

CHAPTER 6

RESULTS OF IMPEDANCE SPECTROSCOPIC STUDIES

6.1 Introduction

The most important characteristic of solid polymer electrolytes is their electrical properties and in particular ionic conductivity. Impedance spectroscopy is a non-destructive technique that is being used as a successful tool to investigate the electrical properties of systems such as polymer electrolytes (Benavente et. al, 2000). Using this technique, impedance measurements can be made in wide frequency ranges. Analysis of the impedance data is often made by a complex impedance method, which involves plotting the impedance imaginary part Z_i against the real part, Z_r (Z_i vs Z_r).

From the Cole-Cole plot, the bulk resistance of each sample is determined. The electrical conductivity is calculated using the equation, $\sigma = d/R_b A$, where σ is the ionic conductivity, d is the thickness of the sample, R_b is the bulk resistance and A is the electrode-electrolyte contact area. The conductivity of a polymer electrolyte is the sum of all conducting species in the host media, ie.,

$$\sigma = \sum \sigma_i$$

where ' i ' is the type of conducting species which may include single ions such as Li^+ and Γ , or contact ions that do not contribute to conductivity.

In this work, the salt concentration and temperature dependent conductivity of PEO based electrolytes were studied by impedance spectroscopy. The effect of fillers and the macromolecules such as calix4 and calix6 on the ionic conductivity and dielectric behaviours of the electrolytes was also analyzed.

6.2 Ionic Conductivity of PEO-LiI complexes

Salt-in-polymer complexes exhibit a combination of properties that make them potentially attractive for applications as electrolyte material in batteries, solar cells and smart windows (Kananov et al., 2002). For this reason, extensive research efforts have been undertaken over the past three decades to optimize and to understand the characteristics of ionic transport in these polymer-based ion conductors. Complexes of poly (ethylene oxide) with alkali metal salts belong to the most frequently investigated prototype systems.

PEO has the ability to solvate relatively high salt concentrations in their amorphous state. This is related to a unique conduction mechanism involving the creation of free volume, arising from the dynamics of the polymer chains, that led to design strategies for new polymer electrolytes in which crystallinity was suppressed and segmental motion maximized (Gray et al., 1997). This in turn, led to some enhancement in ionic conductivity at room temperature. However, despite innovative designs of flexible polymers and the synthesis of salts containing asymmetric anions capable of suppressing crystallinity, the ionic conductivity has been persistently limited to 10^{-4} S cm^{-1} at room temperature. This is particularly true for salts consisting of large polarisable anions and small cations such as NaI, LiTf, which are of technological relevance (Adams et al., 2003 and Patel et al., 2007). In the present work we are dealing with PEO complexed with alkali metal iodide, LiI from room temperature to 100° C.

The increase in salt concentration in polymer electrolytes causes an increase in the number of charge carriers, and consequently an increase in ionic conductivity. Meanwhile, the decrease in the ionic conductivity of PEO – LiI electrolytes for higher

salt concentrations can be assigned to the decrease either in mobility or in the number of free charge carriers or both and to the increase of the degree of crystallinity of PEO. Maurya et. al.,(1992). It can be observed that the bulk resistance changes with LiI concentration. From $\sigma = d/R_bA$ we can calculate the conductivity of PEO-LiI samples at different temperatures, which is listed in Table 6.1.

Table 6.1: Ionic conductivity of PEO-LiI system from temperature to 100°C

Temp °C	Lil 4wt.% S/cm	Lil 6wt.% S/cm	Lil 8wt.% S/cm	Lil 10wt.% S/cm	Lil 12wt.% S/cm	Lil 14wt.% S/cm
RT	1.22E-04	1.24E-04	1.35E-04	1.54E-04	1.28E-04	1.02E-04
40	1.56E-04	2.04E-04	2.52E-04	2.65E-04	2.34E-04	2.42E-04
50	2.04E-04	2.80E-04	3.22E-04	3.50E-04	2.86E-04	3.10E-04
60	2.84E-04	3.20E-04	3.42E-04	3.86E-04	3.61E-04	3.33E-04
70	3.28E-03	3.58E-03	3.68E-03	4.08E-03	3.82E-03	3.62E-03
80	3.81E-03	3.68E-03	3.74E-03	4.24E-03	4.02E-03	3.71E-03
90	4.23E-03	4.34E-03	4.48E-03	4.53E-03	4.10E-03	3.88E-03
100	4.36E-03	4.42E-03	4.58E-03	4.62E-03	4.28E-03	4.02E-03

When salt dissolves in polymer and dissociates to ions, it generates carrier ions which increases the ionic conductivity. According to Weston and Steele (1982), PEO interacts with inorganic salts and therefore, can solvate salts such as LiI, LiSCN and LiClO₄ etc. The solvated ions present mobility in the polymeric solvent, giving significant ionic conductivity to the material. The room temperature ionic conductivity is due to the amorphous phase, which we have shown in the XRD analysis. Figure 6.1 represents the impedance spectrum for pure PEO and Fig 6.2: (a)- (f) represents the impedance spectra for PEO with LiI at different weight percentages (4 wt. % - 14 wt. %) at room temperature.

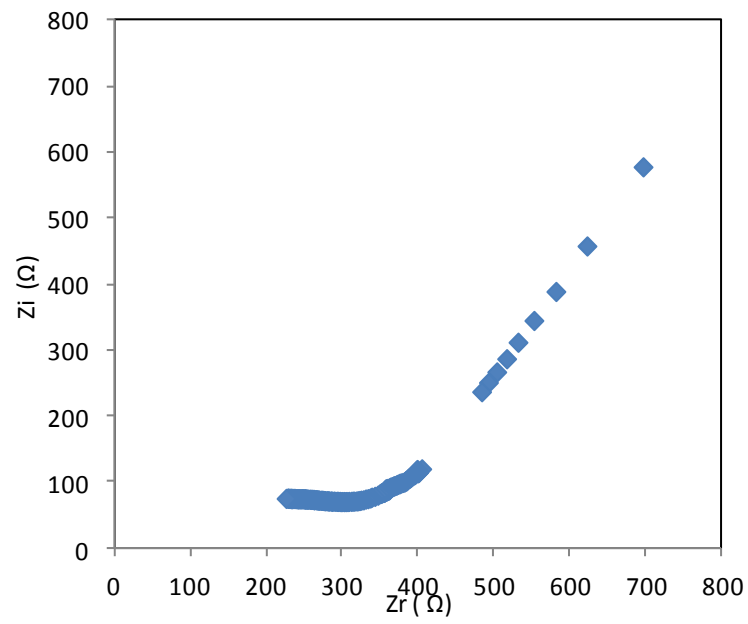


Figure 6.1: Impedance plot of PEO at room temperature

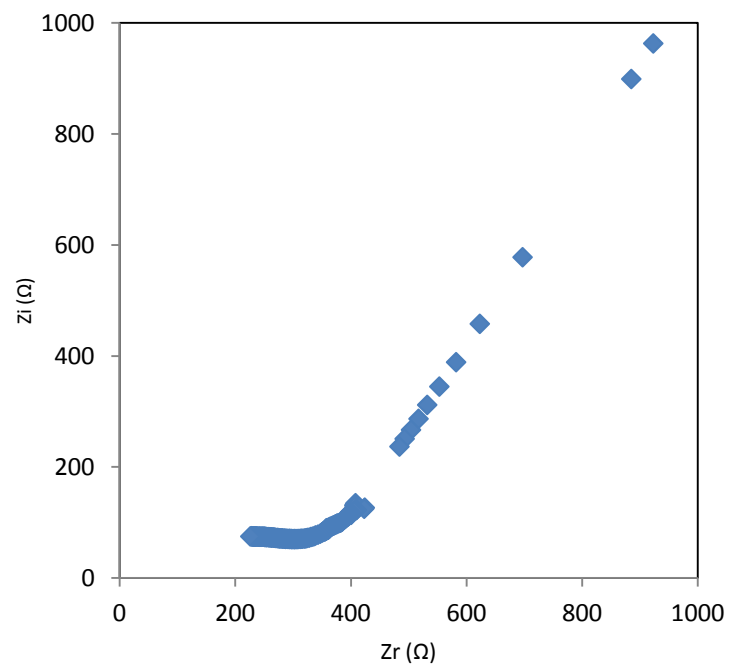


Figure 6.2 (a): Impedance plot of 96 wt.% PEO:4 wt.% LiI at room temperature

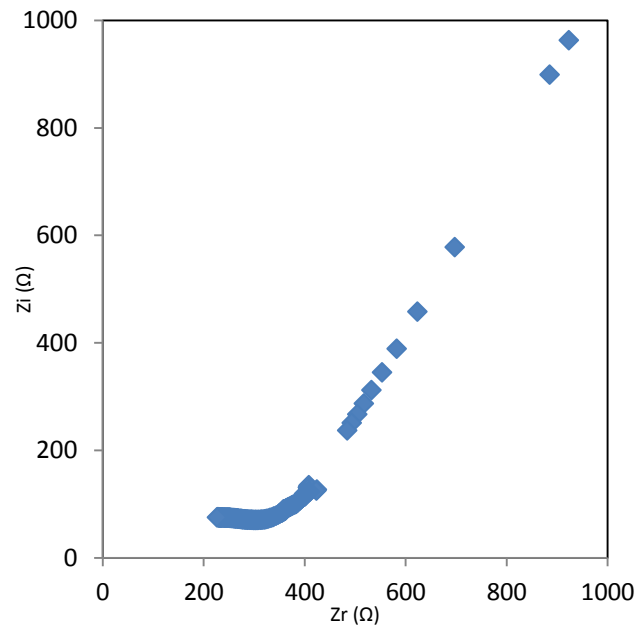


Figure 6.2 (b): Impedance plot of 94 wt.% PEO: 6 wt.% LiI at room temperature

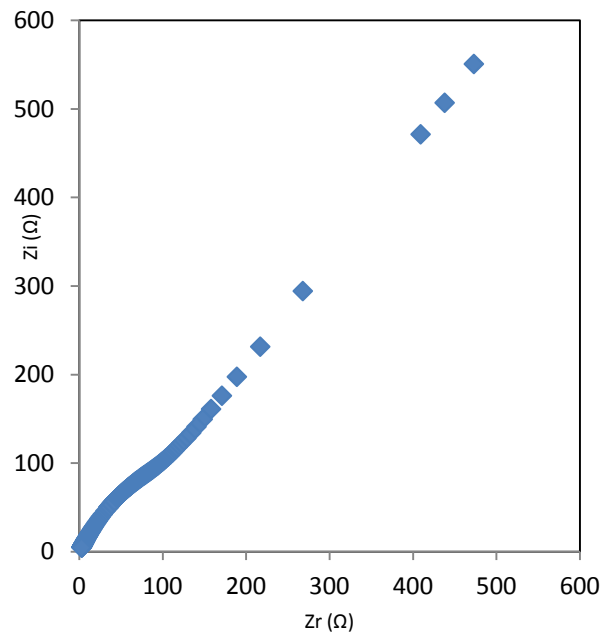


Figure 6.2 (c): Impedance plot of 92 wt.% PEO : 8wt.%LiIatroomtemperature

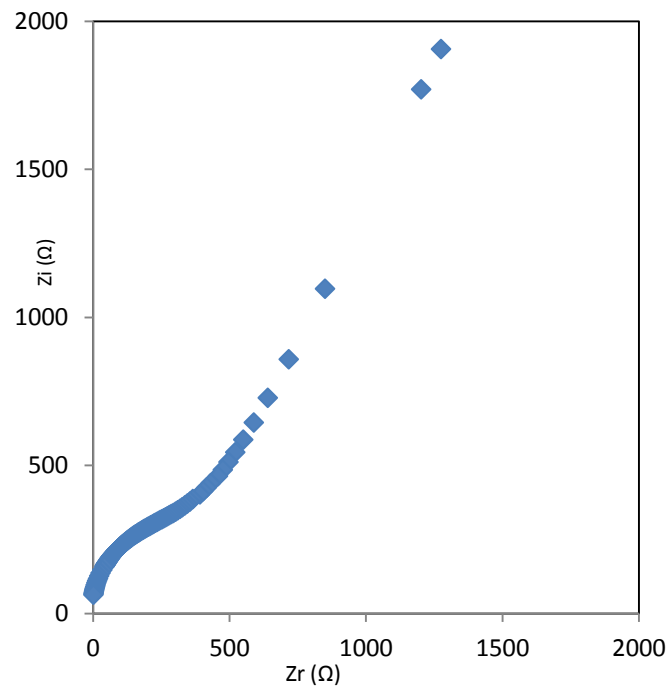


Figure 6.2(d): Impedance plot of 90 wt.% PEO:10 wt.% LiI at room temperature

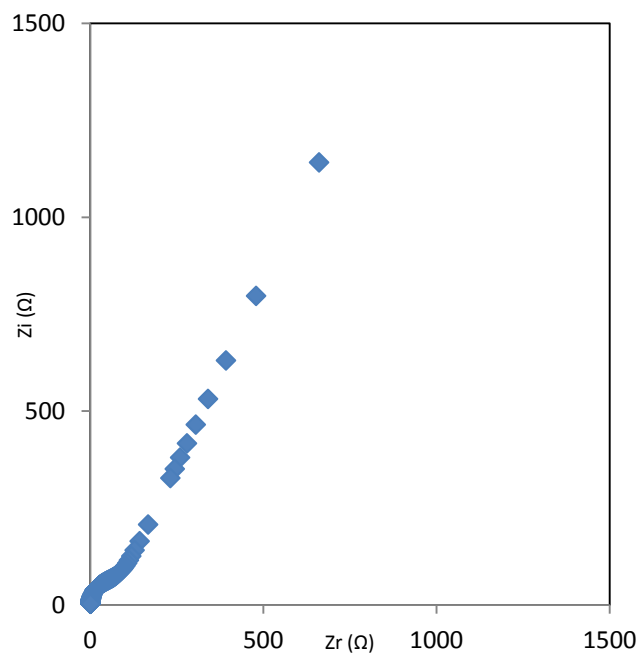


Figure 6.2(e): Impedance plot of 88 wt.% PEO:12 wt.% LiI at room temperature

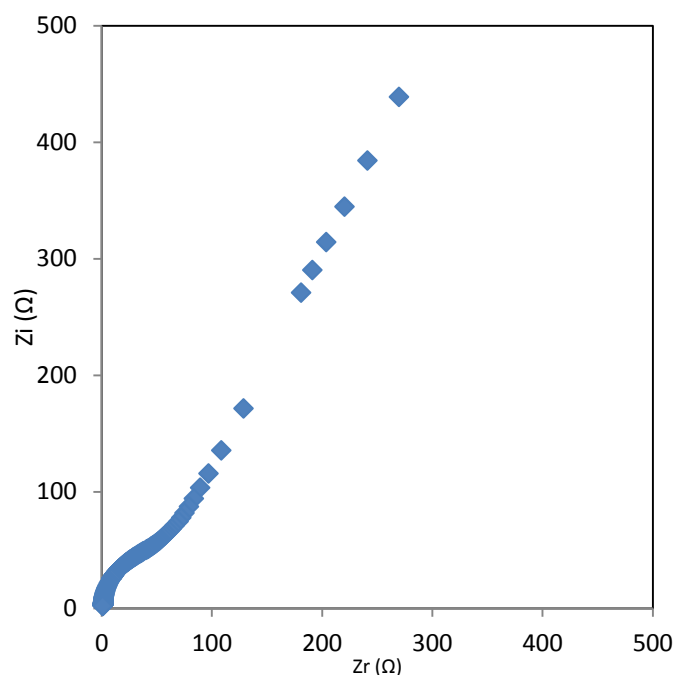


Figure 6.2(f): Impedance plot of 86 wt.%PEO-14 wt.%LiI at room temperature

Figure 6.3 represents the ionic conductivity of PEO:LiI at different wt. % of LiI at room temperature. It can be seen that the conductivity increases and reaches the highest value of $1.54 \times 10^{-4} \text{ S cm}^{-1}$ for PEO: LiI (90:10). It is well known that ionic conductivity occurs in the amorphous region of the polymer (Berthier et al., 1983, and Wright et al., 1975). This observation can therefore be attributed to the availability of conducting ions supplied by the incorporated salt and to the increasing amorphous nature of the material as a result of polymer-salt complexation (Carini et al.,1992). However, for higher salt concentrations (LiI > 10 wt %), the conductivity drops due to the ion association, which could lead to the increase in the degree of crystallinity. The trend is clearly shown in Figure 6.3 and such behaviour has been observed for many PEO based electrolyte systems (Sekhon et al., 1995).

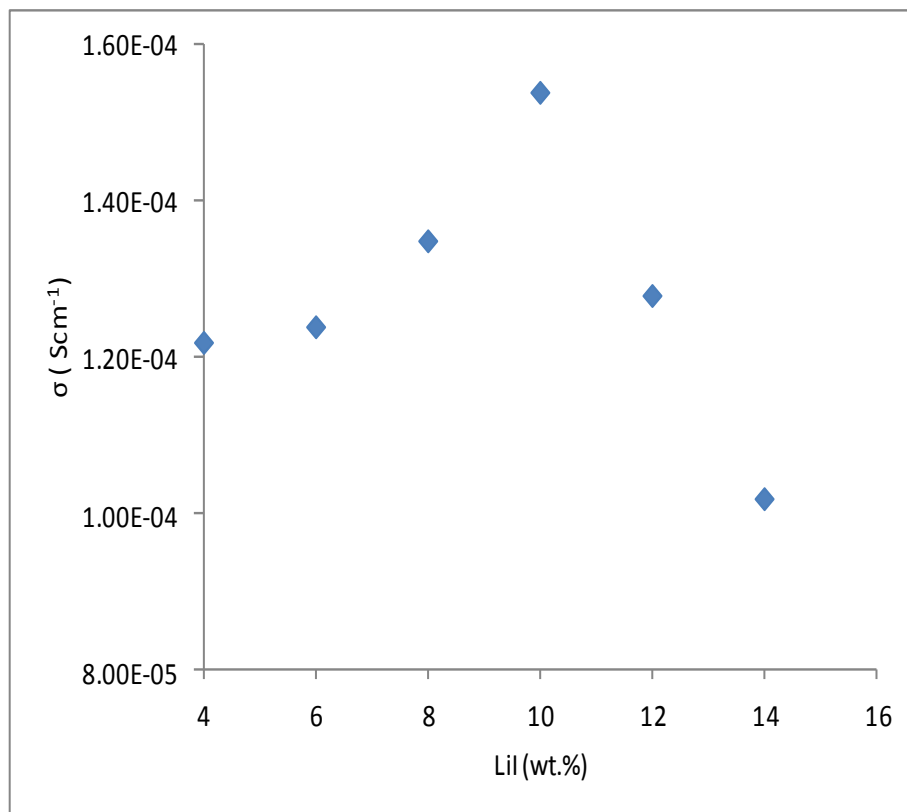


Figure 6.3: The conductivity variation of different wt. % of LiI at room temperature

To determine the conductivity at elevated temperatures, the samples were heated in steps from RT to 100⁰ C. The Cole-Cole plots of the samples at selected temperatures (temperature at 70⁰ C and 100⁰ C) are shown in Fig 6.4 (a)- (e) and Fig 6.5(a)-(e). The ionic conductivity values at elevated temperatures are shown in Table 6.1.

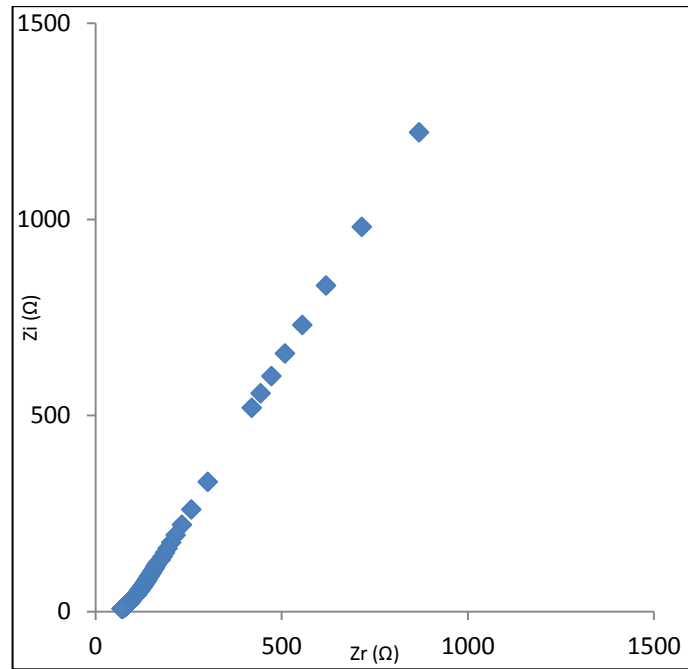


Figure 6.4(a) : Impedance plot of PEO:LiI ; 96 wt.% 4 wt.% at 70^oC temperature

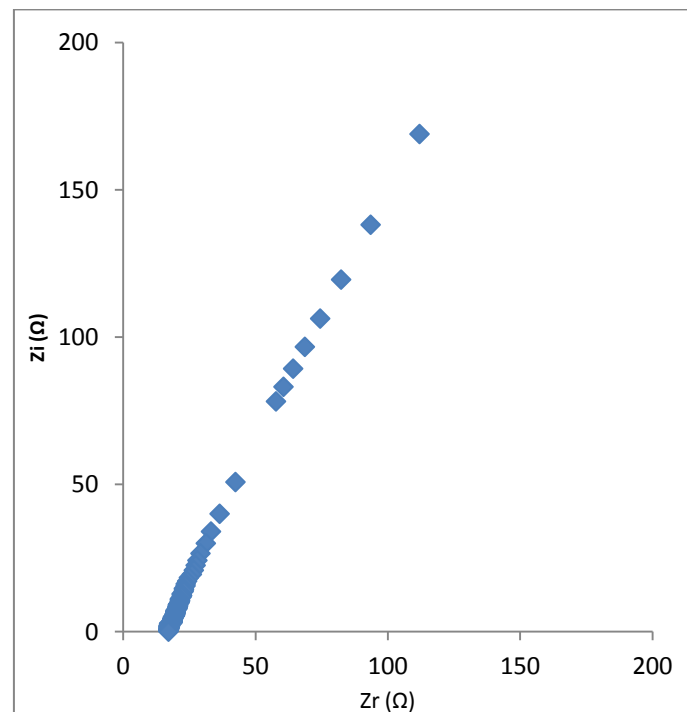


Figure 6.4(b): Impedance plot of PEO:LiI; 94 wt.%: 6 wt.% at 70^o C temperature

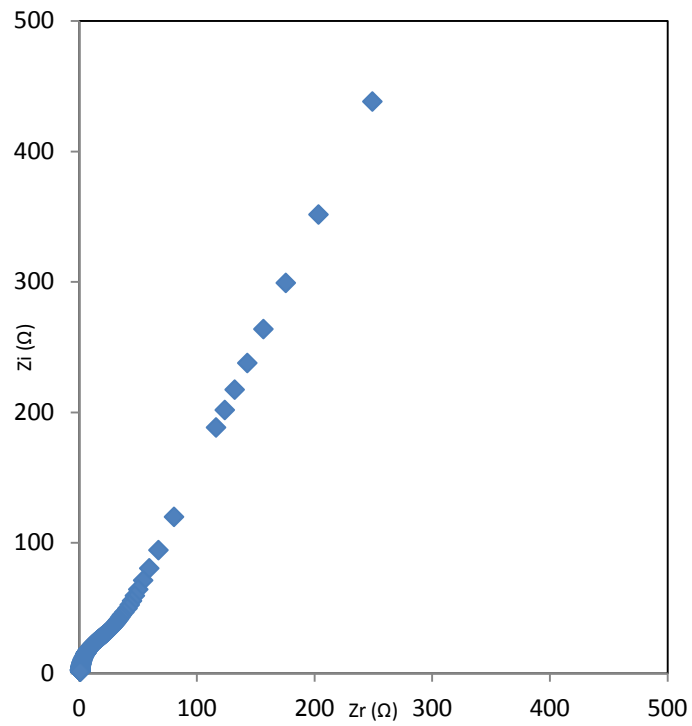


Figure 6.4(c): Impedance plot of (c) PEO:LiI, 94 wt.%: 8 wt.% at 70°C temperature

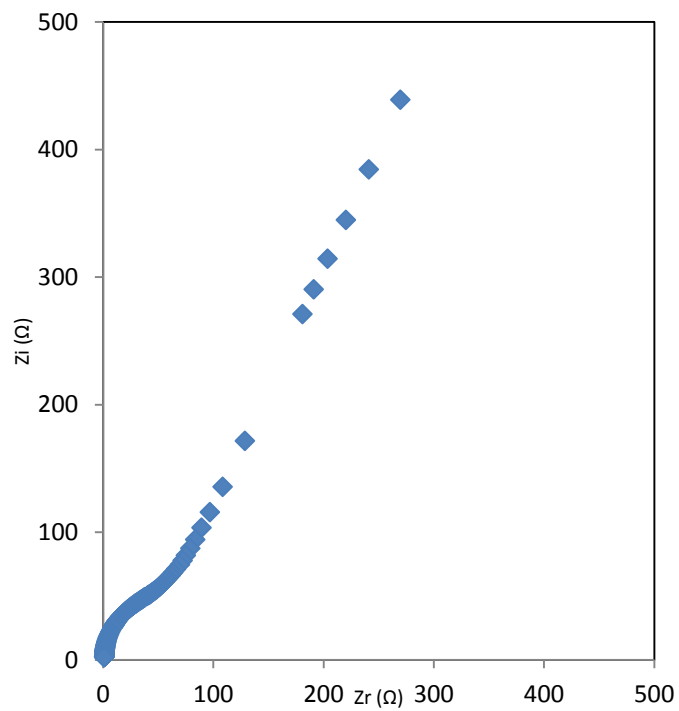


Figure 6.4(d): Impedance plot of PEO:LiI ; 92 wt.%: 10 wt.% at 70°C temperature

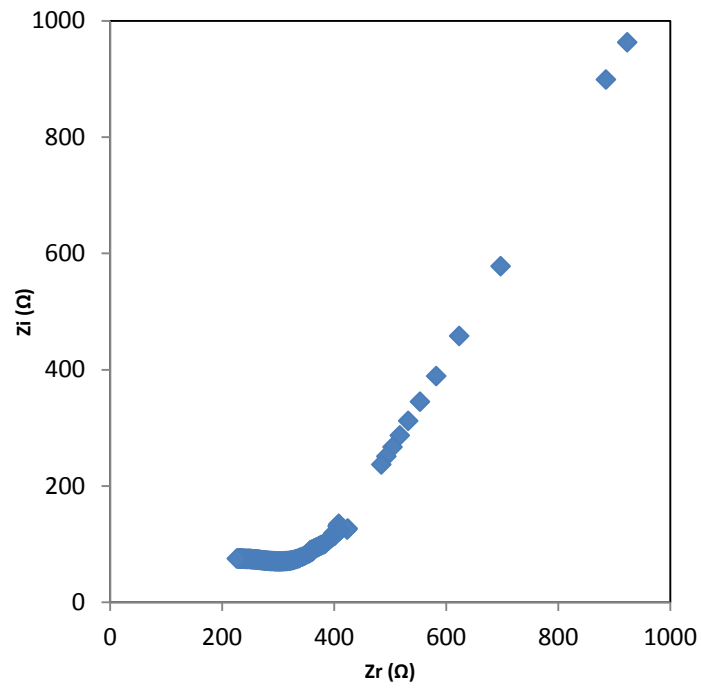


Figure 6.4(e): Impedance plot of PEO:LiI; 88 wt. %:12 wt. % at 70°C

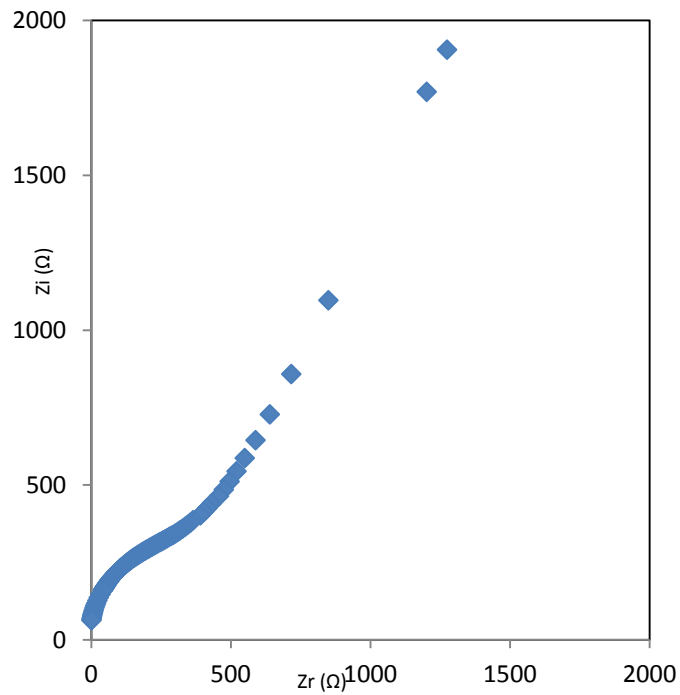


Figure 6.4(f): Impedance plot of 86 wt. %PEO-14 wt. % LiI at 70°C

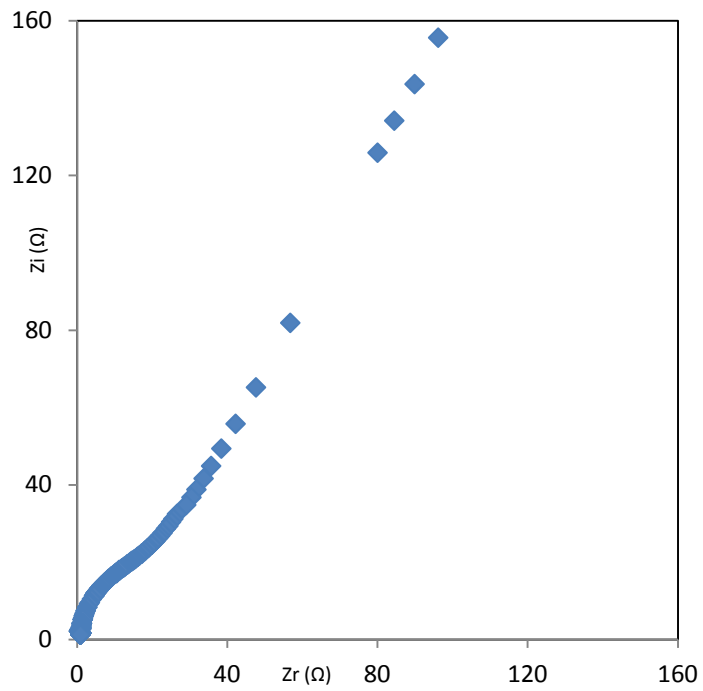


Figure 6.5(a): Impedance plot of PEO : LiI; 96 wt.:%4wt.% at 100°C temperature

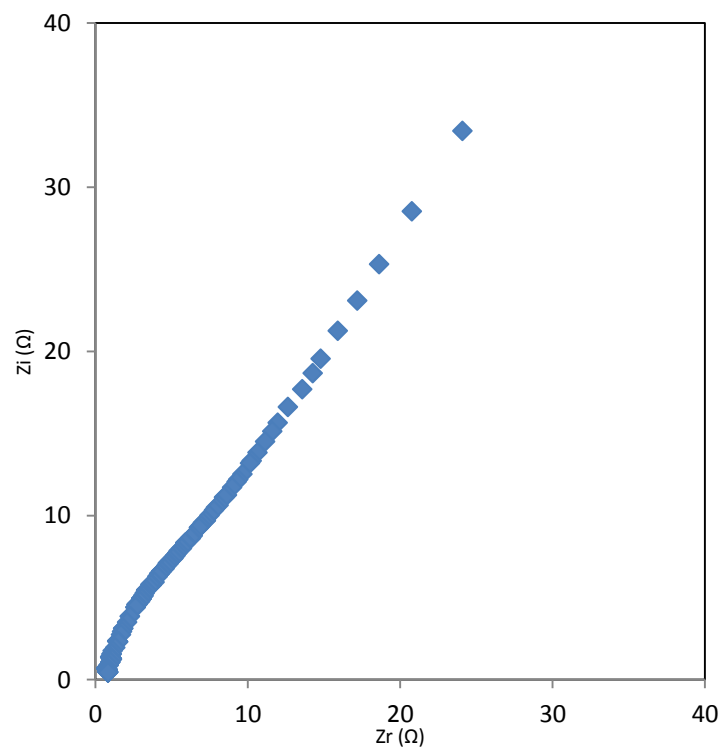


Figure 6.5(b): Impedance plot of PEO:LiI ;94wt.:%6wt.% at 100°C temperature

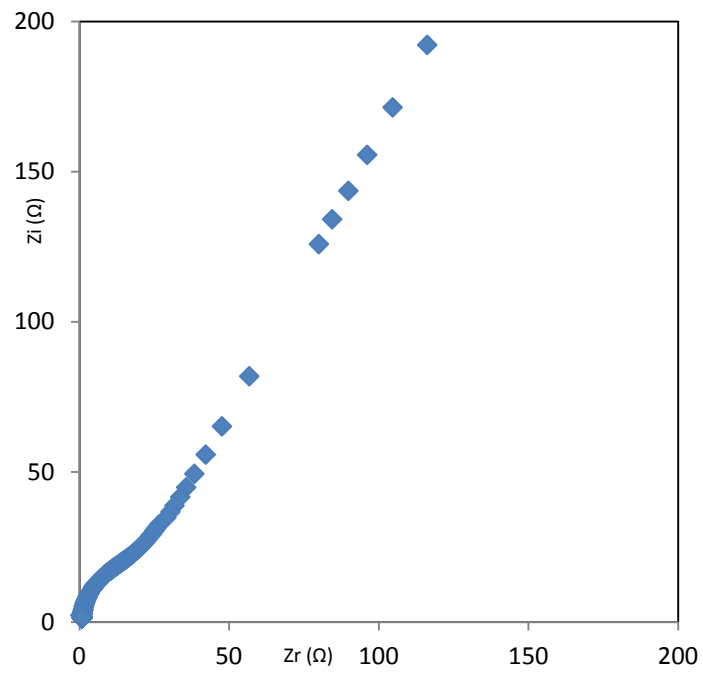


Figure 6.5(c): Impedance plot of PEO:LiI; 92:8 wt% at 100°C temperature

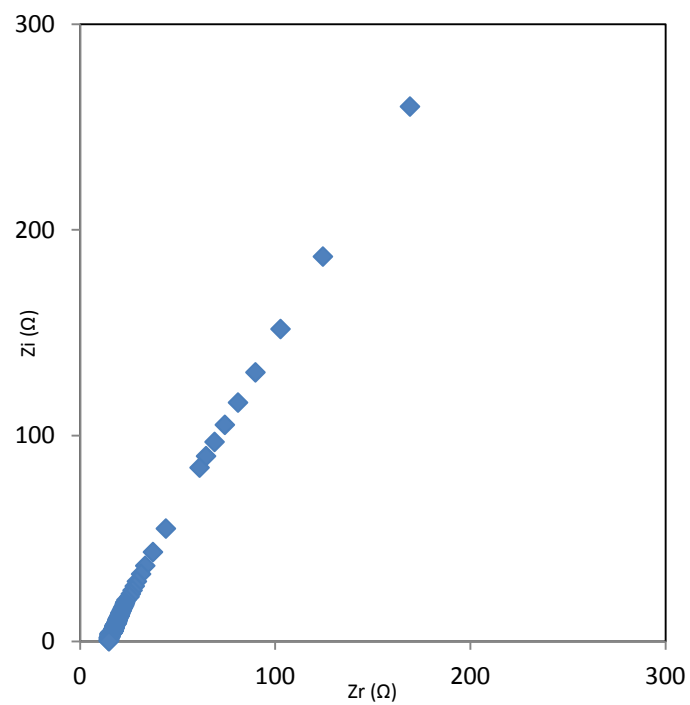


Figure 6.5(d): Impedance plot of PEO:LiI; 90:10wt.% at 100°C temperature

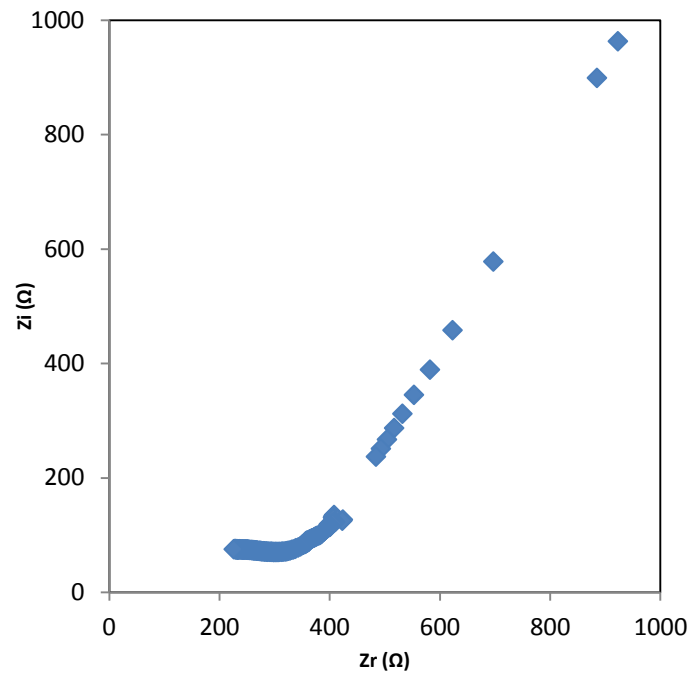


Figure 6.5(e): Impedance plot of PEO:LiI; 88:12 wt.% at 100°C temperature

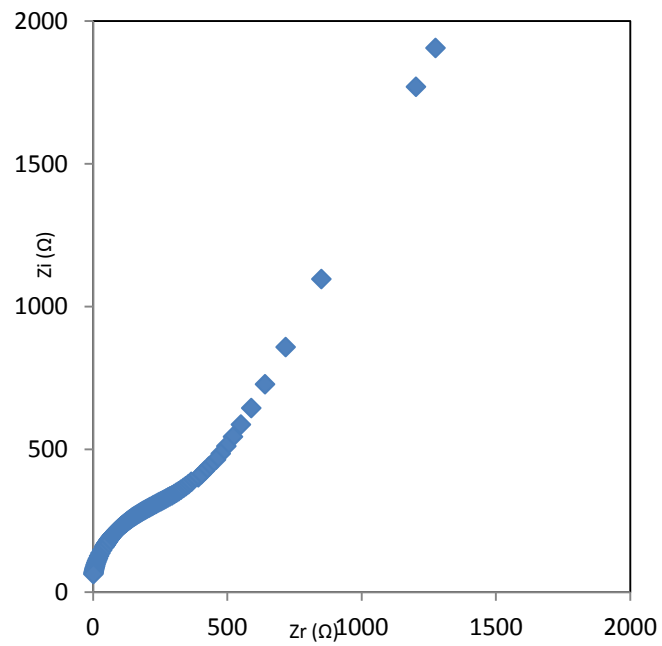


Figure 6.5(f): Impedance plot of PEO :LiI; 86:14wt.% at 100°C temperature

The result shows that at elevated temperature Li^+ ion transport readily occurs corresponds to the increase in ionic conductivity. At higher temperature Li environment is almost purely ionic.

Figure 6.6 represents the plots of $\log \sigma$ versus $1000/T$ at different LiI wt.%. It is clearly shown in Fig 6.6 the ionic conductivity of PEO-LiI samples shows a sharp increase from 60°C to 70°C . The conductivity values increased from 10^{-4} S/cm at 60°C to 10^{-3} S/cm at 70°C in all prepared samples. This is due to the well-known crystalline-amorphous transition of PEO component (Gray et.al. (1997)). The phase transition of solid PEO to liquid PEO increased the mobility of PEO, and also facilitated the fast Li-ion motion in the polymer network upon increase in temperature (Michael et.al 1997). At lower concentration of salts, as the temperature increases, the fraction of free anions reaches a maximum and the fraction of ion pairs and triplets is a minimum. For a higher concentration, the fraction of ion pairs increases with increase in temperature, and the fraction of triplets decreases [Wieczorek et al., 2005]

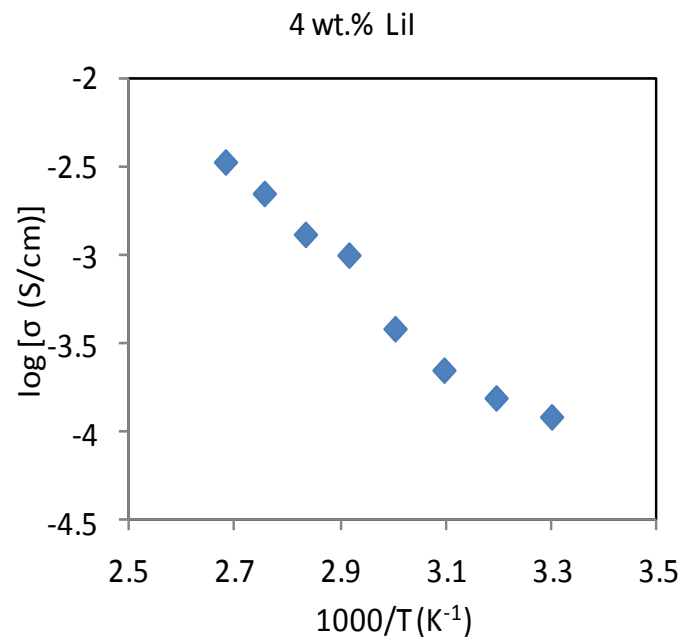


Figure 6.6 (a): Plot for $\log \sigma$ vs $1000/T$ for PEO- LiI 96wt. %:4wt. %

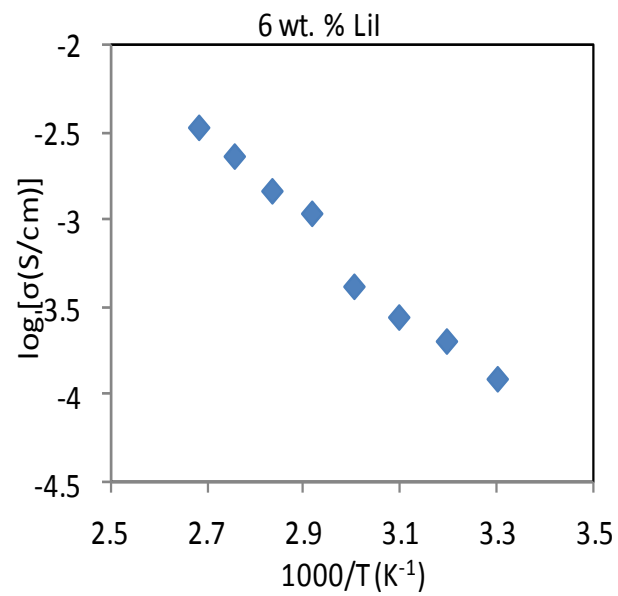


Figure 6.6(b) : Plot for $\log \sigma$ vs $1000/T$ for PEO- LiI 94wt. %:6 wt. %

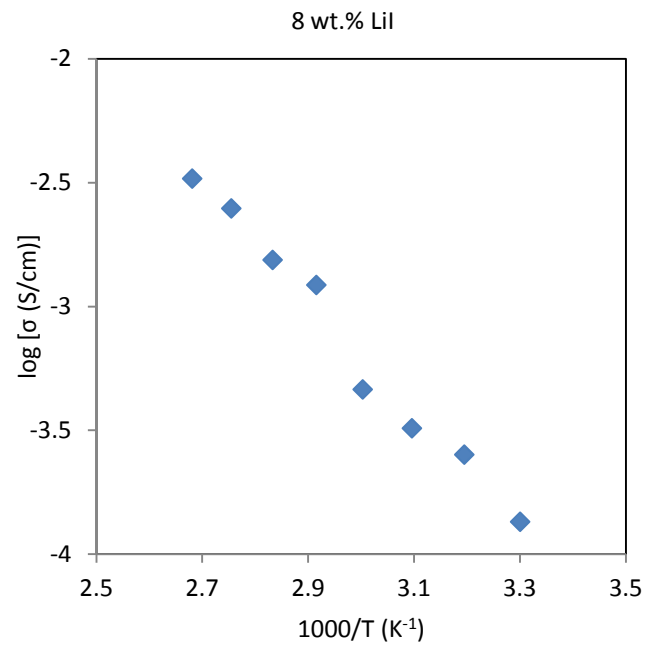


Figure 6.6(c): Plot for $\log \sigma$ vs $1000/T$ for PEO- LiI92wt.%.8wt.%

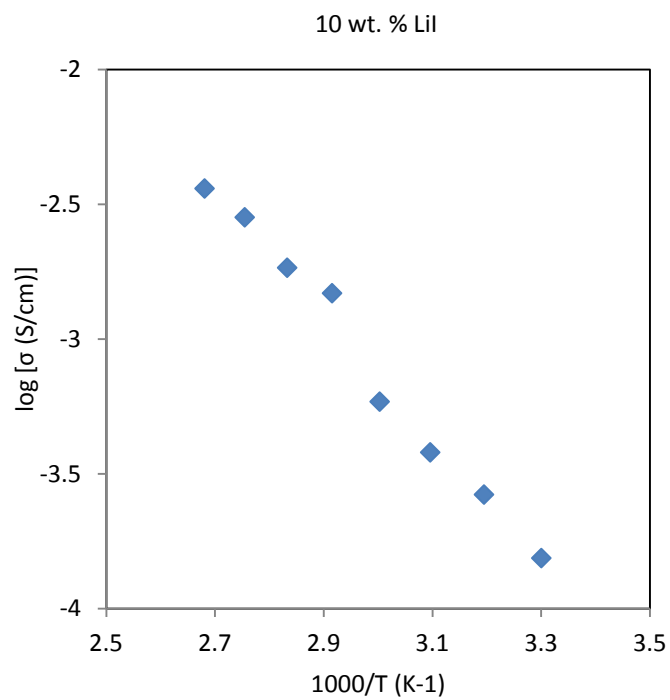


Figure 6.6(d): Plot for $\log \sigma$ vs $1000/T$ for PEO- LiI90wt.%.10wt.%

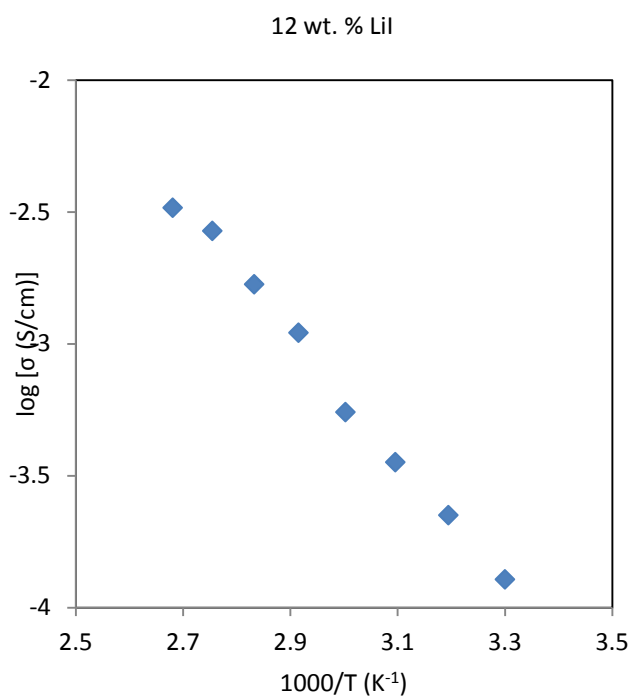


Figure 6.6(e): Plot for $\log \sigma$ vs $1000/T$ for PEO- Lil 88wt.%.12wt.%

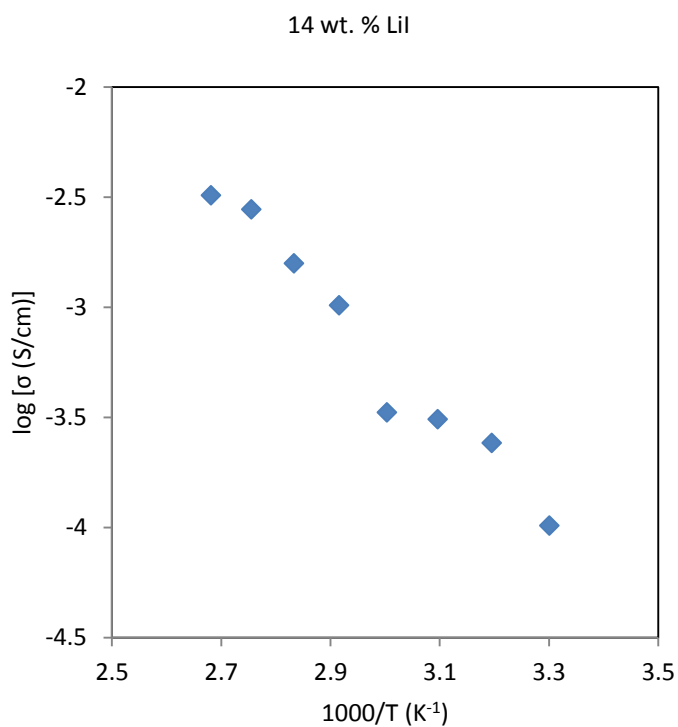


Figure 6.6(f): Plot for $\log \sigma$ vs $1000/T$ for PEO-LiI 86wt.%.14wt.%

6.3 Ionic conductivity of PEO-LiI with Inorganic filler

To improve the mechanical properties of polymer electrolytes without impairing their ionic conductivity, ceramic powder, Al_2O_3 , was added to PEO (90 wt. %): LiI(10 wt. %) system. The effect of adding the inorganic filler like Al_2O_3 is to change the fraction of available oxygen sites, which in turn results in changes to the formation of ionic aggregates (Croce et al., 1998, Scrosati et al., 1999, Scrosati et al., 2000, Appetecchi et al., 2000). The region in which the enhancement of ionic conductivity is observed corresponds to a lowering of the fraction of contact ion pairs and higher aggregates; this is due to the placement of filler molecules in the vicinity of the coordination sphere of the Li^+ cations (Wieczorek et al., 1998). Changes in conductivity result from acid–base type interactions involving polyether oxygen, filler acid or base centers and alkali metal cations. The effect of the filler is to change the formation of ion aggregates. The region in which the enhancement of ionic conductivity is observed corresponds to a decrease in the fraction of contact-ion pairs and high aggregates, this is due to the location of filler molecules in the vicinity of the co-ordination sphere of Li^+ cation. Table 6.2 shows the ionic conductivity increases by the addition of different weight percentages of Al_2O_3 to the highest conducting PEO-LiI sample. As shown in table 6.2 the ionic conductivity increases from 2.98×10^{-4} S/cm to 3.30×10^{-4} S/cm in 5 wt.% to 15 wt.% of Al_2O_3 due to interactions between the surface groups of the ceramic particles and both the PEO segments and the lithium salt anions. When the concentration of dissolved inorganic filler in the polymer matrix increases, the average separation between dissolved ions decreases which in turn increases the ion-ion interaction and the increase in ion aggregates with increasing concentration of filler (Fuoss and Kraus, 1959).

Conductivity decreases with further addition of filler due to less contact ions and ion dissociation. On the low concentration, the fraction of ion pairs decreases with increase in temperature.

Table 6.2: conductivity values for PEO-LiI-Al₂O₃ Room Temperature to 100 °C

Temp/°C	Al ₂ O ₃ 5 wt. % S/cm	Al ₂ O ₃ 10 wt. % S/cm	Al ₂ O ₃ 15 wt. % S/cm	Al ₂ O ₃ 20 wt. % S/cm	Al ₂ O ₃ 25 wt. % S/cm
RT	2.98E-04	3.24E-04	3.30E-04	3.26E-04	3.11E-04
40	3.54E-04	3.62E-04	3.87E-04	3.60E-04	3.34E-04
50	4.52E-04	4.65E-04	4.88E-04	4.66E-04	4.55E-04
60	6.21E-04	6.61E-04	7.33E-04	6.88E-04	6.75E-04
70	1.00E-03	1.05E-03	1.32E-03	1.20E-03	1.09E-03
80	2.04E-03	2.22E-03	2.48E-03	2.31E-03	2.16E-03
90	3.24E-03	3.62E-03	3.88E-03	3.51E-03	3.39E-03
100	4.24E-03	4.61E-03	5.08E-03	4.88E-03	4.66E-03

Figure: 6.7 (a) to (c) show the spectra for high ionic conductivity sample [76.5 wt.% PEO- 8.5 wt.% LiI- 15 wt.% Al₂O₃] at room temperature, 70° C and at 100° C.

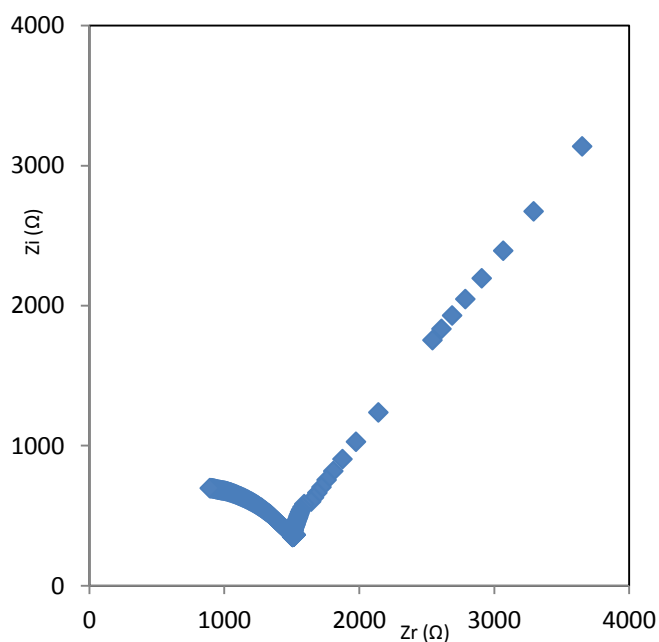


Figure 6.7 (a) : 76.5.0% PEO : 8.5% LiI : 15 %Al₂O₃ at room temperature

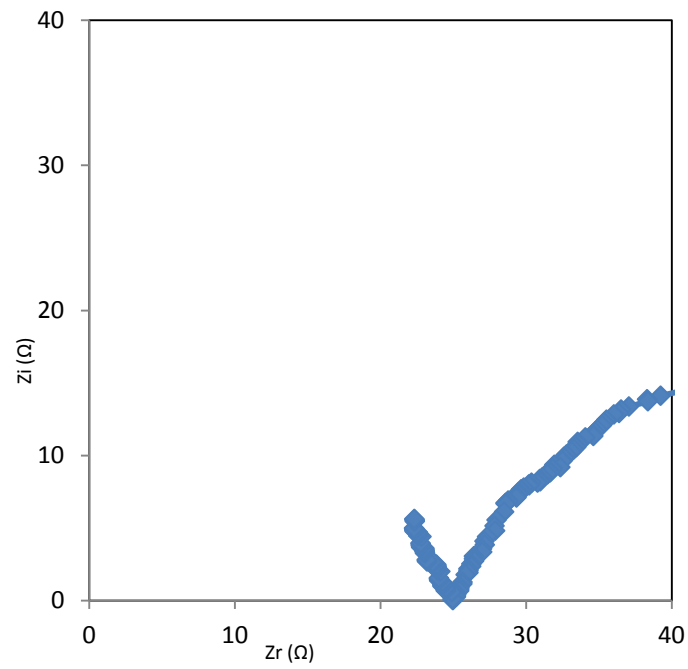


Figure 6.7 (b): 76.5% PEO : 8.5 %LiI : 15 %Al₂O₃ at 70^o C.

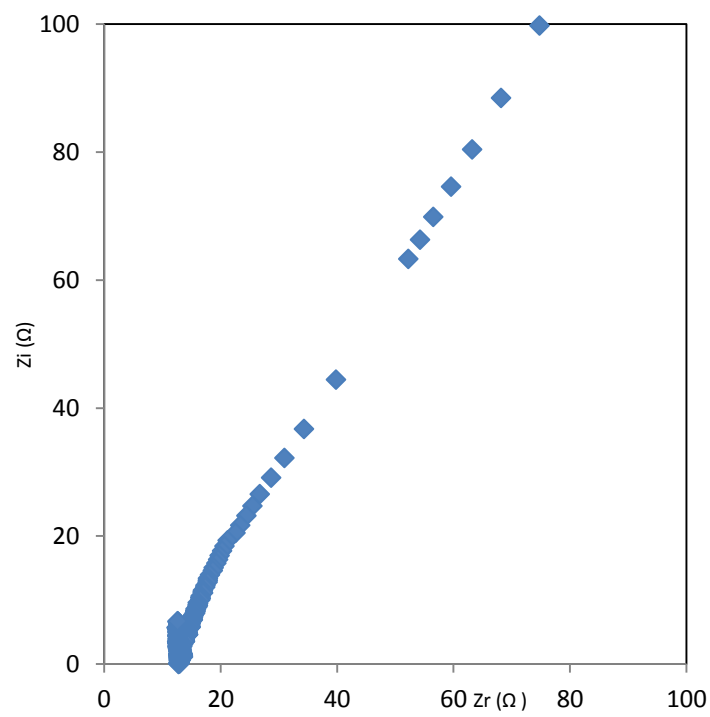


Figure 6.7 (c): 76.5 %PEO : 8.5 %LiI : 15% Al₂O₃ at 100^o C

Figure 6.8 shows the temperature dependent conductivity. The conductivity increases from room temperature to 100°C. The behaviour of the conductivity as a function of the temperature can be fitted by Arrhenius law. The results show that the Al₂O₃ showing the same trend as in PEO-LiI values. At 60°C there is an increase in ionic conductivity shows a maximum value of 7.33×10^{-4} S/cm at 15 wt. % of Al₂O₃, is due to the melting temperature of PEO, which is similar to PEO-LiI complexes.

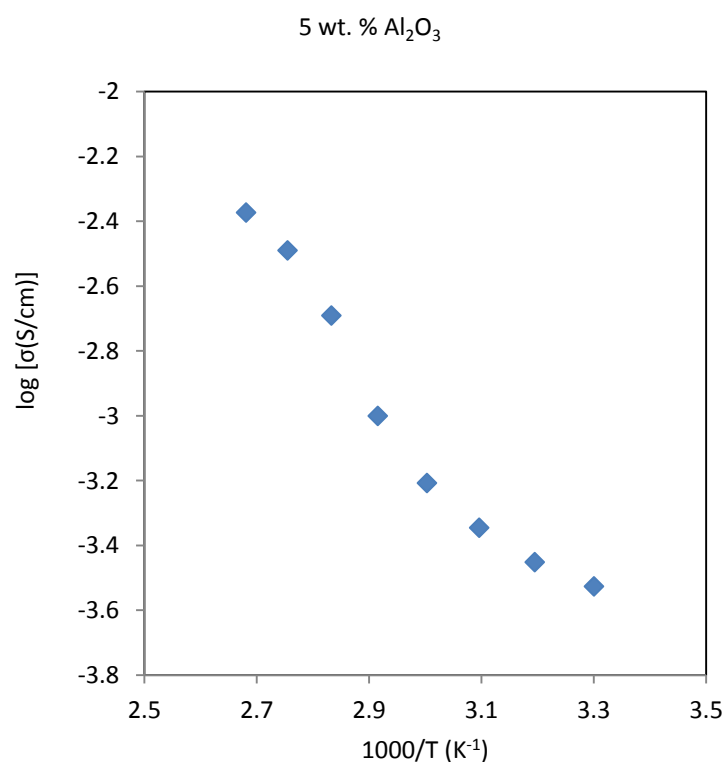


Figure 6.8(a): Plot of $\log \sigma$ vs $1000/T$ 85.5% PEO: 9.5% LiI : 5 % Al₂O₃

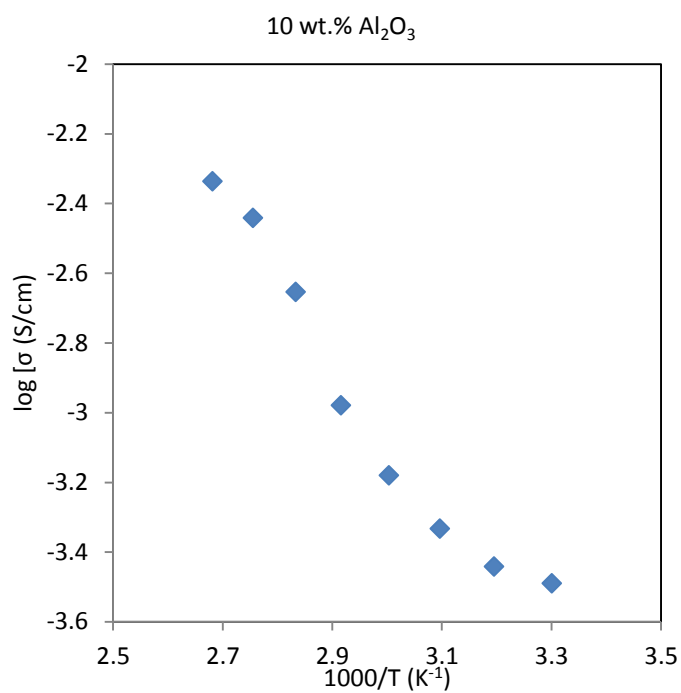


Figure 6.8(b): Plot of $\log \sigma$ vs $1000/T$ 81.0% PEO: 9 % LiI: 10 % Al₂O₃

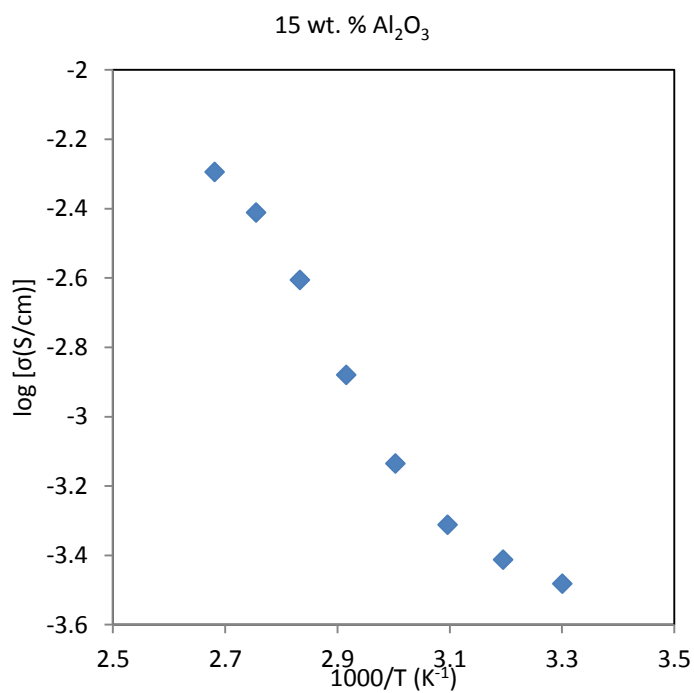


Figure 6.8(c): Plot of $\log \sigma$ vs $1000/T$ 76.5 %PEO : 8.5 % LiI : 15% Al₂O₃

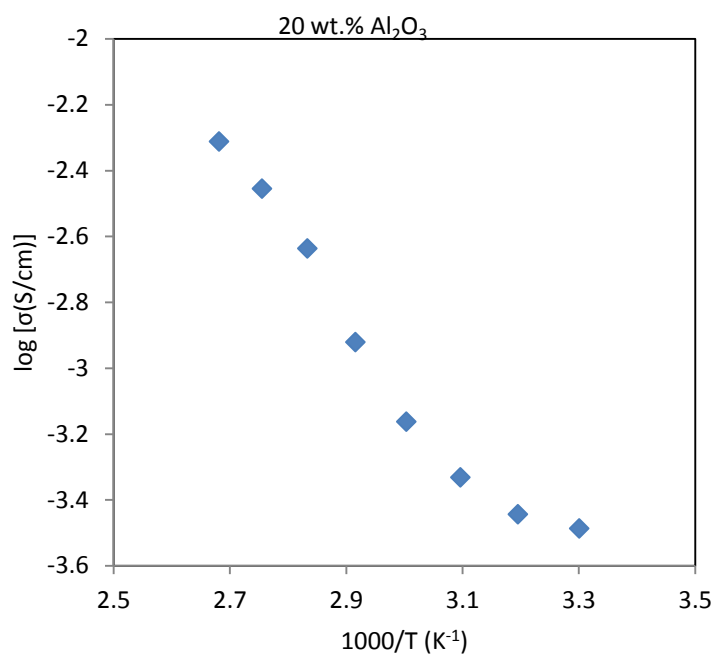


Figure 6.8(d): Plot of $\log \sigma$ vs $1000/T$ 72.0%PEO:8%LiI:20%Al₂O₃

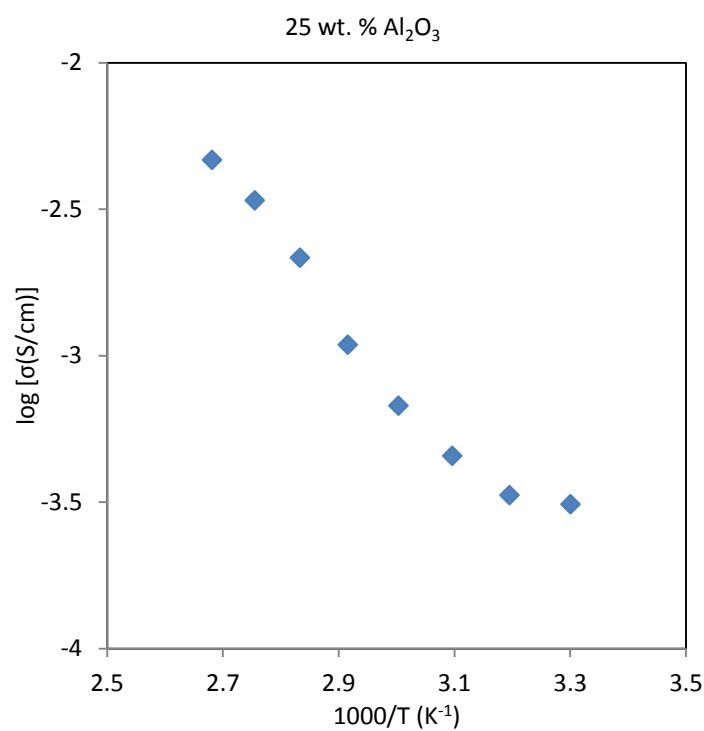


Figure 6.8(e): Plot of $\log \sigma$ vs $1000/T$ PEO-LiI-Al₂O₃, 67.5% PEO : 7.5% LiI : 25% Al₂O₃

These results shown in Figure 6.8 are in agreement with those described in the literature (Choi et.al, 1996). The increase in conductivity at 60⁰ C can be due to the PEO crystallinity change with the formation of space charge in the filler particles. The doping effect on ionic conductivity of inorganic ionic conductor in Li salts were investigated by many authors since the first work of Liang (Liang 1973).

6.4 Ionic conductivity of PEO-LiI with Organic Macromolecules

To improve the electrical properties of solid polymer electrolytes, the work has to focus on the enhancement of the ionic conductivity value. One of the approaches is to add to the polymer electrolyte while in solution a neutral macrocyclic molecule (supramolecular additive) that is capable of forming a complex with the anion of the salt via the interacting centres of the macrocyclic compound. The increase of the t_{Li^+} value after supramolecular polymer electrolyte modification was confirmed experimentally by Wiczorek and co-workers for calix4 and calix6 arene derivatives (Wiczorek et al., 2004). But unfortunately by adding macrocyclic molecules like calix arenes led to a decrease in ionic conductivity by one order. This can be due to the immobilization of anion of the salt by the hydroxyl group of calix arenes. Thus, the lithium cation conductivity was lowered in this case.

To immobilize the anion we add anion receptor calix arenes to the high conducting PEO-LiI sample. As can be seen from Table 6.3 and Table 6.4 conductivity of polymer electrolytes containing calix arenes is lower than the polymer electrolytes with LiI salt.

Table 6.3: the conductivity values for PE:LiI: Calix 4 (1wt.% to5 wt.%) RT to 100 °C

Temp/°C	Calix4 1wt.% (S/cm)	Calix4 2wt.% (S/cm)	Calix4 3wt.% (S/cm)	Calix4 4wt.% (S/cm)	Calix 4 5wt.% (S/cm)
RT	3.04E-05	3.23E-05	4.56E-05	4.09E-05	3.43E-05
40	3.58E-05	4.50E-05	5.00E-05	4.59E-05	4.25E-05
50	5.22E-05	5.41E-05	5.82E-05	5.60E-05	5.43E-05
60	7.72E-05	7.85E-05	8.50E-05	8.00E-05	7.83E-05
70	1.13E-04	1.32E-04	1.49E-04	1.32E-04	1.13E-04
80	2.24E-04	2.31E-04	2.62E-04	2.48E-04	3.26E-04
90	3.50E-04	3.73E-04	5.00E-04	4.67E-04	4.48E-04
100	4.25E-04	4.40E-04	5.20E-04	5.00E-04	5.13E-04

Table 6.4: the conductivity values for PEO:LiI :Calix 6[1wt% to5wt.%) RT to 100 °C

Temp/°C	Calix6 1wt.% (S/cm)	Calix6 2wt.% (S/cm)	Calix6 3wt.% (S/cm)	Calix6 4wt.% (S/cm)	Calix6 5wt.% (S/cm)
RT	2.63E-05	2.79E-05	2.87E-05	2.76E-05	2.72E-05
40	3.29E-05	3.81E-05	4.22E-05	4.08E-05	3.75E-05
50	4.24E-05	4.57E-05	4.80E-05	4.38E-05	4.01E-05
60	6.63E-05	6.88E-05	7.04E-05	6.91E-05	6.59E-05
70	1.08E-04	1.22E-04	1.46E-04	1.33E-04	1.19E-04
80	2.02E-04	2.26E-04	2.48E-04	2.20E-04	2.12E-04
90	3.89E-04	4.22E-04	4.80E-04	4.19E-04	3.87E-04
100	4.82E-04	5.26E-04	5.54E-04	4.89E-04	4.58E-04

The decrease in overall ionic conductivity values of PEO-LiI-calix4 and PEO-LiI-calix6 could be attributed first of all to the decrease of the charge carriers concentration due to anion trapping and additionally, to the high affinity of the carbonyl oxygen atom from the calix arenes to the Li⁺ cation.

At higher temperatures, the conductivity of calix arenes containing samples is similar to the system which does not contain the anion receptor, that is at higher temperature the ionic conductivity increases is due to the increase in ion pairs. The fraction of these charge carriers are charge triplets (Kalita et al., (2005)).

Figure 6.9 (a) to (c) represents the impedance spectra of PEO-LiI-calix 4 system [87.3 wt% PEO : 9.7 wt% LiI :3 wt.% Calix 4] at room temperature, 70⁰ C and 100⁰ C are shown.

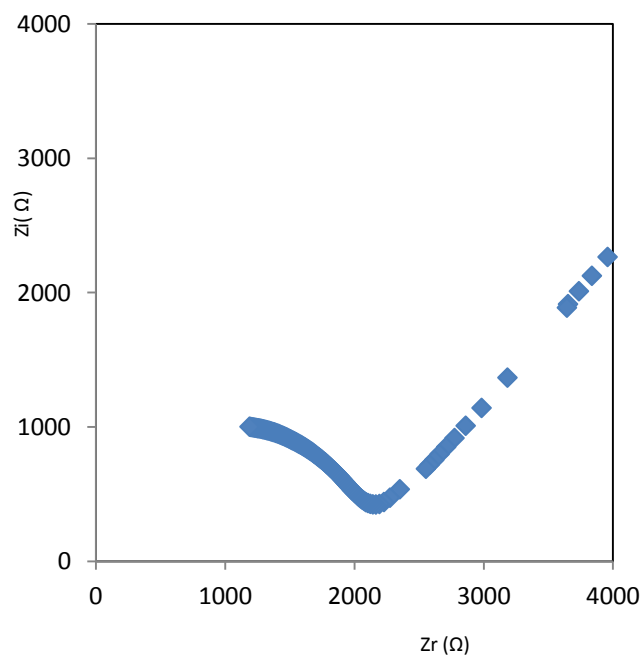


Fig 6.9 (a): 87.3% PEO : 9.7% LiI :3% Calix4at room temperature

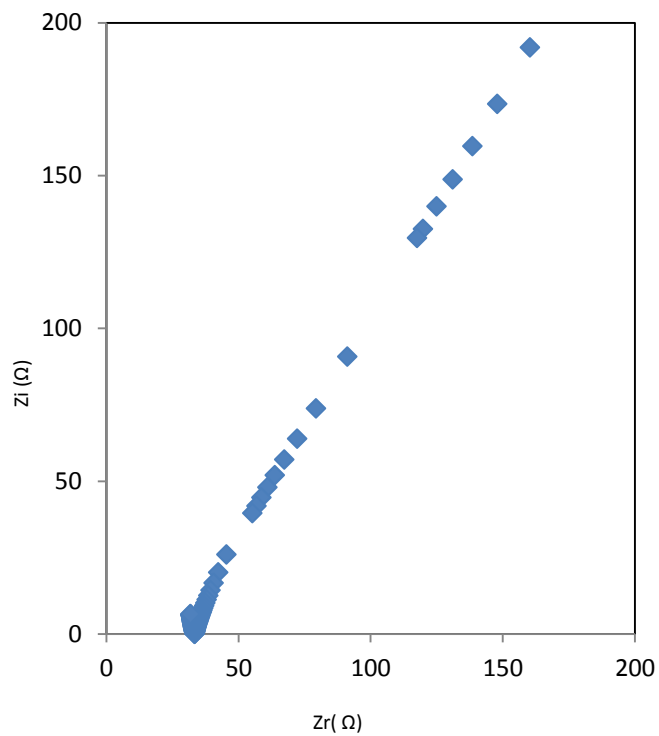


Figure 6.9 (b) : 87.3% PEO : 9.7% LiI :3% Calix 4at 70°C

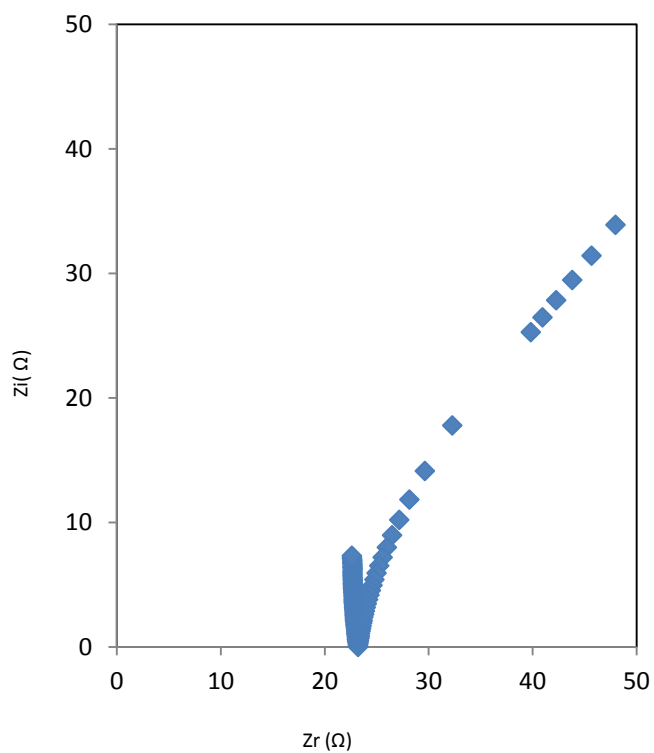


Figure 6.9 (c) : 87.3% PEO : 9.7% LiI :3% Calix 4 at 100° C.

Figure 6.10 (a) to (c) represents the impedance spectra of PEO-LiI-calix 6 [87.3 wt% PEO : 9.7 wt% LiI :3 wt.% Calix 6] at room temperature, 70⁰ C and 100⁰ C are shown .

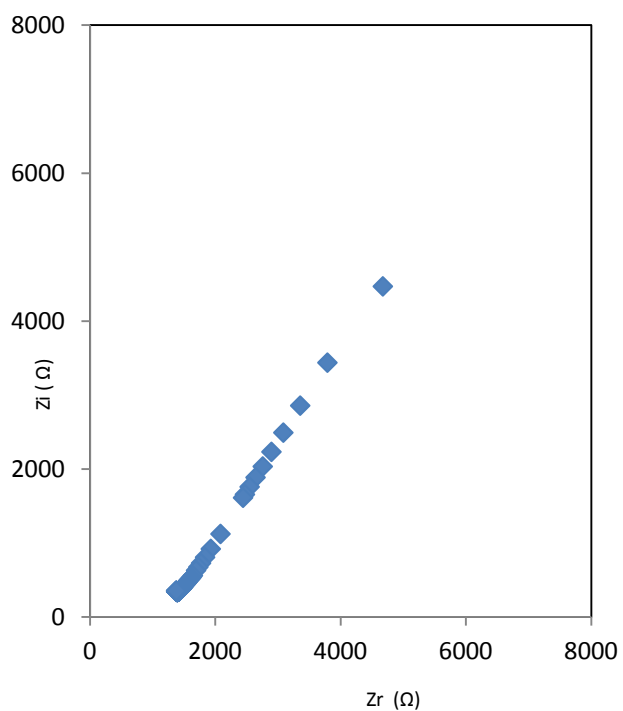


Figure 6.10 (a) : 87.3% PEO : 9.7% LiI :3% Calix6 at room temperature

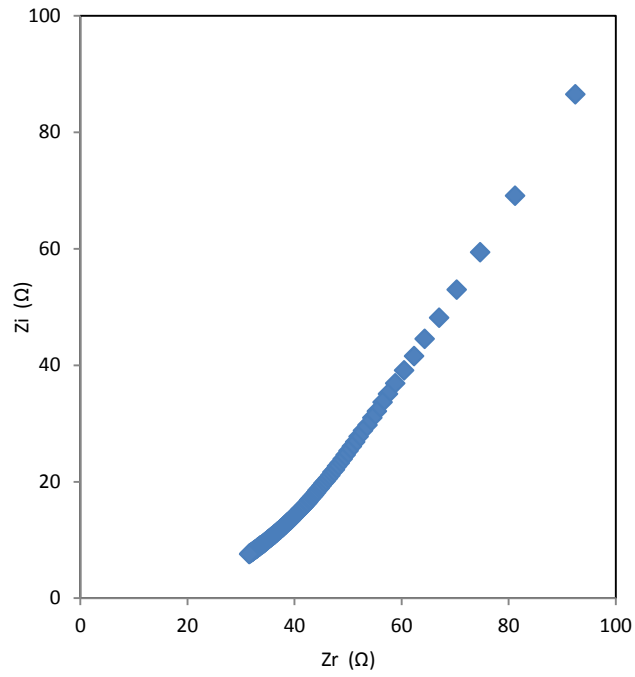


Figure 6.10(b): 87.3% PEO : 9.7% LiI : 3% Calix 6 at 70^o C.

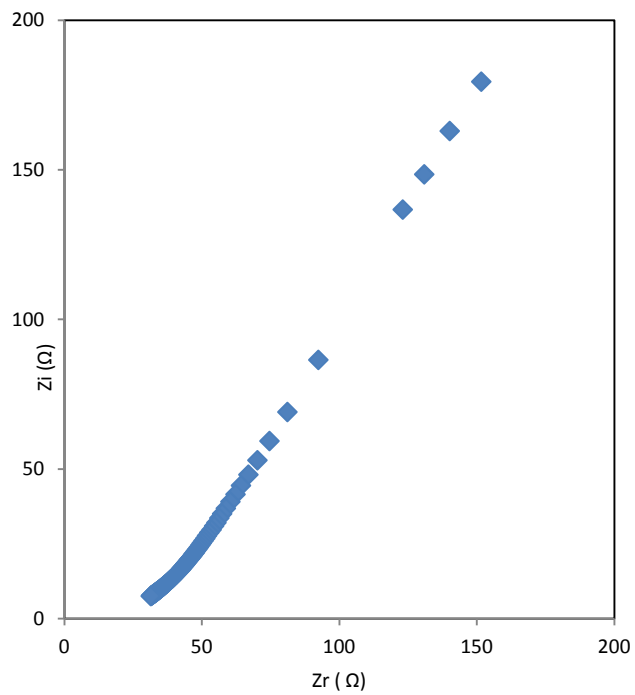


Figure 6.10 (c): 87.3% PEO : 9.7% LiI : 3% Calix 6 at 100^o C

There is variations in ionic conductivity of calix4 and calix6 differs when weight percentage of the molecule increases. The calix at 3 wt. % (87.3% PEO : 9.7% LiI :3% Calix) shows the highest ionic conductivity. The highest conductivity is due to the complexation of calix content with the polymer salt systems which we have discussed in our earlier chapters. The highest conductivity value for 3 wt. % of both calix4 and calix6 arenes might be due to the stronger complexation between the receptor calix molecules with the ethylene oxide chains and the ionic interactions or through ionic aggregates (Kalita et al., 2007).

Figure 6.11 and 6.12 show the temperature dependence of the ionic conductivity for the polymer-salt with Calix4 and polymer-salt with Calix6 systems respectively. From the plot it has been observed that ionic conductivity increases with increase in temperature as well as increase in concentration. The reduction of ionic conductivity on addition of Calix arenes below the melting temperature of PEO may be attributed to the removal of the mobile charge carriers (Anions) by calix arenes. According to Fuoss-Kraus calculations, in the range where a rise in conductivity is noted, the contribution of free ions decreases due to generation of positively charged triplets (Fuoss et al., 1959 and Zalewska et al.,2001).

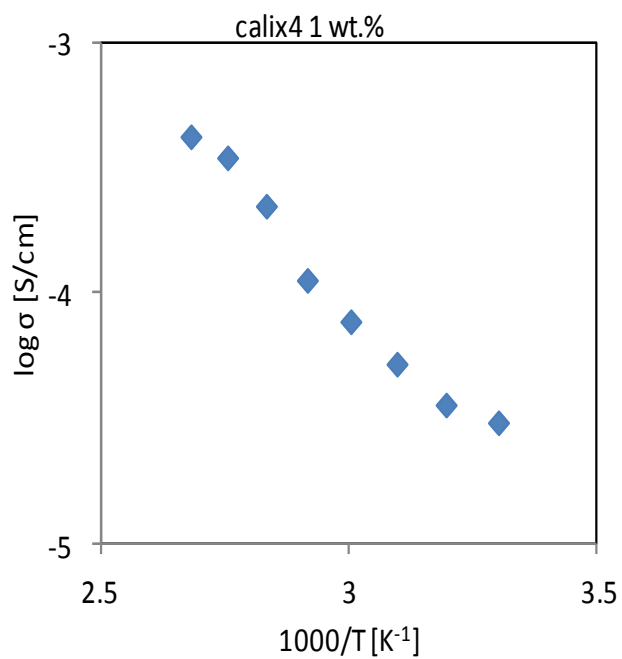


Figure 6.11 (a): 89.1% PEO : 9.9% LiI : 1% Calix 4

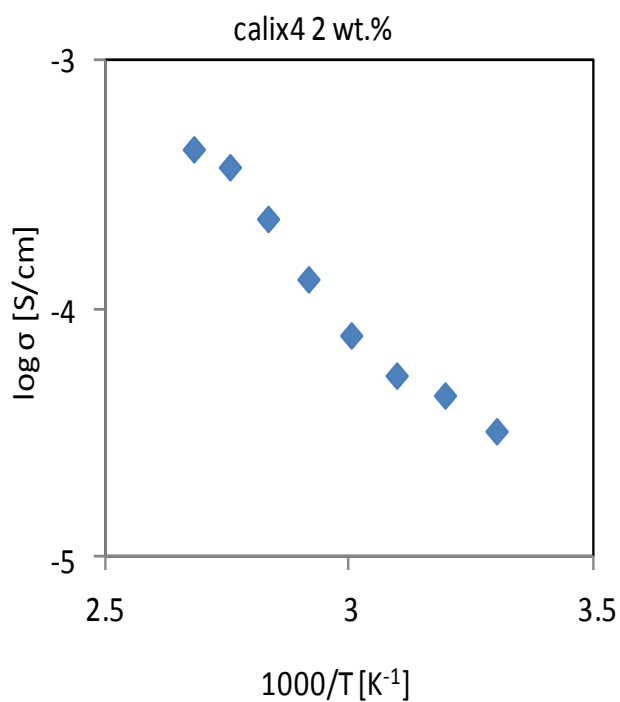


Figure 6.11 (b): 88.2% PEO : 9.8% LiI : 2% Calix4

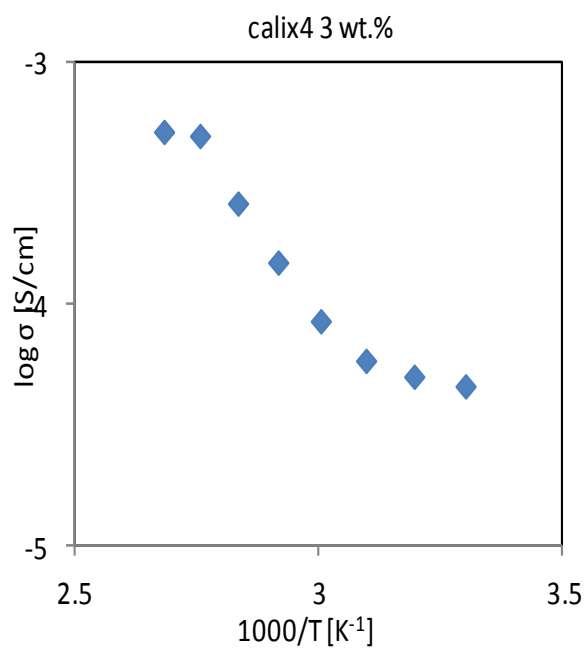


Figure 6.11(c): 87.3% PEO : 9.7% LiI :3% Calix4

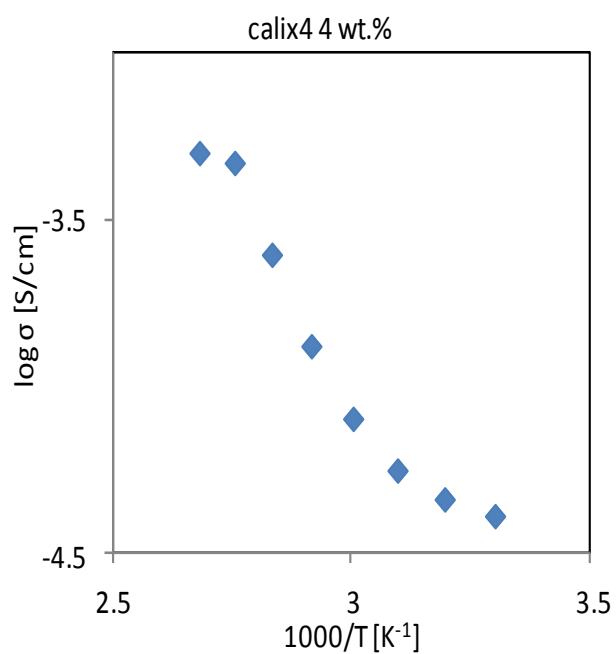


Figure 6.11 (d): 86.4% PEO : 9.6% LiI : 4% Calix 4

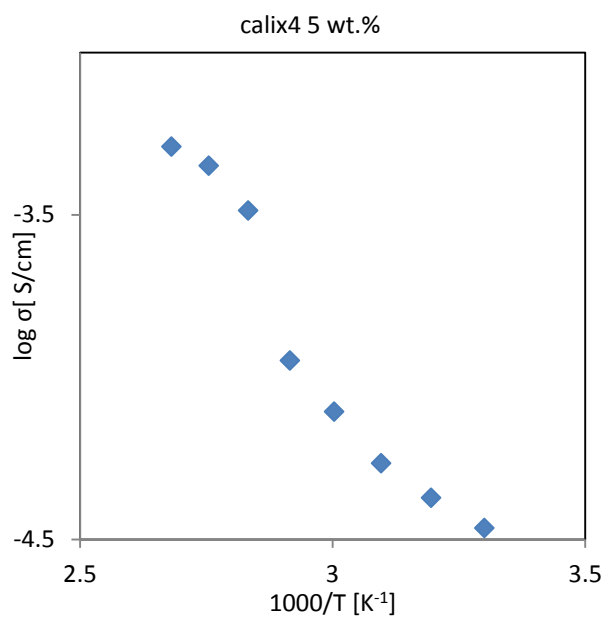


Figure 6.11(e): 85.5% PEO : 9.5% LiI : 5% Calix4

Figure 6.12 shows the temperature dependence of the ionic conductivity for the polymer-salt with Calix6 system.

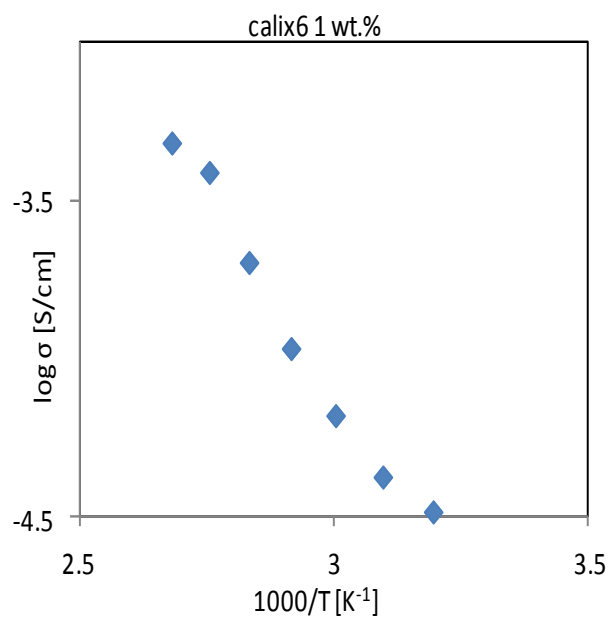


Figure 6.11(a): 89.1% PEO : 9.9% LiI : 1% Calix 6

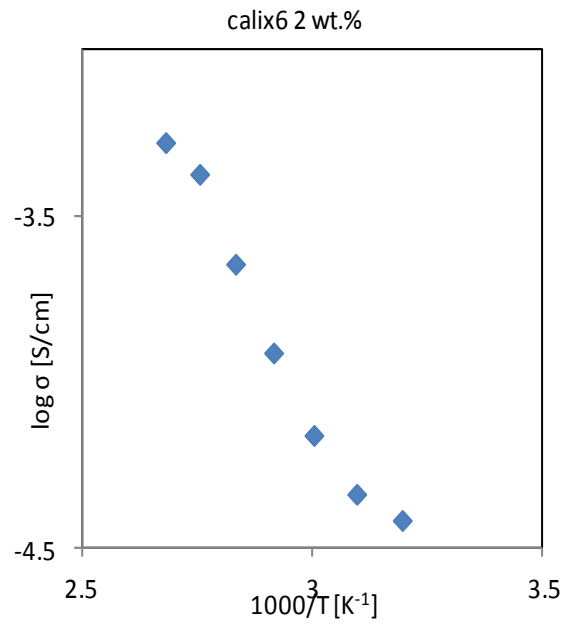


Figure 6.11(c): 88.2% PEO: 9.8% LiI: 2% Calix6

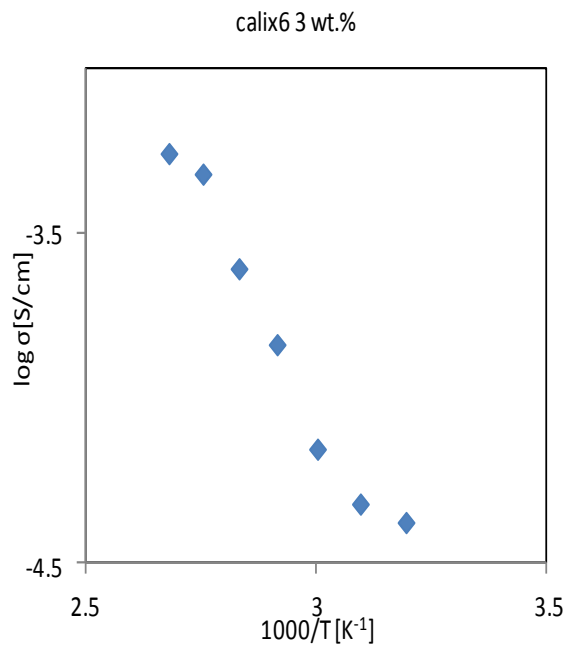


Figure 6.11 (c): 87.3% PEO : 9.7% LiI : 3% Calix6

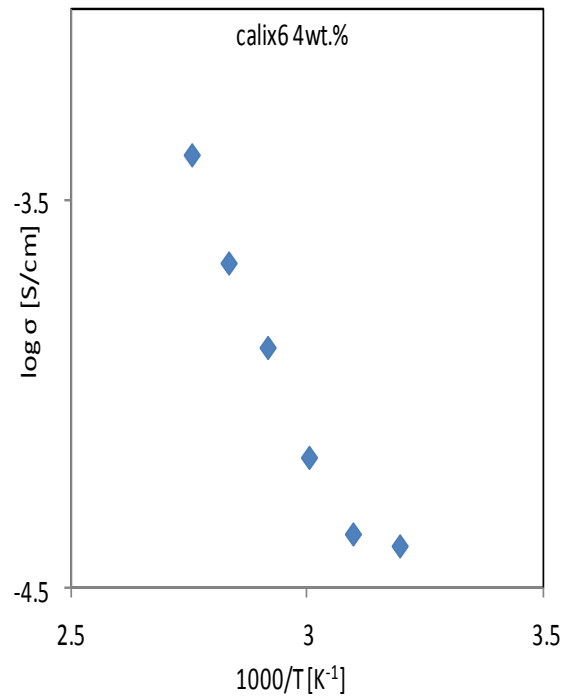


Figure 6.11(d): 86.4% PEO : 9.6% LiI : 4% calix6

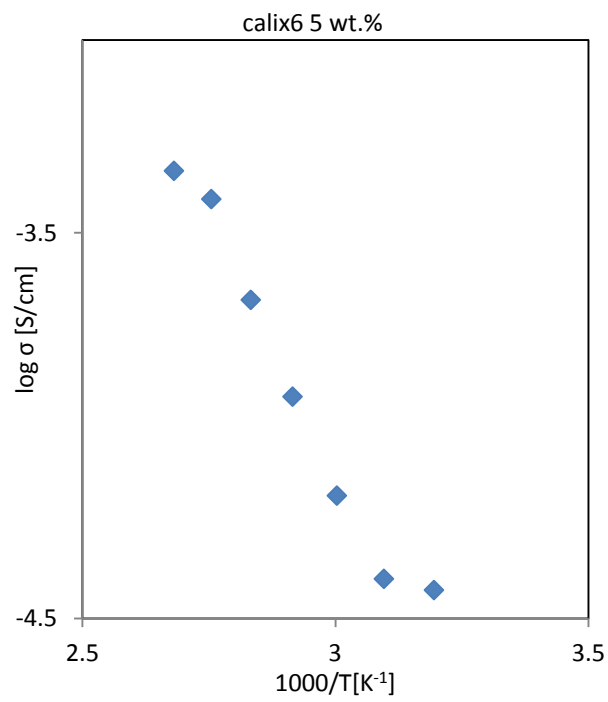


Figure 6.11(e): 85.5% PEO : 9.5% LiI : 5% Calix6

It has been found that the polymer electrolyte system 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 4 and 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix6 exhibit a sharp increase in ionic conductivity at 60°C. It is found that that when temperature increases conductivity increases this is due to the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours inter-chain hopping and intra-chain ion movements, accordingly the conductivity becomes high (Mishra et al., 1998).

In diluted samples the conductivity is almost the same for all series. The decrease in conductivity can be due to the anion-receptor complex formation (Johansson and Jacobsson 2005).

Figure 6.11 summarises the variations of ionic conductivity by the addition of LiI, Al₂O₃, Calix4 arene and Calix6 arene to PEO.

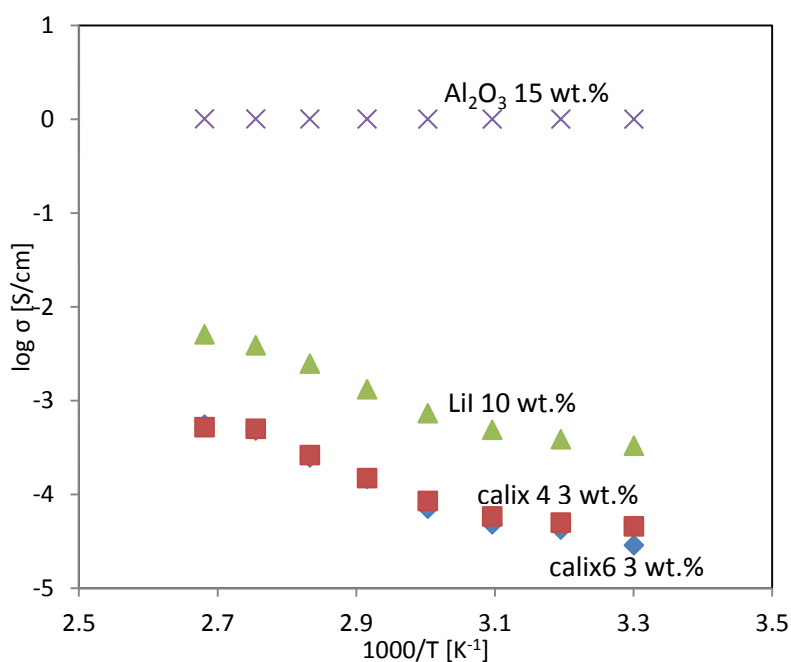


Figure 6.11: variation in ionic conductivity in PEO

6.5 Summary

Due to the low impact on environment, relatively low cost and no risk of electrolyte leakage as well as as good stability Poly(ethylene oxide) based polymer electrolyte are well established. To study the applications, add Poly(ethylene oxide) with with inorganic salt like LiI. Poly(ethylene oxide) - LiI with ceramic fillers. Both system shows an ionic conductivity of 10^{-3} S/cm at 60°C . Both anions and cations are generally mobile in most of the polymer electrolytes, whereas restricting the mobility of the anions without adversely affecting the lithium cation is desirable for battery applications. For this macromolecule like calix arene is added to the poly(ethylene oxide) – LiI system. By adding macromolecule the decrease in conductivity of the membrane is due to the decrease in charge carriers concentration due to anion trapping . The results obtained for conductivity show a clear compatibility for the FTIR and XRD data's that we have been discussing in the earlier chapters.