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Physico-chemical properties of some polymer blended task specific novel S-(+)-2-3-dihydroxy-N, N, N-tributyl-propanaminiumtriflate and 1-(2-propoxy)-3-methylimdazolium-borohydride room temperature ionic liquids

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Two novel chiral ionic liquids S-(+)-2-3-dihydroxy-N, N, N-tributyl-propanaminiumtriflate and 1-(2-propoxy)-3-methylimdazolium-borohydride have been prepared using conventional metathesis reaction. These ionic liquids have been subjected to solution cast method followed by ultrasonication to obtain the corresponding ionic liquid gel polymer electrolytes with poly (vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP), free-standing, rubbery, dimensionally stable films with a high degree of transparency have been obtained. Thermo-gravimetric analysis confirms that the intermediate solvent, acetone used for mixing PVDF-HFP polymer with ionic liquid is completely evaporated after gelation and drying process. Further thermal properties have been analyzed by differential scanning calorimetry. Scanning electron microscopy micrographs show the different surface morphology of the gel electrolytes according to nature of the ionic liquid. The structural information has been extracted by X-ray diffraction. The ionic conductivities of both polymer-ionic liquid blends are in the order of 10^{-3} to 10^{-5} S cm^{-1}. Electrochemical stability window of these polymer electrolytes ranges from 4.0 to 5.0 V. Various physicochemical properties and fast ion conduction in the gel polymer membranes show their promising characteristics as electrolytes in different ionic devices.

Keywords: Ionic liquids, Polymers, Blends, Ionic size, Ionic conductivity

1 Introduction

In the series of fascinating materials of last decades ionic liquids (ILs) are the most studied and discussed material all over the world[1]. Room temperature ionic liquids (RTIL) amongst other IL with specific physicochemical properties attracted many scientists towards their applications in multifarious domains. RTILs are molten salts that own inimitable properties, such as insignificant vapour pressure, excellent thermal stability, non-flammability, high ionic conductivity and a wide electrochemical stability window. They are also used as media for several chemical reactions, like synthesis of conducting polymers, metal oxides, novel compounds, additives, including plasticizers, components of polymer electrolytes, and porogenic agents to polymers[2,3]. Combining ILs with polymer offers the prospect of their potential applications, where they surpass the performance of conventional media such as organic solvents giving advantages in terms of improved safety and a higher operating temperature range[2-5]. However, the most important challenge is how to immobilize ILs in polymer matrices while retaining their sought after properties. The main polymers used in polymer based electrolytes are high molecular weight polymers including poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), poly(1-vinyl pyrrolidone) (PVP), poly(N-methyl acryl amide) (PDMAA), and poly(1-vinyl pyrrolidone-co-vinyl acetate) (P(VP-c-VA))[6-11]. Among them, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), which is a copolymer vastly studied for having good mechanical stability, ease in processing like flexible transparent films and good liquid retention capacity with high ionic conductivity ~ 10^{-3} S cm^{-1} values[11]. The terms like "gel electrolyte", "plasticized electrolyte", "ion gel" and "hybrid film" are used in various applications, including

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*Corresponding author (E-mail: ykb.ssi@gmail.com) transistors, secondary batteries, supercapacitors, electrochromic displays, sensors etc[12-14]. In general, the gel polymer electrolytes consist of salt solution of a polar organic solvent in a polymer host. Nevertheless, there are several problems associated with organic solvents such as volatility and flammability at elevated temperatures during the operation of a battery. To overcome this problem a gel electrolyte, based on a blend of a RTIL and a copolymer exhibits both large specific capacitance (>10 μF/cm^2), allows transistor operation at frequencies greater than 100 Hz and improved polarization response times (1 ms) when used as the gate dielectric in a polymer thin-film transistor[12] has been reported. The high ionic concentration of charge carriers in ILs counters the electrolyte depletion problem with conventional electrolytes and therefore enhances the performance of device[15]. Some of the ionic liquids like 1-ethyl-3-methylimidazolium (EMI$^+$) cation based ILs are less stable toward Li-metal[16,17] and unsuitable for Li battery applications but have many other applications as electroplating metals and semiconductors[18], to enhance the stability of electromechanical actuators[19]. These findings indicate the requirement of new and suitable ionic liquids according to the specific needs like chemical and electrochemical stability of the desired application like sensors, super capacitors and batteries.

The aim of this paper is to study the intensive use of ionic liquids in energy storage devices. Accordingly, the following objectives have been formulated:

(i) Synthesis and characterization of novel task specific ionic liquids
(ii) To obtain polymer blend ionic liquids
(iii) To study morphological, structural, thermal, and electrochemical studies of newly prepared polymer blend ionic liquids
(iv) To validate their application in energy storage ionic devices

In this work, two novel task specific ILs have been prepared for the synthesis of carbonyl compounds by asymmetric reductive amination method. One of them is an imidazolium based whereas the other is a tri alkyl ammonium based RTIL. These reagents have been prepared and effectively used in the synthesis of functionalized amines by reductive amination method. They were found to be efficient in promoting the reductive amination of carbonyl compounds with aromatic amines to afford novel functionalized secondary amines[20]. This work focuses on the development of novel polymer-ionic liquid blend system using two novel ionic liquids separately with host polymer.

2 Experimental Details

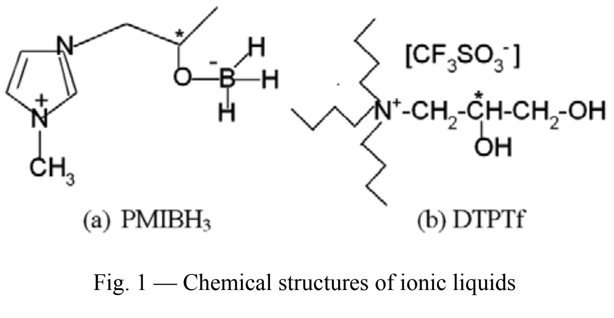
2.1 Synthesis of ionic liquids

2.1.1 S-(+)-2- 3-dihydroxy-N, N, N-tri butyl propanaminium triflate $[(OH)^3(OH)^2C_1C_3N]^+$ (DTPTf)

In a round bottomed 50 cm^3 flask equipped with a condenser and magnetic stirrer, 5 g tributylamine (0.02mol)(Aldrich) and 3 g S-(+)-3-Chloro-1, 2-propanediol (0.02 mol) (Aldrich) were mixed and heated at 120 °C for 12 h. The reaction mixture was washed with 2×30 cm^3 diethyl ether. The drying of organic layer under vacuum gave 70% yield as colorless oily liquid. This reagent is soluble in chloroform, dichloromethane, acetone and ethanol. It is insoluble in water, diethyl ether and *n*-hexane. The S-(+)-2-3-dihydroxy-N,N,N-tributylpropanaminium triflate ionic liquid can be obtained by metathesis of the above ionic liquid with sodium triflate (NaOTf) in DCM followed by regular workup, chemical structure is given in Fig. 1(a). ^{1}H NMR (400 MHz, DMSO-d_6,25 °C, ppm): δ0.90, J=7.3 (q, 9H), 1.28, J=7.32 (m,6H,2'CH_2), 1.61, J=8 (m, 6H, 2'CH_2), 3.34, J=4.5 (m,6H,CH_2-N), 4.75, J=5 (br,1H,2'OH), 4.00, J=5 (br,1H,1'OH), 3.28, J=8 (m,1H,CH-N), 2.92, J=8 (m,1H,CH-N) ,3.40, J=8.8 (m,1H,*CH) 3.62, J=8 (m,2H,1'CH_2); ^{13}C NMR (100 MHz, $CDCl_3$,25^{0}C, ppm): δ 77.3, 77.0,76.7,59.5,23.8, 19.6 and 13.7. IR (KBR) :1044 cm^{-1}(1° C-O str); 1106 cm^{-1}(2^0 C-O ben); 1382 cm^{-1}-1464cm^{-1}(CH str, def, methyl); 2876 and 2963 cm^{-1}(CH str,methyl); 3336 cm^{-1}(O-H str).

2.1.2 1-[(2-propoxy)-3-methylimdazolium-borohydride$[(OBH_3)^2 C_3C_1im]^+$($PMIBH_3$)

In around bottomed 50 cm^3 flask equipped with a condenser and magnetic stirrer, 1 g of 1- (2-hydroxypropyl)-3-methylimidazolium bromide (0.003 mol) (Aldrich) and 40 cm^3 H_2O and 0.14 g of sodium borohydride (0.0037 mol) (Aldrich) were stirred



(a) $PMIBH_3$ (b) DTPTf

Fig. 1 — Chemical structures of ionic liquids

rapidly for 2 min at -20 °C and extracted with CH_2Cl_2 (Aldrich). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. After drying under vacuum for 2 h, the product was obtained in 80% yield as a colorless oily liquid, chemical structure of obtained IL is given in Fig. 1(b). The product was characterized by ^{1}HNMR and gave satisfactory spectroscopic data in accordance with the structure. ^{1}H NMR (400 MHz, DMSO-d_6,25 °C, ppm): δ8.67, (S, 1H), 7.37 & 7.42, J =2.2 & 2.2 (d 2H), 3.38, J=5.1 (S, N-CH_3), 4.32, J= 2.9 (S,1H), 4.13, J=3.6 (S,1H), 4.00, J=5.2 (m,*CH), 3.52, J=3.1 (d,3H).

2.2 Preparation of gel polymer electrolytes

The copolymer, poly (vinylidene fluoride-co-hexaflouropropylene) (PVdF-HFP; ~M.W.400,000), was procured from Sigma-Aldrich. PVdF-HFP and the synthesized ILs, $PMIBH_3$ and DTPTf, were vacuum dried at room temperature and ~80 °C, respectively, for ~12 h prior to use. The gel polymer electrolyte films were prepared by the solution-cast method. In the first step of this method, mixtures of ionic liquids with polymer were prepared. The predetermined amount of PVdF-HFP was dissolved in acetone separately. The ILs was added to this solution in 80:20 (w/w) ratios. These solutions were then stirred magnetically at room temperature for ~24 h and ultrasonicated for few seconds to ensure a homogeneous mixing. The final solutions were casted over glass petri-dishes and allowed for slow evaporation of the solvent. Finally, the free-standing gel polymer electrolyte films were obtained. The gel polymer electrolytes were found in the form of free-standing films of thickness ~200 µm. Images of gel polymer electrolytes are shown in Fig. 2 (a). All the gel films were stored in dry atmosphere to avoid moisture adsorption.

2.3 Physical characterization

Morphological changes due to the addition of ILs into the PVdF-HFP network were characterized using a scanning electron microscope (SEM, JEOL, JSM 5600). The SEM micrographs were taken at low vacuum after sputtering gold on the gel film samples to prepare conducting surfaces. X-ray diffraction (XRD) patterns of the gel polymer electrolyte films were recorded with a high resolution X-ray diffractometer (CuK$_\alpha$ radiation, 40 kV, 100 mA, Rigaku, model Dmax-2200) using Cu-K$_\alpha$ radiation in the Bragg angle (2θ) ranges from 5° to 90°.

Thermal stability and possible phase/structural changes in gel polymer electrolyte films were tested by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was carried out from room temperature to 900 °C under a dynamic dry nitrogen atmosphere at a heating rate of 10 °C/min using a Perkin Elmer TGA system (TGA-7). DSC (TA instruments, Model: Q100) was performed from room temperature (RT) to 400 °C at a heating rate of 10 °C min^{-1} in a static nitrogen atmosphere.

The ionic conductivity of the polymer electrolyte films was evaluated by means of ac impedance spectroscopy using Gamry instrument (Reference 3000, Potentiostatic/ Galvanostat/ ZRA) over the frequency range from 1 Hz to 100 kHz at a signal level of 10 mV. The temperature variation of ionic conductivity was evaluated by Bode plots (σ versus frequency plots). The Bode spectra were recorded using broadband dielectric (C-50, Novocontrole, Germany) over the frequency range from 1 Hz to few MHz for the temperature range from 0 °C (273 K) to 90 °C (363 K) varying at a heating rate of 1 °C/min in dynamic N_2 atmosphere. The low temperature is achieved using liquid nitrogen. There is a provision to achieve further low temperature -50 °C or more using this equipment. The impedance measurements of the gel polymer electrolyte films were performed by sandwiching the film between two stainless steel (SS) electrodes. The electrochemical stability window (ESW) of the films was evaluated by cyclic voltammetry at a scan rate of 1 mV/s. The total ionic transport number (t_{ion}) was obtained by polarization technique. In this technique, a SS| polymer electrolyte| SS cell was polarized by applying a step potential of 1.0 V and the resulting potentiostatic current was monitored as a function of time.

3 Results and Discussion

The structures of cations (DTP^+ and PMI^+) are not spherical, so they can be defined in length and width. The BH_3^- anion, according to the structure, is covalently attached to O to PMI^+. Theoretical calculations (geometry optimization and frequency calculation) were carried out using the density functional theory (B3LYP) methods at 6-31++G(d,p) basis set (Gaussian 09). The ACD drawings of the ionic liquids are shown in Fig. 2.

3.1 Structural analysis

To study the morphological changes due to the addition of DTPTf and $PMIBH_3$ in PVdF-HFP, the

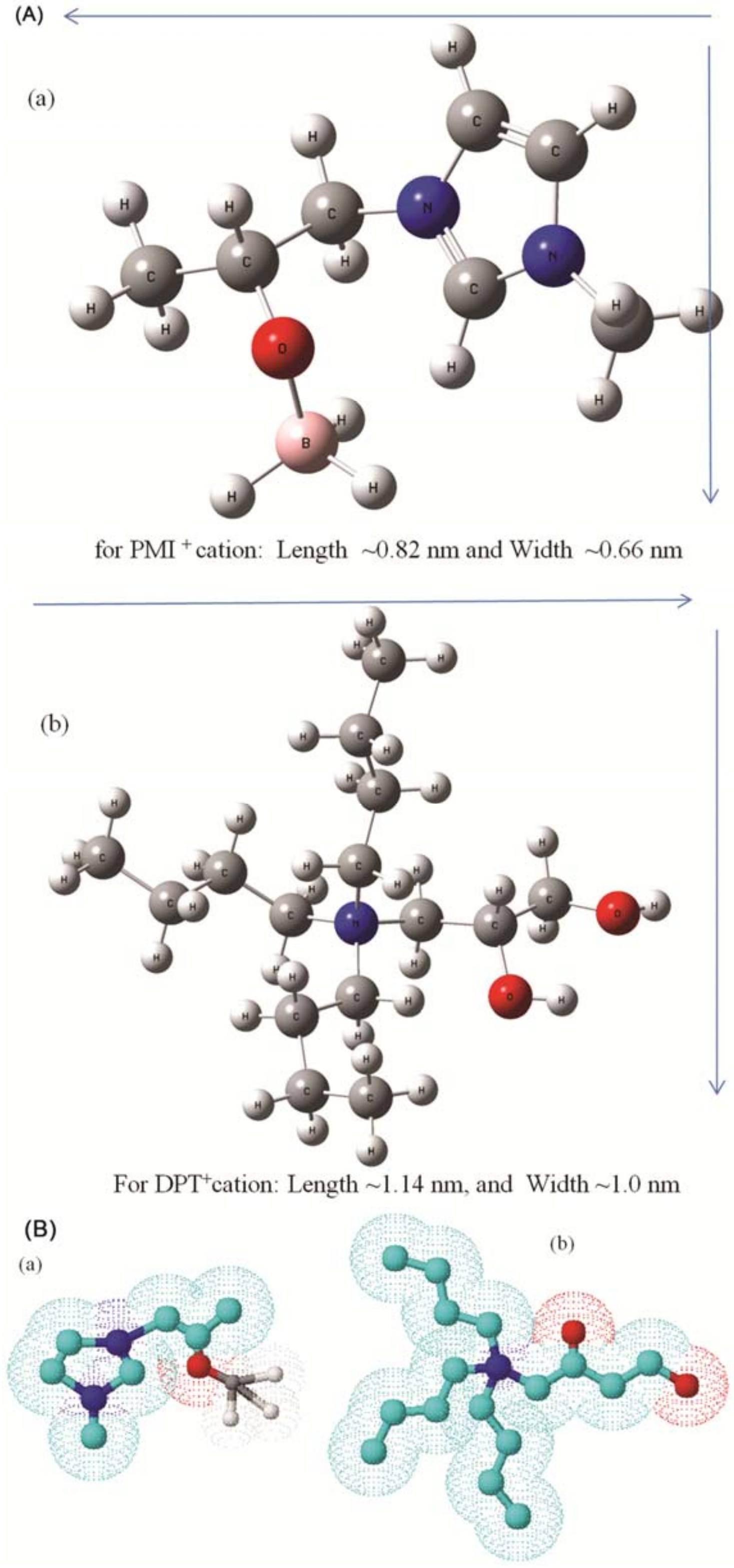


Fig. 2 — (A) Molecular structures and size of (a) PMI$^+$ and (b) DPT$^+$ cations, and (B) ACD drawings of (a) PMIBH$_3$ and (b) DTPTf ionic liquids

comparative SEM images have been recorded, as shown in Fig. 3. When IL is added to the host polymer PVdF-HFP, the composite system appears like a porous surface, indicating that IL fills the porous texture of the host polymer (Fig. 3 (c, d)). The morphological structure of pure PVdF-HFP is looking smoother and less porous in comparison to the blends of ionic liquids with polymer host.

On the dispersion of ionic liquids, the specific changes have been noted in the morphological features; on the addition of 80 wt% of ionic liquid $PMIBH_3$, the PVdF-HFP network shows the granular texture containing well defined spherical balls like entities (Fig. 3 (c)). On the addition of second ionic liquid DTPTf to the PVdF-HFP system, the SEM images are found to be distinctly different. In the material containing 80 wt% DTPTf, the porous texture contains coagulated and distorted granules (Fig. 3(d)). The size of cations is varied largely; the DTP^+ is almost double in comparison to PMI^+ cation. The free volume of the host polymer varied significantly after blending with two different ionic liquid, distinctly observed from the more swollen micrograph of DTPTf based polymer blend.

The above observations indicate that porous and granular texture of the gel polymer electrolytes depend on the physico-chemical properties (viscosity, dielectric constant, etc.) and the structure of ionic liquids, dispersed in the PVdF-HFP network. The changes on the microscopic and molecular scales which are discussed in the following sections have also been observed. It may be noted that the porous structures have the capability of retaining ionic liquid or liquid electrolyte, which provide the network of pathways for the motion of ions that lead to the enhancement in ionic conductivity.

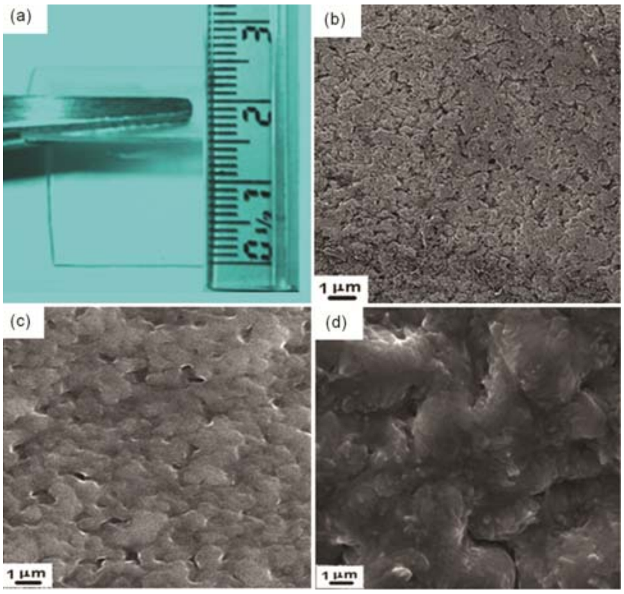


Fig. 3 — Photographs of (a) ionic liquid-polymer blend and SEM images of (b) PVdF-HFP, (c) PVdF-HFP + $PMIBH_3$ and (d) PVdF-HFP +DTPTf

Figure 4 shows the XRD patterns of pure PVdF-HFP, PVdF-HFP+IL composite with the two ILs ($PMIBH_3$ and DTPTf). The XRD pattern of pure PVdF-HFP film shows the typical characteristics of a semi crystalline microstructure with predominant peaks and shoulders at $2\theta = 17.6^o$, 19.7^o, 26.6^o and 38.9^o (Fig. 4(a)). On the addition of ILs ($PMIBH_3$ and DTPTf) these characteristic peaks of polymer diminish, instead broad humps appear between 15^o and 40^o (Fig. 4(b, c)), which indicates the predominantly amorphous nature of the PVdF-HFP+ILs gel electrolyte materials[21]. These humps appear to be the combination of two broad peaks at ~19.7^o and ~26.5^o. Such predominant amorphous nature of gel polymer electrolyte at room temperature is confirmed from DSC studies.

3.2 Thermal properties

Figure 5 shows the TGA curves of pure PVdF-HFP film, PVdF-HFP+$PMIBH_3$ and PVdF-HFP+DTPTf blends. The host polymer PVdF-HFP is highly thermally stable as almost no weight loss occurs up to ~400 °C (Fig. 5(a)). A negligible weight loss (~4 wt%) has been observed at 100 °C for PVdF-HFP-ionic liquid blends (Fig. 5(b, c)), which is mainly due to desorption of moisture. The onset of

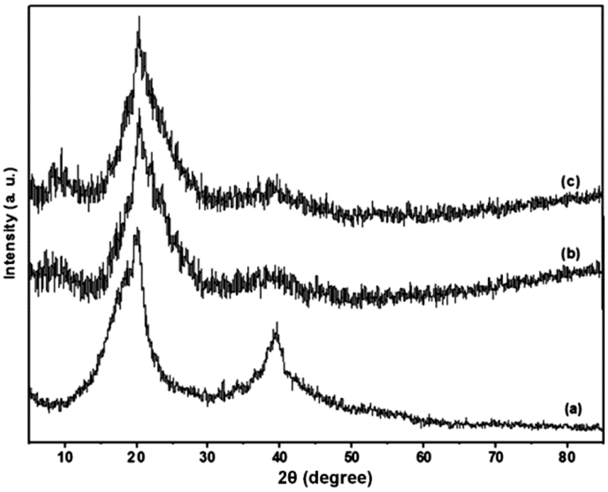


Fig. 4 — XRD patterns of (a) PVdF-HFP, (b) PVdF-HFP + $PMIBH_3$ and (c) PVdF-HFP + DTPTf

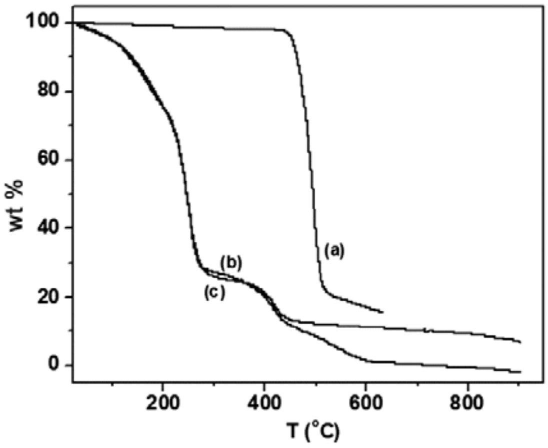


Fig. 5 — TGA curves of (a) PVdF-HFP, (b) PVdF-HFP + $PMIBH_3$ and (c) PVdF-HFP + DTPTf

sharp weight loss is found after ~100 °C for both blends, owing to the evaporation of adsorbed moisture due to hydrophilic nature of ionic liquids and possibly may be due to rapid decomposition of ionic liquids. The initial trend of both kinds of ionic liquids is similar. Further, a plateau region has been observed between ~280 °C and ~400 °C for each blend system (Fig. 5(b, c)). The plateau region is steeper for DTPTf than the plateau of $PMIBH_3$, which indicates the relatively lower thermal stability of DTPTf based polymer blend system over the $PMIBH_3$ based polymer blend systems. There is possible aromatization of carbon chains to form stable carbon solid from $PMIBH_3$ based polymer blend, whereas there is mostly decomposition in the DTPTf based polymer blends attributed to their loose molecular structure. It may be noted that the yield of carbon is quite high in this case of $PMIBH_3$ based polymer blend. Hence the $PMIBH_3$ can be a potential candidate for novel carbon materials like other ionic liquids[19].

The DSC curves of pure PVdF-HFP, PVdF-HFP+$PMIBH_3$ and PVdF-HFP+DTPTf blends are presented in Fig. 6. The following salient features can be dug out from the comparative DSC studies. An endothermic peak appearing at the temperature ~145 °C corresponds to the melting of PVdF-HFP host polymer film. The polymer PVdF-HFP and IL composites show predominant characteristic DSC peaks of IL without any marked changes (Fig. 6 (c)). The melting peak of PVdF-HFP is not seen distinctly, when added to IL, because of its lower proportion and possible overlapping with decomposition of IL beyond 100-125 °C temperature range[22,23].

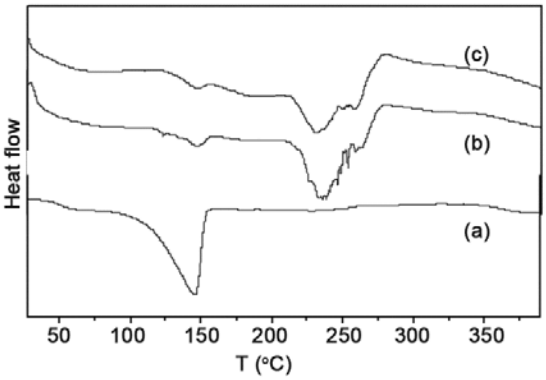


Fig. 6 — DSC curves of (a) PVdF-HFP, (b) PVdF-HFP + $PMIBH_3$ and (c) PVdF-HFP + DTPTf

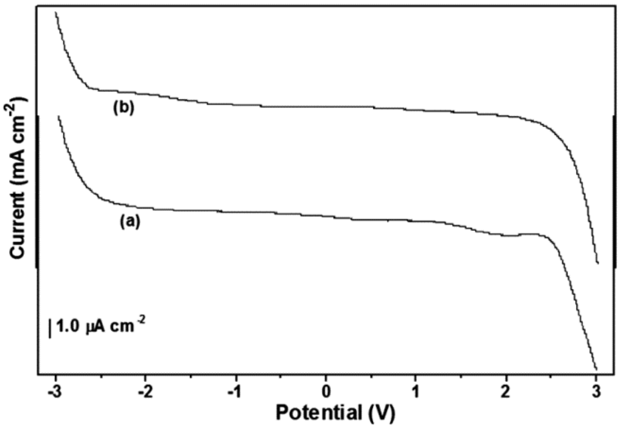


Fig. 7 — CV responses of ionic liquid based gel polymer electrolyte films, (a) PVdF-HFP + $PMIBH_3$ and (b) PVdF-HFP / DTPTf recorded using symmetrical platinum electrodes at a scan rate of 1 mVs^{-1}

3.3 Electrochemical properties: Electrochemical stability and ionic conductivity

The electrochemical stability window (ESW) is the working voltage range over which an electrolyte remains safe and stable. The ESW of the prepared polymer gel electrolytes was evaluated by cyclic voltammetry using symmetrical platinum electrodes. Figure 7 shows the typical cyclic voltammograms of PVdF-HFP/$PMIBH_3$ and PVdF-HFP/DTPTf gel systems, recorded at the scan rate of 1 mV s^{-1}. The voltage range of stability was chosen over which the voltammetric current was almost constant and beyond this region the onset of the increase in current was observed. The oxidation/reduction waves, observed in the voltammograms (which are within the tolerance limit), are possibly due to the presence of adsorbed species like hydroxyl groups and/or due to impurities. The ESW of DTPTf gel electrolyte is in the -2.8 to +2.8 V range (Fig. 7), which is found to be higher as compared to $PMIBH_3$-based electrolytes, i.e., from -2.6

to +2.6 V voltage range[24]. The ESW values obtained are suitable from device application point of view particularly for high performance super capacitors.

Figure 8 shows variation of ionic conductivity with frequency ranges from 10^6 Hz to 1 Hz. The ac conductivity values increase with increasing frequency. These values become constant around 10 kHz, further constant till frequency reached value 10^6 Hz. The constant conductivity values in this plateau region are the exact conductivity values. The ionic conductivity values for the two ILs based polymer blend system show a marked difference at all temperatures ranges 273 K to 363 K (Fig. 8 (a, b)). At room temperature PVdF-HFP+PMIBH$_3$ systems show a conductivity of around 2×10^{-6} Scm^{-1}, while this value is around 1×10^{-2} Scm^{-1} for the PVdF-HFP+DTPTf system that is about four orders of magnitude higher than the former. This large difference in conductivity values may be attributed to the fact that $\mathrm{BH_3^-}$ in PMIBH$_3$ is not an anion in the true sense; it is covalently bonded to the oxygen of the propoxy group of the PMI$^+$ part which prevents PMIBH$_3$to dissociate in the polymer matrix. The conductivity for PVdF-HFP+PMIBH$_3$ system increases by almost three orders of magnitude between 273 K and 383 K where it is almost 6×10^{-4} S cm^{-1}. As usual, this increase may be easily attributed to the increase in the dissociation constant of the C-O bond between the $\mathrm{BH_3^-}$ and propyl-chain.

Figures 9 and 10 show the temperature dependence of ionic conductivity of the two PVdF-HFP+IL gel polymer electrolytes. Both of them follow the Arrhenius behavior. Accordingly, the ionic conductivity relation with temperature can be expressed as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad \ldots (1)$$

where σ_0 is pre-exponential factor, E_a is activation energy and k is Boltzmann constant. The activation energy values are marked on the log(σ) versus 1/T plots for different temperature range. The plot for the PVdF-HFP + DTPTf system has two distinct regions: before and after 60 °C (333 K). The magnitude of the slope is larger (i.e., the activation energy is larger) for

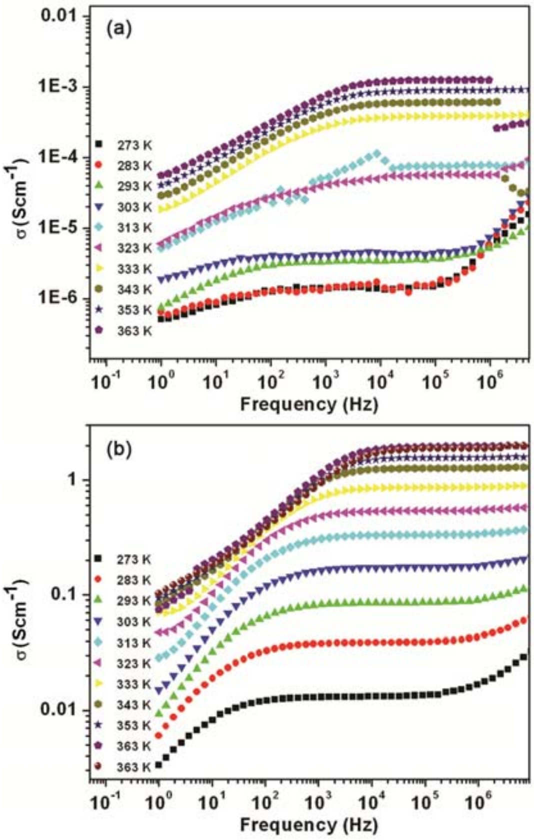


Fig. 8 — Conductivity versus temperature plot for (a) PVdF-HFP+PMIBF$_3$ and (b) PVdF-HFP +DTPTf composite system

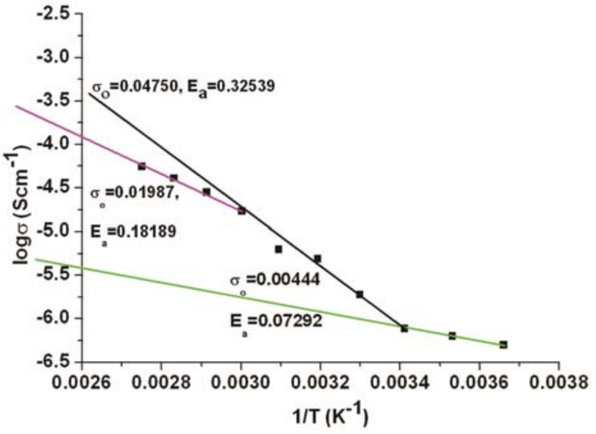


Fig. 9 — Plot of logσ versus 1/*T* for the PVdF-HFP + PMIBH$_3$ system

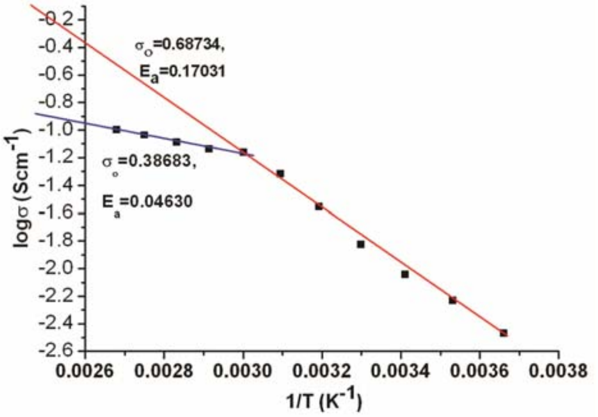


Fig. 10 — Plot of logσ versus 1/T for the PVdF-HFP+DTPTf system

temperatures lesser than 333 K. Both these regions have clear Arrhenius behavior. The decreased slope may be attributed to slight decomposition or evaporation of DTPTf at around that temperature, as can be seen in Fig. 6(c) of TGA and DSC.

Whereas, for the PVdF-HFP+PMIBF$_3$ case, conductivity versus temperature plots more or less has a constant slope at higher temperatures. However, there is a change observed in the slope at around 17 °C (290 K). After 290 K, the activation energy increases slightly. The reason for this increase in activation energy may be the beginning of reduction in the viscosity of the system with temperature[25,27]. Such kind of materials is being reported in various applications[28-30].

4 Conclusions

Novel, chiral, room temperature ionic liquids for applications in gel polymer electrolytes (GPE) have been synthesized, incorporated in a PVdF-HFP matrix to form GPEs and characterized. On the basis of morphological, structural, thermal, and electrochemical studies, the following conclusion have been drawn:

(i) The gel electrolyte films are free-standing and flexible with excellent mechanical/ dimensional integrity.

(ii) Presence of ILs in the system results in a composite with porous surface. For PMIBF$_3$the composite shows spherical granular structures. For DTPTf, the granules are coagulated and distorted, and their size increases with IL content.

(iii) XRD patterns indicate the composite PVdF-HFP + IL system are amorphous.

(iv) The ESW of the two types of gel polymer electrolyte films with ILs PMIBF$_3$ and DTPTf are ~5.8 V (from -2.9 to +2.8 V) and ~5.2 V (from -2.6 to + 2.6 V), respectively.

(v) TGA curves indicate significant decomposition of ILs and small PVdF-HFP chains above 100 °C. DSC behavior for both composite systems show that the PVdF-HFP melting peak is over whelped by the ILs.

(vi) Temperature dependence of ionic conductivity shows the Arrhenius type thermally activated process and has been correlated with the different transitions observed from DSC results. The gel materials can be used as electrolytes in ionic devices for the temperature range from -40 °C to ~100 °C.

In view of above studies, the present PVdF- HFP + IL gel polymer films made from the two different ionic liquids appear to be excellent electrolyte materials in energy storage ionic devices, particularly in electrical double layer capacitors (EDLCs)/super capacitors.

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References

1 Walden P, *Bull Acad Imp Sci*, 8 (1914) 405.
2 Ohno H, *Electrochemical aspects of ionic liquids*, (Wiley, New Jersy), 2005.

3 Rogers R D & Seddon K R, *Ionic liquids: Industrial applications for green chemistry*, (American Chemical Society, Washington DC), 2002.

4 Webber A, Blomgrem G E, Schalkwijk W A & Scrosati B, *Advances in lithium ion batteries*, (Kluwer/Plenum Pub, New York), 2002.

5 Fuller J, Carlin R T & Osteryoung R A, *J Electrochem Soc*, 144 (1997) 3881.

6 MacCallum J R & Vincent C A, *Polymer electrolytes review-1 & 2*, (Elsevier Applied Science, London), 1987 & 1989.

7 Gray F M, *Solid polymer electrolytes: Fundamental and technological applications,* (VCH Publishers, New York), 1991.

8 Gray F M, *Polymer electrolytes,* (Royal Society of Chemistry, Cambridge), 1997.

9 Abraham K M & Alamgir M, *J Electrochem Soc*, 136 (1990) 1657.

10 Jiang Z, Carrol B & Abraham K M, *Electrochim Acta*, 42 (1997) 2667.

11 Saito Capiglia C, Kataoka Y, Kodama H, Quartarone T E & Mustarelli P, *Solid State Ion,*131 (2000) 291.

12 Lee J, Panzer M J, He Y, Lodge T P & Frisbie C D, *J Am Chem Soc*, 129 (2007) 4532.

13 Asai Tominaga, Sumita Y S, Panero M S & Scrosati B, *J Power Sources*, 146 (2005) 402.

14 Shin J H, Henderson W A & Passerini S, *J Electrochem Soc*, 152 (2005) 978.

15 Pandey G P, Kumar Y & Hashmi S A, *Indian J Chem*, 49A (2010) 743.

16 Matsumoto H & Miyazaki Y, *Chem Lett*, 8 (2000) 922.

17 Bonhote P, Dias A P, Papageorgiou N, Kalyanasundaram K & Grätzel M, *Inorg Chem*, 35 (1996) 1168.

18 Endres F, *Electrodeposition from ionic liquids*, Abbott A, Edn MacFarlane, (Wiley-VCH, Weinheim, Germany), 2008.

19 Ding J, Zhou D & Spinks G, Wallace G, Forsyth M & MacFarlane D, *Chem Mater*, 15 (2003) 2392.

20 Rupini B, Pasricha S & Rathi B, *Int J Org Chem,* 3 (2013) 190.

21 Zhang S, Dokko K & Watanabe M, *Mater Horiz*, 2 (2015) 168.

22 Grillone A M, Panero S, Retamal B A & Scrosati B, *J Electrochem Soc*, 146 **(**1999) 27.

23 Chandra S, Sekhon S S & Arora N, *Ionics*, 6 (2000) 112.

24 Ozdemir S, Varlikli C, Oner I, Ocakoglu K & Icli S, *Dyes Pigments*, 86 (2010) 206.

25 Kumar Y, Hashmi S A & Pandey G P, *J Phys Chem C*, 116 (2012) 26118.

26 Shalu S K, Chaurasia S K, Singh R K & Chandra S, *J Phys Chem B,*117 (2013) 897.

27 Sengwa R J, Choudhary S & Sankhla S, *Indian J Eng Mater Sci*, 16 (2009) 395.

28 Choudhary S & Sengwa R J, *Indian J Pure Appl Phys*, 49 (2011) 600.

29 Sengwa R J, Sankhla S & Choudhary S, *Ionics*, 16 (2010) 697.

30 Lim C S & Ramesh S & Majid S R, *Ceram Int*, 39 (2013) 745.