

## Ionic Conductance Behaviour of Plasticized Polymer Electrolytes Containing Different Plasticizers

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**Abstract.** The effect of different plasticizers on the properties of PEO–NH<sub>4</sub>F polymer electrolytes has been studied. Aprotic organic solvents like propylene carbonate (PC), ethylene carbonate (EC),  $\gamma$ -butyrolactone ( $\gamma$ -BL), dimethylacetamide (DMA), dimethylformamide (DMF), diethylcarbonate (DEC) and dimethylcarbonate (DMC) having different values of donor number, dielectric constant, viscosity etc. have been used as plasticizers in the present study. The addition of plasticizer has been found to modify the conductivity of polymer electrolytes by increasing the amorphous content as well as by dissociating the ion aggregates present in polymer electrolytes at higher salt concentrations. The conductivity enhancement with different plasticizers has been found to be closely related to the donor number of the plasticizer used rather than its dielectric constant. The increase in conductivity with the addition of plasticizer has further been found to be dependent upon the level of ion association present in the electrolytes. The variation of conductivity as a function of plasticizer concentration and temperature has also been studied and maximum conductivity of  $\sim 10^{-3}$  S/cm at room temperature has been obtained. X-ray diffraction studies show an increase of amorphous content in polymer electrolytes with the addition of plasticizers.

### 1. Introduction

The electrical and mechanical properties of polymer electrolytes should be sufficiently practical to make their development a consideration when compared with other highly conducting solid electrolytes. The study of polymer electrolytes was initiated by Fenton et al. [1] in 1973 by reporting the complexation of alkali metal salts with polyethylene oxide, but their technological significance was not appreciated until Armand et al. [2,3] in 1978 suggested their applications in solid state batteries. The complexes formed between alkali metal salts and polyethylene oxide (PEO) were found to possess high ionic conductivity, suitable for applications in various solid state ionic devices. This led to research and development on the synthesis of new polymer electrolytes, physical studies and development on the synthesis of new polymer electrolytes, physical studies of their structure, theoretical modeling of the charge – transport processes and physical and chemical properties at the electrolyte/electrode interface.

PEO based polymer electrolytes are one of the most extensive studied system (i.e. solvent free PEO/salt complexes). The electrolytes commonly exhibit conductivity in the range  $10^{-8}$  to  $10^{-4}$  S/cm at temperature between 40 and 100 °C, which limits their practical applications at ambient temperature. Polymer electrolytes should have the following properties for their use in devices:

- high conductivity at room temperature,
- low electronic conductivity,
- good mechanical properties,
- chemical, electrochemical and photochemical stability,
- ease of processing.

The main reasons for low value of conductivity of PEO based polymer electrolytes are:

- higher degree of crystallinity,
- low solubility of salt in the amorphous phase,
- mobility of both cations and anions.

Many attempts have been made to improve the electrical properties of polymer electrolytes [4-19] via various

approaches. All these improvements have been achieved either by reducing the crystallinity or by lowering the glass transition temperature. As it has been reported that in PEO based polymer electrolytes, the amorphous phase is the high conducting phase [20], so in each approach, which is used for enhancement of conductivity at ambient temperature, the initial step is to increase the amorphous content in polymer electrolytes. Out of all the methods used for improving the electrical properties without affecting their mechanical stability, the addition of plasticizer to polymer electrolytes has been most suitable and hence widely studied. The low viscosity, non-volatile and polar nature of different plasticizers are suitable properties for their use in polymer electrolytes. Much work has already been reported [21-37] to study various properties of plasticized polymer electrolytes. In some earlier studies [28, 32-35], it has been reported that the incorporation of plasticizer decreases the glass transition temperature ( $T_g$ ). A decrease in the value of  $T_g$  helps in easy movement of the polymer chains, which results in an increase in conductivity. The increase in conductivity with plasticizer addition has also been reported to depend upon the viscosity of the plasticizer [28].

The dependence of conductivity of PEO-MX type polymer electrolytes on salt concentration has been extensively studied [38-44] and it has been reported that conductivity of polymer electrolytes initially increases with an increase in salt concentration but the rate of increase of conductivity decreases at higher salt concentrations and even saturation is reached in some cases at higher salt concentrations, which is generally explained to be due to the formation of ion aggregates at higher salt concentration. These ion aggregates do not contribute to conductivity. However the dissociation of these ion aggregates shall lead to an increase in carrier concentration ( $n$ ) and hence conductivity. In our earlier study [45] we have found that the addition of plasticizer to polymer electrolytes results in an increase in conductivity which is dependent upon the concentration of the salt and plasticizer in the electrolyte. Dielectric constant of plasticizer also plays an important role in the modification of electrical properties of polymer electrolytes and the addition of plasticizer with dielectric constant higher than that of the polymer (PEO) used results in an increase in conductivity due to the dissociation of ion aggregates in addition to a decrease in the glass transition temperature.

The present study has been undertaken to study in detail the effect of the addition of different plasticizers

with a wide range of dielectric constant ( $\epsilon$ ), viscosity ( $\eta$ ) and donor number (D.N.) values on the dissociation of ion aggregates as well as on the fraction of amorphous content. Plasticizers with dielectric constant higher (PC, EC, DMF,  $\gamma$ -BL, DMA) as well as lower (DEC, DMC) than that of polymer (PEO) have been used in the present study. Polymer electrolytes (PEO-NH<sub>4</sub>F) with different levels of ion aggregation have been studied. X-ray diffraction studies have also been carried out to check the change in amorphous content with the addition of plasticizers.

## 2. Experimental Details

Films of PEO, PEO-NH<sub>4</sub>F and PEO-NH<sub>4</sub>F-different plasticizers were prepared by using high molecular weight polyethylene oxide (PEO) (Aldrich, MW =  $5 \times 10^6$ ), ammonium fluoride (NH<sub>4</sub>F) (Reidel) and different plasticizers viz; ethylene carbonate (EC) (Merck), propylene carbonate (PC) (Aldrich),  $\gamma$ -butyrolactone ( $\gamma$ -BL) (Merck), N,N-dimethylacetamide (DMA) (CDH), N,N-dimethylformamide (DMF) (Merck), dimethyl carbonate (DMC) (Lancaster) and diethyl carbonate (DEC) (Lancaster) by solution casting technique using methanol as the solvent. The solutions of PEO containing different amounts of NH<sub>4</sub>F (expressed as F/O ratio) and appropriate amount of different plasticizers (EC, PC, DMA,  $\gamma$ -BL, DMF, DEC, DMC) (expressed as wt.% of polymer) were mixed uniformly in methanol, and the homogenous solutions were poured in polypropylene dishes. The solvent was allowed to evaporate slowly and the properly dried samples in film form were used for further studies. The electrical conductivity of polymer electrolyte films was measured by using HP 4284A precision LCR meter in 20 Hz – 1 MHz frequency range. The impedance/admittance plots were drawn and conductivity was calculated by using relation:

$$\sigma = G\ell/A,$$

where  $G$  is conductance to be determined from impedance/admittance plots,  $\ell$  is the thickness of films measured by micrometer and  $A$  is the area of cross section of the films. The conductivity of all samples was measured as a function of temperature by placing the sample holder containing the sample in a temperature controlled furnace. The variation of conductivity as a function of salt concentration and plasticizer content was also studied.

### 3. Results and Discussion

The conductivity of PEO-NH<sub>4</sub>F polymer electrolytes was measured as a function of salt (NH<sub>4</sub>F) concentration expressed as F/O ratio and is given in Fig. 1. The variation is similar to that reported for complexes of PEO with different metal salts (MX) [38-44]. The conductivity of PEO (~ 10<sup>-9</sup> S/cm) increases by nearly three orders of magnitude to ~ 10<sup>-6</sup> S/cm with the addition of salt. At low salt concentration values the conductivity increases linearly with the salt concentration and the salt is assumed to be completely dissociated and nearly all ions are available for conduction. With further increase in salt concentration, the conductivity shows a deviation from the linear variation, reaches a maximum value and then shows a small decrease with further increase in salt concentration. The deviation in conductivity from linear variation at medium salt concentration values is explained to be due to the formation of ion aggregates, which do not take part in the conduction process. The formation of ion aggregates increases with further increase in salt concentration and as a result the conductivity even shows a small decrease. At high salt concentration value, more ion aggregates are formed and there is no net increase in the number of free ions even with an increase in salt concentration. The addition of salt (NH<sub>4</sub>F) to polymer (PEO) also results in an increase in the viscosity of polymer electrolyte due to the complexation of salt with polymer which also reduces the mobility and hence conductivity.

The ion aggregate formation in polymer electrolytes has been studied by various experimental techniques and the simplest one is from mass action considerations [46]. If the salt MX dissociates according to:  $MX \rightarrow M^+ + X^-$  with  $K = (M^+)(X^-) / (MX)$  as the equilibrium constant.

If the activities are replaced by concentration, then for weak dissociation let  $c = M^+$

$c \times c / C - c = c^2 / C - c \cong c^2 / C = K$  and therefore  $c = \sqrt{KC}$ , where  $C$  is the concentration of salt (MX). If the salt is strongly dissociated, then  $c \cong C$ .

If ion aggregation is strong i.e.  $K$  is small, then  $\sigma \sim C^{1/2}$  and if ion aggregation is unimportant, then  $\sigma \sim C$ .

From the log - log plot of ionic conductivity vs. salt concentration (log  $\sigma$  vs. log  $C$ ), the linearity of the plot implies that ion aggregation is unimportant and any deviation from linearity suggests the formation of ion-aggregates [47,48].

The above simple method has been used to check the presence of ion aggregates in the present system and Fig.

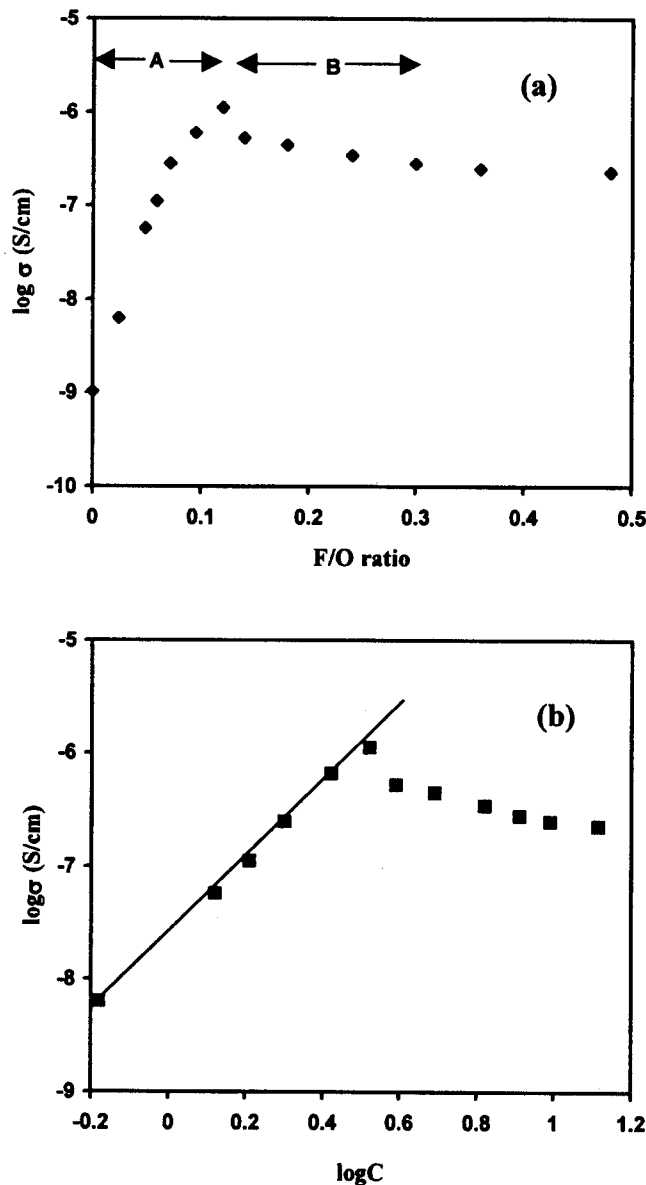


Fig. 1. (a) Variation of conductivity of PEO-NH<sub>4</sub>F polymer electrolytes as a function of salt concentration (expressed as F/O ratio). (b) Variation of conductivity (log  $\sigma$ ) of PEO-NH<sub>4</sub>F as a function of salt concentration (log  $C$ ).

1b shows the plot of log  $\sigma$  vs. log  $C$  for PEO-NH<sub>4</sub>F polymer electrolytes. At low salt concentration values log  $\sigma$  vs. log  $C$  plot is linear in nature which suggests that ions are dissociated whereas in high salt concentration region, this plot shows deviation from linearity which is an indication of the presence of ion aggregates. Thus from Figs. 1a and b, the whole salt concentration range studied could be divided into two regions as follows:

region A : salt is dissociated, absence of ion aggregates (0.0 < F/O < 0.1)

region B : presence of ion aggregates (0.1 < F/O < 0.48)

The maximum value of conductivity of PEO-NH<sub>4</sub>F polymer electrolytes at room temperature as given in Fig. 1 is  $1.11 \times 10^{-6}$  S/cm for sample with F/O ratio 0.12 and this value is quite low and hence not suitable for applications of these polymer electrolytes in various solid state ionic devices. Suitable steps are needed to increase the conductivity of these polymer electrolytes by two to three orders of magnitude without compromising other physical properties like mechanical strength etc.

On the basis of thermal studies, PEO-MX type polymer electrolytes have been reported to be multiphase materials with the amorphous phase as the high conducting phase [20]. An increase in the content of amorphous phase in these polymer electrolytes has been reported [20,49] to result in an increase in conductivity. The addition of plasticizers like PEG, PPG etc. to PEO-MX type polymer electrolytes has been reported [15,16,21,24] to result in an increase in conductivity which is generally explained to be due to an increase in the amorphous content. However if the plasticizer chosen has higher dielectric constant as compared with the polymer, then it can also help in the dissociation of salt as well as in the dissociation of ion aggregates formed at higher salt concentration values.

To study the role of plasticizer in increasing the amorphous content of PEO-NH<sub>4</sub>F polymer electrolytes as well as on the dissociation of ion aggregates formed at higher NH<sub>4</sub>F concentrations, different plasticizers with a wide range of dielectric constant values (2 - 90) were chosen for the present study. The important physical properties of different plasticizers used in the present study are listed in Table 1.

Plasticizers with different values of dielectric constant as given in Table 1 were added to PEO-NH<sub>4</sub>F polymer electrolytes with F/O ratio 0.12 (composition showing maximum value of conductivity). The concentration of

Table 1. Properties of Plasticizers.

Plasticizer	$\epsilon$ at 25 °C	$\eta$ (cP) at 25 °C	D.N	M. P (°C)	d
EC	89*	1.90*	16.4	37-39	1.32
	* at 40 °C				
PC	64.4	2.53	15.1	-55	1.19
$\gamma$ -BL	39.1	1.75	18.0	-45	1.12
DMA	37.8	1.937	27.8	-20	0.93
DMF	36.1	0.80	26.6	-61	0.94
DMC	3.12	0.584	---	2-4	1.07
DEC	2.82	0.748	---	-43	0.98

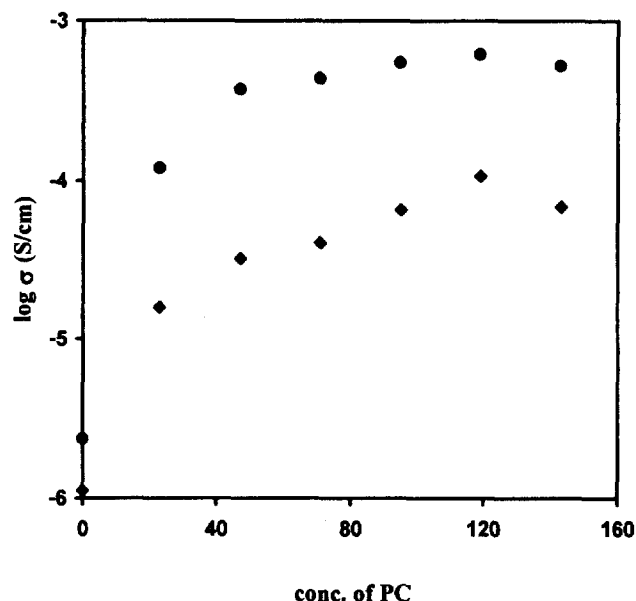


Fig. 2. The dependence of conductivity on plasticizer (PC) concentration (expressed as wt.% of PEO) for PEO-NH<sub>4</sub>F polymer electrolytes with F/O ratio 0.12 at 30 °C (◆) and 60 °C (●).

salt was kept fixed and the amount of plasticizer added was varied. Figure 2 shows the variation of conductivity of PEO-NH<sub>4</sub>F polymer electrolytes at 30 °C and 60 °C as a function of the concentration of propylene carbonate (PC) used as a plasticizer. From Fig. 2 it is observed that at both temperatures, the conductivity increases sharply with the initial small addition of plasticizer and then attains a nearly saturation value. The conductivity has been found to increase by nearly two orders of magnitude with the addition of plasticizer. The variation of conductivity with PC concentration could be explained as follows:

The addition of PC to PEO-NH<sub>4</sub>F polymer electrolytes increases the amorphous content of polymer electrolyte, which results in an increase in conductivity as given in Fig. 2. Once the electrolyte becomes amorphous, then further addition of plasticizer (PC) does not result in more increase in amorphous content and as a result the increase in conductivity is not in the same proportion and even reaches a saturation value. As the concentration of NH<sub>4</sub>F is kept constant, so the effect of plasticizer on salt dissociation (if any) shall be same for samples containing different concentrations of PC. Similar behaviour has been observed in the case of other plasticizers viz EC,  $\gamma$ -BL, DMF, DMA having dielectric constant higher than that of polymer (PEO) used.

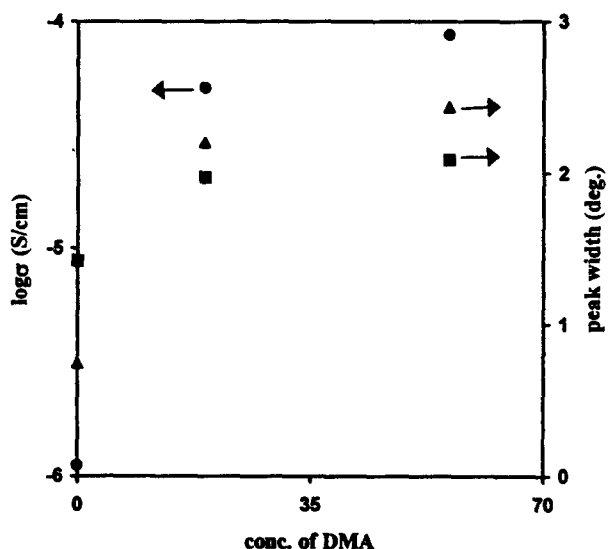


Fig. 3. Variation of conductivity (●) and peak width for XRD lines at 18.736° (■) and 23.12° (▲) of PEO-NH<sub>4</sub>F-DMA polymer electrolytes as a function of DMA concentration.

The increase in amorphous content of polymer electrolytes with the addition of salt/plasticizer has also been studied by using X-ray diffraction. If the line width of X-ray diffraction lines is taken as a measure of the amorphous content of the sample then an increase in amorphous content shall result in an increase in the line width of X-ray diffraction lines. Figure 3 shows the variation of line width of most prominent X-ray diffraction lines at  $2\theta$  values 18.736° and 23.12° as a function of plasticizer (DMA) concentration for polymer electrolyte with F/O value 0.12. Figure 3 shows that line width and hence amorphous content increases with the addition of DMA but the increase is not in the same proportion at higher DMA concentrations. For comparison purposes the variation of conductivity with DMA concentration is also included in Fig. 3. It is observed that the variation of line-width and hence amorphous content as a function of DMA concentration is very similar to the variation in conductivity value, which indicates that an increase in amorphous content leads to higher conductivity value. Similar results have been obtained with other plasticizers.

However the addition of plasticizers viz DEC, DMC having dielectric constant less than that of polymer (PEO) to the PEO-NH<sub>4</sub>F polymer electrolytes does not result in an increase in conductivity as given in Fig. 4. It is observed that initial addition of DEC, DMC to PEO-NH<sub>4</sub>F results in a decrease in conductivity, which can be due to lower value of the dielectric constant of the plasticizer

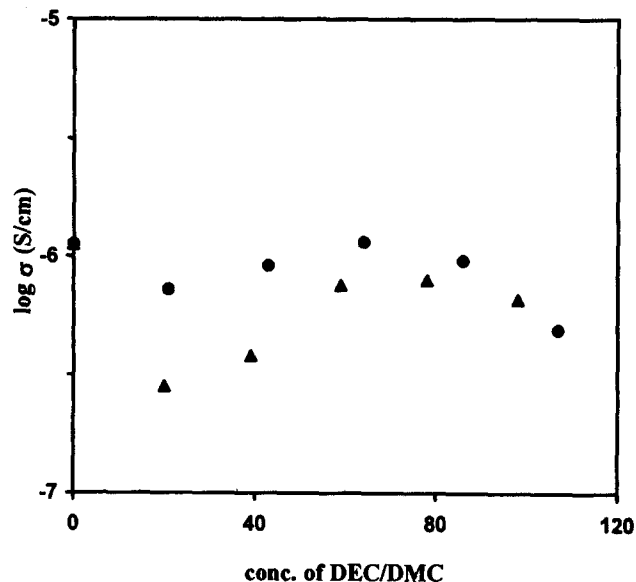


Fig. 4. The dependence of conductivity on plasticizer concentration (expressed as wt.% of PEO) for PEO-NH<sub>4</sub>F polymer electrolytes with F/O ratio 0.12 at 30 °C with DEC (▲) and DMC (●).

used. The small increase in conductivity observed at higher DEC, DMC concentration could be due to an increase in the amorphous content of the polymer electrolytes. Thus the dielectric constant of plasticizer plays an important role in the modification of conductivity of polymer electrolytes as reported earlier [50, 51] also for PEO-NH<sub>4</sub>ClO<sub>4</sub> polymer electrolytes.

The variation of room temperature conductivity of polymer electrolytes (PEO-NH<sub>4</sub>F) having F/O ratio 0.12 as a function of plasticizer (EC, PC,  $\gamma$ -BL, DMA, DMF) concentration has been studied and the results obtained are given in Fig. 5. The following general observations could be made from the results of Figs. 4 and 5:

- (i) the addition of plasticizers like EC, PC,  $\gamma$ -BL, DMA, DMF having dielectric constant higher than that of polymer (PEO) to PEO-NH<sub>4</sub>F polymer electrolytes has been found to result in an increase in conductivity value whereas
- (ii) the addition of plasticizer like DEC, DMC having dielectric constant lower than that of PEO leads to a decrease in conductivity of PEO-NH<sub>4</sub>F polymer electrolytes.
- (iii) the increase in conductivity value with the addition of same amount of different plasticizers (EC, PC,  $\gamma$ -BL, DMA, DMF) (having dielectric constant higher than that of PEO) to PEO-NH<sub>4</sub>F polymer electrolytes is in the following order:

$$\text{DMA} > \text{DMF} > \gamma\text{-BL} > \text{PC} > \text{EC}$$

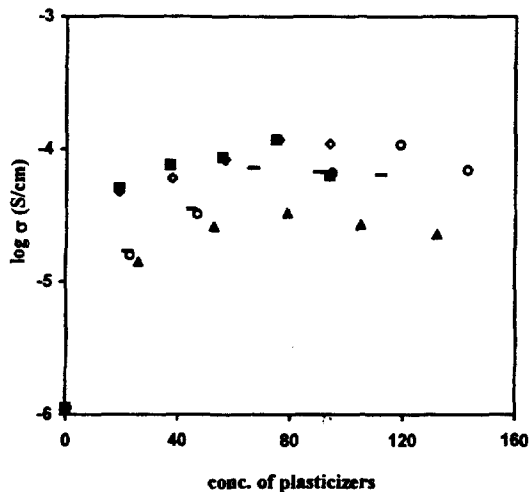


Fig. 5. Variation of conductivity with plasticizer concentration (expressed as wt.% of PEO) for PEO-NH<sub>4</sub>F polymer electrolytes with F/O ratio 0.12 and EC (▲), PC (○),  $\gamma$ -BL (-), DMF (◇), DMA (■) as plasticizers.

This order of increase in conductivity has been found to be more closely related to the donor number of the plasticizers used (listed in Table 1). It is found that as the value of donor number of plasticizer increases, its effect in enhancement of room temperature conductivity also increases expect for EC, which may be due to the high melting point of EC (~ 38 °C). It is in crystalline form at room temperature, due to which the increase in conductivity at room temperature in case of EC is slightly less as compared to PC which has slightly lower donor number (15.1) than EC (16.4).

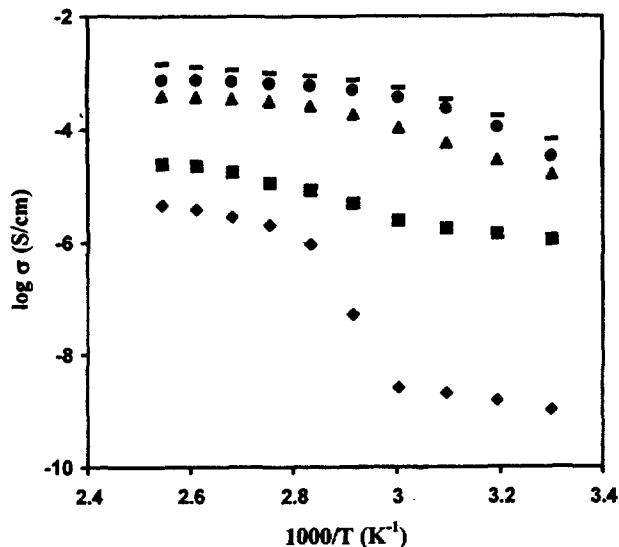


Fig. 6. The temperature dependence of conductivity of pure PEO (◆), PEO-NH<sub>4</sub>F-PC plasticized polymer electrolytes with F/O ratio 0.12 and containing different concentrations of PC (equivalent to 0 (■), 24 (▲), 47 (●) and 95(-) wt.% of polymer).

The conductivity of plasticized polymer electrolytes was also studied as a function of temperature. Figure 6 gives such variation of conductivity as a function of reciprocal temperature for PEO-NH<sub>4</sub>F polymer electrolytes containing different concentrations of PC – a plasticizer with dielectric constant (64.4) higher than that of PEO (~ 5). For comparison purposes variation of conductivity with temperature for PEO and PEO-NH<sub>4</sub>F with F/O ratio 0.12 is also included. Figure 6 shows that the conductivity of pure PEO rises sharply at ~ 60 °C which corresponds to the melting point of PEO and is generally explained to be due to the transition from the semi-crystalline to the elastomer phase. The addition of NH<sub>4</sub>F to PEO results in the complexation of salt with polymer and the resulting polymer electrolyte have conductivity nearly three orders of magnitude higher than that of PEO and secondly there is no sharp increase in conductivity at ~ 60 °C. The addition of PC in different concentrations to PEO-NH<sub>4</sub>F having F/O ratio 0.12 results in further increase in conductivity. The log conductivity vs. reciprocal temperature plots for plasticized polymer electrolytes as given in Fig. 6 are curved in nature which suggests the highly viscous/amorphous nature of polymer electrolytes containing PC. Similar variation of conductivity with temperature has also been observed for PEO-NH<sub>4</sub>F polymer electrolytes containing different concentrations of other plasticizers and the representative results for one more plasticizer i.e. EC are also given in Fig. 7.

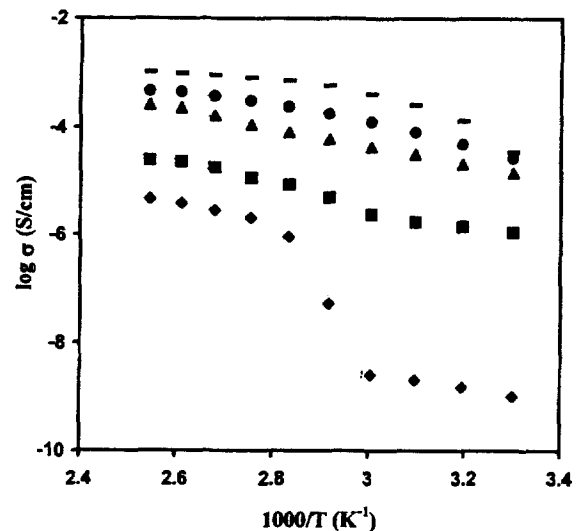


Fig. 7. The temperature dependence of conductivity of pure PEO (◆), PEO-NH<sub>4</sub>F-EC with F/O ratio 0.12 and containing different concentrations of EC (equivalent to 0 (■), 26 (▲), 53 (●) and 79 (-) wt.% of polymer).

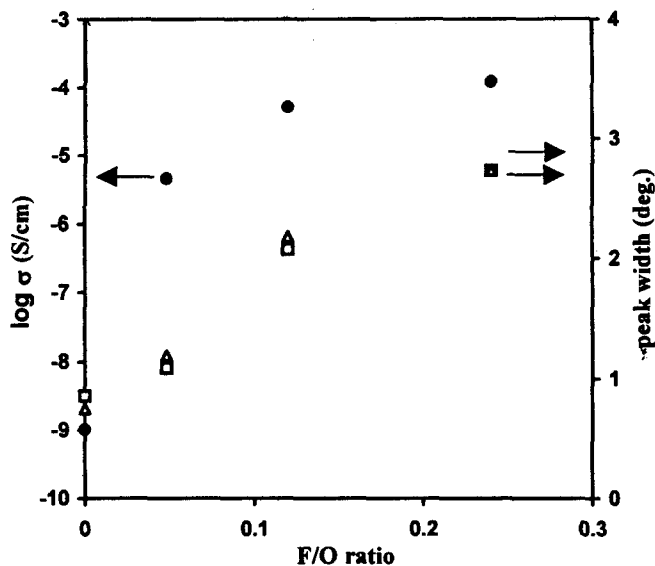


Fig. 8. Variation of conductivity (●) and peak width for XRD lines at 18.736° (□) and 23.12° (Δ) with salt concentration for PEO-NH<sub>4</sub>F-DMA plasticized polymer electrolytes containing fixed amount of DMA.

While discussing the variation of conductivity as a function of temperature in Figs. 6 and 7 it was observed that the conductivity of PEO shows a sharp increase at a temperature of ~ 60 °C corresponding to melting temperature of PEO and has been explained to be due to a transition from the crystalline to elastomer phase [2]. However the addition of salt i.e. NH<sub>4</sub>F has been reported to suppress this transition as shown in Figs. 6 and 7 and it has been explained to be due to the complexation of NH<sub>4</sub>F with PEO which reduces the crystallinity of polymer electrolyte and hence increase in  $\sigma$  at  $T \sim T_m$  is greatly reduced. This was checked by X-ray diffraction studies also. Polymer electrolytes containing same amount of plasticizer i.e. DMA (equivalent to 19 wt.% of polymer) but different concentrations of NH<sub>4</sub>F were studied and Figure 8 shows the variation of linewidth of prominent X-ray lines at  $2\theta$  values 18.736° and 23.12° as a function of NH<sub>4</sub>F concentration alongwith the variation of conductivity. From Fig. 8 it is observed that the linewidth/amorphous content increases with an increase in NH<sub>4</sub>F concentration and similar variation is observed in the conductivity behaviour which suggests that the addition of NH<sub>4</sub>F leads to complexation and hence an increase in amorphous content of polymer electrolytes. Thus the addition of salt/plasticizer to PEO results in an increase in the amorphous content of polymer electrolytes and hence conductivity increases.

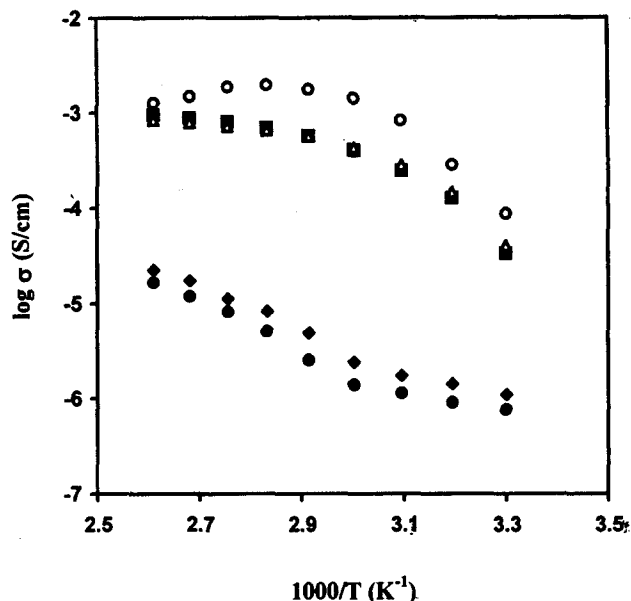


Fig. 9. The variation of conductivity with temperature for unplasticized (◆) and plasticized PEO-NH<sub>4</sub>F polymer electrolytes (F/O = 0.12) containing same amount of DEC (●), EC (■), PC (Δ) and DMA (○).

Equal amount of different plasticizers (PC, EC, DMA and DEC) was added to PEO-NH<sub>4</sub>F polymer electrolytes having F/O ratio 0.12. Figure 9 shows the variation of conductivity with temperature for these plasticized polymer electrolytes along with the results for unplasticized PEO-NH<sub>4</sub>F. Figure 9 shows that the conductivity of electrolytes with plasticizers having dielectric constant higher than that of PEO (i.e. PC, EC and DMA) is higher than the unplasticized PEO-NH<sub>4</sub>F in the whole (studied) temperature range, whereas the conductivity of electrolytes plasticized with DEC (having dielectric constant lower than that of PEO) is lower than that of unplasticized PEO-NH<sub>4</sub>F polymer electrolytes. The nature of the  $\log \sigma$  vs. reciprocal temperature curve for plasticized polymer electrolytes containing PC, EC and DMA is curved which suggests the amorphous nature of these polymer electrolytes.

As discussed earlier, the addition of plasticizer to polymer electrolytes results in an increase in amorphous content, which is high conducting phase [20], and hence conductivity increases. The plasticizer (due to its higher dielectric constant value as compared with that of the polymer (PEO)) can also help in the dissociation of salt as well as that of ion aggregates, which are formed at higher salt concentrations in polymer electrolytes. In above section, the increase of amorphous content with plasticizer addition was studied for polymer electrolytes

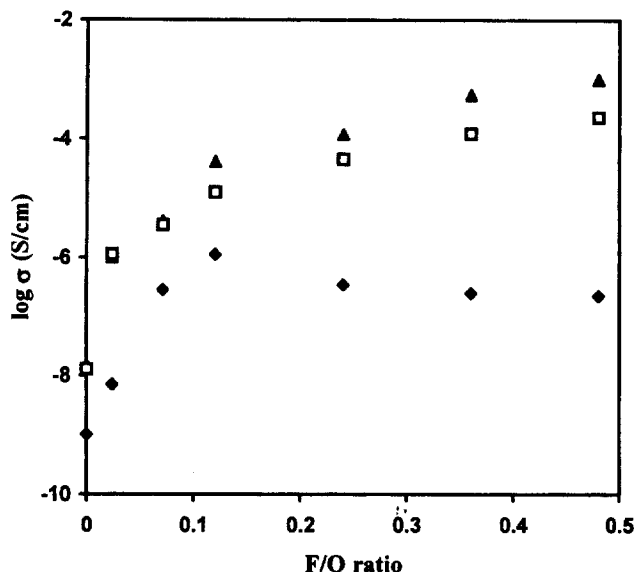


Fig. 10. Dependence of conductivity on salt concentration (expressed as F/O ratio) of unplasticized (◆) and plasticized PEO-NH<sub>4</sub>F (F/O = 0.12) with same amount of DMA (▲) and PC (□).

containing a fixed concentration of NH<sub>4</sub>F (F/O = 0.12). To study the effect of the plasticizer on the dissociation of salt and ion aggregates, samples with different levels of ion aggregation i.e. in regions A and B of Fig. 1a have been chosen. In this case the concentration of the plasticizer was kept constant and same amount of plasticizer was added to polymer electrolytes having different concentrations of NH<sub>4</sub>F.

The variation of conductivity of PEO-NH<sub>4</sub>F polymer electrolytes as a function of salt concentration (F/O ratio) with plasticizer (PC, DMA) and without plasticizer is shown in Fig. 10. The conductivity of plasticized polymer electrolytes is higher than that of the corresponding unplasticized electrolytes at all salt concentrations but the increase in conductivity with plasticizer addition has been found to depend upon the salt concentration. The increase in conductivity is small in region A (low salt concentration region) and is larger in region B (higher salt concentration region). The relative increase in conductivity ( $\sigma/\sigma_0$ ), where  $\sigma$  and  $\sigma_0$  are the values of conductivity of PEO-NH<sub>4</sub>F polymer electrolytes with and without the plasticizer respectively, has been calculated and plotted as a function of salt concentration (F/O ratio) in Fig. 11. The increase in conductivity with the addition of plasticizer is very small and nearly constant in region A, however it increases with salt concentration in region B – region in which ion aggregates are present and rise

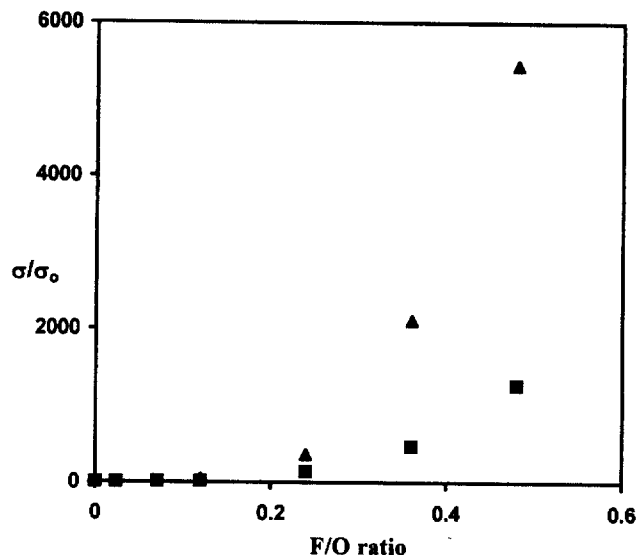


Fig. 11. The relative increase in conductivity ( $\sigma/\sigma_0$ ) of PEO-NH<sub>4</sub>F polymer electrolytes as a function of salt concentration (F/O ratio) with the addition of same amount of DMA (▲) and PC (■).

sharply with further increase in salt concentration. The results of Fig. 10 and Fig. 11 could be explained as follows:

- in region A i.e. at low salt concentration values, the increase in conductivity with the addition of plasticizer is nearly same for samples with different salt concentration values. In this region, the increase in conductivity is mainly due to an increase in the amorphous content of polymer electrolytes. Due to low salt concentration, ion aggregates are not present in this region as shown in Fig. 1b.
- in region B i.e. at high salt concentration values, the increase in conductivity with plasticizer addition increases with an increase in salt concentration. In this region, the formation of ion aggregates takes place as discussed earlier in Fig. 1b, so the addition of plasticizer with dielectric constant higher than that of PEO helps in the dissociation of ion aggregates. The dissociation of ion aggregates leads to an increase in the number of free ions ( $n$ ) which become available for conduction and hence conductivity ( $\sigma = nq\mu$ ) increases.
- maximum increase in  $\sigma$  is observed for polymer electrolytes with F/O ratio 0.48 i.e. containing maximum salt concentration studied. For this concentration, an increase in conductivity by a factor of more than 5000 has been observed with the addition



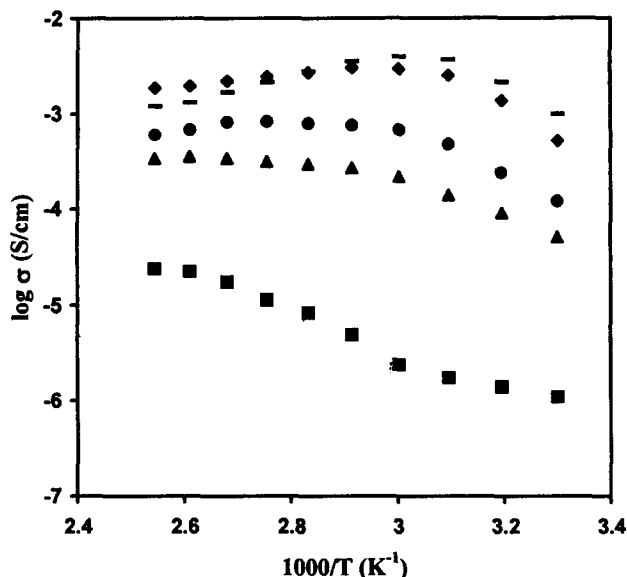


Fig. 12. Variation of conductivity with temperature for unplasticized (■) and plasticized PEO-NH<sub>4</sub>F polymer electrolytes (containing same amount of DMA) with F/O = 0.12 (▲), 0.24 (●), 0.36 (◆) and 0.48 (-).

of plasticizer. The maximum value of conductivity approaching  $\sim 10^{-3}$  S/cm has been obtained in this case. Similar results have also been obtained with other plasticizers viz EC,  $\gamma$ -BL, DMF, etc. having dielectric constant higher than that of the polymer used.

The dependence of conductivity of plasticized polymer electrolytes (PEO-NH<sub>4</sub>F-DMA) on salt concentration was also studied over 25 °C – 125 °C temperature range and the results are shown in Fig. 12. The plot of log conductivity vs. reciprocal temperature is given for plasticized polymer electrolytes PEO-NH<sub>4</sub>F-DMA containing same amount (equivalent to 19wt% of PEO) of plasticizer and having different concentration of the salt i.e. for F/O = 0.12, 0.24, 0.36, 0.48. For reference the results for unplasticized PEO-NH<sub>4</sub>F polymer electrolytes (F/O = 0.12) are also included in Fig. 12. It is observed that at all temperatures studied (25-125 °C), the conductivity of plasticized polymer electrolytes increases with an increase in salt concentration. The formation of ion aggregates in PEO-NH<sub>4</sub>F polymer electrolytes at higher salt concentrations and their dissociation with the addition of high dielectric constant/donor number plasticizers was also studied from mass action considerations [46] point of view. According to this, if ion aggregates are not present, then log  $\sigma$  vs. log C plot shall be a straight line and any deviation from straight-line behaviour suggests the

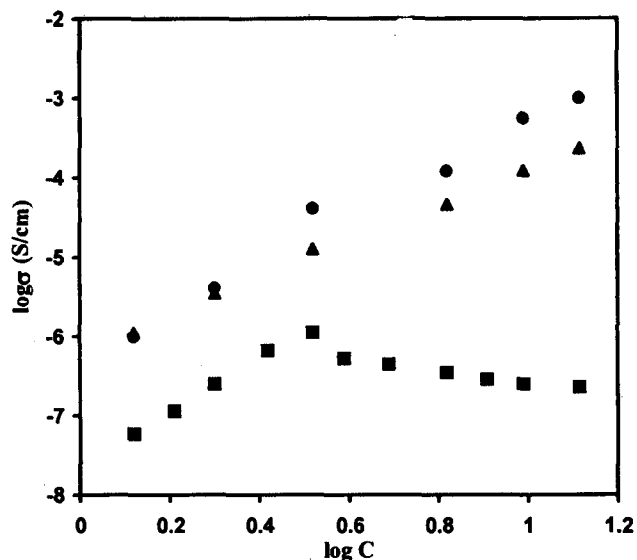


Fig. 13. Log  $\sigma$  vs. log C for unplasticized (PEO-NH<sub>4</sub>F) (■) and plasticized (PEO-NH<sub>4</sub>F-DMA) (●), (PEO-NH<sub>4</sub>F-PC) (▲) polymer electrolytes.

presence of ion aggregates as given in Fig. 1. Figure 13 shows the log  $\sigma$  vs. log C plot for PEO-NH<sub>4</sub>F polymer electrolytes alongwith for polymer electrolytes plasticized with PC i.e. (PEO-NH<sub>4</sub>F-PC) and with DMA i.e. (PEO-NH<sub>4</sub>F-DMA). The amount of plasticizer (PC, DMA) added is same in each case.

For unplasticized polymer electrolytes, a straight line behaviour is observed in the low salt concentration region ( $0.0 < F/O < 0.1$ ) and plot deviates considerably at higher salt concentration region ( $0.12 \leq F/O \leq 0.48$ ) which suggests the presence of ion aggregates in the high salt concentration region (B). The same plot for polymer electrolytes plasticized with PC shows a nearly straight-line behaviour with only small deviation at higher salt concentration values, which suggests that most of the ion aggregates get dissociated with the addition of PC. Similar behaviour is observed for polymer electrolytes plasticized with DMA. The plot shows small deviation at higher salt concentration values only. A comparison of plots for unplasticized polymer electrolytes with plasticized polymer electrolytes suggests that the dissociation of ion aggregates takes place with the addition of plasticizers. This results in an increase in the value of conductivity due to an enhancement in carrier concentration as given in Figs. 10 and 11. Thus the addition of plasticizer to polymer electrolytes results in an increase in conductivity by increasing the amor-

phous content of polymer electrolytes as well as by dissociating ion aggregates formed at higher salt concentration values.

#### 4. Summary

The addition of plasticizers (EC, PC,  $\gamma$ -BL, DMA, DMF) with dielectric constant greater than that of PEO to PEO-NH<sub>4</sub>F polymer electrolytes has been found to result in an increase in conductivity value, which further depends upon the concentration of salt as well as on the amount of plasticizer added. The magnitude of increase in conductivity with the addition of same amount of different plasticizers (having dielectric constant higher than that of PEO) to PEO-NH<sub>4</sub>F polymer electrolytes has been found to be closely related to the donor number of plasticizer. The increase in conductivity is more for plasticizer with higher donor number. The higher value of donor number/dielectric constant results in increasing the conductivity by dissociating ion aggregates, which are present in polymer electrolytes at higher salt concentrations in addition to increasing the amorphous content. The addition of plasticizers (DEC, DMC) with dielectric constant less than that of polymer used (PEO) does not result in enhancement in conductivity.

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