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## Glass transition, viscosity, and conductivity correlations in solutions of lithium salts in PEGylated imidazolium ionic liquids

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### ABSTRACT

Ionic liquids (ILs) are attractive as non-volatile and non-flammable electrolytes for lithium ion batteries. In this study, ionic conductivities of the solutions of lithium salts in ILs derivatized with poly(ethylene glycol) (PEG) were correlated with the viscosities and glass transition temperatures of these solutions. The ILs studied include 1-(monomethoxy PEG)-3-methylimidazolium bistriflamide and 1-( $\omega$ -perfluoroalkyl PEG)-3-methylimidazolium bistriflamide, the properties of which were compared with 1-(monomethoxy PEG)-3-methylimidazolium iodide, 1-( $\omega$ -perfluoroalkyl PEG)-3-methylimidazolium iodide, and 1-hexyl-3-methylimidazolium iodide. Binary solutions of lithium salts, lithium bistriflamide or lithium iodide, in ILs with common anions, were characterized using electrochemical impedance spectroscopy, cone and plate viscometry, and differential scanning calorimetry. Although the dissolution of the lithium salt would increase the concentration of charge-transporting ions in the solution, a decrease in conductivity was observed. The decrease was related to an increase in the glass transition temperature and an increase in viscosity. It was found that for a particular IL and lithium salt combination, the variation of viscosity or ionic conductivity with temperature could be characterized by the Vogel–Fulcher–Tammann expression,  $\exp\{A+BT_0/(T-T_0)\}$ , with fixed values of parameters  $A$  and  $B$ , that were independent of the concentration of the lithium salt in the solutions, and only temperature  $T_0$ , as the concentration-dependent parameter, which showed correlation to the glass transition temperatures of the solutions.

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### 1. Introduction

Ionic liquids (ILs) are nonflammable, electrochemically stable, and exhibit exceptionally low vapor pressures even at relatively high temperatures, which make them attractive as thermally safe solvents for lithium ion battery electrolytes [1–6]. These electrolytes are commonly prepared by dissolving lithium salts, such as  $\text{LiClO}_4$ ,  $\text{LiCl}$ ,  $\text{LiSCN}$ ,  $\text{LiTf}_2\text{N}$ , and  $\text{LiPF}_6$  in the IL solvent. Contrary to the expectation that an increase in the concentration of charge carriers in the electrolyte solution, because of the addition of lithium salt, would increase the conductivity of the solution, a decrease in conductivity is actually observed [7–13]. A primary objective of the present work is to develop a phenomenological understanding of the factors responsible for this decrease.

Poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) based solvents have been widely used as electrolyte materials for lithium ion batteries [14–20]. The basic oxygen atoms of the PEG tail coordinate with  $\text{Li}^+$  atoms and promote solubility of lithium salts [21,22]. The hopping of  $\text{Li}^+$  ions between the oxygen coordination sites in PEO or PEG can contribute to lithium conduction in these electrolytes, in addition

to the vehicular diffusion mechanism [20,23–25]. In a previous study, we synthesized and investigated the thermal and transport properties of imidazolium ILs functionalized with methoxy-terminated PEG, and found that PEGylation imparted lower molar mass normalized viscosities compared with the conventional 1,3-dialkylimidazolium ILs [1,26]. Moreover, the ionicity imparted by the imidazolium head group significantly improved the thermal stability of the polyether compounds [1]. The PEGylated ILs also showed excellent electrochemical stability in a  $\text{LiMn}_2\text{O}_4/\text{Li}$  cell [1].

In these PEGylated imidazolium ILs, H-bonding interactions between the PEG tail and the imidazolium ring are expected to “solvate” the cation and weaken electrostatic interactions between the cation and anion. Thus, these ILs were less viscous than 1,3-dialkylimidazolium ILs of comparable molecular weight [26]. In a subsequent study, we found that perfluoroalkyl-terminated PEG tails resulted in an increase in viscosity without a significant loss of conductivity [27].

We report herein the effect of the addition of a lithium salt on the conductivity, viscosity, and glass transition temperature of imidazolium ILs with PEGylated cations, previously synthesized and characterized by us [26,27]. In addition, a conventional 1,3-dialkylimidazolium IL, namely 1-hexyl-3-methylimidazolium iodide ([HexMeIm][I]), and its mixtures with  $\text{LiI}$ , were also studied. Based on a previous study [28],

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which showed that charge delocalization in cation and anion has a strong effect on the transport properties of the IL, ILs with two different anions, bistriflamide and iodide, were included in the present study. In contrast to iodide, which is a charge localized anion, bistriflamide is a highly charge delocalized anion. The selection of the two aforementioned ILs in the present study was based on these considerations, with a specific focus on the conduction effects of charge delocalization.

## 2. Theoretical considerations

### 2.1. Viscosity and glass transition

Arrhenius fluids exhibit a linear relationship between  $\ln \eta$  and  $1/T$ , where  $\eta$  is the viscosity and  $T$  is the absolute temperature. However, glass-forming liquids (including ILs) show a non-linear behavior, which is well-described by the Vogel–Fulcher–Tammann (VFT) equation [13,28,29], Eq. (1), and its variations [30,31]:

$$\ln \eta = \ln \eta_0 + \frac{BT_0}{T-T_0} \quad (1)$$

wherein,  $\eta_0$ ,  $B$ , and  $T_0$  are temperature-independent parameters of the model.

Eq. (1) can also be written in the form of Eq. (2):

$$\ln \eta = A + \frac{B}{\left(\frac{T}{T_0}\right) - 1} \quad (2)$$

where  $B$  is a parameter that characterizes the “fragility” of the IL and  $A$  is a constant [32].  $T_0$  is related to the glass transition temperature,  $T_g$ , and is lower by up to about 50 °C than the empirical  $T_g$ , as will be shown in this article.

According to Angell [32], viscous liquid behavior during cooling can be classified on the basis of “fragility”. “Strong” liquids show resistance to structural change and exhibit little reorganization with variation in temperature (near  $T_0$ ), and have higher values of  $B$  [28]. On the other hand, “fragile” liquids have glassy structures that change rapidly at their  $T_g$  and are associated with lower values of  $B$ . At temperatures significantly greater than  $T_0$ , the activation energy of viscosity is equal to  $RBT_0$ , where  $R$  is the gas constant [28].

### 2.2. Relationship between conductivity and viscosity

The ionic conductivity,  $\sigma$ , of a pure IL can be expressed as:

$$\sigma = F(c_+ \mu_+ + c_- \mu_-) = \frac{Fe}{k_B T} (c_+ D_+ + c_- D_-) \quad (3)$$

where  $F$  is the Faraday's constant;  $e$  is the magnitude of the charge carried by an electron;  $c_+$  and  $c_-$  represent the concentrations of free cations and anions, respectively;  $\mu_+$  and  $\mu_-$  represent the mobilities of the cations and anions, respectively;  $k_B$  is the Boltzmann's constant;  $T$  is the absolute temperature; and  $D_+$  and  $D_-$  represent the diffusivities of the cation and anion, respectively.

The molar concentrations of the free cations and the anions are related to the molar concentration,  $c_{IL}$ , of the IL as follows:

$$c_+ = c_- = \alpha_{IL} c_{IL} \quad (4)$$

where  $\alpha_{IL}$  is the fraction of the IL that has dissociated (and therefore, contributes to ionic current).  $\alpha_{IL}$  is related to the Haven ratio that can be determined from pulsed field gradient NMR experiments [28,33]. In the case of a pure IL,

$$c_{IL} = \frac{1}{V_{IL}} = \frac{\rho_{IL}}{MW_{IL}} \quad (5)$$

where  $V_{IL}$  is the molar volume,  $\rho_{IL}$  is the density, and  $MW_{IL}$  is the molecular weight of the IL. From Eqs. (3), (4), and (5):

$$\Lambda = \frac{\sigma}{c_{IL}} = \frac{Fe \alpha_{IL}}{k_B T} (D_+ + D_-) \quad (6)$$

where  $\Lambda$  is the molar conductivity of the IL.

Diffusion coefficients of cations and anions can be related to viscosity via the Sutherland–Einstein relation [28]:

$$D_{\pm} = \frac{k_B T}{C \pi r_{\pm} \eta} \quad (7)$$

where  $C$  is a constant,  $\eta$  is the viscosity of the IL, and  $r_+$  and  $r_-$  are the radii of the cationic and anionic diffusing species.

From Eqs. (6) and (7):

$$\Lambda = \frac{Fe \alpha_{IL}}{C \pi \eta} \left( \frac{1}{r_+} + \frac{1}{r_-} \right) \quad (8)$$

If  $\alpha_{IL}$ ,  $r_+$ , and  $r_-$  are constants, molar conductivity at different temperatures would be inversely proportional to viscosity of the IL.

In the case of a solution of IL and lithium salt (LiX, where X denotes the anion), Eq. (3) can be rewritten as:

$$\begin{aligned} \sigma &= F(c_+ \mu_+ + c_- \mu_- + c_{Li^+} \mu_{Li^+} + c_{X^-} \mu_{X^-}) \\ &= \frac{Fe}{k_B T} (c_+ D_+ + c_- D_- + c_{Li^+} D_{Li^+} + c_{X^-} D_{X^-}) \end{aligned} \quad (9)$$

Overall charge neutrality requires:

$$c_+ + c_{Li^+} = c_- + c_{X^-} \quad (10)$$

The concentrations of ions are related to the total concentrations,  $c_{LiX}$  and  $c_{IL}$ , of the lithium salt and IL in the solution, and the respective dissociated fractions,  $\alpha_{LiX}$  and  $\alpha_{IL}$ , by:

$$c_{Li^+} = c_{X^-} = \alpha_{LiX} c_{LiX} \quad (11)$$

and

$$c_+ = c_- = \alpha_{IL} c_{IL} \quad (12)$$

From Eqs. (9) to (12):

$$\sigma = \frac{Fe}{C \pi \eta} \left[ \alpha_{IL} c_{IL} \left( \frac{1}{r_+} + \frac{1}{r_-} \right) + \alpha_{LiX} c_{LiX} \left( \frac{1}{r_{Li^+}} + \frac{1}{r_{X^-}} \right) \right] \quad (13)$$

If  $\alpha_{IL}$  and  $\alpha_{LiX}$  are equal to 1 (that is, all IL and salt molecules are dissociated),

$$\sigma = \frac{Fe(c_{IL} + c_{LiX})}{C \pi \eta} \left[ \frac{c_{IL}}{c_{IL} + c_{LiX}} \left( \frac{1}{r_+} + \frac{1}{r_-} \right) + \frac{c_{LiX}}{c_{IL} + c_{LiX}} \left( \frac{1}{r_{Li^+}} + \frac{1}{r_{X^-}} \right) \right] \quad (14)$$

Thus, the molar conductivity of the solution is:

$$\Lambda = \frac{\sigma}{c_{IL} + c_{LiX}} = \frac{Fe}{C \pi \eta} \left[ x_{IL} \left( \frac{1}{r_+} + \frac{1}{r_-} \right) + (1-x_{IL}) \left( \frac{1}{r_{Li^+}} + \frac{1}{r_{X^-}} \right) \right] \quad (15)$$

where, in a binary solution,  $x_{IL}$  is the mole fraction of IL in the solution.

When all variables, except  $\eta$ , on the right of Eq. (15) are independent of temperature,  $\Lambda$  is inversely proportional to  $\eta$ . A log–log plot of  $\Lambda$  vs.  $1/\eta$  (the Walden plot [34]) would be a straight line of unit slope.

The ionicity of ILs has been classified on the basis of the location of the log  $\Lambda$  vs. log  $\eta^{-1}$  plot relative to a hypothetical line of unit slope and zero intercept [35,36]. ILs whose Walden plots lie below this line are called “subionic”, while those with Walden plots above the line are called “superionic”. The subionic nature is generally attributed to the existence of tight (undissociated) pairs that do not contribute to ionic conductivity.

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