CHAPTER V
INFRARED SPECTROSCOPY
5.1 Introduction

Infrared spectroscopy was used to detect the existence of the specific interactions in polymer electrolytes. It is a powerful tool to study the mechanism of interpolymer miscibility through the bond formation; both qualitatively and quantitatively. The pure Polyethylene Oxide has two bands at 1360 and 1340 cm\(^{-1}\) have crystalline phase and 1350 cm\(^{-1}\) corresponds to amorphous phase of PEO \(^{(1,2)}\).

The vibration spectra can be calculated by the local mode method \(^{(4)}\). In this method the slow motions are calculated by using classical simulation techniques. The fast vibrations can be determined using quantum mechanical calculations for each vibration and configuration. The local effective potential function can be calculated by

\[
V^{\text{eff}}(Q) = K_0 + K_2 Q^2 + K_3 Q^3 + K_4 Q^4
\]

This potential function will be utilized to solve the 1-Dimensional Schrödinger equation

\[
\frac{\hbar}{4\pi M} \left[ \frac{d^2}{dQ^2} + V^{\text{eff}}(Q) \right] \psi(Q) = E \psi(Q)
\]

Where \(M\) is the G matrix of normal mode analysis \(^{(3)}\). The characteristics ratio as a limit of \(C_n\) as \(n \rightarrow \infty\) is defined as

\[
C_n = \frac{\langle r^2 \rangle}{\sum l_i^2}
\]

Where \(\langle r^2 \rangle\) is the mean square end-to-end distance of the chain, \(n\) is the number of bonds and \(l_i\) are the lengths of the bonds.
Infrared spectroscopy has been widely used for the identification of the functional groups in organic compounds because of the fact that their spectra are generally complex and numerous maxima and minima can be used for comparison purpose. In fact, the infrared absorption spectrum of an organic compound represents one of its true physical properties.

From application and instrumentation point of view, the infrared region has been subdivided into three parts.

(i) Near infrared region \(14290 - 400 \text{ cm}^{-1}\) (0.7 – 2.5 \(\mu\text{m}\))
(ii) Middle infrared region \(4000 - 666 \text{ cm}^{-1}\) (2.5 – 15 \(\mu\text{m}\))
(iii) Far infrared region \(700 - 200 \text{ cm}^{-1}\) (14.3 – 50 \(\mu\text{m}\))

In the present investigation, the infrared spectrum of polymer electrolyte films was recorded on a JASCO FT/IR-5300 spectrophotometer in the range of \(400 - 4000 \text{ cm}^{-1}\).

The infrared spectrum of a simple diatomic molecule may contain a great many lines while that of poly-atom may be extraordinarily complex, even though some of the details of fine structure are blurred by insufficient resolving power. Although in favorable cases much information may be obtained about bond lengths and angles or at least the general shape of the molecule, in others even the assignment of observed bands to particular molecular vibrations is not trivial.
Assignments are based mainly on experience with related molecules on the band contour (from which the type of vibrations parallel or perpendicular can usually be deduced). Consideration of the symmetry of the molecule is also important because this determines which vibrations are likely to be infrared active. Fortunately the usefulness of IR spectroscopy extends far beyond the measurement of precise vibrational frequencies and the molecular structural features. Because of the 3N-6 and 3N-5 rules it is evident that a complex molecule is likely to have an infra-red spectrum exhibiting a large number of normal vibrations. Each normal mode involves some displacement of all, or nearly all the atoms in the molecule, but while in some of the modes all atoms may undergo approximately the same displacement, in others the displacements of a small group of atoms may be much more vigorous than those of the remainder. Thus we may divide the normal modes into two classes: the skeletal vibrations, which involve many of the atoms to much the same extent, and the characteristic group vibrations, which involve a small portion of the molecule, the remainder being more or less stationary.

For organic molecules these usually fall in the range 1400-700 cm\(^{-1}\) and arise from linear or branched chain structures in the molecule. Group frequencies are usually almost independent of the structure of the molecule as a whole and, with a few exceptions; fall in the regions well above and well below that of the skeletal modes. The vibrations of light atoms in terminal groups (for example -CH\(_3\), -OH, -C≡N etc.,) are of high frequency, while those of heavy atoms (-C-Cl, -C-
Br, metal-metal etc.) are low in frequency. Their frequencies and consequently their spectra are highly characteristic of the group, and can be used for analysis.

More detailed investigations of the complexation of iodine, NaI, KI, and LiClO₄ and fillers doped polyethylene oxide has been performed with the help of infrared vibrational spectroscopic studies using Jasco FT/IR-5300 spectrophotometer.

5.2 RESULTS AND DISCUSSIONS

The pure PEO spectra was broad and intense γ (CH₂) band centered at 2888 cm⁻¹ in Pure PEO splits into two small bands in the PEO/alkali metal halides electrolytes. This may be due to the interaction between the oxygen atoms of the pure PEO chain and the inter layer cation. As compared to bulk PEO, another major difference is in the positions of the mid IR band of the interpolated PEO. The CH₂ deformations in this region are sensitive to the PEO chain structure to distinguish PEO and host layers. The helical PEO has a structure in which the O-CH₂-CH₂-O has an all-gauche conformation (5). The percentage of transmission was increased and shifted towards lower frequencies and was observed in order of 1%, 2%, 5% and with filler TiO₂ (1%). Figure 5.5 deals with exact difference of transmission of wavelengths of Pure, Iodine (2%), Iodine (5%) and Iodine (2%) + TiO₂ (10%) spectra's were presented. We also observed new peaks in filler doped samples.
We observed in Chapter 3 large spherulites with diameter of about 175μm in PEO/LiClO$_4$ electrolyte. In addition, the crystal boundaries connect closely with each other. Only a little continuous amorphous phase among the crystal domain was observed. With other dopants, the spherulites become much smaller with diameter of about 25μ, and the fraction of amorphous increases greatly. All the amorphous domains form a continuous pathway, where Li$^+$ cation can move freely and quickly with most of the polymer section. Hence the conductivity increases in the polymer electrolytes.

Figures 5.6 and 5.7 depict the IR spectra's of PEO with NaI (2%) and NaI (5%). The exact transmission peaks are compared with pure PEO and NaI doped samples are represented in figure 5.8. It is clearly observed that there are bands of transmission peaks in NaI (2%) samples and the band with wave numbers of NaI (5%) are also identified. PEO like character of the material (6-9) in the alcohol groups C-OH and O-H stretching absorption is seen in our IR spectra's. The IR absorption bands of carbonyl groups (around 1700-1800cm$^{-1}$) and O-H stretching (3200cm$^{-1}$) are not detected, a contribution to these components from acetal moieties, in which carbon is bonded to more than one alkoxyl group, is observed. The transmission IR spectra gives information related to the entire sample of the PEO.

Figure 5.9 and Figure 5.10 shows the IR spectra of PEO with KI (2%) as toluene solvent and PEO with KI (2%) The IR spectra of Pure PEO and PEO complexed with KI are shown in figure 5.11. The intensity of aliphatic C-H
stretching vibration band observed around 2950 cm\(^{-1}\) in PEO is found to increase with increasing the concentration of KI salt in the PEO.

IR spectroscopy is a useful tool for studying the interactions of inorganic electrolytes with polymeric matrices. The present systems diagnostic bands for complexation are, the carbonate carbonyl stretching frequency (1741 cm\(^{-1}\)), the carbonate C-O frequency (1275 cm\(^{-1}\)) and the C-O-C ether stretching frequency (1113 cm\(^{-1}\)). For the characteristic frequency of the carbonyl unit no significant changes are observed (other than broadening of bands). With increasing salt concentrations in the system NaI/PEO, a broadening of the bands is first observed. Figure 5.16 depicts the IR spectra of Pure PEO, PEO with LiClO\(_4\) (2%), PEO with LiClO\(_4\) (5%), PEO with LiClO\(_4\) (2%) and TiO\(_2\) (20%), PEO with LiClO\(_4\) (1%) and filler BaZnTiO\(_3\) (20%). This observed chemical shift to be attributed that the electrons surrounding the Li anion deprived by the addition of the filler. In other words the attractive force between the Li cation and anion is reduced by the negative charge in TiO\(_2\). The IR spectra indicate that the existence of fillers enhances the dissolution of the Li salt and thus increase the fraction of free anion. However the balanced attractive forces among the fillers ether groups and Li cations produce an optimum conductivity.

Therefore the appearance of new peaks along with changes in existing peaks in the IR-spectra directly indicates the complexation of PEO with alkali metal salts. The carbonyl stretching band at 1800 cm\(^{-1}\) is sensitive to the complexation of the Li\(^+\) cations to the carbonyl oxygen. The perturbation to the carbonyl band in the presence of Li salts arises from complexation of Li\(^+\) action to
the carbonyl oxygens are more expensive and the larger the complexation, larger the spectrum perturbation. This is indirect evidence that the Li⁺ is somehow complexed to the PEO site chains. As increasing amounts of iodine are added to PEO, its carbonyl band broadens and shifts to lower frequencies in a manner consistent with previously reported IR spectra on LiClO₄ dissolved in PEO(2).

From the IR spectra shown in Figure (5.1-5.12) and from the Table-1, the following changes in the spectral feature have been observed by comparing the spectrum of complexed PEO with that of PEO polymer:

(a) The intensity of the aliphatic O-H stretching vibrations band observed around 3512 cm⁻¹ in pure PEO and is found to decrease in alkali metal complexed PEO samples.

(b) The intensity of the aliphatic C-H stretching vibrations band observed around 2956 cm⁻¹ in pure PEO is found to decrease in alkali metal complexed PEO samples.

(c) The width of the C-O stretching band observed around 1277 cm⁻¹ in pure PEO is found to decrease in alkali metal complexed PEO samples.

(d) Several new peaks around 2888.66 cm⁻¹, 1969.36 cm⁻¹, 952.57 cm⁻¹ and 437.83 cm⁻¹ have been observed in complexed PEO.

(e) The peak observed in pure PEO at 527 cm⁻¹ will disappeared.
(f) The peak observed in pure PEO at 3783 cm$^{-1}$ disappeared in almost all the alkali metal complexed PEO samples.

(g) Some of the peaks observed in pure PEO around 3659 cm$^{-1}$, 2956 cm$^{-1}$, 1951 cm$^{-1}$, 1814 cm$^{-1}$, 823 cm$^{-1}$ are found to be shifted in some complexed PEO samples due to the addition of alkali metal salts in the polymer.

The complexation of the PEO with alkali metal salts have been studied by using vibration spectroscopic studies (10-15). The appearance of new peaks along with the changes in the existing peaks in the IR spectra directly indicates the complexation of PEO with alkali metal halides. The decrease in the width of 1100 cm$^{-1}$ band was assigned to C-O symmetrical and asymmetrical stretching (13-15) suggesting the coordination/complexation of the salt with PEO. The details of the vibrational bands observed in these compounds are given in Table-5.1
Figure 5.1 Shows the IR spectra of Pure PEO
Figure 5.2 Shows the IR spectra of PEO with Iodine (2%)
Figure 5.3 Shows the IR spectra of PEO with Iodine (5%)
Figure 5.4 Shows the IR spectra of PEO with Iodine (5%) and TiO$_2$ (10%)
Figure 5.5. IR Spectra's of Pure, 2% Iodine, 5% Iodine and I (5%) + TiO₂ (10%) for comparison
Figure 5.6 Shows the IR spectra of PEO with NaI (2%)
Figure 5.7 Shows the IR spectra of PEO with NaI (5%)
Figure 5.8. IR spectra's of Pure, 2% Nal and 5% Nal for comparison
Figure 5.9 Shows the IR spectra of PEO with KI (2%) (Toluene solvent)
Figure 5.10 Shows the IR spectra of PEO with KI (2%) (Acetonitril solvent)
Figure 5.11. IR spectras of Pure, 2% KI (toluene solvent) and 2% KI (acetonitril solvent)
Figure 5.12 Shows the IR spectra of PEO with LiClO$_4$ (2%)
Figure 5.13 Shows the IR spectra of PEO with LiClO₄ (5%)
Figure 5.14 Shows the IR spectra of PEO with LiClO$_4$ (1%) and TiO$_2$ (20%)
Figure 5.15 Shows the IR spectra of PEO with LiClO₄ (1%) and BaZnTiO₃ (20%)
Figure 5.16. IR spectra of Pure, 2% LiClO₄, 5% LiClO₄ and LiClO₄ (2%) + TiO₂ (20%), LiClO₄ (1%) and BaZnTiO₃ (20%) for comparison
TABLE 5.1: Various Vibrational bands observed in the IR spectra of PEO with metal alkali halides with fillers

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<th>PEO+ Iodine (5%)</th>
<th>PEO+ Iodine (5%)+ TiO₂ (10%)</th>
<th>PEO+ NaI (2%)</th>
<th>PEO+ NaI (5%)</th>
<th>PEO+ KI (2%)</th>
<th>PEO+ KI (2%)</th>
<th>PEO+ LiClO₄ (2%)</th>
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