

Conductivity modification in polymer electrolyte–crown ether complexes

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ABSTRACT

Polymer electrolyte (PEO:NH₄I) has been complexed with dibenzo-24-crown-8 ether (DB24C8). The conductivity of the complexes has been measured as a function of the crown ether composition. The conductivity of this system is an order of magnitude higher than for the PEO:NH₄I system. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been done to know about the thermal behaviour of the complexes. The conformational changes have been detected by Fourier transform infrared (FTIR) spectroscopy. Conductivity modification in the complexes has been explained by the chain-like formation in the complexes, increased amorphous phase and the enhanced free volume determined by positron annihilation lifetime spectroscopy (PALS).

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1. Introduction

The search is still on for new solid electrolytes for the use in solid-state electrochemical devices. Polymer electrolytes have an important role in solid-state ionic devices. This is due to their special properties like ease of fabrication, good mechanical property, good electrode–electrolyte contact and reasonably high ionic conductivity. Polymer electrolytes, formed by a salt dissolved in a high solvating polymer, such as poly ethylene oxide-[CH₂CH₂-O]_n, have been extensively studied. Due to the mechanism of ion transport in polymer electrolytes, it is of interest to know how it would be affected when the polymer electrolytes are complexed with special structured molecules/compounds (in the present case, crown ether). Crown ethers are macrocyclic ligands first characterized in 1967 by Charles Pederson [1]. Crown ethers are particularly interesting compounds since they have a lot of equal or similar acceptor groups. They are a special class of organic compounds that form complexes with inorganic cations. Crown ethers are well known for their selectivity towards alkali and alkaline earth metals [2,3] and many salts. This property has been extensively used in designing ion selective electrodes. Crown ethers are also used as models for studying the ion transport in biological membranes. In the complexation process, the metal ion is partially or completely solvated and fits in the crown ether cavity [4,5]. The stability of alkali and alkaline earth metal ions with crown ethers in non-aqueous solvents are known to be much higher than in water. In general, in the regular ethers, only weak complexes are formed but in certain polyethers (where multiple interactions are possible), the complexes are much stronger. The stability of crown

ether complexes depends on the match between the diameter of the cation and the cavity size of crown ether. The polymer electrolyte chosen for the present study has a special structure in which the cation (NH₄⁺) weakly bonds with the ether oxygen of the polymer chain while the anion (I⁻) hangs out [6]. During the conformational changes in the polymer chain, when two NH₄⁺ ions come near to each other, there is a probability of jump of H⁺ ions from one site to another thereby giving rise to ion conduction. Due to this reason, it is desirable to have flexibility or amorphous phases in the polymer (which is a solid solvent for the ionic charge carriers).

There are several approaches that have been adopted to improve the conductivity of the polymer electrolytes like; (i) modification of the host PEO by addition of plasticizers, (ii) copolymerization, (iii) dispersal of different types of dispersoids/fillers etc. In this paper, the effect of addition of crown ether on the structural and electrical behaviour of the polymer electrolyte complexes with crown ether are being reported. Some earlier work using crown ethers in polymer electrolyte systems are reported in ref. [7–10]. In all the cases, the conductivity has been enhanced due to the structure of the crown ether, which is perfectly arranged to allow the metal ions to enter and interact with oxygen lone pairs and form a strong complex. Also, the exterior of the crown ether is nonpolar, which allows the cation to move more easily and the addition of the crown ether to the polymer electrolyte leads to a reduction of cation–anion interaction and thus, promotes salt dissociation.

2. Experimental

Polyethylene oxide (PEO) (mol.wt. ~6 × 10⁵, Aldrich), NH₄I (Himedia), and dibenzo-24-crown-8 ether (Merck) were used as the starting chemicals. Both PEO and NH₄I were dissolved in distilled

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methanol and stirred for 3–4 h at 40 °C. When this polymeric complex solution became highly viscous, it was poured into polypropylene petri dishes. The films were dried in room temperature for 7–8 days and then were further dried in vacuum ($\sim 10^{-3}$ Torr) for 2–3 h to eliminate traces of the solvent. On the basis of composition dependence of conductivity, the 90:10 wt.% ratio ($\text{NH}_4^+/\text{EO} = 0.034$) of PEO: NH_4I was identified as the highest conducting composition.

For making the polymer electrolyte–crown ether complexes, in the PEO: NH_4I (90:10) viscous solution, the crown ether in chloroform was added in the desired ratio (0.1–0.9 wt.%). The resulting mixture was further stirred till a viscous solution formed for casting of the films of [PEO: NH_4I : \times wt.% crown ether]. Above 0.9 wt.% of crown ether, the films were mechanically unstable. For drying the films, the procedure described above was adopted. Vacuum evaporated aluminum electrodes were used for electrical contacts. To avoid shrinkage of films during electrode formation, the films were fixed to the mask by an adhesive.

For the conformational changes, the FTIR spectra were recorded in the range 400–4000 cm^{-1} using Perkin-Elmer FTIR spectrometer.

The XRD of the polymer electrolyte and its complexes were done using D8 Advance X-ray diffractometer (Bruker) using $\text{CuK}\alpha$ radiation at a scan rate 0.02°/s.

Thermal response was recorded by DSC (DSC Pyris, Perkin Elmer). The temperature program, after calibrating the apparatus in flowing Ar atmosphere, was separated into three cycles where the heating rate was 20 K/min in each run. Before starting the measurement, the sample was cooled down to -100 °C. In the first run, the sample was heated to 100 °C in order to remove the remaining solvent from the films. The second (cooling) and third (heating) runs were used to observe and quantify the respective quantities. The temperature range of these steps was also -100 °C to 100 °C.

TGA (for thermal stability) was carried out in nitrogen atmosphere at a scan rate of 5 °C/min by Mettler Toledo setup.

The bulk electrical conductivity (σ_b) of the different polymer electrolyte–crown ether complexes was determined by complex impedance spectroscopy in the frequency range (1 mHz–100 kHz) using Hioki LCR Hitester (model 3522-50). The errors in the measurements were $|\Delta|: \pm 0.08\%$ rdg. and $\theta: \pm 0.05^\circ$. It must be noted that each conductivity data point is an average of 64 readings (inbuilt in the software).

A general outline of the methodology and limitations of the interpretation have been discussed in an earlier publication [11–13]. PALS is based on the model of Tao and Eldrup, which states that the pick-off lifetime of an orthopositronium (o-Ps) is well correlated to the free volume hole size in polymers. Positron annihilation experiments were performed in a fast coincidence setup with a homemade temperature-controllable sample holder under high vacuum conditions as described elsewhere [14]. Polymer–electrolyte samples were cut into small pieces and stacked in Al-pans up to ~ 500 μm to ensure complete positron absorption in the samples. Al-pans were covered and glued with Kapton foil, and then a stack of two Al-Pans and 1 MBq Na22 source were mounted in to the sample holder in vacuum (approximately 10^{-4} mbar).

Positron annihilation spectra were recorded with approximately 5×10^6 annihilation events, typically within several hours. Evaluation was performed with the LT9.0 routine program [15], using the common background subtraction and the final resolution function which was determined as a sum of two Gaussians with full widths at half maximum of approximately 282 ps and 490 ps, with a fixed ratio of 80% and 20%, respectively. After testing several variations, for all spectra, the following evaluation conditions were chosen. Three lifetime components were fitted with $\tau_{\text{p-Ps}} \sim 125$ ps $<$ $\tau_{\text{positron}} \sim 500$ ps $<$ $\tau_{\text{o-Ps}} \sim 2$ ns. No dispersion and free fitting for all lifetimes and intensities were applied. To reduce the statistical noise, we averaged suitably over the temperature dependence and plotted the data as function of crown ether concentration.

3. Results and discussion

The dibenzo-24-crown-8 ether is a representative of macrocyclic polyethers, which are widely used in chemistry, chemical technology and medicine. Its structure is shown in Fig. 1 (a).

FTIR is a tool used to confirm the complexation between the polymer and the salt as well as the interactions between the various constituents [16–20]. The FTIR spectra of the polymer electrolyte and the polymer electrolyte–crown ether complexes with different weight percentage of crown ether are shown in Fig. 2. The infrared spectra of these polymer complexes vary according to the composition. The band assignments for pure PEO are listed in Table 1. They are C–O–C stretching mode at 940 and 1093 cm^{-1} , CH_2 twisting at 1249 cm^{-1} , CH stretching mode at 2887 cm^{-1} , CH_2 wagging mode at 842 cm^{-1} , asymmetric stretching mode at 1960 cm^{-1} and CH_2 scissoring mode at 1466 cm^{-1} . These bands give evidence of the presence of PEO.

The magnitude of the shift in the vibrational spectra is linked to the size of the cavity in the crown ether. If the cation is of comparable (slightly smaller) size then the cavity, the ion will be located centrally in the cavity. Several complexes with this type of structure have been reported [26,27]. When the cations are either too large or too small for the cavities, other type of structures like chain or sandwich are obtained [28,29]. Size of the NH_4^+ ion is ~ 2.86 Å, and the cavity size of dibenzo-24-crown-8 is greater than 4 Å. The shift will be greater if the cation is of approximately the size of the cavity [28]. In the system under study, the shifting of peaks is small because of the large size difference of the cation and the cavity in DB24C8.

Broadening of C–O–C stretching mode at 1093 and 940 cm^{-1} (as shown in Fig. 2(b)) indicates that the salt has complexed with the polymer as NH_4^+ ion is expected to bond with ether oxygen of PEO. The NH stretching bands of NH_4^+ are at 3160 cm^{-1} and ~ 3020 cm^{-1} . Shifting of

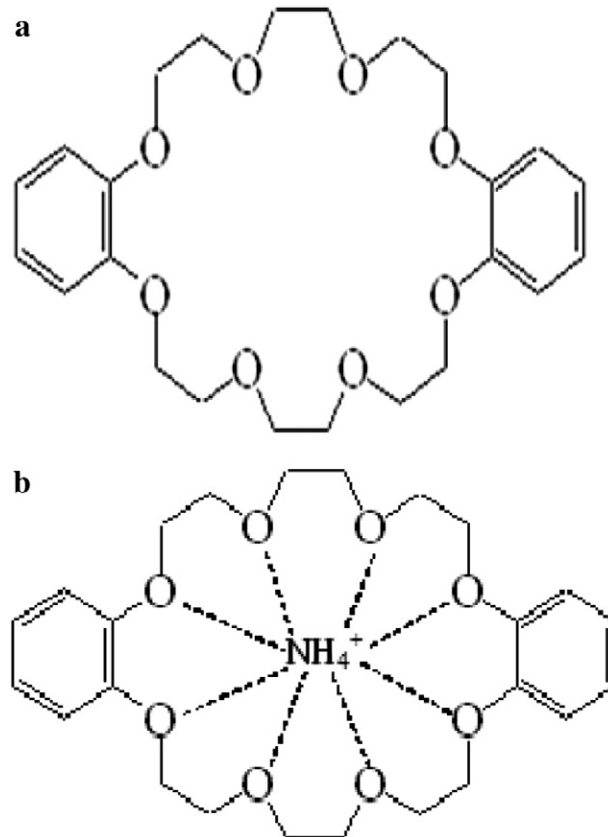


Fig. 1. Structure of (a) dibenzo-24-crown-8 ether and (b) dibenzo-24-crown-8 complex with ammonium salt.

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