



Shear dependent viscosity of poly(ethylene oxide) in two protic ionic liquids



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ABSTRACT

Steady shear viscosity measurements have been performed on 100 kDa poly(ethylene oxide) (PEO) dissolved in the protic ionic liquids ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) and in water. The zero shear viscosity in all three solvents increases with polymer concentration, falling into three concentration regimes corresponding to dilute, semi-dilute and network solutions. Huggins plots reveal three distinct solvent conditions: good (water), good-theta (EAN) and theta (PAN). However, differences in the transition concentrations, power law behaviour of the viscosities, and relaxation times arising from shear thinning in the two ILs can be directly related to the effects of solvent nanostructure.

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1. Introduction

Ionic liquids (ILs) are pure salts with melting points less than 100 °C. Low melting points are achieved employing by large, bulky ions, such that charges are often delocalised over large molecular volumes by resonance, reducing the strength of electrostatic interactions, while also hindering packing into a crystal lattice. A wide array of forces operate between the IL ions, including electrostatic, van der Waals, hydrogen bonding, and solvophobic [1] contributions. ILs have attracted interest as lubricants [2–12], solvents for synthesis and catalysis [13–23], as continuous phases for particle dispersions [24–28], amongst many other applications [29–31].

Ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) are two protic ILs that differ only in the length of the cation alkyl chain. Both EAN and PAN have a sponge-like bulk nanostructure [32,33], which results from electrostatic and hydrogen bonding attractions between the anion and cation groups leading to the formation of charged domains. The cation alkyl chains are repelled from these charged regions, and cluster together into apolar regions within the bulk liquid. The presence of a solid [34] or air [35] interface flattens the bulk structure into a more ordered arrangement, which is a general phenomenon for many protic and aprotic ILs [36,37]. EAN and PAN also form extended hydrogen bond networks within the polar domains between ammonium and nitrate groups. The hydrogen bonds in both liquids are relatively

long, bent, and bifurcated [38]. The extensive hydrogen bonding network invites comparison to water, and a variety of studies have shown that EAN and PAN (along with other related protic ILs) are effective solvents for surfactant self-assembly [39–41] and dissolved polymers [42–44]. The morphology of these dissolved species in the bulk [44] and adsorbed at solid [42,43] and air [45,46] interfaces are similar to aqueous systems in many respects [47–50].

Poly(ethylene oxide) (PEO) is a linear homopolymer. PEO is water soluble due to hydrogen bonding with ethylene oxide groups, and it is thought that similar interactions lead to high solubility in EAN [51] and PAN, such that the polymer is solubilised into the liquids polar domains. This is supported by molecular dynamics simulations of PEO in the aprotic IL 1,3-dimethylimidazolium hexafluorophosphate, which revealed that the average distance between the cation and the PEO ether oxygen is less than the average separation between the cation and anion [52]. This implies that the ether oxygen forms hydrogen bonds with the cation, resulting in solvation.

Rheological studies of aprotic ILs have revealed both Newtonian and non-Newtonian behaviour, depending on the IL species [53,54], the presence of a co-solvent [55], dissolved polymers [56], suspended particles [57], emulsion droplets [58], and surfactants [59]. Protic ILs have not been as extensively investigated; the effect of surfactant micelles on flow has been probed [60–62], as have mixtures or protic ILs with water or acetonitrile [63,31].

In this manuscript the steady-shear viscosity of PEO–PAN and PEO–EAN solutions as function of polymer concentration and

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temperature is described, and compared with the behaviour of PEO in water. The amphiphilic nanostructure of PAN is significantly stronger (more segregated) than that of EAN [32,33]. Examining the viscoelastic properties of PEO in EAN and PAN elucidates the effect of increasing the IL cation alkyl chain length, hydrogen bond network density, and IL nanostructure on both the polymer morphology and liquid viscosity in ILs. These findings are expected to be applicable for polymers dissolved into other ILs, including those from the aprotic family.

2. Experimental methods

PAN and EAN were prepared by reacting equimolar amounts of propylamine (Sigma Aldrich) and ethylamine (Sigma Aldrich) with concentrated nitric acid (Merck) in excess water. The solution temperature was maintained at 283 K to prevent the formation of oxide impurities. Excess water was removed by rotary evaporation at 303 K followed by nitrogen purging and heating at 378–383 K for 12 h, to yield colourless liquids with water content undetectable by a Karl Fischer titration. The resulting room temperature ILs consist of ethylammonium (EA⁺), or propylammonium cations (PA⁺) with nitrate anions. EAN has a melting point of 285 K, a density of 1.21 g/mL and is 45 times more viscous than water at 293 K. PAN has a melting point of 277 K a density of 1.15 g/ml and has a viscosity of 86.6 mPa s at 293 K.

Poly(ethylene oxide) (Sigma Aldrich) with $M_w = 100$ kDa was dried in a vacuum oven for 24 h before use. The polydispersity index of the material is typically between 1.1 and 1.2. PEO solutions in PAN, EAN and Milli-Q water were prepared and stirred for at least 24 h prior to testing.

Steady shear viscosity measurements were performed with a Physica MC 301 rheometer (Anton-Paar GmbH, Austria) using a plate – truncated cone geometry under a nitrogen atmosphere to prevent water ingress. A cone with a diameter of 50 mm, a cone angle of 0.98° and a cone truncation of 94 μm was used. Temperature was kept constant at 293 K using a Peltier heating plate. The shear stress (τ) as function of the shear rate ($\dot{\gamma}$) was measured in the range of 0.02–2000 s⁻¹. Apparent viscosity (η) was calculated using $\eta = \tau/\dot{\gamma}$.

3. Results and discussion

Over the range of shear rates examined, both EAN and PAN were Newtonian at 293 K, with $\eta = 86.6$ mPa s for PAN and $\eta = 41.5$ mPa s for EAN (see Fig. 1). They remained Newtonian at higher temperatures of 363 K, but their viscosities were markedly reduced to 11.8 mPa s and 7.6 mPa s, respectively (data not shown). These are consistent with recently reported results by ourselves and others [64,65], and with the greater degree of amphiphilic nanostructuring in PAN compared with EAN.

Fig. 1 shows viscosity as a function of shear rate for various concentrations of 100 kDa PEO in EAN, PAN and water at 293 K. For all three solvents, the solution viscosity increases markedly with PEO concentration, but the absolute viscosities are up to 2 orders of magnitude higher in the ILs than water at similar polymer concentrations. At low PEO concentrations the solutions are Newtonian across the shear range for all three liquids. However, when the polymer concentration is increased, shear thinning is observed in all three solvents. This effect is smallest for aqueous PEO solutions, where slight shear thinning is seen only at the highest polymer concentrations. This is consistent with Ebagninin et al.'s recent rheological characterisation of aqueous PEO solutions [66]; while they found no shear thinning of 100 kDa solutions up to $\dot{\gamma} = 1000$ s⁻¹, higher molecular weight PEOs clearly exhibited shear thinning.

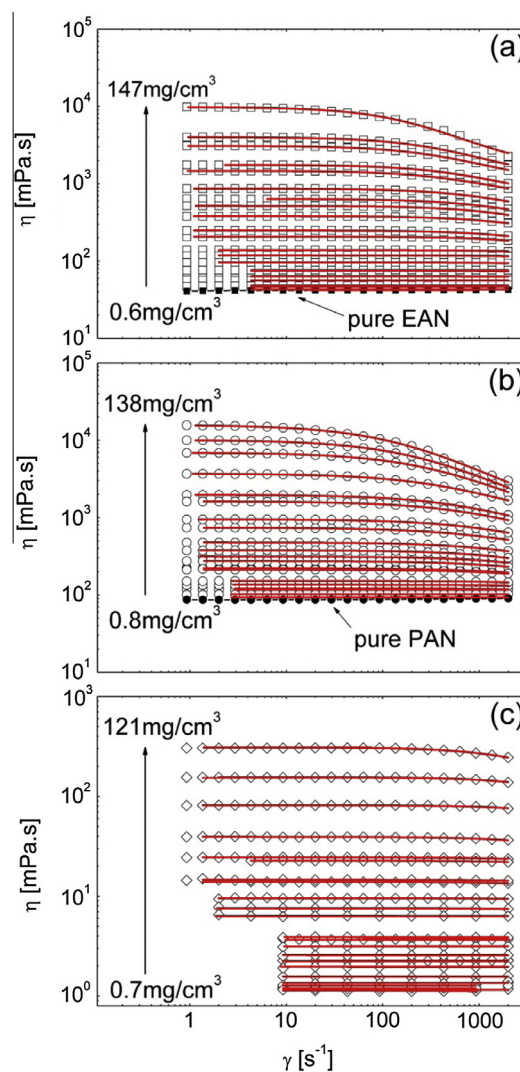


Fig. 1. Apparent viscosity vs. shear rate for various PEO–EAN (a), PEO–PAN (b), and PEO–water (c) solutions at 293 K. Open symbols denote the experimental data, full symbols denote the pure ILs and lines represent fits to the data.

In the ILs, shear thinning is more pronounced in PAN than EAN, and the shear rate at which shear thinning begins decreases with increasing PEO concentration. We have previously observed some shear thinning in EAN and PAN at very high shear rates. However, over the range investigated here, these non-Newtonian responses must be a consequence of the dissolved PEO [66].

The shear rate dependent viscosities can be analysed using the Cross equation [66,67]:

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (\lambda \cdot \dot{\gamma})^m} \quad (1)$$

where η is the experimental apparent viscosity at shear rate $\dot{\gamma}$, η_0 is the extrapolated zero shear solution viscosity, and η_{∞} is the solution viscosity at infinite shear rate. In this fit η_{∞} values are set equal to the last data point accessible in the experiment [66]. λ is time constant, so $1/\lambda$ is the shear rate at which the viscosity has fallen half way from η_0 to η_{∞} , and m describes the dependence of the viscosity on the shear rate in the shear thinning part of the curve. Fits of the Cross equation to the experimental data (Fig. 1) yield excellent agreement over the entire range of shear rates.

Zero-shear viscosities of PEO solutions in all three solvents are shown in Fig. 2. For each solvent, three regimes with distinct

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