

## CHAPTER 5

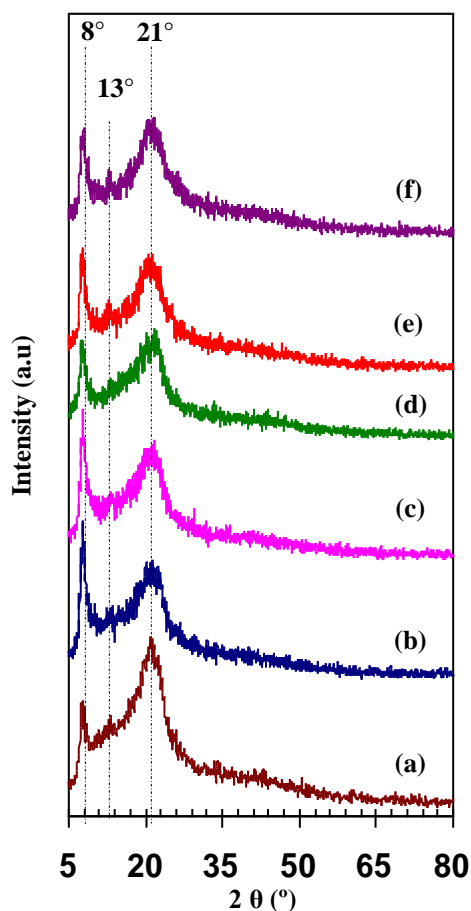
### PLASTICIZED MC-NH<sub>4</sub>NO<sub>3</sub> SYSTEM

#### 5.0 Introduction

The important parameter in the study of solid polymer electrolytes is conductivity. Currently, researchers are putting a lot of efforts to develop polymer electrolytes with excellent conductivity for application as separator in electrochemical devices such as batteries, capacitors, fuel cells, electrochromic devices and solar cells. The polymer-salt electrolytes only give room temperature conductivity around  $10^{-7}$  S cm<sup>-1</sup> and this is not sufficient in any application. To increase the conductivity, several methods have been tried of which plasticization is one of them. Plasticization is the addition of suitable chemical compounds with high dielectric constant and low viscosity to the polymer-salt electrolyte. Rajendran and Uma (2000) used dibutyl phthalate (DBP) as plasticizer in PMMA-LiBF<sub>4</sub> polymer electrolytes and obtained conductivity enhancement up to  $4.5 \times 10^{-3}$  S cm<sup>-1</sup> at 304 K. Every *et al.* (1996) studied the effect of water and DMSO as plasticizer in poly (2-acrylamido-2-methyl-propane-1-sulphonic acid) doped with lithium carbonate and sodium carbonate and found that the plasticization with water gives a higher conductivity compared to DMSO because water is a better coordinating solvent than DMSO.

## 5.1 X-ray diffraction (XRD) analysis

Figure 5.1 displays the X-ray diffractogram of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system at room temperature.



**Figure 5.1: XRD diffractogram for (a) 75MC25AN0PEG, (b) 71.25MC23.75AN5PEG, (c) 67.5MC22.5AN10PEG, (d) 63.75MC21.25AN15PEG, (e) 80MC20AN20PEG, (f) 56.25MC18.75AN25PEG**

It can be seen that, the 64 wt.% MC-21 wt.% NH<sub>4</sub>NO<sub>3</sub>-15 wt.% PEG is highly amorphous compared to samples containing other concentrations of PEG. This is based on the lower intensity of the peak at  $2\theta = 8^\circ$  and an increase in broadness of the peak at  $2\theta = 21^\circ$ . These results can be explained following Hodge *et al.* (1996) criterion as in Section

4.1. The degree of crystallinity of the samples with PEG concentration was evaluated and listed in Table 5.1.

**Table 5.1: Data of the degree of crystallinity of the samples**

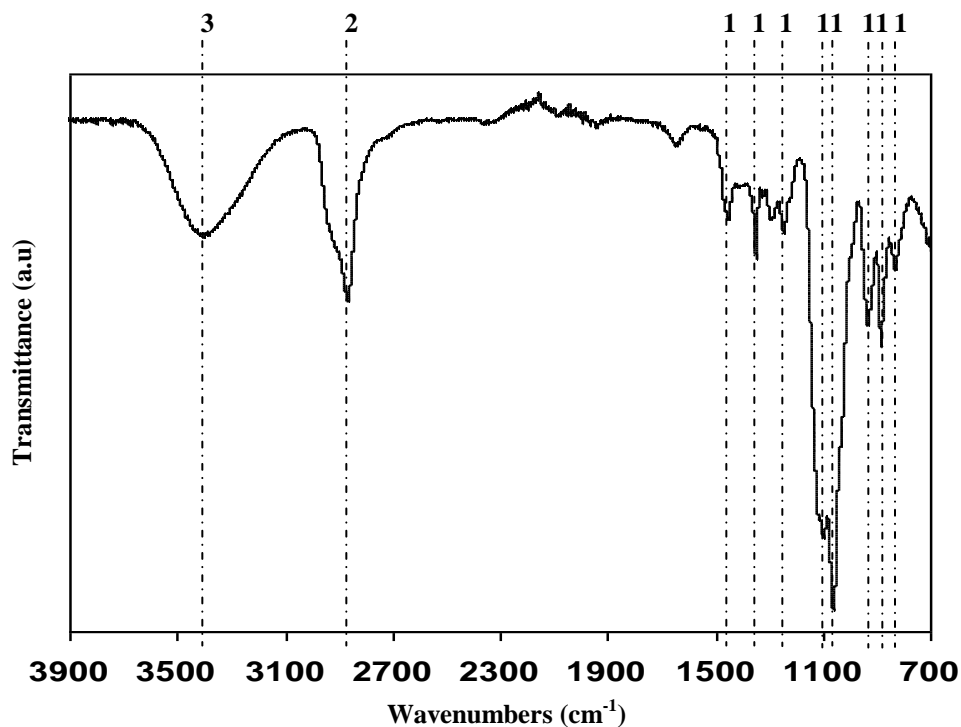
PEG concentration (wt.%)	$I_T$	$I_C$	$X_C$ (%)
5	0.5516	0.0237	4.2966
10	0.5218	0.0241	4.6186
<b>15</b>	<b>0.5005</b>	<b>0.0143</b>	<b>2.8571</b>
20	0.5407	0.0202	3.7359
25	0.5357	0.0161	3.0054

The decrease in crystallinity of the samples with PEG concentration from 5 to 15 wt.% reveals that the amorphous nature of the plasticized system increases up to 15 wt.% PEG. Beyond that, the crystalline fractions increase indicating that the samples are more crystalline. A new peak observed at  $2\theta \approx 13^\circ$  for samples containing 20 and 25 wt.% PEG is due to the formation of partially crystalline entities and it implies that the samples containing more than 15 wt.% PEG is less amorphous. Similar to the unplasticized system, the more amorphous sample is expected to exhibit high conductivity value.

## 5.2 Fourier Transform Infrared (FTIR) analysis

In order to study the complexation in plasticized MC-NH<sub>4</sub>NO<sub>3</sub> polymer electrolytes system, it is important to determine if there is an interaction between MC and PEG and PEG with NH<sub>4</sub>NO<sub>3</sub>. The interaction between MC and NH<sub>4</sub>NO<sub>3</sub> (AN) is already discussed in

Chapter 4. Poly (ethylene glycol) (PEG) with molecular structure HO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>-H was used as a plasticizer in this work and FTIR have revealed significant absorption bands as displayed in Figure 5.2 while the vibrational modes and wavenumbers are listed in Table 5.2.



**Figure 5.2: FTIR spectrum for pure PEG**

**Table 5.2: Vibrational modes with corresponding wavenumbers for pure PEG**

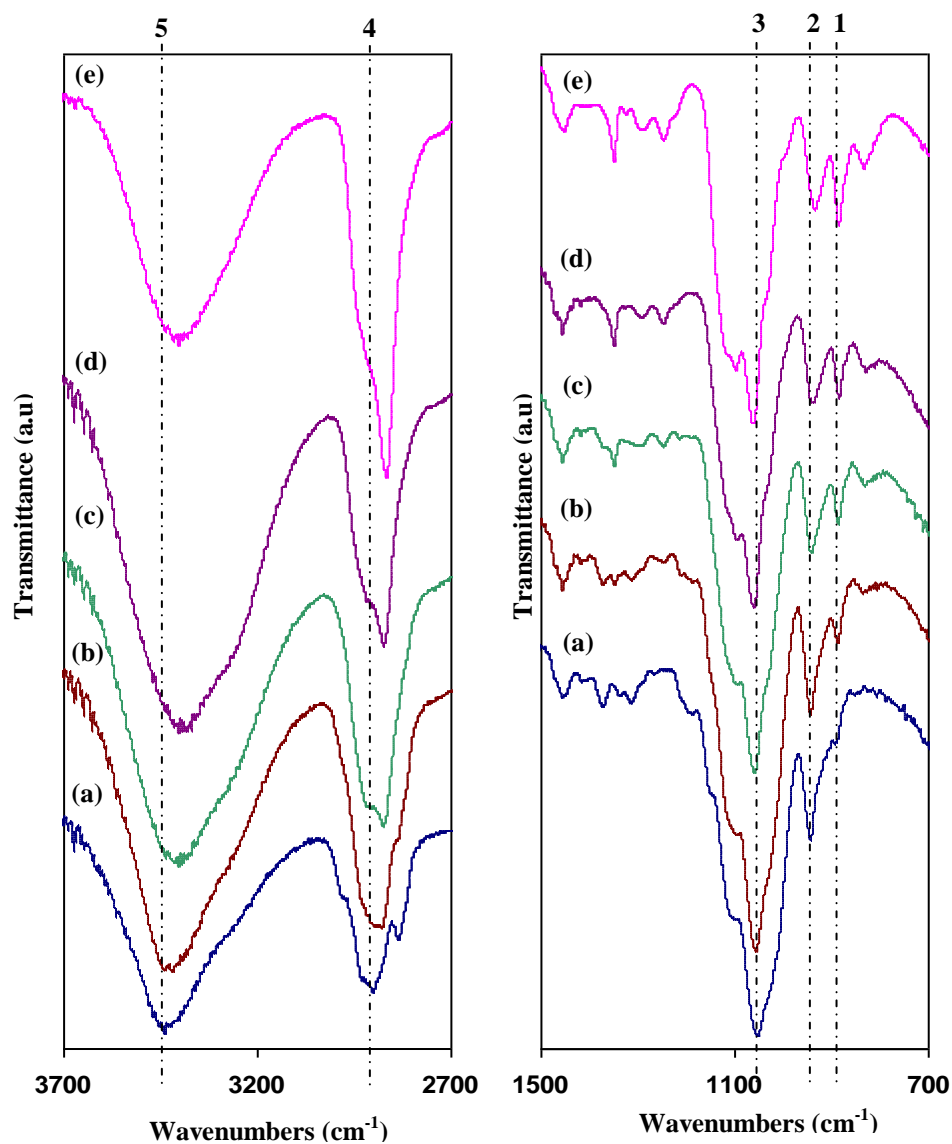
No.	Wavenumber (cm <sup>-1</sup> )	Assignment
1	833, 885, 936, 1061, 1098, 1247, 1349, 1452	C-O-C bonds or ether groups stretching
2	2867	CH <sub>2</sub> or alkyl stretching
3	3403	O-H or hydroxyl groups stretching

According to Mansur *et al.* (2004), ether groups stretching in PEG can be observed from 1050 to 1150 cm<sup>-1</sup>, alkyl (R-CH<sub>2</sub>) stretching modes can be observed in the wavenumber region between 2850 to 3000 cm<sup>-1</sup> and the hydroxyl group can be located in the wavenumber region between 3200 and 3600 cm<sup>-1</sup>. The vibrational bands of PEG were found at 833, 885, 936, 1061, 1098, 1247, 1349 and 1452 cm<sup>-1</sup> corresponding to the different vibrational modes of C-O-C bonds in PEG [Fang *et al.*, 2009; Zhang *et al.*, 2010; Kolhe and Kannan, 2003]. Other vibrational bands can be found at 2867 and 3403 cm<sup>-1</sup> and can be ascribed to CH<sub>2</sub> and O-H stretching bands respectively.

Interactions between MC and PEG were investigated at different concentrations of PEG as shown in Figure 5.3 while Table 5.3 lists the vibrational modes and wavenumbers exhibited in MC-PEG system.

**Table 5.3: Vibrational modes with corresponding wavenumbers for pure MC, MC-PEG and pure PEG**

Samples	Locations for MC (cm <sup>-1</sup> )				
	1	2	3	4	5
	Ring stretching of MC	-	C-O stretching	C-H stretching	O-H stretching
Pure MC	894	944	1053	2902	3440
75MC25PEG	887	944	1057	2879	3416
50MC50PEG	886	943	1060	2876	3403
25MC75PEG	885	940	1061	2874	3403
Pure PEG	885	936	1061	2867	3403
	C-O-C bonds	C-O-C bonds	C-O-C bonds	CH <sub>2</sub> stretching	O-H stretching
	1	2	3	4	5
	Locations for PEG (cm <sup>-1</sup> )				



**Figure 5.3: FTIR spectra for (a) pure MC, (b) 75MC25PEG, (c) 50MC50PEG, (d) 25MC75PEG, (e) pure PEG**

The figures show that when MC and PEG mixed together, the C-O-C bonds of PEG initially at  $1061\text{ cm}^{-1}$  gets shifted to  $1057\text{ cm}^{-1}$  at 25 wt.% PEG concentration. The band then gets shifted to  $1060\text{ cm}^{-1}$  when the concentration of PEG reaches 50 wt.%. For 75 wt.% of PEG, the characteristic peak of MC-PEG is located at almost the same position as the characteristic peak of the ether group in pure PEG. In short, C-O stretching in the spectrum of the samples is located nearer to that of pure PEG or MC depending on which component is more in the composition. This result is almost similar to that reported by

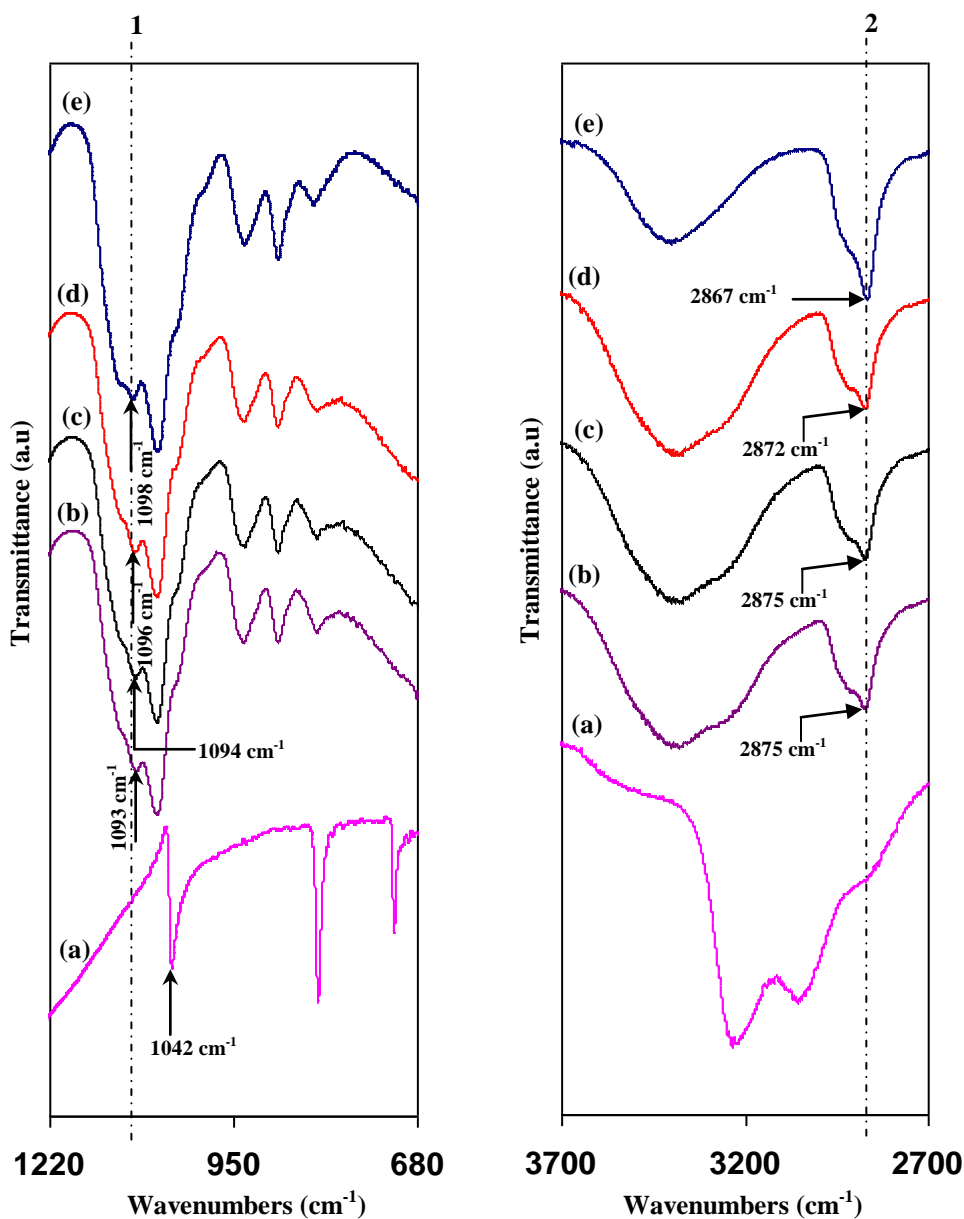
Subban and Arof (2004) although they used PVC as polymer host and DMF as a plasticizer. They found that, when PVC is mixed with DMF, the O=C-N stretching mode of DMF at 661 cm<sup>-1</sup> initially gets shifted to 658 cm<sup>-1</sup> at 20 and 50 wt.% DMF concentration. The band then shifted to 660 cm<sup>-1</sup> for sample contains 80 wt.% DMF.

Changes in the spectra are also noted at the vibrational bands 885 and 936 cm<sup>-1</sup> attributed to ether group of PEG and 894 and 944 cm<sup>-1</sup> due to ring stretching of MC. When different amounts of MC were dissolved in different concentrations of PEG, these peaks shifted to lower or higher wavenumbers depending on how much of MC or PEG is in that sample.

A shift of PEG's CH<sub>2</sub> stretching at 2867 cm<sup>-1</sup> to 2879 cm<sup>-1</sup> were also observed when MC was dissolved in 25 wt.% PEG. This band then shifted to lower wavenumbers when higher PEG concentrations were used to dissolve MC (2874 cm<sup>-1</sup> for sample of MC which was dissolved in 75 wt.% PEG. This is nearer to CH<sub>2</sub> stretching of pure PEG).

The obvious shifting of wavenumber can also be seen in Figure 5.3 at the band attributed to O-H stretching in the region 3200 to 3700 cm<sup>-1</sup> which was shown by line number five. O-H stretching of pure PEG at 3403 cm<sup>-1</sup> did not change for samples containing 50 and 75 wt.% PEG indicating that the action of PEG is more prominent at the higher PEG concentration and on the other hand, when 25 wt.% PEG was added, the O-H stretching shifted to 3416 cm<sup>-1</sup>. The shift is interpreted by the dipole-dipole interactions or hydrogen bonding between O-H groups of MC and PEG molecules.

The PEG-NH<sub>4</sub>NO<sub>3</sub> interactions were investigated and the FTIR spectra are displayed in Figure 5.4. Interaction can be said to occur when NH<sub>4</sub><sup>+</sup> of the salt bonds weakly with the oxygen atom of the ether group in the PEG plasticizer. From the present study, C-O-C bands are observed to shift to lower wavenumbers from 1098 cm<sup>-1</sup> in the spectrum of pure PEG to 1093 cm<sup>-1</sup> in the spectrum of NH<sub>4</sub>NO<sub>3</sub> doped PEG. Figure 5.4 also presents spectrum of the samples in the region from 2700 to 3700 cm<sup>-1</sup>.



**Figure 5.4:** FTIR spectra for (a) pure AN (NH<sub>4</sub>NO<sub>3</sub>), (b) 95PEG5AN, (c) 97.5PEG2.5AN, (d) 99PEG1AN (e) pure PEG



The CH<sub>2</sub> stretching band of pure PEG was initially observed at 2867 cm<sup>-1</sup>. With increasing concentrations of NH<sub>4</sub>NO<sub>3</sub> from 1.0, 2.5 and 5.0 wt.%, this band further shifted to 2872 cm<sup>-1</sup> for PEG containing 1.0 wt.% NH<sub>4</sub>NO<sub>3</sub> and 2875 for PEG containing 2.5 and 5.0 wt.% NH<sub>4</sub>NO<sub>3</sub>. The shifting of C-O-C and CH<sub>2</sub> stretching bands in the plasticizer-salt system implies the interaction between PEG and NH<sub>4</sub>NO<sub>3</sub> has occurred. Table 5.4 lists the vibrational modes and wavenumber of PEG-AN system.

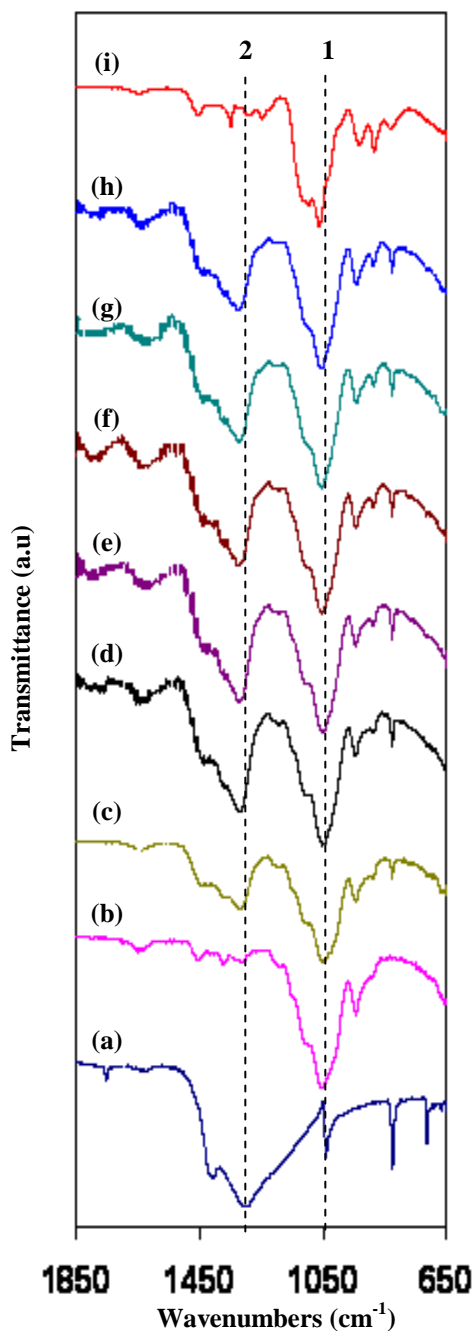
**Table 5.4: Vibrational modes with corresponding wavenumbers for pure AN, AN-PEG and pure PEG**

Samples	Locations for AN (cm <sup>-1</sup> )	
	1	2
	v(NO) of NO <sub>3</sub> <sup>-</sup>	-
Pure AN	1042	-
95PEG5AN	1093	2875
97.5PEG2.5AN	1094	2875
99PEG1AN	1096	2872
Pure PEG	1098	2867
	C-O-C bonds	CH <sub>2</sub> stretching
	1	2
	Locations for PEG (cm <sup>-1</sup> )	

To determine the interaction of PEG and the effect of its presence in MC-NH<sub>4</sub>NO<sub>3</sub> samples, the FTIR studies were employed with different concentrations of PEG added to the MC-NH<sub>4</sub>NO<sub>3</sub> system as shown in Figure 5.5.

From the present study, the effect of adding PEG plasticizer in MC-NH<sub>4</sub>NO<sub>3</sub> system in the region 650 to 1850 cm<sup>-1</sup> is shown by the shift in C-O stretching bands of 75MC25AN which was initially at 1053 cm<sup>-1</sup> and of PEG which was initially at 1061 cm<sup>-1</sup>. The C-O

peak shifted to 1058 cm<sup>-1</sup> with addition of 25 wt.% PEG. The changes in the spectra can also be observed at 1318 cm<sup>-1</sup> when PEG was added. The shifting of this band to higher wavenumbers indicates that complexation occurred in plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system.



**Figure 5.5:** FTIR spectra for (a) pure NH<sub>4</sub>NO<sub>3</sub>, (b) pure MC, (c) 75MC25AN0PEG, (d) 71.25MC23.75AN5PEG, (e) 67.50MC22.50AN10PEG, (f) 63.75MC21.25AN15PEG, (g) 80.00MC20.00AN20PEG, (h) 56.25MC18.75AN25PEG, (i) pure PEG

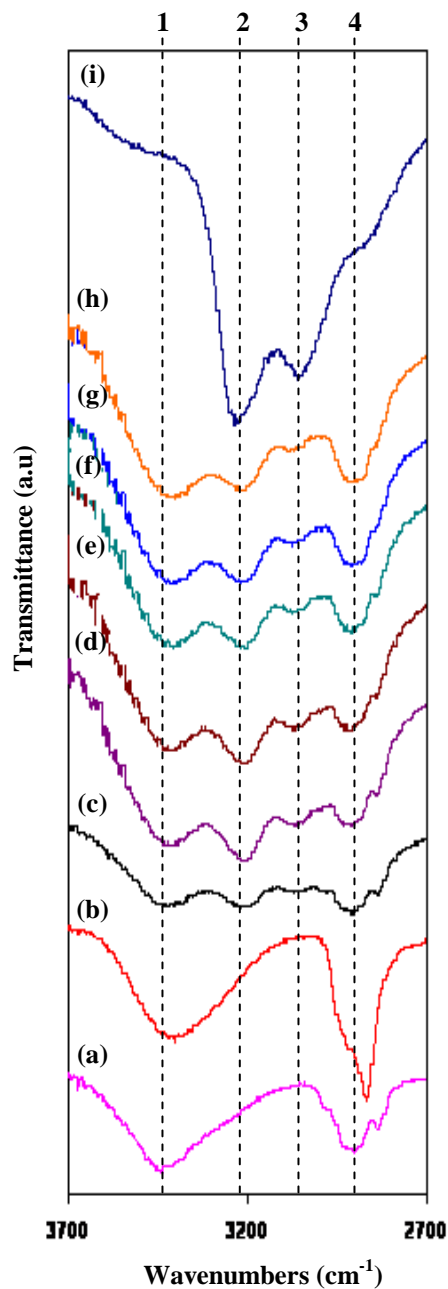
Table 5.5 lists the vibrational modes and wavenumbers of MC-AN-PEG system in the region 650 to 1850 cm<sup>-1</sup>.

**Table 5.5: Vibrational modes with corresponding wavenumbers for pure AN, pure MC, 75MC25AN, MC-AN-PEG and pure PEG**

Samples	Locations of AN (cm <sup>-1</sup> )	
	1	2
	$\nu(\text{NO})$ of NO <sub>3</sub> <sup>-</sup>	$\nu_s(\text{NO})_2$ of NO <sub>3</sub> <sup>-</sup>
Pure AN	1042	1300
Pure MC	1053	1314
75MC25AN0PEG	1051	1318
71.25MC23.75AN5PEG	1053	1317
67.5MC22.5AN10PEG	1053	1322
63.75MC21.25AN15PEG	1056	1322
80MC20AN20PEG	1055	1325
56.25MC18.75AN25PEG	1058	1326
Pure PEG	1061	1326
	C-O stretching	-
	1	2
	Locations for MC/PEG (cm <sup>-1</sup> )	

The effects of PEG in MC-NH<sub>4</sub>NO<sub>3</sub> system can also be observed in the region of O-H and C-H stretching bands of MC and PEG and N-H stretching band of NH<sub>4</sub>NO<sub>3</sub> respectively as shown in Figure 5.6. In the system plasticized with PEG, the band attributed to N-H stretching, remains unshifted implying that no interaction was detected in PEG-AN system at this location. The C-H stretching of 75MC25AN at 2910 cm<sup>-1</sup> has shifted to 2913 cm<sup>-1</sup> when PEG was added from 5 to 25 wt.%. The shift of C-H stretching band in the plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system implies the interaction between PEG and MC-NH<sub>4</sub>NO<sub>3</sub> system has occurred. With increasing concentration of PEG, the band at 3437 cm<sup>-1</sup> due to

O-H stretching band of 75MC25AN is observed to shift to lower wavenumber. This is probably due to the interaction between MC and PEG and MC and AN since PEG and AN did not give any interaction at this location.



**Figure 5.6:** FTIR spectra for (a) pure MC, (b) pure PEG, (c) 75MC25AN0PEG, (d) 71.25MC23.75AN5PEG, (e) 67.50MC22.50AN10PEG, (f) 63.75MC21.25AN15PEG, (g) 80.00MC20.00AN20PEG, (h) 56.25MC18.75AN25PEG and (i) pure NH<sub>4</sub>NO<sub>3</sub>

Table 5.6 lists the vibrational modes and wavenumbers of MC-AN-PEG system in the region 2700 to 3700 cm<sup>-1</sup>.

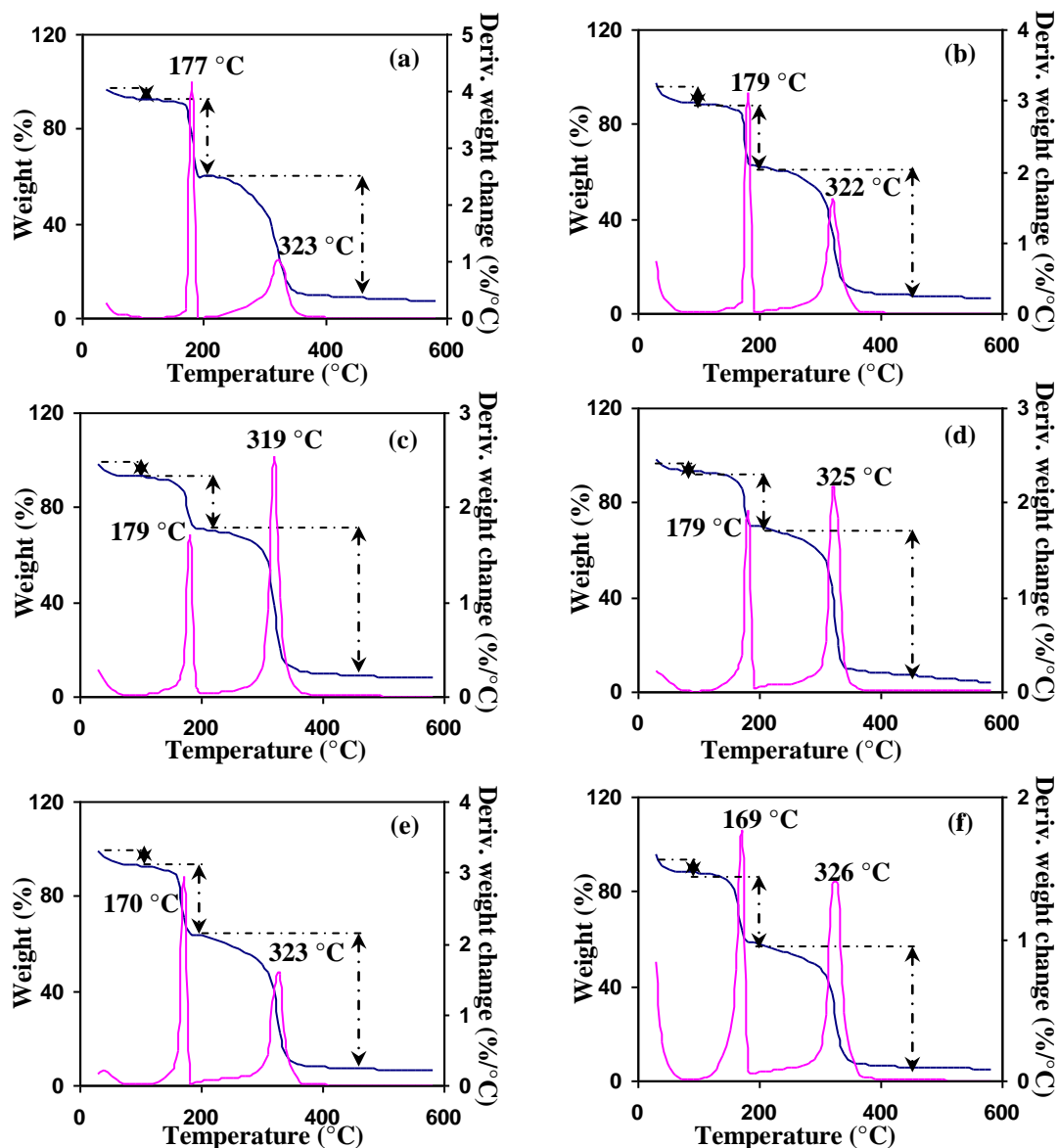
**Table 5.6: Vibrational modes with corresponding wavenumbers for pure AN, pure MC, 75MC25AN, MC-AN-PEG and pure PEG**

Samples	Locations of AN (cm <sup>-1</sup> )			
	1	2	3	4
	O-H stretching	N-H stretching	N-H stretching	C- H stretching
Pure AN	-	3236	3058	-
Pure MC	3440	-	-	2902
75MC25AN0PEG	3437	3214	3089	2910
71.25MC23.75AN5PEG	3412	3214	3089	2913
67.5MC22.5AN10PEG	3407	3214	3089	2913
63.75MC21.25AN15PEG	3407	3214	3089	2913
80MC20AN20PEG	3402	3214	3089	2913
56.25MC18.75AN25PEG	3440	3214	3089	2913
Pure PEG	3403	-	-	2867

### 5.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was used to study the thermal degradation of materials. Figure 5.7 depicts the TGA and DTGA curves for plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system. A slight weight decrease shown in Figure 5.7 started below 100 °C due to the loss of free water. From the thermogram, it can be observed that decomposition of plasticized samples occur in 3 stages. DTGA<sub>maxima</sub> for samples with 5 to 15 wt.% PEG is stable up to between

177 and 179 °C but for polymer-salt samples with 20 and 25 wt. % PEG, the DTG<sub>maxima</sub> decreased to ~170 °C.



**Figure 5.7:** TG and DTG curves for (a) 75MC25AN0PEG, (b) 71.25MC23.75AN5PEG, (c) 67.50MC22.50AN10PEG, (d) 63.75MC21.25AN15PEG, (e) 60MC20AN20PEG (f) 56.25MC18.75AN25PEG

The temperature range, DTG<sub>maxima</sub> and weight losses (%) are given in Table 5.7 for plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system.

**Table 5.7: Thermogravimetric (TGA) data of the plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system.**

Samples	No. of degradation stage	Temperature range (°C)	DTGA <sub>max</sub> (°C)	% weight loss	
75.00MC25.00 AN0PEG	1	25-100		8	Water loss
	2	100-200	177	<b>32</b>	AN decomposed
	3	200-450	323	<b>51</b>	MC decomposed
71.25MC23.75 AN5PEG	1	25-100		10	Water loss
	2	100-200	179	<b>27</b>	AN decomposed
	3	200-450	322	<b>54</b>	MC decomposed
67.50MC22.50 AN10PEG	1	25-94		7	Water loss
	2	94-212.5	179	<b>23</b>	AN decomposed
	3	212.5-450	319	<b>61</b>	MC decomposed
63.75MC21.25 AN15PEG	1	25-86		7	Water loss
	2	86-205.5	179	<b>23</b>	AN decomposed
	3	205.5-450	325	<b>63</b>	MC decomposed
80.00MC20.00 AN20PEG	1	25-100		7	Water loss
	2	100-189	170	<b>29</b>	AN decomposed
	3	189-450	323	<b>57</b>	MC decomposed
56.25MC18.75 AN25PEG	1	25-94		12	Water loss
	2	94-200	169	<b>30</b>	AN decomposed
	3	200-450	326	<b>52</b>	MC decomposed

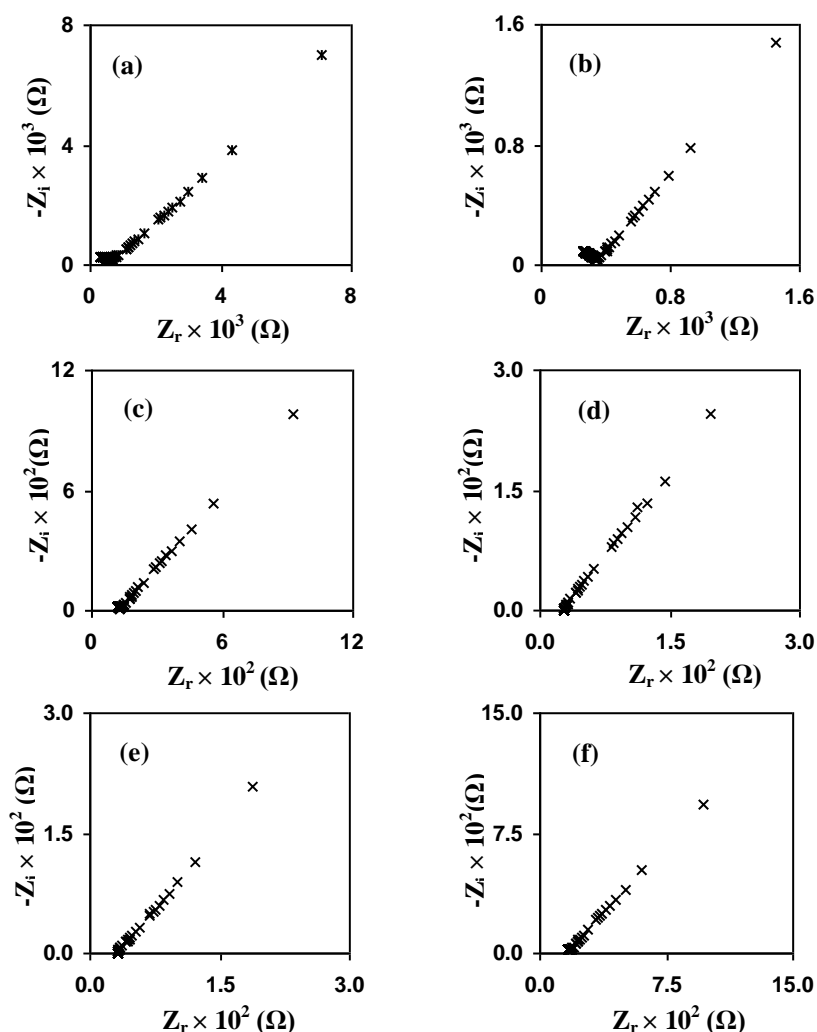
**DTGA: differential thermogravimetric analysis**

## 5.4 Electrochemical Impedance Spectroscopy (EIS) analysis

The effect of low molecular weight poly (ethylene glycol), as a plasticizer in the MC-NH<sub>4</sub>NO<sub>3</sub> system was also investigated using electrochemical impedance spectroscopy (EIS) to determine the bulk resistance and conductivity of plasticized polymer electrolytes.

### 5.4.1 The effect of PEG 200 on conductivity of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system

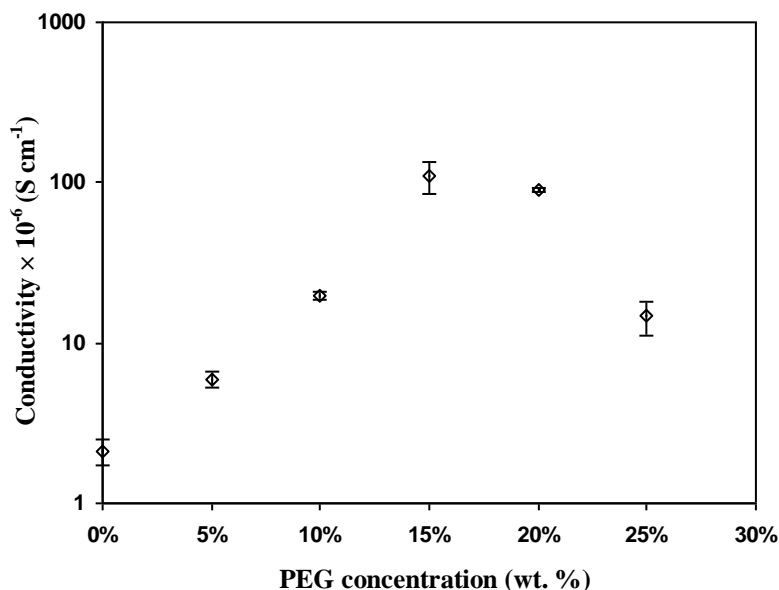
Figure 5.8 depicts the Cole-Cole plots for plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system.



**Figure 5.8: Cole-Cole plot for (a) 75MC25AN0PEG, (b) 71.25MC23.75AN5PEG, (c) 67.50MC22.50AN10PEG, (d) 63.75MC21.25AN15PEG, (e) 60MC20AN20PEG (f) 56.25MC18.75AN25PEG**



The Cole-Cole plots show that there is an inclined straight line. The bulk resistance was obtained from the intersection of the spike on the real impedance-axis. It can be observed that, the values of  $-Z_i$  and  $Z_r$  decreased from sample (a) to sample (d) then increased again for samples (e) and (f).



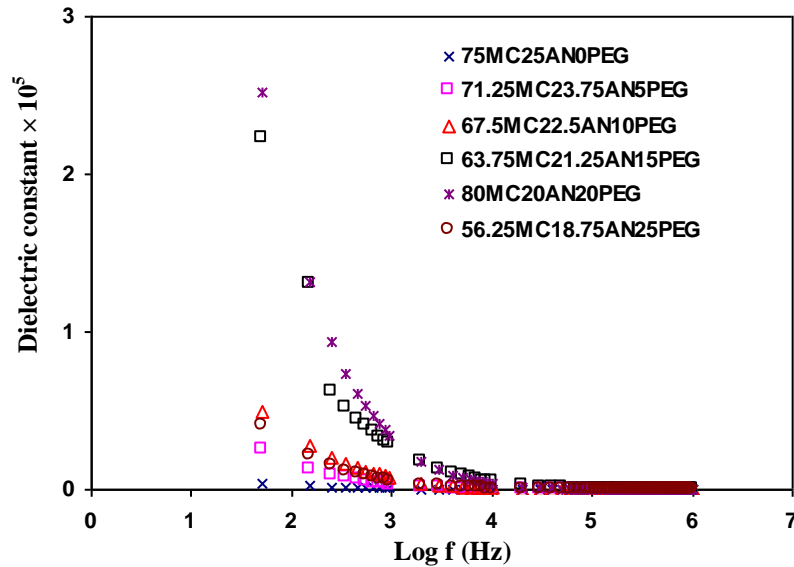
**Figure 5.9: Room temperature ionic conductivity of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> with PEG**

Figure 5.9 depicts the ionic conductivity of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system at room temperature. It can be observed that, conductivity increased from  $2.10 \times 10^{-6}$  S cm<sup>-1</sup> to  $1.10 \times 10^{-4}$  S cm<sup>-1</sup> with addition of PEG up to 15 wt.%. After that, the conductivity decreased. The increase in the ionic conductivity with PEG concentration up to 15 wt.% is due to the increase of amorphous content in the materials as proven by x-ray diffractogram in Figure 5.1. According to Kumar and Sekhon (2002), PEG with low molecular weight helps in ion transport mainly by increasing the amorphous content, which is reported to be the high conducting phase as well as by increasing the free volume. After 15 wt.% PEG concentration, the amorphous content of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system is decreased based on the raising of the degree of crystallinity as listed in Table 5.1, hence, verify that

the ionic conductivity of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system at higher PEG concentration decreased.

#### 5.4.2 Dielectric behavior of room temperature conductivity

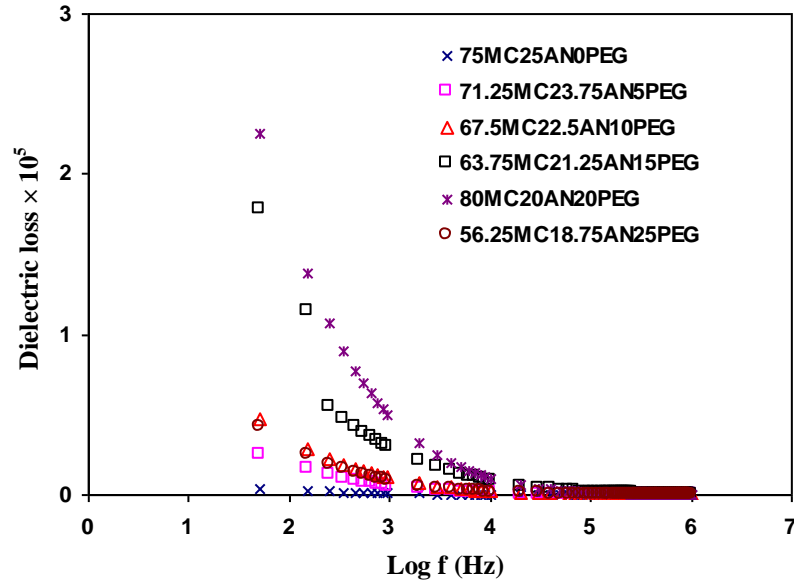
Dielectric behavior was studied to help in understanding the conductive behavior of polymer electrolyte [Ramesh *et al.*, 2002]. Figure 5.10 presents the variation of dielectric constant with frequency for different weight percentage of PEG.



**Figure 5.10: Dielectric constant versus log frequency plot plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

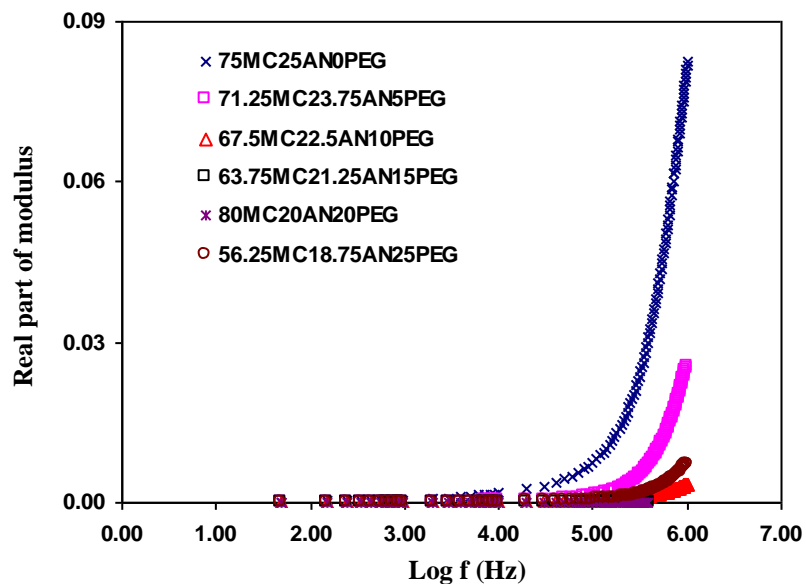
From the plots, it can be seen that the dielectric permittivity decreased with increasing frequency and achieved a constant value at higher frequencies. Similar behavior was observed for other plasticized polymer electrolytes [Pradhan *et al.*, 2009]. The value of dielectric constant is initially high but begins to drop with increasing frequency because the dipoles of the samples are not able to follow the field variations at high frequencies [Raja *et al.*, 2004]. Karan *et al.* (2008) suggested that the drop of dielectric constant at high frequencies is due to electrode polarization effects.

The variation of dielectric loss with frequency for different weight percentage of PEG is depicted in Figure 5.11. Dielectric loss decreases with increasing frequency. This is also due to the increase of polarizability at the electrode.

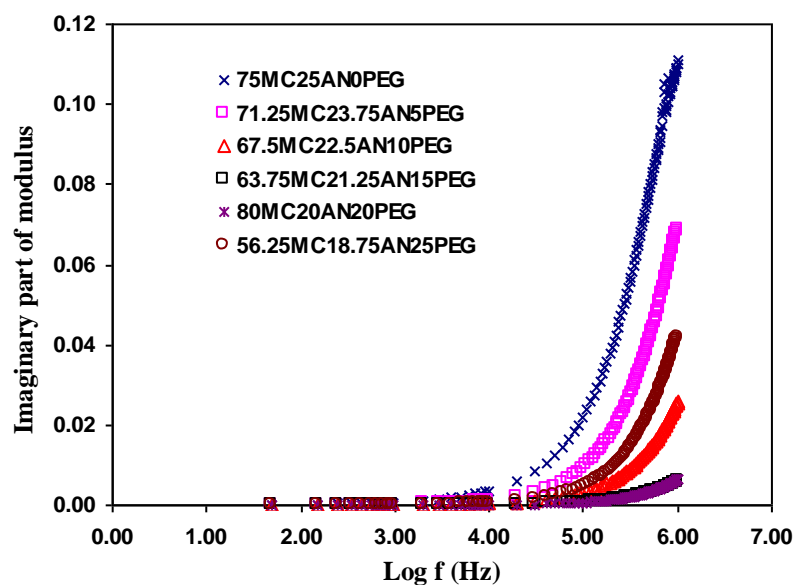


**Figure 5.11: Dielectric loss versus log frequency plot plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

The variation of real and imaginary parts of modulus with frequency for different weight percentage of PEG is depicted in Figure 5.12 and 5.13 respectively. In both of the plots, there are no relaxation peaks observed.

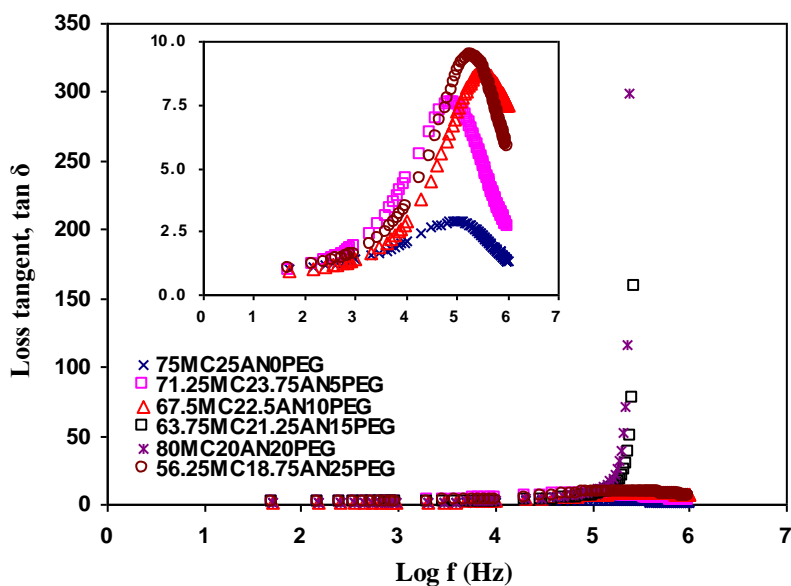


**Figure 5.12: Real part of modulus versus log frequency plot plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**



**Figure 5.13: Imaginary part of modulus versus log frequency plot plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

Figure 5.14 shows the variation of loss tangent ( $\tan \delta$ ) at different frequencies with different weight percentages of PEG.



**Figure 5.14: Loss tangent versus log frequency plot plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

A relaxation peak was observed for the sample without PEG and samples with 5, 10 and 25 wt.% PEG. It can be seen that, the intensity of peak increases with increasing PEG

content. From the plot of loss tangent versus frequency, the relaxation time can be calculated. With increasing conductivity, the relaxation time decrease as shown in Figure 5.15.

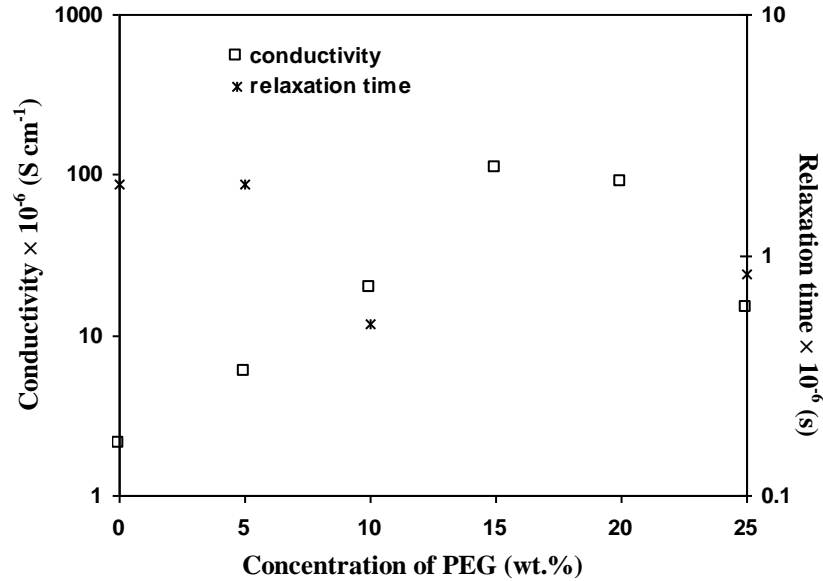
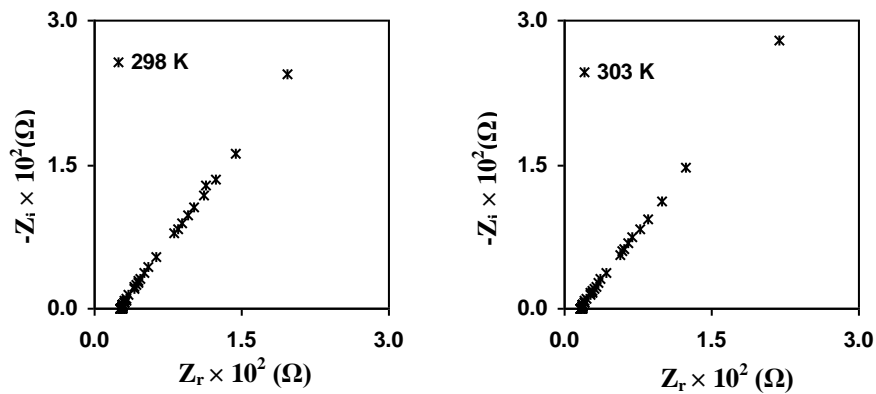


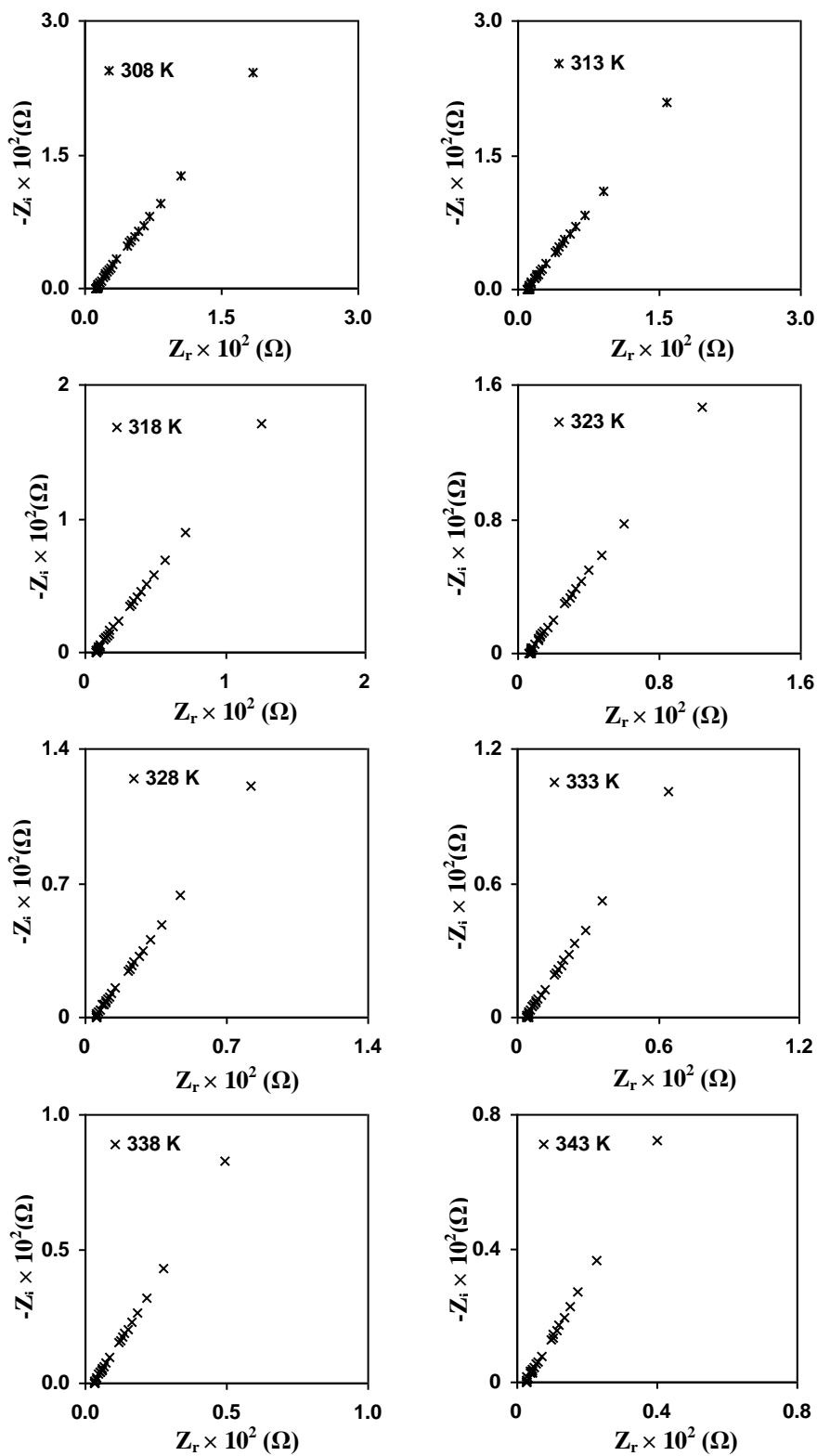
Figure 5.15: The dependence of conductivity and relaxation time on PEG concentration at room temperature

#### 5.4.3 The effect of temperature on conductivity of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system

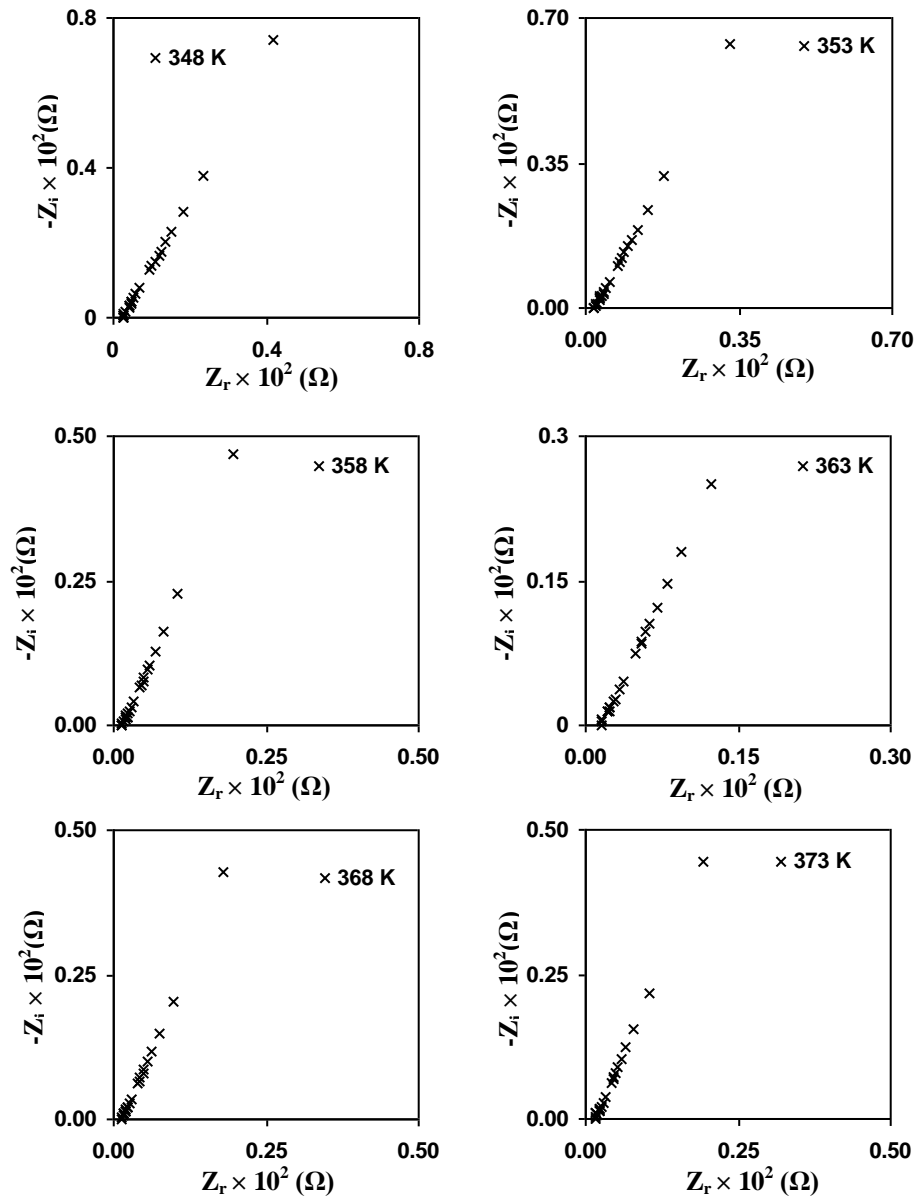
The Cole-Cole plots of the highest conducting sample in plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system at different temperatures are shown in Figure 5.16.



...FIGURE 5.16 CONTINUED...



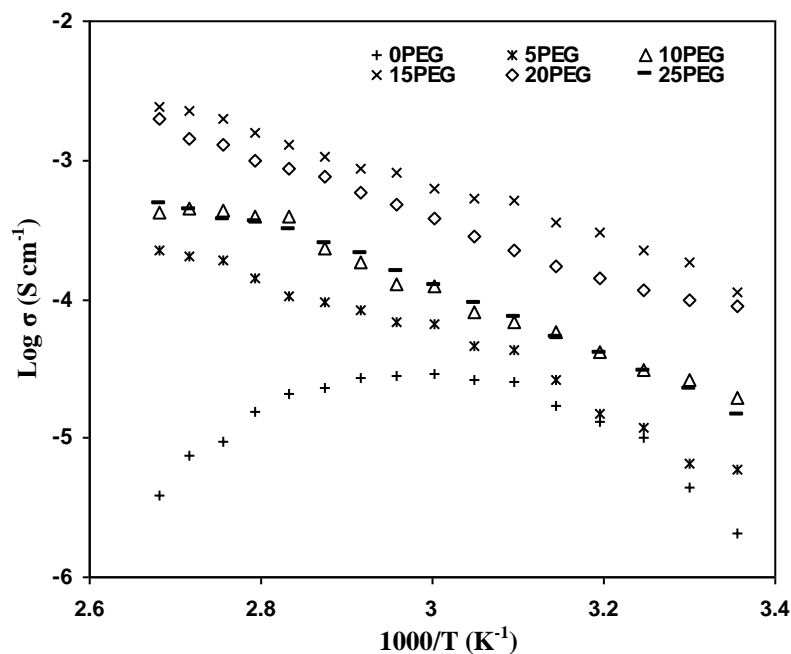
...FIGURE 5.16 CONTINUED...



**Figure 5.16: The Cole-Cole plot for the highest conducting sample of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system at various temperatures**

The plot shows a low frequency spike suggesting that only capacitive component prevails in the polymer electrolytes. From Figure 5.16, it is observed that, as the temperature increases, the bulk resistance decreases from 22.80  $\Omega$  at room temperature to 2.71  $\Omega$  at 373 K. The temperature-dependent of ionic conductivity was studied to investigate the mechanism of ionic conduction. Figure 5.17 depicts the variation of

temperature dependence of ionic conductivity for plasticized sample of MC-NH<sub>4</sub>NO<sub>3</sub> system.



**Figure 5.17: Temperature dependence of ionic conductivity for samples of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

Unlike the conductivity-temperature relationship of MC doped with NH<sub>4</sub>NO<sub>3</sub> samples, the conductivity increases with increase in temperature up to 100 °C. The regression value,  $R^2$  was determined to be 0.99. The conductivity-temperature relationship exhibits Arrhenius-like behavior. According to Park and Ruckestein (2001), among the many plasticizers for MC, PEG is most suitable for the preparation of proton conducting electrolytes. This is because PEG is sufficiently hygroscopic enabling it to retain moderate moisture in the polymer and improves flexibility of the membrane without decreasing its mechanical strength. Therefore, the conductivity of the sample does not drop after 333 K but continues to increase as temperature is increased to 373 K. From the temperature dependent of ionic conductivity, the activation energy was calculated and listed in Table 5.8.



**Table 5.8: The activation energy,  $E_a$  of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

Plasticizer concentration (wt.%)	Activation energy (eV)
5	0.47
10	0.44
15	0.37
20	0.41
25	0.45

In this work, the highest conducting sample is that containing 15 wt.% and it also has the lowest activation energy.

#### 5.4.4 Transport parameters of plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system

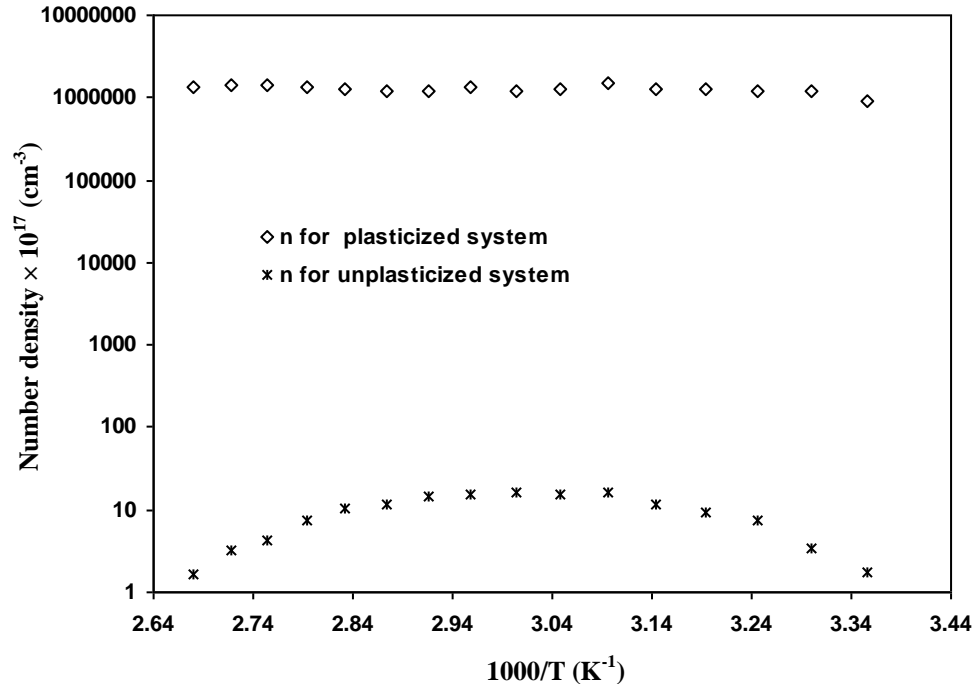
The number density, mobility and diffusion coefficient of the charge carriers in the polymer electrolytes was calculated using the Rice and Roth (1972) model. Table 5.9 lists the transport parameters.

**Table 5.9: Transport parameters for plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

Samples	$\tau$ (s) $\times 10^{-11}$	$\nu$ (cm s <sup>-1</sup> ) $\times 10^3$	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) $\times 10^{-9}$	$n$ (cm <sup>-3</sup> ) $\times 10^{22}$	$D$ (cm <sup>2</sup> s <sup>-1</sup> ) $\times 10^{-10}$
71.25MC23.75AN5PEG	1.58	9.50	0.20	18.70	0.05
67.55MC22.5AN10PEG	1.64	9.15	0.73	17.00	0.19
63.75MC21.25AN15PEG	1.77	8.47	7.73	08.93	2.00
60MC20AN20PEG	1.69	8.85	2.08	26.70	0.54
56.25MC18.75AN25PEG	1.61	9.32	0.40	23.20	0.10

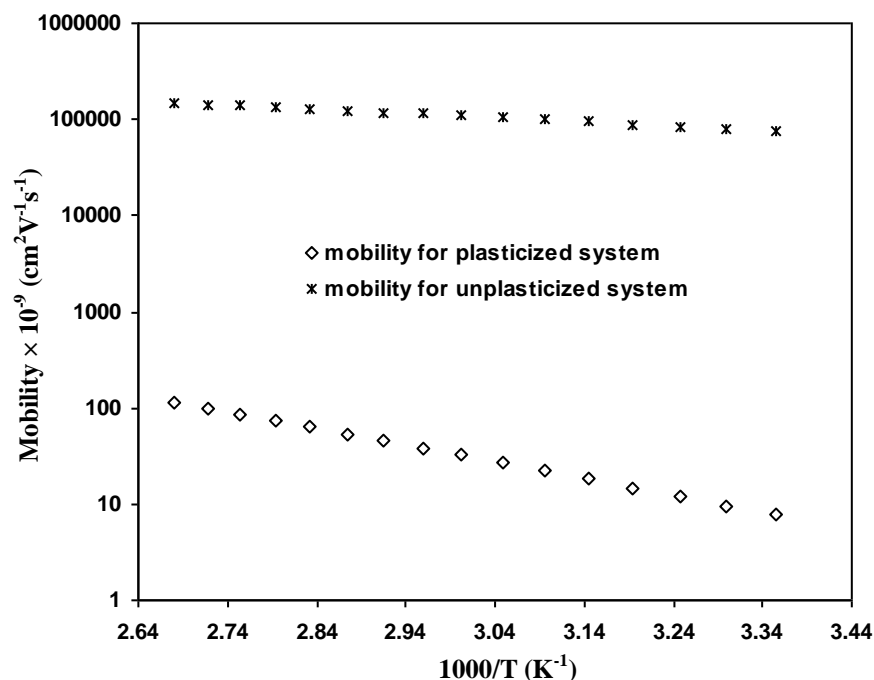
The jump distance between the transit sites,  $\ell$  used in this work was 1.5 nm. The mobility increases from  $0.20 \times 10^{-9} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  to  $7.73 \times 10^{-9} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  as the concentration of PEG increases from 5 to 15 wt.% PEG and then decreased. This trend follows the trend of conductivity versus concentration of PEG. The diffusion coefficient trend is also the same. However, the trend of number density of mobile ions is opposite to the trend of conductivity. It can be inferred that, in this work, conductivity is dependent on mobility and diffusion coefficient of charge carriers.

The Rice and Roth model was also employed to the temperature dependence of conductivity. Figures 5.18, 5.19 and 5.20 depict the temperature dependence of number density, mobility and diffusion coefficient of the highest conducting sample in plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system.



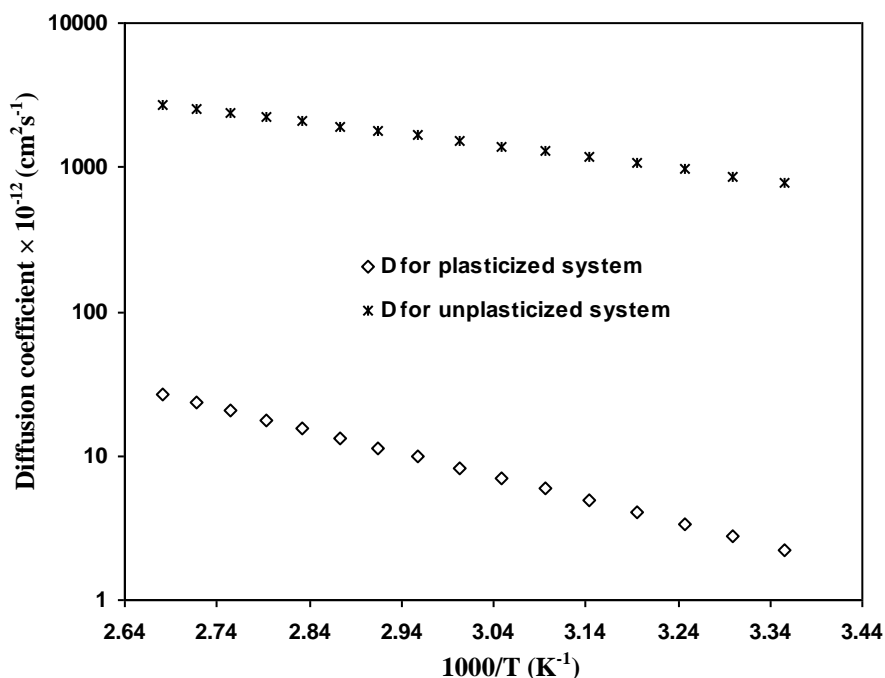
**Figure 5.18: Temperature dependence of number density for the highest conducting sample in unplasticized and plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

Number density of mobile ion seems to remain constant at all temperatures studied indicating that the plasticizer has maximized the dissociation of salt. For the unplasticized system ion recombination has taken place leading to lower number density of mobile ions. Mobility in the plasticized system is thermally assisted but its magnitude is lower than that of the unplasticized system.



**Figure 5.19: Temperature dependence of mobility for the highest conducting sample in unplasticized and plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

The magnitude of the diffusion coefficient for the plasticized system is less than that of the unplasticized system. Hence, the conductivity is more dependent on number density of mobile ions when temperature increases from room temperature to 373 K for the plasticized system. Although the number density is almost independent of temperature with addition of PEG, its magnitude is more than three times higher than that of the unplasticized system.



**Figure 5.20: Temperature dependence of diffusion coefficient for the highest conducting sample in unplastized and plasticized MC-NH<sub>4</sub>NO<sub>3</sub> system**

## 5.5 Summary

In this chapter, we prepared plasticized MC-NH<sub>4</sub>NO<sub>3</sub> samples using poly (ethylene glycol) (PEG). The room temperature conductivity enhancement was two orders of magnitude higher. Conductivity only occurs in amorphous phase. From X-ray diffractogram, it was proven that, the highest conducting sample is least crystalline (most amorphous) compared to other samples. FTIR studies show that, there is interaction between MC-PEG due to hydrogen bonding between the molecules of the materials. PEG also interacts with NH<sub>4</sub>NO<sub>3</sub> when the C-O-C stretching of PEG shifted to lower wavenumbers. Conductivity-temperature relationship shows that this system obeys Arrhenius rule. The conductivity increased up to 100 °C with addition of PEG. The

activation energy was evaluated from gradient of log conductivity versus  $1000/T$ . The highest conducting sample has the lowest activation energy. Using the Rice and Roth model, it was inferred that the increase in conductivity with addition of PEG and temperature is governed by mobility, diffusion coefficient and number density of mobile ions although the number density of mobile ions are almost constant in the temperature range investigated.