

A Comparative Study on the Role of the Plasticizer on (PEO+KBrO₃) Polymer Electrolytes

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ABSTRACT

The PEO based polymer electrolyte has significant foremost investigation area due to high conductivity. In this present study (PEO+KBrO₃) polymer electrolyte have been prepared by solution-cast technique. Dimethylformamide [DMF] was used as plasticizer to (PEO+KBrO₃) polymer electrolytes. The transport properties of these polymers electrolytes are studied by using the d.c. conductivity in the temperature range of 303-373K. The effect of the plasticizer on the d. C. conductivity studied has been investigated. It was observed that, conductivity have been enhanced by addition of plasticizer.

Keywords: Poly(propylene oxide), Polymer electrolytes, d.c. Conductivity, Plasticizer.

1. INTRODUCTION

In current years, extensive concentration has been devoted to polymer materials, which in mixture with suitable metal salts, give electrolytes of the growth of sophisticated high energy electrochemical devices, e.g., batteries/fuel cells, electrochemical display devices / smart windows, photo electrochemical cells, etc. [1–5]. The main advantages of polymeric electrolytes are their mechanical properties, ease of fabrication of thin films of desirable sizes and their ability to form proper electrode / electrolyte contact. Primarily the studies in this field are committed to PEO-based polymer electrolytes using alkali salts, e.g., LiBF₄, LiPF₆ and LiB(C₆H₅)₄ [6], LiSCN [7], LiSO₃CF₃ and LiClO₄ [8], NaSCN [9], NaYF₄ [10], KYF₄ [11], etc. Several PEO-based polymer electrolytes are also reported with salts of divalent and transition metal cations such as halides of Zn, Cd, Mg, Pb, Cu, Fe, Ni, Co [12–14]. Some proton conducting polymer electrolytes have been reported based on PEO complexed with ammonium salts such as NH₄SCN and NH₄SO₃CF₃ [15], NH₄ClO₄ [16, 17], NH₄I [18].

In this present report Dimethylformamide [DMF] was used as plasticizer and using solution-cast technique (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolytes have been prepared. The performance of the plasticizer was experimentally investigated by the d. C. conductivity studied.

2. EXPERIMENTAL

Films (thickness about 100 to 150 μm) of pure PEO poly(propylene oxide) (Aldrich, molecular weight 6 × 10⁵) and various compositions of complexed films of (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) were prepared with weight ratios of (90:10), (80:20) and (70:30) by a solution-cast technique using methanol water-free solvent. In this present investigation Dimethylformamide (DMF) used as plasticizer for (PEO+KBrO₃) polymer electrolytes. The solutions were stirred for 15 to 20 h, cast onto polypropylene dishes and then evaporated slowly at room temperature. The final products were vacuum-dried thoroughly at 10⁻³ Torr [19]. The dc conductivity was measured by means of an in-house conductivity set-up [19] in the temperature range 303 to 373 K. The dc-conductivity was studied as a function of temperature and composition using d. c. conductivity setup.

3. RESULTS AND DISCUSSION

(i). Composition dependence of the conductivity:

Fig. 1 shows the composition dependence of the conductivity of (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolytes at different temperatures. The conductivity values of (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) electrolyte systems are given in Table 1 for different temperatures. From Fig. 1 and Table 1 the following features can be observed [20]:

(a) The conductivity of pure PEO is about $1.8 \times 10^{-10} \text{ S.cm}^{-1}$ at RT and increases with the relative concentration of KBrO₃. The change in magnitude is of the order of 100 times in (PEO+KBrO₃) (90:10 and 80:20) and 1000 times in (PEO+KBrO₃+Plasticizer) (90:10 and 80:20) electrolyte systems compared to that of pure PEO polymer.

(b) The enhancement of the conductivity is about three or four orders of magnitude if 10% of electrolyte is added to the polymer. A smaller concentration would of course result in smaller conductivities. The data in Fig. 1 also indicate that there is a kind of saturation at larger concentrations.

(c) A comparison of the conductivity of (PEO+KBrO₃+Plasticizer) electrolyte with that of (PEO+KBrO₃) electrolyte shows that the conductivity is enhanced by a factor of 10, due to the addition of plasticizer to (PEO+KBrO₃).

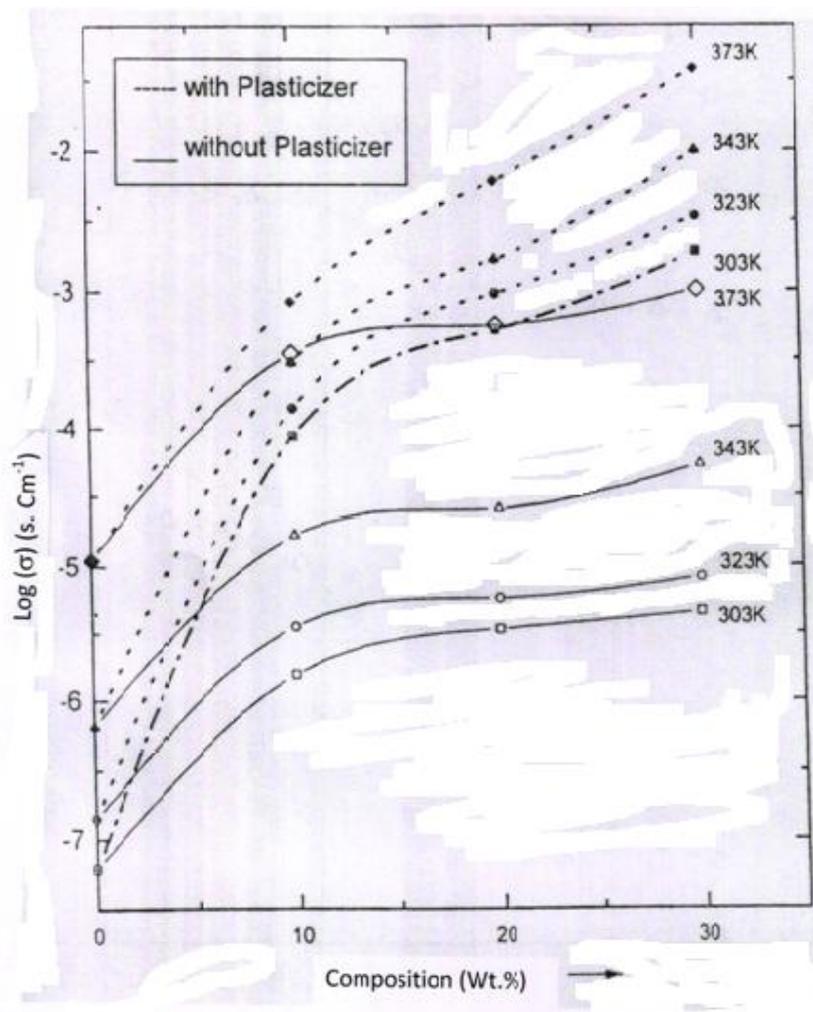


Fig.1. Composition dependence of d.c. conductivity of (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolytes at different temperatures.

Table-1. Comparison of conductivity data of (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolytes.

Polymer Electrolyte	Conductivity (S. Cm ⁻¹)	
	303K	373K
PEO	1.80X10 ⁻¹⁰	8.00X10 ⁻⁸
(PEO+KBrO ₃) (90:10)	1.67X10 ⁻⁸	7.00X10 ⁻⁸
(PEO+KBrO ₃ +Plasticizer) (90:10)	9.51X10 ⁻⁷	5.99X10 ⁻⁵
(PEO+KBrO ₃) (80:20)	5.71X10 ⁻⁸	8.00X10 ⁻⁶
(PEO+KBrO ₃ +Plasticizer) (80:20)	5.69X10 ⁻⁶	4.36X10 ⁻⁵
(PEO+KBrO ₃) (70:30)	7.72X10 ⁻⁸	9.80X10 ⁻⁶
(PEO+KBrO ₃ +Plasticizer) (70:30)	2.04X10 ⁻⁵	2.75X10 ⁻⁴

(ii). Conductivity vs. Temperature:

Fig. 2 shows the conductivity vs. Temperature ($\log \sigma$ vs. $\frac{10^3}{T}$) plots for pure PEO and different compositions of (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolytes in the temperature range 303–373K. From the conductivity–temperature plots, the following features are observed. Within the temperature range under study, the conductivity is found to increase with temperature in polymer PEO, (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolyte systems.

From Fig. 2, the conductivity–temperature plots follow an Arrhenius nature throughout, but with two different activation energies above and below the melting point (T_m) of the polymer. In region I (i.e. below T_m), the conductivity of pure PEO increases slowly with temperature up to 70°C. At 70°C, there is a sudden increase in conductivity. In region II (i.e. above T_m), the conductivity again increases with increasing temperature. This behaviour is identical for both (PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolyte systems. The increase in conductivity is about 10 times larger in the (PEO+KBrO₃+Plasticizer) polymer electrolyte compared with the (PEO+KBrO₃) electrolyte.

At T_m (which corresponds to the melting point of the polymer) there is a transition from a semi-crystalline phase to an amorphous phase. Due to the phase change, the conductivity shows a sudden increase at T_m . According to Druger et al. [21-22], in polymer electrolytes, the change of conductivity with temperature in region I is explained as being due to segmental motion which results in an increase in the free volume of the system. The increase in free volume would also facilitate the motion of ionic charge [23]. Thus the segmental motion either permits the ions to hop from one site to another site or provides a pathway for ions to move, or, in other words, the segmental movement of the polymer facilitates the transitional ionic motion. From this it is clear that the ionic motion is due to a combination of ionic transitional motion /hopping and the dynamic segmental motion of the polymer, which assists the ionic motion. However, as the amorphous region progressively increases (region II), the polymer chains acquire faster internal modes in which bond rotations produce segmental motion. This, in turn, favours hopping inter-chain and intra-chain ion movement and the conductivity of the polymer electrolyte thus becomes high. The existence of two regions in the conductivity–temperature plots has been observed in a number of PEO-based polymer electrolytes [24-26].

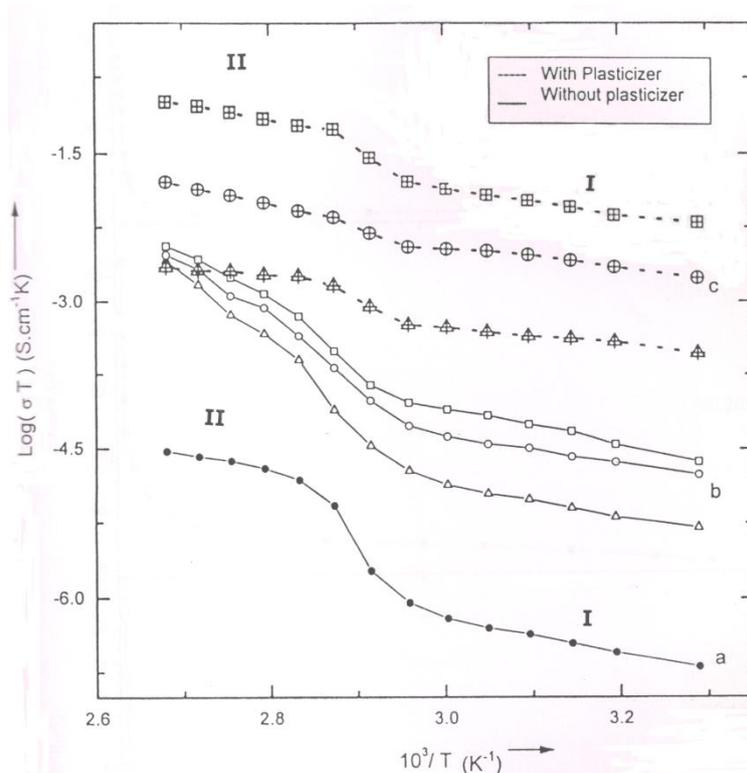


Fig. 2. The temperature dependence of d. c. Conductivity (a) Pure PEO, (b) (PEO+KBrO₃) and (c) (PEO+KBrO₃+Plasticizer) polymer electrolyte systems.

(iii). Effect of the plasticizer (DimethylFormamide [DMF]) on the polymer:

A plasticizer having a low molecular weight and is a non-volatile substance, when added to a polymer, improves its flexibility and utility. The plasticizer substantially reduces the brittleness of many polymers because its addition in small quantities markedly reduces the glass transition temperature (T_g) of the polymer. This effect is due to a reduction in the number of cohesive chains. Plasticizer molecules (being relatively small in size compared to polymer molecules) penetrate into the polymer matrix and establish attractive forces between the plasticizer molecules and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thus enhance the conductivity. The conductivity of the polymer electrolyte, therefore, is increased by plasticizer addition [19].

4. CONCLUSIONS

(PEO+KBrO₃) and (PEO+KBrO₃+Plasticizer) polymer electrolyte systems were fabricated by using the solution casting method. The addition of plasticizer (DMF) to a polymer electrolyte leads to an increase in conductivity by more than a factor of 10 in plasticizer-added polymer electrolyte systems as compared with the pure polymer electrolyte system.

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