 2.7 M $LaCl_3$ experiment where pressure was measured in situ and are assigned from the uncertainty in the spectral measurement (±30 MPa). See the Supporting Information for discussion of pressure uncertainties. Lines are exponential fits to three of the solution values.

There are two important terms affecting these relaxation rates. For most aqueous solutions in a high magnetic field, the time scale of tumbling of small molecules is shorter than the inverse Larmor frequency, which causes the longitudinal and transverse relaxation rates to be equal: $1/T_1 = 1/T_2$. In this "extreme-narrowing" limit the relaxation rate for quadrupolar nuclei in solution, such as ^{139}La ($I = 5/2$) and ^2H ($I = 1$) is given by Equation (1),[9]

$$\frac{1}{T_{2Q}} = \frac{1}{T_{1Q}} = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \langle \chi^2 \rangle \tau_c \qquad (1)$$

where I is the spin of the nucleus in question, τ_c is the correlation or reorientation time because of molecular tumbling, and $\langle \chi^2 \rangle$ is the mean square of the zero-average, fluctuating quadrupolar coupling constant. Values of the quadrupolar coupling constants are known for ^2H and ^{139}La nuclei. In $LaCl_3 + {}^2H_2O$ solution at 20 °C, $\langle \chi \rangle_{rms} = 237.7 \pm 10$ kHz[10] and $\langle \chi \rangle_{rms} = 3.1$–$3.4$ MHz[10e,11] values for ^2H and ^{139}La have been calculated from experimental data and Equation (1). Lang, Ludemann, and co-workers[3f] report $\langle \chi \rangle_{rms} = 230$ MHz for ^2H up to 0.9 GPa and noted that it increases to $\langle \chi \rangle_{rms} = 264$ MHz in 11 M LiCl solutions. The quadrupolar coupling constant $\langle \chi \rangle_{rms}$ for ^{139}La in $La(ClO_4)_3$ solutions is identical to that in $LaCl_3$ solutions at ambient pressures.[11]

The correlation time, τ_c, is strongly affected by solution viscosity, which modulates the rates of random diffusive movements and varies considerably with pressure. The link between viscosities and correlation times is usually treated using a version of the Stokes–Einstein Equation (2),[5]

$$\tau_c = \frac{\eta \kappa V_m}{kT} \qquad (2)$$

where V_m is the hydrodynamic volume and η is the macroscopic viscosity. This approach ignores details of the nuclear spin relaxation pathways but is appropriate for the experiments described here. The parameter κ describes coupling of translation and rotation during relaxation[13] and is usually set to unity so that V_m can be treated as the effective hydrodynamic volume for the ^2H_2O molecule, or the solvated La^{III} complex. Since viscosity increases with pressure, the time scale of molecular tumbling changes with pressure and causes the value of τ_c to increase.

For most solutions in this study, the relaxation time of ^2H reflects only nuclei in bulk solution and not solvation spheres. For solutions containing structure-making cations such as La^{3+}(aq), the rotation of ^2H_2O molecules that are tightly bound in solvation spheres has only a small effect on the local structure of the liquid.[14] Chloride ions have been shown to have little effect on the effective volume of the ^2H_2O molecule.[15] Changes in viscosity with pressure exert the dominant controls on relaxation. The T_1 values for ^2H in various $LaCl_3$ solutions vary by roughly a factor of 2–3 as a function of electrolyte concentration (Figure 1 b) and this range can bind the effects of viscosity changes alone over our pressure range.

However, for ^{139}La relaxation, T_1 relaxation rates are affected by viscosity but also from quadrupolar interactions of a small set of La^{III} complexes: La^{3+}(aq), $LaCl^{2+}$(aq), and $LaCl_2^+$(aq). The ^{139}La T_1 values, in contrast to those of ^2H, vary more with solution composition and pressure (Figure 2), suggesting that viscosity changes alone do not fully account for the variation in ^{139}La T_1 values. The effects of concentration on ^{139}La relaxation clearly diminish with increased pressure. Furthermore, if the correlation times of the two nuclei, ^{139}La and ^2H, are controlled only by a single bulk variable, such as solution viscosity, the ratio of T_1 values for ^2H and ^{139}La should be constant and independent of pressure. A plot of the ratio of these values for the 2.7 M $LaCl_3$ solution (see Figure S4 in the Supporting Information) is constant to within 10 % at $P > 0.6$ GPa indicating that the ^{139}La NMR relaxation is well correlated with ^2H relaxation at higher pressures. Clearly viscosity is a dominating variable and becomes increasingly important at higher pressures.

The trend toward convergence of ^{139}La T_1 values beyond $P \gtrsim 1.2$ GPa indicates that the product $(\chi^2 \cdot \tau_c)$ becomes progressively insensitive to solution composition at elevated pressures. Any process that changes the electric field gradient at the ^{139}La nucleus, and these include ion pairing or rapid ligand exchanges, could affect relaxation through the quadrupolar coupling constant. At the time when the Lee et al. paper[5] was published (1974), there was no firm evidence for complexation of La^{3+} and Cl^- although the authors clearly knew of this possibility. There have since been careful NMR,[10e,16] X-ray,[17] vibrational,[18] and other spectroscopic[19] studies of the reactions given in Equations (3) and (4)

$$La^{3+}(aq) + Cl^-(aq) \leftrightarrow LaCl^{2+}(aq) \tag{3}$$

$$La^{3+}(aq) + 2\,Cl^-(aq) \leftrightarrow LaCl_2{}^+(aq) \tag{4}$$

and these are supported by theoretical studies.[20] Equilibrium constants (K_1; K_2) for reactions (3) and (4) have been tabulated[21] and Migsidov, Williams, and Wagner[22] organized the observations into parameters for the Helgeson–Kirkham–Flowers (HKF) model, allowing predictions to elevated temperatures and pressures.

Values of K_1 and K_2 are shown as a function of pressure in Figure 3. The equilibrium constants are small, consistent with weak outer-sphere ion-pairing reaction, and diminish further with increased pressure. The trend is consistent with the favoring of more highly solvated ions with pressure because solvent water molecules can be packed into a smaller volume. There are reports of ion pairing for $La(ClO_4)_3$ solutions[18] but these constants have not been parameterized for elevated pressures. Ion pairing would be weaker and yet would undoubtedly trend the same as the chloride data.

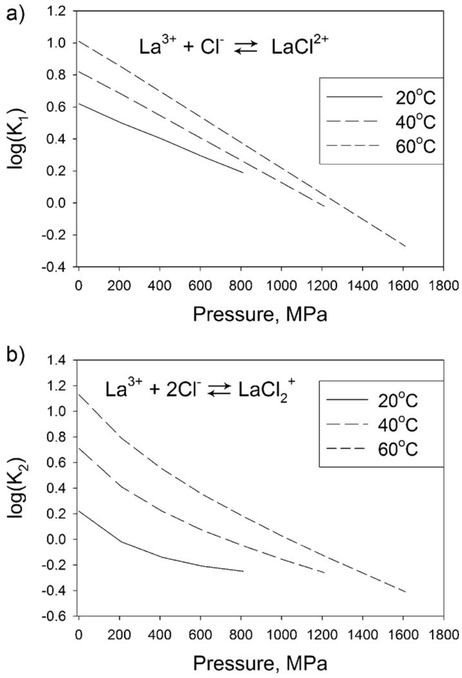

Figure 3. Estimated equilibrium constants for a) reaction (3) and b) reaction (4).[22]

However, a large fraction of the La^{III} is present as $LaCl^{2+}$ and $LaCl_2{}^+$ at all pressures. A quick calculation illustrates the magnitude–the equilibrium constants for Equations (3) and (4) are $K_1 = 10^{0.19}$ and $K_2 = 10^{-0.25}$, at pressures of 0.80 GPa. At this pressure, 77% of La^{III} is present as $La^{3+}(aq)$ with the remainder as $LaCl^{2+}(aq)$ and $LaCl_2{}^+(aq)$. The estimates are crude but show ion pairing even at the highest pressures. (For the calculations we use the extended Debye–Hückel equation for activity corrections in our least concentrated solution, 0.1 M $LaCl_3$, with $A = 0.5042$, $\mathring{a} = 5.0$ Å for La^{III} ions, $\mathring{a} = 3.0$ Å for Cl^-, $B = 0.3288$ $(kg\,mol^{-1})^{-0.5}$ Å and $\dot{B} = 0.0410$ $km\,mol^{-1}$. Choice of another model for activity corrections makes no essential difference.) The key result is that interconversion of La^{3+}, $LaCl^{2+}$, and $LaCl_2{}^+$ is not negligible even at high pressures.

Our observation that ^{139}La T_1 values converge at $P \gtrsim 1.2$ GPa indicates that the electric field gradients at the ^{139}La nuclei are becoming uniform even in the presence of large speciation differences. Viscosity effects are clearly dominating, but such a case would arise if all La^{III} species interconvert by rapid rates of ligand substitution at very high pressures. If such rapid rates were occuring, the exchanging ligands must be dominated by solvation waters because we observe limited influence of changes in anion concentrations. Rates of solvent exchange for La^{3+} fall into the range of $10^{8.5}$–$10^9\ s^{-1}$,[23] which is near the Smoluchowski limit of diffusion-controlled reactions and cannot reach the 10^{-12} s timescales of nuclear reorientation. More likely is that rapid ligand substitutions diminish the electric field gradients, and thus χ, at high pressures.

The major goal of this work was to show that a simple new NMR probe design can be used for solute spectroscopy at geochemical pressures. Uncertainties in pressure can also be reduced to a few tens of megapascals when the ruby is included in the cell, as is illustrated in the table-of-contents picture, because this geometry reduces the error in pressure to the precision of the fluorescence wavelength measurement, rather than the statistics associated with use of an external calibration scale.

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