

3 Electrical Characterization Studies

The polymer electrolyte, which has been prepared as per the method described in chapter 2 were dried and analysed for various characteristics. The electrical conductivity of the polymer electrolytes was immediately measured by impedance spectroscopy.

3.1 Impedance Analysis

Organic polymer electrolytes show little conductivity with increasing salt content as well as inorganic salts (117). Table 3.1 provides concentration of salt, polymer and the resulting conductivity values. The conductivity versus composition curve is shown in Fig. 3.1. From Fig. 3.1, it can be observed that the ionic conductivity of the polymer electrolyte is increased with increasing salt content.

Results & Discussion I

This increase in ionic conductivity with increasing salt content may be due to the increase in number of charge carriers in the polymer electrolyte. The conductivity attains its maximum value of 10^{-3} S/cm at 15% of salt content. After that composition, the conductivity begins to decrease with increasing salt content. This decrease in ionic conductivity with increasing salt content may be due to the fact that the polymer cannot incorporate more salt beyond certain composition. The excess salt could have increased the crystallinity of the complex as observed by some other workers (147-148).

3 Electrical Characterization Studies

The polymer electrolyte, which has been prepared as per the method described in chapter 2 were dried and analysed for various characteristics. The electrical conductivity of the polymer electrolytes was immediately measured by ac-impedance spectroscopy.

3.1 ac-Impedance Analysis

3.1.1 Unplasticized Systems

Organic polymers are generally used as insulators. Many polymers show little conductivity with $10^{-12} \sim 10^{-18}$ S/cm due to some contaminants such as solvents or ions [117]. Table 3.1 provides concentration of salt, polymer and the resulting conductivity values. The conductivity versus composition curve is shown in Fig. 3.1. From Fig. 3.1, it can be observed that the ionic conductivity of the polymer electrolyte is increased with increasing salt content.

This increase in ionic conductivity with increasing salt content may be due to the increase in number of charge carriers in the polymer electrolyte. The conductivity attains its maximum value of 10^{-7} S/cm at 15% of salt content. After that composition, the conductivity begins to decrease with increasing salt content. This decrease in ionic conductivity with increasing salt content may be due to the fact that the polymer cannot incorporate more salt beyond certain composition. The excess salt could have increased the crystallinity of the complex as observed by some other workers [147-148].

Table 3.1 Conductivity of the polymer electrolyte with increasing salt content

Composition	Conductivity (s/cm)
95 : 5 (PVDF : LiBF ₄)	1.3×10^{-9}
90 : 10 (PVDF : LiBF ₄)	1.8×10^{-7}
85 : 15 (PVDF : LiBF ₄)	3.6×10^{-7}
80 : 20 (PVDF : LiBF ₄)	2.6×10^{-7}
70 : 30 (PVDF : LiBF ₄)	2.2×10^{-7}

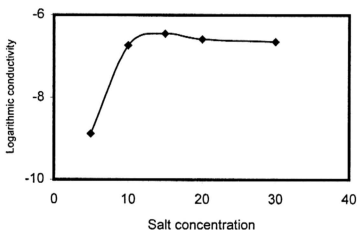


Fig.3.1. Log σ versus salt concentration for PVDF based polymer electrolytes

It has been reported that in order to have a high ionic conductivity the salt must be in a dissociated state but not in a crystalline state [116]. There is strong anion-cation interaction leading to a formation of electrically neutral species unable to participate in the ionic conduction. Thus, the ionic conductivity of the polymer electrolyte is decreased beyond a particular composition.

From the ac-impedance studies, it can be observed very clearly that there is a possible complexation between the salt and the polymer system. Because of this complexation between the salt and the polymer, the conductivity of the polymer electrolyte system increases with increasing salt content until an optimising concentration has been reached. From this study, the composition for the highest ion conducting polymer electrolyte is chosen for further studies.

Belcore's hybrid polymer electrolyte gives ionic conductivity close to 10^{-3} S/cm. This high ionic conductivity in hybrid polymer electrolyte is due to several plasticizers. Several plasticizers are used to dissolve 1 M of lithium salts. We have also achieved an ionic conductivity towards the order of 10^{-3} S/cm in hybrid polymer electrolytes [149]. In the present work, PVDF, salt and the plasticizers were dissolved in the solvent. As usual, the films were formed and the conductivities were measured.

3.1.2 Plasticized Systems

The ionic conductivity which has been obtained from the PVDF: LiBF_4 composition is 10^{-7} S/cm (high conducting sample). This room temperature ionic conductivity is very low for any particular use in batteries or any other devices and needs to be enhanced. One of the approaches to enhance ambient ionic conductivity is to incorporate a low molecular weight diluent or plasticizer [150]. In polymer language, the term plasticizer refers to a species, which will decrease the glass transition temperature of the polymer electrolyte [63] and hence increase the segmental mobility. These plasticizers are usually highly dielectric and low viscous

solutions [33]. The role of the plasticizer among others [150], is to enhance the ionic conductivity by increasing the dissociation of the salt which will increase the number of mobile carriers. The impedance spectra for all the polymer electrolyte films which has been analyzed in the present study is shown in Fig. 3.2(a-d), 3.3 (a-d) and 3.4(a-d) for DMF, MF and EC respectively.

All the Cole-Cole plots for the plasticized polymer electrolyte film show a depressed semi-circular nature with a tail at the low frequency end. This straight line at low frequencies is due to the diffusion impedance at the electrode electrolyte interface, followed by a semicircle with a Z' intercept at a higher frequency range. This kind of response is the characteristic of the polymer electrolytes having ionic conductivity. From the real axis intercept, the bulk resistance of the polymer electrolyte sample is calculated and tabulated. Table 3.2 gives the conductivity values at ambient condition for various plasticizers, which is employed in the present study.

3.2 Choice of the Better Plasticizer for Conductivity Enhancement

The ionic conductivity values for different plasticizers are shown in Table 3.2. The plot of conductivity and the plasticizer content is shown in Fig. 3.5. The ionic conductivity values for all the polymer electrolytes, ranges from 10^{-6} to 10^{-4} S/cm. The maximum conductivity which has been obtained from the present study at ambient condition is 10^{-4} S/cm. This conductivity is at the lower end of the useful range for application of polymer electrolytes in solid state batteries.

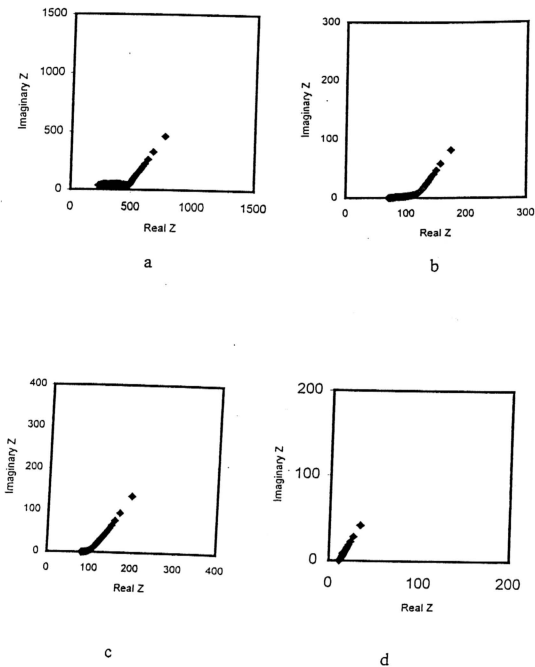
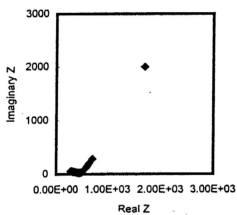
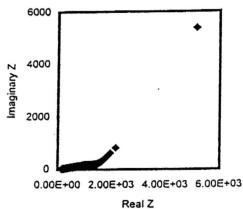


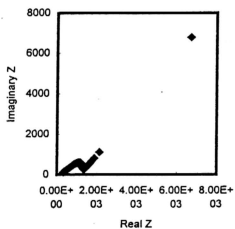
Fig.3.2. Cole-Cole plots for DMF based polymer electrolytes (a) DMF 1 (b) DMF 3 (c) DMF 4 (d) DMF 6



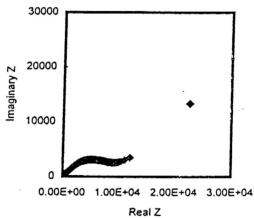
a



b



c



d

Fig.3.3. Cole-Cole plots for MF based polymer electrolytes (a) MF 1 (b) MF 3 (c) MF 4 (d) MF 6

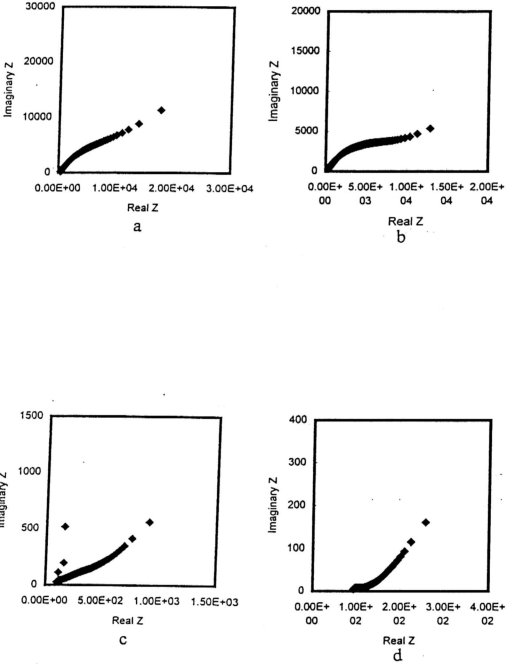


Fig.3.4. Cole-Cole plots for EC based polymer electrolytes (a) EC 1 (b) EC 3 (c) EC 4 (d) EC 6

Table 3.2 Ionic conductivity values and the name of the Polymer electrolyte

Name of the electrolyte	Composition	Conductivity (s/cm)
DMF 1	PVDF-LIBF ₄ : DMF (95:5)	1.0 x 10 ⁻⁴
DMF 2	PVDF-LIBF ₄ : DMF (90:10)	1.9 x 10 ⁻⁴
DMF 3	PVDF-LIBF ₄ : DMF (85:15)	2.2 x 10 ⁻⁴
DMF 4	PVDF-LIBF ₄ : DMF (80:20)	2.7 x 10 ⁻⁴
DMF 5	PVDF-LIBF ₄ : DMF (70:30)	2.3 x 10 ⁻⁴
DMF 6	PVDF-LIBF ₄ : DMF (60:40)	6.1 x 10 ⁻⁵
MF 1	PVDF-LIBF ₄ : MF (95:5)	8.8 x 10 ⁻⁶
MF 2	PVDF-LIBF ₄ : MF (90:10)	1.2 x 10 ⁻⁵
MF 3	PVDF-LIBF ₄ : MF (85:15)	1.2 x 10 ⁻⁴
MF 4	PVDF-LIBF ₄ : MF (80:20)	1.0 x 10 ⁻⁴
MF 5	PVDF-LIBF ₄ : MF (70:30)	2.3 x 10 ⁻⁵
MF 6	PVDF-LIBF ₄ : MF (60:40)	1.3 x 10 ⁻⁶
EC 1	PVDF-LIBF ₄ : EC (95:5)	1.6 x 10 ⁻⁶
EC 2	PVDF-LIBF ₄ : EC (90:10)	1.7 x 10 ⁻⁶
EC 3	PVDF-LIBF ₄ : EC (85:15)	3.2 x 10 ⁻⁶
EC 4	PVDF-LIBF ₄ : EC (80:20)	1.5 x 10 ⁻⁴
EC 5	PVDF-LIBF ₄ : EC (70:30)	9.4 x 10 ⁻⁵
EC 6	PVDF-LIBF ₄ : EC (60:40)	7.1 x 10 ⁻⁵

Abbreviation:

PVDF : Poly (vinylidene fluoride); DMF : Dimethyl Formamide

MF : Methyl Formate; EC: Ethylene Carbonate

From Fig. 3.5, it can be observed that the polymer electrolytes containing the DMF plasticizer has higher ionic conductivity than the electrolytes containing MF and EC plasticizers. In the case of EC and MF plasticizer based polymer electrolyte system, the maximum conductivity is almost the same i.e., about 10^{-4} S/cm. The increase in conductivity until the optimizing plasticizer concentration is probably due to the increase in dissociation of the salt by the respective plasticizers.

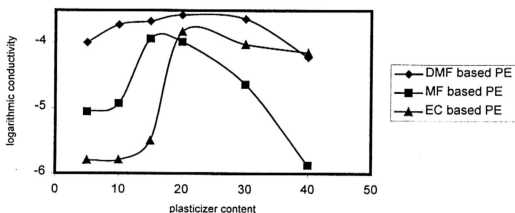


Fig. 3.5. Log σ versus composition of plasticizer

From Fig. 3.5, it can be observed that the conductivity value initially increases with increasing plasticizer content and after attaining the maximum conductivity, the σ value begins to decrease. This increase and decrease in conductivity for various plasticizers content is also observed in other systems [129] and may be due to the formation of linkages between the plasticizer itself, thus causing it to crystallize resulting in the decrease in electrical conductivity [151]. This limiting composition of plasticizer content is varied with respect to the plasticizer. In the case of DMF, MF and EC is 20%, 15% and 20% respectively.

From Fig. 3.5, it can also be observed that the DMF plasticizer based polymer electrolyte gives high ionic conductivity at ambient temperature in all the composition when compared with EC and MF. The role of the plasticizers in polymer electrolyte is to reduce the glass transition temperature [63]. It was shown at an early stage, that this low glass transition temperature resulted in higher ionic conductivities of polymer electrolyte. In this aspect, we expect that the DMF plasticizer decrease the glass transition temperature more when compared with other plasticizers and make the segmental motion of the polymer more flexible [51].

3.3 Dielectric Relaxation Studies

If the plasticizer dissociates more salt into ions then the dielectric constant value of the plasticized samples should increase. Fig. 3.6 to 3.8 shows the dielectric constant for the plasticized and unplasticized systems. From this, it can be observed that the plasticized polymer electrolyte system has a higher dielectric constant than the unplasticized system. Thus, the ionic conductivity is high in the case of plasticized system because the plasticizer has increased the dissociation of the salt [152]. Fig 3.9 to 3.11 shows the dielectric loss for the plasticized and unplasticized system. The dielectric loss also increases with decrease in frequency. This is due to the free charge motion within the material [153]. These values are due to free charge buildup at the interface between the material and the electrode. At low frequencies, ϵ' and ϵ'' value increase indicating that the electrode polarization phenomena makes significant contribution. Since capacitance, $C \propto \epsilon$ the conductivity depression at low frequency implies the capacitive nature of the double layer between the electrolyte and the electrode.

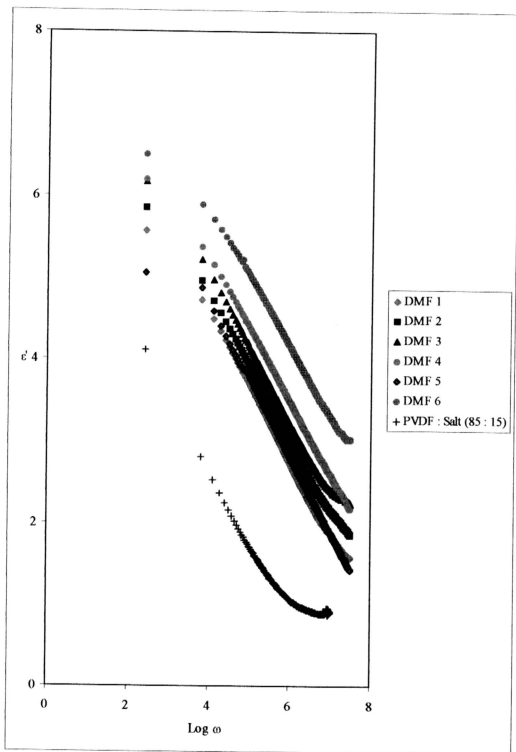


Fig. 3.6. ϵ' versus $\log \omega$ at different plasticizer concentrations for DMF and highest conducting unplasticized polymer electrolyte [PVDF : LiBF₄ (85 : 15)]

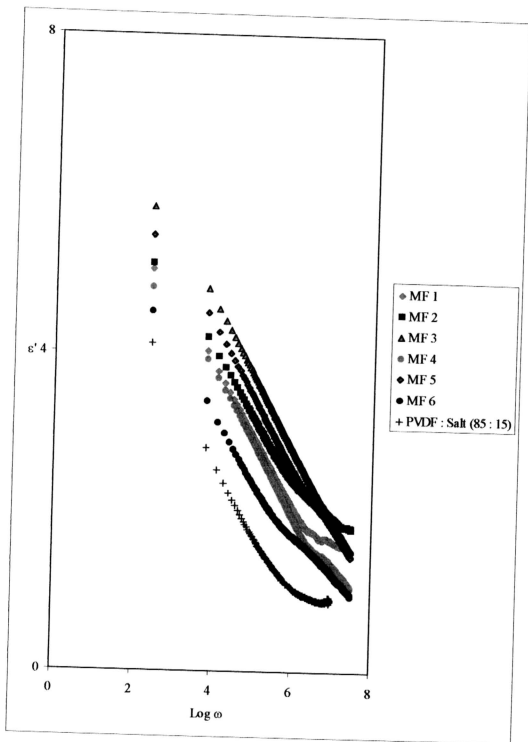


Fig 3.7. ϵ' versus $\log \omega$ at different plasticizer concentrations for MF 3 and highest conducting unplasticized polymer electrolyte [PVDF : LiBF₄ (85 : 15)]

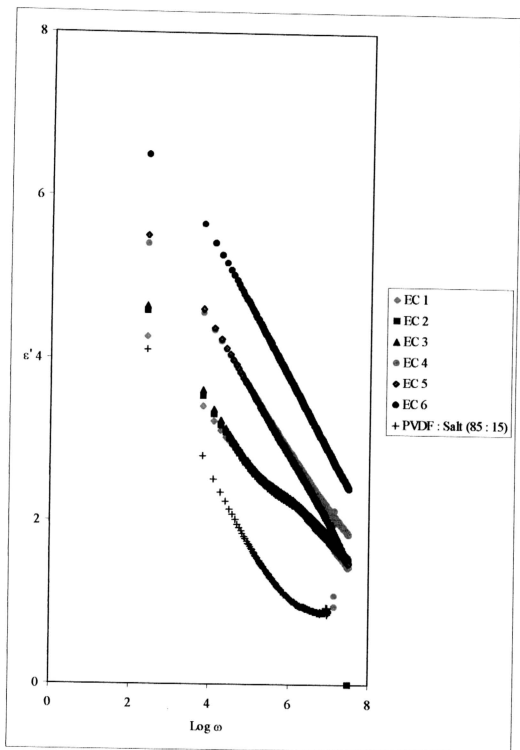


Fig 3.8. ϵ' versus $\log \omega$ at different plasticizer concentrations for EC and highest conducting unplasticized polymer electrolyte [PVDF : LiBF₄ (85 : 15)]

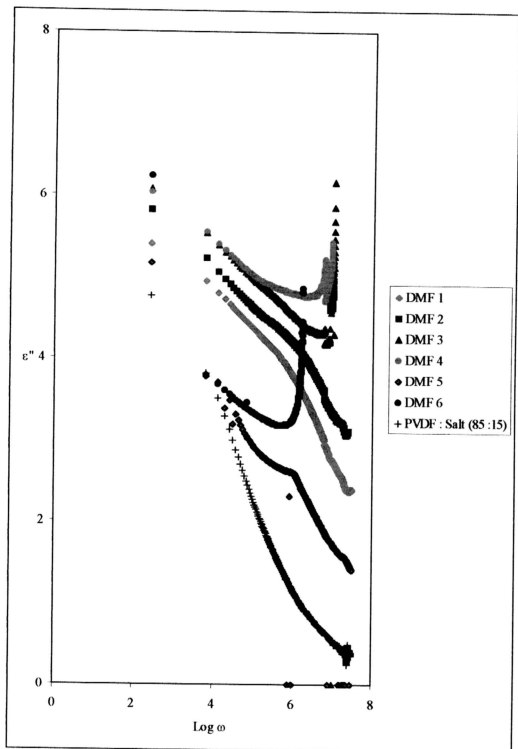


Fig 3.9. ϵ'' versus $\log \omega$ at different plasticizer concentrations for DMF and highest conducting unplasticized polymer electrolyte [PVDF : LiBF₄ (85 : 15)]

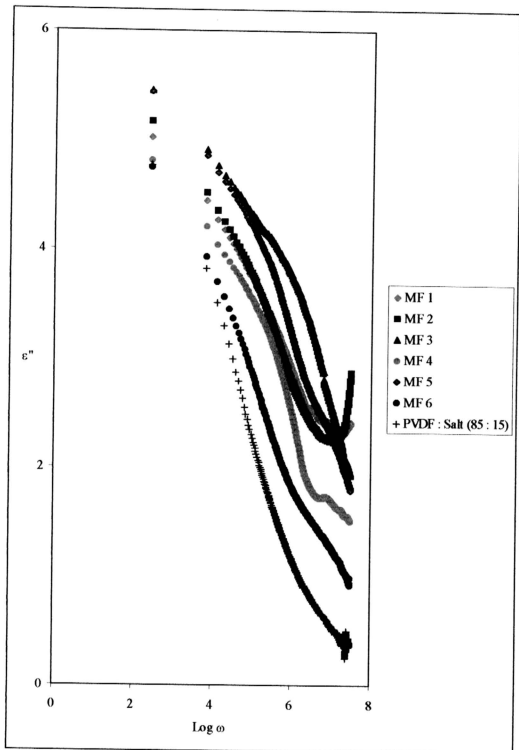


Fig 3.10. ϵ'' versus $\log \omega$ at different plasticizer concentrations for MF and highest conducting unplasticized polymer electrolyte [PVDF : LiBF_4 (85 : 15)]

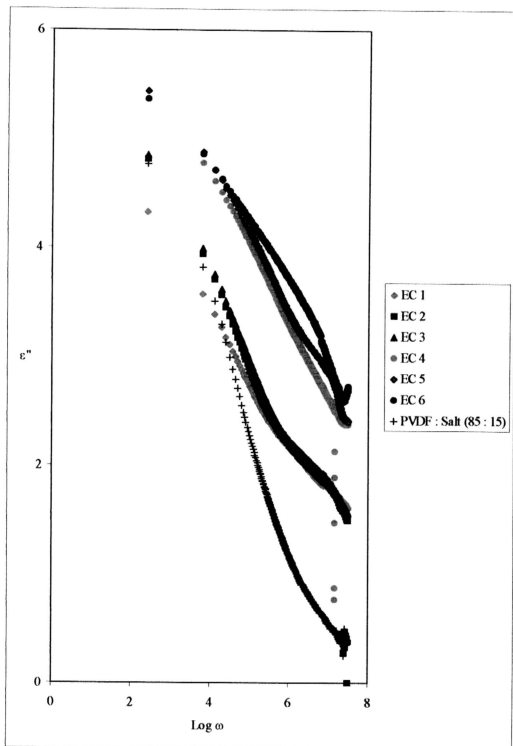


Fig 3.11. ϵ'' versus $\log \omega$ at different plasticizer concentrations for EC and highest conducting unplasticized polymer electrolyte [PVDF : LiBF₄ (85 : 15)]

Although the dielectric constant of EC is more than that of DMF, the DMF plasticizer gives a higher ionic conductivity. The comparative studies on DMF and PC based polymer electrolyte system clearly shows the fact that DMF is showing good performance than PC although the dielectric constant of PC is higher than that of DMF [150]. The conductivity value reported for DMF plasticizer for LiClO_4 in the liquid form is in the range of 10^{-2} S/cm when compared with PC system.

This high ionic conductivity of the DMF based plasticizer is because of the fact that the DMF is having strong co-ordination with lithium salts [154]. This strong co-ordination decreases the cation-polymer interaction and thereby decreases the glass transition temperature of the system. Thus, the conductivity is high at ambient temperature in liquid form. This has been confirmed by NMR studies [150]. Not only, this strong interaction with lithium salts gives it an advantage; it is also having strong affinity with the polymer. Depletion of the plasticizer from the polymer electrolyte system appears to be not very strong significantly at ambient temperature [154].

3.4 Ion Conduction Mechanism

In order to understand the ion conduction mechanism in plasticizer based polymer electrolyte system, conductivity-temperature measurements were carried out for the polymer electrolyte with highest ionic conductivity for different types of plasticizers (DMF, MF and EC). In the present study, the temperature chosen is from room temperature to 100°C . Table 3.3 gives the ionic conductivity values, which has been obtained in the present study for different temperatures. Fig. 3.12 depicts the $\log \sigma T$ versus $1000/T$ (K^{-1}) for the three different plasticizer based polymer electrolytes,

exhibiting the highest room temperature ionic conductivity. From the temperature dependent ionic conductivity plots, the regression values are calculated. The regression values are found to be 0.90, 0.91 and 0.92 respectively for DMF, MF and EC plasticizer based polymer electrolytes. These regression values are close to unity and it strongly suggesting that the temperature dependent ionic conductivity for all the plasticized systems follow Arrhenius type behaviour.

Table 3.3 Temperature and conductivity values for polymer electrolytes

Temperature (K)	1000/T (K ⁻¹)	log σT (DMF 4)	log σT (MF 3)	log σT (EC 4)
310	3.32	-1.18	-1.46	-1.22
323	3.10	-1.14	-1.41	-1.18
333	3.00	-1.12	-1.37	-1.14
343	2.92	-1.09	-1.19	-1.10
353	2.83	-1.06	-1.11	-1.07
363	2.75	-0.99	-1.07	-1.01
373	2.68	-0.73	-1.02	-0.85

The Arrhenius behaviour of temperature dependent ionic conductivity of the polymer electrolyte sample hints at the possibility of cation transport quite similar to that of the ionic conductivity mechanism in ionic crystals. In ionic crystals, the ions jump to neighbouring vacant sites and therefore if the activation energy decreases with plasticizer content, then the ionic conductivity increase to a higher value.

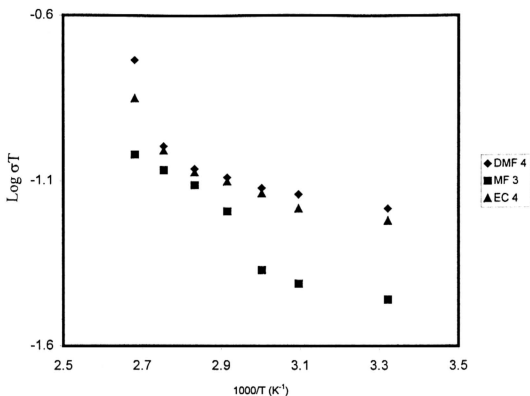


Fig 3.12. $\log \sigma T$ versus $1000/T$ (K⁻¹)

The activation energy, which is the combination of the energy of defect formation and energy of defect migration can be calculated from the plots. The activation energy for the DMF, MF and EC based plasticizers are 0.25 eV, 0.62 eV and 0.29 eV respectively. From the activation energy calculation, it can be concluded that the activation energy is lowest for the DMF plasticizer based polymer electrolytes followed by the EC and then MF based polymer electrolytes. The trend in conductivity too is highest for the DMF plasticizer based polymer electrolytes followed the EC and then MF based polymer electrolytes. This kind of conductivity mechanism is reminiscent of the original view of Armand [32].

3.5 Summary

The ionic conductivity of the plasticized and unplasticized polymer electrolytes was analysed in the present study by ac-impedance spectroscopy. From ac-impedance spectroscopy studies, the ambient temperature ionic conductivity of the unplasticized polymer electrolyte system is found to be in the order of 10^{-7} S/cm and this ionic conductivity is very low for any particular use. The ionic conductivity of the unplasticized polymer electrolyte system is enhanced further by the addition of plasticizers such as DMF, MF and EC. The ambient temperature ionic conductivity of the plasticized polymer electrolyte system is found to be in the order of 10^{-4} S/cm. This high ionic conductivity of the plasticized system may be attributed to the dissociation of more salt by the plasticizer and thereby increasing the number of mobile ion species in the polymer electrolyte. The main role of the plasticizer is to reduce the glass transition temperature and thereby increase the flexibility of the polymer backbone. It is also observed that the ionic conductivity of the DMF plasticizer based polymer electrolyte at ambient temperature is highest compared with other plasticizers used in the present study. It is because of the fact that the plasticizer DMF could probably reduce the glass transition temperature more compared to the other plasticizer used in the present study and it is also having strong affinity towards the salt and the polymer. This high affinity towards salt makes more facile path for ion conduction and the interactions with polymer suppress the depletion of the plasticizer at ambient temperature from the polymer electrolyte.