NMR spectroscopy of some electrolyte solutions to 1.9 GPa

Gerardo Ochoa [a], Christopher A. Colla [b], Peter Klavins [c], Matthew P. Augustine [a,*],
William H. Casey [a,b,*]

[a] *Department of Chemistry, University of California, Davis, 1 Shields Ave, Davis, CA 95616, USA*
[b] *Department of Earth and Planetary Sciences, University of California, Davis, 1 Shields Ave, Davis, CA 95616, USA*
[c] *Department of Physics, University of California, Davis, 1 Shields Ave, Davis, CA 95616, USA*

Abstract

Nuclear-magnetic resonance (NMR) spectra of CsCl and LaCl$_3$ in D$_2$O/H$_2$O solutions were collected up to pressures of 1.9 GPa using a new NMR probe design that considerably extends the pressure range available for geochemical experiments. The longitudinal-relaxation times (T_1) for ^{2}H compare well with those reported in the previous studies of Lee et al. (1974), who examined lower pressures, and indicate that the probe functions properly. In some experiments, ^{133}Cs and ^{1}H NMR spectra could be taken on solutions to pressures well beyond the nominal freezing pressure of D$_2$O or H$_2$O to form Ice VI (near 0.9 GPa). Freezing to form the high-pressure ice is kinetically slow on an experimental time scale (minutes to hours). The data indicate that the electrolyte concentrations increase the freezing pressure of the solution. This result means that solution NMR spectra can be collected at pressures that are nearly twice the nominal freezing pressure of pure D$_2$O or H$_2$O. Pulsed-magnetic-field-gradient NMR methods are used to independently measure the self-diffusion coefficient of H$_2$O in these solutions, which yields estimates of solution viscosity via the Stokes–Einstein relation. The increased viscosity accounts for the pressure variation of T_1 values as rates of molecular tumbling are affected. Accounting for such changes is essential if NMR spectral line widths are used to infer pressure-enhanced rates of geochemical reactions, such as interconversion of aqueous complexes.
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1. INTRODUCTION

A common geochemical model of electrolyte solutions, the Helgeson-Kirkham-Flowers (HKF) model, describes the partial molar properties of solutes using an expression containing the dielectric constant of water and solute-specific variables derived from fits to experimental data. When this model is coupled to thermodynamic data for minerals, it can be used to estimate solubilities and speciation information at high pressures and temperatures (Shock and Helgeson, 1988; Tanger and Helgeson, 1988; Shock et al., 1989; Anderson and Crerar, 1993; Shock and Koretsky, 1995; Sverjensky et al., 1997, 2014; Schulte et al., 2001). Recently the HKF model was extended to 6.0 GPa and 1200 °C via molecular-dynamic estimates of the dielectric constant of water (Pan et al., 2013; Sverjensky et al., 2014). These new pressure and temperature limits inspired the design of a nuclear magnetic resonance (NMR) probe for examining solute speciation at higher pressures (Pautler et al., 2014; Ochoa et al., 2015).

There is a rich literature on high-pressure NMR spectroscopy, but this earlier work is generally limited to pressures less than 0.5 GPa (see Ballard et al., 1996), with heroic exceptions (Jonas, 1980; Lang and Lüdemann,

1993; de Langen and Prins, 1995; Ballard et al., 1998). These earlier designs generally employed milliliter-sized samples. In contrast, the design described in the present paper has a 10–15 microliter sample volume (Fig. 1) and can reach pressures of 2.0 GPa. The early work was directed at detailing solvent motions and relaxation mechanisms (Lee and Jonas, 1971; Lee et al., 1974; Akai and Jonas, 1976; Jonas et al., 1976; Defries and Jonas, 1977; Jonas, 1980; Lamb et al., 1981; Lamb and Jonas, 1981; Lang and Lüdemann, 1993; Ballard et al., 1998). High-pressure NMR was then extended to estimate the activation volumes of homoleptic reactions (Merbach and Vanni, 1977; Asano and Noble, 1978; Ducommun et al., 1979a,b, 1980; Monnerat et al., 1981; Swaddle and Merbach, 1981; Meyer et al., 1982; Hugi-Cleary et al., 1985, 1987; Cossy et al., 1987; Minirale, 1989; Pittet et al., 1990; Takagi et al., 1994; Drljaca et al., 1998a; Swaddle et al., 2005; Dees et al., 2007) with an intent of assigning mechanisms to ligand-exchange reactions (Helm and Merbach, 2005). The work has been reviewed several times (Asano and Noble, 1978; Eldik et al., 1989; Drljaca et al., 1998b). Diamond-anvil technologies, of course, can reach much higher pressures but are limited to nanoliter sample volumes or less, which are too small for studying solutes in water (e.g., Meier et al., 2015).

In this paper, the NMR spectroscopy of a fully dissociated electrolyte (CsCl, LaCl$_3$) is studied in order to reproduce the earlier work of Lee et al. (1974) and to demonstrate the utility of the new probe design. Time constants for the longitudinal relaxation (T_1) of ^{2}H were measured on aqueous CsCl in D$_2$O and compare well with the original work. In addition, values of T_1 were determined for ^{133}Cs and ^{2}H NMR in the solutions and were compared to previous work on LaCl$_3$ (Lee and Jonas, 1971; Lee et al., 1974; Ochoa et al., 2015). The CsCl and LaCl$_3$ solutions were chosen because Jonas' group not only measured the T_1 values for these solutions, but also measured viscosities via the rolling-ball method at high pressures. Knowing the viscosity of an experimental solution is important because this controls rates of molecular tumbling and thus affects the widths of NMR spectral peaks.

2. EXPERIMENTAL METHODS

All cesium chloride (CsCl) solutions were prepared by dissolving the anhydrous salt into deuterium oxide solvent (D$_2$O). Lanthanum chloride (LaCl$_3$) solutions were made similarly but in H$_2$O with a resistance of 18 MΩ. Solution compositions were verified by coulometric titration for the chloride ion. All pD and pH measurements were made with a combination electrode and calibrated using standard buffers in H$_2$O. The pD values were calculated using: pD = pH + 0.4 (Kręzel and Bal, 2004).

The design of the high-pressure NMR probe is described in earlier papers (Pautler et al., 2014; Ochoa et al., 2015) and only the highlights are mentioned here. This high-pressure NMR probe is distinct from previous designs (e.g., Ballard et al., 1996, 1998) because it employs a small solenoid coil made of Berylco-25 wire wrapped around cylindrical capsule of PEEK© (Polyether ether ketone) tubing containing 10–15 μL experimental solution. The cylindrical capsule is sealed at each end (Fig. 1.A) with waterproof epoxy. The solenoid is fabricated from 28 gauge beryllium-copper wire and fed through small holes in the assembly where it is sealed with Stycast© epoxy mixed with a small amount of Al$_2$O$_3$ powder (Fig. 1.B). A ruby attached to a 200 μm fiber-optic cable is also passed through the feedthrough, just below the RF coil, and sealed. Pressure was monitored in situ using ruby fluorescence where movement of the R1 peak with pressure (Piermarini et al., 1975; Mao et al., 1986) could be monitored using an Ocean Optics HR4000 UV–vis spectrometer. To ensure that the lowest-pressure measurements were accurate, we confirmed the ruby-fluorescence calibration via a four-wire resistance measurement on manganin wire (Supplemental Information). The correlation is nearly exact (Supplemental Information) but we use the fluorescence estimates of pressure throughout this paper because they can be made in situ.

The ^{133}Cs and ^{2}H NMR data were acquired using a 300 MHz (7.0 T) Oxford Instruments 78-mm-bore superconducting magnet interfaced to a spectrometer controlled by Tecmag Orion® software. The ^{2}H T_1 measurements were acquired using a standard inversion-recovery pulse sequence with a calibrated π/2 time of 15.8 μs and a relaxation delay of 3 s (applied peak-to-peak radiofrequency voltage of 130 V with a circuit Q ∼ 11). The ^{133}Cs T_1 measurements were acquired using a saturation-recovery pulse sequence with a calibrated π/2 of 9 μs and a relaxation delay of 100 ms. The probe includes a cooling jacket through which water was circulated at 25(±2) °C from an external water bath. The two degree range corresponded to a diurnal variation. Temperature in the probe was checked with a Type T thermocouple. The experimental range in temperature during an experiment was much smaller at 25 °C (±0.5 °C).
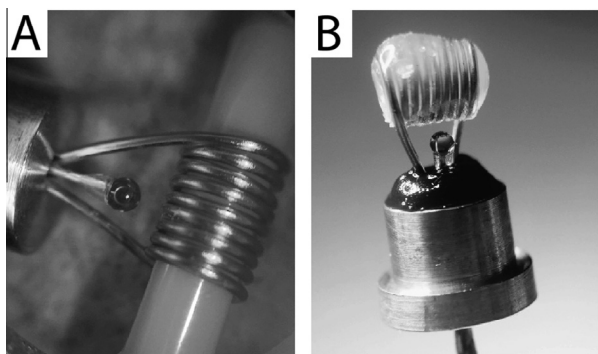

Fig. 1. The microcoil geometry, showing the 1-mm-diameter ruby sphere that is attached to a fiberoptic cable for pressure measurements and calibration. (A): Solenoid and ruby before a solution sample has been placed in the 10–15 μL PEEK© tubing container, and before trimming, with no Stycast© added to seal the beryllium-copper feedthrough. The coil length is 3.4 mm and the coil diameter is 2.7 mm. (B): The solenoid ready for an experiment. The sample is sealed into the tubing and the assembly is sealed with Stycast© mixed with Al$_2$O$_3$ powder.