Correlation between ionic conductivity and fluidity of polymer gel electrolytes containing NH$_4$CF$_3$SO$_3$

HARINDER PAL SINGH, RAJIV KUMAR and S S SEKHON*

Department of Applied Physics, Guru Nanak Dev University, Amritsar 143 005, India

Abstract. Nonaqueous polymer gel electrolytes containing ammonium triflate (NH$_4$CF$_3$SO$_3$) and dimethyl-acetamide (DMA) with polymethylmethacrylate (PMMA) as the gelling polymer have been synthesized which show high value of conductivity (~ 10^{-2} S/cm) at 25°C. The conductivity of polymer gel electrolytes containing different concentrations of NH$_4$CF$_3$SO$_3$ shows a small decrease with the addition of PMMA and this has been correlated with the variation of fluidity of these gel electrolytes. The small decrease in conductivity with PMMA addition shows that polymer plays the role of stiffener and this is supported by FTIR results which also indicates the absence of any active interaction between polymer and NH$_4$CF$_3$SO$_3$ in these gel electrolytes.

Keywords. Ionic conductivity; ion aggregates; FTIR spectroscopy; gels; fluidity.

1. Introduction

Proton conducting polymer electrolytes are materials of current interest due to their possible use in proton exchange membrane fuel cells (PEMFC), display devices, supercapacitors etc (Colomban 1992; Laforgue *et al* 1999; Cronin *et al* 1999; Paoli *et al* 2001; Perry and Fuller 2002). Solvent free polymer electrolytes based on the complexation of high molecular weight polyethylene oxide (PEO) and polypropylene oxide (PPO) with various ammonium salts have been studied in detail (Daniel *et al* 1988; Chandra *et al* 1990; Prusinowska *et al* 1994; Oradd *et al* 2000; Kumar and Sekhon 2002). Polymer electrolytes obtained by the complexation of ammonium triflate (NH$_4$CF$_3$SO$_3$) with PEO and PPO were also reported (Stainer *et al* 1984; Ansari *et al* 1985) in early eighties but due to their lower conductivity they were not persued thereafter.

Polymer gel electrolytes are another category of polymer electrolytes in which the solvent is retained in the electrolyte and these show high value of conductivity approaching 10^{-2} S/cm at room temperature. These electrolytes belong to solvent–salt–polymer hybrid system in which the salt solution is immobilized by the addition of a suitable polymer matrix (Feuillade and Perche 1975; Tsuchida *et al* 1983; Abraham and Alamgir 1990). The solvent provides the conducting medium whereas polymer provides mechanical stability to these electrolytes (Webber 1991; Sekhon *et al* 1998). The membrane presently being used in PEMFC is very expensive and as its conductivity depends upon humidity level, it can be used

over a limited range of temperature only (Slade *et al* 1983). Due to this there is a growing need for developing an alternative proton conducting membrane which possess high value of conductivity and is also suitable for use over a wide temperature range. This is the motivation for the present work.

In the present paper, polymer gel electrolytes containing NH$_4$CF$_3$SO$_3$ in dimethylacetamide (DMA) and with polymethylmethacrylate (PMMA) as the gelling polymer have been studied. Conductivity, pH and viscosity of liquid and polymer gel electrolytes have been studied as functions of salt concentration, polymer concentration and temperature. FTIR studies have also been carried out to check the interaction between salt, solvent and polymer.

2. Experimental

Ammonium trifluoromethanesulphonate (NH$_4$CF$_3$SO$_3$) (Aldrich), dimethyl-acetamide (DMA) (dielectric constant = 37·8, viscosity = 1·937 cP at 25°C) (Merck) and polymethylmethacrylate (PMMA) (Aldrich, av. mol. wt. 120,000) have been used as the starting materials in the preparation of liquid and gel electrolytes. Liquid electrolytes were prepared by dissolving NH$_4$CF$_3$SO$_3$ in different concentrations (expressed as molarity value) in DMA and then gel electrolytes were obtained by adding PMMA in different amounts (expressed as wt% of liquid electrolyte) to the liquid electrolytes along with continuous stirring. The conductivity was measured by complex impedance spectroscopy using HP4284A precision LCR meter in the 20 Hz–1 MHz frequency range with a cell using platinum electrodes, details of which have been published earlier (Sekhon *et al* 1998). The viscosity of electrolytes was measured by Fungilab rotating viscometer model Visco

*Author for correspondence (sekhon_apd@yahoo.com)

Basic L and pH was measured by Systronics pH meter model 335. Room temperature FTIR spectra of all the samples was recorded in the 400–4000 cm^{-1} range by Perkin Elmer FTIR spectrometer.

3. Results and discussion

The electrical conductivity of liquid electrolytes prepared by adding $NH_4CF_3SO_3$ in different concentrations to DMA was measured and the variation of conductivity with salt concentration is given in figure 1. At low salt concentrations, the conductivity increases linearly and the conductivity of solvent ($\sim 10^{-6}$ S/cm) has been found to increase by four orders of magnitude to a value of $\sim 10^{-2}$ S/cm even at low concentration (0·1 M) of salt. $NH_4CF_3SO_3$ upon dissociation in solvent with high dielectric constant provides free ions, which take part in the conduction process and as a result conductivity increases. With further increase in salt concentration, conductivity reaches a maximum value of $3·65 \times 10^{-2}$ S/cm and then shows a small decrease at higher salt concentrations. The decrease in conductivity at higher salt concentrations is due to the presence of ion aggregates which do not take part in the conduction process, along with an increase in viscosity which would also result in lower conductivity (Bohnke *et al* 1993a; Southall *et al* 1996). The viscosity of electrolytes was also measured and its variation with the concentration of $NH_4CF_3SO_3$ is given in figure 2. The viscosity increases with an increase in salt concentration although the increase is very small. However, distinction must be made between macro and micro viscosity, the

viscosity measured experimentally is macroscopic in nature whereas it is the microscopic viscosity which is inversely related to mobility and hence conductivity (Bohnke *et al* 1993b).

The formation of ion aggregates at higher salt concentrations was also checked by mass action considerations (Ratner 1987). According to this method, if all the ions are present as free ions, then the plot between log *s* and log *C* (where *s* and *C* are the conductivity and concentration of salt in the electrolyte, respectively) shall be a straight line and if ion aggregates are formed then the plot between log *s* and log *C* shall show a deviation from straight line behaviour. A graph plotted between log *s* and log *C* for liquid electrolytes containing $NH_4CF_3SO_3$ in DMA is given in figure 3. At low salt concentrations the plot shows a straight-line behaviour whereas at high salt concentrations it shows deviation from straight line behaviour and the deviation increases with an increase in salt concentration. This suggests the presence of ion aggregates at higher salt concentrations, which is in agreement with the conductivity results given in figure 1.

The dissociation of $NH_4CF_3SO_3$ in the solvent shall give rise to free NH_4^+/H^+ ions and their concentration shall vary with a change in salt concentration. As the pH of an aqueous solution depends upon the concentration of free H^+ ions [pH = – log (H^+(aq.))] so any change in H^+ ion concentration shall be reflected in the pH of the electrolyte. pH of liquid electrolytes was, therefore, measured as a function of $NH_4CF_3SO_3$ concentration and the results are given in figure 4. For comparison the variation of log conductivity with salt concentration is also included in figure 4. The pH of liquid electrolytes decreases sharply
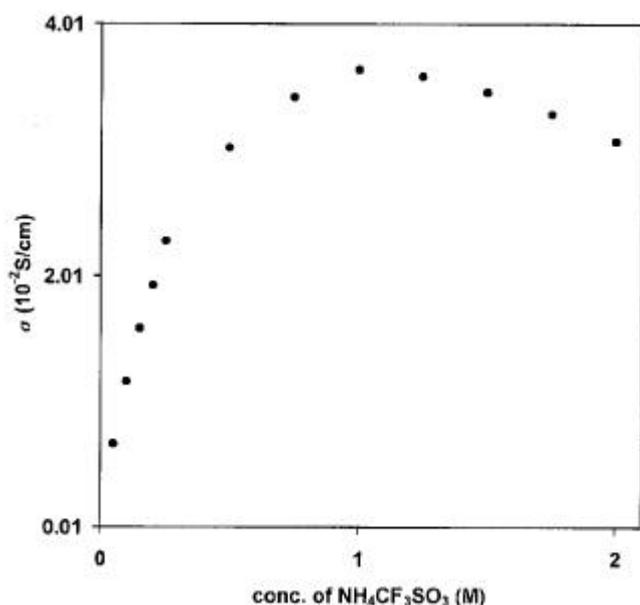
**Figure 1.** Variation of conductivity (*s*) of liquid electrolytes as a function of $NH_4CF_3SO_3$ concentration.
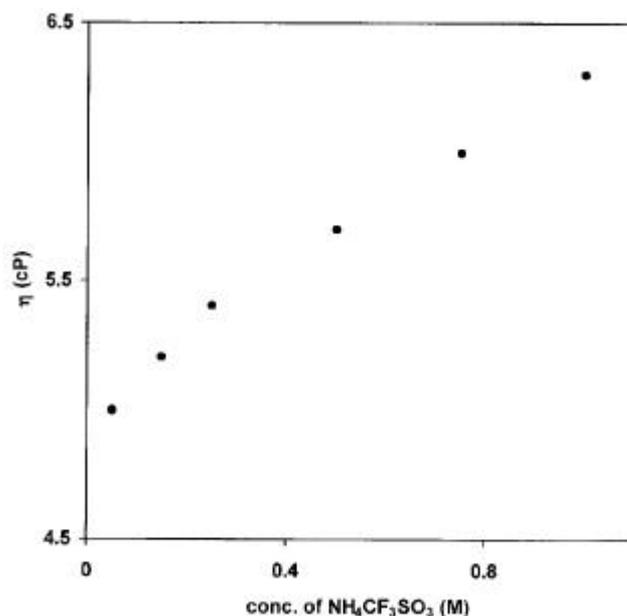
Figure 2. Variation of viscosity (*h*) of liquid electrolytes as a function of $NH_4CF_3SO_3$ concentration.

with the addition of even a small amount (0·1 M) of NH$_4$CF$_3$SO$_3$ which indicates that free ions are provided by the salt. With further increase in salt concentration, pH decreases slowly and reaches a nearly saturation value at higher salt concentrations up to 2 M. The small change in pH at higher salt concentrations indicates that H$^+$ ions provided by the salt are not free and may result in the formation of ion aggregates. These results are also in agreement with the conductivity variation which also increases from 10^{-6} S/cm to 10^{-2} S/cm with the addition of NH$_4$CF$_3$SO$_3$ and thereafter reaches a near saturation value which suggests that no new free H$^+$ ions are available for conduction and H$^+$ ions provided by an increase in salt concentration are used in the formation of ion aggregates. These results are consistent with the results of mass action considerations as given in figure 3.

The electrical conductivity of polymer gel electrolytes obtained by the addition of PMMA to liquid electrolytes was measured as a function of PMMA concentration and the results are given in figure 5. As the formation of ion aggregates depends upon salt concentration so liquid electrolytes containing different levels of ion aggregation i.e. different concentrations of NH$_4$CF$_3$SO$_3$ (0·1, 0·25, 0·5, 0·75 and 1 M), were used in the preparation of gel electrolytes. The results of figure 5 show that conductivity of liquid electrolytes containing different concentrations of NH$_4$CF$_3$SO$_3$ decreases with an increase in PMMA content but the decrease is small and is by a factor and not by an order. The conductivity of polymer gel electrolytes containing 4 and 10 wt% PMMA was also measured as a function of salt concentration and the results are given in figure 6. For comparison the variation of conductivity with salt concentration for liquid electrolyte is also in-

cluded in this figure. The results show that conductivity of gel electrolytes is lower than the corresponding liquid electrolytes at all salt concentrations but the difference is very small and is by a factor only. The small change in conductivity observed with the addition of PMMA as given in figures 5 and 6 suggests that the polymer does not play an active role in the conduction process and acts as a stiffener only (Sekhon *et al* 1998).
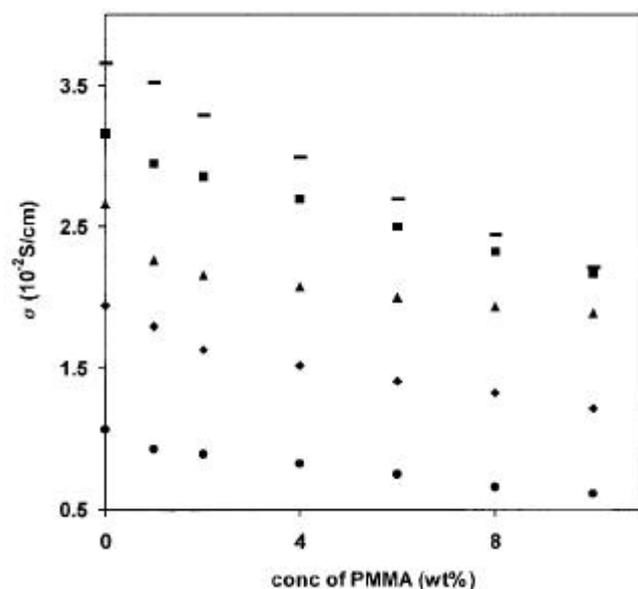
As the addition of polymer provides dimensional stability to the electrolytes by increasing its viscosity so the
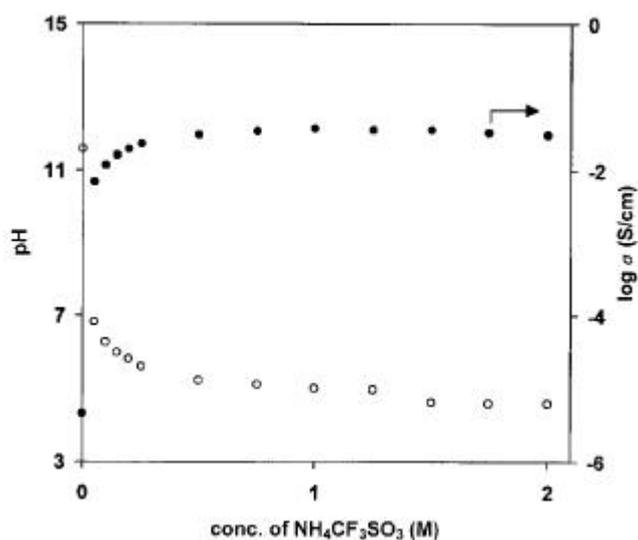
Figure 4. pH (o) and log conductivity (•) variation for liquid electrolytes with NH$_4$CF$_3$SO$_3$ concentration in DMA.
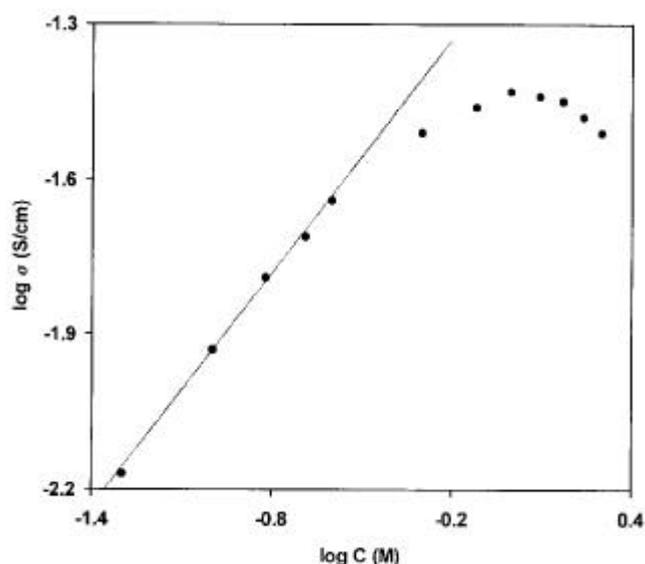
Figure 3. Log conductivity vs log salt concentration plot for liquid electrolytes containing NH$_4$CF$_3$SO$_3$ in DMA.
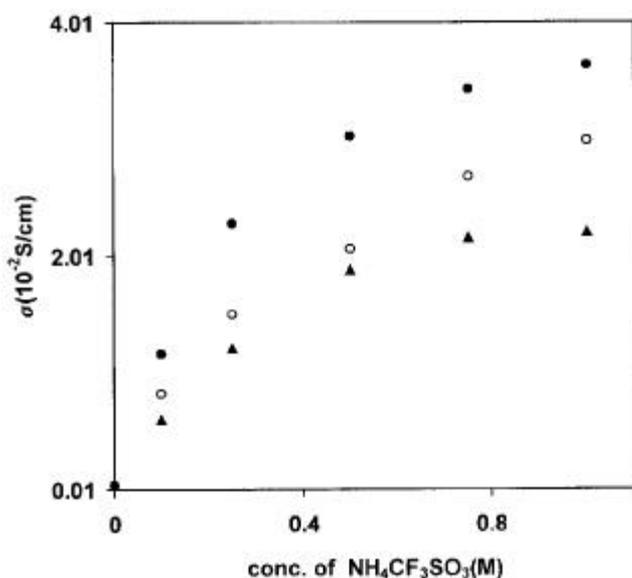

Figure 5. Conductivity as a function of PMMA concentration for polymer gel electrolytes containing 0·1 (•), 0·25 (♦), 0·5 (▲), 0·75 (■) and 1 M (–) NH$_4$CF$_3$SO$_3$ in DMA.

effect of polymer on the viscosity of electrolytes was also studied and fluidity ($f = h^{-1}$) was calculated which is given by

$$f = (e^2/6pr)\, n s,$$

where e is an electronic charge, r the effective radius of the diffusing species, n the number density of charge carriers and s is conductivity. The fluidity is directly proportional to the conductivity of the electrolytes. The variation of fluidity with PMMA concentration for gel electrolytes containing different concentrations of $NH_4CF_3SO_3$ in DMA is given in figure 7. Fluidity has been found to decrease with PMMA concentrations and its comparison with conductivity results (given in figure 5) shows a close correlation and a decrease in fluidity has been found to result with a decrease in conductivity.

The conductivity and viscosity of polymer gel electrolytes obtained by adding 10 wt% PMMA to 1 M solution of $NH_4CF_3SO_3$ in DMA were also measured as a function of temperature and the variation of log conductivity and log fluidity with reciprocal temperature is given in figure 8. For comparison the variation of conductivity of liquid electrolytes (1 M $NH_4CF_3SO_3$ in DMA) with temperature is also included in this figure. The conductivity of liquid and gel electrolytes increases with an increase in temperature and the variation for gel electrolytes is similar to that observed for the corresponding liquid electrolytes which suggests liquid-like behaviour of these gel electrolytes. The fluidity of gel electrolytes also increases with an increase in temperature and follows Arrhenius behaviour. Both fluidity and conductivity are directly related to each other and an increase in fluidity results in higher mobility which enhances the conductivity of the electrolytes.

The role of PMMA in these polymer gel electrolytes along with the possible interactions between salt, solvent and polymer was studied by FTIR spectroscopy and FTIR spectra of DMA (a), $NH_4CF_3SO_3$ (b), liquid electrolyte containing 1 M $NH_4CF_3SO_3$ in DMA (c) and the corresponding gel electrolytes containing 10 wt% PMMA (d) are given in figure 9. The spectra of $NH_4CF_3SO_3$ show bands at 1251 and 764 cm^{-1} due to the symmetric and asymmetric stretch of CF_3^- and bands at 1031 and 640 cm^{-1} due to the symmetric and asymmetric stretch of SO_3^-,
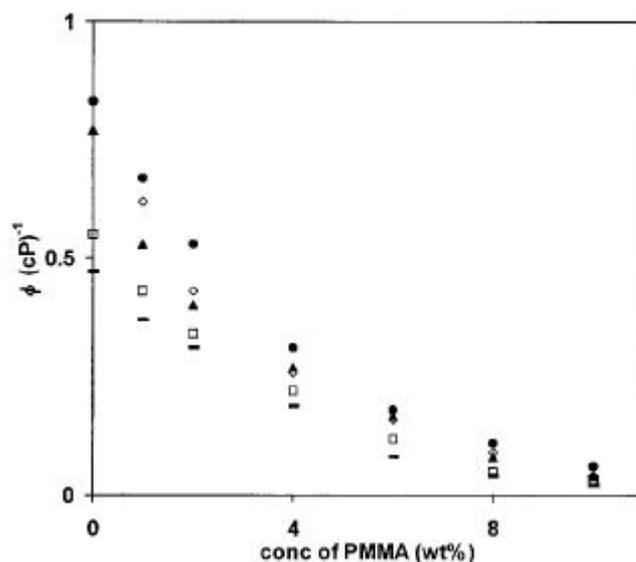
Figure 7. Variation of fluidity (f) with PMMA concentration for gel electrolytes containing 0·1 (●), 0·25 (◊), 0·5 (▲), 0·75 (□) and 1 M (–) $NH_4CF_3SO_3$ in DMA.

Figure 6. Conductivity as a function of $NH_4CF_3SO_3$ concentration for gel electrolytes containing 0 (●), 4 (o) and 10 (▲) wt% PMMA.
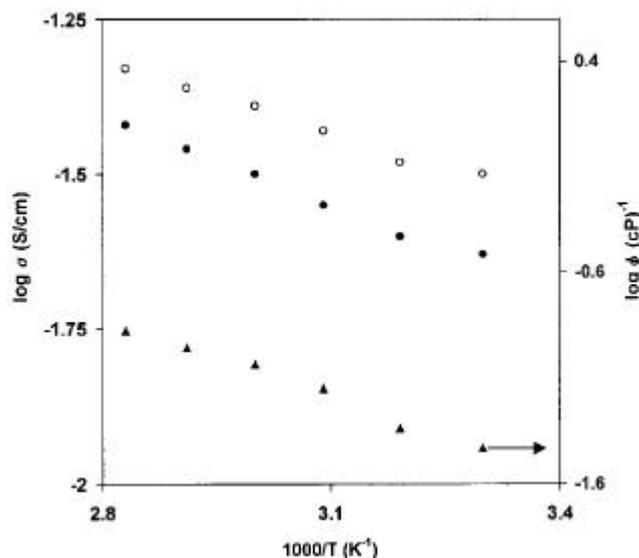
Figure 8. Variation of log s with reciprocal temperature for liquid electrolyte (o) containing 1 M $NH_4CF_3SO_3$ in DMA and log s (●) and log f (▲) of corresponding gel electrolytes containing 10 wt% PMMA.
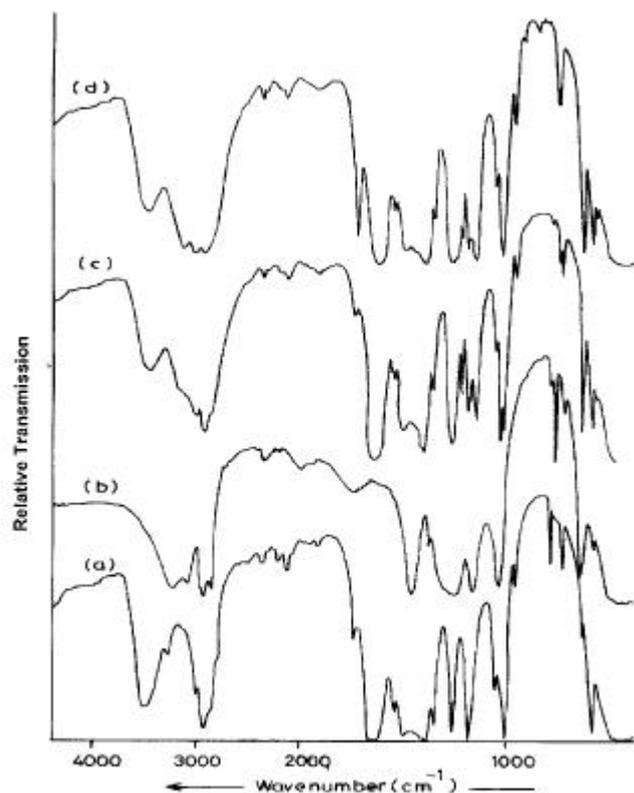
Figure 9. FTIR spectra of dimethylacetamide (a), ammonium triflate (b), liquid electrolyte containing 1 M NH$_4$CF$_3$SO$_3$ in DMA (c) and the corresponding gel electrolytes containing 10 wt% PMMA (d).

respectively. The peak observed at 1456 cm^{-1} is due to NH$_4^+$ bending whereas peaks in the 3000–3200 cm^{-1} range are due to the symmetric and asymmetric stretching of NH$_4^+$ group. The spectra of DMA shows peaks at 1643 and 1549 cm^{-1} associated with the carbonyl group of DMA and symmetric and asymmetric stretching of N–H (Silverstein and Webster 1997; Socrates 1998).

In the case of liquid electrolytes when NH$_4$CF$_3$SO$_3$ is added to DMA, the 1643 cm^{-1} peak shifts to lower wavenumber side. The shifting of peak at 1643 cm^{-1} associated with carbonyl of DMA to lower wavenumber side suggests that interactions are taking place between the salt and the solvent. Also the peak observed at 1456 cm^{-1} which has been assigned to be due to NH$_4^+$ bending disappears and this also suggests that there are some kind of interactions taking place between salt and solvent. The shifting of 1251 and 764 cm^{-1} peaks to higher wavenumber side could be due to the presence of ion aggregates, which was also reflected in the conductivity behaviour as given in figures 1 and 3. The addition of PMMA to liquid electrolytes results in the broadening of peaks around 3000 cm^{-1} and could be due to the overlapping of C–H band of PMMA and N–H band of DMA. No other major change in the spectra has been observed with PMMA addition, which suggests the

absence of any interaction between polymer and liquid electrolytes. This shows that PMMA plays a passive role and mainly acts as a stiffener which is consistent with the results obtained from conductivity studies on these electrolytes.

4. Conclusions

Nonaqueous polymer gel electrolytes containing NH$_4$ CF$_3$SO$_3$ with high conductivity of ~ 10^{-2} S/cm at 25°C have been synthesized. The increase in free H$^+$ ion concentration with the addition of salt has been studied by pH measurements. The variation of conductivity and viscosity with salt concentration, polymer concentration and temperature has been studied and the decrease in conductivity with PMMA concentration has been found to be closely related to a decrease in the fluidity of the electrolytes. FTIR studies show the absence of an interaction between PMMA and liquid electrolyte which suggests that PMMA plays the role of a stiffener in these gel electrolytes.

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