

Synthesis

[Ch][PRO] ILs was prepared using a new potentiometric titration method reported in the paper by Serena De Santis, Giancarlo Masci, Francesco Casciotta, Ruggero Caminiti, Eleonora Scarpellini, Marco Campetella and Lorenzo Gontrani, (*Phys. Chem. Chem. Phys.* May 2015 – accepted), based on the titration of choline hydroxide with a slight excess of solid amino acid which is then back titrated with choline hydroxide.

This method has shorter preparation time, stoichiometry within $\pm 1\%$, no use of organic solvents, very high yields (close to 100 %), high reproducibility with respect to the methods reported in the literature, thus resulting more environmentally friendly. The product was dried *in vacuo* for 24h at 50 °C, and the water content, determined with a Karl Fischer moisture titrator (831 KF Coulometer Metrhom), was less than 0.2 wt %.

X-Ray

About 0.5 ml of liquid were introduced in anamorphous quartz capillary (2 mm radius), that was afterward sealed with a Teflon band and kept in dry atmosphere, just before the measurements.

The X-Ray experiment(WAXS) was carried out on a Bruker D8 Advance with DaVinci design diffractometer (angle dispersive) equipped with a Mo K α X-Ray tube ($\lambda = 0.7107 \text{ \AA}$), whose radiation was focused onto the sample with Göbel mirrors. The 2θ angle range available was 2.75-142° with a step of 0.25° within the Bragg-Brentano para-focusing geometry. The scattered intensity was gathered with the Lynxeye XE Energy-Dispersive 1-D detector. □

Primary data were processed, performing the necessary corrections for the background and sample adsorption and subtracting the independent atomic scattering, to obtain the “total (static) structure function $I(Q)$, that is equal to:

$$I_{EXP}(Q)_{E.U} = \sum_{i=1}^N x_i f_i^2 + I(Q)$$

(1)

$I(Q)$ constitutes the structurally sensitive part of the scattering intensity $I_{E. U.}(Q)$ – expressed in electron units, and is due to the interference contributions from different atoms.

The variable Q is the magnitude of the transferred momentum, and depends on the scattering angle (2θ), according to the relation $Q = 4\pi (\sin \theta / \lambda)$.

The Fourier-transform of the structure functions yields the radial distribution function $D(r)$ of the system:

$$D(r) - 4\pi^2 \rho_0 = \frac{2r}{\pi} \int_0^\infty Q I(Q) \sin(rQ) M(Q) dQ \quad (2)$$

$M(Q) = \frac{f^2_N(0)}{f^2_N(Q)} \exp(-0.01Q^2)$ is a modification function used to improve the curve resolution of both experimental and theoretical structure functions (see below) at high Q .

If the second term of the subtraction, which corresponds to uniform distribution, is dropped the Differential Correlation Function $Diff(r)$, containing only the structural contribution to the distribution function, is obtained. The connection between experiment and theory resides in the following relation relating $I(Q)$ and the structural correlations among the particles of the liquid that describe its structure¹:

$$I(Q) = \sum_{i=1}^N \sum_{j=1}^N x_i x_j f_i f_j H_{ij}(Q) \quad (3)$$

where we have introduced the partial structure functions H_{ij} defined in terms of pair correlation functions $g(r)$ by the Fourier integral

$$H_{ij}(Q) = 4\pi \rho_0 \int_0^\infty r^2 (g_{ij}(r) - 1) \frac{\sin(Qr)}{Qr} dr \quad (4)$$

(ρ_0 is the bulk number density of the system, x_i are the numerical concentrations of the N species and f_i their Q -dependent X-Ray scattering factors).

The comparison between experimental and model data is carried out using both $QI(Q)M(Q)$ and $Diff(r)$, while for the discussion of the model characteristics both $g_{ij}(r)$ and $Diff(r)$ are employed, depending on the distance range considered. Several studies demonstrating the validity of this experimental-computational approach have been published so far (see, e. g. Ref. 2-3); all the functions were calculated using in-house codes purposely written by R. Caminiti and L. Gontrani.

Small Angle Diffraction experiments (SAXS) were collected on a Bruker AXS D8 Advance focusing powder diffractometer operating in transmission mode in θ/θ geometry, equipped with a Cu-K α X-Ray tube ($\lambda = 1.5418 \text{ \AA}$). Samples were charged in 2 mm diameter quartz capillaries, whose charging funnels were sealed using Parafilm. Capillaries were fixed upside down using bee-wax, to a standard goniometer head and aligned along the beam path. The instrument is fitted with focusing Göbel mirrors along the incident beam, Soller slits on both incident (2.3° horizontal divergence) and diffracted (radial) beams, and a Vantec-1 position sensitive detector (PSD). Data were measured in step-scan mode in the $2-40^\circ$ angular range, step-size 0.022° and 1s counting time.

Computational Details

In order to provide a full characterization of the structure of the liquid within the relevant range of radial distances that are accessible to experiments, we have performed two different simulations of the bulk system composed by an equal number of [Pro] anions and [Cho] cations. The first simulation was performed employing classical molecular dynamics within periodic boundary conditions, using the AMBER program package (GPU version of PMEMD) and the Gaff force field on a bulk system composed by 250 ionic pairs of IL. The partial atomic charges were however recomputed owing to the RESP method using the B3LYP electronic density. The resulting charges have been scaled by 0.8 to roughly account for polarization effects. Pre-equilibration took 2 ns of

physical time and the simulation temperature was set to 300 K; a productive simulation followed (5 ns).

The same equilibration protocol was applied to a smaller simulation box (55 ion pairs) to obtain a thermalized starting structure for *ab initio* molecular dynamics simulations with the program package CP2K, using the Quickstep module and the orbital transformation for faster convergence. The electronic structure was calculated by means of the PBE functional⁴, with an explicit Van der Waals correction that includes the empirical dispersion correction (D3) by Grimme⁵. Basis sets of the kind MOLOPT-DZVP-SR-GTH and GTH pseudopotentials⁶ were used. The time step was chosen to be 0.5 fs and the simulation temperature was set to 350 K using the Nosé-Hoover chain thermostat. After 5 ps of equilibration, a 32 ps production trajectory in the NVT ensemble was performed. To determine the free energy landscape of H-bond interaction, we employed the Umbrella Sampling technique⁷ on a little box composed by 3 ion pairs. In our model, the biasing potential was a function of the *collective variable* O(Cho)---O(Pro) distance, and we performed 22 constrained simulations overall, each one of them lasting for 20 ps. The unbiased probabilities of the collective variable was then easily recovered from the biased simulations using the weighted histogram analysis method WHAM⁸.

1 C. J. Pings and J. Waser, *J. Chem. Phys.*, 1968, **48**, 3016

2 L. Gontrani, F. Ramondo, G. Caracciolo and R. Caminiti, *J. Mol. Liq.* 2008, **139(1)**, 923

3 M. Macchiagodena, F. Ramondo, A. Triolo, L. Gontrani and R. Caminiti, *J. Phys. Chem. B*, 2012, **116(45)**, 13448–13458

4 G. K. H. Madsen, *Phys. Rev. B*, 2007, **75**, 195108

5 S. Grimme, *J. Comput. Chem.* 2006, **27**, 1787–1799

6 S. Goedecker, M. Teter and J. Hutter, *Phys. Rev. B* 1996, **54**, 1703–1710

7 G. M. Torrie and J. P. Valleau, *J. Comput. Chem.* 1977, **187**, 1977

8 S. Kumar, D. Bouzida, R. H. Swendsen, P. A. Kollman and J. Rosenberg, *J. Comput. Chem.* 1992, **13**, 1011

