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Conformation of poly(ethylene oxide) dissolved in ethylammonium nitrate

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Abstract

Small angle neutron scattering has been used to investigate the morphology of 38 kDa PEO dissolved in ethylammonium nitrate (EAN) in the dilute and semidilute concentration regions. At infinite dilution the radius of gyration, Rg, is 8.1 nm. This value decreases through the dilute regime according to a concentration (c) dependence of Rg ~ c⁻⁰.²⁴, while above the overlap concentration a c⁻¹ dependence is followed. These differ from aqueous solution behavior, which we attribute to EAN being a less good solvent for PEO than water, and is in fact close to a θ solvent. The polymer structure on length scales less than 3 nm is unaffected by increasing polymer concentration, suggesting that the overall decrease in coil dimensions is a consequence of tighter packing of ~3 nm polymer ‘blobs’ into a smaller volume.
Introduction

Ionic liquids (ILs) are solvents that consist entirely of ions which are typically bulky and sterically hindered, resulting in melting points below 100 °C. ILs often exhibit low volatility, high conductivity, and a capacity to dissolve unusual combinations of solutes. The ability to change their physical properties through systematic variation in the molecular structure of the ions has led to research interest in a diverse range of fields including particle stabilization, lubrication, synthesis, catalysis, extractions, in solar cells, as solvents for surfactant self assembly and polymers, solid - liquid and liquid - air interfacial phenomena, amongst many others.

Ethylammonium nitrate (EAN) is a protic IL that was discovered a century ago. It is synthesized by proton transfer from nitric acid to ethylamine, which results in ethylammonium cations (EA+) and nitrate anions. The melting point of EAN is 12˚C, its viscosity is about 30 times higher than that of water and it has a density of 1.21 g/ml. EAN has a pronounced nanostructure, which results from an extensive H-bonding network and strong electrostatic attractions between the ethylammonium cation and the nitrate anion, generating solvophobic attractions between cation ethyl chains. In combination, these forces favor the formation of a bicontinuous sponge-like nanostructure consisting of separate ionic and apolar regions. In the vicinity of a macroscopic interface, the sponge-like structure flattens, and a more pronounced layered arrangement results.

The extensive hydrogen bond network of EAN has stimulated a plethora of studies into molecular self assembly in EAN and its protic analogues, with particular attention paid to surfactant micelles and liquid crystal phases. Because the tailgroup of surfactants can be accommodated within the apolar domains of EAN’s nanostructure, surfactant solubility is high, and critical micelle concentrations can be orders of magnitude higher than in water. This makes surfactants inefficient in bulk EAN, as much higher concentrations must be used to produce the same effects as in aqueous systems.
The situation is even more pronounced at charged surfaces. Although polyoxyethylene nonionic surfactants with long alkyl chains do adsorb from EAN onto graphite by a solvophobic interaction, no adsorption is observed at concentrations up to 30 wt% on silica or mica, due to competition from strongly-bound ethylammonium cations. This means that surface properties cannot be modified by surfactant adsorption from EAN solution as in aqueous systems. However, when the number of ethylene oxide units is increased, there are more surface attachment points per molecule, and this tips the balance in favour of adsorption; the adsorption of poly(ethylene oxide) (PEO) homopolymers and amphiphilic Pluronic copolymers (PEO-\(b\)-poly(propylene oxide)-\(b\)-PEO) at the EAN – silica interface has been observed. AFM force curve measurements suggest that PEO adsorbs to the silica – EAN interface with a compact, mushroom morphology. This is in contrast with PEO adsorbed at the water – silica interface, which has a brush conformation. The reason for this difference is unresolved, but may be a consequence of EAN being a poorer solvent for PEO compared to water.

PEO is reported to be soluble in numerous ionic liquids. PEO – IL solutions show promise for many applications including \(\text{CO}_2\) capture, in solar cells and in batteries. Similar to aqueous systems, PEO lower consolute temperatures in ILs are concentration and molecular weight dependant; variation in the ion structure permits control over the cloud point. The molecular origin of PEO temperature stability in ILs is not clear, but in water the effect of salt species on PEO-water solutions is usually explained in terms of the Hofmeister series. Aqueous cloud points vary with ion species due to charging along the polymer chains (salting-in) or a disruption of the water structure close to the polymer chain (salting-out). The anion is generally of greater consequence for such effects. However, Hofmeister effects are only seen at low ionic strength in water, because in high salt concentrations electrostatic forces are screened, resulting in solution properties that are similar to neutral polymers in salt free solutions. The high ionic strength of ILs means that electrostatic interactions are effectively screened.
This investigation probes the structure of PEO solutions in EAN using small angle neutron scattering (SANS). A fully deuterated PEO (d-PEO) and hydrogenous EAN (h-EAN) system is required to achieve scattering contrast for this study; the similarity of the refractive indices of EAN and PEO render optical techniques such as light scattering unsuitable. The extension, conformation and polymer – solvent interactions between PEO and EAN are evaluated and discussed. Only one paper has previously examined the morphology of PEO in an IL.\textsuperscript{30} Triolo \textit{et al.} used small angle neutron scattering to probe the structure of 27.3 KDa PEO dissolved in the aprotic IL 1-butyl-3-imidazolium tetrafluoroborate ([Bmim][BF$_4$]). While [Bmim][BF$_4$] was reported to be a good solvent for PEO, the random coil was smaller than for corresponding aqueous systems, and its dimensions decreased more rapidly with increasing polymer concentration. While both EAN and [Bmim][BF$_4$] are nanostructured,\textsuperscript{18,37,38} they differ in several respects, notably in the physical dimensions of the ions and the capacity of EAN to form a three dimensional hydrogen bond network. This study will examine the morphology of PEO dissolved in EAN, and the results obtained will be contrasted with aqueous and [Bmim][BF$_4$] systems.

\textbf{Experimental Section}

Hydrogenous ethylammonium nitrate (h-EAN) was prepared by reacting equimolar amounts of ethylamine (Sigma Aldrich) and conc. nitric acid (BASF) in excess water. The solution temperature is maintained at 8 - 10 °C to prevent the formation of oxide impurities. Water is removed by rotary evaporation at 50 °C, then purging with nitrogen and heating at 105 – 110 °C for 12 h. This method results in H$_2$O contents undetectable by Karl-Fischer titration.

Fully deuterated poly(ethylene oxide) (d-PEO) with molecular weight of 38 kg/mol and a polydispersity index of 1.06 was purchased from Polymer Source Inc. (Canada) and was used without further treatment. d-PEO – h-EAN solutions with concentrations between 0.1 wt% to 10 wt% (or 1 – 122 mg/cm$^3$) were prepared a few days prior to measurements.
Small angle neutron scattering (SANS) experiments were performed at the QUOKKA beamline at the Bragg Institute (ANSTO, Australia) using 1mm path-length Hellma Cells. The neutron wavelength was 4.94 Å with a 6% wavelength spread. 2-dimensional SANS spectra were collected at a distance of 2 m and 12 m providing a overall q-range of 0.1 to 0.5 Å⁻¹. The integration time was 1800 s for the 2 m and 10000 s for the 12 m distance. Data reduction were performed using the NIST reduction software including QUOKKA specific extensions. The h-EAN background was subtracted from the spectra after the data reduction process. All experiments were conducted at 22 °C.

**Results and Discussion**

A number of factors affect the conformation of a dissolved polymer chain, but the solvent quality and polymer concentration are usually the most important. Solvent quality refers to the relative favorability of polymer–polymer and polymer–solvent interactions. If polymer-solvent interactions are energetically favoured an extended conformation results and chain entropy controls the coil dimension. If monomer – monomer interactions are more favoured the polymer adopts a globular structure to minimize the interaction area with the solvent. These interactions are well understood in molecular solvents but the situation is more complex in ILs due to the heterogeneous bulk liquid morphology. In addition to polymer-solvent interactions, the extension of polymer coils is also influenced by the interactions between neighbouring coils, which is concentration dependent. In the dilute regime, polymer coils are relatively separated from one another and coil extension is determined mainly by solvent interactions, such that the radius of gyration (Rg) only weakly decreases with polymer concentration. The concentration at which contact between adjacent polymer chains become appreciable is known as the overlap concentration (c*), and denotes the beginning of the semidilute regime. In this regime, the polymers form a non-connected network with a characteristic mesh size smaller than Rg, and which decreases rapidly with increasing
concentration. At high concentrations, the loose polymer network present in the semidilute regime is transformed into a highly entangled arrangement with properties similar to a polymer melt. In this study the concentration-dependent morphology PEO dissolved in EAN in the dilute and the semidilute concentration regimes is examined, and the favourability of PEO – EAN interactions is ascertained.

SANS spectra for 38 kDa d-PEO dissolved in h-EAN at concentrations between 1 mg/cm$^3$ and 122 mg/cm$^3$ are presented in Figure 1. Repeat measurements of the same samples 48 hours apart confirmed that PEO dissolved in EAN is stable to aggregation over this time period. This is in stark contrast to PEO dissolved in water, where light scattering experiments reveal that the polymers start to agglomerate after a short time (~24h), even though water is a good solvent for PEO. The absence of PEO agglomerates in EAN might be a consequence of steric effects relating to the solvent or the viscosity of EAN being 30 times greater than that of water.

The form of the data for all concentrations in Figure 1 is consistent with a polymer coil. The scattering intensity increases with concentration up to 24 mg/cm$^3$, but the shape of the scattering function remains the same, indicating that the coil morphology is largely unchanged. This means that interactions between neighboring polymers are weak, consistent with the dilute regime. At higher polymer concentrations (60 and 122 mg/cm$^3$) the scattered intensity at low scattering vectors (q) decreases, and the shape of the scattering function changes. This is a consequence of the dimension of the polymer coil being reduced and/or overlaps between chains becoming appreciable, such that there are fewer long length scale correlations and more short distance correlations. This change is consistent with moving from the dilute into the semidilute regime.
Figure 1: Scattered neutron intensity as a function of scattering vector, \( q \), for d-PEO - h-EAN solutions at various polymer concentrations. Red lines are Debye model fits.

For the extraction of the \( R_g \) values model fits were applied to the experimental data (Fig. 1 red lines). The scattering of a polymer coil with excluding volume effects is described by:

\[
I(q) = \frac{I_0}{\nu U^{1/2} \gamma(2\nu, U)} - \frac{1}{\nu U^{1/\nu} \gamma(1, U)}
\]  

(1)

where \( I_0 \) is scaling factor, \( \gamma \) is the incomplete gamma function and \( \nu \) is Flory’s excluded volume parameter which is connected to the Porod exponent (\( m \)) via: \( \nu = 1/m \), \( m \) is evaluated separately at high \( q \) values (compare Figure 4).

\[
U = \frac{q^2 R_g^2 (2\nu + 1)(2\nu + 2)}{6}
\]  

(2)

Least square fits were performed with \( R_g \) and the \( I_0 \) as fit parameter and \( \nu = \text{const} \). The extracted \( R_g \) values as function of concentration are summarized in Figure 2. For concentrations less than 24 mg/cm\(^3\), \( R_g \) decreases weakly with increasing concentration (\( R_g \sim c^{-0.24} \)), in accordance with previous results for PEO dissolved in [Bmim][BF\(_4\)].\(^{30}\) At higher concentrations \( R_g \) decreases much
more strongly with concentration \((R_g \sim c^{-1})\), reflecting the change in the form of the scattering data at the same concentrations in Figure 1. This confirms that \(c^*\) lies between 24 and 60 mg/cm\(^3\).

**Figure 2:** \(R_g\) as evaluated from polymer coil model fits versus concentration. Red lines show linear regression fits to the data. Dashed line shows the calculated overlap concentration, \(c^*\).

In the dilute solution regime, and at low \(q\), the scattered intensity can be approximated by the Zimm formula.\(^{44}\)

\[
\frac{Kc}{I(q)} \approx \frac{1}{M_w} \left(1 + \frac{q^2 R_g^2}{3}\right) + 2A_c c
\]

where \(c\) is the concentration of the polymer in g/cm\(^3\), \(M_w\) its molecular weight, and \(K = \left(\Delta \rho / \rho_{d\text{-PEO}}\right)^2 N_A^{-1}\) is the contrast factor, in which \(\Delta \rho\) is the difference in scattering length density between the polymer and the solvent (\(\Delta \rho = 5.96 \times 10^{-6}\) Å\(^2\)), \(\rho_{d\text{-PEO}}\) is the density of d-PEO (1.27 g/cm\(^3\)) and \(N_A\) is the Avogadro constant. This gives \(K = 3.6 \times 10^{-3}\) mol cm\(^2\)/g\(^2\). \(A_2\) is the second virial coefficient, describing polymer – polymer interactions in the presence of a solvent. Repulsions between polymers in a good solvent give \(A_2 > 0\), \(A_2 = 0\) at the theta condition, and attractions between polymer chains in poor solvents give \(A_2 < 0\).
Zimm analysis allows the determination of the unperturbed coil dimension (radius of gyration at infinite dilution) as well as the molecular weight of the polymer by extrapolation of the scattering data to zero concentration and zero angle\textsuperscript{45}. Figure 3 shows a Zimm plot ($Kc/I(q) \text{ vs } (q^2 + c \times \text{const.})$) of the scattering data in the dilute solution regime, showing extrapolations to $q^2 = 0$ (green line) and $c = 0$ (blue line). At higher concentrations, the data is nonlinear. This yields $M_w = 39.6$ kDa, which is acceptably close to the 38 kDa stated by the supplier. The second virial coefficient of $1.6 \times 10^{-6}$ cm$^3$ mol g$^{-2}$ is positive, but much smaller than $2.2 \times 10^{-3}$ cm$^3$ mol g$^{-2}$ measured in water\textsuperscript{46} or $2.0 \times 10^{-3}$ cm$^3$ mol g$^{-2}$ measured in [bmim][BF$_4$].\textsuperscript{30} The PEO chains thus interact in the presence of EAN close to 0 conditions.

![Zimm plot](image)

**Figure 3:** Zimm plot for d-PEO in H-EAN for concentrations between 1 and 60 mg/cm$^3$ (most right). Full dots represent the experimental data, red lines are linear fits to the experimental data, open dots are the extrapolation of the experimental data to $q^2 = 0$, green full line is the fit to open dots. The blue line represents the Zimm plot for the extrapolation in the limit of zero concentration.

The unperturbed $R_g$ of PEO in EAN is 8.1 nm, which is considerably smaller than the 9.6 nm obtained for the same molecular weight PEO in water ($R_{g,H2O} = 0.215M_w^{0.58}$),\textsuperscript{46} consistent with water being a better solvent for PEO. A more compact morphology in EAN is in good agreement with previous reports of poor headgroup solvation for oligo-ethylene oxide surfactants in micelles.\textsuperscript{8}
hemimicelles adsorbed at the graphite EAN interface,\textsuperscript{9} and adsorbed at the air–EAN interface.\textsuperscript{14,15} Similarly, adsorbed layers of PEO at the silica–EAN interface adopt a compact mushroom conformation rather than an extended brush layer like that formed in water.\textsuperscript{29}

For dilute polymer solutions in good solvents (for instance polystyrene in CS\textsubscript{2} \textsuperscript{47}) $R_g$ is found to decrease as $c^{-0.125}$, consistent with theoretical predictions.\textsuperscript{47,48} We observe a much stronger $c^{-0.24}$ dependence for PEO in EAN, which is similar to previous observations for d-PEO dissolved in the aprotic ionic liquid [Bmim][BF\textsubscript{4}].\textsuperscript{30} This suggests that such scaling of coil dimensions with concentration may be a general feature of ionic liquid solvents.

Curiously, the same scaling of $R_g$ is observed for polyelectrolytes in salt-free aqueous solutions.\textsuperscript{49-51} Polyelectrolyte chain conformation is a consequence of forces that operate on three different length scales. At short distances, the local monomer structure is a consequence of thermal energy and morphologies similar to those observed for a neutral polymer result. Over intermediate distances (a few monomer units) electrostatic repulsion between monomer groups result in chain extension, but over larger distances these repulsions are screened and a random flight structure results. Similar behaviour might be generated for PEO in EAN and other ILs by a preferential affinity of the cation or anion for PEO, for example by H-bonding of the ammonium group to the ether oxygen or solvophobic association of ethyl groups. This would lead to enrichment of one ion along the PEO chain, giving rise to similar electrostatic forces on intermediate length scales as in polyelectrolyte solutions.

Calculation of $c^*$\textsuperscript{52} using this extrapolated $R_g = 8.1\text{nm}$ suggests $c^* = 29 \text{ mg/cm}^3$, which is in excellent agreement with the experimental data. In the semi-dilute region, we observe a $c^{-1}$ dependence of the correlation length or apparent $R_g$, which is expected for entangled polymer solutions.\textsuperscript{53}

Figure 4 shows the asymptotic behaviour at $qR_g >> 1$, which results from the local arrangement of monomer units within each polymer coil. At high $q$ the intensity decays according to $I(q) \sim q^{-m}$;
For fully extended polymer chains $m = 1$, while for chain in a $\theta$ solvent $m = 5/3$. Higher values of $m$ correspond to a more compact morphology. In the dilute regime an exponent of $1.62\pm0.02$ is observed, consistent with a Gaussian conformation, and that the level of solvation is close to the $\theta$ condition. This is more compact than that reported for dilute solutions of PEO in good solvents like water ($m = 1.44$) or methanol ($m = 1.55$). In contrast, $m = 2$ has been reported for d-PEO dissolved in [Bmim][BF$_4$] in the dilute regime, which is a consequence of less extended coils.

In the semidilute regime the high $q$ scattering follows $I(q) \sim q^{-1.38}$. This significant reduction in $m$ is primarily a consequence of the polymer coil adopting a more elongated arrangement at higher concentrations. As the polymer concentration is increased, the (average) spherical morphology becomes unfavourable as a sphere can only occupy 74% of the available volume. A slightly more elongated conformation will space fill more effectively, even if inter chain entanglements are appreciable.

Figure 4: Double logarithmic SANS spectra for various concentration of d-PEO in h-EAN (symbols) together with linear fits (red lines) in the high $q$ – range (concentrations in mg/cm$^3$ are 1 (○), 2 (●), 5 (□), 11 (■), 24 (◊), 60 (♦) and 122 (○)).

In the high $q$ region, the scattering arises from correlations between segments in individual coils, and is independent of interactions. This is shown in Figure 5, where the scattering normalized by
concentration is very similar for all samples examined at $q > 0.2 \, \text{Å}^{-1}$. This means that, PEO can be regarded as $\sim 3 \, \text{nm}$ d-PEO ‘blobs’, inside which the proximity of monomers to one another is independent of concentration.

![Figure 5](image)

**Figure 5**: Scattering spectra normalized by concentration for various d-PEO - h-EAN solutions

The H-bonding capacity of EAN has been widely credited for its ability to promote amphiphilic self-assembly, and recent studies have shown that EAN itself exhibits a form of amphiphilic self-assembly. Both characteristics may play a role in its solvent quality for PEO. Recent molecular dynamic simulations of 1,3-dimethylimidazolium hexafluorophosphate ([Emim][PF$_6$]) dissolved in a PEO matrix found that the distance between the cation and the PEO ether oxygen is less than the average distance between the cation and the anion, which suggests that the cation is solvated by ether oxygens, and recent light scattering experiments by Villari et al. have provided experimental support for this result. However, the presence of PEO did not significantly disturb the position of the anion relative to the cation. This suggests that hydrogen bonds between the ethylammonium cation and the PEO chain play a key role in solubility. As solvation of the ether oxygens by ammonium is governed by a competition with the anion, we would predict that a better H-bonding anion should reduce the solubility of PEO. Preliminary measurements indicate that PEO is not soluble in ethylammonium formate, which is consistent with this prediction.
Further, the simulation suggested that [Emim][PF₆] did not change the \textit{trans} and \textit{gauche} arrangements about the C-C and C-O bonds, due to the large volume of the cations involved. As EAN ions are somewhat similar in size, similar behaviour might be expected. The absence of a cloud point for PEO in EAN up to at least 150°C may suggest that the nature of the interactions between the polymer and the solvent, and therefore the PEO morphology and polarity,\textsuperscript{59} are largely unaffected by temperature.

Conclusions

The concentration dependant morphology of PEO dissolved in EAN has been determined through analysis of SANS spectra. At infinite dilution the PEO \(R_g\) is 8.1 nm, slightly less than the value obtained in water of 9.4 nm. A more contracted conformation implying that EAN is a less good solvent for PEO than water, which was confirmed by calculation of the 2\textsuperscript{nd} virial coefficient using Zimm analysis. The value obtained was only slightly greater than zero, suggesting that EAN is a good solvent for PEO but very close to a \(\theta\) solvent. As concentration increases through the dilute regime \(R_g\) decreases according to a \(R_g \sim c^{-0.24}\) dependence due to steric interactions between neighboring coils. This rate of decay is greater than that observed in aqueous systems which is a consequence of the reduced coil dimension in EAN shifting the overlap concentration to higher values. This means that steric effects do not occur until higher polymer concentrations are reached, but once they do occur they are stronger. The same concentration dependence has been reported for PEO in an aprotic ionic liquid,\textsuperscript{30} and for a polyelectrolyte in low salt conditions, which could mean that one of the ionic liquid ions has greater affinity for the PEO chain than the other, resulting in a net charge. In the semidilute regime the average polymer coil shape changes from a sphere to slightly more elongated arrangement to space fill more effectively, and loose interpenetration of chains can occur. The higher rate of decay (\(R_g \sim c^{-1}\)) above the overlap concentration reflects the rapid change in the PEO interconnected network mesh size. Both above and below the overlap
concentration, the arrangement of monomers on length scales of less than 3 nm is unaffected by increasing polymer concentration. This suggests that the overall decrease in coil dimension that occurs is a consequence of tighter packing of ~ 3 nm polymer ‘blobs’ into a smaller volume. Inside the dimensions of the ‘blob’ the proximity of monomers to one another is unaffected.

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