Conductivity studies of new polymer electrolytes based on the poly(ethylene glycol)/sodium iodide system

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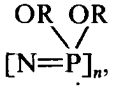
The conductivity behaviour of the system poly(ethylene glycol) (PEG)–sodium iodide (NaI) has been studied by varying the ratio of the metal salt and PEG. A maximum conductivity of $10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ is observed for $\mathrm{PEG_{10}NaI}$ samples at 25°C. The conductivity increases by two orders of magnitude as compared to pure PEG and has been shown to be due to ionic carriers. This behaviour is similar to that exhibited by the analogous poly(ethylene oxide) system.

(Keywords: poly(ethylene glycol); sodium iodide; ionic conductivity; polymer electrolytes; solid state batteries)

INTRODUCTION

There is currently wide interest in the area of research into polymer electrolytes because of their potential in electrochemical applications such as high energy density solid state batteries. However, relatively few polymers have been studied from the point of view of polymer electrolytes[1,2]. Among the polymer systems reported, poly(ethylene oxide) (PEO) is the most widely studied in terms of its complexation behaviour with several metal salts[3,4]. PEO–metal salt complexes exhibit high ionic conductivities at or near ambient temperatures, making them attractive candidates for electrochemical applications. However, the poor mechanical strength of PEO electrolytes at the high conducting region is a severe drawback. Alternative strategies in this area include synthesis of new types of polymers such as polyphosphazenes containing polyoxy substituents  $[\mathrm{N{=}P(OR)_2}]_n$, $\mathrm{R = {-}CH_2CH_2O{-}CH_2CH_2{-}O{-}CH_3}$ (ref. 5), or improving the mechanical strength of PEO by blending with additives. Poly(ethylene glycol) (PEG) has been used as a plasticizer for PEO-based polymer electrolytes[6]. However, there are no reports on the metal salt complexes of pure PEG. In view of the similar structures of PEO and PEG, owing to the presence of similar repeating units[7], it is expected that the metal salt complexes of the latter would exhibit high ionic conductivities comparable to those observed in the former system. MacCallum *et al.*[8] have shown that end-acetylated PEG, of average molecular weight 400, functions as a polymer electrolyte when complexed with $\mathrm{LiCF_3SO_3}$ and $\mathrm{LiClO_4}$.

We have undertaken a detailed investigation on the ionic transport studies of various PEG–metal salt complexes. We report here the findings of our investigations on the ionic conductivity behaviour observed in PEG–sodium iodide (NaI) polymer–salt electrolytes.

EXPERIMENTAL

Pure PEG ($M_w = 8000$) and anhydrous NaI (purity 99+%) were procured from Aldrich (USA). NaI was dried overnight under vacuum at ~100°C. Appropriate amounts of PEG and NaI were dissolved in methanol separately and then added together. The resulting solution was stirred and cast on a Teflon plate then left in a moisture-free atmosphere for 48 h to evaporate the solvent slowly at room temperature. The film formed was again dried in a vacuum oven at ~50°C with pressure ~1 mm Hg for 24 h in order to remove any trace of solvent present. The electrolyte films (thickness ~100 μm) obtained were stored in a desiccator over $\mathrm{P_2O_5}$. For conductivity studies, these films were sandwiched between stainless steel electrodes, melted and cooled in order to obtain a good electrical contact. The a.c. conductivity measurements were performed after loading the sample/electrode assembly into a sample holder, using an HP 4274A impedance analyser. The sample holder was kept inside a sealed glass tube with a dynamic vacuum to prevent uptake of moisture by the polymer–salt electrolyte films and the experiment was carried out in the heating cycle at a very slow heating rate.

Since d.t.a. studies usually give an error of ±2°C in determining the melting points, a hot plate visual microscope was employed. Melting points were determined at a very slow heating rate with a precision of 0.5°C. X-ray powder diffraction studies were carried out for the phase analysis. Since the samples were highly hygroscopic, the sample films were coated with 'Krylon' acrylic spray paint which is transparent to X-rays. The i.r. studies were made with KBr diluent on a Perkin-Elmer model no. 1320.

RESULTS AND DISCUSSION

Figure 1 shows the conductivity (σ) *versus* temperature ($\log\sigma$ *versus* $1/T$) plots for pure PEG and PEG complexed with NaI at various oxygen:sodium ion ratios. The conductivity results of pure PEG are in agreement with the values reported previously[9]. According to

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Kimura and Yasuda[9], the conductivity in pure PEG is electronic in nature. The d.c. polarization studies performed on pure PEG with stainless steel blocking electrodes in vacuum (1 mm Hg) at room temperature (25°C) also suggest that the dominant charge carriers in pure PEG are electronic in nature and not ionic. However, the possibility of oxygen ion conduction is not totally ruled out, since the polarization studies are not made in a completely oxygen-free atmosphere. Similar studies performed on PEG complexed with NaI reveal that the electronic conduction is negligible compared to the ionic conduction. (For example, PEG_{10}–NaI representing an oxygen:sodium ratio of 10, shows an electronic conductivity at least two orders of magnitude less than the ionic conductivity exhibited at 25°C.)

It is evident from *Figure 1* that the conductivity of PEG is increased by a few orders of magnitude by the addition of NaI. The conductivity increases as the salt concentration increases, attaining a maximum for an oxygen:sodium ratio of 10. It is worthwhile to compare the occurrence of the maximum conductivity composition for a similar isostructural system. Interestingly, PEO, having a similar structure, also exhibits a maximum conductivity at the composition $PEO_{10}NaI$[10,11]. A maximum conductivity of $10^{-6}\,\Omega^{-1}\,cm^{-1}$ is observed for $PEG_{10}NaI$ and PEG_6NaI samples at 25°C, which is higher by a factor of 5×10^2 than that of pure PEG.

Figure 1 also displays the variation of conductivity with temperature. The log σ *versus* $1/T$ plots display two regions, namely a low temperature region where the conductivity behaves in the Arrhenius manner and a high temperature region in which the logarithm of conductivity varies non-linearly (in a curved manner) with respect to the inverse temperature. The two regions are separated by a 'knee' temperature at which a conductivity jump by orders of magnitude is observed.

Since PEG has a high degree of crystallinity, as observed from X-ray diffraction and i.r. spectroscopy, the low temperature Arrhenius behaviour could be explained by the usual thermodynamic point defect mechanisms, namely creation of vacancies or interstitial sites in equilibrium with temperature. The activation energy (energy of formation and migration of defects) associated with this process for the samples studied are listed in *Table 1*. It can also be noted from the table that the activation energy changes systematically and attains a minimum value for the composition 12:1, which is the same as the composition corresponding to the minimum melting point. This kind of behaviour is consistent with the established behaviour of the solid solution type of ionic salt systems[12,13].

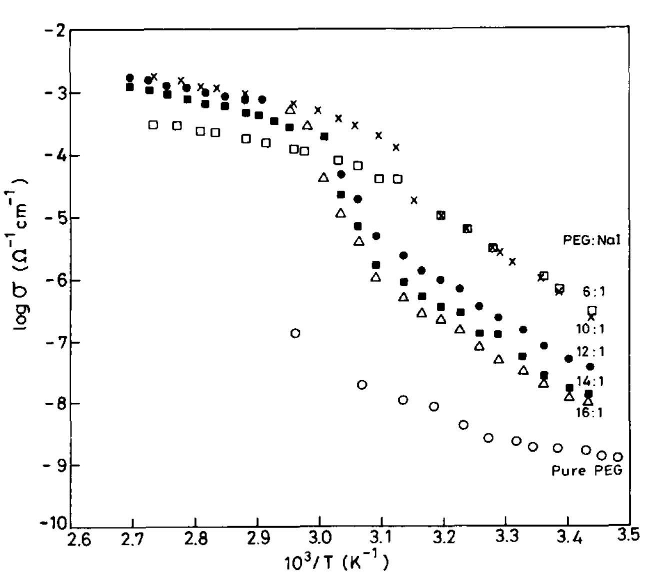

Figure 1 Logarithm of conductivity *versus* inverse temperature for the PEG–NaI system at various oxygen:sodium ion ratios

Table 1 Activation energy and melting point of PEG–NaI system

Composition	Activation energy (eV)	Melting point (°C)
Pure PEG	–	62
$PEG_{16}NaI$	1.23	50.5
$PEG_{14}NaI$	1.21	49
$PEG_{12}NaI$	1.20	52
$PEG_{10}NaI$	1.28	55
PEG_6NaI	1.28	110

X-ray diffraction studies suggest that the NaI dissolves completely in PEG up to an oxygen:sodium ratio of 10:1. There was no direct evidence for the complex formation observed in the i.r. spectrum recorded between wavenumbers 600 and 4000 cm^{-1}. The i.r. bands observed for pure PEG ($M_w = 8000$) and PEG complexed with NaI are as follows. Pure PEG: 2940(m), 2882(s), 2820(m), 2800(m), 2730(w), 2685(w), 1462(m), 1448(w), 1410(w), 1354(m), 1337(s), 1277(m), 1238(m), 1146(s), 1105(s), 1060(m), 952(m), 938(m), 836(m). PEG:NaI(12:1): 2920(s), 2880(s), 2815(w), 1470(m), 1458(m), 1355(m), 1287(w), 1246(m), 1130(s), 1100(s), 1025(m), 975(w), 936(m), 840(w).

The bands corresponding to pure PEG are in agreement with earlier studies[14,15]. No structural change was observed because of the salt complexation. However, the peak position corresponding to that of the antisymmetric C–O–C stretching mode at 1060 cm^{-1} for pure PEG was shifted down by about 35 cm^{-1}, while the shifts in the other peaks were relatively smaller, suggesting that the force constant of C–O–C stretching mode is considerably affected. This leads to an indirect confirmation of the complex formation of oxygen ion with that of the foreign sodium ion. According to X-ray studies, the complex formation seems to attain a saturation limit at the 10:1 ratio and further addition of NaI salts remains as a separate phase. The conductivity also attains a saturation limit at a ratio of 10:1 and the sample corresponding to the ratio 6:1 has the same conductivity as that of $PEG_{10}NaI$.

The melting point studies suggest that the 'knee' temperature observed in the figure is the melting temperature. The samples become highly viscous liquids above this temperature. The conduction mechanism proposed for the crystalline phase can no longer be applicable in this region and hence a non-Arrhenius behaviour is observed, as expected. MacCallum *et al.*[8] have carried out studies aimed at delineating the mechanism of conduction in polyether electrolytes by studying the conductances of $LiClO_4$ and $LiCF_3SO_3$ in a low molecular weight end-acetylated PEG. They attribute the conduction to ion pairs, triplets and higher charged aggregates, and not to single ions. Since the low molecular weight PEG is not crystalline, and is a liquid, the mechanism proposed for this system might also be applicable above the melting temperature for the high molecular weight PEG–NaI polymer electrolyte reported in this work. However, other theories, such as the free-volume theory[3,4], should also be investigated to explain the conduction mechanism in the region above the melting temperature.

CONCLUSION

The present study has shown that the PEG–NaI polymer salt complexes show a large enhancement in ionic conductivity as compared to pure PEG. The conductivity behaviour is essentially similar to that observed in comparable PEO systems. In view of this, PEG seems to be an attractive candidate for further detailed studies with several other metal salts.

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