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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 100kDa 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.

I. 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 solvophobic¹ 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 solid³⁴ or air³⁵ 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-assembly³⁹⁻⁴¹ and dissolved polymers.⁴²⁻⁴⁴ The morphology of these dissolved species in the bulk⁴⁴ 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 EAN⁵¹ 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 of protic ILs with water or acetonitrile.^{63,64}

In this manuscript the steady-shear viscosity of PEO–PAN and PEO–EAN solutions as function of polymer concentration and 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 in to other ILs, including those from the aprotic family.

II. Experimental methods

PAN and EAN were prepared by reacting equimolar amounts of propylamine (Sigma Aldrich) and ethylamine (Sigma) 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) with $M_w = 100$ kDa was dried in a vacuum oven for 24 hours 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 hours 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 $94\mu\text{m}$ 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 $0.02 - 2000 \text{ s}^{-1}$. Apparent viscosity (η) was calculated using $\eta = \tau/\dot{\gamma}$.

III. Results and Discussion

Over the range of shear rates examined, both EAN and PAN were Newtonian at 293 K, with $\eta = 86.6 \text{ mPa.s}$ for PAN and $\eta = 41.5 \text{ mPa.s}$ for EAN (see Figure 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,^{65,66} and with the greater degree of amphiphilic nanostructuring in PAN compared with EAN.

Figure 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;⁶⁷ while they found no shear thinning of 100 kDa solutions up to $\dot{\gamma} = 1000 \text{ s}^{-1}$, higher molecular weight PEOs clearly exhibited shear thinning.

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.⁶⁷

Figure 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.

The shear rate dependent viscosities can be analysed using the Cross equation^{67,68}:

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

where η is the experimental apparent viscosity at shear rate γ , 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.⁶⁷ 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 (Figure 1) yield excellent agreement over the entire range of shear rates.

Zero-shear viscosities of PEO solutions in all three solvents are shown in Figure 2. For each solvent, three regimes with distinct power-law slopes can be discerned. Table 1 lists the transition concentrations and the respective slopes obtained for each solvent.

Figure 2: Zero shear viscosity vs. concentration of PEO solutions. c^* and c^{**} denote positions at which the gradients change. Lines represent power law fits to the different regimes (see Table 1).

In the most dilute regime all three solvents exhibit power law behaviour with virtually identical exponents $\eta_0 \sim c^{0.24 \pm 0.02}$. At higher concentrations a change in slope occurs indicating the onset of chain overlap. The overlap concentration, c^* , depends on the solvent, as does the effect of increased concentration on η_0 ; a scaling of 1.04, 1.31 and 1.38 is found for water, PAN and EAN, respectively, within this semi-dilute regime. At even higher concentrations the slope changes again at c^{**} (see Figure 2), yielding exponents of 2.55

(water), 2.46 (PAN) and 3.05 (EAN) in the “network” regime. A concentrated network regime was not present at the concentration under investigations. A comparison of the slope values obtained for the three solutions reveal that the exponent values in all regimes are significantly smaller compared to literature values for larger molecular weight PEO.⁶⁷ This is most likely a consequence of the PEO chains being small thus the scaling behaviour of an “ideal polymer chain” is not fulfilled and a deviation of power law results.

Table 1: Summary of zero shear viscosity parameters for 100 kDa PEO solutions in water, EAN and PAN.

Solvent	Slope for various regimes			Transition conc. [mg/ml]		[η] [ml/mg]	k_H	[η]c*
	I	II	III	c^*	c^{**}			
PAN	0.23	1.31	2.46	9.1	57	0.086	0.53	0.78
EAN	0.26	1.38	3.05	10.2	53	0.081	0.43	0.83
water	0.24	1.04	2.55	6.2	32	0.127	0.40	0.79

At the lowest concentrations examined, where all solutions were Newtonian, PEO forms a dilute solution. Here, below c^* , the size of the polymer chain depends only weakly on concentration. Unperturbed (infinite dilution) chain dimensions may be obtained via the intrinsic viscosity, [η], using the Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad \text{Eq 2}$$

Where η_{sp} is the specific viscosity, $\left(\frac{\eta_0}{\eta_{solvent}} - 1 \right)$.

Figure 3: Huggins plots for dilute PEO solutions.

A plot of η_{sp} as a function of concentration produces a straight line with the intercept equal to η_{sp} and the slope equal to the Huggins coefficient (k_H). k_H is smaller in a good solvent (where polymer/solvent interactions are favoured over polymer/polymer interactions) than in poor solvent (polymer/polymer interactions favoured over polymer/solvent interactions); k_H is less than 0.5 in a good solvent, between 0.5 – 0.7 in a theta solvent, and greater than 0.7 in a poor solvent. Huggins plots for the three systems investigated are presented in Figure 3, and the derived k_H values are shown in Table 1.⁶⁹

The observed k_H of 0.40 for PEO in water is consistent with values for a good solvent, and lies within the range reported previously for aqueous solutions of PEO of comparable molecular weights, ranging from 86 kDa – 250kDa.⁶⁹ The overlap concentration in water, $c^* = 6.2 \text{ mg/cm}^3$ (see Figure 2 and Table 1), is approximately equal to the reciprocal of the intrinsic viscosity, or in our case 7.9 mg/ml. This agrees well with values of 11.8 and 8.73 mg/ml reported previously for 100 kDa and 112 kDa aqueous PEO solutions.^{67,70} Within the approximation of little chain perturbation in the dilute regime, this can be used to estimate the radius of gyration (R_g) via⁷⁰

$$R_g = \left(\frac{3M_w[\eta]}{4\pi N_A} \right)^{1/3}$$

This yields $R_g = 17.1$ nm in water, in excellent agreement with the 17.7 nm expected from the light scattering results of Devanand and Selser, who found $R_g = 0.0215M_w^{0.583}$ nm.⁶⁹

The Huggins coefficient for PEO in EAN is somewhat larger, 0.43, as is expected for approaching a θ solvent, and larger still in PAN ($k_H = 0.53$) which is typical for a theta solvent. The intrinsic viscosities of PEO in both ILs are also much lower than in water, consistent with the observed higher overlap concentrations, and smaller radii of gyration than in water. For PEO, R_g calculated as above is 14.7 nm in EAN and 15.0 nm in PAN.

The concentration dependence of zero shear viscosity for PEO – EAN solutions are consistent with recent morphological studies performed using small angle neutron scattering (SANS) on deuterated 36 kDa PEO in hydrogenous EAN.⁴⁴ In the dilute regime, EAN is better than a theta solvent for PEO (but not as good a solvent as water), and the polymer conformation is close to an “ideal” Gaussian coil. At these concentrations, the coils are separated from one another, so the coil extension is determined mainly by solvent – polymer interactions. This means that the radius of gyration only weakly decreases with polymer concentration, and consequently the viscosity increases only slightly.

The previously measured R_g for a 38 kDa PEO in EAN at infinite dilution by SANS was 8.1 nm.⁴⁴ Combining the SANS and rheology (admittedly limited) two data points gives a scaling law of $R_g = 0.017M_w^{0.57}$ nm for PEO in EAN, which suggests that the smaller PEO chain is the result of a smaller rigid segment length in EAN than in water, as well as slightly poorer solvent quality.

In the semi-dilute regime the size of the Gaussian coils decreases, but the ideal coil morphology is maintained. SANS measurements revealed that the morphology of PEO “blobs”⁷¹⁻⁷³ less than 3 nm were unaffected by concentration, so coil size changes are a result of changes at larger length scales. At these concentrations, polymer coils interact sterically with their neighbours, leading to contraction of individual coils without changing the

conformation significantly. Nonetheless, the increased number of polymer coils and the stronger interactions between them results in the concentration dependence on viscosity being stronger in the semi-dilute regime than in the dilute regime. When the polymer concentration exceeds c^{**} , the shape of the polymer coil changes as interactions between neighbouring chains take effect. Rather than a random flight chain, SANS experiments revealed an elongated structure. At higher concentrations, elongated structures are favoured as they space fill more effectively than spheroidal coils. The higher polymer concentration, combined with the fact that chain – chain entanglements are increased for the elongated structures compared to the spheroidal structures due to the higher contact area, which means that viscosity depends more strongly with concentration in this regime. In the “network” regime, polymer entanglements are pronounced and viscosity increases strongly with concentration (see Figure 2).

As Figure 1 shows, no shear thinning is detected below c^* in EAN or PAN. As PEO concentration is increased beyond c^* , the onset of shear thinning occurs at progressively lower shear rates. The time constant, λ , obtained from the Cross model (Eq. 1) is a measure of the relaxation time of the system back into its unperturbed or equilibrium state. In polymer solutions shear thinning may occur for two main reasons. Firstly, adjacent polymer chains disentangle as shear is applied. When the polymer concentration is high, there are a large number of entanglements between neighbouring polymer chains. This means that when shear is applied to the solution the probability of disentanglement occurring is high, and the onset of shear thinning occurs at low shear rates. At low polymer concentrations, the degree of entanglement is lower, so the probability of disentanglement upon the application of shear is lower, and shear thinning is noted at higher shear rates. Secondly, shearing induces a uniaxially elongated alignment of polymer coils along the flow direction which reduces the polymer coil area perpendicular to the flow direction and reduced viscosity results.

λ versus concentration (top) and viscosity (bottom) for PEO – EAN and PEO – PAN solutions are presented in Figure 4 for PEO concentrations greater than 26.6 mg/cm³ where shear thinning is observed. Solutions of PEO in both EAN and PAN fall into two regions; λ initially rises steeply up to c^{**} , after which it increases more gradually. λ is more strongly affected by concentration below c^{**} because there are fewer interactions between polymer chains, and hence each new interaction that occurs when concentration is increased has a large effect. Above c^{**} , there are many polymer entanglements, so when the polymer concentration is increased by the same amount as below c^{**} the proportion of new entanglements is lower, and thus λ is less strongly affected.

λ versus η_0 (Figure 4b) follows a single power-law relationship $\eta_0 \sim \lambda^x$. This suggests that the underlying relaxation mechanisms as a function of shear and for the increase in viscosity and λ are the same. As polymer concentration is increased, the number of polymer entanglements increases. Additionally, the polymer is more confined by neighbouring coils and this impedes motion of the polymer chain. Both effects increase the coil relaxation time, and thus the viscosity.

Figure 4: Relaxation time as function of (a) concentration and (b) η_0 of PEO solutions in PAN (dots) and EAN (squares). Lines represent linear fits to the experimental data.

Although PEO solutions in PAN are more viscous than those in EAN, their viscous and rheological responses have many similarities. Recall that EAN and PAN are both nanoheterogeneous solvents, and that the bulk structure of PAN is stronger than that of EAN, meaning that the polar and apolar domains are more distinct. The hydrophobic regions in PAN are also larger as a result of the longer cation alkyl chain and identical ammonium and nitrate charged moieties. As the PEO chains are solvated by these ionic polar domains, the Huggins coefficients for EAN and PAN can be interpreted as being that of a suitably-weighted average solvent of the two domains.

Like PEO – EAN, PEO – PAN solutions exhibit three regimes of zero shear viscosity as a function of concentration (Figure 2). The slopes in each region are slightly lower for PAN, with the difference becoming more marked at higher concentrations. This is also a consequence of the reduced polar volume in PAN; as the cation alkyl chain is longer in PAN,

the volume fraction of the polar phase relative to the apolar phase is smaller. This means that at any polymer concentration, the volume of polar phase ‘solvent’ available to the polymer is lower in PAN than EAN, so transitions occur at lower concentrations. The unperturbed radius of gyration determined from c^* for PAN is 15 nm which is quite similar to the value determined for EAN within error.

Concentrated PEO – PAN solutions also shear thin like those for EAN, but have longer relaxation times (Figure 4a) at the same concentrations. This is not simply due to the higher solvent viscosity. Figure 4b has a higher gradient (0.97 for PAN versus 0.85 for EAN), which suggests a greater level of entanglements between neighbouring polymer coils in PAN versus EAN at the same concentration. This is again consistent with lower polar phase volume in PAN increasing the effective polymer concentration.

Conclusion

The flow behaviour of PEO in PAN and EAN is heavily influenced by the underlying nanostructure of the solvents. Changing the polar/apolar volume ratio affects the average solvent quality, seen through the intrinsic viscosity and the Huggins parameter, as the PEO is preferentially solvated by charged groups rather than alkyl chains. Similar to the ability of water to form hydrogen bonds with the EO along the polymer chain, the ammonium head groups of the cations (EA^+ and PA^+) fit onto the structure of the PEO backbone; their hydrogen bonding ability effectively solvates the EO segments. These polar regions are good solvents for PEO, but the average solvent behaviour is influenced by the presence of non-polar domains. This leads to similar radii of gyration of PEO in EAN and PAN in dilute solution.

Although the concentration-dependent viscosity of PEO in these ILs is typical of many polymer solutions, showing dilute, semi-dilute and network regimes, the transition

concentrations and power-law viscosity behaviour in the semi-dilute and network regimes also reflect solvent nanostructure. The transition to entangled chains at c^{**} occurs at lower concentrations in PAN because there is less good solvent (polar volume fraction) available than in EAN. This is also seen in the pronounced shear thinning that occurs in both ILs in semidilute and network concentration ranges.

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

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