Chapter 5

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5.4 Summary (160)
5.1 Introduction

Present thesis work is to study the ion transport studies of polymer salt complexes. Currently two types of materials are attracting great attention, (1) sodium based system with the hope to address drawbacks related to Li\(^+\) based systems (flammable, limited availability in nature, cost etc.) and (2) proton conducting materials. The second category of materials are useful for electrochromic devices, fuel cells, humidity sensors etc. They are generally based on acids and/or ammonium salts. Literature survey has indicated that ion dynamic behavior of ammonium salts based systems are negligibly studied.

Hence present system is dedicated to understand the ion dynamics of ammonium salt based systems. Same as in previous section three different anions (Cl\(^-\), I\(^-\) and PF\(_6^-\)) are selected. Ammonium salts consisting these anion are doped in same synthesized host polymer and prepared materials are analyzed on the same line of action as followed in previous chapter.

5.2 Experimental Details

5.2.1 Materials used

Triethylenetetramine (Loba Chemie), 1-3 propane sultone (Sigma-Aldrich), NH\(_4\)PF\(_6\) (Sigma-Aldrich), NH\(_4\)I (Loba Chemie), NH\(_4\)Cl (Loba Chemie), Glutaraldehyde (GA- Loba Chemie) and Methanol (Fisher Scientific) were used for synthesis of materials.

5.2.2 Preparation of polymer electrolyte films

In present case also the same preparation methodology is followed as was adopted for preparation of sodium salt systems and discussed in section 4.2.2, except that sodium salts are replaced by ammonium salts.
5.3 Results and Discussion

5.3.1 Structural study

In polymer-salt complexes salt is expected to act as a plasticizer also. This plasticizing behavior is observed in case of sodium salt doped materials. Here also XRD analysis has been carried out to confirm the plasticizing behavior. The X-ray diffraction (XRD) pattern of pure ZW and ZW + NH$_4$I containing different amounts of salt are shown in figure 5.01.

![X-ray diffraction profiles of pure ZW and ZW + x wt % NH$_4$I](image)

**Fig 5.01:** X-ray diffraction profiles of pure ZW and ZW + x wt % NH$_4$I

In the XRD pattern of pure ZW polymer a broad peak is observed nearly at 22°. After doping the salt broadness of the peak increases with increasing salt concentration. This increase in FWHM confirms that, in case of ammonium salt based systems also, with increasing the salt concentration, amorphosity of the polymer–salt complexes increases and salt acts as a plasticizer (Aji, M.P. et al., 2012). As discussed in previous (section 4.3.1) chapter, interaction between charge carrier and polymer segment hinders the alignment during the solution cast procedure and hence the crystallinity decrease after addition of salt. As the salt concentration increases, hindrance goes on increasing and...
hence amorphosity increases and after a certain limit of salt concentration system becomes completely amorphous.

5.3.2. Transference number and conductivity analysis

Ionic transference number confirms the electrolytic nature of the material. Here also DC polarization method (details discussed in Chapter 2) is used for estimation of ionic transference number. Figure 5.02 shows the polarization curve for ZW + NH₄I system and similar curves are obtained for the other two systems also. For all the three systems \( t_{\text{ion}} > 0.95 \) is obtained which indicates the electrolytic nature of the synthesized material.

Fig 5.02: Polarization curve for ZW +50 wt % NH₄I system

Nyquist plots for studied systems are shown in figure 5.03(a) ZW + NH₄Cl, 5.03(b) ZW + NH₄I and 5.03(c) ZW + NH₄PF₆. All the Nyquist plots consist of two regions (i) semi circle towards the high frequency region and (ii) spike towards the low frequency. Semicircle towards high frequency side is associated with bulk effect of material whereas the low frequency spike is correlated to the double layer capacitance at the blocking electrodes representing the polarization effect at electrode/electrolyte interface (Kim, C. et al., 1999; Bruce, P.G. et al., 1995). In the complex impedance plot,
intercept at real axis changes with salt concentration illustrating that total conductivity is mainly due to ionic conduction (Jacob, M.M.E. et al., 1997). Distribution of relaxation time causes the depression in semicircle. If the ion transport is Debye type then the centre of semicircle lies on the $Z'$ axis but if the system has distributed relaxation time then instead of a perfect semicircle having centre of $Z'$ axis a depressed semicircle, whose centre is below $Z'$ axis, is observe.
Depressed semicircle and tilled spike are correlated with leaky capacitor which are designated as constant phase element (CPE) (Omari, M.E. et al., 1998; Ahmad, M.M. et al., 2002). In inset of figure 5.03(b), an equivalent circuit is presented, which is a parallel and series combination of bulk resistance ($R_b$) and leaky capacitors CPE1 and CPE2 respectively. CPE1 is related with bulk and CPE2 is related with electrode electrolyte interface capacitor. At low salt concentration less number of charge carriers are coming to electrode and hence value of double layer capacitor is small so the curve is dominated by charge transfer resistance, whereas at higher salt concentration number of charge carriers are larger hence the value of double layer capacitor is large and Nyquist plot at low frequency portion is dominated by capacitive nature. In polymer-salt complexes conductivity varies with addition of salt and passes through minima and maxima. Therefore, it indicates that in polymer-salt complexes, dissociation of salt and numbers of available charge carriers are not directly related to the amount of salt concentration. In present study also, same phenomena is observed for all the three salts as shown in figure 5.04. Here also the smaller anion ($\text{Cl}^-$) based system is the highest.
conducting system, which indicates that probably anion is the dominating charge carrier in the present series also. Here NH₄I system is the less conducting than NH₄PF₆ containing system which may be attributed to greater possibility of polyiodide formation in NH₄I system (Kumar, M. et al., 2012). It seems that polyiodide present in the system has greater size than PF₆⁻ and hence the maximum conductivity achieved for NH₄I system is smaller than that of NH₄PF₆ based system.

Trend shown in figure 5.04 are the typical behavior of polymer–salt complexes. The detailed explanation is given in previous chapter. To understand the effect of salt concentration on dissociation of salt and/or number of charge carriers, fractional number of dissociated charge carriers (N/N₀) as a function of salt concentration three systems are plotted as shown in figure 5.05. This is a typical behavior of polymer–salt complexes.

Fig 5.04: Variation of conductivity with salt concentration for three ammonium salts.
Fig 5.05: Variation of fractional number of dissociated charge carriers with salt concentration for three salt systems.

To understand the conductivity behavior further, total numbers of charge carriers are calculated. Figure 5.06 shows values of the numbers of charge carriers (N) as a function of salt concentration for ZW + NH₄I, ZW + NH₄Cl and ZW + NH₄PF₆ systems.

Fig 5.06: Variation of total number of charge carriers with salt concentration for three ammonium salt systems.
As discussed in previous chapter different methods could be found in literature for the calculation of the number of charge carriers (Klein, R.J. et al., 2006; Wang, Y. et al., 2013). Since these formulas are derived after many assumptions, hence the calculated number of charge carriers varies from method to method. Hence here also the estimated values are used for qualitative discussion only. In all the three systems, number of charge carriers have a minimum, when plotted as a function of salt concentration. It is associated with ion- pair formation in the mid salt concentration range.

### 5.3.3 Temperature dependent conductivity study

![Graph of conductivity vs temperature for ammonium systems](image)

**Fig 5.07:** Variation of conductivity with temperature for three different ammonium systems for maximum conducting salt wt%.

Figure 5.07 shows the temperature dependent conductivity for maximum conducting material of all the ammonium salt based systems. The continuous increase in the conductivity with temperature may also be attributed to increase in the amorphosity. Due to increase in the amorphous nature, the polymer chain acquires faster internal modes in which bond rotation produces segmental motion. This supports interchain and
intrachain hopping of ions and conductivity of the polymer electrolytes thus becomes high.

In studied temperature range all the conductivity vs 1000/T curves are showing a linear nature indicating Arrhenius type of behavior which can be given by following equation-

\[
\sigma = \sigma_0 \exp \left( - \frac{E_a}{k_B T} \right)
\]  

(5.01)

where \(\sigma_0\) is pre-exponential factor, \(E_a\) is activation energy, \(k_B\) is Boltzmann’s constant, and \(T\) is the ambient temperature. The activation energy is calculated using above equation and shown in table 5.01.

<table>
<thead>
<tr>
<th>Polymer electrolyte system</th>
<th>Conductivity (Scm(^{-1}))</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZW + NH(_4)Cl</td>
<td>1.30x10(^{-2})</td>
<td>0.32</td>
</tr>
<tr>
<td>ZW + NH(_4)I</td>
<td>5.65x10(^{-4})</td>
<td>0.28</td>
</tr>
<tr>
<td>ZW + NH(_4)PF(_6)</td>
<td>3.31x10(^{-3})</td>
<td>0.25</td>
</tr>
</tbody>
</table>

5.3.4  Frequency dependent conductivity study

As discussed in the chapter 4 that ion dynamics of any system could be easily understood by analyzing the conductivity curve as a function of frequency. Changing value of exponent with frequency indicates that different ion dynamics exist in the entire frequency region and it is only a statistical probability that a particular type of ion dynamics exists in a particular frequency region. Figure 5.08, 5.09 and 5.10 shows the frequency dependent conductivity curve at different temperature for ZW + NH\(_4\)Cl, ZW + NH\(_4\)I and ZW + NH\(_4\)PF\(_6\) systems and in inset of figure 5.08, 5.09 and 5.10 with salt concentration. Here also the conductivity curve can be divided into three regions. Polarization region (region I) towards low frequency, dc conductivity region (region II)
indicated by a plateau in the mid frequency region and the dispersion region (region III) observed towards higher frequency side.

**Fig 5.08:** Frequency dependent conductivity curve at different temperature for ZW + NH$_4$Cl system and in inset with salt concentration.

**Fig 5.09:** Frequency dependent conductivity curve at different temperature for ZW + NH$_4$I system and in inset with salt concentration.
Another way to analyzing these three curves is by dividing (after removing the polarization region) them into two- (i) thermally active region and (ii) thermally inactive region. Jonscher region is thermally active region. With increasing temperature the plateau region and dispersive region, shifts towards upward side whereas high frequency side curves have a tendency to collapse and such type of trend indicates a presence of cage movement of ions (NCL/SLPL type phenomenon) (Leon, C. et al., 2002).

5.3.5 Scaling of conductivity data

Variation of salt concentration and/or temperature may influence the conductivity by changing number of charge carriers and/or mobility or they may also affect the underlying charge transport mechanism. Scaling the conductivity data is a simple technique to differentiate between two. Scaling is nothing but overlapping of different data sets in to a single master curve after applying a suitable normalizing technique. In present thesis Ghosh and Pan technique of scaling is followed. Here also the scaling parameter $\sigma_0$ and $\omega_p$ are estimated by method proposed in section 3.3.7.
Fig. 5.11: Scaling of frequency dependent curves at different salt concentrations and with temperature (in inset) for (a) ZW + NH$_4$PF$_6$ and (b) ZW + NH$_4$I system.

Figure 5.11 shows the scaled conductivity curve in complete experimental frequency range with different salt concentrations and in inset with temperature for ZW + NH$_4$PF$_6$ and ZW + NH$_4$I systems. Overlapping of the curves in to a single curve indicates that the charge transport mechanism is independent of composition and temperature i.e. doping concentration and temperature are affecting the charge concentration and mobility.
only. In case of NH₄PF₆ based system at 40% and 50% salt concentration $\omega_p$ was out of range hence scaling could not be realized. In case of NH₄I system at 10% and 20% salt concentration JPL region is not observed in the studied frequency range, hence these could not be included in scaled curve. The scaled conductivity spectra, with respect to salt concentration and temperature, collapsed in to a single master curve including UPL as well as SLPL region. This can be interpreted as existence of a single phenomenon for all the curves in complete experimental frequency range (Patro, L.N. et al., 2009; Sidebottom, D.L. et al., 1999; Roling, B. et al., 2000). For NH₄Cl based system, even at room temperature, $\omega_p$ was out of studied frequency range for all the salt concentration, hence scaling was not possible in this case.

5.3.6 Dielectric study

Figures 5.12(a&b), 5.13 (a&b) and 5.14 (a & b) show the variation of $\varepsilon'$ and $\varepsilon''$ (in inset) with salt concentration and temperature for ZW + NH₄Cl, ZW + NH₄I and ZW + NH₄PF₆ systems respectively. Both real and imaginary parts of dielectric constant rise sharply towards low frequency region due to electrode polarization effect. At high frequency, the periodic reversal of the electric field is so fast that excess ion diffusion in the direction of the electric field is not feasible. The polarization due to charge accumulation decreases leading to decrease in the value of $\varepsilon'$ and $\varepsilon''$ (Bhaskaran R. 2006). The low frequency relaxation shoulder seen in the loss curve is attribute to macroscopic polarization of the ionic charge carriers in the alternating field (Klein, R.J. et al., 2006; Macdonald, J.R. et al., 1953). The relaxation peaks shift towards higher frequency side with salt and temperature. Relaxation time decreases with salt and temperature due to increase in flexibility of the matrix (Aji, M.P. et al., 2012). Decrease in relaxation time with salt concentration can be correlated with plasticizing effect of added salt is indicated by XRD analysis.
Fig. 5.12: Variation of mod value of dielectric constant (5.12 a) and dielectric loss (5.12 b) with angular frequency at different temperature and in inset at different salt concentration for ZW + NH₄Cl system.
Fig. 5.13: Variation of mod value of dielectric constant (5.13 a) and dielectric loss (5.13 b) with angular frequency at different temperature and in inset at different salt concentration for ZW + NH₄I system.
Fig. 5.14: Variation of mod value of dielectric constant (5.14 a) and dielectric loss (5.14 b) with angular frequency at different temperature and in inset at different salt concentration for ZW + NH₄PF₆ system.
Fig. 5.15: Variation of $\frac{\partial \log \epsilon'}{\partial \log \omega}$ with $\log \omega$ at different salt concentrations for ZW + NH$_4$Cl system.

Fig. 5.16: Variation of $\frac{\partial \log \epsilon'}{\partial \log \omega}$ with $\log \omega$ at different salt concentrations for ZW + NH$_4$I system.
Fig. 5.17: Variation of $\frac{\partial \log \varepsilon'}{\partial \log \omega}$ with $\log \omega$ at different salt concentrations for ZW + NH$_4$PF$_6$ system.

Derivative curve ($\frac{\partial \log \varepsilon'}{\partial \log \omega}$ vs log $\omega$) of log $\varepsilon'$ vs. log $\omega$ passes through a dip, as shown in figure 5.15, 5.16 and 5.17 for different systems by varying the salt concentration. The frequency of dip is shifting towards the higher frequency with increasing salt concentration, it confirms the plasticization effect of salt.

5.3.7 Loss tangent and relaxation behavior study

Dielectric spectra are further analyzed in terms of loss tangent. Loss tangent is the ratio of dielectric loss and dielectric constant. $\tan\delta$ vs log $\omega$ curve can be analyzed to understand the distribution in relaxation time. As we know, the dispersion in electric function at higher frequency can be studied in terms of stretched Kohlrausch function (Williams, G. et al., 1970);

$$\varphi(t) = \exp\left(\frac{-t}{\tau}\right)^{\beta}$$

(5.02)

where $\tau$ is the characteristic relaxation time and $\beta$ represents the Kohlrausch-William-Watts (KWW) exponent. $\beta = 1$ represents the Debye type ion relaxation nature
whereas $\beta < 1$ indicates distribution of relaxation time. The exponent $\beta$ in the present case is determined using the FWHM value of the tan$\delta$ peak except for ZW + NH$_4$Cl at 50% salt concentration. Table 5.02 shows the calculated value of $\beta$ with salt concentration for NH$_4$Cl, NH$_4$I and NH$_4$PF$_6$ systems.

**Table 5.02:** KWW exponent ($\beta$) with salt concentration for ZW + NH$_4$Cl, ZW + NH$_4$I and ZW + NH$_4$PF$_6$ systems.

<table>
<thead>
<tr>
<th>Salt wt%</th>
<th>$\beta_{\text{NH}_4\text{Cl}}$</th>
<th>$\beta_{\text{NH}_4\text{I}}$</th>
<th>$\beta_{\text{NH}_4\text{PF}_6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.72</td>
<td>0.54</td>
<td>0.74</td>
</tr>
<tr>
<td>20</td>
<td>0.64</td>
<td>0.20</td>
<td>0.72</td>
</tr>
<tr>
<td>30</td>
<td>0.72</td>
<td>0.70</td>
<td>0.73</td>
</tr>
<tr>
<td>40</td>
<td>0.70</td>
<td>0.69</td>
<td>0.76</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>0.59</td>
<td>0.78</td>
</tr>
</tbody>
</table>

For all the cases, $\beta$ is less than 1, indicating a non-Debye type relaxation prevailing in the systems. It is a typical behavior of disordered systems.

In case of polymer electrolytes ion conduction relaxation is observed in higher frequencies range hence tan$\delta$ is analysed in log$\omega$ = 2 to 8 range. Variation of loss tangent as a function of frequency having different salt concentrations are shown figure 5.18(a), 5.19(a) and 5.20(a) for ZW + NH$_4$I, ZW + NH$_4$PF$_6$ and ZW + NH$_4$Cl systems. Well defined relaxation peaks can be seen in the curves. tan$\delta$ increases with frequency because the active component (ohmic) of current increases and it dominates over the reactive component (capacitive). After a peak tan$\delta$ decreases with frequency because active component is independent of frequency and reactive component increases in proportion to the frequency (Chopra, S. et al., 2003). The presence of relaxation peak or resonance in loss tangent can be explained as follows. The observed loss peaks also shifts towards higher frequency side with salt concentration. Since salt itself acts as a plasticizer (Aji, M.P. et al., 2012) hence amorphismity of the matrix increases due to which movement of charge carriers becomes easy resulting in shifting of peaks towards higher frequency side. To understand the effect of salt concentration on conduction mechanism the loss tangent
curve is further analyzed. The peaks are deconvoluted using “peak fit” software to understand the effect of salt concentration on conduction mechanism relaxation.
Fig. 5.18: (a) Variation of loss tangent with frequency at different salt concentration for ZW + NH₄I system (b) deconvoluted spectra of loss tangent of ZW + NH₄I system and (c) variation of conductivity and different relaxation times with salt concentrations respectively.
Fig. 5.19: (a) Variation of loss tangent with frequency at different salt concentration for ZW + NH₄PF₆ system (b) deconvoluted spectra of loss tangent for ZW + NH₄PF₆ system and (c) variation of conductivity and different relaxation times with salt concentrations respectively.
Figure 5.20: (a) variation of loss tangent with frequency at different salt concentration for ZW + NH₄Cl system, (b) deconvoluted spectra of loss tangent for ZW + NH₄Cl system and variation of (c) conductivity and different relaxation times with salt concentrations respectively.

Figure 5.18(b), 5.19(b) and 5.20(c) show the deconvoluted peaks for all concentrations of NH₄I, NH₄PF₆ and NH₄Cl based system respectively. As discussed in previous chapter, assignment of peaks to any phenomenon is generally perception based. The two peaks observed in studied pure polymer loss tangent curve, are normal mode \( (\omega_{\text{nor}}) \) relaxation and segmental mode relaxation \( (\omega_{\text{seg}}) \). As expected on addition of salt normal mode peak shifted towards lower frequency side and was out of studied frequency range.

On addition of salt, \( \omega_{\text{seg}} \) changes its strength and position according to conductivity, and hence associated with polymer segment assisted ion motion and denoted as \( \omega_1 \) in doped material. A new peak appears on higher frequency side which also changes its position with salt concentration and is denoted by \( \omega_2 \). The \( \tan\delta \) behavior can be better understood in terms of relaxation time \( \tau (= 1/\omega_{\text{peak}}) \). \( \tau_1 (= 1/\omega_1) \) and \( \tau_2 (= 1/\omega_2) \) are plotted in figure 5.18(c), 5.19(c) and 5.20(c) for NH₄I, NH₄PF₆ and NH₄Cl systems along with DC conductivity. In case of NH₄Cl system \( \tau_1 \) and \( \tau_2 \) for 50% salt
concentration could not be estimated because for this system resonance peak due to pseudo inductance dominated over the ion relaxation peak as shown in inset of figure 5.20(a).

For NH$_4$Cl and NH$_4$PF$_6$, $\tau_1$ and $\tau_2$ are following an inverse behavior in comparison to $\sigma_0$. Such kind of behavior of relaxation time is associated with polymer segment assisted ion transport mechanism. Hence for these two systems $\tau_1$ and $\tau_2$ are associated with relaxation of cation and anion. Since the smaller anion based system is having highest conductivity hence it is concluded that anion is the dominating charge carrier hence the peak with higher strength and towards higher frequency is associated with anion ($\tau_2$). In case of NH$_4$I system $\tau_1$ follows an inverse trend with $\sigma_0$ and hence is correlated with segment assisted anion motion. $\tau_2$ does not follow an expected trend. In case of NH$_4$I system due to iodine’s tendency of making poliyodides, ion-ion interaction may be very strong and hence $\tau_2$ may be associated with ‘ion mode’ relaxation. As observed in NaI based system here also at 50% salt concentration the relaxation time decreases sharply. At this salt concentration N/N$_0$ is very small which indicates formation of ion pair and hence a decrease in relaxation time is expected at this salt concentration. Hence, exceptionally high frequency peak (indicated as $\tau_3$ as in figure 5.19c) seems to be associated with a new phenomenon. Here also $\tau_3$ is associated with direct diffusion of ion through relaxation of ion- pair. Since ion pairing is required for such kind of transport hence though they are faster than polymer segment assisted motion but number of mobile charge will decrease and hence its peak strength decreases.

5.3.8 Electric modulus study

As discussed in previous chapter, the space charge polarization effect at lower frequency is so dominating that system’s dielectric relaxation phenomenon are obscured and hence ‘Electric modulus’ (M*) is also studied which suppresses the electrode polarization effect. Modulus analysis provides the information about the conductivity relaxation and ion dynamics (Kyritsis, A. et al., 1995; Ghosh, S. et al., 2003; Almond, D.P. et al., 1983; Karmakar, A. et al., 2012).
Figure 5.21, 5.22 and 5.23 show the variation of imaginary part of complex modulus with frequency at different temperatures and in inset at different salt concentration for NH₄I, NH₄PF₆ and NH₄Cl based systems respectively. The small value of modulus towards low frequency region confirms the ion conduction. Modulus peaks separate the region where ions are mobile over long distances (left side of peak) and where the ions are spatially confined to their potential wells (right side of peak) (Karmakar, A. et al., 2012). As the temperature increases, the movement of the charge carriers becomes faster due to increase in the flexibility of the material leading to decrease in the relaxation time and hence a shift is observed in the M'' peak towards higher frequency side. This behavior suggests that the relaxation is thermally activated.

The broadness of the M'' vs ω curve can be interpreted as distribution of relaxation time.

**Fig. 5.21:** Variation of mod of imaginary part of complex electric modulus with frequency at different temperatures and in inset at different salt concentration for ZW + NH₄I system.
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Fig. 5.22: Variation of mod of imaginary part of complex electric modulus with frequency at different temperatures and in inset at different salt concentration for ZW + NH₄PF₆ system.

Fig. 5.23: Variation of mod of imaginary part of complex electric modulus with frequency at different temperatures and in inset at different salt concentration for ZW + NH₄Cl system.

~ 159 ~
5.4 Summary

Ammonium salt based systems have similar behavior as that of sodium salt based systems. Here also the smaller anion containing system is exhibiting the highest conductivity indicating that probably in present series of systems, anions are the dominating charge carriers. XRD analysis has indicated the plasticization behavior of salt. Conductivity data is successfully scaled by estimating the scaling parameters as proposed in section 3.3.7. Here also in Cl\(^-\) and PF\(_6^-\) containing system two relaxations peaks are observed which inversely followed the \(\sigma_0\) and hence are associated with with polymer segment \(-\)assisted ion motion. In case of I\(^-\) based system here also \(\tau_2\) does not follow expected trend, and at 50% NH\(_4\)I concentration a fast relaxation peak is observed and here also it is associated with direct diffusion of ion.