

SUPPORTING INFORMATION

Unusual linear dependency of viscosity with temperature in ionic liquid/water mixtures#

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Temperature dependent variation of ^1H NMR spectra of C2 proton	SI-1
Experimental section	SI-2

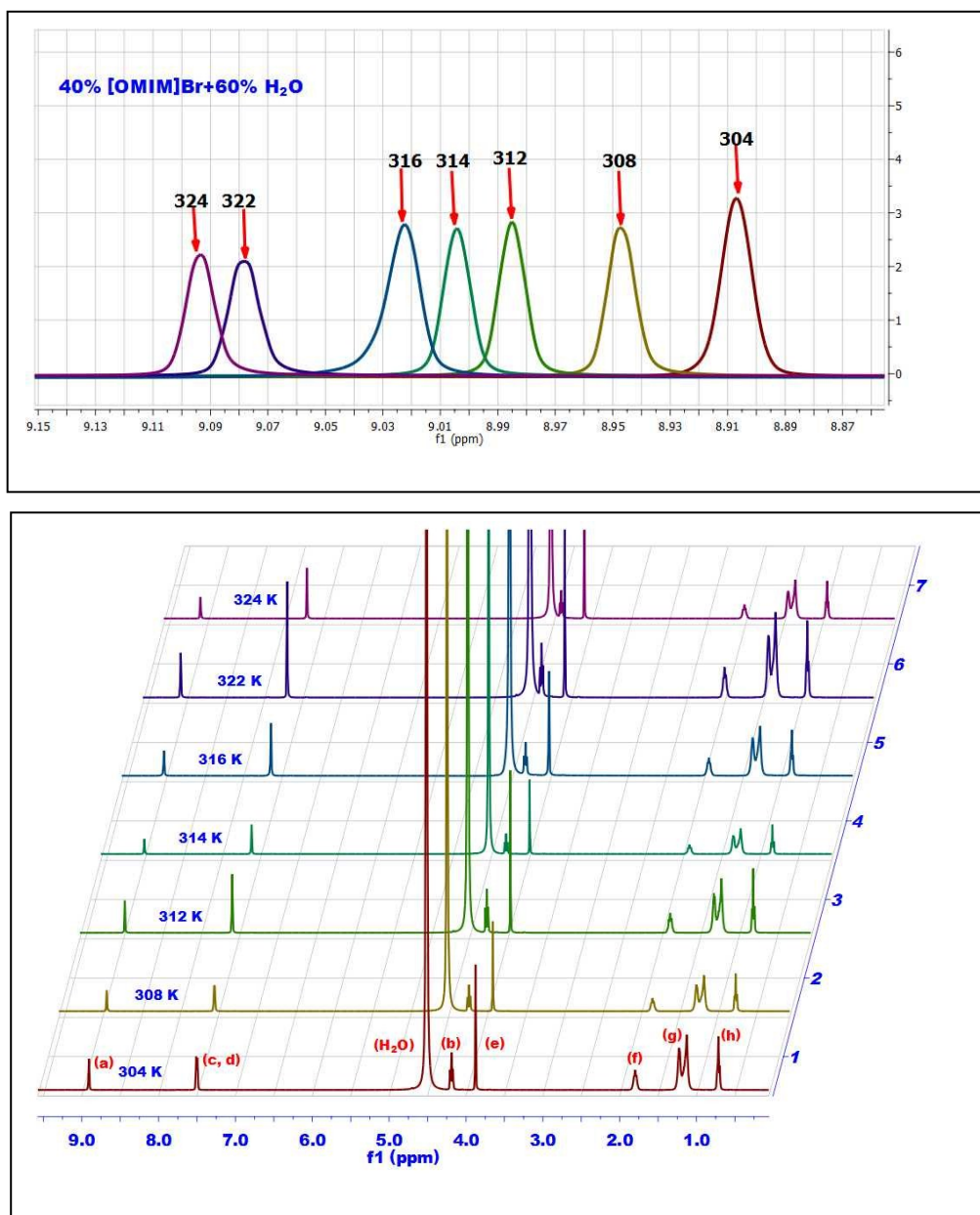


Figure 1. Temperature dependent variation of ^1H NMR spectra of C2 proton (top) and its corresponding full spectrum (bottom) has been presented in its 40% (w/w) of [OMIM]Br in water.

Experimental Section

Materials: 1-bromooctane (purity, > 99%) and 1-Methylimidazole (purity, > 99%) were obtained from Sigma Aldrich and used after distillation. LiClO₄ (purity, > 99.99%) was obtained from Fluka Analytical and before its use it was dried for around 48 h at 130 °C to remove any absorbed moisture. Deuterium oxide, D₂O has been used as the internal standard in all the NMR experiments and was obtained from the Sigma Aldrich with 99.9 atom % D.

Synthesis of Ionic Liquids: 1-Octyl-3-methylimidazolium bromide ([OMIM]Br) was synthesized according to the reported procedure.^[1-4] After its synthesis, it were dried under high vacuum for 8-10 h with a constant heating of 70 °C. The ¹H NMR spectra of this ionic liquid show good agreement with that reported in the literature.^[1-4] The aqueous salt solutions of LiClO₄ were prepared in deionized water (specific conductance < 0.55 × 10⁻⁶ S cm⁻¹) with an accuracy of ± 0.0002 mol kg⁻¹ and all the ternary mixtures were prepared by adding the ionic liquids (w/w) into the aqueous Li⁺ salt solutions (w/w).

Viscosity Measurements: A Brookfield-ultra rheometer with a cone plate arrangement has been used for the measurement of viscosity of all the ionic liquid solutions. The samples required in each measurement are 0.5 ml. All the temperature dependent viscosity measurements have been carried out with an accuracy of ±0.1%. A Julabo temperature thermostat bath has been used to control the temperature of the experimental set up. The viscosity (η) values of the solutions were obtained through the equation as:

$$\eta = (100/RPM) (TK) (\text{Torque}) (SMC) \quad (2)$$

where RPM , TK (0.09373) and SMC (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated by taking the reported viscosity data of aqueous solutions of $CaCl_2$, $MgCl_2$ and $[BMIM][BF_4]$ in different concentration.^[5, 6] The accuracy of the instrument was obtained as $\pm 1\%$. The reported experimental viscosity data are the average of triplicate measurements with a precision of 0.25%.

NMR Measurements: All the NMR experiments were performed on a Bruker-AV400 spectrometer with a 9.4 T superconducting magnet (Larmor frequencies $\nu_0 = 400$ MHz).^[7] The sample are placed in a 5 mm (outside diameter) NMR tube in their neat condition and D_2O in a capillary tube was used as external lock. The temperature dependent NMR measurements have been taken with an accuracy of $\pm 0.1\%$. The temperature of the experiment was controlled by a Bruker BVT-3200 temperature controller unit. The samples were thermally equilibrated for 30 min before the start of each experiment. Self-diffusion coefficient of ionic liquids and H_2O molecules were measured by using a standard Bruker pulse field gradient spin echo (PFGSE) experiment with longitudinal eddy current delay.^[8] All the spectral data has been acquired with 50 ms diffusion delay time (Δ) and 3.5 ms bipolar gradient pulse time (δ) by varying the gradient strength (g). The values of self-diffusion coefficients has been calculated from the experimental data using an online Bruker T_1/T_2 utility program by fitting the signal intensity (area) to the following equation.^[9]

$$I = I_0 \exp [-\gamma^2 g^2 \delta^2 D (\Delta - \delta/3)] \quad (1)$$

where I and I_0 are the measured and equilibrium signal intensity, respectively. δ is the duration of the magnetic field gradient g , γ is the gyromagnetic ratio of the nuclei (1H), Δ is the diffusion time and D is the self-diffusion coefficient. The measured self-diffusion coefficients are fitted

well with the equation 1 suggesting that the diffusion are of free in nature. A sample plot of the signal intensity with the gradient strength for the 40% (w/w) composition of [OMIM]Br in water is given in the figure 2.

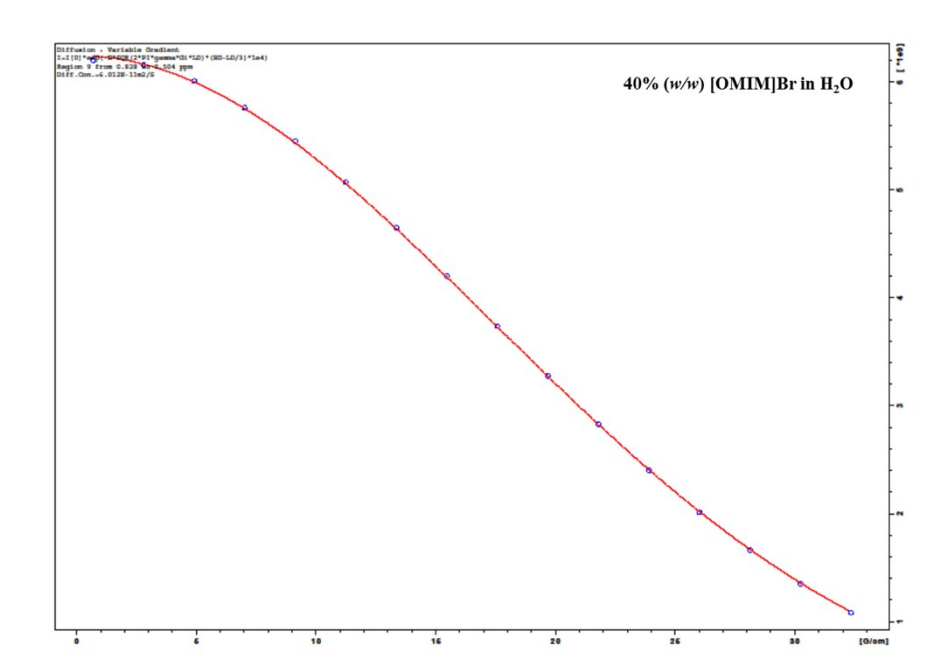


Figure 2. A sample plot showing the signal intensity with the gradient strength for the C2-proton in its 40% (w/w) composition of [OMIM]Br in H₂O at 300 K.

References

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