CHAPTER 4

FOURIER-TRANSFORM INFRA RED SPECTROSCOPY STUDIES ON PEO - LiI ELECTROLYTES AND ITS COMPOSITES

4.1 Introduction

Progress in portable consumer electronic devices has seen an urgent need for the development of new flexible batteries with high specific energy. Since the 1970's, great attention has been devoted to study solid polymeric electrolytes. Interest in this area is the result of pioneering measurements on ionic conductivity in the polymer-salt complexes reported by Wright and co-workers and the realization of their technical importance by Armand (Gray, 1991 and Daiso Co.Ltd. Elastomers Technical Report). The continuous interest on polymeric electrolytes is related to their use in different electrochemical devices. Following Wright's work, poly (ethylene oxide) or PEO salt systems have become an important new class of electrolytes for use in high specific energy rechargeable lithium batteries. PEO is the most extensively used polymer host since it exhibits good electrochemical stability and can dissolve high salt concentrations to form solid polymeric electrolytes with high ionic conductivity (Watanabe et al. (1987), Kim et al. (2003) and Watanabe et al. (1983)). However, PEO based polymer electrolytes show reasonable ionic conductivity only above its melting temperature. Ion conduction only occurs within the amorphous region of the polymeric electrolyte. A lot of efforts have been put to suppress the crystallinity of the PEO polymer host and increase its amorphous nature to enhance the ionic conductivity.

In this chapter, the technique of FTIR is used to probe the interactions between the different constituents in the PEO polymer electrolyte systems. Therefore, the occurrence of complexation can be confirmed. FTIR spectroscopy was used by Papke et al.

(Kennelly 1983) and many workers (Jonscher 1978 and Shastry and Rao 1991) to provide information on cation-oxygen interactions in a wide range of PEO-metal salt systems. FTIR spectroscopic studies were also carried out to investigate the formation of ion pairs/clusters in the polymeric materials investigated. Apart from that, FTIR spectroscopy is also used to determine the types of PEO phases, amorphous or crystalline, present in the polymer films and to establish interactions between the polymer, salt and filler. Such interactions may induce changes in the location of the vibrational modes in the spectrum of the material. The structure of PEO is shown as in Figure 4.1
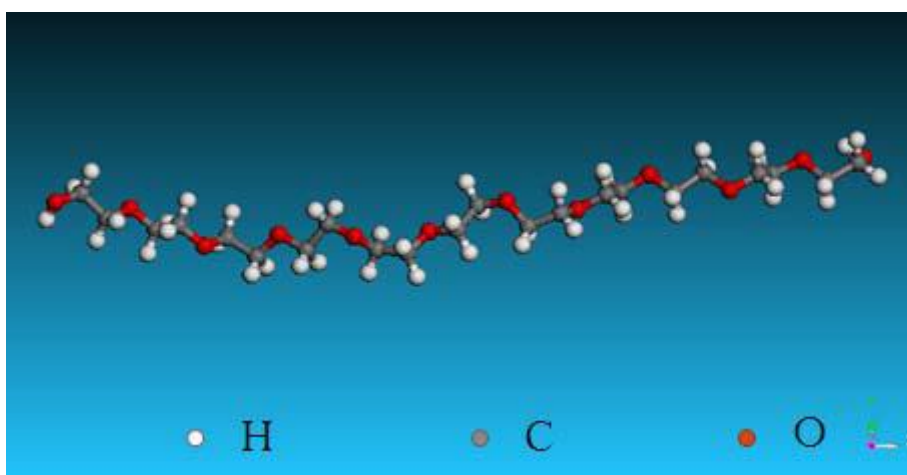

Figure 4.1: A segment of a polyethylene oxide chain

From Figure 4.1, it is expected that Fourier transform infrared spectrum should show bands due to CH_2, C-O and C-O-C vibrations (Matsura, et.al, 1986). However in the spectrum of PEO based materials the most important band(s) are probably the C-O and C-O-C bands. This is because the interaction of the salt is expected to occur at the oxygen atom of PEO when the salt was added to the polymer. Most of the bands were found to be sensitive to the changes in LiI concentration. The iodide band can be observed at the 1620 cm^{-1} (Pawlowska et al., 2007).

The basic ionic species that must be present are Li^+ and I^- ions. Due to the bigger size of the I^- anion (around 220 picometers), the transference number of the I^- should be greater than the transference number of Li^+. The low transference number of Li ions in PEO based polymer electrolytes has been reported by many researchers and in most cases it is below 0.4 (Armand et al., 2001, Watanabe et al., 1995, and Alloin et al., 1997). Low ionic conductivity can be the result of the poor salt dissociation. Typically in solid polymer electrolytes besides free ions, ion aggregates are also present (Wieczorek et al., 1998a, Marcinek et al., 2005, Wieczorek et al., 2005b).   The low lithium ion transference number results from stronger interaction between Li^+ cations and the polar atom of the polymer matrix in comparison with that of the corresponding anions. As a result, the mobility of the anions is higher in comparison with that of the Li^+ cations (Staunton,et.al., 2005, Stoeva et.al., 2003, Christie, et al., 2005). For device applications, high cation and low anion transference numbers are required. To do this, the anions must be immobilised. Immobilisation of the I^- anion can be achieved by adding anion trappers such as calix 4 and calix 6 which are neutral supramolecules. These have a number of interacting centres that can interact with anions of the salt and immobilize them. Such immobilization can be deduced from the FTIR spectra which is one of the aims of this chapter.

4.2 Proof of PEO-LiI Complex formation

There is clear evidence for complexation with addition of different concentrations of LiI. Fig 4.2 shows the FTIR spectra of pure PEO, pure LiI and PEO with different wt. % of LiI content, from 4 wt. % to 14 wt. % in the 1000 to 1200 cm $^{-1}$ wave number region are shown.

In the case of pure PEO, the C-O-C band splits into three peaks at 1148, 1095 and 1058 cm^{-1}. With increase in weight percentage of LiI, the C-O-C band shifts. These shifts indicate the formation of the Li^{+}--O- C associates in the electrolytes. It has been reported that the C-O-C band maximum is centred between 1096 and 1099 cm^{-1} (Zukowska et al, 2007). The shifting of the peak shows a clear evidence for the complexation.
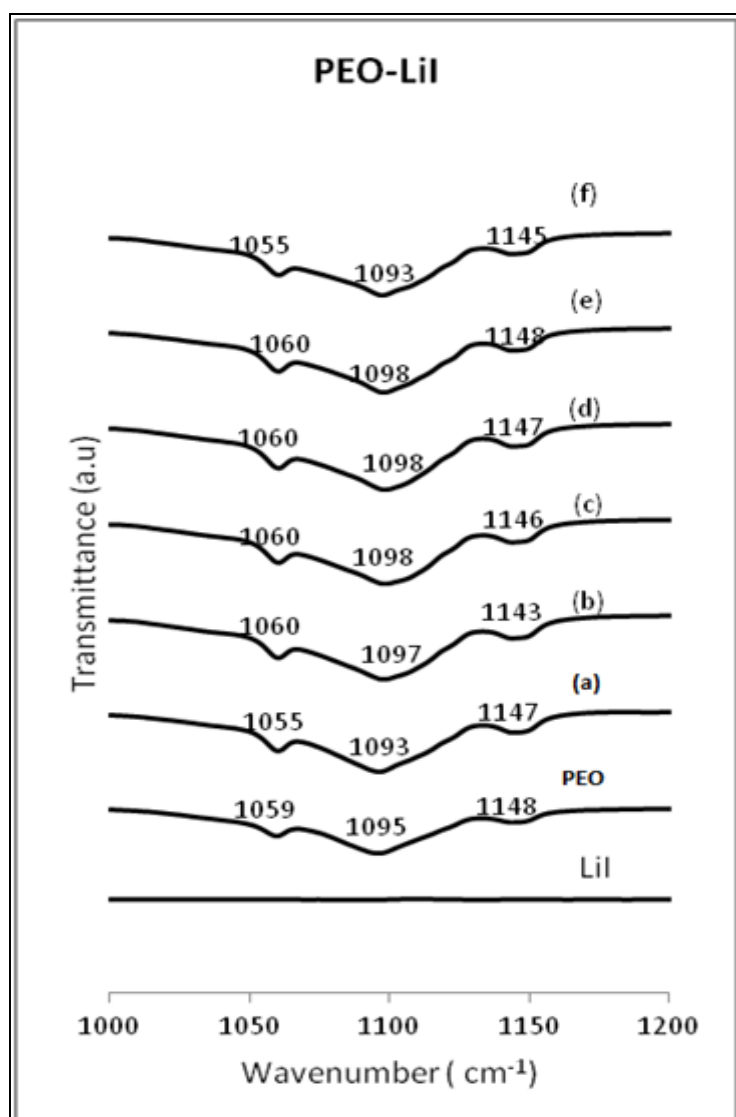

Figure 4.2 : FTIR spectra of pure PEO, and LiI ; (a) PEO- 4wt.% LiI, (b) PEO- 6wt.% LiI, (c) PEO- 8wt.% LiI (d) PEO-10wt.% LiI, (e) PEO-12wt.% LiI and (f) PEO-14wt.% LiI.

Addition of 4wt. % LiI shifts the peaks to 1147, 1093 and 1055 cm^{-1}, for 6 wt.% to 1143, 1097 and 1060 cm^{-1}, for 8 wt. % to 1146, 1098 and 1060 cm^{-1}, for 10 wt.% to1147, 1098 and 1060 cm^{-1}, for 12 wt.% to 1148, 1098 and 1060 cm^{-1} and addition of 14 wt. % LiI shifts the C-O-C peaks to 1145, 1093 and 1055 cm^{-1}.

The shifts indicate interactions between Li^{+} of the salt and the oxygen atom of the polymer. This shows that complexation has occurred. Hence this peak requires closer examination. It can be seen in Fig 4.2 there is no peaks in the LiI spectrum in this wavenumber region. So the peaks appearing in the spectrum for different weight percentage of salt are solely due to the incorporation of salt into the polymer matrix.

In Figure 4.3 when different amounts of salt is incorporated into the PEO matrix, CH$_2$ band in the spectrum of PEO at 1332 cm^{-1} become broader indicating a reduction of PEO crystallinity (Xi and Tang, 2005; Wieczorek,et al., 1998). The peak at 1332 cm^{-1} for pure PEO and the polymer salt complexes are shown in Figure 4.3. The peak shifts when salt concentration increases. It is also noted that there is no peak in the spectrum of LiI in this wave number region. Introduction of LiI salt into the pure polymer would modify the degree of crystallinity of the PEO.
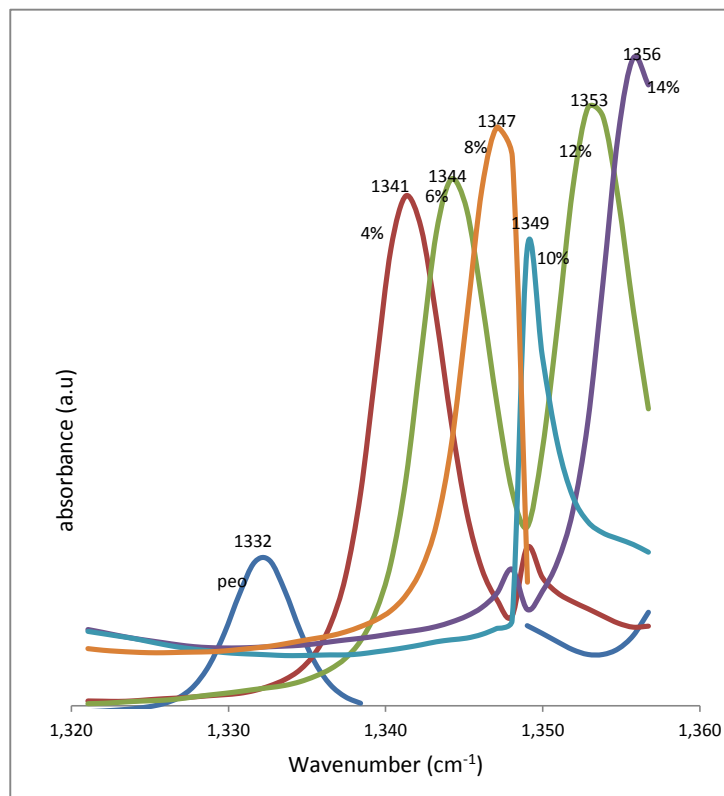
Figure 4.3: Changes in the peak position of the CH$_2$ band on addition of different weight percentage of LiI

The shift in this peak supports the occurrence of complexation i.e.,the interaction between the cation of the salt and the oxygen donor atom of the polymer. Since CH$_2$ band is the characteristic of the PEO crystalline phase, the degree of crystallinity of the polymer-salt complexes can be indicated by the broadness or full width at half maximum (FWHM) of this peak [Xi et al, 2005 and Wieczorek et. al 1998]. Wang et al, 2007 has shown that for PEO-LiClO$_4$ there are two clear CH$_2$ peaks at 1343 and 1360 cm^{-1}. The broadness can be estimated by using FWHM of the peak which was originally near 1340 cm^{-1}.

Figure 4.4 shows the FWHM of the CH$_2$ peak at 1332 cm^{-1} for different salt concentration. The FWHM increases with LiI concentration until 10 wt. % of LiI. This indicates that the amorphousness of the peak increases with LiI concentration and the

sample with 10 wt% of LiI is the most amorphous. With increase in LiI concentration above 10 wt%, the samples have become more crystalline. These results predict that the sample with 10 wt% LiI should exhibit the highest room temperature ionic conductivity.
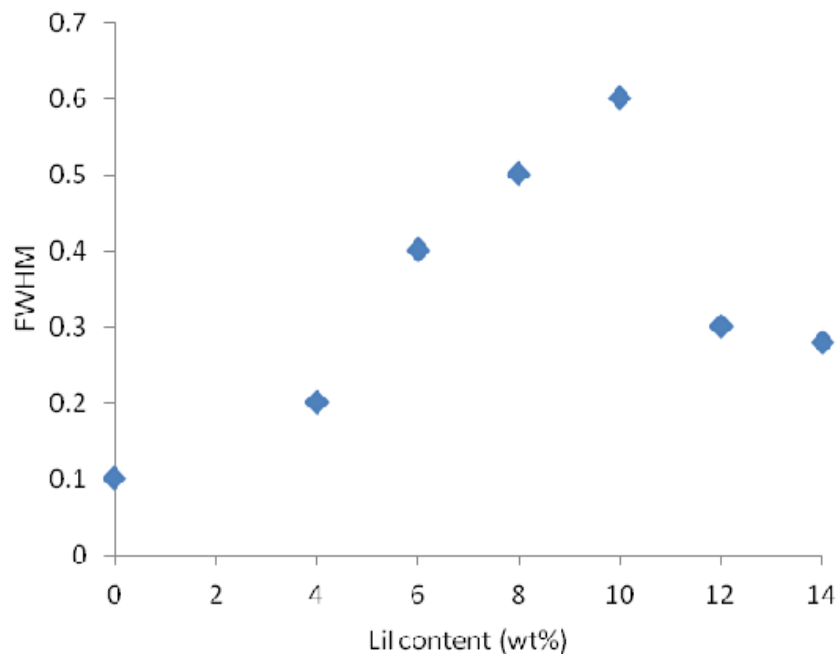

Figure 4.4: Full Width at Half Maximum (FWHM) for the peak 1332 cm^{-1} at different LiI concentration

According to Kalita et al, (2007) the peak at 1279 cm^{-1} for pure PEO is also characteristic of the crystallinity phase. This peak gets broader as the LiI content increases. This is shown in Fig 4.5. In the present work this peak shifts from 1279 cm^{-1} in pure PEO to 1284 cm^{-1} in 14 wt. % of LiI, 1282 cm^{-1} for 12 wt. %, 1282 cm^{-1} for 10 wt. % 1281 cm^{-1} for 8 wt. %, 1283 cm^{-1} for 6 wt. % and 1281 cm^{-1}for 4 wt.% of LiI. Pawlowska et al.(2007) had studied similar system in samples of PEO-LiCF$_3$SO$_3$.
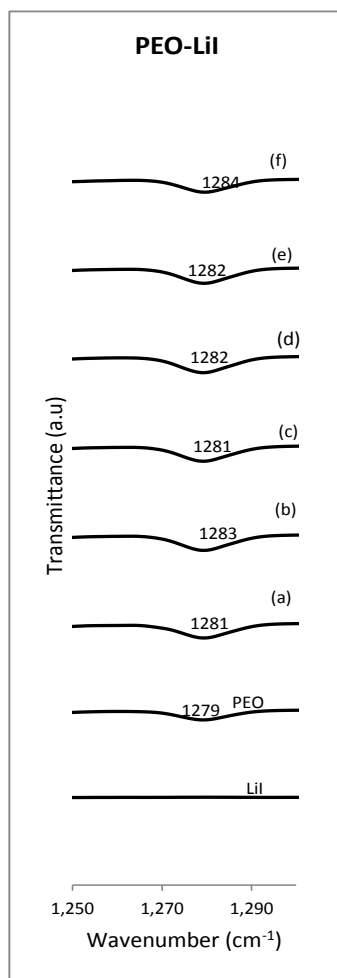
Figure 4.5: FTIR spectra of PEO, LiI and PEO with LiI (a) 96wt.% PEO : 4wt% LiI, (b) 94 wt.% PEO : 6 wt.% LiI, (c) 92 wt.% PEO : 8 wt.% LiI, (d)90 wt.% PEO : 10 wt.% LiI, (e) 88 wt.% PEO : 12wt.% LiI, (f) 86wt.% PEO : 14wt.% LiI

The FWHM for the peak originally near 1279 cm^{-1} is obtained from analysis done using the Ominic Software is displayed in Figure 4.6. Again as in Figure 4.4, the sample with salt content of 10 wt.% is the most amorphous. Since ion conduction occurs only in the amorphous region, it may therefore be predicted that this sample should exhibit the highest room temperature ionic conductivity in the PEO-LiI system.
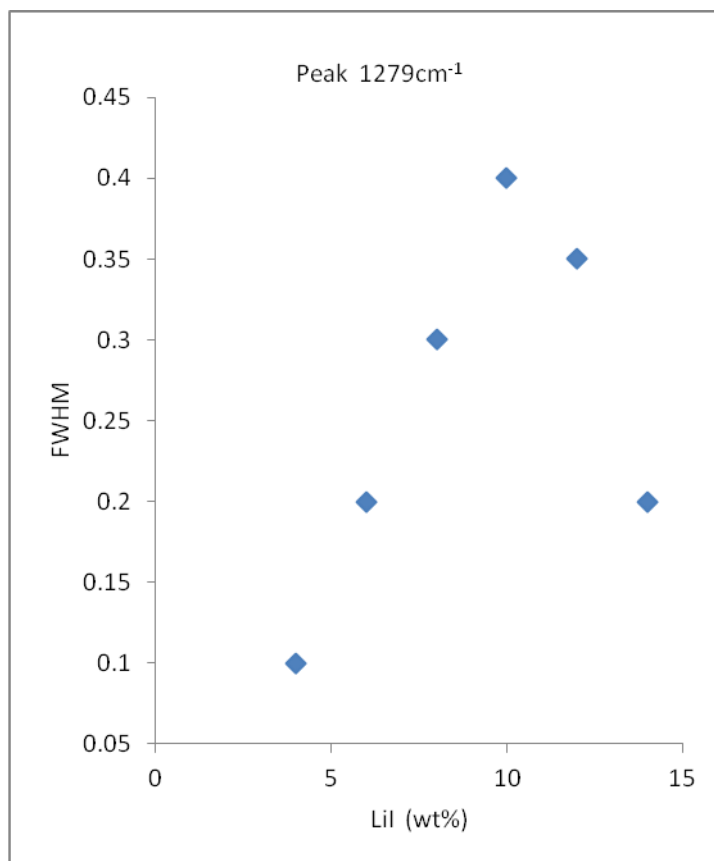
Figure 4.6: Full Width at Half Maximum for the peak 1279 cm⁻¹ at different LiI content

Figure.4.4 and Figure 4.6 are proofs of the use of FTIR in revealing the degree of amorphousness of the different samples prepared.

Figure 4.7 shows a peak for I⁻ at 1619 cm⁻¹. When LiI was incorporated into the PEO polymer, the peak gets shifted between 1628 cm⁻¹ to 1660 cm⁻¹ as the LiI wt% increases. According to Golodnitsky the LiI peak can be seen at 1610 cm⁻¹. Here the peak of pure LiI is located at 1619 cm⁻¹ which is upshifted to 1660 cm⁻¹ and gets broader as the percentage of the LiI increases. The shifting indicates the occurrence of complexation and the broadening indicates that the complex has become more amorphous and other moieties such as contact ions have formed (Golodnitsky, et. al, 2002).
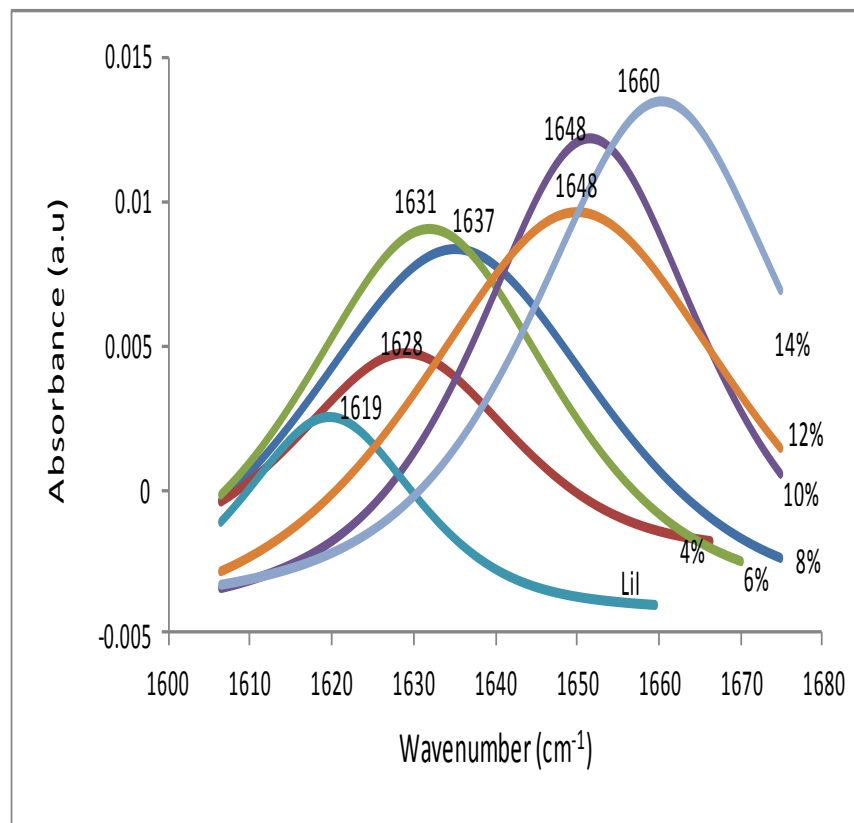
Figure 4.7: Changes in the peak position of the LiI band on addition of different weight percentage of LiI

There is no peak observed in the PEO spectrum in this wave number region. The peak at 1619 cm^{-1} in the pure LiI spectrum shifts to 1660 cm^{-1} as shown in Figure 4.7. Table 4.1 shows the shifting of the peak after the addition of different wt. % of LiI and FWHM of the peaks.

Table 4.1: shifting of peaks at different wt. % of LiI

	Peak shifts (cm^{-1})	Change in FWHM (cm^{-1})
LiI	1619	0
PEO + 4 wt. % LiI	1628	32.4144
PEO + 6 wt. % LiI	1637	33.6496
PEO + 8 wt. % LiI	1631	34.4171
PEO + 10 wt. % LiI	1648	37.0834
PEO + 12 wt. % LiI	1648	36.7215
PEO + 14 wt. % LiI	1660	35.9408

On complexation with PEO, the peak at 1619 cm^{-1} is that of I^- become broadened. This is due to increase in amorphous nature or the formation of other entities containing I^-. A possible entity is Li^+I^- contact ion pair as depicted in Figure 4.8.
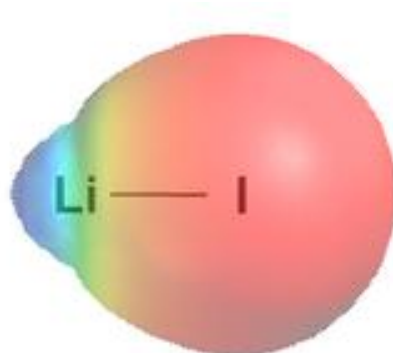
Figure 4.8: Schematic representation of Li^+I^-

If contact ion pair exists then the peak observed in this wave number region can be deconvoluted into two peaks as shown in Figure. 4.9 (a) to (f) with the peak at the lower wave number representing free ions and the higher wave number representing contact ions.
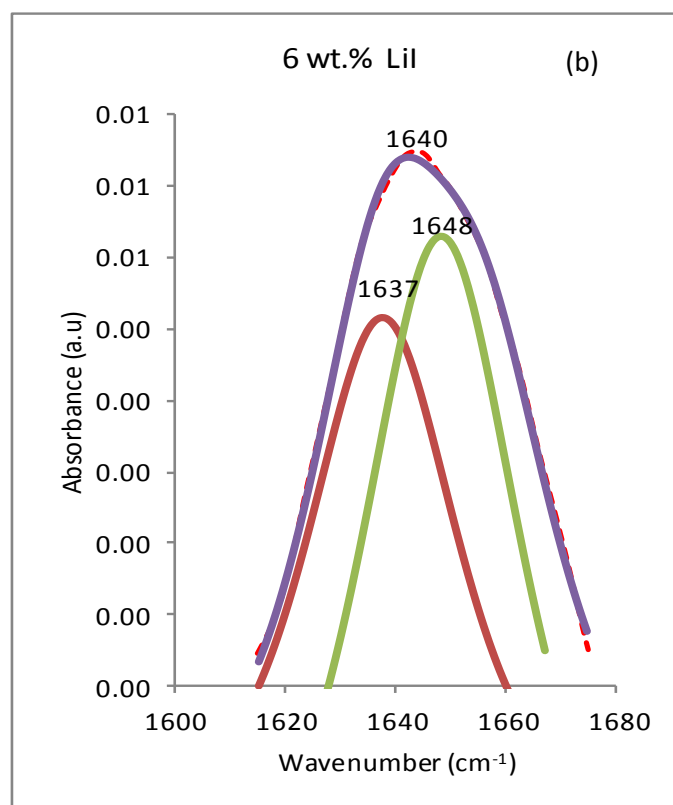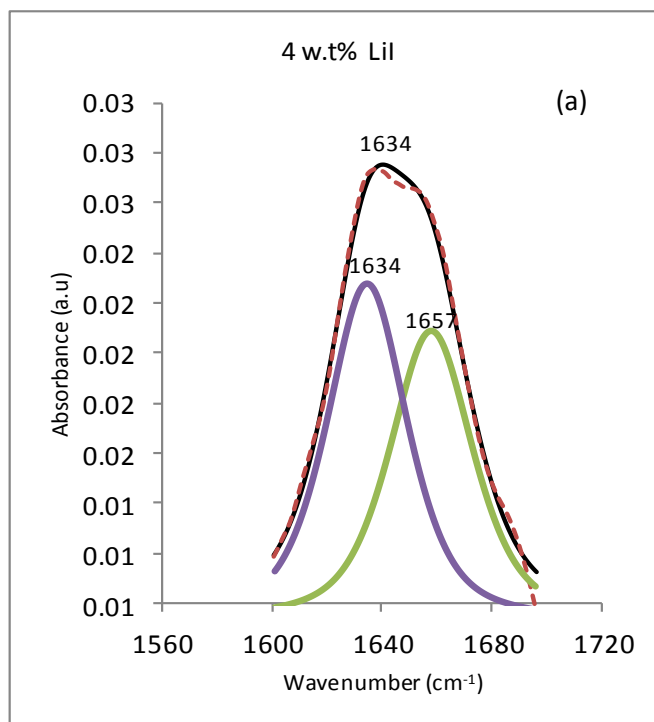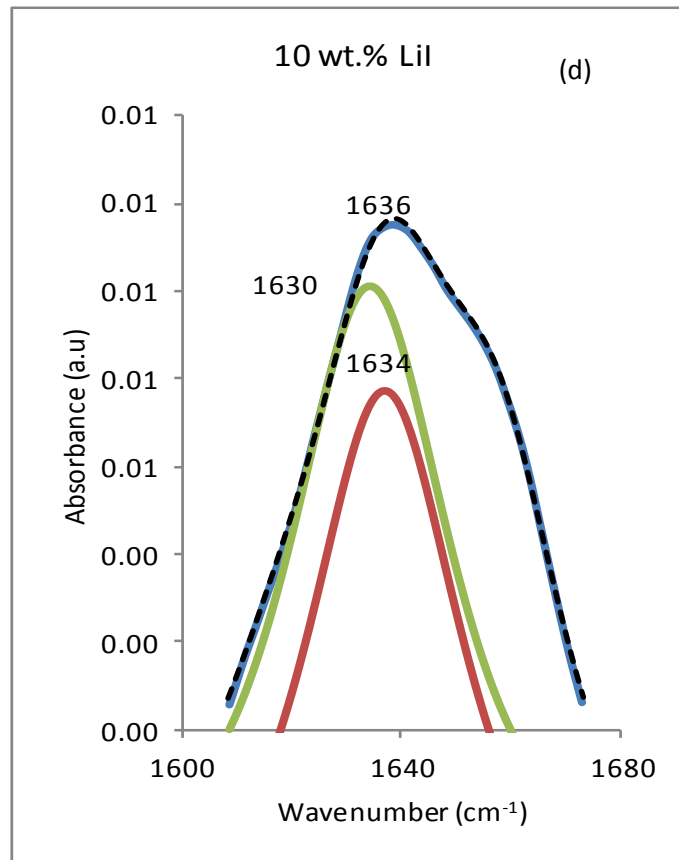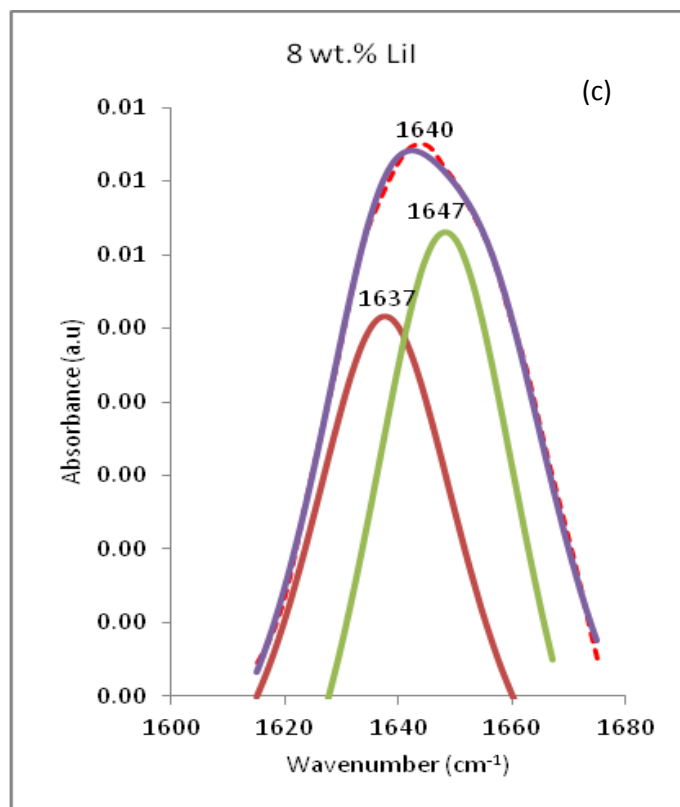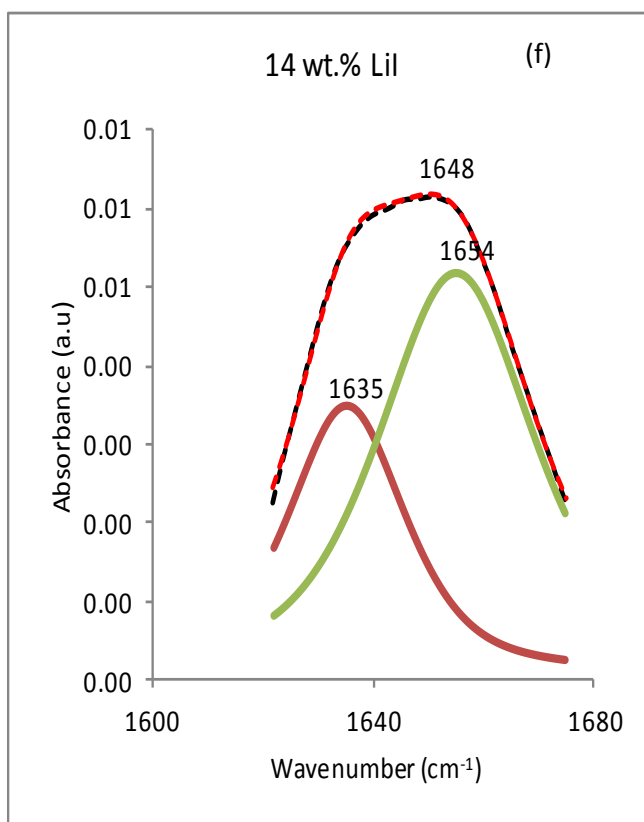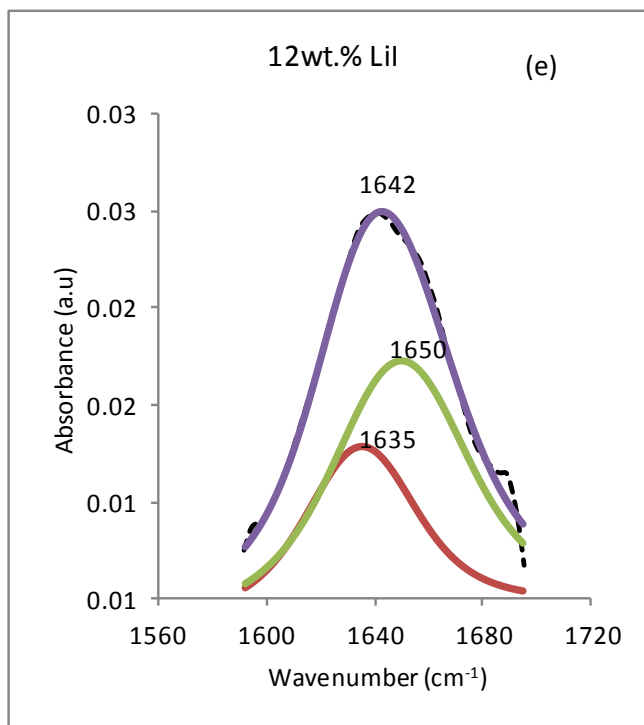
Figure 4.9: Deconvoluted iodide peak.

From the Figure 4.9(a)-(f) can be seen that the free ion peaks are located at 1634 cm^{-1}for 4 wt.%, 1637 cm^{-1} for 6 wt.% and 8 wt.%, 1634 cm^{-1} and 1630 cm^{-1} for 10 wt%,1635 cm^{-1} for 12 wt.% and 1635 cm^{-1} for 14 wt.% of LiI respectively. The contact ion peaks are located at 1657 cm^{-1} for 4 wt.%, 1648 cm^{-1} for 6 wt.%, 1648 cm^{-1} for 8 wt.%, 1636 cm^{-1} and 1634 cm^{-1} for 10 wt.%, 1650 cm^{-1}and 1642 cm^{-1} for 12 wt.% and 1654 cm^{-1}and 1648 cm^{-1} for 14 wt.% of the LiI respectively.

The ratio of the area of the free ion peak to the total area of both peaks can give the percentage of free ions. Figure 4.10 depicts the graph of percentage of free ions that shows a maximum at 10 wt% LiI indicating that this sample should exhibit the highest conductivity at room temperature for the PEO-LiI system, based on free ion number density.
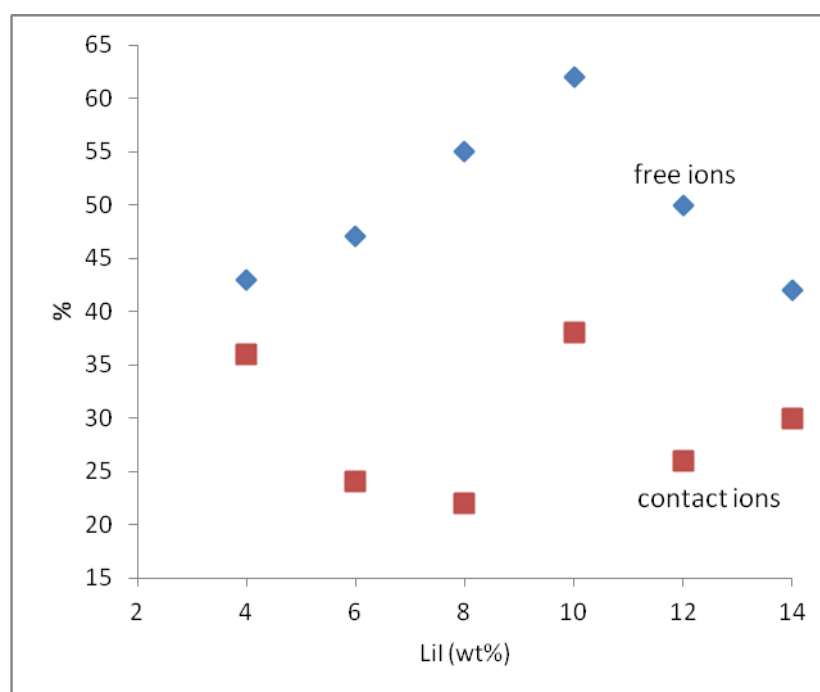

Figure 4.10: Percentage of free ions for different wt% of LiI

It has been shown that FTIR can indicate the presence of free ions and other moieties present in the sample.

4.3 Complex formation by the addition of Al_2O_3

To enhance the transport properties of PEO-based composite polymer electrolytes various types of ceramic powders e.g.Al_2O_3 or TiO_2 have been added (Zukowska, et al., 2007). The role of a ceramic filler is not only to prevent crystallization but also to promote interactions between PEO, filler surface and the ionic species which in turn increases the transport properties of polymer electrolytes (Wieczorek,et al., 2000 and Magistris and et,al 1999). The incorporation of Al_2O_3 acidic group can form structural modifications via Lewis acid–base reactions between the ceramic surface states and the PEO segments, as proposed by Wieczorek et al.,(1995) and Przyluski et al.,(1995). According to the Wieczorek model, the oxygen atom in the Lewis acid, -OH groups on the Al_2O_3 surface would compete with the ether oxygen in PEO for the Lewis acid lithium cations for the formation of complexes with the PEO chains, as well as with the anions of the added LiI salt (Croce et al., 1992). Thus, the ceramics would act as cross-linking centers for the PEO segments, thus lowering the polymer chain reorganization tendency and promoting an overall structure stiffness. Such a structure modification would provide Li^+ ions conducting pathways at the ceramics surface, this accounting for the improvement in ionic transport.

Increase in ionic conductivity should result from changes in ionic association due to ion-ion and ion-polymer interactions involving an inorganic or organic additive. These interactions led to lowering of the electrolyte viscosity and changes in the fraction of ionic associates. According to the model of Wieczorek and co-workers, the final conductivity of composite electrolyte depends on the equilibrium of the Lewis acid-base

reactions involving additive, a matrix polymer and salt (with cations acting as Lewis acid and anions as Lewis bases). The Lewis acid-base model is also useful for designing fillers which might act as anionic receptors, thus, possibly increasing the cation transport number.

The use of inorganic fillers such as Al_2O_3 proved to be one of the most effective as demonstrated by Scrosati's group (Croce et al., 1999; and Appetecchi et al., 1998). Due to the competition between acidic–OH groups of aluminas or other inorganic fillers compete with the alkali metal cations in the formation of complexes with polyether chains, leads to changes in the crystalline structure of the PEO based electrolytes. In these systems the Lewis base alumina surface groups seem to interact with alkali metal cations. These types of acid-base interactions result in the formation of amorphous phases, thus increasing the amorphous domain and enhance conductivity. The formation of different types of complexes in composite polyether electrolytes can be studied experimentally using FTIR spectroscopy.

In Figure 4.11, there are three clear peaks in the spectrum of PEO at 1058, 1092 and 1145 cm^{-1}. These peaks are the contribution of C-O-C band in pure PEO which gets shifted by the formation of complex ions.
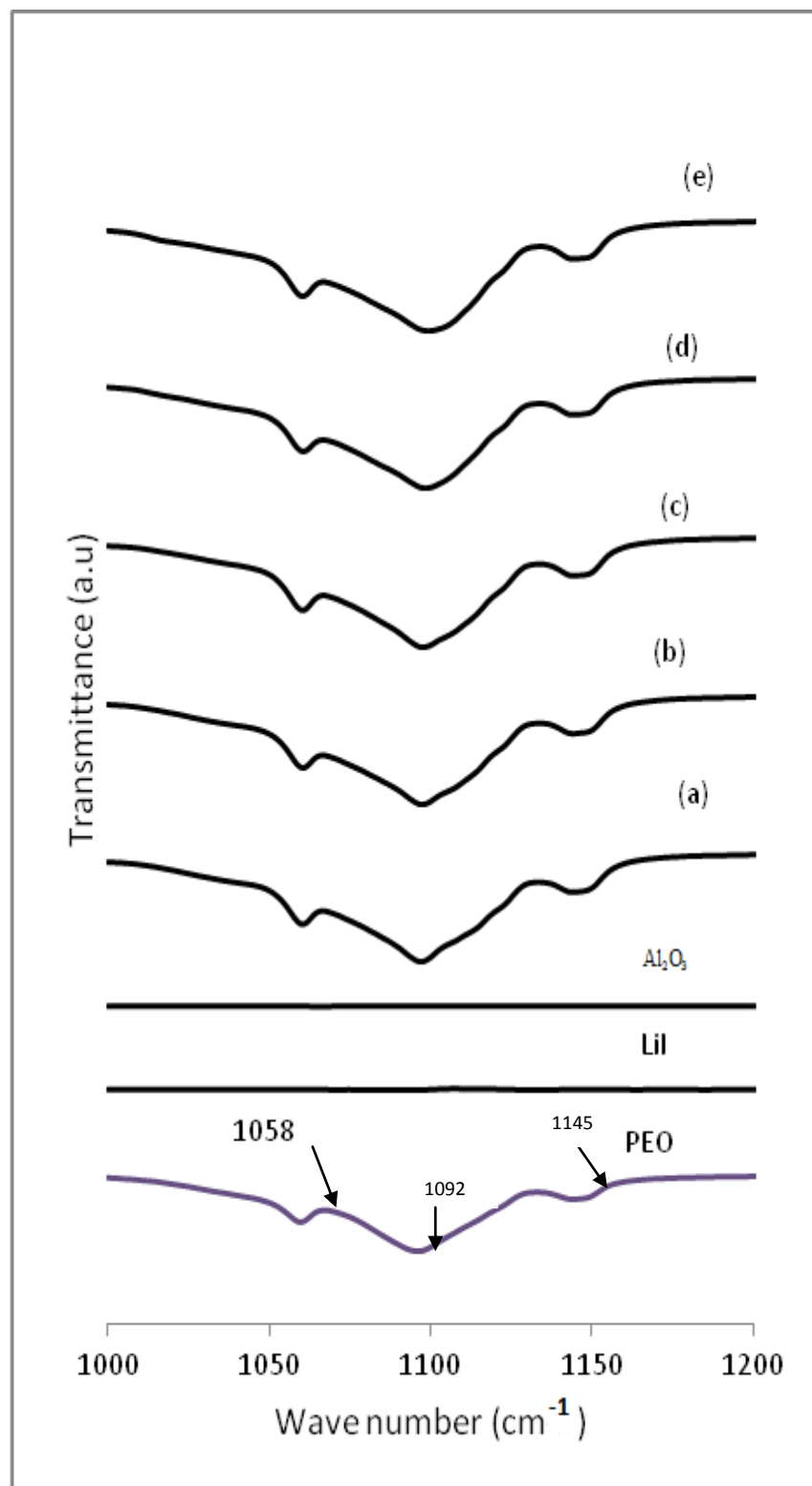
Figure 4.11: PEO, LiI, Al $_2$O$_3$ and PEO-LiI–Al$_2$O$_3$. (5-25wt%) (a) 85.5wt. %PEO:9.5wt.% LiI:5wt. %Al$_2$O$_3$, (b) 81.0 wt.% PEO: 9wt.%LiI:10wt.%Al$_2$O$_3$, (c) 76.5wt.% PEO :8.5wt.% LiI:15 wt.%Al$_2$O$_3$, (d) 72.0wt. %PEO : 8wt.% LiI:20wt.% Al$_2$O$_3$, (e) 67.5wt.% PEO : 7.5wt.% LiI : 25wt.% Al$_2$O$_3$

Table 4.2 represents the shifting of the C-O-C peak by the addition of different weight percentages of Al_2O_3

Table 4.2: shifting of C-O-C peak

Wave number of C-O-C peak in PEO-LiI cm^{-1}			
Pure PEO	1058	1092	1145
(a)with 5wt% Al_2O_3	1057	1097	1147
(b)with10wt% Al_2O_3	1058	1098	1148
(c)with15wt% Al_2O_3	1060	1100	1148
(d)with 20wt% Al_2O_3	1062	1102	1149
(e)with 25wt% Al_2O_3	1050	1099	1146

Here changes are due to Al_2O_3 competing with the ether oxygen in PEO to form Lewis acid complexes. Fig 4.12 shows the characteristic crystallinity peak at 1279 cm^{-1} that has become broader and shifted to around 1281 cm^{-1} after the incorporation of inorganic filler to the polymer-salt system showing an increase in amorphous phase (Kalita et al, 2007). The elimination of the crystallinity and existence of a stable amorphous phase are desirable for a material to have high conductivity. A faster ionic transport takes place in the amorphous phase in which the conductivity is about two to three orders of magnitude greater as compared with the crystalline phase (Scrosati et al., 1993).
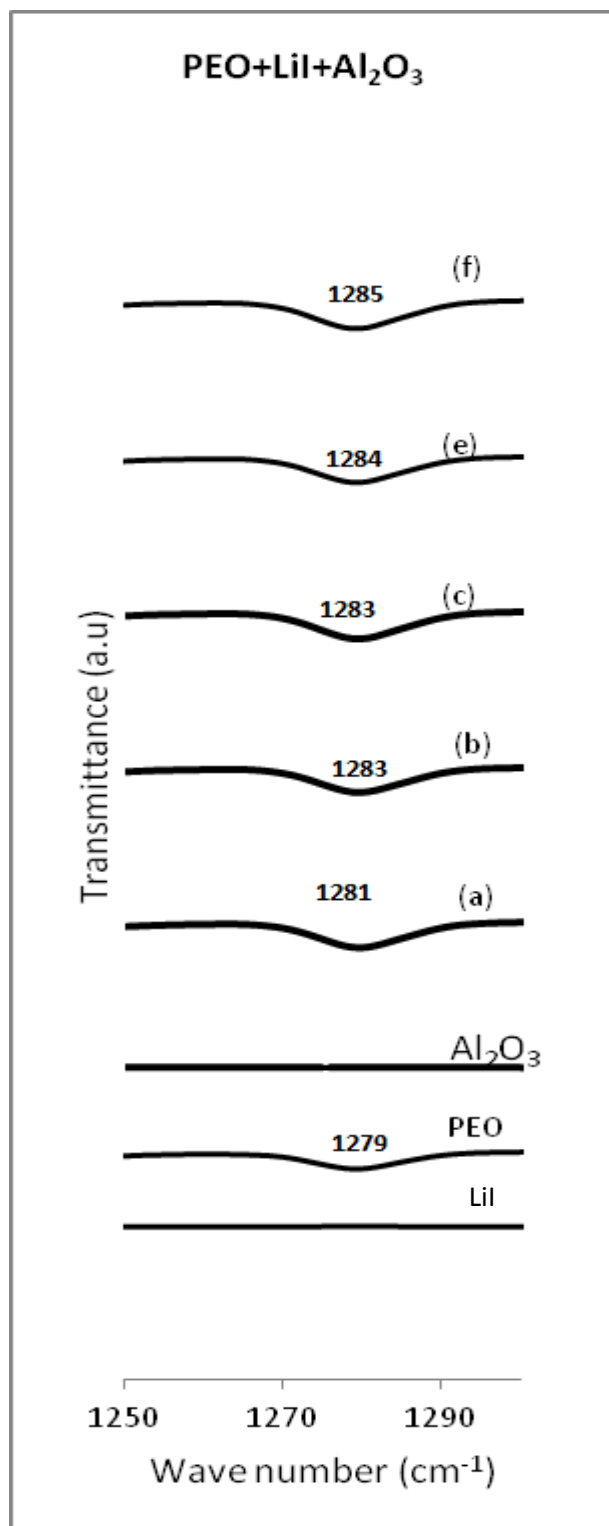
Figure 4.12: LiI, PEO, Al₂O₃ and PEO-LiI–Al₂O₃. (5-25wt%)   (a) 85.5 wt.%PEO:9.5wt.% LiI:5wt. %Al₂O₃, (b) 81.0wt.% PEO: 9%wt.LiI:10wt.%Al₂O₃, (c) 76.5wt.% PEO :8.5wt.% LiI:15wt. %Al₂O₃, (d) 72 .0 wt.%PEO : 8wt.% LiI:20wt.% Al₂O₃, (e) 67.5wt.% PEO : 7.5wt.% LiI : 25wt.% Al₂O₃

Table 4.3: represents the wave numbers shifting of crystallinity peak after the addition of different wt. %,5 wt.% 25 wt.% of Al_2O_3. To study this peak more in detail, the FWHM of the peak is determined.

Table 4.3: Shifting of crystallinity peak

PEO-LiI-Al_2O_3	Shifts / cm^{-1}	Change in FWHM (cm^{-1})
PEO	1279	0
5 wt.% Al_2O_3	1281	36.672
10 wt.% Al_2O_3	1283	38.247
15 wt.% Al_2O_3	1283	43.350
20 wt. % Al_2O_3	1284	39.740
25 wt. % Al_2O_3	1285	30.841

Figure 4.13: shows the change in the FWHM of the peak at 1279 cm^{-1}.
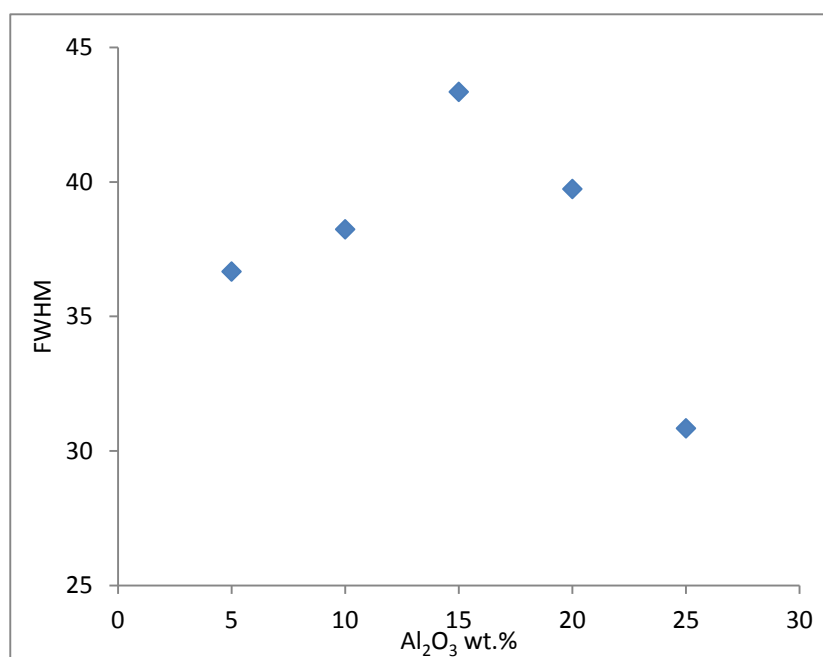
Figure 4.13: FWHM for peak at 1279 cm^{-1}

From the Figure 4.13 it can be seen that the addition of Al_2O_3 increases the amorphous nature of the most amorphous 90 wt. % PEO-10 wt. % of LiI sample in the PEO-LiI system. This indicates that the sample 76.5 wt. % PEO-8.5 wt. % LiI-15 wt. % Al_2O_3 should exhibit the highest conducting sample in the composite PEO-LiI-Al_2O_3 system.

Fig 4.14 shows the change in LiI peak after the addition of Al_2O_3. For the addition of 5 wt. % to 25 wt. % of Al_2O_3, the peak shifts from 1619 cm^{-1} to 1659 cm^{-1}. This is due to the complexation of Al_2O_3 with the polymer electrolyte.
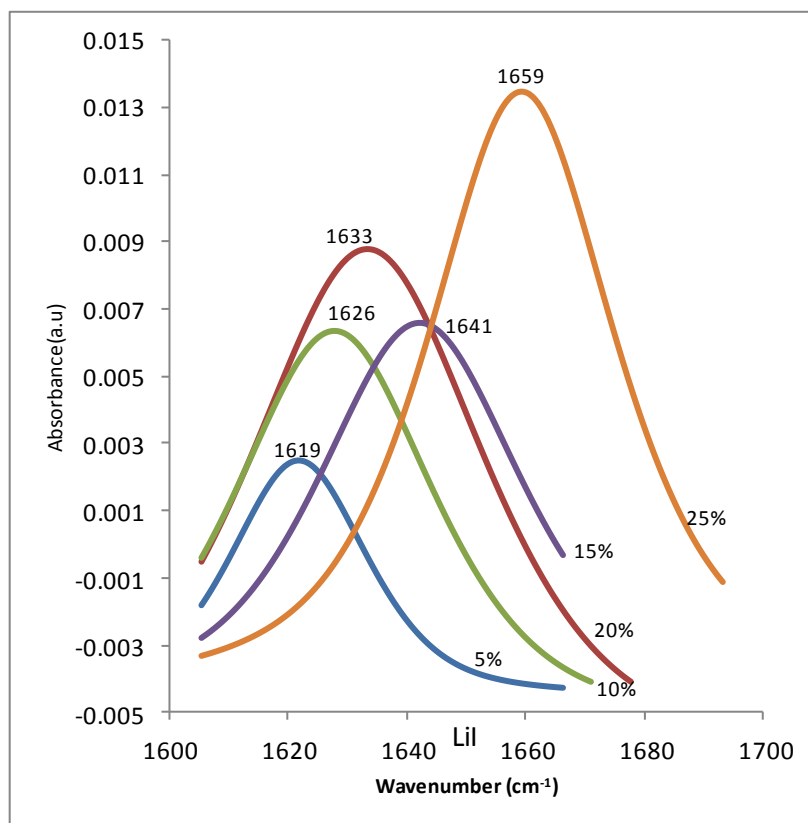
Figure 4.14: Changes in the peak position of the LiI band on addition of different weight percentage of Al_2O_3

The peak at 1619 cm^{-1} is that of I$^-$. On complexation with PEO, this peak can be observed to broaden. The broadening can be due to the increase in amorphous nature of the samples and the presence of contact ions.

The ratio of the area of the free ion peak to the total area of both free ions and contact ion pair peaks can give the percentage of free ions. Figure 4.15 depicts that the graph of percentage of free ions and contact ion pair peaks. At 15 wt. % of Al$_2$O$_3$ indicates that it should exhibit the higher conductivity at room temperature for the PEO-LiI-Al$_2$O$_3$ system. This is because of the higher percentage of free ions which contributes to the ionic conductivity is higher for 15 wt.% of Al$_2$O$_3$.
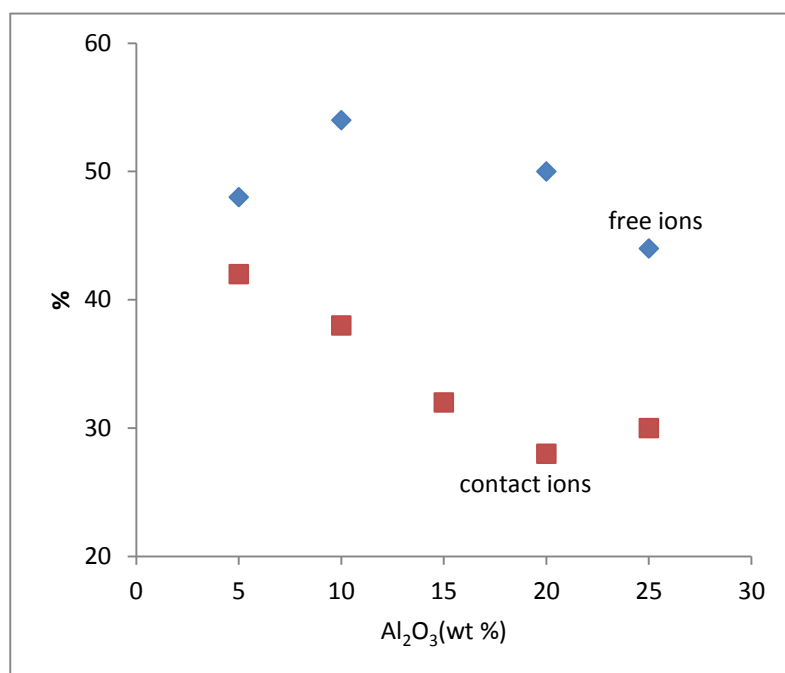
Figure 4.17: Percentage of free ions and contact ions for different wt% of Al$_2$O$_3$

Figure 4.18 depicts the deconvoluted peaks at 1619 cm^{-1} for LiI in the PEO – LiI – Al$_2$O$_3$ systems. From the deconvoluted peaks we have calculated the percentage of contact ion pairs and percentage of free ions.
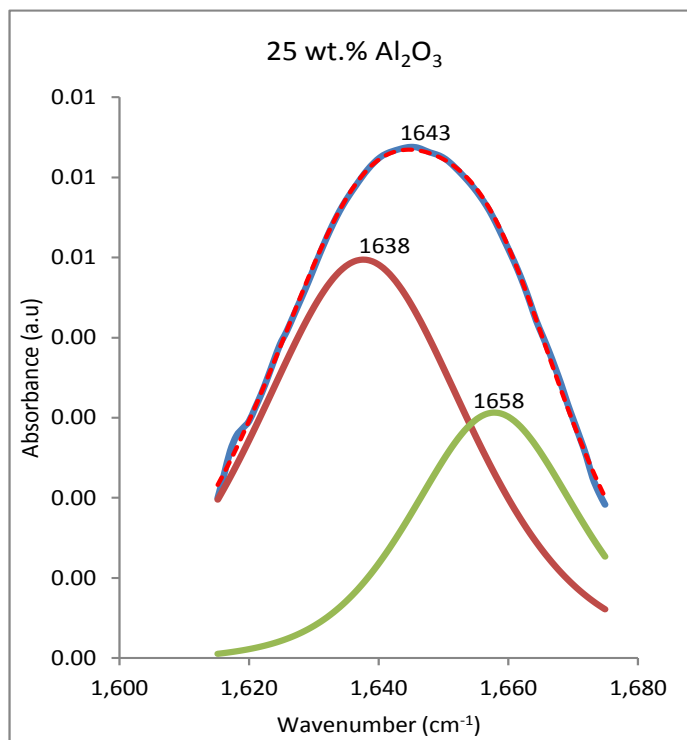
15 wt.% Al$_2$O$_3$

20 wt.% Al$_2$O$_3$
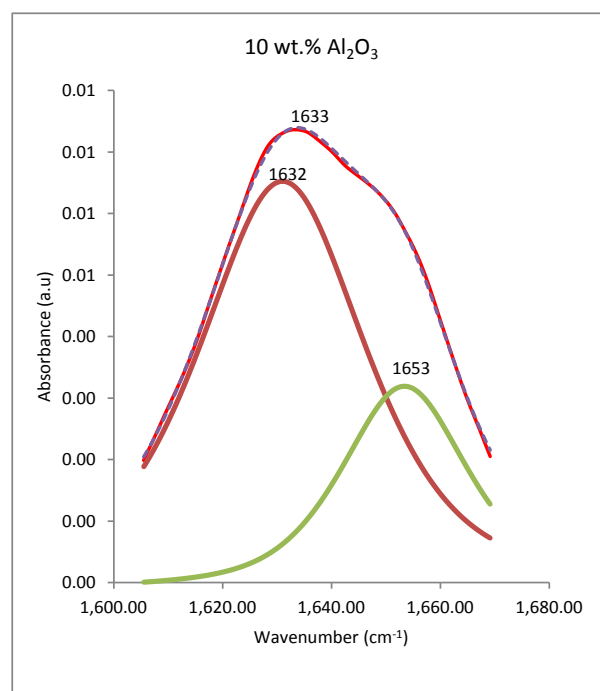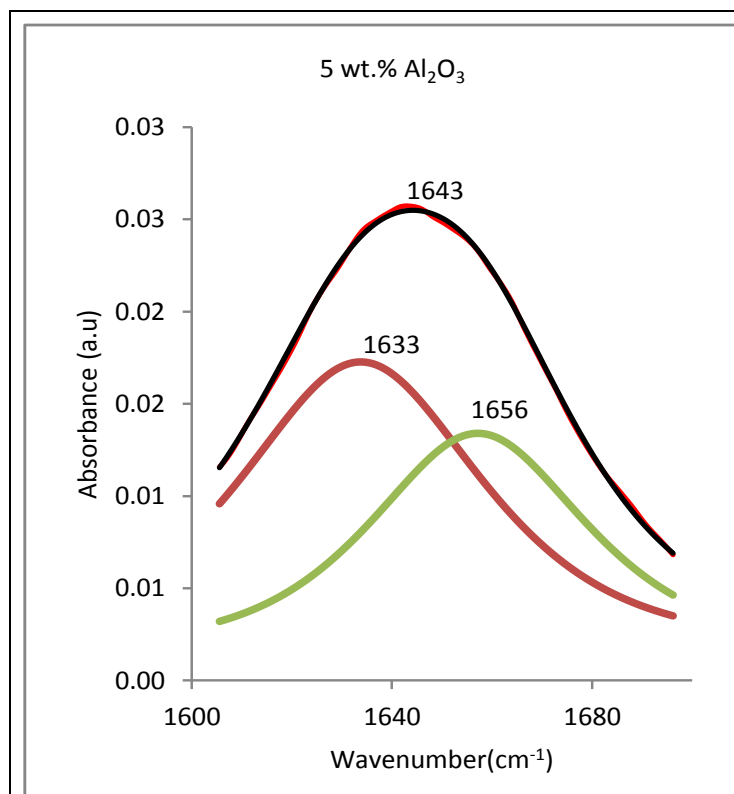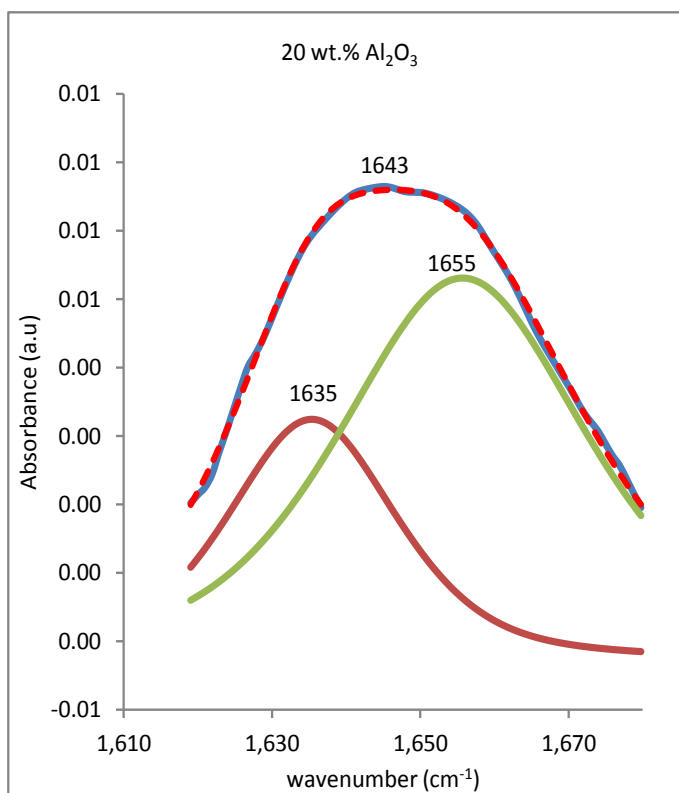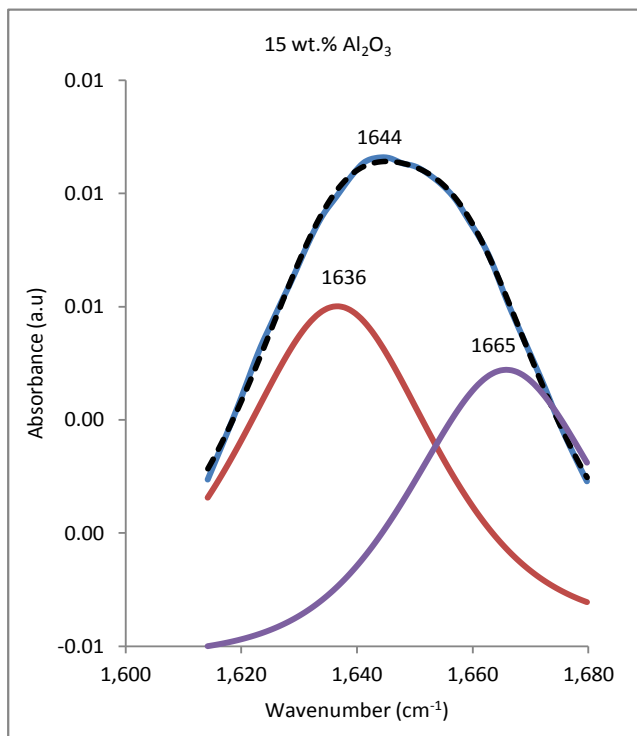
Figure 4.18 : Deconvoluted peak for 1640 cm^{-1} for PEO-LiI- Al$_2$O$_3$ system.

The free ion peaks are located at 1633 cm^{-}1 and 1643 cm^{-1}for 5 wt.%, for 10 wt.% 1632 cm^{-1} and 1633 cm^{-1}, for 15 wt.% free ions are at 1635 cm^{-1} and 1643 cm^{-1}, for 20 wt.% of Al$_2$O$_3$ free ions can be seen at 1636 cm^{-1}, 1644 cm^{-1} and for 25 wt.% it is at 1638 cm^{-1}, 1643 cm^{-1} respectively.

The contact ions for 5 wt.% of Al$_2$O$_3$ is at 1656 cm^{-1}, that of 10 wt.% is at 1653 cm^{-1}, 20 wt.% of Al$_2$O$_3$ is at 1655 cm^{-1} and for 25 wt.% it is at 1665 cm^{-1}.

4.4   Complexation of PEO – LiI –Calix4 and PEO-LiI-Calix6 system.

In polymer electrolytes both anions and cations are mobile. For device applications we need to restrict the mobility of anions without adversely affecting the cations. There are some theoretical predictions which justify the use of anionic receptors as additives enhancing cation transport number in polymeric electrolytes (Johanson 2003 and Johanson et al., 2005)

. It has been shown that calix4 arenes are very effective to complex with iodide and triflate anions (Kalita et al 2005, Blazejczyk et al 2004 and Blazejczyk et al 2005). FTIR spectroscopy is a convenient tool for studying associations in systems with macrocyclic additives. The incorporation of macromolecules in a PEO environment can considerably reduce the crystallinity of the polymer host (Stephan et al., 2010). The most pronounced change is observed for the C-O vibration in the spectra of PEO–LiI-Calix4 and PEO–LiI-Calix6. Through these interactions the anion can be immobilised and can increase the cation transference number [Kalita et al., 2005].

Apart from the C-O-C peak shifting due to complexation, we can observe in Figure, 4.19 some other interactions of calix4 arenes with PEO-LiI systems. The peak at 1652 cm^{-1} can be superposition of peaks attributed to weakly and strongly associated carbonyl group of the calix molecule. The peak at 1700 cm^{-1} corresponds to free carbonyl group of the receptor molecules (Pawlowska et,al., 2007). This indicates by the addition of macromolecules to polymer salt system there is stronger hydrogen bonds formed between the receptor molecule and the oxygen atom in the polymer molecule.
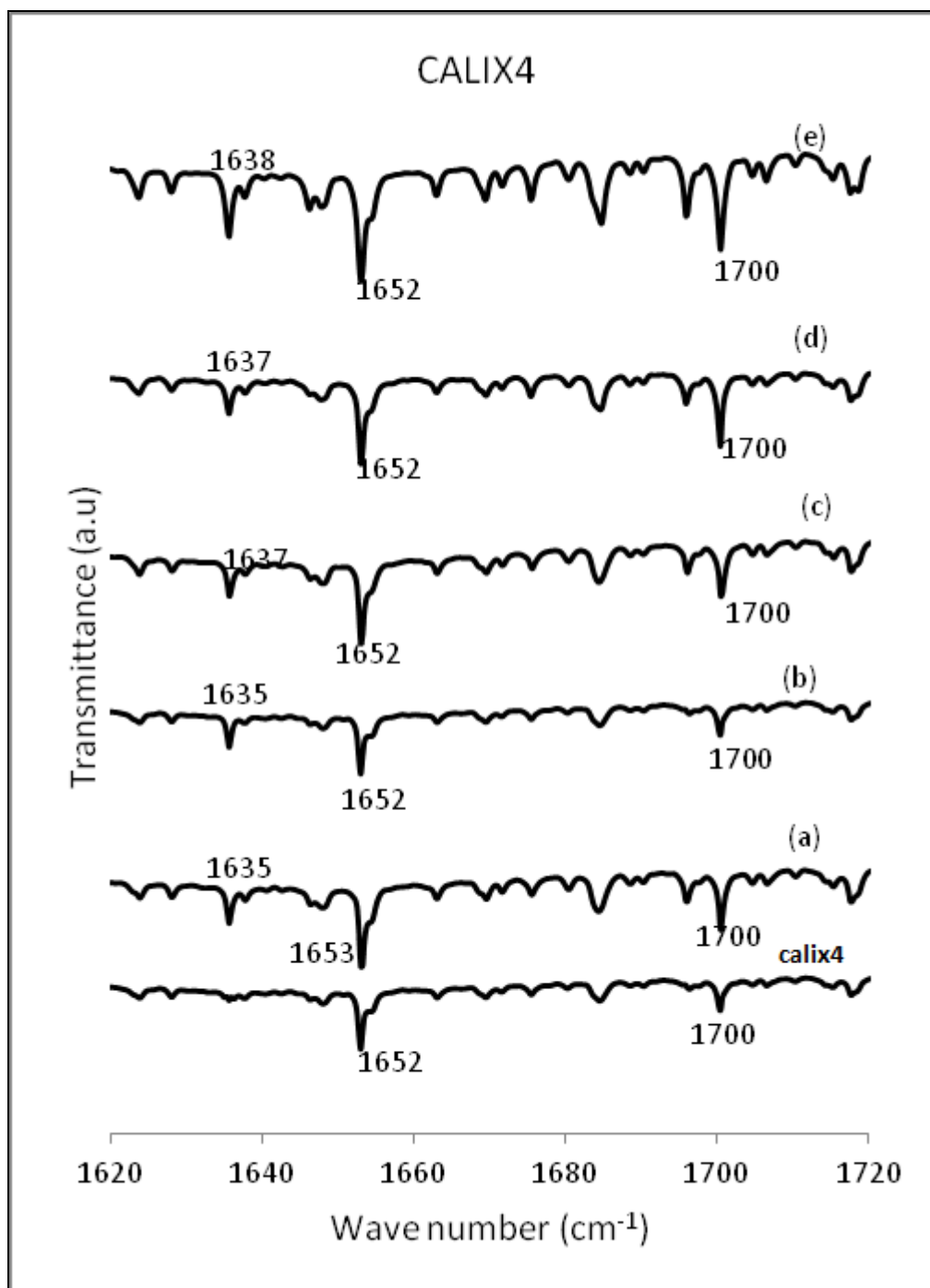
Figure 4.19: FTIR spectra of Calix 4 and PEO –LiI –calix 4(1%- 5%); (a)89.1wt.% PEO : 9.9 wt.% LiI : 1 wt.% Calix 4, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 4, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3wt.% Calix 4 (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix 4,(e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix 4

Figure 4.20 shows the shifting of LiI peak after the addition of different wt.% of

calix4. It can seen that after the addition of the macromolecule, the peak representing I⁻

shifted from 1619 cm^{-1} to 1638 cm^{-1}.
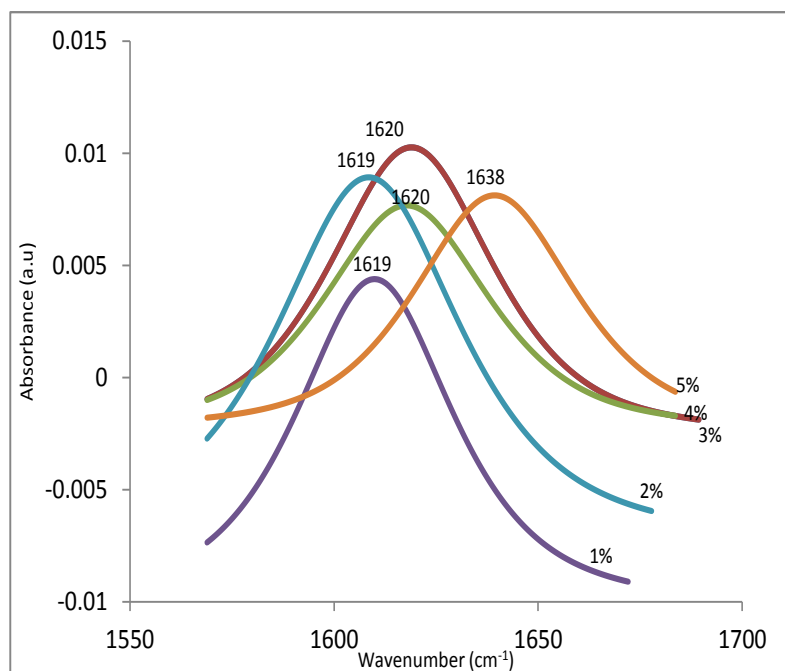
Figure 4.20: LiI peak upon addition of different wt% of calix4

Figure 4.20 also depicts the broadening of Iˉ band after the addition of the macromolecules calix4. The broadening indicates that the complex has become more amorphous and other moieties such as contact ions has formed.

Figure 4.21 shows the deconvoluted Iˉ peak. From the figure we can observe that the percentage of free ions and contact ions formed according to the wt.% of calix arenes. The free ions are located at low wave number range whereas contact ions are at high wave number range.
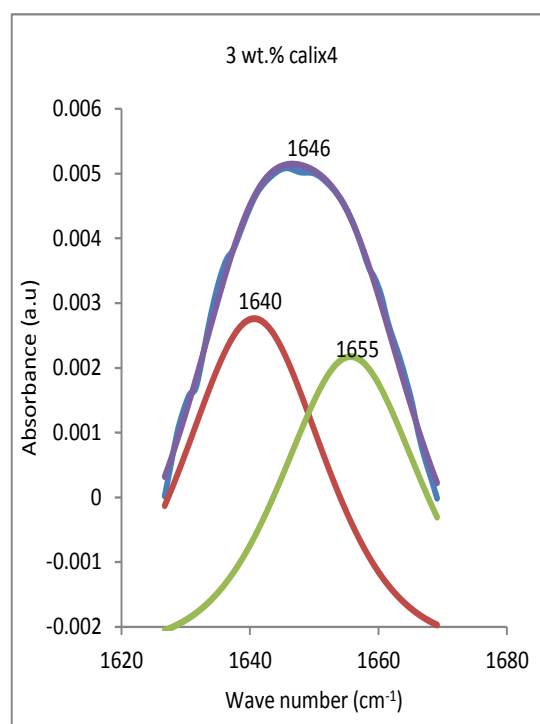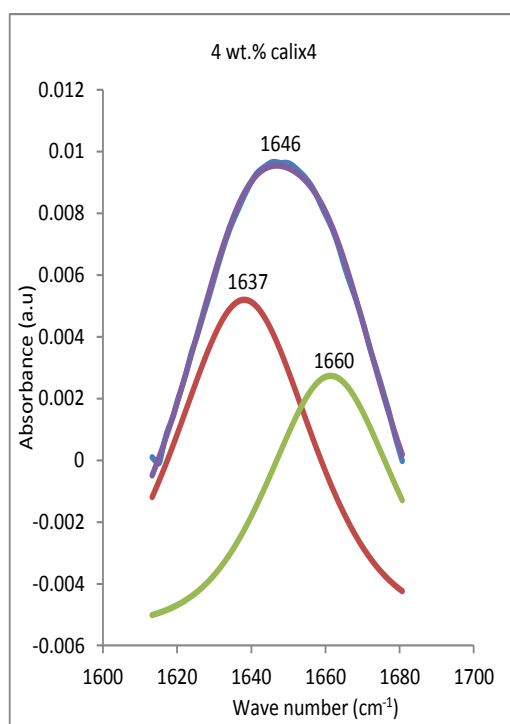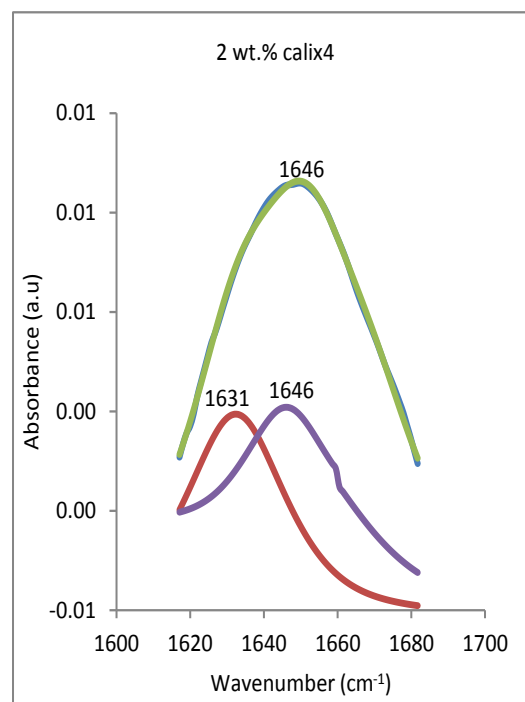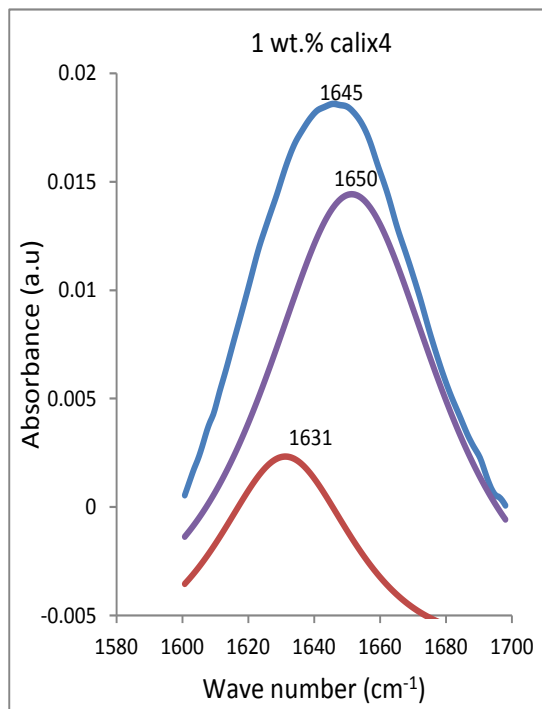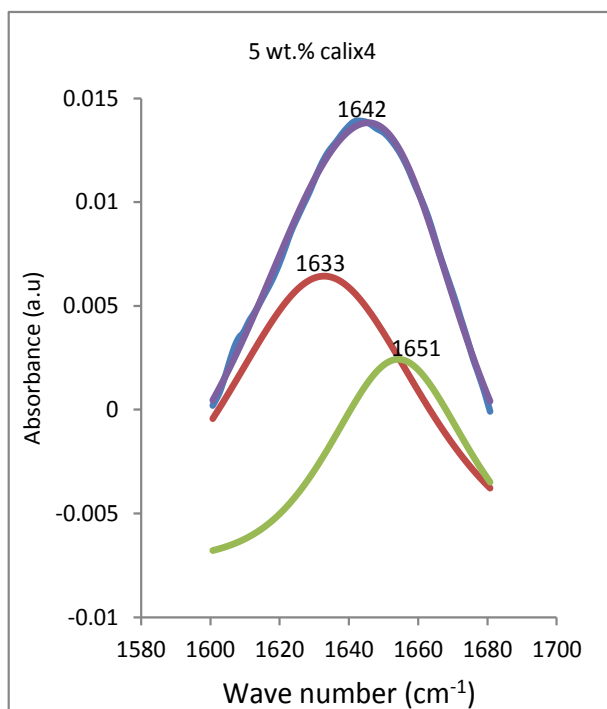
Figure 4.21: Deconvoluted LiI peak for PEO-LiI- Calix4 system.

In the deconvoluted LiI peak in Figure 4.21 for 1 wt.% of calix4 the free ion peak is located at 1631 cm^{-1}, for 2 wt.% it is at 1631 cm^{-1}, 1640 cm^{-1}, for 3 wt.% it is at 1640 cm^{-1} and for 4 wt.% and for 4 wt.% and 5 wt.% of calix4 the free ion peaks are at 1637 cm^{-1} and 1633 cm^{-1}. The contact ion pairs are at 1650 cm^{-1} and 1645 cm^{-1} for 1 wt.%, 1646 cm^{-1} at 2 wt.%, 1655 cm^{-1} and 1646 cm^{-1} for 4 wt.% and 1651 cm^{-1} and 1642 cm^{-1} for 5 wt.% of calix4.

According to Blazejczk et al, 2004 supramolecules such as calix arenes in the polymer electrolyte environment promote the formation of strong hydrogen anion-receptor bonds in competition with anion-cation and other interactions.

Figure 4.22 shows a broader peak at 1278 cm^{-1}, which is attributed to the presence of crystallinity of the sample. The peak gets broader and it gets shifted as the concentration

of calix4 increases. Crystallinity peak of calix4 at 1278 cm^{-1} gets shifted to 1283 cm^{-1}, 1281 cm^{-1}, 1283 cm^{-1}, 1281 cm^{-1} and to 1282 cm^{-1}on addition of 1, 2, 3, 4 and 5 wt.% calix4.
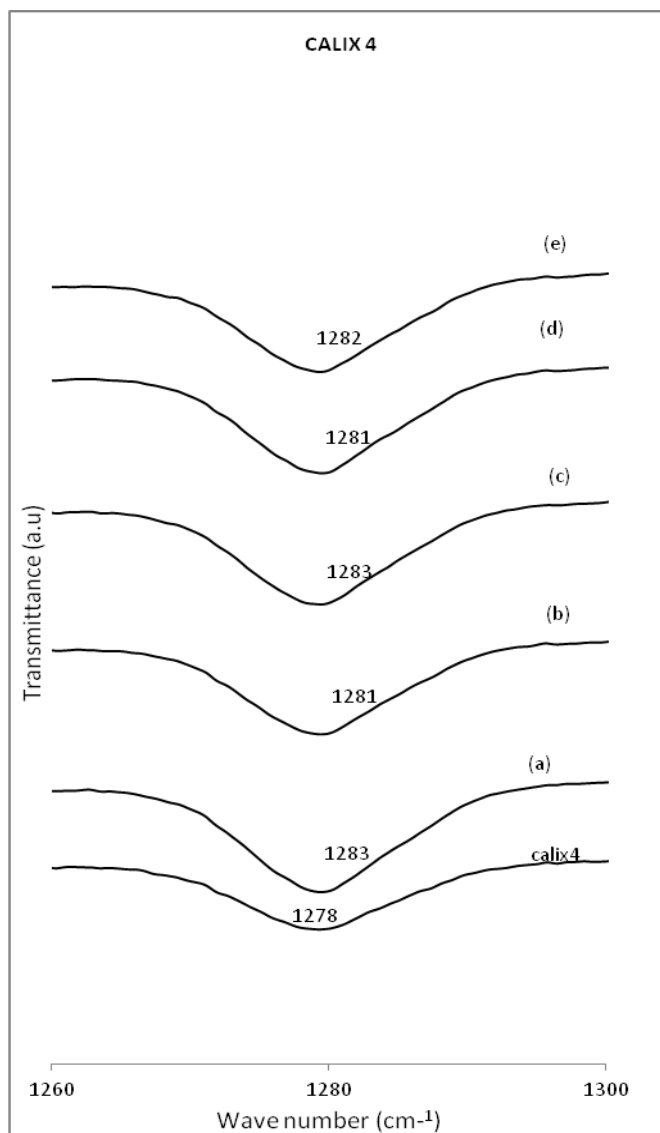

Figure 4.22: FTIR spectra of Calix 4 and PEO –LiI –calix 4(1%- 5%); (a)89.1 wt.% PEO : 9.9 wt.% LiI : 1wt.% Calix 4, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 4, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 4 (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix 4,(e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix 4

Figure: 4.23 shows the FWHM of the peak 1278 cm^{-1} which is obtained from the Ominic Software. The FWHM shows that at 3 wt.% of calix4 the peak is getting much more broader compared to the other wt.%, so we can confirm that there is complexation between the LiI salt with the calix4 arene molecule which reduces the crystallinity of the system.
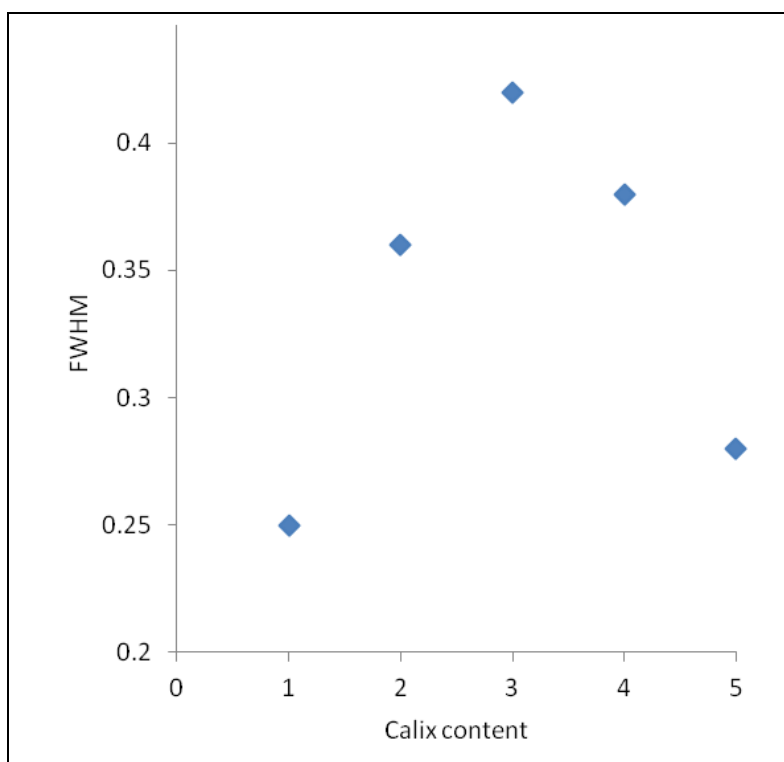

Figure 4.23: FWHM for peak 1278 cm^{-1}in the PEO-LiI-Calix4 system.

Figure 4.24 shows the linking of polyether chains by hydrogen bonds is supported by the shift of C-O-C vibrations. The C-O-C vibration of pure calix occurs at 1060 cm^{-1} and it gets shifted to 1061 cm^{-1} and 1062 cm^{-1} as the concentration of Calix4 increases. Here the complexation occurs between the linking of polyether chains by hydrogen bonds and due to the weak interactions between the polyether oxygen atom and calix4 molecules. It shows Γ peak broadening which indicates that the complex has become

more amorphous and other moieties such as contact ions has also formed in the PEO-
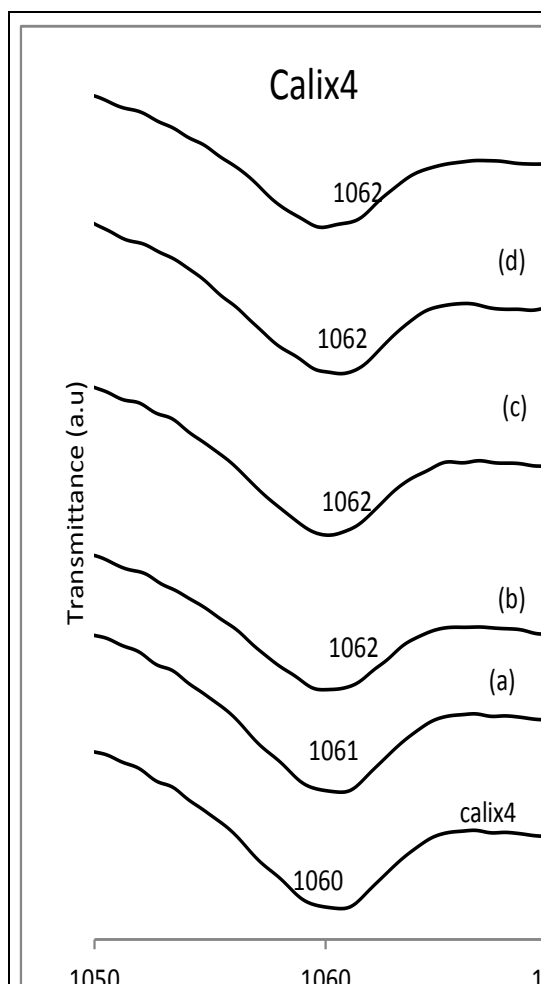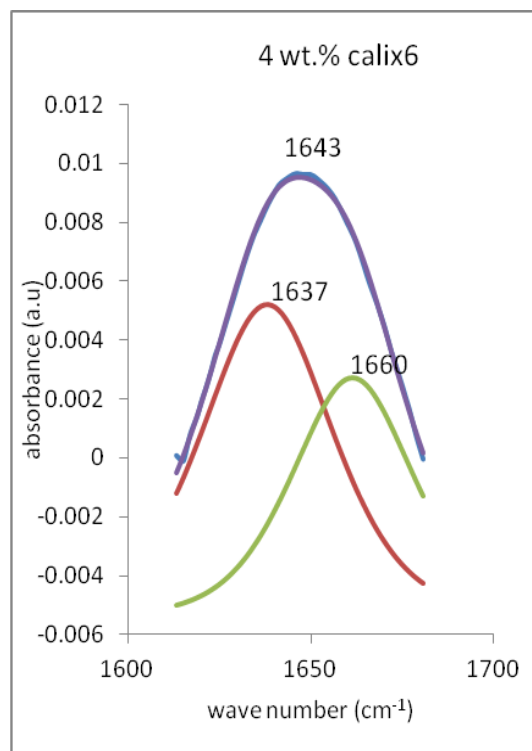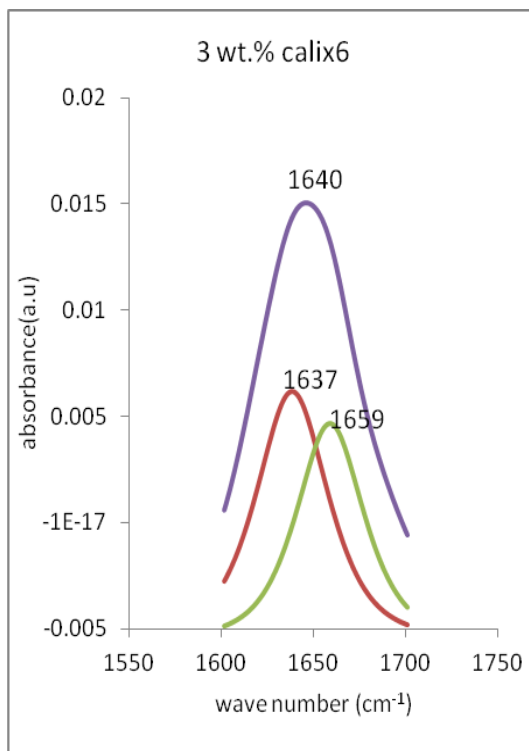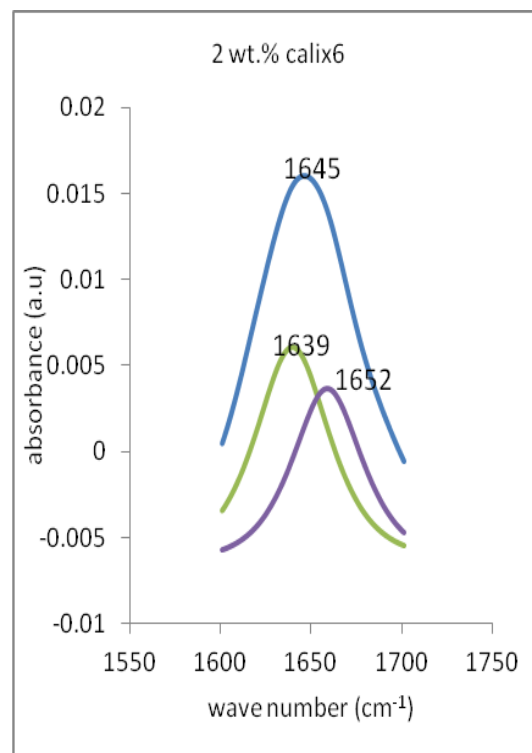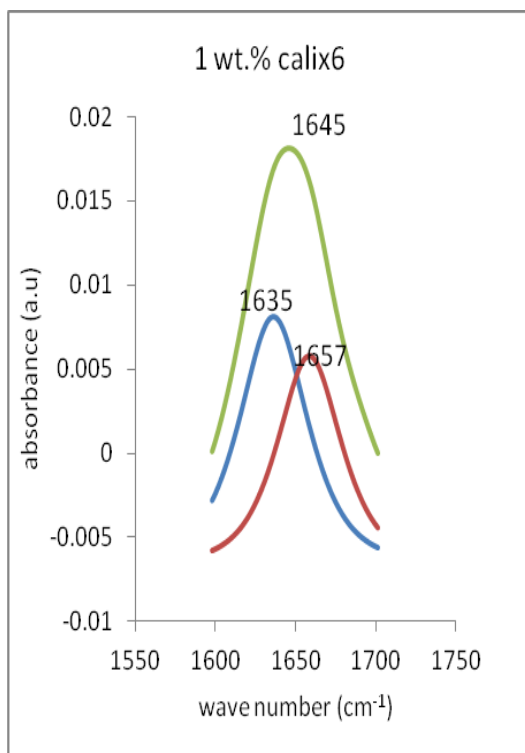
LiI –calix6 system.

Figure 4.24: FTIR spectra of Calix4 and PEO –LiI –calix 4(1%- 5%); (a)89.1wt.% PEO : 9.9 wt.% LiI : 1 wt.% Calix 4, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 4, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 4 (d) 86.4 wt.% PEO : 9.6wt.% LiI : 4 wt.% Calix 4,(e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5wt.% Calix 4

Same trend can be obtained by the addition of calix6 molecule to PEO-LiI system. In

Figure 4.25 represents the deconvoluted peaks for the LiI peak at 1640 cm^{-1}. From the

deconvoluted peak we can measure the formation of free ions and contact ions by the
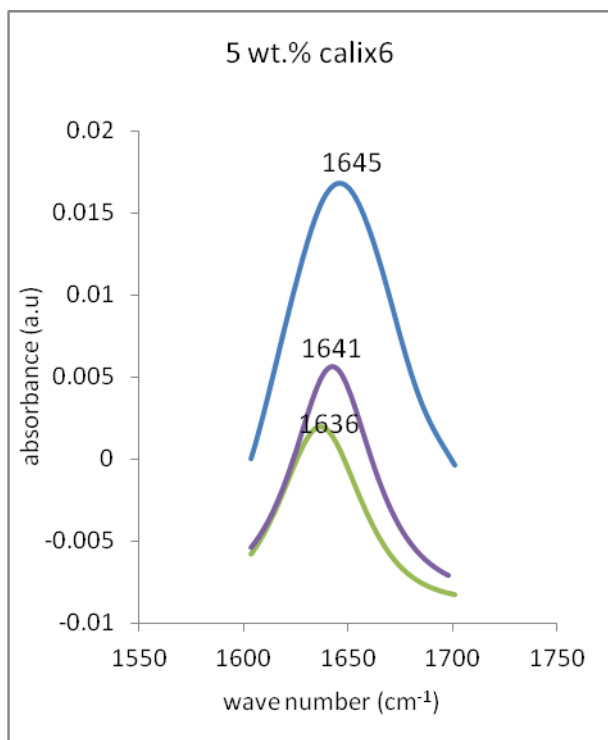
addition of different wt.% of calix6.

Figure 4.25: Deconvoluted peak for 1640 cm^{-1} for PEO-LiI- Calix6 system

The free ion peaks are located at 1635 cm^{-1} for 1 wt.% of calix6, at 2 wt.% it can be seen at 1639cm^{-1}, for 3 wt.% it is at 1637 cm^{-1} and for 4 wt.% and 5 wt.% it is at 1637 cm^{-1} and 1636 cm^{-1}. The contact ions are at 1657 cm^{-1} and 1645 cm^{-1} for 1 wt.% of calix6, 1645 cm^{-1} and 1652 cm^{-1} for 2 wt.%, 1640 cm^{-1} and 1659 cm^{-1} for 3 wt.%, 1643 cm^{1}, 1660 cm^{-1} for 4 wt.% and 1659 cm^{-1}, 1641 cm^{-1} and 1645 cm^{-1} for 5 wt.% calix6.

Figure 4.26 represents the percentage of free ions and contact ions in PEO-LiI-calix6 system. The percentage of free ion increase to maximum for 3wt.% of calix4 and calix6 system and starts decreasing whereas the percentage of contact ions decreases to minimum for 3 wt% of calix4 and calix6 systems.
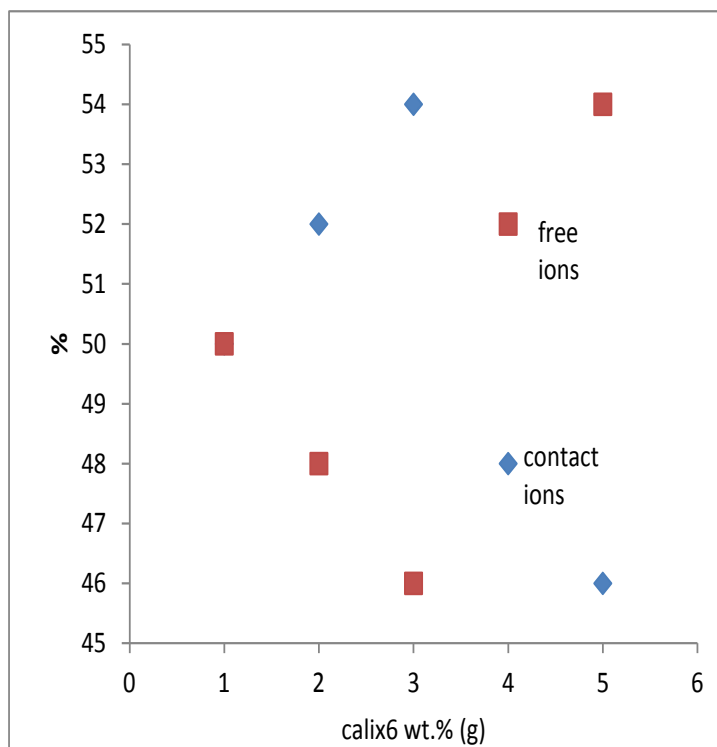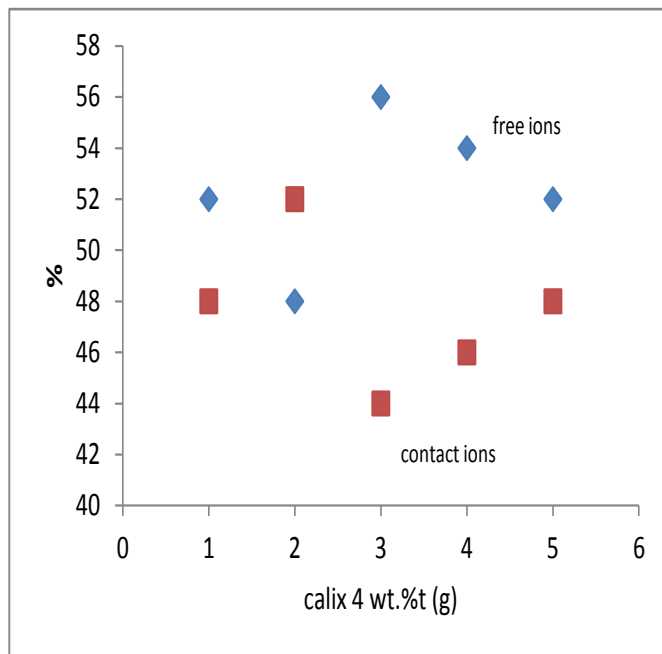
Figure 4.26: The % free ions and contact ions in the PEO-LiI-Calix system

Figure 4.27 and 4.28 also show the similar interactions between polymer - salt complex with the calix6 arenes as in calix4.

In Figure 4.27 the peak at 1652 cm^{-1} can be superposition of peaks attributed to weakly and strongly associated carbonyl group of the calix compounds. The peak at 1700 cm^{-1} corresponds to free carbonyl group of the calix molecules. In the spectra, peak for lithium iodide appears at 1635 cm^{-1} which originally appear at 1619 cm^{-1} in the PEO-LiI system (Pawlowska et al. 2007). These shifting shows by the addition of macromolecules to polymer salt system there is stronger interactions may occur linking calix6 arene and cation Li$^+$ and weaker ones between anions I$^-$ and calix arenes.
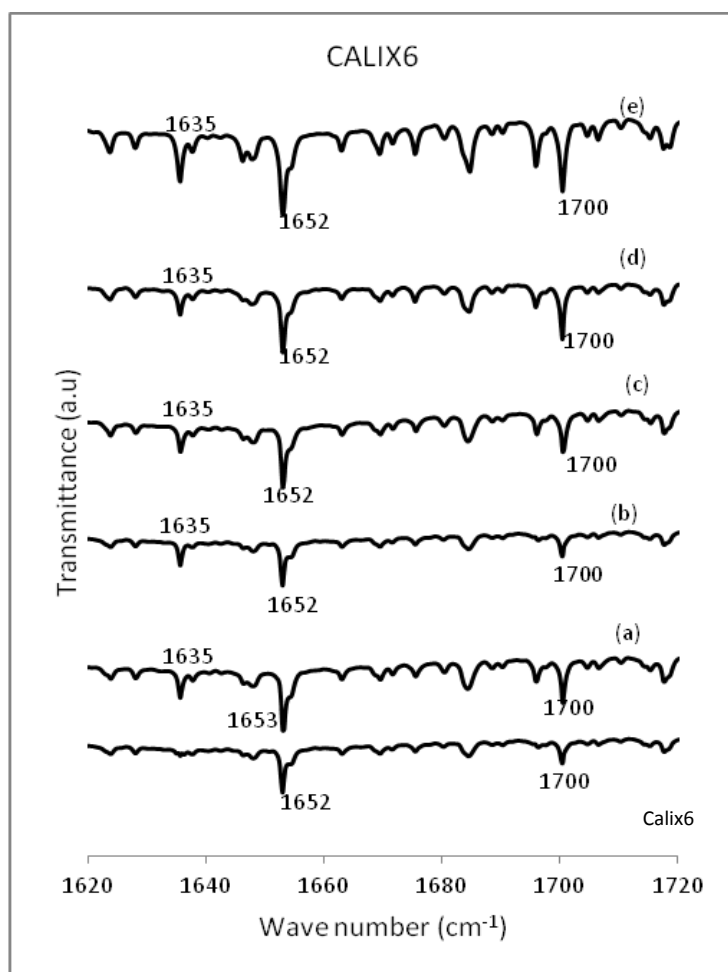

Figure 4.27: FTIR spectra of Calix 6 and PEO –LiI –calix 6(1%- 5%); (a)89.1wt.% PEO : 9.9 wt.% LiI : 1wt.% Calix 6, (b) 88.2wt.% PEO : 9.8wt.% LiI : 2 wt.% Calix 6, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 6 (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix6, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix6

Figure 4.28 depicts the crystallinity peak. For pure calix6 the crystallinity peak appears at 1279 cm^{-1}, it gets broader and shifted to 1280 cm^{-1} for 1 wt. %, 1282 cm^{-1} for 2 wt. %, 1280 cm^{-1} for 3 wt. %, 1281 cm^{-1} for 4 wt. %, and 1282 cm^{-1} for 5 wt. % calix6 containing samples. The broadening can be shown in Figure 4.29 by measuring the FWHM of the peak.
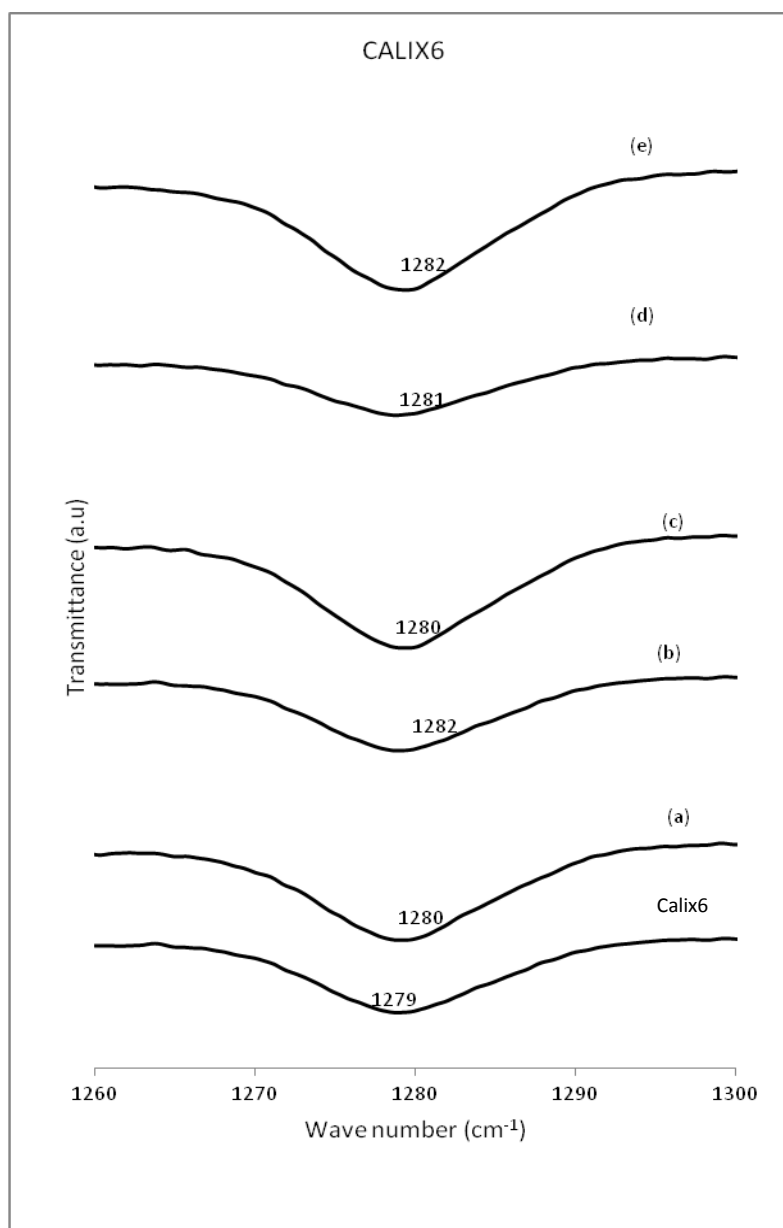

Figure 4.28: FTIR spectra of Calix6 and PEO –LiI –calix 6(1%- 5%); (a)89.1 wt.% PEO : 9.9 wt.% LiI : 1 wt.% Calix 6, (b) 88.2 wt.% PEO : 9.8 wt.% LiI : 2 wt.% Calix 6, (c) 87.3 wt.% PEO : 9.7 wt.% LiI :3 wt.% Calix 6 (d) 86.4 wt.% PEO : 9.6 wt.% LiI : 4 wt.% Calix6, (e) 85.5 wt.% PEO : 9.5 wt.% LiI : 5 wt.% Calix6

Figure 4.29 depicts the FWHM for peak at 1279 cm^{-1} where can observe that at 3 wt.% of calix6 the amorphous nature increases. The FWHM is calculated using Ominic software.
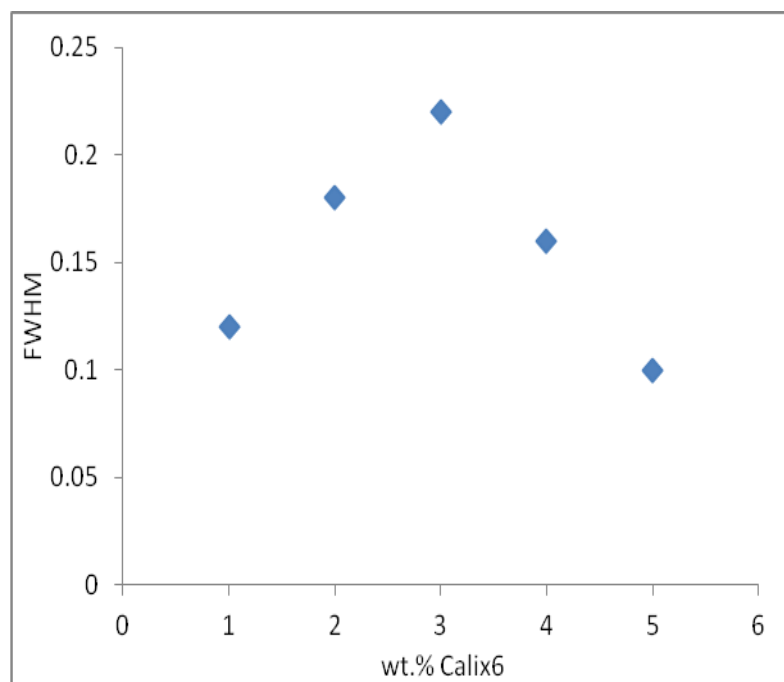

Figure 4.29: The FWHM for peak at 1279 cm^{-1}

In Figure 4.30, the C-O-C vibration of pure calix6 occurs at 1098 cm^{-1} and its gets broader and shifted to 1106 cm^{-1} as the wt.% of Calix6 increases to 5 wt. % due to the complexation between the linking of polyether chains by hydrogen bonds and due to the weak ionic interactions.
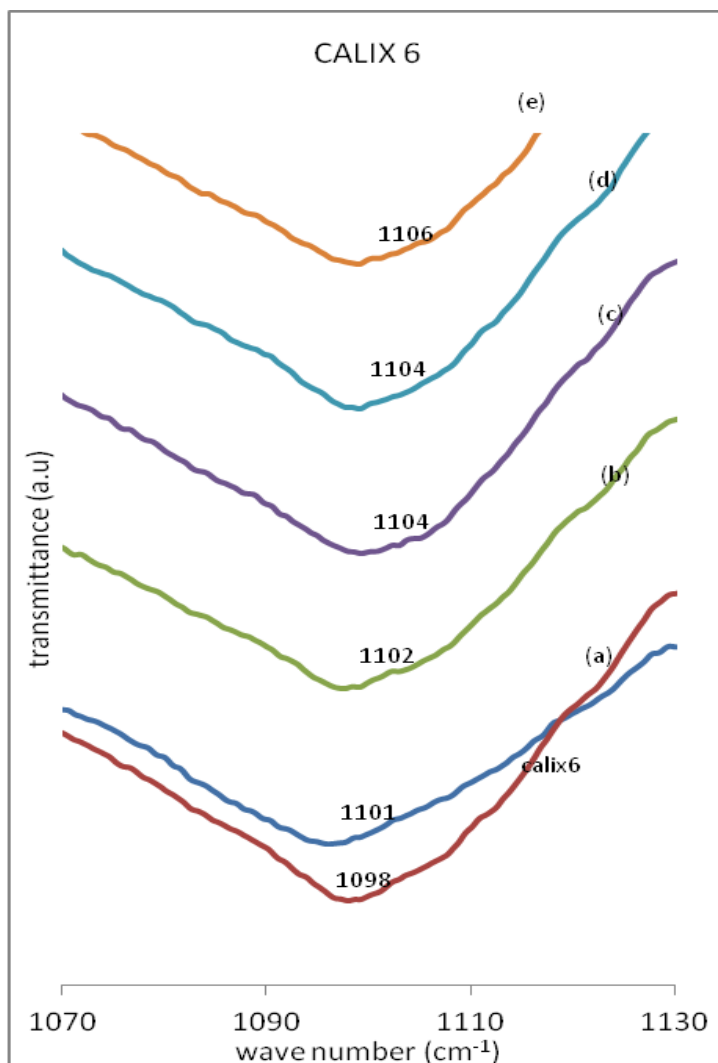
Figure 4.30: FTIR spectra of Calix 6 and PEO –LiI –calix 6(1%- 5%); (a)89.1wt.% PEO : 9.9wt.% LiI : 1wt.% Calix 6, (b) 88.2wt.% PEO : 9.8wt.% LiI : 2wt.% Calix 6, (c) 87.3wt.% PEO : 9.7wt.% LiI :3wt.% Calix 6 (d) 86.4wt.% PEO : 9.6wt.% LiI : 4wt.% Calix6, (e) 85.5wt.% PEO : 9.5wt.% LiI : 5wt.% Calix6

From all these shifting and broadening of the peaks there is indication that complexation happens between calix arenes with the polymer salt system. To confirm complexation we need to study about this in more detail in the XRD and Conductivity measurement chapters.
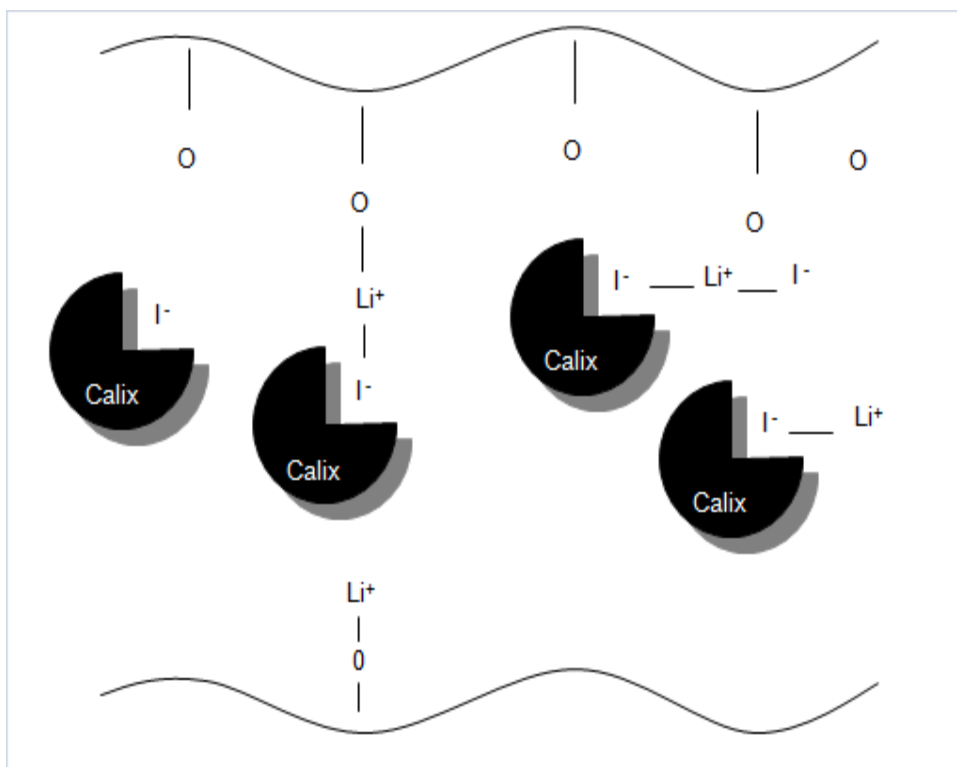
Figure 4.31: A diagram illustrating the various types of the activity of the active filler against the anions of the polymeric electrolyte Ciosek et al., 2007.

The peaks, far less intense are also found in the FTIR spectra of polymer salt systems with organic additives calix4 and calix6 arenes. It shows that there are interactions between polymer salt system and the additives.

The study of FTIR data of calix6 arenes and calix4 arenes has shown that it has higher ability to form complexes with polymer matrix. The shifting of LiI band had shown that the I^- may be bonded to the free OH group through dipole interactions or through weak van der Waal forces. On the basis of our results we can assume that calix arene derivatives may be successfully used as receptors to immobilise the I^- anions as shown in the above diagram. We can confirm the complexation of polymer salt system with organic macromolecule anion receptor with XRD studies that we are dealing with in the following chapter.

Figure 4.32 and Figure 4.33 had shown the immobilisation of I⁻ by dipole forces or
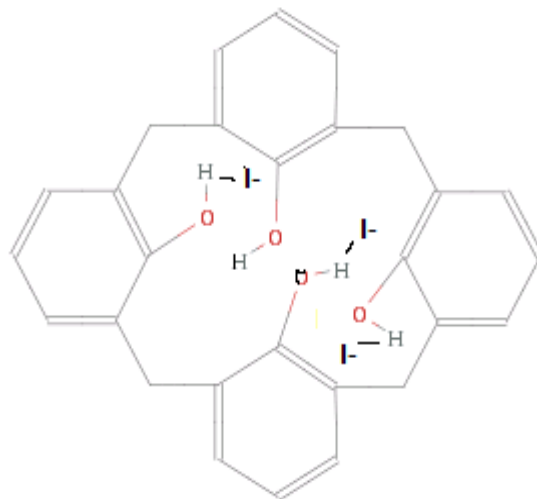
weak van der Waal forces in calix4 and calix6 molecules.

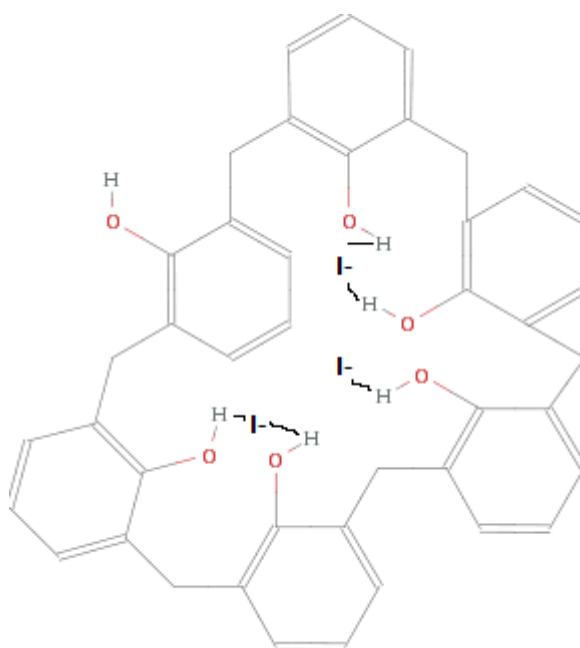**Figure 4.32 : The possible anion trapping in calix4 arenes**

Figure 4.33: The possible anion trapping in calix6 arenes.

Figure 4.34 is the pictorial representation for anion trapping in calix arenes. I^- might be the large guest molecule trapping inside the calix due to the weak dipole interactions.
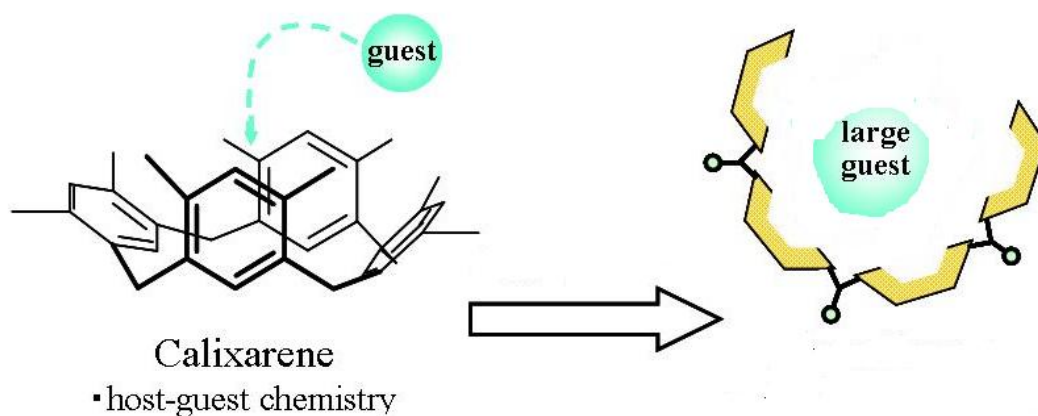

Figure 4.34: Pictorial representation of anion trapping in calix arenes [Paul Karpcho, 2007]

4.5 Summary

It is well known that ion motion is not simply the diffusion of a single ion or ion cluster, but rather involves the formation of different coordination environments around the mobile ions. The increase in conductivity is due to the ion-ion and ion-polymer interactions caused by the filler. By adding filler like Al_2O_3 and macromolecules like Calix4 and calix6 which helps in preventing crystallization of polymer chains. It also, in particular in promoting specific interactions between the surface groups and both the PEO segments and the electrolyte ionic species. This study will help to verify the observations in the X-ray diffractograms in the next chapter.FTIR spectroscopy is an effective tool for examining such conformational changes. From our studies FTIR spectroscopy studies we have confirmed

- there is occurrence of complexation between PEO and LiI salt

- formation of ion pairs/clusters

- by adding LiI salt, inorganic Al_2O_3 and organic macro molecules like calix4 and calix6 arenes the crystallinity of polymer electrolyte reduces and it becomes more amorphous.

- complexation occurs due to the hydrogen and weak ionic interactions between the LiI and polymer.

- The decrease in conductivity is due to the anion trapping in the calix4 and calix6 arenes by weak van der Waal's forces and dipole dipole interactions.

These modifications reflect complexation between the salt molecule with the polymer inorganic and organic fillers. This can contribute in the enhancements of the ionic conductivity over a wide range of temperature,that we are going to deal with in the following chapter.