SUPPORTING INFORMATION

Alkyl Chain Length and Temperature Effects on Structural Properties of

Pyrrolidinium-based Ionic Liquids: a Combined Atomistic Simulation and Small

Angle X-ray Scattering Study

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1. Methodology Section

1.1. Simulation Methodology

The all-atom force field used in the simulation was transferred from APPLE&P potential (Atomistic Polarizable Potential for Liquids, Electrolytes, & Polymers) developed by Grant Smith's group.[1] All parameters were transferred to exp-6 force field without any alteration except that the polarizability term was excluded from the potential.[2] The partial charges of carbon groups beyond the fourth carbon near the

pyrrolidium ring were all set to zero except the terminal methyl group. All the simulations were conducted using the Gromacs MD package. The cubic simulation box consisting of 125 ion pairs was sufficiently equilibrated at 1 bar and 298 K for 4 ns after energy minimization followed by a 4-ns production run. A linear mean square displacement and the density without significant variation confirmed the equilibrium state of the simulation box. Timesteps of 1 fs were adopted. All bonds were constrained using the LINCS algorithm. Particle-mesh Ewald summation was used for the long-range interaction with a 1.1 nm cutoff. The Nosé-Hoover thermostat and Parrinello-Rahman barostat were used respectively for the temperature coupling and pressure coupling. A larger box size containing 250 ion pairs was tested, which reproduced all the peaks in the structure function without significant variation compared with the system size used in this study.

For the structure function calculation for small angle x-ray scattering, the simulations were completed using the above protocol in the isothermal-isobaric ensemble at 1 bar and 298 K, 348 K and 363 K respectively. The total structure function and partial structure function respectively, were calculated based on the atom correlation functions using the following equations.[3]

$$S(Q) = 1 + \frac{\sum_{\alpha\beta} \chi_\alpha \chi_\beta f_\alpha(Q) f_\beta(Q) 4\pi \int_0^{r_c} [g_{\alpha\beta}(r) - 1] r^2 \frac{sin(Qr)}{Qr} dr}{\left[\sum_\alpha \chi_\alpha f_\alpha(Q) \right]^2}$$

$$S_{\alpha\beta}(Q) = 1 + 4\pi\rho \int_0^{rc} [g_{\alpha\beta}(r) - 1] r^2 \frac{sin(Qr)}{Qr} dr$$

χ_α and χ_β is the fraction of atom species α and β, Q is the wave number, $f_\alpha(Q)$ is the form factor of atom specie α, $g_{\alpha\beta}(r)$ is the correlation function of atom species α and β, and r_c is the integration cutoff which equals one half of the simulation box.

1.2. Small Angle X-ray Scattering Experiment

Small angle x-ray scattering measurements on $[C_nMPy][Tf_2N]$ with $n=3$, 4, 6, 8 and 10 were performed using the Anton Paar *SAXSess mc²* instrument at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory. The coherent scattering intensity, $I_{coh}(q)$ was collected as a function of the absolute value of the scattering vector, $q = |\vec{q}| = 4\pi sin(\theta)/\lambda$ where λ is the wavelength and 2θ is the scattering angle. The instrument, tuned to the Cu k_α wavelength, has a sealed tube source equipped with Göbel mirror optics and, with an image plate attachment, effectively measures in the $0.01 - 2.8$ Å^{-1} q-range. The ionic liquids were synthesized by using methods described previously.[4] The samples were contained in sealed quartz capillary tubes with a1-mm outer diameter and 0.01mm wall thickness. The temperature was controlled using an

Anton Paar TCS 300 unit capable of maintaining the temperature within ± 0.1℃.

Measurements were conducted at 23, 75 and 90 ℃ once the sample container temperature

equilibrated and as the temperature was ramped in each direction to check the reversibility of the observed changes. Measurements were conducted at 20 kV and 50 mA. Raw scattering data corrections included normalization to the incident beam intensity and sample attenuation by collecting counts behind the transparent nickel beam stop, and background scattering subtraction. Water scattering was used to calibrate all scattering intensities to absolute units of differential scattering cross section per unit volume, $I(Q) = (\frac{1}{V})d\Sigma / d\Omega \,(\mathrm{cm}^{-1})$. The structure functions, $S(Q)$, were computed by using the program PDFgetX2[5] where the data was corrected according to:

$$S(Q) = \frac{(I(Q) - \sum_i \chi_i f_i^2)}{(\sum_i \chi_i f_i)^2}$$

Here, χ_i and f_i are the atomic concentration and the form factor or atomic species i, respectively. Additionally, the data were corrected for sample self-absorption, multiple scattering, and a small amount of Compton scattering. The room-temperature $S(Q)$ data for the series is displayed in Figure 4. The position and amplitude of the two peaks below 1 Å^{-1} were found by fitting two Gaussian functions simultaneously to the $S(Q)$ data in the region 0.01 – 1 Å^{-1}. A parabolic function serves as a good approximation to the baseline that was subtracted for fitting either a Gaussian or Lorentzian function. The Gaussian function was able to fit the low alkyl chain ionic liquids better so it was used systematically in the entire series for consistency.

Reference:

(1)   Borodin, O. Polarizable Force Field Development and Molecular Dynamics Simulations of Ionic Liquids. *J. Chem. Phys. B* **2009**, *113*, 11463-11478.

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(5)   Qiu, X.; Thompson, J. W.; Billinge, S. J. L. Pdfgetx2: A Gui-Driven Program to Obtain the Pair Distribution Function from X-Ray Powder Diffraction Data. *J. Appl. Cryst.* **2004**, *37*, 678.
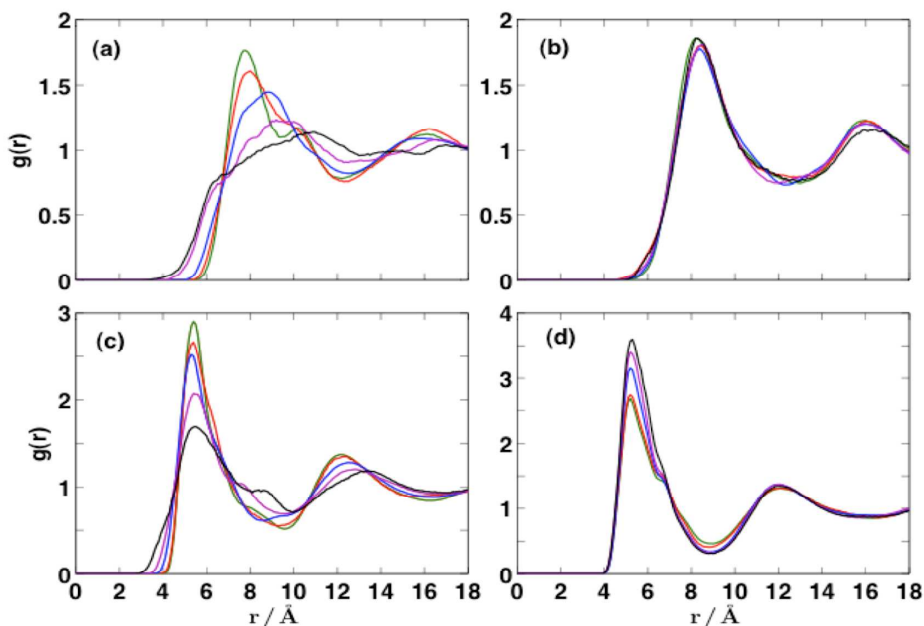
2. Supporting Figures

Figure S1. Center of mass radial distribution functions at 298 K of a) cation-cation b) anion-anion c) cation-anion and d) pyrrolidinium ring-anion for *n*=3 (green), 4(red), 6(blue), 8(purple) and 10(black).
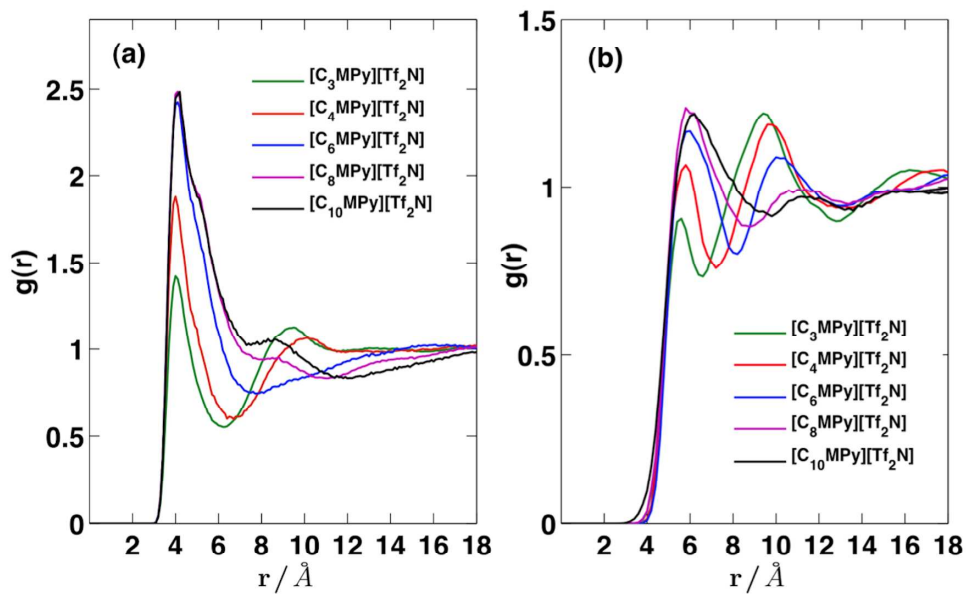
Figure S2. Center of mass radial distribution function at 298 K of a) terminal carbon b) alkyl chain
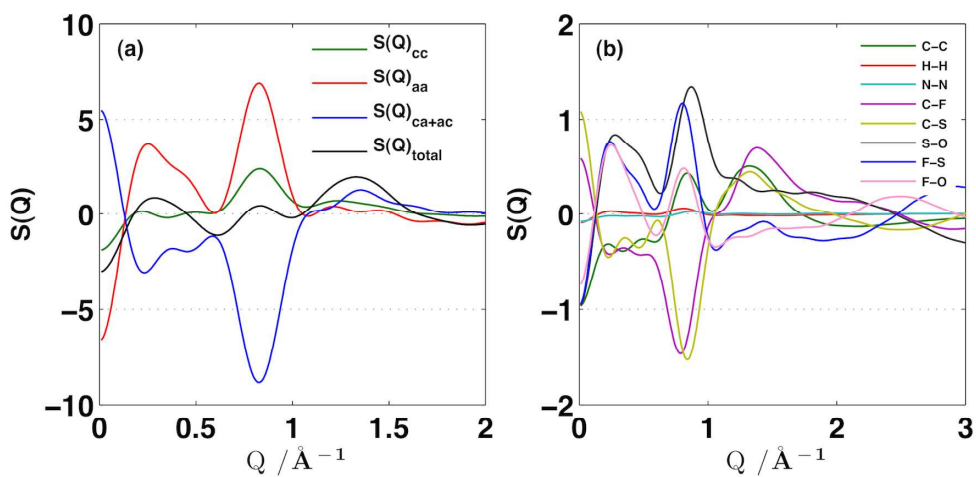

Figure S3. (a) X-ray weighted subcomponents of $S(Q)$ contributed by cation-cation, cation-anion and anion-anion correlations compared with total structure function at 298 K

of [C$_{10}$MPy][Tf$_2$N] ; (b) x-ray weighted atomic subcomponents of $S(Q)$ in
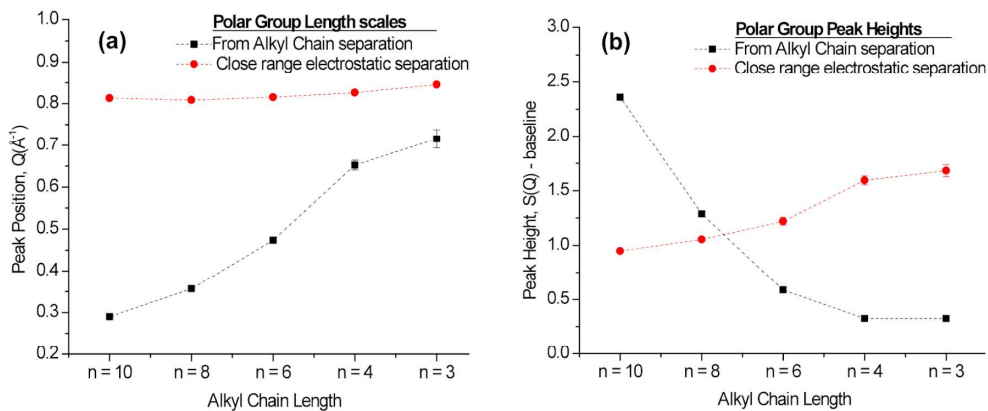
[C$_{10}$MPy][Tf$_2$N].

Figure S4. Peak positions (3a) and peak heights (3b) as a function of alkyl chain length obtained for pyrrolidinium-based RTILs by SAXS at 298K. 3a) The characteristic length scale corresponding to close-range electrostatically-ordered polar group correlations (I$_E$ peak, in red) is relatively invariant whereas the separation corresponding to alkyl-chain-separated polar groups (I$_A$ peak, in black) decreases with decreasing chain length shown by the shift to higher values in reciprocal space. 3b) As the chain length decreases, the alkyl-separated distance becomes comparable to the electrostatically-separated length resulting in overlap and increased intensity.
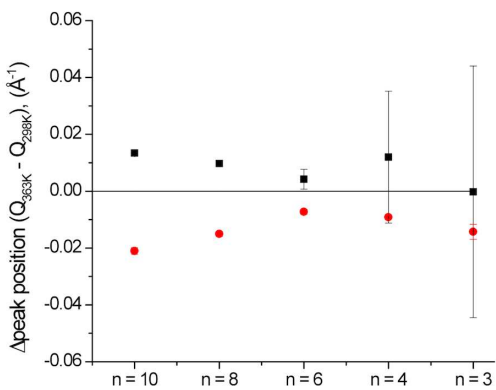
Figure S5. Total change in peak position for pyrrolidinium-based RTILs obtained by SAXS as a function of temperature from 298 K to 363 K for the two polar group peaks. Black squares (■) denote changes in the low-Q peak position, due to the alkyl chain separated distance and red circles (●) denote changes in the electrostatically separated distance (higher Q). Negative (positive) values indicate the peak shifted to lower (higher) Q with increasing temperature. For $n = 3$ and $n = 4$ the shift in the low-Q peak was smaller and statistics in this region introduced the larger error bars.