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Transport properties and intermolecular interactions in binary mixtures based on the protic ionic liquid ethylimidazolium triflate and ethylene glycol†

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1 Supplementary Information

The phase behaviour of the pure components, EG and C_2HImTfO, and some of the binary mixtures was investigated by differential scanning calorimetry (DSC). Figure SI-1 shows that all samples are liquid at 30 °C, but also that the heat of fusion decreases with the content of EG. This in turn indicates that the liquid mixtures tend towards becoming glass forming liquids, in contrast to the pure protic ionic liquid C_2HImTfO that easily crystallizes. The DSC traces of the binary mixtures reveal a glass transition temperature, T_g, at around -110 °C.

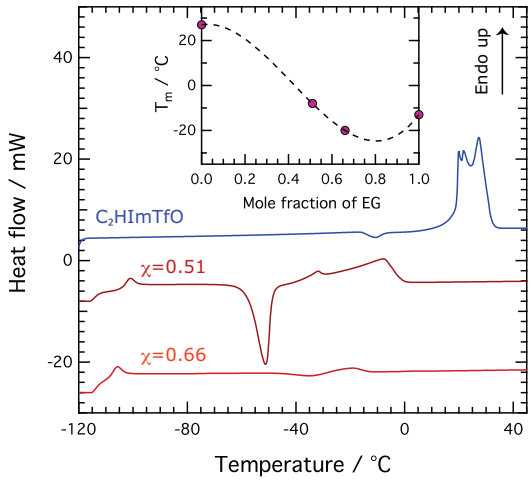

Figure SI-1. DSC traces recorded during the heating scan for the pure ionic liquid C_2HImTfO and two binary EG/C_2HImTfO mixtures. The inset shows the compositional dependence of T_m.

The increase in ionic conductivity detected upon addition of EG is moderate if compared to the increase measured when adding water, Figure SI-2A. The same difference is observed when comparing the effect on the self-diffusion coefficient of the C_2HIm cation, Figure SI-2B. The larger effect of water is likely a consequence of its lower viscosity (0.9 mPa·s at 25 °C) if compared to that of EG (16 mPa·s at 25 °C). It is also notable that the composition at which a maximum conductivity is observed is shifted from χ∼0.9 (water) to χ∼0.6 (EG). It is interesting that the different effects of water and EG on the transport properties (*i.e.* conductivity, diffusivity and ionicity) can not simply be explained by the acidity of the –OH groups, given that the dissociation constants are very similar (the pK_a being 14.00 for water and 14.22 for EG).

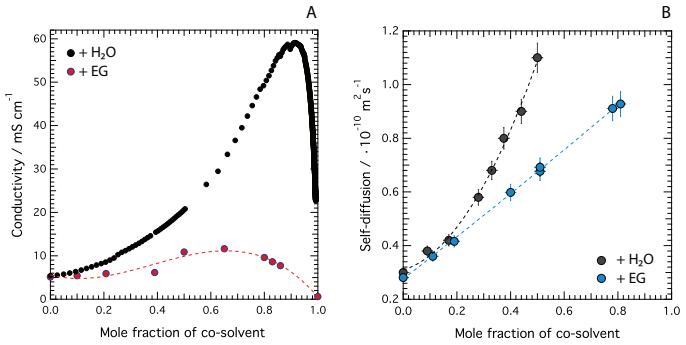

Figure SI-2. Ionic conductivity (A) and self-diffusion coefficient of the imidazolium cation (B) as a function of added water or ethylene glycol to the protic ionic liquid C_2HImTfO.

The thermal stability of the EG/C_2HImTfO mixtures with a mole fraction of EG equal to 0.5 was examined by thermogravimetric analysis (TGA), covering the temperature range 25–500 °C and using a heating rate of 10 °C/min, Figure SI-3. This figure shows two mass loss phenomena. The first one starting at 114 °C (with about 20% loss from the initial weight) is attributed to the loss of added ethylene glycol, which displays a lower evaporation point in the mixture than in the neat state (T_b of pure EG ≈ 197 °C). The second mass loss starting at 330 °C is attributed to the decomposition of C_2HImTfO. Altogether, these results show that the binary mixture EG/C_2HImTfO is useful for real applications in *ie.g.* fuel cells up to 110 °C, only slightly better than aqueous based electrolytes which are limited to 80 °C.

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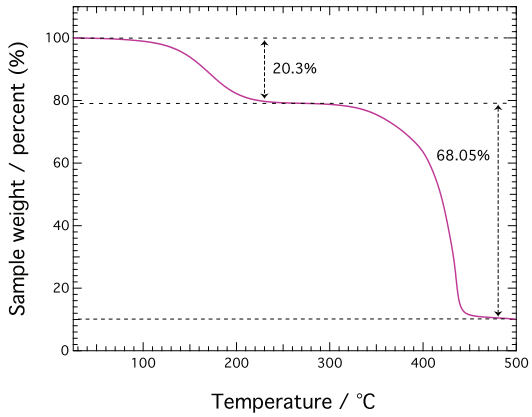

Figure SI-3. Thermogravimetric analysis of the EG/C_2HImTfO mixture with a mole fraction of EG equal to χ=0.5.

Table 1 Density (ρ) and viscosity (η) values of the binary mixtures EG/C_2HImTfO as a function of the mole fraction of ethylene glycol (χ) measured at 30 °C.

χ_{EG}	ρ (gr·cm^{-3})	η (Pa·s)
0	1.428	0.041.
0.2	1.401	0.028
0.41	1.364	0.020
0.53	1.337	0.010[a]
0.6	1.316	0.016
0.8	1.242	0.013
1.0	1.106	0.014

[a]This value was extrapolated from the fit of the other experimental data.

Table 2 Excess self-diffusion (expressed as D_{NH}/D_{cation}), ionicity (expressed as $\Lambda_{imp}/\Lambda_{NMR}$), self-diffusion coefficient of the TfO anion (expressed in 10^{-10} m^{2}s^{-1}, D_{anion}), self-diffusion coefficient of the C_2HIm cation (expressed in 10^{-10} m^{2}s^{-1}, D_{cation}) and ^{1}H NMR line widths of the NH and OH nuclei ($\Delta\nu$, in Hz) as a function of the mole fraction (χ) of ethylene glycol present in the EG/C_2HImTfO mixtures.

χ_{EG}	D_{NH}/D_{cation}	$\Lambda_{imp}/\Lambda_{NMR}$	D_{anion}	D_{cation}	$\Delta\nu_{NH}$	$\Delta\nu_{OH}$
0	1.00	0.57	0.25	0.28	16.9	-
0.1	0.99		0.31	0.36	19.1	11.2
0.2	0.99	0.48	0.35	0.42	21.2	10.7
0.39	1.10	0.39	0.50	0.6	37.8	17.4
0.51			0.60	0.69	31.9	0.47
0.65	1.16	0.76			87.0	35.4
0.8	1.17	0.72	0.99	0.92	467.5	72.5
0.86	1.19				502.3	63.9
1.0	-		-	-	-	10.4