

Polymer Electrolytes Based on Room Temperature Ionic Liquid: 2,3-Dimethyl-1-octylimidazolium Triflate

Boor Singh and S. S. Sekhon*

Department of Applied Physics, Guru Nanak Dev University, Amritsar-143005, India

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Room temperature ionic liquid (DMOImTf) based upon 2,3-dimethyl-1-octylimidazolium cation and trifluoromethanesulfonate or triflate (CF_3SO_3)[−] anion has been synthesized and shows conductivity of 5.68 mS/cm and viscosity of 26.4 cP at 25 °C. Ion conducting polymer electrolytes based on polymers (poly(ethylene oxide) (PEO) and polyvinylidene fluoride-*co*-hexafluoropropylene (PVdF-HFP)) and ionic liquid (DMOImTf) were prepared in film form by the casting technique. The conductivity of polymer electrolytes containing 0.5 M LiCF_3SO_3 in PEO:DMOImTf taken in equal weight ratio increases with the addition of propylene carbonate (PC) while its mechanical stability improved by dispersing nanosize fumed silica. However, polymer electrolytes containing PVdF-HFP and ionic liquid show a high value of conductivity (10^{-4} – 10^{-3} S/cm) alongwith better mechanical stability.

Introduction

Room temperature ionic liquids (RTILs) that consist only of cations and anions are being extensively studied due to their unique properties such as negligible vapor pressure, nonflammability, high ionic conductivity, and good thermal and electrochemical stability. A wide range of ionic liquids reported in the literature includes superacidic,¹ basic,² hydrophilic and water miscible,³ and hydrophobic and water immiscible.⁴ Ethylammonium nitrate with a melting point of 14 °C was the first room temperature molten salt reported by Walden⁵ in 1914 and much of the earlier work was on eutectic mixtures of aluminum chloride with other salts.^{6,7} Reports of air- and water-stable non-chloroaluminate ionic liquids^{8,9} and their applications in various fields generated renewed interest in these materials. The most important and widely studied^{10–17} cations include dialkylimidazolium and pyridinium derivatives and bulky and soft anions such as $[\text{PF}_6]^-$, $[\text{BF}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$, and $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$. In dialkylimidazolium cations an increase in the alkyl chain length increases the hydrophobicity of ionic liquids.¹⁸ Substituting the halide ions with tetrafluoroborate $[\text{BF}_4]^-$, hexafluorophosphate $[\text{PF}_6]^-$, trifluoromethanesulfonate $[\text{CF}_3\text{SO}_3]^-$, and bistrifluoromethanesulfonate $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ anions results in progressively more hydrophobic salts^{19,20} and results in ionic liquids with low melting and high thermal stability.^{21,22} The very low vapor pressure of ionic liquids has led to their use as a green solvent in environmentally friendly reactions and separation processes.^{23–25} Ionic liquids with different organic cations have also been suggested for electrolyte applications.^{25,26,30} Different polymer electrolytes containing ionic liquids obtained by polymerization of ionic liquids,^{13,28–29} inclusion of different polymers in ambient temperature ionic liquids,^{33,14} ionic liquid–polyelectrolyte systems,^{29,31} and polymer gel electrolytes containing hydrophilic and hydrophobic ionic liquids^{32,33} have been reported to possess high conductivity suitable for applications. The effect of addition of plasticizer and inert insulating matrix on the conductivity behavior of polymer electrolytes containing

semicrystalline/amorphous polymer in an ionic liquid will also be interesting. RTILs being themselves ionic conductors can find applications in various electrochemical devices and in this direction ion conducting polymer electrolytes containing polymers and RTILs prepared in the film form can be interesting electrolytes, which is the motivation for the present work.

In the present study synthesis and experimental results of the melting point, density, viscosity, and ionic conductivity for 2,3-dimethyl-1-octylimidazolium trifluoromethanesulfonate (DMOImTf) and polymer electrolytes containing DMOImTf in poly(ethylene oxide) (PEO) and polyvinylidene fluoride-*co*-hexafluoropropylene (PVdF-HFP) has been presented. The variation of viscosity and ionic conductivity of RTIL and of polymer electrolytes containing RTIL with temperature has been studied. The role of PEO, which is semicrystalline, and PVdF-HFP, which is a highly amorphous polymer, on the conductivity behavior of polymer electrolytes has been studied. The addition of propylene carbonate and nanosize fumed silica to PEO-based polymer electrolytes containing RTIL and their effect on the conductivity and mechanical properties has also been investigated.

Experimental Section

Synthesis of Ionic Liquid. 1,2-Dimethylimidazole (Merck) (9.6 g, 0.1 mol) and 1-bromooctane (Spectrochem) (19.3 g, 0.1 mol) were mixed in a round-bottomed flask equipped with reflux condenser and maintained at 140 °C for 40 min. The emulsion formed initially turned into a yellow viscous solution which was then cooled for 20 min and 2,3-dimethyl-1-octylimidazolium bromide was obtained in quantitative yield. The anion exchange reaction was carried out by using a solution of lithium trifluoromethanesulfonate or lithium triflate (LiCF_3SO_3) (Aldrich) in double distilled deionized water and this aqueous solution was slowly added to the magnetically stirred solution of 2,3-dimethyl-1-octylimidazolium bromide and the mixture was stirred for 20 min. The organic layer was extracted with dichloromethane (SRL) and separated from the aqueous layer. The organic layer was then washed with double distilled deionized water until it was free from lithium bromide. The

* Address correspondence to this author. Fax: +91-183-2258820. E-mail: sekhon_apd@yahoo.com.

absence of LiBr was also checked by taking a small amount of ionic liquid, which was then digested with nitric acid and perchloric acid, and the mixture was then heated to obtain a highly viscous mass that was dissolved in very dilute hydrochloric acid and the test for Br^- anion was performed. The negative test indicated the absence of any LiBr in the ionic liquid. Residual water from the ionic liquid was removed by azotropic distillation with benzene using a Dean–Stark trap and then benzene was removed under reduced pressure.

Polymer Electrolytes Containing Ionic Liquid. Polymer electrolytes containing PEO (Aldrich, $M_w = 5 \times 10^6$) and PVdF-HFP (Fluka, $M_w = 130\,000$) in ionic liquid (DMOImTf) were prepared by the solution casting method. In this method stoichiometric quantities of ionic liquid and polymer were dissolved in acetonitrile/methanol and the mixture was stirred to obtain a uniform viscous solution, which was then poured into polypropylene dishes. The solvent was allowed to evaporate slowly and polymer electrolytes in the film form were obtained. These films were stored under dry conditions and used for different studies. For preparing polymer electrolytes containing propylene carbonate (PC) (Merck) and fumed silica (Aldrich, average particle size 7 nm), PC and fumed silica in the required amounts were also added to the starting solution.

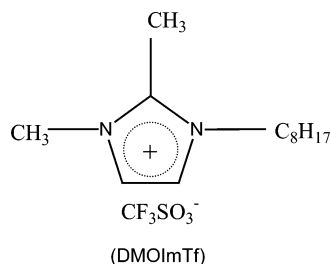
NMR. The ^1H and ^{13}C NMR spectra were obtained on a spectrometer (JEOL, AL-300 MHz) at 300 and 75 MHz, respectively, in CDCl_3 , using tetramethylsilane (TMS) as internal standard. Chemical shifts are expressed as δ (ppm) downfield from TMS. Mass spectra were performed on a LC-Agilent 100 Series mass spectrometer.

Conductivity. The ionic conductivity of different electrolytes was determined by the complex impedance method in the 5–80 °C temperature range by using a special cell with platinum electrodes for RTIL and a cell with pressure contact stainless steel electrodes for polymer electrolytes containing RTIL in the film form. The experiments were performed with a computer interfaced Hioki 3532-50 LCR Hitester and HP 4284A precision LCR meter in the frequency range 42 Hz to 5 MHz and 20 Hz to 1 MHz, respectively.

Viscosity. Viscosity of the ionic liquid was measured with a Fungilab rotating viscometer (Model Basic L) and the temperature was controlled within ± 0.1 °C with a Julabo water circulator (F-12 EC).

Results and Discussion

2,3-Dimethyl-1-octylimidazolium triflate (DMOImTf) synthesized as above has the following structure:



The structure of ionic liquid was confirmed by ^1H and ^{13}C NMR and mass spectrometer measurements. The abbreviations used to explain the multiplicity are the following: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet; J , coupling constant.

DMOImTf. ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 0.87 (t, 3H, $-\text{CH}_3$, $J = 6.6$ Hz); 1.26–1.32 (m, 10H, $5 \times \text{CH}_2$); 1.76–

1.80 (m, 2H, $-\text{CH}_2$); 2.59 (s, 3H, $-\text{CH}_3$); 3.79 (s, 3H, $-\text{CH}_3$); 4.02 (t, 2H, $-\text{CH}_2$, $J = 7.5$ Hz); 7.17, 7.20 (dd, 2H, $J = 2.1$ Hz).

^1H NMR shows a second-order AB kind of spectrum in the aromatic region, due to a very small difference in the chemical shift values of the two vicinal protons. The peak is a doublet of doublet appearing at δ 7.162, 7.169, 7.200, and 7.207. The inner two peaks have gained in intensity at the cost of the outer two peaks and mainly dictate the chemical shift values. $\Delta\delta$ (11 Hz) is comparable to J (2 Hz) giving a complex pattern.

^{13}C NMR, DEPT-135 (CDCl_3 , 75 MHz) δ (ppm) 9.39 (CH_3 , +ve), 13.77 (CH_3 , +ve); 22.29 (CH_2 , -ve); 26.00 (CH_2 , -ve); 28.70 (CH_2 , -ve); 28.73 (CH_2 , -ve); 29.42 (CH_2 , -ve); 31.41 (CH_2 , -ve); 35.06 (CH_3 , +ve); 48.46 (CH_2 , -ve); 120.68 (Ar, +ve); 122.50 (Ar, +ve); 143.52 (Ar, absent in DEPT-135). Mass spectrum (ESI) m/z 209 (DMOIm^+), 148.7 (CF_3SO_3^-). Yield 90%.

DMOImTf with a melting point of -38 °C is a room temperature ionic liquid and its physical properties are listed in Table 1. The water content of DMOImTf as measured by the

TABLE 1: Some Physical Properties of DMOImTf

ionic liquid	mp (°C)	conductivity at 25 °C (in S/cm)	viscosity at 25 °C (in cP)	density (in g/cm^3)
DMOImTf	-38	5.68×10^{-3}	26.4 ^a	1.15

^a With 0.55 wt % water content.

Karl Fisher titration method was 0.55 wt %.

The viscosity of DMOImTf is less than that reported for 1-butyl-3-methylimidazolium triflate²⁶ and this may be due to a decrease in the magnitude of positive charge on the imidazolium cation because of the positive inductive effect of the octyl chain. Thus the net force of attraction between the cation and anion will decrease resulting in the diminution in the ionic character of DMOImTf, which decreased viscosity. The viscosity of the ionic liquid has also been found to depend on the amount of water present in the ionic liquid.

The variation of conductivity and viscosity of DMOImTf with temperature in the 5–80 °C temperature range is given in Figure 1. The large decrease in viscosity from 62.3 to 6.8 cP will lead

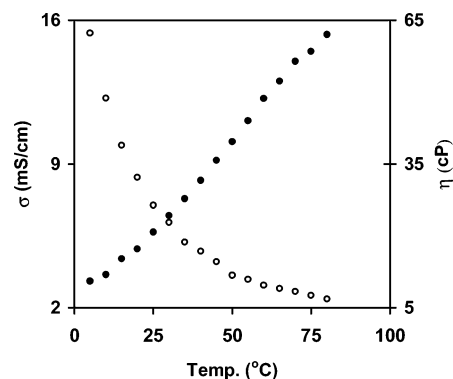


Figure 1. Conductivity (σ) (●) and viscosity (η) (○) of DMOImTf as a function of temperature.

to an increase in mobility ($\mu = q/6\pi\eta r$) and is accompanied by an increase in conductivity by 1 order of magnitude from 3.3×10^{-3} to 1.53×10^{-2} S/cm in the same temperature range. Although the conductivity of DMOImTf is quite high, it could not be used in various applications due to its liquid nature at room temperature. This drawback can be overcome by complexing ionic liquid with different polymers (PEO, PVdF-HFP) and obtaining the electrolytes in the film form.

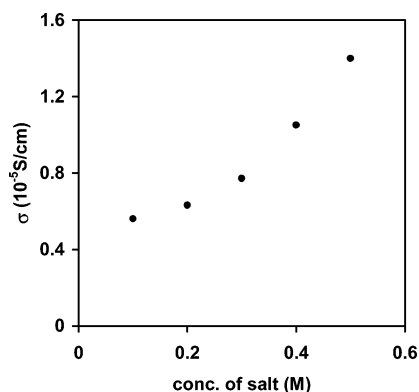


Figure 2. Variation of conductivity (at 25 °C) of PEO + DMOImTf (in equal weight ratio) with LiCF₃SO₃ concentration.

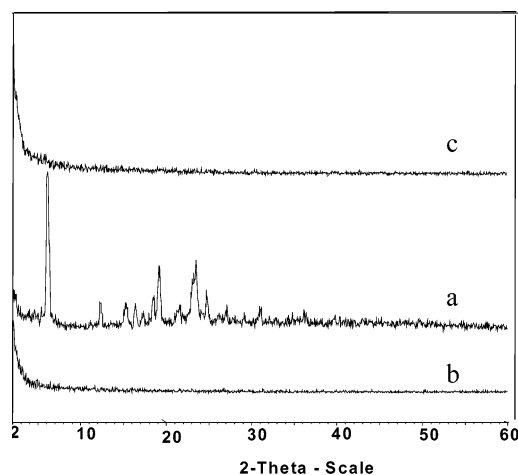


Figure 3. X-ray diffraction pattern of (a) PEO + DMOImTf, (b) PEO + DMOImTf + 0.5 M LiCF₃SO₃, and (c) PVdF-HFP + DMOImTf.

Polymer Electrolytes Containing RTIL in PEO. Polymer electrolytes containing PEO and DMOImTf in equal weight ratio show a conductivity of 7.25×10^{-6} S/cm at 30 °C. The addition of polymer generally results in a decrease in conductivity and similar results have earlier been reported with other ionic liquids also.^{30,32–33} Lithium triflate in different concentrations was then added to polymer electrolytes containing PEO and DMOImTf in equal weight ratio and the variation of conductivity with salt concentration is given in Figure 2. The conductivity increases with the concentration of salt and reaches a value of 1.4×10^{-5} S/cm at 0.5 M salt concentration. The salt provides more free ions and the salt due to the large anion also has a plasticizing effect on polymer electrolytes. This was checked by recording the X-ray diffraction pattern of these electrolytes as given in Figure 3. As PEO is semicrystalline in nature so peaks at d values (in Å) of 5.81, 4.63, 3.795, 3.295, and 2.475 observed in the spectra of PEO + DMOImTf are due to crystalline PEO. However, the sample containing 0.5 M LiCF₃SO₃ is amorphous, which is due to the plasticizing effect of salt. The addition of salt also increases the amorphous content, which is the high conducting phase in polymer electrolytes containing PEO, and this results in an increase in conductivity as given in Figure 2.

The variation of conductivity with temperature over the 10–80 °C temperature range for the electrolytes (a) DMOImTf, (b) PEO + DMOImTf, (c) PEO + DMOImTf + 0.5 M LiCF₃SO₃, (d) PEO + DMOImTf + 0.5 M LiCF₃SO₃ + PC, and (e) PEO + DMOImTf + 0.5 M LiCF₃SO₃ + PC + fumed silica

is given in Figure 4. The conductivity of ionic liquid is quite high and does not vary much over the temperature range studied.

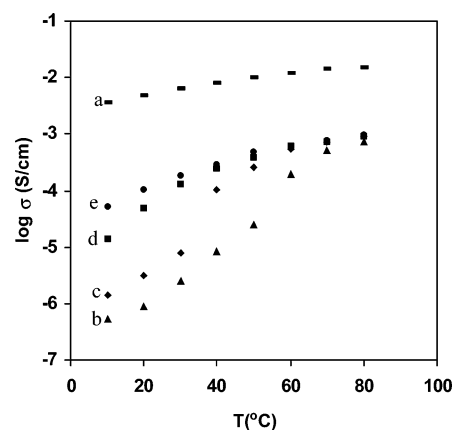


Figure 4. Conductivity of (a) DMOImTf, (b) DMOImTf + PEO, (c) DMOImTf + PEO + 0.5 M LiCF₃SO₃, (d) DMOImTf + PEO + 0.5 M LiCF₃SO₃ + PC, and (e) DMOImTf + PEO + 0.5 M LiCF₃SO₃ + PC + fumed silica as a function of temperature.

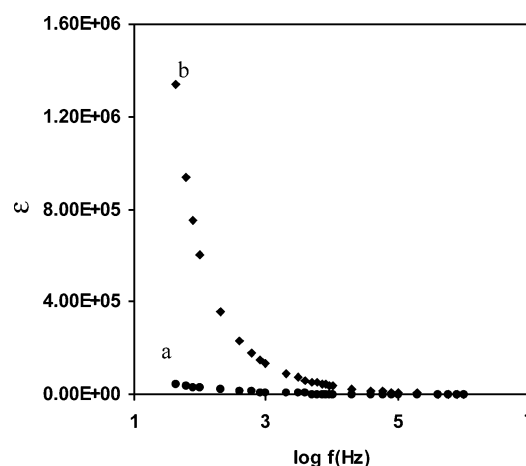


Figure 5. Variation of dielectric constant (at 25 °C) of (a) DMOImTf + PEO + 0.5 M LiCF₃SO₃ and (b) DMOImTf + PEO + 0.5 M LiCF₃SO₃ + PC as a function of frequency.

The conductivity of PEO + DMOImTf increases by nearly 3 orders of magnitude above 65 °C, which is the melting temperature of PEO, and is generally explained to be due to a transition from the semicrystalline to the amorphous phase at the melting temperature.³⁵ For polymer electrolytes containing 0.5 M LiCF₃SO₃, the conductivity is higher than those without salt at all temperatures and the transition to high conducting phase takes place at lower temperatures (35–40 °C). The presence of a large number of ions in the IL may also lead to the formation of ion aggregates and the addition of plasticizer has been reported to increase the conductivity by 1 order of magnitude.¹⁴ The low value of conductivity of these polymer electrolytes in the low-temperature range ($T < T_m$) may be due to the crystalline nature of PEO along with the presence of ion aggregates which do not take part in the conduction process.

The addition of propylene carbonate (PC) to the above polymer electrolytes results in an increase in conductivity at low temperatures ($T < T_m$) by 1 order of magnitude and, second, no sharp increase in conductivity is observed at any temperature. The net dielectric constant of polymer electrolytes has been found to increase with the addition of PC as given in Figure 5 and this results in the dissociation of ion aggregates into free ions along with an increase in the amorphous content of these electrolytes at temperatures below T_m . The absence of any sharp change in conductivity with temperature suggests the amorphous nature of these polymer electrolytes and conductivity in the

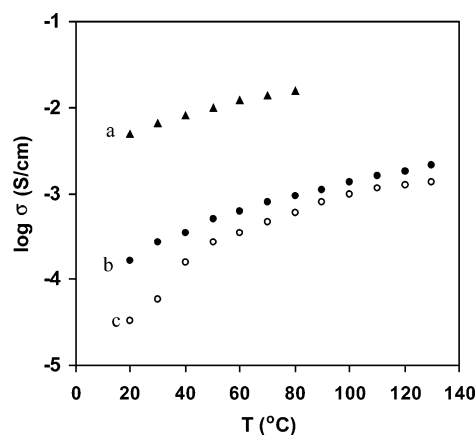


Figure 6. Conductivity of (a) DMOImTf, (b) DMOImTf + PVdF-HFP, and (c) DMOImTf + PVdF-HFP + 0.5 M LiCF₃SO₃ as a function of temperature.

10^{-4} – 10^{-5} S/cm range is observed at all temperatures in the 10–80 °C temperature range.

Polymer electrolytes containing ionic liquid and having compositions b, c, and d show a high value of conductivity ($>10^{-4}$ S/cm) at all temperatures above T_m where PEO is present in the amorphous phase. As a result the films become sticky and do not possess good mechanical properties and hence may not be suitable for device applications. The mechanical properties of the polymer electrolyte films were improved by dispersing nanosize fumed silica to the plasticized polymer electrolytes and the resulting films were found to have much better mechanical strength along with an increase in conductivity. The conductivity results as given in Figure 4 show that films containing fumed silica have higher conductivity than other electrolytes and conductivity $>10^{-4}$ S/cm has been obtained at temperatures above 20 °C. The increase in conductivity with the addition of fumed silica is due to the formation of a high conducting interfacial region between the particles of the fumed silica and polymer electrolytes.^{36,37} The above results indicate that PEO-based plasticized polymer electrolytes containing RTIL and fumed silica possess good mechanical properties along with a high value of conductivity and are thus suitable for use in devices.

Polymer Electrolytes Containing RTIL and PVdF-HFP. PVdF-HFP is a copolymer and is highly amorphous and films containing this polymer generally possess good mechanical properties. Polymer electrolytes containing DMOImTf and PVdF-HFP in equal weight ratio and those containing 0.5 M LiCF₃SO₃ were prepared and the variation of conductivity with temperature is given in Figure 6. The results for DMOImTf are also included for comparison purposes. The conductivity of electrolytes containing RTIL and polymer is quite high, 1.68×10^{-4} S/cm at 20 °C, which increases to 2.12×10^{-3} S/cm at 130 °C. There is no sharp change in conductivity as was observed in the case of electrolytes containing PEO (Figure 4) and films have been found to be amorphous by X-ray diffraction studies as given in Figure 3. The addition of 0.5 M LiCF₃SO₃ to the above polymer electrolytes, however, leads to a small decrease in conductivity and at all temperatures above 100 °C a high conductivity of $\sim 10^{-3}$ S/cm is obtained, which is lower by only 1 order of magnitude than that for the IL. The conductivity of the same order has also been reported^{32,33} for PVdF-HFP-based polymer gel electrolytes containing ionic liquids. The high value of conductivity of these electrolytes along with better mechanical properties is desirable for their possible use in devices.

Conclusions

Room temperature ionic liquid 2,3-dimethyl-1-octylimidazolium triflate (DMOImTf) has been synthesized and shows a conductivity of 5.68 mS/cm and a viscosity of 26.4cP at 25 °C. The ionic conductivity of polymer electrolytes containing DMOImTf in PEO increases with the addition of propylene carbonate and the dispersion of nanosize fumed silica improves its mechanical strength along with an improvement in conductivity. However, polymer electrolytes containing DMOImTf in PVdF-HFP show good mechanical strength along with high conductivity (10^{-4} – 10^{-3} S/cm) in the 20–140 °C temperature range. These polymer electrolytes containing RTIL with high conductivity and good mechanical strength are potential electrolytes for use in various devices.

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Supporting Information Available: The dependence of the viscosity on the amount of water present in the ionic liquid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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