

Electronic Supplementary Information (ESI)

Molecular Dynamics involving Proton Exchange of a Protic
Ionic Liquid-Water Mixture studied by NMR Spectroscopy

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Lineshape analysis for the NH peak at different temperatures shows the same behaviour as the OH peak, Figure S1. The NH peak is wider than the OH peak at all temperatures due to the proton coupling to ^{14}N .

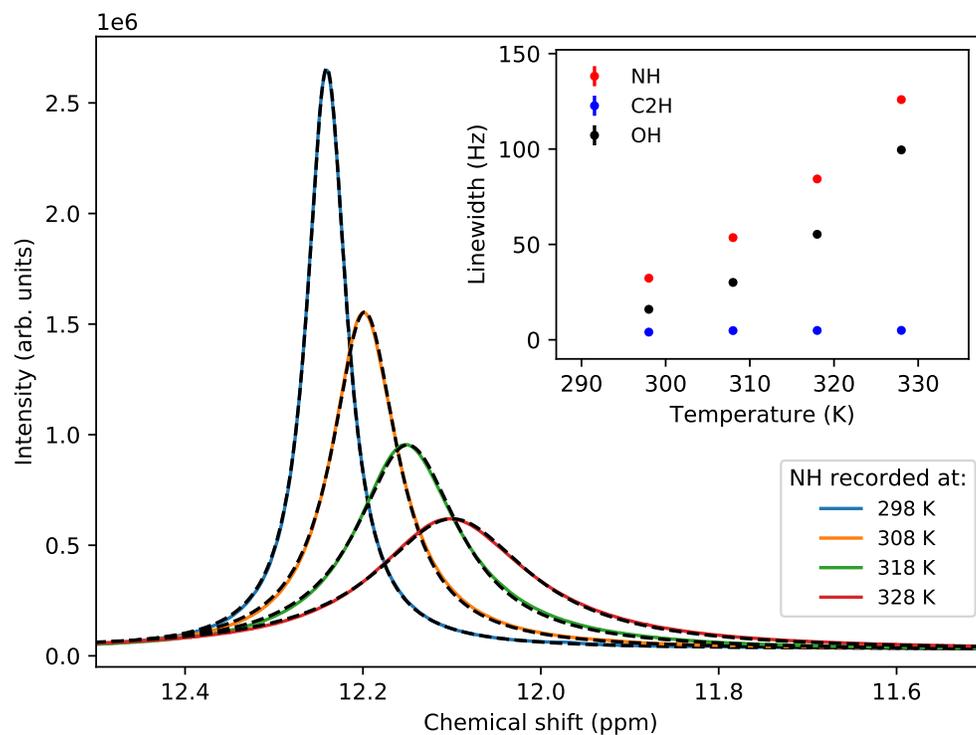


Figure S1: The effect of temperature on the proton exchange rate as reflected in the NH peak linewidth. The inset is a plot of linewidths versus temperature for the two exchanging signals (NH and OH) and one non-exchanging (C²H).

An example of a 2D-EXSY spectrum is shown in Figure S2. The cross peaks between NH and OH signals are due to cross relaxation caused by nuclear Overhauser effect (NOE) and/or chemical exchange. Based on the experimental parameters chosen for the NMR experiment, most importantly the mixing time, the NOE is sometimes not detected. No cross peaks are observed in our EXSY spectra, such as the one shown below, indicating that NOE cannot be detected here. The presence of cross peaks between NH and OH is, therefore, attributed solely to relaxation due to chemical exchange since intermolecular NOE is even weaker than intramolecular.

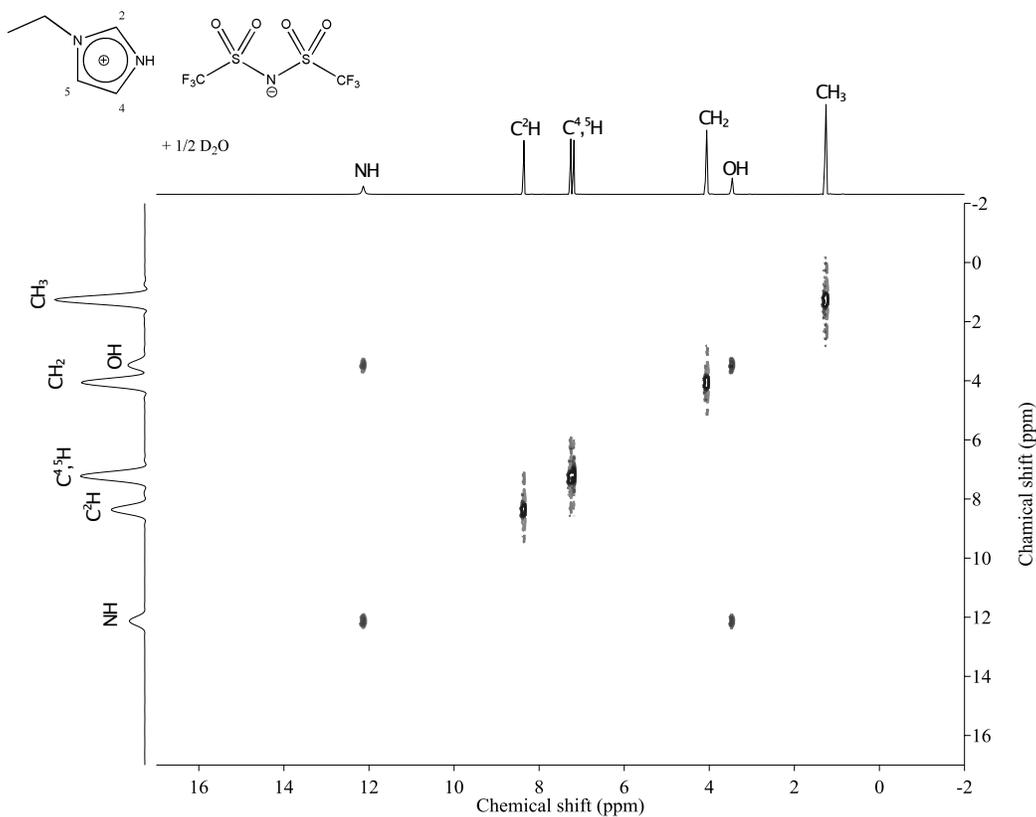


Figure S2: 2D-EXSY spectrum of C₂HimNTf₂-water mixture with a mixing time, τ_m , of 50 ms in Topspin's standard NOESYHPR pulse sequence.

Solution to Kärger differential equations (S1) for a two cite exchange such as in this case is presented in the literature² with a rather confusing notation. The solutions are provided below, equation (S2), with slight changes in notation. The results of simulation based on equation S2 are shown in figure S3. The model seems to be more successful in producing initial slopes. We suspect the reason might be that the residence time of the proton (as measured with lineshape analysis and EXSY, ~ 50 ms) is not exactly in the middle of the time scale range probed with PFG experiments (25, 50, 100, 200, 500, 1000 ms).

$$\frac{dM_i}{dt} = -(\gamma\delta g)^2 D_i M_i - k_i M_i + k_j M_j \quad (\text{S1})$$

$$\frac{dM_j}{dt} = -(\gamma\delta g)^2 D_j M_j + k_i M_i - k_j M_j$$

$$M_i = \left[\frac{M_{i,0}}{2} - \left(\frac{\omega M_{i,0} - k_j M_{j,0}}{2\Omega} \right) \right] \exp[-(v - \Omega)t] \\ + \left[\frac{M_{i,0}}{2} + \left(\frac{\omega M_{i,0} - k_j M_{j,0}}{2\Omega} \right) \right] \exp[-(v + \Omega)t] \quad (\text{S2})$$

$$M_j = \left[\frac{M_{j,0}}{2} + \left(\frac{\omega M_{j,0} + k_i M_{i,0}}{2\Omega} \right) \right] \exp[-(v - \Omega)t] \\ + \left[\frac{M_{j,0}}{2} - \left(\frac{\omega M_{j,0} + k_i M_{i,0}}{2\Omega} \right) \right] \exp[-(v + \Omega)t]$$

$$v = \frac{1}{2} (k_i + k_j + D_i m^2 + D_j m^2)$$

$$\omega = \frac{1}{2} (k_i - k_j + D_i m^2 - D_j m^2)$$

$$\Omega = \sqrt{\omega^2 + k_i k_j}$$

$$m = (\gamma\delta g)^2$$

²C.S. Johnson, "Effects of chemical exchange in diffusion-ordered 2D NMR spectra", *Journal of Magnetic Resonance, Series A*, 1993, **102**, 214-218

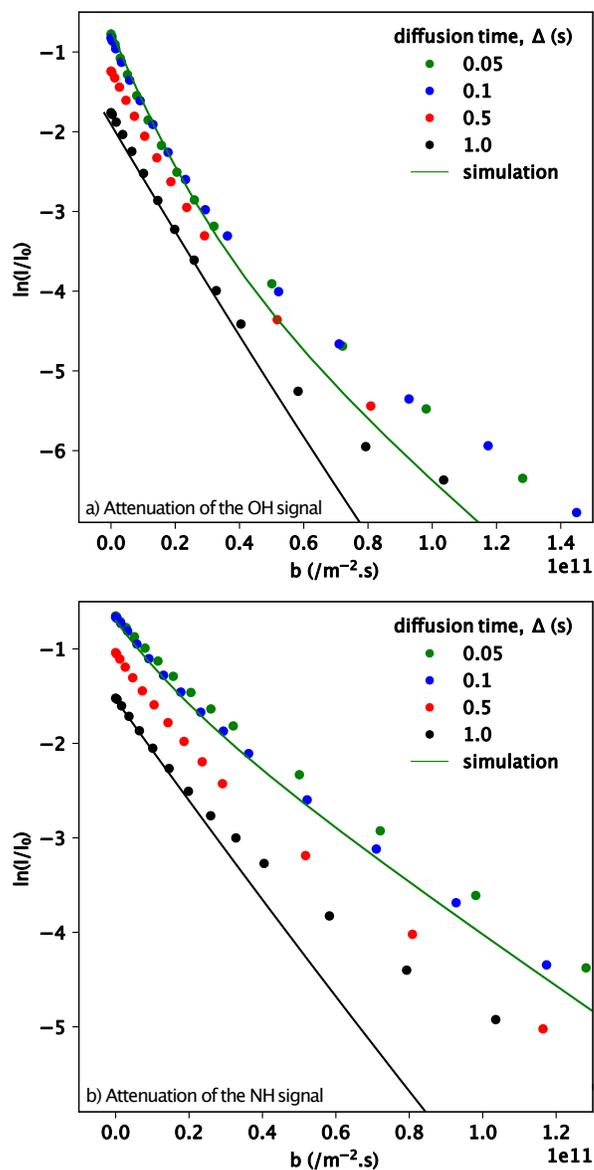


Figure S3: Attenuation of the two exchanging signals deviating from a mono-exponential behaviour. The solid lines are simulated result for two sets of data (for the shortest and the longest diffusion times) for each signal based on equation S2. The error bars are smaller than the symbol sizes.