Solubility, ionic conductivity and viscosity of lithium salts in room temperature ionic liquids†

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Lithium salts used in batteries have poor solubility in many common room temperature ionic liquids, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI). Lithium salt solutions in ionic liquids that contain the thiocyanate anion, in contrast, can be prepared at concentrations as high as 4 M. The solubility of three common lithium salts (LiClO$_4$, LiSCN and LiTFSI) used in lithium batteries were measured for four room temperature ionic liquids including 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$), 1-butyl-3-methylimidazolium acetate (bmimACET), 1-butyl-3-methylimidazolium thiocyanate (bmimSCN) and EMITFSI. The solubility was determined using Fourier Transform Infrared Attenuated Total Reflectance spectroscopy (FTIR-ATR), which was an efficient method for determining electrolyte solubility in electrolyte solvents. The ionic conductivity of room temperature ionic liquids with thiocyanate containing anions with high concentrations of lithium salts was determined using AC impedance. There was an optimal lithium salt concentration in the ionic liquid in terms of maximum ionic conductivity for the solutions.

Introduction

Initial excitement over ionic liquids resulted from their environmental advantage over traditional organic solvents. The use of ionic liquids with negligible vapor pressure as a replacement for organic solvents promises to decrease the emission of organic solvents into the environment by eliminating evaporative loss of solvent.[1–9] Additionally, the interest in ionic liquids extends beyond the environmental impact of these solvents, including the possible use of lithium ion batteries in zero emission electric vehicles or low emission hybrid vehicles.[10–12]

Room temperature ionic liquids have received increased attention for use in secondary lithium batteries.[13–21] The 1-ethyl-3-methylimidazolium (EMI) cation has been the focus of studies due to its tendency to form low viscosity solutions with a wide range of anions. However, the EMI cation has been reported to be electrochemically unstable in some systems due to a cathodic limiting potential. In order to progress the use of imidazolium cation based ionic liquids, a recent report concluded that increasing the chain length of alkyl substituents on imidazolium cations has improved the performance of lithium batteries based on room temperature ionic liquids.[22] Another recent limitation of ionic liquid based batteries reported the relatively poor solubility of the lithium salt in the ionic liquid containing electrolyte layer as possibly reducing performance.[23] There is a dearth of information on the solubility of ionic compounds in general and lithium salts in particular in room temperature

ionic liquids.[44] To our knowledge, there is no study of lithium salts in room temperature ionic liquids in the literature. The intent of this study is to increase the knowledge base of lithium salt solubility in ionic liquids.

In this paper we present a detailed study of the solubility of three lithium salts, used in lithium batteries, in four common ionic liquids. The ionic liquid EMITFSI was chosen due to its regular use in lithium battery studies. The other ionic liquids contained longer alkyl substituents on the imidazolium cation and a variety of anions. We validated a Fourier Transform Infrared Attenuated Total Reflectance spectroscopy (FTIR-ATR) method for determination of the solubility of an electrolyte solute in an electrolyte solvent. The solubility study was restricted to 25 °C as this would be the lowest temperature and lowest solubility the salts have under practical storage conditions for a lithium battery. The ionic conductivity of solutions with significant lithium salt solubility were performed over a range of 25 to 75 °C, as these temperatures would represent the normal range of operation for such devices.

Results and discussion

The solubility of lithium salts in room temperature ionic liquids was measured using FTIR-ATR. We extended the work of Dunuwila and Berglund which measured the solubility of a molecular species, maleic acid, in water, in which a transmission ratio was used at two wavelengths (one specific to the solvent and one specific to the solute) to determine the solubility limit of the lithium salt in the ionic liquid.[24,25] We validated the use of this technique for determining electrolyte solubility by repeating these experiments with a series of electrolytes in water *versus* published values. Representative FTIR-ATR spectra of a lithium

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salt (lithium perchlorate) in an ionic liquid (bmimSCN) solution are shown in Fig. 1. As the concentration of the lithium salt increases in solution, its infrared peak increases in intensity at ~1350 cm⁻¹. As the concentration of the lithium salt increases in the solution, the peak of the ionic liquid solvent decreases in intensity at ~1450 cm⁻¹. As a result, as the concentration of the lithium salt increases in the ionic liquid, the transmission ratio of the lithium salt peak to the ionic liquid solvent peak increases. When the solubility limit of the lithium salt is reached in the ionic liquid, the transmission ratio becomes constant.
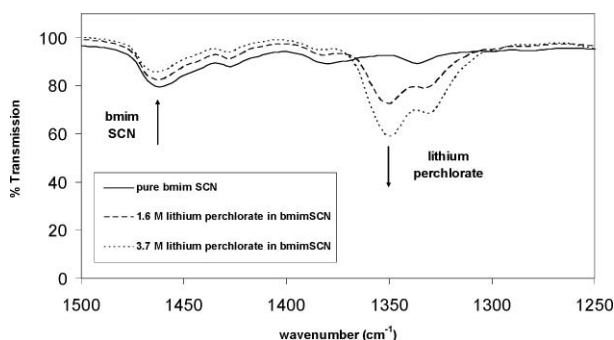

Fig. 1 Representative FTIR-ATR spectra of a lithium salt (LiClO₄) in an ionic liquid (bmim SCN) solution are shown.

As seen in Fig. 1, the decrease in intensity of infrared transmission bands of ionic liquid bmimSCN (at 1460 cm⁻¹) relative to lithium perchlorate (at 1380 cm⁻¹) is readily apparent. As the maximum lithium salt concentration in the ionic liquid is reached, the ratio of the two peaks reach a constant value. Fig. 2 shows the transmission ratios for the three different lithium salts as a function of concentration studied in bmimSCN. From a plot of this type, the maximum solubility can clearly be determined. Similar experiments were carried out for all three lithium salts in the four different ionic liquids used in these experiments (data not shown).
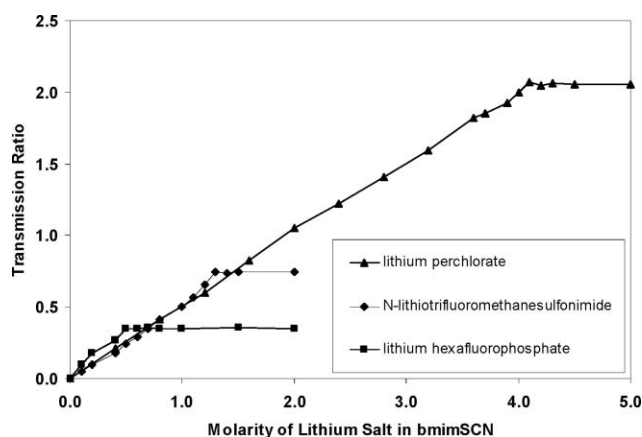

Fig. 2 The transmission ratios for the LiClO₄, LiTFSI and LiPF₆ as a function of lithium salt concentration in bmimSCN.

Table 1 reports the solubility of the three lithium salts in the four ionic liquids as determined by this method. The highest concentration of all three lithium salts was the greatest in bmimSCN. Surprisingly, bmimSCN was able to solubilize LiClO₄ in excess of a 4 M solution. It was also clear that the

Table 1 The solubility of the lithium salts in room temperature ionic liquids as determined by FTIR-ATR at 25 °C

	bmimACET	bmimSCN	bmimPF₆	EMITFSI
LiTFSI	0.18 M	1.3 M	0.06 M	0.4 M
LiClO₄	0.10 M	4.1 M	0.09 M	0.3 M
LiPF₆	0.34 M	0.60 M	0.08 M	0.1 M

bmim PF₆ ionic liquid was the poorest solvent for the lithium salts studied. Although in EMITFSI the solubility for LiTFSI (0.4 M) and LiClO₄ (0.3 M) was reasonable, it was a poor solvent for LiPF₆ (0.1 M). Furthermore, EMITFSI was a poor solvent for lithium salts compared to bmimSCN. This is the first study of salt solubility in ionic liquids. In recent studies of molecular solubility in ionic liquids, the nature of the anion has been found to be a dominating factor in solubility trends.[26] From Table 1, it can be seen that our data agreed with these results for electrolyte solubility in electrolyte solvents. Additionally, models such as COSMO-RS have been useful in predicting solubility behavior in ionic liquids based on electrostatic and dispersion interactions.[27–30] The major parameters from the COSMO-RS approach for predicting solubility in ionic liquids were found to be misfit, van der Waals interaction energies and H-bonding.[31] As the current study does not involve molecules with moieties of H-bonding donors, misfit and van der Waal interactions may likely explain the current solubility results. The sigma moments, molecular descriptors derived from COSMO-RS, are measures of polarity or polarizability on the molecular surface. When the bmim cation is kept constant, a trend for solubility is observed for all three lithium salts based on the anion. The order of solubility follows: thiocyanate > acetate > hexafluorophosphate. Considering the sigma moment is based on the polarization charge density, it is reasonable to consider that the most polarizable anion (⁻SCN) was the best solvent for the lithium salts and that the least polarizable anion (PF₆⁻) was the poorest solvent for all of the salts.

The expected end use of these solutions is for application in lithium batteries. As a result of the exceptional solubility of LiClO₄ and LiTFSI in the bmimSCN, the ionic conductivities of these solutions were measured using AC Impedance. As seen in Fig. 3a and 3b, the temperature dependence of the ionic conductivity of the LiTFSI/bmimSCN and LiClO₄/bmimSCN, respectively, was measured in the range of 25 to 75 °C. As expected, the ionic conductivity of the mixtures decreased with decreasing temperature. The ionic conductivity of a solution is directly related to the number, charge and mobility of the carrier ions. However, as the lithium salt concentrations increased, the ionic conductivity of the salt solutions did not necessarily decrease as the viscosity of the solution increased. This was surprising as the increase in viscosity should reduce the mobility of the carrier ions.

Fig. 4a depicts the ionic conductivity of the LiTFSI salt in bmimSCN solvent mixture as a function of LiTFSI concentration. In the only other report of ionic conductivity of a lithium salt/ionic liquid mixture as a function of lithium salt concentration, 1,2-dimethyl-3-propylimidazolium TFSI was mixed with LiTFSI. In this study where there was a common ion between the lithium salt and ionic liquid, the increasing lithium salt concentration resulted in a decrease in ionic conductivity.
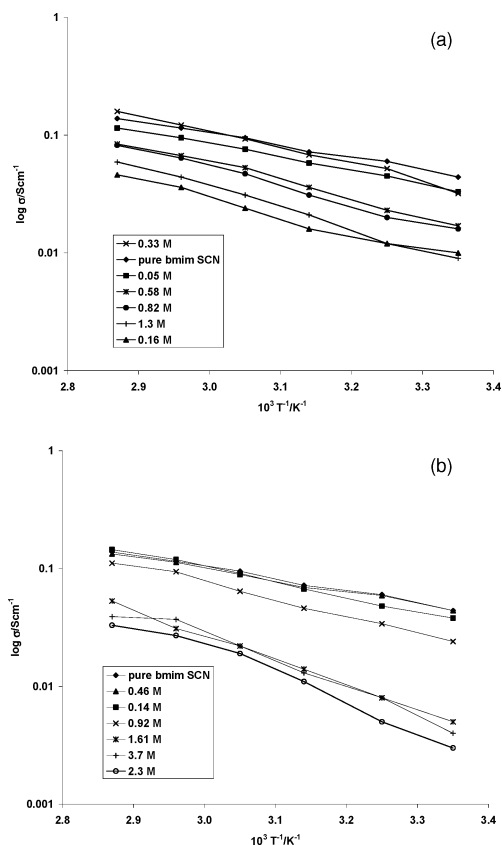
Fig. 3 (a) Ionic conductivity of LiTFSI/bmimSCN mixtures as a function of temperature in the range of 25 to 75 °C. (b) Ionic conductivity of LiClO₄/bmimSCN mixtures as a function of temperature in the range of 25 to 75 °C.
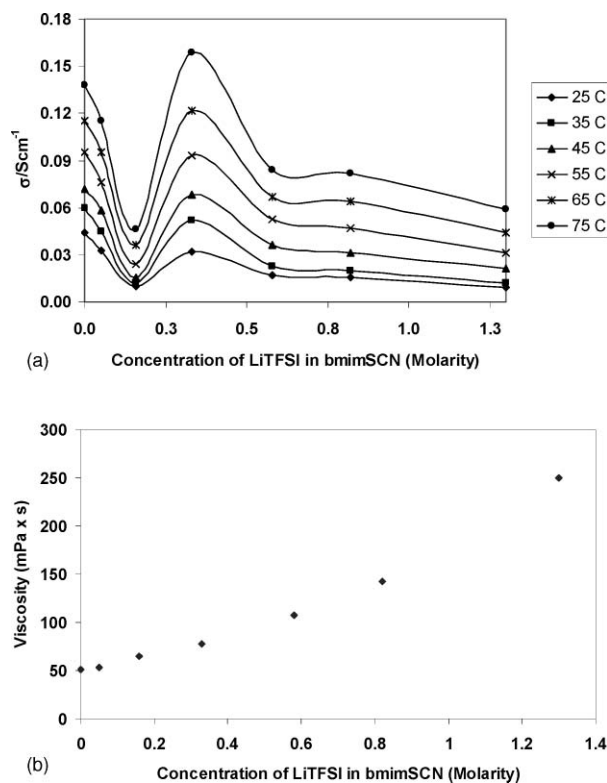
Fig. 4 (a) Ionic conductivity of LiTFSI/bmimSCN mixtures as a function of LiTFSI concentration in the range of 25 to 75 °C. (b) Viscosity of LiTFSI/bmimSCN mixtures as a function of LiTFSI concentration at 25 °C.

This was explained by the increasing viscosity of the more concentrated solutions, which in turn would lower the mobility of the carrier ions.[21] However, in our study, we found that there was actually an optimal concentration of lithium salt for the mixture in terms of ionic conductivity. Initial loading of the lithium salt decreased the ionic conductivity of the mixture. A subsequent increase in the loading of lithium salt concentration in the mixture resulted in a notable increase in ionic conductivity before decreasing again with added lithium salt. The viscosity of the the LiTFSI salt in bmimSCN mixture as a function of LiTFSI concentration at 25 °C is depicted in Fig. 4b. The viscosity of the mixture increases with a corresponding increase in lithium salt concentration.

There is increasing evidence that the properties of room temperature ionic liquids are more comparable to that of molecular organic solvents than that of high temperature molten salts. The theory for the relationship between viscosity of electrolyte solutions and concentration of the salt in non electrolyte solvents has been explained by the Jones-Dole equation:[34]

$$\eta_r = \eta/\eta_0 = 1 + AC^{1/2} + BC + DC^2$$

where η is the viscosity of the salt solution, η_0 is the viscosity of the pure solvent, C is the concentration of the salt, and A, B and D are coefficients. The $AC^{1/2}$ term is typically not relevant at concentrations greater than 0.05 M.[35] The BC term is prevalent at salt concentrations greater than 0.5 M is due to volume effects

and ion solvent interactions.[36] The DC² term is credited to ion-ion and ion-solvent interactions at concentrations between 0.5 and 2.0 M.[37] Dilute electrolyte solutions in non-electrolyte solvents has been described by Debye–Hückel-Onsager equation.[38] However, this model does not correctly predict the conductivity behavior of concentrated ionic solutions.[39–41] However, quasi lattice theory has been modified for conductivity and has been validated for the prediction of conductivity for lithium salts in organic solvents.[39,42,43]

Presumably, the effective number of carrier ions increases with added lithium salt and results in an increase in conductivity. However, the viscosity continues to increase with added lithium salt as predicted by the Jones Dole relationship. At some point, however, the effective mobility of the ionic carrier decreases as a result of the increase in viscosity. This leads to a maximum of conductivity. Although this phenomenon is typically observed around 1 M for electrolytes in organic solvents, the maximum of conductivity for the electrolytes in an electrolyte solvent occurred at approximately 0.4 M in the LiTFSI in bmimSCN and LiClO₄ in bmimSCN mixtures.

A similar trend is seen in Fig. 5a where the ionic conductivity of a mixture of LiClO₄ in bmimSCN is plotted against the concentration of LiClO₄. The viscosity of the LiClO4 salt in bmimSCN mixture as a function of LiClO4 concentration at 25 C is depicted in Fig. 5b.

In summary, we found that the nature of the anion played a significant role in the solubilization of lithium salts in ionic liquids. FTIR-ATR was an efficient technique for determining
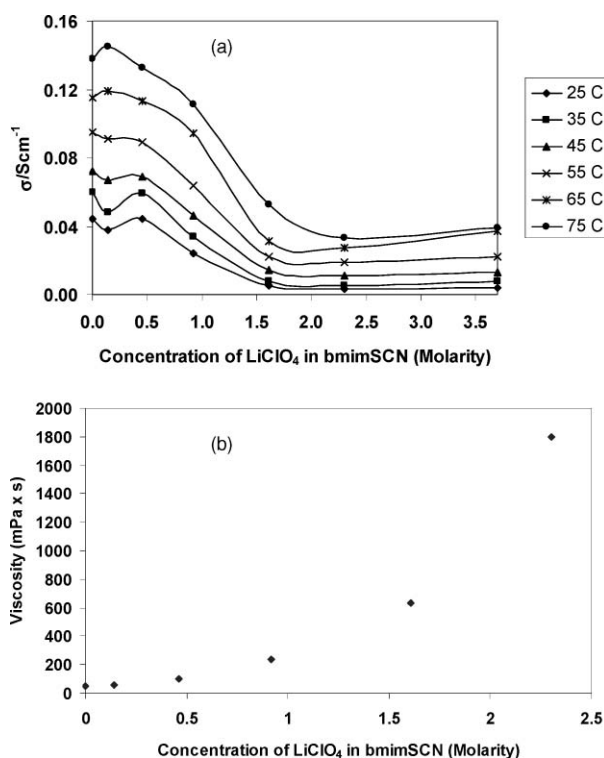
Fig. 5 (a) Ionic conductivity of LiClO$_4$/bmimSCN mixtures as a function of LiTFSI concentration in the range of 25 to 75 °C. (b) Viscosity of LiClO$_4$/bmimSCN mixtures as a function of LiClO$_4$ concentration at 25 °C.

solubility of electrolytes in ionic liquids. There appears to be an optimal concentration of lithium salts dissolved in ionic liquids for the greatest ionic conductivity. Future efforts will explore the use of systematic variation of anion structure to determine if there are trends in solubility of lithium salts based on specific ionic liquid structure. Models like COSMO-RS could be used to provide a more definitive insight to the variables that determine electrolyte solubility in electrolyte solvents. These efforts could be used to improve lithium batteries based on ionic liquid electrolytes.

Experimental section

Reagents and sample preparation

1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$), 1-butyl-3-methylimidazolium acetate (bmimACET), 1-butyl-3-methylimidazolium thiocyanate (bmimSCN), lithium perchlorate (LiClO$_4$), lithium hexafluorophosphate (LiPF$_6$) and N-lithiotrifluoromethanesulfonimide (LiTFSI) were used as received from Sigma-Aldrich. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) was synthesized in as described in the literature.[32,33] Lithium salt solute was weighed out into a volumetric flask and ionic liquid solvent was added to the desired volume to prepare each solution. A series of solutions were prepared increasing the mass of lithium salt added until supersaturation was observed in terms of a turbid, cloud point by eye. The system was stirred for one week at room temperature in an inert atmosphere to allow maximum solubility to be reached at 25 °C.

AC impedance measurements

The ionic conductivity (σ) was measured by AC impedance spectroscopy in the temperature range of 25 to 75 °C. Two platinum wires with a 1 mm diameter were sealed in glass and polished to a mirror finish. The platinum disk electrodes were placed in 1″ × 1″ × 0.5″ Teflon blocks held together with screws. A third platinum wire was introduced from the side of the apparatus before the screws were tightened to serve as the reference electrode. The sample cell constant was standardized by taking impedance measurements of 1.00, 0.100, and 0.0100 M KCl (aq) solutions of known conductivity and found to be 3.80 cm^{-1}. The measurements were taken on a CH Instruments 601B Electrochemical Analyzer over the frequency range of 1 Hz to 1 MHz with an AC excitation of 5 mV. Conductivity measurements were performed in a Tenney Junior environmental chamber. Samples were heated to 75 °C and allowed to thermally equilibrate for 20 minutes. An impedance spectrum was collected at that temperature, then the temperature was lowered by 10 °C and the sample was allowed to thermally equilibrate for 20 minutes before the next scan was taken. Measurements were made at 75, 65, 55, 45, 35, and 25 °C. R$_{bulk}$ was determined from the Nyquist plot and was divided into the cell constant to calculate ionic conductivity.

Solubility measurements

In situ measurements of solubility were performed using a Thermo Electron Corporation Nicolet Avater 370 DTGS with a Pike Technolgies Miracle ATR accessory equipped with a TempPRO Isothermal Temperature Control Accessory. The lithium salt solution was added to the ATR crystal at 25 °C. Spectra were obtained in triplicate at each concentration of lithium salt. Concentrated slurries were not formed due to the fact that any settled solid lithium salt would possibly interfere with the optical measurement. The method was validated by measuring the solubility of both potassium carbonate in water and potassium sulfate in water and comparing these values to the known values for these common electrolytes.

Viscosity measurements

A Ubbelohde 10 mL glass viscometer was standardized with distilled water. All liquids were at 20 °C and atmospheric pressure. Each liquid was tested three times, and the average run time was used to calculate the viscosity.

Acknowledgements

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