A quantitative ionicity scale for liquid chloride salts

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Supporting information:

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1. Materials:

[Hmim]Cl was synthesized according to a modified literature procedure, such that the 1:1 salt was obtained.[1]

2. Methods:

2.1 Experimental:

^{35}Cl relaxation experiments performed with [Hmim]Cl were carried out with Bruker AVANCE 600 MHz (B_0= 14.1 T) and 500 MHz (B_0=11.7 T) NMR spectrometers using Bruker's standard 5 mm Z-gradient BBO probe. The operating frequencies for ^{35}Cl were 58.80 and 49.00 MHz, respectively, and for ^{13}C 150.90 MHz and 125.76 MHz. ^{1}H DOSY measurements were carried out with Bruker AVANCE 400 MHz (B_0 = 9.4 T) with similar 5 mm Z-gradient BBO probe. The resonance frequency for proton was 399.75 MHz.

The spin-lattice relaxation time, T_1, was measured by the inversion recovery pulse sequence ($180^\circ - \tau - 90^\circ - RD$) with relaxation delay $RD > 10T_1$. ^{13}C relaxation measurements were made under inverse gated Waltz decoupling. 90° pulses for both nuclei were equal or less than 10 μs. Sixteen τ values were used to acquire ^{35}Cl relaxation data. Number of scans varied from high temperature 400 scans to 20,000 near T_1 minimum where the broadening of the ^{35}Cl signal made observations more demanding. The total experiment time for one relaxation measurement was few minutes at high temperatures and 1.7 h at low ones. Twenty two τ values and 32 scans were used to acquire the ^{13}C data. Sixteen dummy scans were used to compensate the possible warming of the sample due to the decoupling. The total experiment time for one relaxation measurement of ^{13}C was 3.5 h. T_1 relaxation experiments of ^{13}C were measured in triplicate as were T_1 experiments of ^{35}Cl, at fixed

temperatures. However, T_1 of ^{35}Cl for the temperature dependence plot was measured only once at every temperature.

Data was processed using area-fit in Bruker's T_1 module of the Xwinnmr or TopSpin program. There was no evidence of non-exponential recovery in either case. We estimate the error for experimental T_1 of ^{13}C to be better than 10%. Due the very short T_1 and broad peak of ^{35}Cl, the errors increased when $T_1 < 0.1$ ms and, therefore, the maximum error for ^{35}Cl experimental data is 10-15 % over the whole temperature range.

The Arrhenius type equation, $T_1 = T_{1o} \exp^{\frac{E_a}{RT}}$, was fitted to high temperature points of the $\ln(T_1)$ vs. 1000/T plot, where T is the temperature, as given in Figure 1 below. The line on the low temperature points is drawn using the same fitted equation with the negative slope, $\frac{-E_a}{R}$.
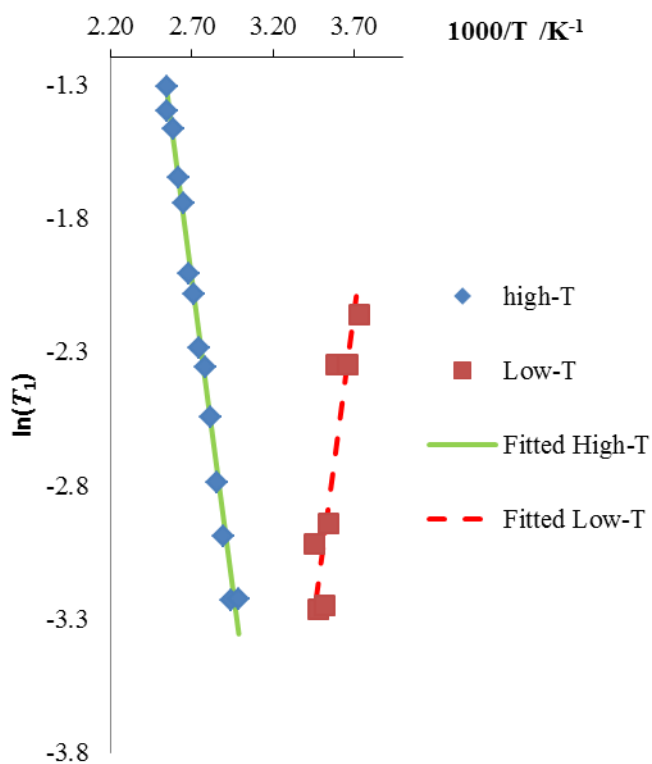
Figure 1. Arrhenius plot of $^{35}Cl^-$ variable temperature T_1 data.

The spin-spin relaxation time, T_2, was determined from half-height of the line width. Because of the broad ^{35}Cl lines, we assumed the inhomogeneity of the magnetic field have not much effect on the line width. Therefore, $T_2 = 1/(\pi \Delta \nu_{1/2})$ where $\Delta \nu_{1/2}$ is the line width at the half-height of the peak.[2]

2D-DOSY measurements were made with the stimulated echo pulse program with bipolar gradient pulses and a longitudinal eddy current delay (ledbpgp2s from Bruker pulse sequence library). The $90°$-pulse for proton was 8.1 μs and we used 12 ms sine shaped gradients. The FIDs were collected into 32k data points leading to 2.5 s acquisition time. The relaxation delay was also 2.5 s. The diffusion time was 200 ms. The gradient strength was increased from 5% to 95% of the maximum strength of 53.5 G cm^{-1} in 64 steps with signal average of 4 scans for every step. The total experiment time was about 22 minutes.

FIDs were apodized with exponential multiplication (LB = 1) and zero filled before Fourier transform. Diffusion coefficients and DOSY displays were obtained using Bruker's DOSY module of the Xwinnmr or TopSpin program.

Temperature was controlled by a Bruker BVT-3000 temperature unit. The correct temperature was set with a Bruker standard calibration samples of 80% glycol in [D6]DMSO and 4% of methanol in methanol-D_4. The temperature was let to stabilize an hour before the measurement. The accuracy of the sample temperature has been estimated to be $1°$.

2.2 Calculations:

2.2.1 Correlation times and $|C_Q|(^{35}Cl^-)$:

$|C_Q|(^{35}Cl^-)$ values were determined by first solving the T_1 relation (Equation 1) over two magnetic fields (11.7 T, and 14.1 T), at the specified temperatures, for the corresponding correlation time, τ_Q. We employed the following relation shown in Equation 1,

$$\frac{R_{1,500}}{R_{1,600}} = \frac{8UU^2 + VV^4\left(32UU^2 + 20\right) + VV^2\left(40UU^2 + 25\right) + 5}{25UU^2 + 20UU^4 + VV^2\left(32UU^4 + 40UU^2 + 8\right) + 5} \tag{1}$$

Equation 1. Rate equation used to solve for $|C_Q|(^{35}Cl^-)$ at various temperatures.

We used values of $R_{1,n} = \dfrac{1}{T_{1,n}}$ (for T_1 at $n = 500$ MHz, 600 MHz), and substituted $UU = \omega_{500}\tau_Q$ and $VV = \omega_{600}\tau_Q$, to obtain τ_Q. Once the correlation time was found at each temperature, $|C_Q|(^{35}Cl^-)$ was easily obtained. Where T_2 values were used in conjunction with T_1 values, we followed a procedure reported in reference 3.

2.2.2 Anisotropic rotational diffusion coefficients for [Hmim]$^+$ in Table 2 of the main text were obtained using a method described in reference 4.

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2.2.3 Friction coefficients in Table 2 of the main text were calculated according to equations given in reference 5 using parameters given in Table 1.

Table 1. Parameters required for calculation of friction coefficients.

IL	T / K	V_m / dm^3 mol^{-1}	Reference	σ / mS cm^{-1}	Reference
[Hmim]Cl	373	0.103	this work	4.146	this work
[C$_2$mim]Cl	377	0.134^a	6-8	31.88	9

^{a} Calculated from densities reported in given references, extrapolated to 377 K. T is the temperature, V_m is the molar volume and σ is the specific conductivity.

The density of [Hmim]Cl was determined using a 2.00 mL volumetric flask, calibrated with distilled water. Samples were added to the mark and weighed using an analytical balance, in triplicate, over three temperatures, in the range 298.25- 346.65 K. The value at 373 K was obtained by extrapolation. The specific conductivity of [Hmim]Cl was obtained from variable temperature microwave dielectric relaxation spectroscopy (DRS) measurements, described in reference 10 over the temperature range 303 - 353 K, with extrapolation to 373 K.

2.2.4 Diffusion coefficients were obtained for Cl$^-$ in this work according to $D_{rot.} = \dfrac{1}{6\tau_Q}$

(rotational) and $D_{trans.} = \dfrac{2a_{Cl}^2}{9\tau_Q}$ (translational),[11] with a_{Cl} = 1.81 x 10^{-8} cm.

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