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Conformation of poly(ethylene oxide) dissolved in the solvate ionic liquid [Li(G4)]TFSI

Zhengfei Chen,^a Paul A. FitzGerald,^b Gregory G. Warr,^b Rob Atkin,^{a*}

^a Newcastle Institute for Energy and Resources, The University of Newcastle, Callaghan, NSW, Australia

^b School of Chemistry, The University of Sydney, Sydney, NSW 2006 Australia

*rob.atkin@newcastle.edu.au

Abstract

The conformation of 38 kDa PEO in a solvate ionic liquid (SIL), lithium tetraglyme bis(trifluoromethanesulfonyl)amide ([Li(G4)]TFSI) from dilute to concentrated solution regimes has been determined by small angle neutron scattering and rheology. SANS analysis reveals that [Li(G4)]TFSI is better than a theta solvent (theta-good) for PEO. The variation of the radius of gyration (R_g) and viscosity as a function of polymer concentration allow the overlap concentrations, c^* and c^{**} , to be identified at 13 mg/mL and 50 mg/mL, respectively, which are similar to values reported previously for conventional ionic liquids. Unlike water and conventional ionic liquids, [Li(G4)]TFSI cannot form hydrogen bonds with PEO. Thermal gravimetric analysis indicates that the solvation of PEO by [Li(G4)]TFSI is a consequence of PEO forming coordinate bonds with the lithium by displacing the anion, but without displacing the glyme molecule.

Key words: SANS, solvate ionic liquids, PEO confirmation, rheology

TOC Graphic

PEO dissolves in [Li(G4)]TFSI via coordination with Li^+ .

Introduction

Over the last decade, ionic liquids (ILs) have attracted substantial research attention for catalysis,^{1,2} surfactant self-assembly,³⁻⁸ materials synthesis,⁹⁻¹³ lubrication,¹⁴⁻¹⁶ electrochemistry,^{17,18} and their nanostructure in the bulk¹⁹⁻²¹ and at interfaces.²²⁻²⁵ In a recent review article, Angell *et al.* classified ILs into four categories: aprotic, protic, inorganic ILs and solvate ILs (SILs).²⁶ In SILs, ligand molecules strongly coordinate with cations or anions, forming complex ions.

The Watanabe group have reported a series of SILs prepared from equimolar mixtures of methyl-terminated oligoethers (or glymes, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$, abbreviated *Gn*) and certain alkali metal (Li, Na and K) salts.²⁷⁻³⁰ Solvate ILs are classified as “good” or “poor” depending on the relative affinities of the glyme ligand and anion for the cation.³¹ For example, $[\text{Li}(\text{G4})]\text{TFSI}$ is a good solvate IL because the weakly basic TFSI (bis-trifluoromethanesulfonimide) anion does not compete effectively for Li^+ , and stable complex cations ($[\text{Li}(\text{G4})]^+$) result. Molecular dynamic simulations suggest that, on average, G4 oxygen's occupy 4.5 of the lithium ion's 5 coordination sites, with the TFSI anion occupying the remaining 0.5 sites relatively weakly.³² Conversely, mixing lithium nitrate (LiNO_3) with G_4 results in a mixture of $[\text{Li}(\text{G4})]^+$, NO_3^- , Li^+ and free glyme, in equilibrium, due to the strongly basic NO_3^- anion competing to solvate Li^+ .²⁸ The resultant mixture is classified as a poor solvate IL.³¹ Good SILs have properties similar to conventional ILs, including low melting point, negligible vapour pressure, high ionic conductivity, and wide electrochemical windows. SILs formed from lithium salts are attractive charge storage electrolytes due to the very high Li^+ content and relatively low viscosity.^{27,30,33} Polymers such as polyethylene oxide (PEO) are frequently added to electrolytes in these devices as they can suppress dendrite growth during the cycling of lithium metal. Therefore, in addition to being interesting from a fundamental standpoint, understanding the interactions between PEO and SILs is important for enabling the use of SILs in devices.

Several groups have examined the solubility of PEO in conventional protic and aprotic ILs.³⁴ PEO is soluble in many conventional imidazolium-based ILs, including 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ($[\text{EMIM}]\text{TFSI}$),³⁵ 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}][\text{PF}_6]$),^{36,37} 1-ethyl-3-methylimidazolium methylsulfate ($[\text{EMIM}][\text{EtSO}_4]$),³⁸ 1-ethyl-3-

methylimidazolium tetrafluoroborate ([EMIM]BF₄),³⁹ and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄),^{39,40} due to the hydrogen bonding interactions between the imidazolium cations and PEO chains. However, Rodriguez *et al.* reported that 1-alkyl-3-methylimidazolium chloride ([C_nMIM][Cl]) and PEO were not miscible and formed biphasic liquid mixtures.⁴¹ This is likely because hydrogen bonding between the imidazolium cations and Cl⁻ anions are preferred over PEO – cation H-bonds.⁴¹

The properties of polymer solutions depend on the chain conformation, described in terms of the radius of gyration R_g , which is the average root-mean-squared distance of any point in the polymer coil from its centre of mass. The size of a polymer chain is determined by the solvent quality. Polymer solvents are categorised as poor, theta (θ) or good solvents.⁴² In a good solvent, favourable interactions between the polymer and the solvent lead to the chain adopting a more swollen conformation. In a poor solvent, the chain collapses because polymer – polymer interactions are more favourable than those between the polymer and solvent. In the theta condition, polymer - polymer and polymer - solvent attractions are equal. The theta condition is observed in polymer melts,^{43,44} where the polymer is the solute and the solvent, and other systems.^{45,46} The polymer coil size, expressed as R_g , is related to its molecular weight by $R_g = KM^\nu$, where K is a constant that depends on the polymer type and ν is the Flory exponent. In general, ν is 0.6 for a good solvent, 0.5 for a θ solvent and 0.33 for a poor solvent.⁴⁷

There are relatively few studies of PEO conformation in ILs. Small angle neutron scattering (SANS) has been used to probe PEO in ethylammonium nitrate (EAN),⁴⁸ and rheology has been used to study PEO in EAN and propylammonium nitrate (PAN).⁴⁹ The conformation of PEO in [BMIM]BF₄ has been investigated using SANS⁵⁰ and atomistic simulations.⁴⁰ These studies reveal that [BMIM]BF₄ is a good solvent for PEO, and PAN is a theta solvent, while EAN is an intermediate theta-good solvent. The atomistic simulations show that the solvation free energy of PEO in [BMIM]BF₄ is more negative than for water, attributed to strong hydrogen bonding between PEO and the imidazolium cation.⁴⁰ PEO is soluble in EAN and PAN due to hydrogen bonds between the cation ammonium protons and the PEO ether oxygens, and EAN is a better solvent for PEO than PAN because it can form more hydrogen bonds per unit volume.⁵¹

The R_g and viscoelastic properties of dissolved polymers are characterised by two concentrations. The coil overlap concentration (c^*) defines the crossover from dilute region to the semidilute region. In the dilute regime, gentle decreases in R_g and increases in viscosity are noted as the chains are relatively isolated and interact weakly with one another. In the semi-dilute regime, R_g decreases more strongly with increasing polymer concentration as repulsive interactions from neighbouring chains cause the coils to contract.⁴² These repulsions, along with inter chain entanglements, cause the viscosity to increase more strongly with concentration in this regime. c^{**} defines the crossover from semidilute to concentrated regime. Above c^{**} there is significant overlap of polymer chains and R_g tends to a constant value. Here the polymer chains approach the θ condition (unperturbed size) because polymer – polymer interactions dominate as the overall composition changes from solvent-rich towards polymer melt. Viscosity increasing dramatically with concentration in this regime because chain entanglements increase as the solvent volume fraction decreases.

In this work, we use SANS and rheology to examine the conformation of PEO (38 kDa) in [Li(G4)]TFSI. At high concentrations a mixture of hydrogenous and deuterated PEO is used to achieve zero average contrast (ZAC) which enables R_g to be extracted even when there is significant overlap of the coils.^{42,52,53} c^* and c^{**} are determined from the change in R_g and viscosity as a function of polymer concentration, and the solvent quality from data fitting and Zimm analysis. These experiments, combined with thermal gravimetric analysis (TGA) results, provide insight into the mechanism by which PEO is solubilised in [Li(G4)]TFSI.

Experimental Section

The solvate IL, [Li(G4)]TFSI, was prepared by mixing equimolar tetraglyme (G4) (Sigma Aldrich) and bis(trifluoromethanesulfonyl)amide (LiTFSI) (Sigma Aldrich) at 50 °C with constant stirring on a hot plate overnight. The clear solvate IL was further dried at 120 °C for 3 hours and the water content was 0.04 wt% determined by Karl Fisher titration. Fully deuterated poly(ethylene oxide) (d-PEO) with molecular weight of 38 kDa was obtained from Polymer Source (Canada). The corresponding hydrogenous poly(ethylene oxide) (h-PEO) was purchased from Fluka. d-PEO-[Li(G4)]TFSI, d-PEO and h-PEO-[Li(G4)]TFSI, and h-PEO-

Li(G4)]TFSI solutions from 0.1 to 11 wt% were prepared several days prior to measurement to ensure complete mixing.

Small angle neutron scattering (SANS) experiments were conducted using the QUOKKA beamline⁵⁴ at ANSTO (Australia) using 1 mm path-length Hellma Cells. An incident wavelength of 5.0 Å ($\Delta\lambda/\lambda = 0.07$) was used with sample-to-detector distances of 2 m and 12 m to provide a q range of 0.006 to 0.34 Å⁻¹. Raw SANS data were reduced to 1D data in IGOR Pro with reduction procedures provided by NIST modified for use on QUOKKA.⁵⁵ All experiments were carried out at room temperature.

At high polymer concentrations, when there is significant overlap of chains, isotope labelling can be used to determine polymer dimensions. The general equation that describes the coherent neutron cross section per unit volume, $I(q)$, for solutions of identical deuterated and hydrogenous polymers, is given by⁴²

$$I(q)/nN^2 = \varphi(1 - \varphi)(b_H - b_D)^2P(q) + [\varphi b_D + (1 - \varphi)b_H - b_s(v_p/v_s)]^2S(q). \quad (1)$$

In equation (1), $P(q)$ is the single-chain form factor which contains information on the intramolecular correlations (e.g. R_g); $S(q)$ is the total scattering structure factor which contains information both on intra- and intermolecular correlations between monomer units and is related to both R_g and the correlation length (ξ). The scattering vector q is $4\pi\lambda^{-1} \sin \theta$, in which λ is the neutron wavelength and 2θ is the scattering angle; n and N are the number density and degree of polymerization of the polymer molecules; b_H , b_D , and b_s are the scattering lengths of the hydrogenous and deuterated monomeric units, and the solvent; v_p/v_s is the ratio of specific volumes for polymer and solvent; φ is the volume fraction of polymer chains that are deuterated.

Rheological measurements of h-PEO-[Li(G4)]TFSI solutions were performed on a TA Instruments AR-G2 rheometer using the cone and plate arrangement with a cone of 40 mm diameter and angle of 1° 59' 36".

Shear dependent viscosities were measured by increasing the shear rate from 1 to 1000 s⁻¹. All

measurements were maintained at 25 °C. A thermogravimetric analysis (TGA) of 5 wt% 35 kDa PEO in pure G4 and [Li(G4)][TFSA] was performed respectively on a TG/TDA analyser (PerkinElmer) from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under nitrogen gas flow (20 mL min⁻¹).

Results

SANS data for d-PEO dissolved in [Li(G4)]TFSI (bulk contrast) at low concentrations (between 1.4 mg/mL and 48.5 mg/mL) is shown in Figure 1. When the PEO is fully deuterated, $\varphi = 1$ and the first term on the right-hand side of equation (1) is zero. This means that fits to the total scattering $S(q)$ using the polymer excluded volume effect (eq. 2 and 3)⁵⁶ can be used to determine R_g and the Flory exponent (ν) for each PEO concentration, where I_0 is the scaling factor and γ is the incomplete gamma function.

$$I(q) = \frac{I_0}{vU^{\frac{1}{2\nu}}} \gamma\left(\frac{1}{2\nu}, U\right) - \frac{1}{vU^{\frac{1}{\nu}}} \gamma\left(\frac{1}{\nu}, U\right), \quad (2)$$

$$\text{where } U = \frac{q^2 R_g^2 (2\nu+1)(2\nu+2)}{6} \quad (3)$$

Data fits using this model are shown in Figure 1 (solid lines) and the fitting parameters are presented in Table 1. The Flory exponent is constant over the full concentration range at 0.55 ± 0.02 .

Figure 1. SANS intensity for d-PEO-[Li(G4)]TFSI solutions with background subtracted. Lines are Polymer Excluded Volume model fits to the data.

Table 1. Fitting parameters for d-PEO- [Li(G4)]TFSI solutions.

[PEO] (mg/mL)	Excluded volume fit		Ornstein-Zernike
	R_g (Å)	Flory exponent, ν	ξ (Å)
1.43	69	0.54	45
2.78	67	0.54	42
4.37	67	0.54	42
8.84	60	0.54	38
13.3	55	0.55	34
19.5	48	0.56	30
33.8	39	0.56	23
48.4	31	0.57	19

In polymer solutions, ξ is the average distance between adjacent contact points, which is independent of molecular weight but decreases when inter chain repulsions become appreciable at higher concentrations.⁵⁷ For the data in Figure 1, ξ can be determined from $S(q)$ using the Ornstein-Zernike formula⁵⁸:

$$I(q) = I_0/(1 + q^2\xi^2) \quad (4)$$

The fits obtained using the Ornstein-Zernike formula are shown in the Supporting Information (SI) in Figure S1, and the ξ values are presented in Table 1.

The SANS data in Figure 1 can also be analysed using the Zimm formula:⁵⁹

$$\frac{Kc}{I(q)} \approx \frac{1}{M_w} \left(1 + \frac{q^2 R_g^2}{3} \right) + 2A_2c \quad (5)$$

in which c is the polymer concentration, and M_w its molecular weight. $K = (\Delta\rho/\rho_{PEO})^2 N_A^{-1}$, is the contrast factor, where $\Delta\rho$ is the difference in neutron scattering length density between PEO and the solvent ($\Delta\rho = 5.23 \times 10^{-6} \text{ Å}^{-2}$), ρ_{PEO} is the apparent density of PEO (1.2 g cm^{-3}), N_A is the Avogadro constant, and A_2 is

the second virial coefficient. $A_2 > 0$ in a good solvent due to favourable polymer – solvent attractions, $A_2 = 0$ at the θ condition and $A_2 < 0$ in a poor solvent due to polymer – polymer interactions being preferred. A Zimm plot ($Kc/I(q)$ vs $(q^2 + c)$) of the SANS data is shown in Figure 2 with extrapolations to $c = 0$ and $q = 0$,⁶⁰ revealing that the fully swollen coil size (R_g at infinite dilution) is 86 Å.

Figure 2. Zimm plot of d-PEO-[Li(G4)]TFSI solutions at concentration between 1 and 20 mg mL⁻¹. Open dots and open squares are the extrapolation of the experimental data to $c = 0$ and $q^2 = 0$, respectively.

At higher PEO concentrations the ZAC condition is used to resolve the polymer conformation. ZAC is achieved by using $\varphi = 0.16$ (meaning that of the total added PEO 16 vol% is d-PEO and 84 vol% is h-PEO) such that $\varphi b_D + (1 - \varphi)b_H = b_s(v_p/v_s)$. SANS data for the ZAC samples are shown in Figure 3. Under the ZAC condition, the second part of the right-hand side of equation (1) is zero, and R_g is determined from $P(q)$ using a Guinier-Porod model (eq. 6 and 7)⁶¹:

$$I(q) = G \exp\left(\frac{-q^2 R_g^2}{3-s}\right) \quad \text{for } q \leq q_1 \quad (6)$$

$$I(q) = \frac{D}{q^d} \quad \text{for } q \geq q_1 \quad (7)$$

where d is the Porod exponent ($d = v^{-1}$) and s is the dimensional variable. s describes the 3 dimensional shape of the scatters: $s = 0$ for globular objects, $s = 1$ for rods, and $s = 2$ for lamellae.⁶¹ G and D are the

Guinier and Porod scale factors, respectively.⁶¹ The solid lines in Figure 2 are fits using this model, and the fit parameters are given in Table 2.

Figure 3. SANS intensity for PEO-[Li(G4)]TFSI solutions at ZAC with background subtracted. Lines are Guinier-Porod model fits to the data.

Table 2. Guinier-Porod fitting parameters for the solutions of d-PEO and h-PEO in [Li(G4)]TFSI under ZAC.

[PEO] (mg/mL)	R_g (Å)	Porod exponent, d	Dimensional variable, s
49.2	40	1.9	0.28
71.7	38	1.9	0.29
113	38	1.9	0.25
141	38	1.9	0.27

Figure 4 shows viscosity as a function of shear rate from 1 to 1000 s⁻¹ for PEO solutions in [Li(G4)]TFSI as a function of concentration at 25 °C. The viscosity increases significantly with increasing the PEO concentration. The neat solvent is a Newtonian fluid in the whole shear range, but in the PEO solutions, thinning occurs at higher shear rates (above ~250 s⁻¹). This is consistent with previous results for PEO in EAN, PAN,⁴⁹ and in water,⁶² and is attributed to disentanglement of adjacent polymer chains under shear.

Figure 4. Apparent viscosity vs shear rate for various PEO-[Li(G4)]TFSI solutions at 25 °C.

Discussion

In polymer solutions, the solvent quality indicates whether polymer – polymer or polymer – solvent interactions are favoured. In a good solvent, favourable polymer – solvent interactions lead to chain swelling while in a poor solvent polymer – polymer interactions are stronger leading to contraction of the coil. In this work, the solvent quality is assessed via the Flory exponent derived from the fits the SANs data in the bulk contrast (Figure 1) and ZAC (Figure 2), and the Zimm plot shown in Figure 3.

For the bulk contrast and ZAC samples, the Flory exponents are 0.55 ± 0.02 and 0.53 respectively. The second virial coefficient, A_2 , determined from the Zimm plot is $0.7 \times 10^{-3} \text{ cm}^3 \text{ mol g}^{-2}$. These results indicate that [Li(G4)]TFSI is between a theta and good solvent for PEO. Second virial coefficients for PEO in water, EAN and [BMIM]BF₄ are 2.2×10^{-3} ,⁶³ 1.6×10^{-6} ,⁴⁸ and $2 \times 10^{-3} \text{ cm}^3 \text{ mol g}^{-2}$,⁵⁰ respectively. That is [Li(G4)]TFSI is a slightly less good solvent for PEO than water or [BMIM]BF₄, but better than EAN. This is striking, because PEO solubility in EAN is attributed to hydrogen bonds between cation hydrogens and ether oxygens, and Li(G4)]TFSI cannot form hydrogen bonds. R_g at infinite dilution from the Zimm plot analysis is 86 Å . This is between the values of 96 Å for water⁶³ and 81 Å for EAN,⁴⁸ and is again consistent with the differences in solvent quality.

The R_g and ξ values for the PEO solutions as a function of concentration are shown in Figure 5. For the bulk contrast samples, R_g first decreases slightly from 69 Å to 67 Å, and then decreases more rapidly with increasing concentration. This change in slope indicates the chain overlap concentration c^* , where the system transitions from the dilute into the semidilute regime. c^* is estimated to be 13 mg/mL from the intersection of the best fit lines. c^* for the same molecular weight PEO in EAN was found to be 28 mg/mL, consistent with the polymer coils being less swollen by a poorer solvent. In the semidilute regime, R_g follows a $c^{-0.25}$ dependence, similar to its behavior in EAN ($R_g \sim c^{-0.24}$)⁴⁸ and [BMIM]BF₄ ($R_g \sim c^{-0.25}$).⁵⁰

Figure 5. Radius of gyration, R_g , and correlation length, ξ , as function of PEO concentration (open symbols) and viscosity of PEO-[Li(G4)]TFSI solutions as function of PEO concentration (closed circles).

Similar trends are seen in the concentration dependence of ξ . At low concentrations, where inter chain interactions are minimal, ξ is approximately constant at 40 Å. As chains become compressed at higher concentrations in the semi dilute regime, ξ decreases sharply to around 20 Å.

As the extent of overlap between polymer coils increases with concentration through the semidilute regime, bulk contrast SANS tends to underestimate R_g at higher concentrations. This is because excluded volume effects are largely negated by intermolecular effects at polymer high concentrations.⁴⁴ However, using a mixture of d- and h-PEO under the ZAC conditions enables the coil dimensions in concentrated mixtures to be accurately determined.

Figure 5 confirms this: R_g determined using zero average contrast sample at 49 mg/mL is 40 Å, whereas the apparent R_g under bulk contrast conditions is 31 Å at the same concentration. Using ZAC conditions, R_g decreases very slightly from 40 Å to 38 Å, before remaining constant up to the highest concentration investigated. R_g is expected to tend towards a constant value at in the concentrated regime as polymer – polymer interactions become more prevalent and a theta-like condition is approached, and this suggests that c^{**} lies in the range 50-70 mg/mL. The dimensional variable (s) determined from the fits to the data is 0.2 (c.f. Table 2), suggesting that the polymers remain in a globular conformation ($s = 0$) even at these high concentrations.

Crossover concentrations, c^* and c^{**} , can also be determined from plots of viscosity as a function of polymer concentration, also shown in Figure 5 for PEO in [Li(G4)]TFSI. In Figure 5 the rate of change of viscosity with polymer concentration is nonlinear and typical of polymer solutions. In the dilute regime the viscosity of polymer solutions increases weakly with polymer concentration as interactions between chains are weak. In the semidilute regime, inter chain repulsions and entanglements increase so the viscosity increases more rapidly with concentration, while in the concentrated regime polymers are networked and significantly less mobile, so the viscosity increases strongly with polymer concentration. Thus c^* and c^{**} are revealed by the breakpoints in the viscosity data. This analysis suggests that c^* is 13 mg/mL, identical to that determined from the bulk contrast SANS experiment, and that c^{**} is 50 mg/mL, which is in the range expected from the ZAC scattering results. This value is less than that determined for EAN (57 mg/mL) and PAN (53 mg/mL)⁴⁹ but greater than in water (32 mg/mL), consistent with the variation in solvent quality.

The relationship between the relative viscosity (η_{sp}) and polymer concentration, c , in dilute solution may be described by the Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad (8)$$

where $\eta_{sp} = \frac{\eta_0}{\eta_{solvent}} - 1$, $[\eta]$ is the intrinsic viscosity, and k_H is the Huggins coefficient. k_H also provides an indication of the solvent quality. Fits to the viscosity data in the dilute regime give $k_H = 0.42$, which lies in the expected range for a good solvent ($k_H < 0.5$),⁴⁹ and is very similar to $k_H = 0.4$ found for PEO in water.

Thus, consistent with the SANS analysis, the viscosity data also suggests that [Li(G4)]TFSI is a theta - good solvent for PEO.

We now turn to the nature of the interactions between PEO and [Li(G4)]TFSI that produce theta - good solvency. PEO solubility in water, EAN, PAN and [BMIM]BF₄ is generally attributed to hydrogen bond donation from the solvent to the EO group ether oxygens. However, for [Li(G4)]TFSI, there are no hydrogen bond donors on either the [Li(G4)] cation or TFSI anion. PEO solubility in [Li(G4)]TFSI must either be due to attractions between PEO and lithium and/or PEO and G4.

In pure [Li(G4)]TFSI, the glyme molecule complexes Li⁺ in a crown ether like conformation to form the complex cation.²⁸ As PEO and glymes are both formed from EO units, this raises the possibility that PEO solvation in [Li(G4)]TFSI might result from the PEO ether oxygens forming coordinate bonds with lithium. In pure [Li(G4)]TFSI, it has been shown experimentally that there are negligible free glymes.⁶⁴ Therefore, for PEO – lithium coordinate bonds to form, the Li must have an accessible and available co-ordination site, or the glyme molecule must be partially or fully displaced.

Most Li⁺ complexes are 4 or 5 coordinated (although higher and lower coordination numbers are known⁶⁵) and typical coordination numbers for LiX-PEO complexes are 4 to 6.^{66,67} Recent molecular simulations suggest that the average coordination number (Li⁺/O) in [Li(G4)]TFSI is 4.5, with 0.5 Li⁺ coordinated by the oxygen in the anion.³² However, in a “good” SIL such as [Li(G4)]TFSI, the Li⁺-anion coordination is weaker than Li⁺-O in the glyme.³² Given the structural similarities between the PEO and glyme it may reasonably be expected that PEO displaces TFSI which could produce the observed solubility. However, it is unclear whether the PEO can also displace the G4. To resolve this, we performed TGA on a 5 wt% solution of PEO in [Li(G4)]TFSI, shown in Figure 6. For comparison, we also examined 5 wt% PEO in pure G4. The TGA curves for pure glyme and pure [Li(G4)]TFSI have been reported previously.²⁸

Figure 6. TGA curves of 5 wt% PEO in pure G4 and [Li(G4)]TFSI under N₂.

The published pure glyme data²⁸ and our 5 wt% PEO in G4 results are very similar until 95% of the mass is lost. At this point our data has a plateau that persists to about 350 °C, the thermal decomposition temperature of PEO. This shows that the glyme is lost from the system at the same temperature regardless of whether PEO is present or not, and that the PEO decomposition temperature is insensitive to the presence of glyme. Thus these results suggest no strong interactions between PEO and G4, as expected based on their chemical structures; only van der Waals interactions are expected.

The TGA traces for 5 wt% solution of PEO in [Li(G4)]TFSI and pure [Li(G4)]TFSI²⁸ are also remarkably similar over the entire temperature range. For pure [Li(G4)]TFSI, strong interactions between the glyme and lithium cause the G4 to be retained at higher temperatures.^{28,64} In poor SILs, where the interactions between the glyme and metal ion are weak and free glyme is present, significant mass loss is seen at lower temperatures. Therefore, if PEO displaced G4 from the lithium salt in the 5 wt% PEO in [Li(G4)]TFSI sample, mass loss due to free glyme at ~ 200°C would be observed. As it is not, this means that PEO does not entirely displace the G4 from Li.

The absence of free glyme in the 5 wt% PEO in [Li(G4)]TFSI sample combined with weak interactions between PEO and pure G4 lead us to suggest that the dominant mechanism of PEO solvation in

[Li(G4)]TFSI is the formation of coordinate bonds between PEO and the Li by displacement of weakly-bound anions. This is markedly different from water and conventional ILs, where solubility is a consequence of hydrogen bonding. It is possible that the PEO *partially* displaces the G4 to enable more than 0.5 bonds with each [Li(G4)]TFSI, but this is a detail which we cannot currently discern. Experiments are already underway examining PEO solubility and structure in different SILs that may help to resolve this issue.

Conclusions

SILs based on lithium salts have great potential as electrolytes due to their high lithium concentration and mobility. PEO is frequently added to Li based electrolytes to prevent dendrite formation during cycling, which causes a short circuit and device failure. In this work we have studied the structure of PEO dissolved in a solvate ionic liquid for the first time. Most of the characteristic values for the system is similar to those for PEO in conventional ILs, which is surprising because conventional ILs solvate PEO via hydrogen bonds whereas PEO appears to dissolve in the SIL via coordinate bonds between EO oxygens and Li in the complex [Li(G4)] cation. Despite this, in most respects the behaviour of PEO in [Li(G4)]TFSI is typical of polymer solutions.

The radius of gyration and Flory exponents determined from fits to the SANS data, the second virial coefficient from Zimm analysis and the Huggins coefficient determined from rheology all suggest that [Li(G4)]TFSI is better than a theta solvent PEO; it is a poorer solvent than water but slightly better than EAN and PAN despite their dense H-bond networks. The c^* of 13 mg/mL, determined from the dependence of R_g and viscosity on PEO concentration in [Li(G4)]TFSI is lower than in EAN and PAN, which is also consistent with a more expanded chain. c^{**} is also lower, consistent with the differences in solvent quality.

TGA results for PEO in [Li(G4)]TFSI solution are essentially identical to that of the pure SIL. This means that PEO forms a coordinate bond with the lithium ion without completely displacing the glyme molecule; if glyme molecules were displaced then they would be lost from the sample at lower temperatures. Currently

we are unable to determine whether the average number of coordinate bonds between the lithium glyme by lithium – PEO bonds; it is possible that the glyme molecules are partially displaced.

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References

- 1 V. I. Parvulescu and C. Hardacre, *Chem. Rev.* 2007, **107**, 2615-2665.
- 2 F. van Rantwijk and R. A. Sheldon, *Chem. Rev.* 2007, **107**, 2757-2785.
- 3 J. L. Anderson, V. Pino, E. C. Hagberg, V. V. Sheares and D. W. Armstrong, *Chem. Commun. (Cambridge, U. K.)* 2003, 2444-2445.
- 4 R. Atkin, S. M. C. Bobillier and G. G. Warr, *J. Phys. Chem. B* 2010, **114**, 1350-1360.
- 5 T. L. Greaves and C. J. Drummond, *Chem. Soc. Rev.* 2008, **37**, 1709-1726.
- 6 D. F. Evans, A. Yamauchi, R. Roman and E. Z. Casassa, *J. Colloid Interface Sci.* 1982, **88**, 89-96.
- 7 Z. Chen, P. A. FitzGerald, Y. Kobayashi, K. Ueno, M. Watanabe, G. G. Warr and R. Atkin, *Macromolecules* 2015, **48**, 1843-1851.
- 8 Z. Chen, T. L. Greaves, R. A. Caruso and C. J. Drummond, *J. Phys. Chem. B* 2015, **119**, 179-191.
- 9 H. C. Lin, P. W. de Oliveira, I. Grobelsek, A. Haettich and M. Veith, *Z. Anorg. Allg. Chem.* 2010, **636**, 1947-1954.
- 10 D. S. Jacob, A. Joseph, S. P. Mallenahalli, S. Shanmugam, S. Makhluף, J. Calderon-Moreno, Y. Koltypin and A. Gedanken, *Angew. Chem., Int. Ed.* 2005, **44**, 6560-6563.
- 11 Z. Li, L. Yu, L. Zheng, N. Li, S. Han and G. Li, *J. Dispersion Sci. Technol.* 2008, **29**, 1029-1034.
- 12 A. K. Mishra, N. H. Kim and J. H. Lee, *J. Membr. Sci.* 2014, **449**, 136-145.
- 13 Z. Chen, T. L. Greaves, R. A. Caruso and C. J. Drummond, *J. Mater. Chem.* 2012, **22**, 10069-10076.
- 14 H. Li, M. W. Rutland and R. Atkin, *Phys. Chem. Chem. Phys.* 2013, **15**, 14616-14623.
- 15 H. Li, R. J. Wood, M. W. Rutland and R. Atkin, *Chem. Commun. (Cambridge, U. K.)* 2014, **50**, 4368-4370.
- 16 J. Sweeney, F. Hausen, R. Hayes, G. B. Webber, F. Endres, M. W. Rutland, R. Bennewitz and R. Atkin, *Phys. Rev. Lett.* 2012, **109**, 155502.
- 17 H. Li, F. Endres and R. Atkin, *Phys. Chem. Chem. Phys.* 2013, **15**, 14624-14633.
- 18 H. T. Liu, Y. Liu and J. H. Li, *Phys. Chem. Chem. Phys.* 2010, **12**, 1685-1697.
- 19 R. Hayes, S. Imberti, G. G. Warr and R. Atkin, *Phys. Chem. Chem. Phys.* 2011, **13**, 3237-3247.
- 20 R. Hayes, S. Imberti, G. G. Warr and R. Atkin, *J. Phys. Chem. C* 2014, **118**, 13998-14008.
- 21 T. Murphy, R. Hayes, S. Imberti, G. G. Warr and R. Atkin, *Phys. Chem. Chem. Phys.* 2014, **16**, 13182-13190.
- 22 M. Mezger, H. Schröder, H. Reichert, S. Schramm, J. S. Okasinski, S. Schöder, V. Honkimäki, M. Deutsch, B. M. Ocko, J. Ralston, M. Rohwerder, M. Stratmann and H. Dosch, *Science* 2008, **322**, 424-428.
- 23 B. McLean, H. Li, R. Stefanovic, R. J. Wood, G. B. Webber, K. Ueno, M. Watanabe, G. G. Warr, A. Page and R. Atkin, *Phys. Chem. Chem. Phys.* 2015, **17**, 325-333.

- 24 A. Elbourne, K. Voitchovsky, G. G. Warr and R. Atkin, *Chem. Sci.* 2015, **6**, 527-536.
- 25 A. M. Smith, K. R. J. Lovelock, N. N. Gosvami, P. Licence, A. Dolan, T. Welton and S. Perkin, *J. Phys. Chem. Lett.* 2013, **4**, 378-382.
- 26 C. Austen Angell, Y. Ansari and Z. Zhao, *Faraday Discuss.* 2012, **154**, 9-27.
- 27 T. Tamura, T. Hachida, K. Yoshida, N. Tachikawa, K. Dokko and M. Watanabe, *J. Power Sources* 2010, **195**, 6095-6100.
- 28 K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko and M. Watanabe, *J. Phys. Chem. B* 2012, **116**, 11323-11331.
- 29 K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko and M. Watanabe, *J. Am. Chem. Soc.* 2011, **133**, 13121-13129.
- 30 C. Zhang, A. Yamazaki, J. Murai, J.-W. Park, T. Mandai, K. Ueno, K. Dokko and M. Watanabe, *J. Phys. Chem. C* 2014, **118**, 17362-17373.
- 31 T. Mandai, K. Yoshida, K. Ueno, K. Dokko and M. Watanabe, *Phys. Chem. Chem. Phys.* 2014, **16**, 8761-8772.
- 32 S. Tsuzuki, W. Shinoda, M. Matsugami, Y. Umebayashi, K. Ueno, T. Mandai, S. Seki, K. Dokko and M. Watanabe, *Phys. Chem. Chem. Phys.* 2015, **17**, 126-129.
- 33 T. M. Pappenfus, W. A. Henderson, B. B. Owens, K. R. Mann and W. H. Smyrl, *J. Electrochem. Soc.* 2004, **151**, A209-A215.
- 34 N. Winterton, *J. Mater. Chem.* 2006, **16**, 4281-4293.
- 35 Z. F. Bai, M. W. Nagy, B. Zhao and T. P. Lodge, *Langmuir* 2014, **30**, 8201-8208.
- 36 S. K. Chaurasia, R. K. Singh and S. Chandra, *J. Raman Spectrosc.* 2011, **42**, 2168-2172.
- 37 L. T. Costa and M. C. C. Ribeiro, *J. Chem. Phys.* 2006, **124**, 184902.
- 38 J. M. Harner and D. A. Hoagland, *J. Phys. Chem. B* 2010, **114**, 3411-3418.
- 39 H.-N. Lee and T. P. Lodge, *J. Phys. Chem. Lett.* 2010, **1**, 1962-1966.
- 40 J. Mondal, E. Choi and A. Yethiraj, *Macromolecules* 2014, **47**, 438-446.
- 41 H. Rodriguez, M. Francisco, M. Rahman, N. Sun and R. D. Rogers, *Phys. Chem. Chem. Phys.* 2009, **11**, 10916-10922.
- 42 G. Cheng, W. W. Graessley and Y. B. Melnichenko, *Phys. Rev. Lett.* 2009, **102**, 157801.
- 43 L. L. Cai and S. Granick, *Adv. Colloid Interface Sci.* 2001, **94**, 135-150.
- 44 G. D. Wignall and Y. B. Melnichenko, *Rep. Prog. Phys.* 2005, **68**, 1761-1810.
- 45 G. Adamo, A. Pelissetto and C. Pierleoni, *J. Chem. Phys.* 2013, **139**, 034901.
- 46 A. L. Kholodenko and K. F. Freed, *J. Chem. Phys.* 1984, **80**, 900-924.
- 47 B. Hammouda and D. L. Ho, *J. Polym. Sci., Part B: Polym. Phys.* 2007, **45**, 2196-2200.
- 48 O. Werzer, G. G. Warr and R. Atkin, *J. Phys. Chem. B* 2011, **115**, 648-652.
- 49 J. A. Smith, G. B. Webber, G. G. Warr, A. Zimmer, R. Atkin and O. Werzer, *J. Colloid Interface Sci.* 2014, **430**, 56-60.
- 50 A. Triolo, O. Russina, U. Keiderling and J. Kohlbrecher, *J. Phys. Chem. B* 2006, **110**, 1513-1515.
- 51 K. Fumino, A. Wulf and R. Ludwig, *Angew Chem Int Edit* 2009, **48**, 3184-3186.
- 52 J. S. King, W. Boyer, G. D. Wignall and R. Ullman, *Macromolecules* 1985, **18**, 709-718.
- 53 M. Benmouna and B. Hammouda, *Prog. Polym. Sci.* 1997, **22**, 49-92.
- 54 E. P. Gilbert, J. C. Schulz and T. J. Noakes, *Physica B: Condensed Matter* 2006, **385-386**, Part 2, 1180-1182.
- 55 S. R. Kline, *J. Appl. Crystallogr.* 2006, **39**, 895-900.
- 56 B. Hammouda, *Adv. Polym. Sci.* 1993, **106**, 87-133.
- 57 M. Adam and M. Delsanti, *Macromolecules* 1977, **10**, 1229-1237.
- 58 H. E. Stanley *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press, Oxford, 1971.
- 59 B. H. Zimm, *J. Chem. Phys.* 1945, **13**, 141-145.
- 60 C. B. Shogbon, J.-L. Brousseau, H. Zhang, B. C. Benicewicz and Y. A. Akpalu, *Macromolecules* 2006, **39**, 9409-9418.
- 61 B. Hammouda, *J. Appl. Crystallogr.* 2010, **43**, 716-719.
- 62 K. W. Ebaginin, A. Benchabane and K. Bekkour, *J. Colloid Interface Sci.* 2009, **336**, 360-367.
- 63 K. Devanand and J. C. Selser, *Macromolecules* 1991, **24**, 5943-5947.
- 64 K. Ueno, R. Tatara, S. Tsuzuki, S. Saito, H. Doi, K. Yoshida, T. Mandai, M. Matsugami, Y. Umebayashi, K. Dokko and M. Watanabe, *Phys. Chem. Chem. Phys.* 2015, **17**, 8248-8257.
- 65 U. Olsher, R. M. Izatt, J. S. Bradshaw and N. K. Dalley, *Chem. Rev.* 1991, **91**, 137-164.
- 66 J. D. Londono, B. K. Annis, A. Habenschuss, O. Borodin, G. D. Smith, J. Z. Turner and A. K. Soper, *Macromolecules* 1997, **30**, 7151-7157.