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## Effects of Bu<sub>3</sub>MeNTf<sub>2</sub>N Ionic Liquid Addition on Conductivity of PVC- NH<sub>4</sub>Tf Polymer Electrolytes

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### ABSTRACT

Solid polymer electrolytes (SPEs) with poly (vinyl) chloride (PVC) doped with a fixed amount of ammonium trifluoro methane sulfonate (NH<sub>4</sub>Tf) and with varying concentrations of ionic liquid butyltrimethyl ammonium bis (trifluoromethyl sulfonyl) imide (Bu<sub>3</sub>MeNTf<sub>2</sub>N) were synthesised via solution cast technique. PVC-NH<sub>4</sub>Tf- Bu<sub>3</sub>MeNTf<sub>2</sub>N-based SPEs with 15 wt % Bu<sub>3</sub>MeNTf<sub>2</sub>N exhibit conductivity of  $1.56 \times 10^{-4} \text{ Scm}^{-1}$  at room temperature. The ionic conductivity is attributed to the dissociation of NH<sub>4</sub>Tf facilitated by Bu<sub>3</sub>MeNTf<sub>2</sub>N. Results of XRD indicate that the most amorphous film has the highest conductivity and this is corroborated by the results of DSC. FTIR spectra revealed that Bu<sub>3</sub>MeNTf<sub>2</sub>N has weak interaction suggesting that it acts mainly as a lubricant to facilitate polymer segmental motion.

**Keywords:** polymer electrolytes; ionic liquid; ionic conductivity; XRD; infra-red spectroscopy.

### 1. INTRODUCTION

Plasticisation (Hadi et al., 2020) has been one of the methods adopted by researchers to increase the conductivity of polymer electrolytes apart from formation of composite polymer electrolytes (Pradhan et al., 2011). Plasticising solvents such as EC (Wang et al., 1996), PC (Starkey et al., 1997), DMF (Subban et al., 2004), PEG (Srivastava et al., 2000) and other low molecular weight aprotic solvent with high dielectric constant and low viscosity has often been used to achieve plasticising effects in polymer electrolytes. Of late, ionic liquid (IL) which consists of an organic and bulky cation with inorganic anion have been used as a plasticising agent (Cheng et al., 2007, Mohammad et al., 2013, Anuar et al., 2012, Missan et al., 2010). Rather, the ions in IL exists in alternating layers of cation and anions extending several ion layers (Missan et al., 2010). Thus, IL on its own cannot be used as electrolytes in batteries which involve migration of specific target ions. On the other hand, IL can be used as electrolytes in capacitors and actuators which does not involve migration of specific target ions. Hence many different forms of IL incorporated polymer electrolyte have been reported. In most reports, the polymer electrolyte is composed of a polymer doped with inorganic salt and IL or IL doped with inorganic salt and polymer (Cheng et al., 2007, Mohammad et al., 2013, Anuar et al., 2012) while in the work reported by Missan et. al. (Missan et al., 2010), the polymer electrolyte is composed of a polymer with IL and filler. From the mass of work reported for IL incorporated polymer electrolytes, although interactions are observed between IL and the other components of the polymer electrolyte (Mohammad et al., 2013, Anuar et al., 2012), the role

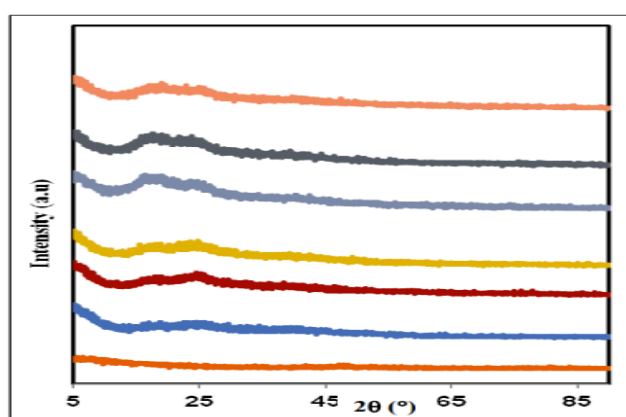
played by IL is still unclear. In this work, ionic liquid Bu<sub>3</sub>MeNTf<sub>2</sub>N is used as a plasticiser to enhance the conductivity of PVC-NH<sub>4</sub>Tf based polymer electrolytes. The ionic conductivity, some structural and thermal properties are presented in this paper. This type of polymer electrolyte enhances the development of a new generation of devices which improves the stability and performance of the devices due to the solid nature of the electrolyte which is PVC as polymer host of proton conducting polymer electrolyte and Bu<sub>3</sub>MeNTf<sub>2</sub>N ionic liquid as a plasticizer are a novelty in this research.

## 2. METHODOLOGY

PVC and NH<sub>4</sub>Tf were mixed with Bu<sub>3</sub>MeNTf<sub>2</sub>N in various wt.% ratio with ratio of PVC-NH<sub>4</sub>Tf fixed at 70:30 wt. %. Solution cast films were obtained by pouring the solution into glass petri dishes, which were dried at room temperature. The films formed were further dried in a vacuum oven at 313 K for 24 hours. Impedance was measured using HIOKI 3532-50 LCR Hi-Tester for frequency ranging from 100 Hz to 1 MHz. DSC was measured at heating rate of 20°Cmin<sup>-1</sup> in nitrogen atmosphere using Perkin-Elmer Q100/200 DSC. FTIR measurements were carried out using Perkin-Elmer FTIR Spectrometer with resolution of 4 cm<sup>-1</sup> while XRD were recorded using X'pert Pro Analytical Diffractometer for 2θ varying from 5° to 90°.

## 3. RESULTS AND DISCUSSION

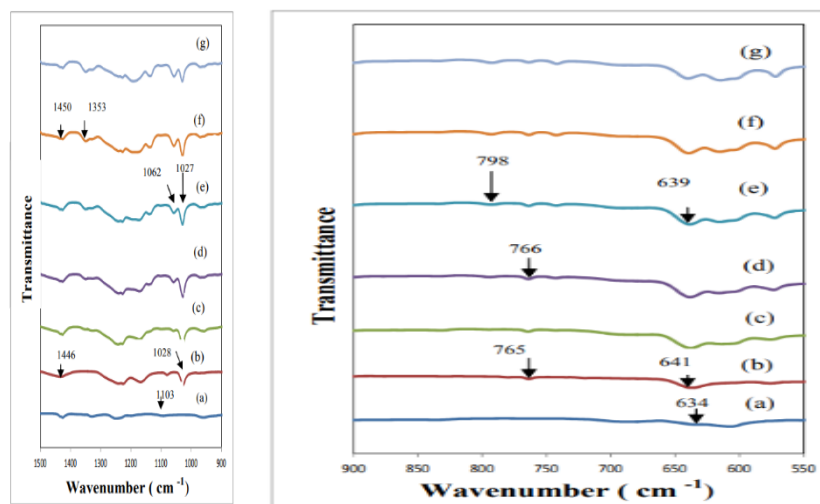
To investigate the effects of ionic liquid addition on the nature of PVC-NH<sub>4</sub>Tf complex, XRD studies were carried out. Figure 1 shows the XRD patterns of pure PVC film, PVC-NH<sub>4</sub>Tf complex at 70:30 wt. % ratio and PVC-NH<sub>4</sub>Tf-Bu<sub>3</sub>MeNTf<sub>2</sub>N complex with different amounts of Bu<sub>3</sub>MeNTf<sub>2</sub>N. The XRD pattern of pure PVC shows its predominant characteristic broad peak from 2θ = 13 to 30° with centre at 25° indicative of the low crystalline nature of PVC. On addition of NH<sub>4</sub>Tf in PVC a broad hump appeared with two peaks at 2θ = 14 and 24°. The intensity of the broad hump is observed to increase substantially with increasing concentration of Bu<sub>3</sub>MeNTf<sub>2</sub>N (Figure 1 c-e) which shows a decrease in degree of crystallinity of the polymer electrolyte.



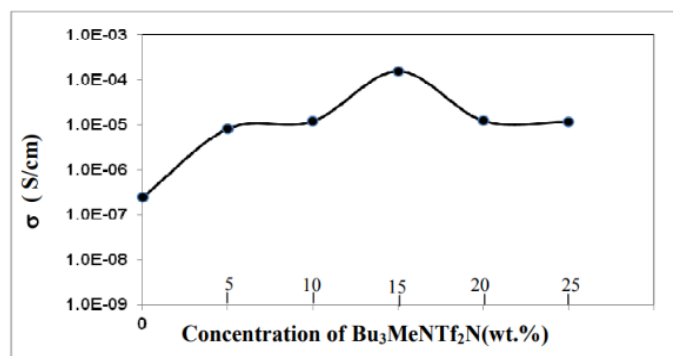
**Figure 1.** XRD spectra of a) PVC b) PVC-NH<sub>4</sub>Tf complex with 70:30 wt. % ratio and PVC-NH<sub>4</sub>Tf- Bu<sub>3</sub>MeNTf<sub>2</sub>N complex with c) 95: 5 (d) 90:10 (e) 85:15 (f) 80:20 (g) 75:25 wt. % ratio.

Interaction between components of the polymer electrolyte is investigated by FTIR whose spectra are displayed in Figure 2 for the samples studied in this work. The IR peak

corresponding to C-Cl stretching at  $634\text{ cm}^{-1}$  (Figure 3) of PVC shifted to higher wavenumber at  $639\text{ cm}^{-1}$  in all the PVC-NH<sub>4</sub>Tf-Bu<sub>3</sub>MeNTf<sub>2</sub>N complexes enunciating the interaction between C-Cl and NH<sub>4</sub><sup>+</sup> /H<sup>+</sup>. CF<sub>3</sub> symmetric deformation of NH<sub>4</sub>Tf (spectrum not shown) at  $764\text{ cm}^{-1}$  remains unshifted at  $765\text{ cm}^{-1}$  in PVC-NH<sub>4</sub>Tf and  $766\text{ cm}^{-1}$  in PVC-NH<sub>4</sub>Tf-Bu<sub>3</sub>MeNTf<sub>2</sub>N complexes with not much change in intensity and shape upon increase in IL concentration indicating that the IL interacts weakly with the polymer and salt suggesting its lubricating action. The band at  $764\text{--}766\text{ cm}^{-1}$  implies the presence of a highly associated triflate ion Li<sub>2</sub>Tf<sup>+</sup> (Starkey et al., 1997) indicating presence of 'free' ions in the sample which contributes to its conductivity. The shift of SO<sub>3</sub> symmetric stretching of NH<sub>4</sub>Tf at  $1032\text{ cm}^{-1}$  to lower wavenumber at  $1027\text{ cm}^{-1}$  in PVC-NH<sub>4</sub>Tf-IL complexes indicate presence of free ions (Mohammad et al., 2013) which also contributes to the conductivity of the system. Complexation of the IL (IR spectrum not shown) results in changes in the frequencies of bands associated with it: combination of C-S and S-N stretching, S-N-S asymmetric stretching and C-SO<sub>2</sub>-N bonding at  $791$ ,  $1054$  and  $1342\text{ cm}^{-1}$  respectively. This is shown in Fig. 2, where it is seen that the combined C-S and S-N stretching at  $791\text{ cm}^{-1}$  shifted to  $798\text{ cm}^{-1}$  disclosing that there is interaction between the IL and components of the polymer electrolyte. The intensity of this band however did not change much with increased IL concentration indicating a weak interaction thereby suggesting that it acts more like a lubricant.



**Figure 2.** FTIR spectra of a) PVC b) PVC-NH<sub>4</sub>Tf complex with 70:30 wt. % ratio and PVC - NH<sub>4</sub>Tf- Bu<sub>3</sub>MeNTf<sub>2</sub>N complex with c) 95: 5 (d) 90:10 (e) 85:15 (f) 80:20 (g) 75:25 wt. % ratio with different wavenumber ( $\text{cm}^{-1}$ )



**Figure 3.** Ionic conductivity dependence on concentration of Bu<sub>3</sub>MeNTf<sub>2</sub>N in wt. %.

The variation of room-temperature ionic conductivity of PVC-NH<sub>4</sub>Tf with respect to Bu<sub>3</sub>MeNTf<sub>2</sub>N content is presented in Figure 3. A sudden initial increase of almost one order of conductivity is observed when 5 wt. % of ionic liquid is added to the PVC complex. Thereafter a gradual increase in the conductivity is observed on further addition of IL up to a maximum of  $1.56 \times 10^{-4} \text{ Scm}^{-1}$  for 15 wt.%. Beyond this composition, the ionic conductivity decreased. Presence of Bu<sub>3</sub>MeNTf<sub>2</sub>N increased the conductivity up to three times when compared to the IL free sample. The initial increase in conductivity is attributed to the enhancement of ionic mobility due to plasticisation of the PVC complex. The amorphous phase of the PVC complex increases with increasing Bu<sub>3</sub>MeNTf<sub>2</sub>N content up to 15 wt. % resulting in the increase in conductivity. This is corroborated by XRD results which showed that the complex with 15 wt.% IL is the most amorphous. Addition of IL has shown presence of free ions due to dissociation of salt leading to an increase in the number of charge carriers. The incorporation of Bu<sub>3</sub>MeNTf<sub>2</sub>N into this polymer-salt system has produced more mobile ions and has also lowered the viscosity that led to increase in ionic mobility which consequently led to increase in conductivity (Missan et al., 2010).

#### 4. CONCLUSION

PVC- NH<sub>4</sub>Tf- Bu<sub>3</sub>MeNTf<sub>2</sub>N proton conducting polymer electrolytes have been prepared by solution cast technique. Highest ionic conductivity was obtained for the electrolyte PVC-NH<sub>4</sub>Tf: Bu<sub>3</sub>MeNTf<sub>2</sub>N with weight ratio of 85:15 with a value of  $1.56 \times 10^{-4} \text{ Scm}^{-1}$ . XRD and DSC results showed that the Bu<sub>3</sub>MeNTf<sub>2</sub>N containing polymer electrolyte films were more amorphous and flexible with improved thermal stability. FTIR showed that Bu<sub>3</sub>MeNTf<sub>2</sub>N acts as a plasticizer with weak interaction in the polymer system.

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