

Supporting information

Switchable long-range double layer force observed in a protic ionic liquid

Nicklas Hjälmarsson¹, Rob Atkin², Mark W. Rutland^{1,3}*

¹Surface and Corrosion Science, KTH Royal Institute of Technology, SE-10044 Stockholm,
Sweden

² Priority Research Centre for Advanced Fluids and Interfaces, The University of Newcastle,
Callaghan, NSW 2308, Australia

³Chemistry, Materials and Surfaces, SP Technical Research Institute Sweden, SE-11428
Stockholm, Sweden

Corresponding Author

*mark@kth.se

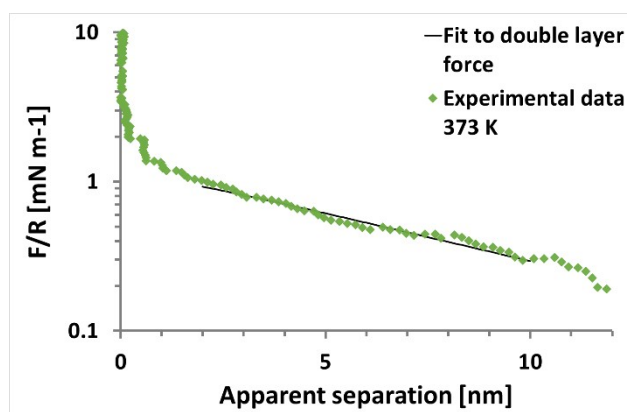


Figure S1. Measured force against apparent separation for EAN at 373 K. Poisson-Boltzmann theory was used to fit the long-range interaction using a constant potential and unlike surfaces

to an electric double layer force with a decay length of 6.3 nm. Values for the surface potentials (not necessarily unique) of -85 and -75 mV were returned from the fit.

Rheology

Rheological measurements of EAN were performed on a Malvern Kinexus Rheometer (Worcestershire, UK) between 293 K and 393 K using a concentric cylinder configuration.

The gap between the cylinders was 5.12 mm and the system was allowed a 5 min equilibrium period after each temperature had been reached. A viscosity value from each temperature was extracted from the Newtonian region and used to construct the Arrhenius plot in Figure S2.

The viscosity data demonstrated an Arrhenius type behaviour (single activation energy).

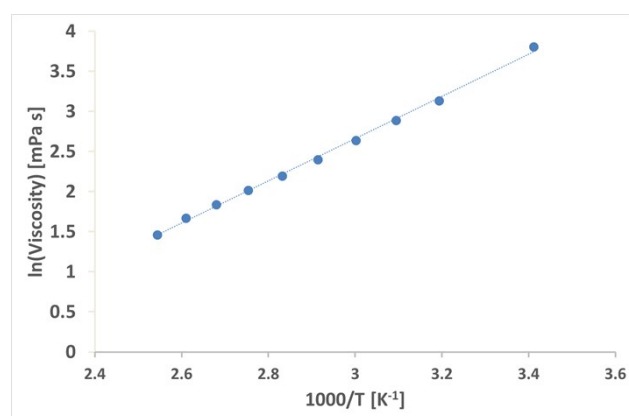


Figure S2. Measured shear viscosities for neat EAN between 293 and 393 K.

The effect of water on surface interactions in EAN

As discussed in the main article, It is known from previous studies that water can affect the decay length and the effective surface potential for ionic liquids. Below, three independent reasons are given for why it is unlikely that water is causing the abrupt transition from complete screening at 353 K to the apparent association of ions at 373 K and 393 K.

- Figure 1 and Figure S1 show clear oscillatory forces for the measured temperatures and in the landmark paper by Horn *et al.* in 1988 it was demonstrated that these oscillatory forces are weakened for EAN by increasing the water content.¹ A later paper by Atkin

et al. confirmed these results using a different technique so it is clear that significant amounts of water (*ca* 5 wt %) will disrupt the interfacial ordering of EAN at surfaces.² Such a disruption is clearly not observed here.

- The viscosity of EAN is very sensitive to the water content and from drainage measurements (albeit performed solely at lower temperatures, 298-353 K) the viscosity was extracted which matched that of the bulk value (measured independently).^{3,4} Thus the water content was well below 1 wt%.
- The effect of temperature is to reduce the water content (the synthesis of EAN uses temperatures around 383 K to drive off the water, thus the screening behaviour cannot be due to *increased* water content). Furthermore, since the decay lengths for 373 and 393 K are similar it is unlikely that there are significant changes in water content over this range.

Temperature dependence on decay length

For the case of a dilute electrolyte behaviour, the decay length, κ^{-1} , can be calculated according to the Debye model using:

$$\kappa^{-1} = \sqrt{\frac{k_B T \epsilon_0 \epsilon_r}{e^2 \sum \rho_i z_i^2}} \quad (\text{S1})$$

where k_B is the Boltzmann's constant, T is the temperature, ϵ_0 and ϵ_r are the permittivities of vacuum and the relative dielectric constant of the medium, respectively, e is the electronic charge, ρ_i is the number density of ion species i and z_i is the valence. Such a treatment predicts a $T^{1/2}$ -dependence of the Debye length. While the measured values at 373 K and 393 K are strictly equal within the formal error measurements, these values were returned independently of this approach and are consistent with this T dependence.

References

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2. J. A. Smith, O. Werzer, G. B. Webber, G. G. Warr and R. Atkin, *J Phys Chem Lett*, 2010, **1**, 64-68.
3. R. Zarrougui, M. Dhahbi and D. Lemordant, *J Solution Chem*, 2015, **44**, 686-702.
4. N. Hjalmarsson, R. Atkin and M. W. Rutland, *Phys Chem Chem Phys*, 2016, **18**, 9232-9239.