Effect of dielectric constant of solvent on the conductivity behavior of polymer gel electrolytes

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Non aqueous polymer gel electrolytes are currently attracting considerable attention due to their use as electrolytes in solid state batteries, fuel cells, supercapacitors, etc. [1–3]. Polymer gel electrolytes belong to a salt–solvent-polymer hybrid system in which the salt solution is immobilized with the addition of a suitable polymer matrix [4, 5]. The solvent helps in the dissociation of the salt and also provides a conducting medium and should generally have high dielectric constant—which ensures the dissociation of salt, low viscosity—which shall result in higher mobility and low melting point and high boiling point—so that the electrolyte could be used over a wide range of temperature [6]. If a single solvent with suitable properties is not available, then a binary/ternary solvent mixture can also be used [7].

The addition of polymer to salt solution increases the viscosity of the electrolytes accompanied by a small decrease in conductivity, which suggests that the polymer generally plays the role of a stiffener only [8–10]. However recent results on proton conducting polymer gel electrolytes containing weak acids indicate that the addition of polymer can also lead to an increase in the conductivity and gel electrolytes with conductivity higher than the corresponding liquid electrolytes have been reported [11, 12]. This increase in conductivity with polymer addition has been found to depend upon the dissociation constant of acid, dielectric constant of solvent and molecular weight of the polymer used [6, 13, 14]. The present study has been undertaken to investigate the role of the dielectric constant of the solvent on the conductivity behavior of polymer gel electrolytes. Lithium ion conducting polymer gel electrolytes containing lithium trifluoromethanesulphonate ($LiCF_3SO_3$), different single/binary solvents based on dimethylacetamide (DMA) and diethylcarbonate (DEC) with polymethylmethacrylate (PMMA) as the gelling polymer have been synthesized and the variation of conductivity and viscosity with the concentration of salt, polymer and the dielectric constant (ε) of the solvent has been studied.

Liquid electrolytes were prepared by dissolving $LiCF_3SO_3$ in different concentrations (expressed as molarity values) in DMA, DEC and in binary mixtures of DMA and DEC taken in different volume ratios. Polymer gel electrolytes were then obtained by adding PMMA in different ratios (expressed as wt.% of liquid electrolyte) to the liquid electrolytes alongwith continuous stirring. Electrical conductivity was measured by complex impedance spectroscopy with HP4284A precision LCR meter in the 20 Hz to 1 MHz frequency range and using a cell with platinum electrodes [12, 15]. The viscosity was measured by Fungilab rotating viscometer (Visco Basic L) and temperature was maintained within an accuracy of ±0.1 °C by Julabo water circulator F 12 EC.

The variation of conductivity at 25 °C with salt concentration for liquid electrolytes containing $LiCF_3SO_3$ in DMA ($\varepsilon = 37.8$), DEC ($\varepsilon = 3.2$) and binary solvent mixtures of DMA and DEC taken in 1:4 ($\varepsilon = 10.0$) and 1:30 ($\varepsilon = 4.2$) volume ratios is given in Fig. 1. The variation of conductivity with salt concentration depends upon the dielectric constant of the solvent. In the case of electrolytes containing high ε solvent (DMA), the salt is fully dissociated and as a result the conductivity increases sharply even with the addition of a small amount of salt and then reaches a saturation value which is generally explained to be due to the formation of ion aggregates which do not take part in the conduction process [16]. However in the case of electrolytes containing low ε solvent (DEC), the conductivity increases slowly with an increase in salt concentration and does not reach a saturation value even upto 1 M concentration. The conductivity of electrolytes containing DEC is lower by 1–3 orders of magnitude than those containing DMA at all salt concentrations and this may be due to the lower ε of DEC due to which the salt is not fully dissociated in the electrolytes. For electrolytes containing binary solvent mixtures of DMA and DEC with dielectric constant in between that of DMA and DEC, the conductivity variation is intermediate. At different salt concentrations, the conductivity has been observed to increase with an increase in the dielectric constant of the solvent used [6]. An increase in ε leads to more and more dissociation of the salt which increases the free ion concentration and as a result conductivity increases.

The variation of the conductivity of liquid electrolytes containing 0.5 M $LiCF_3SO_3$ in different solvents was also studied as a function of the dielectric constant of the solvent and the results are given in Fig. 2. With an increase in the dielectric constant of the solvent from 3.2 (DEC) to 37.8 (DMA), the conductivity at 25 °C has been found to increase by nearly four orders of magnitude from $\sim 10^{-6}$ to $\sim 10^{-2}$ S/cm.

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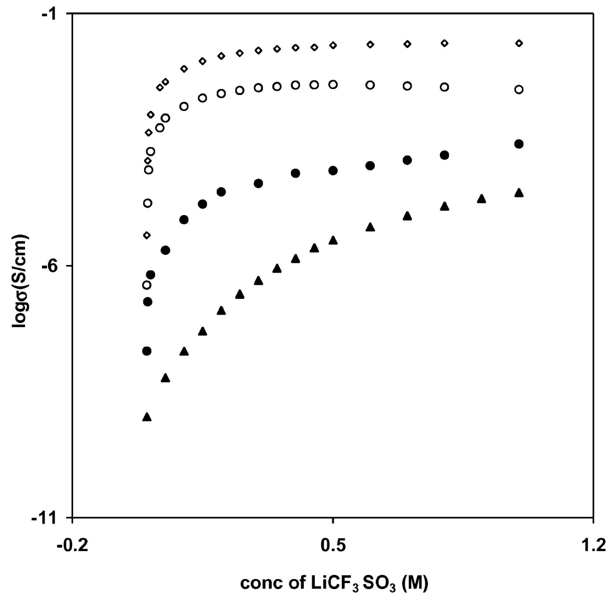

Figure 1 The variation of conductivity of liquid electrolytes as a function of $LiCF_3SO_3$ concentration in DMA (◇), binary solvent mixtures (DMA:DEC) taken in the 1:4 (○), 1:30 (●) and DEC (▲) volume ratios.

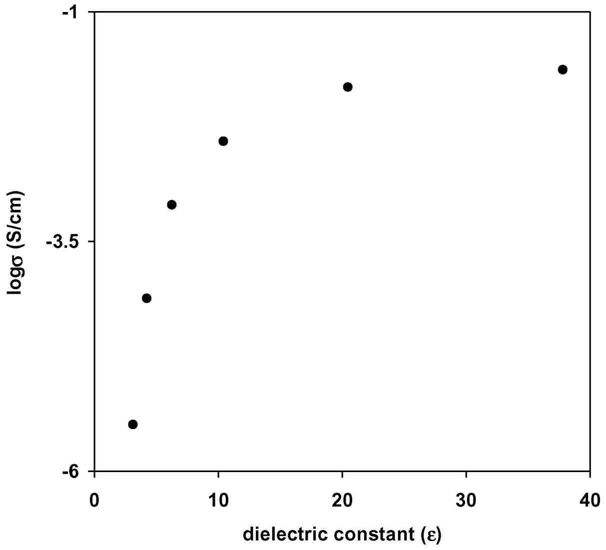

Figure 2 Change of conductivity of with dielectric constant (ε) of solvent for liquid electrolytes containing 0.5 M $LiCF_3SO_3$ in different solvents.

However the increase in the conductivity with dielectric constant is more at low ε than at high ε of the solvent. Once the salt gets dissociated then further increase in dielectric constant shell not lead to a corresponding increase in conductivity as observed in Fig. 2.

The conductivity of polymer gel electrolytes obtained by adding PMMA to liquid electrolytes containing 0.5 M $LiCF_3SO_3$ in DMA and DEC was measured as a function of PMMA concentration and the results are given in Fig. 3. The conductivity of polymer gel electrolytes containing DMA decreases with PMMA addition whereas for gel electrolytes containing DEC, conductivity increases with the addition of PMMA. In the case of gel electrolytes containing DMA the salt is fully dissociated in the liquid electrolytes due to the higher dielectric constant of solvent and the addition of PMMA increases the viscosity of electrolytes which shall lead to lower mobility and as a result conductivity decreases [9]. Whereas in gel electrolytes containing DEC, the salt is not fully dissociated due to the lower ε of solvent and some undissociated salt shall be present in these electrolytes. The addition of PMMA in addition to increasing the viscosity shall also result in the dissociation of undissociated salt present in the electrolytes which shall increase free ion concentration [12] and hence increase in conductivity is observed. The increase in viscosity of polymer gel electrolytes with the addition of PMMA was also measured and variation of viscosity at 25 °C for polymer gel electrolytes containing 0.5 M $LiCF_3SO_3$ in DMA and DEC with PMMA concentration is given in Fig. 4. The viscosity increases with the addition of PMMA and the small increase may be due to the lower molecular weight (15,000) of PMMA used in the present study.

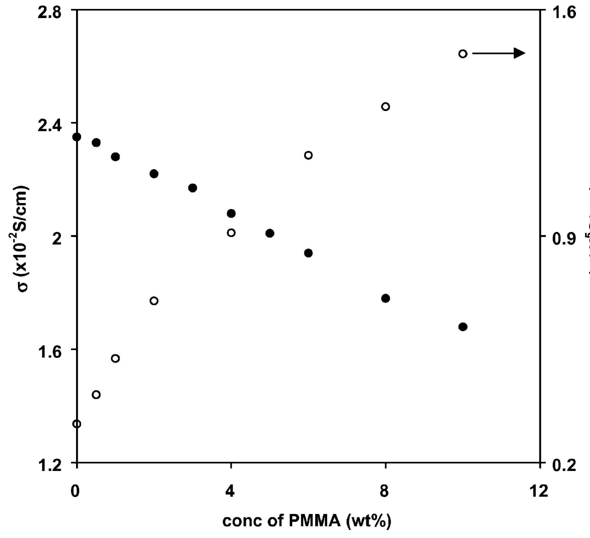

Figure 3 Variation of conductivity with PMMA concentration for polymer gel electrolytes containing 0.5 M $LiCF_3SO_3$ in DMA (●) and DEC (○).

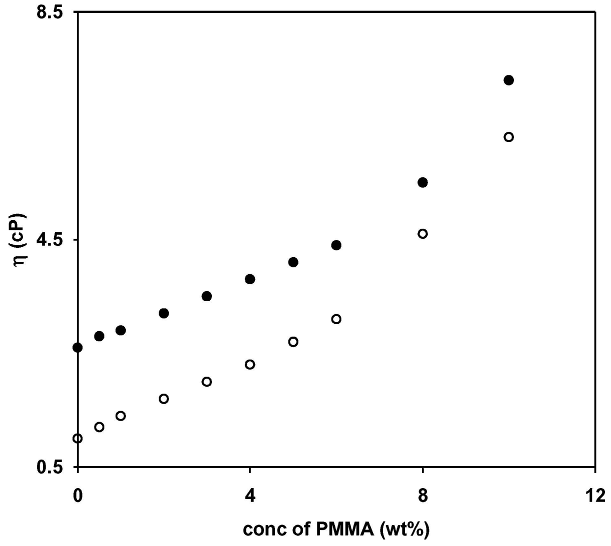

Figure 4 Viscosity as a function of PMMA concentration for polymer gel electrolytes containing 0.5 M $LiCF_3SO_3$ in DMA (●) and DEC (○).

The effect of dielectric constant of the solvent on the conductivity behaviour was further investigated by using polymer gel electrolytes containing solvents

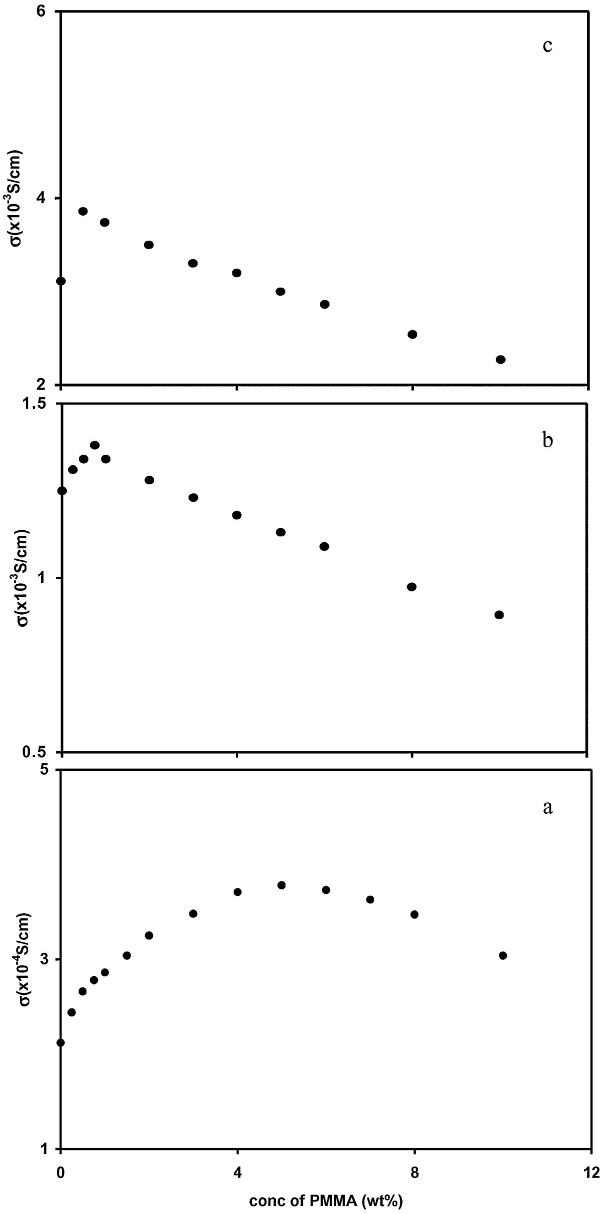

Figure 5 Conductivity as a function of PMMA concentration for polymer gel electrolytes containing 1 M $LiCF_3SO_3$ in different binary solvent mixtures (DMA:DEC) taken in 1:30 (a), 1:10 (b) and 1:4 (c) volume ratios.

with dielectric constant in between those of DMA and DEC; namely, binary solvent mixtures of DMA and DEC taken in 1:1 ($\varepsilon = 20.5$), 1:4 ($\varepsilon = 10.0$) and 1:30 ($\varepsilon = 4.2$) volume ratios. The variation of conductivity of polymer gel electrolytes containing 1 M $LiCF_3SO_3$ in above solvents with PMMA concentrations is given in Fig. 5. The conductivity variation with PMMA concentration shows behaviour intermediate between that observed for electrolytes containing DMA and DEC as given in Fig. 3. For electrolytes containing DMA and DEC in 1:30 volume ratio ($\varepsilon = 4.2$), the conductivity shows a maxima and does not increase for all concentrations of PMMA as observed for electrolytes containing DEC (Fig. 3). With the use of binary solvent of DMA and DEC in 1:4 volume ratio ($\varepsilon = 10.0$) which has higher dielectric constant, the maxima in conductivity shifts to lower PMMA concentration. The use of a solvent with still higher dielectric constant (DMA and DEC in 1:1 volume ratio with $\varepsilon = 20.5$) leads to only a small increase in conductivity at very low concentration of PMMA and conductivity decreases at all other concentrations of PMMA as observed for electrolytes containing DMA as given in Fig. 3. With an increase in the dielectric constant of the solvent, the amount of undissociated salt present in the electrolytes also decreases and accordingly the increase in conductivity with PMMA addition which has been explained to be due to the dissociation of undissociated salt also decreases. Thus the conductivity behaviour of polymer gel electrolytes as a function of PMMA concentration has also been found to depend upon the dielectric constant of the solvent used. The conductivity decreases with the addition of PMMA for polymer gel electrolytes containing high dielectric constant solvents whereas conductivity increases in the case of gel electrolytes containing low dielectric constant solvents. The role of polymer has also been observed to depend upon the presence of undissociated salt in the electrolytes. The dielectric constant of the solvent thus plays an important role in the conductivity behaviour of polymer gel electrolytes.

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