

## CHAPTER 6

### ELECTROCHEMICAL STUDIES OF CHITOSAN ELECTROLYTES

#### 6.1 INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is an important tool to determine the conductivity of a polymer electrolyte. This experiment will measure impedance of a material and with proper analysis, the conductivity of the material can be calculated. The objectives of this study are to determine the conductivity of the electrolytes prepared in this work, to study the effect of conductivity when chitosan is blended with PVA and PEO and added with  $\text{NH}_4\text{I}$  salt and finally, to investigate the effect of incorporating ionic liquid (IL) into the highest conducting chitosan- $\text{NH}_4\text{I}$  electrolyte.

#### 6.2 COLE-COLE PLOTS OF CHITOSAN ELECTROLYTES

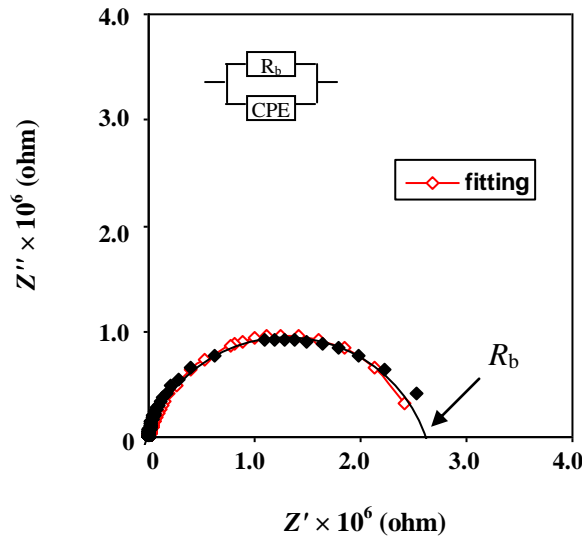
Figure 6.1 shows the complex impedance plot obtained for the pure chitosan film at room temperature 303 K. Bulk resistance,  $R_b$  is determined by extrapolating the depressed semicircle to the real axis. The ionic conductivity of  $9.7 \times 10^{-10} \text{ S cm}^{-1}$  is obtained. From the figure, it can be observed that the plot of imaginary impedance,  $Z''$  against real impedance,  $Z'$  takes the shape of a depressed semicircle indicating that the material can be represented by a parallel combination of bulk resistance and constant phase element (CPE) (inset in Figure 6.1) which arises due to the ion migration in the bulk of the electrolyte and also due to different relaxation times of the ions. The centre of the semicircle being below the real impedance axis, strengthens the inference that the

ions have a distribution of relaxation times. The expressions for the real and imaginary parts of the impedance related to this equivalent circuit are given below:

$$Z' = \frac{R_b + R_b^2 k^{-1} \omega^p \cos(\pi p/2)}{1 + 2R_b k^{-1} \omega^p \cos(\pi p/2) + R_b^2 k^{-2} \omega^{2p}} \quad (6.1)$$

$$Z'' = \frac{R_b^2 k^{-1} \omega^p \sin(\pi p/2)}{1 + 2R_b k^{-1} \omega^p \cos(\pi p/2) + R_b^2 k^{-2} \omega^{2p}} \quad (6.2)$$

Here  $k^{-1}$  corresponds to the capacitance value of the CPE element,  $\omega$  is angular frequency ( $\omega = 2\pi f$  where  $f$  is frequency),  $p$  is related to the deviation from the vertical axis in the  $Z''$  versus  $Z'$  plot and  $R_b$  is bulk resistance. The estimated value of  $k^{-1}$  for pure chitosan film at room temperature is  $5 \times 10^{-10}$  F.



**Figure 6.1: Cole-Cole plot of pure chitosan film at room temperature**

Figures 6.2 to 6.4 represent the Cole-Cole plots for the chitosan-salt (Ch9), chitosan-PVA-salt (CV5) and chitosan-PEO-salt (CEO7) systems, respectively at 303 K. All the three Cole-Cole plots show the semicircle shape with spike implying that a double layer response occurs at the electrode-electrolyte interface [Michael *et al.*, 1997]. The impedance plot can be best represented by an equivalent circuit composed of a parallel

combination of a resistor and a constant phase element (CPE) which is connected in series with another CPE. Electrolytes with the designation of Ch9, CV5 and CEO7 exhibit the conductivity of  $3.73 \times 10^{-7} \text{ S cm}^{-1}$ ,  $1.77 \times 10^{-6} \text{ S cm}^{-1}$  and  $3.66 \times 10^{-6} \text{ S cm}^{-1}$ , respectively. It can be observed that the conductivity has increased by almost one order of magnitude in samples with blended electrolyte films. Therefore, blending of chitosan with conducting polymers like PVA and PEO enhances the ionic conductivity. The expressions for the real and imaginary parts of the impedance related to this equivalent circuit are given below:

$$Z' = \frac{R_b + R_b^2 k_1^{-1} \omega^{p_1} \cos(\pi p_1/2)}{1 + 2R_b k_1^{-1} \omega^{p_1} \cos(\pi p_1/2) + R_b^2 k_1^{-2} \omega^{2p_1}} + \frac{\cos(\pi p_2/2)}{k_2^{-1} \omega^{p_2}} \quad (6.3)$$

$$Z'' = \frac{R_b^2 k_1^{-1} \omega^{p_1} \sin(\pi p_1/2)}{1 + 2R_b k_1^{-1} \omega^{p_1} \cos(\pi p_1/2) + R_b^2 k_1^{-2} \omega^{2p_1}} + \frac{\sin(\pi p_2/2)}{k_2^{-1} \omega^{p_2}} \quad (6.4)$$

The estimated value of  $k^{-1}$  for Ch9, CV5 and CEO7 at room temperature is  $2.0 \times 10^{-7} \text{ F}$ ,  $1.85 \times 10^{-7} \text{ F}$  and  $3.8 \times 10^{-8} \text{ F}$ , respectively.

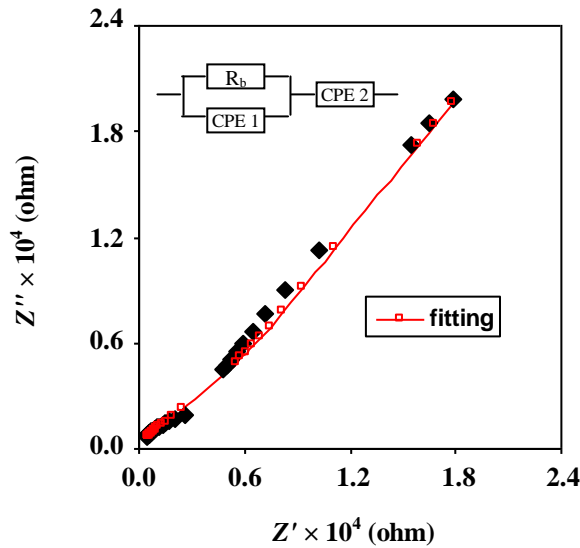


Figure 6.2: Cole-Cole plot of Ch9 electrolyte at room temperature

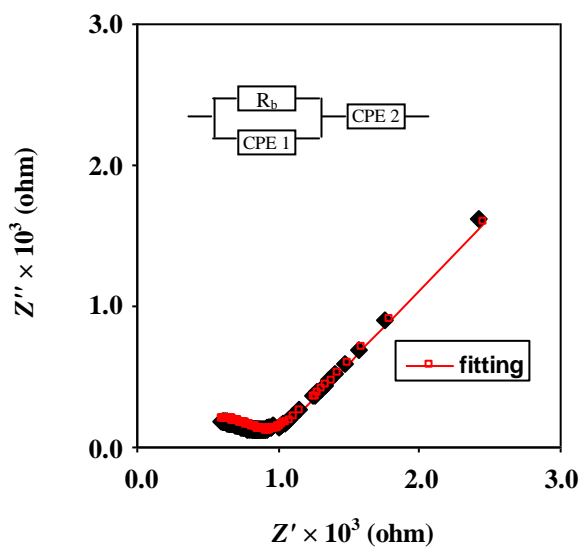


Figure 6.3: Cole-Cole plot of CV5 electrolyte at room temperature

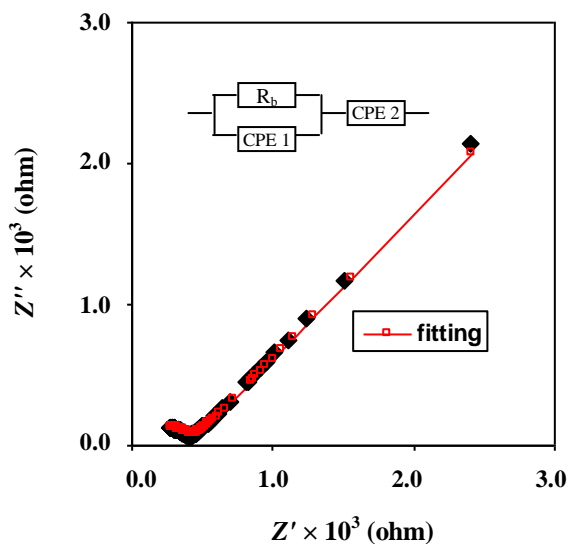


Figure 6.4: Cole-Cole plot of CEO7 electrolyte at room temperature

The complex impedance plot for the CIL5 sample in the chitosan-salt-ionic liquid system is displayed in Figure 6.5. As can be seen from the figure, the Cole-Cole plot reveals only the spike which implies that electrode polarization is dominant. Thus, its physical model can best be described by an equivalent circuit comprising a resistor connected in series with a CPE [Govindaraj *et al.*, 1995]. An increment in conductivity

by almost two orders of magnitude from  $3.73 \times 10^{-7} \text{ S cm}^{-1}$  to  $3.43 \times 10^{-5} \text{ S cm}^{-1}$  can be observed when 50 wt.% BMII ionic liquid was incorporated into the chitosan  $\text{NH}_4\text{I}$  sample. The expressions for the real and imaginary parts of the impedance related to this equivalent circuit are given below:

$$Z' = R_b + \frac{\cos(\pi p_2/2)}{k_2^{-1} \omega^{p_2}} \quad (6.5)$$

$$Z'' = \frac{\sin(\pi p_2/2)}{k_2^{-1} \omega^{p_2}} \quad (6.6)$$

The estimate value of  $k^{-1}$  for pure CIL5 electrolyte at room temperature is  $2.2 \times 10^{-5} \text{ F}$ .

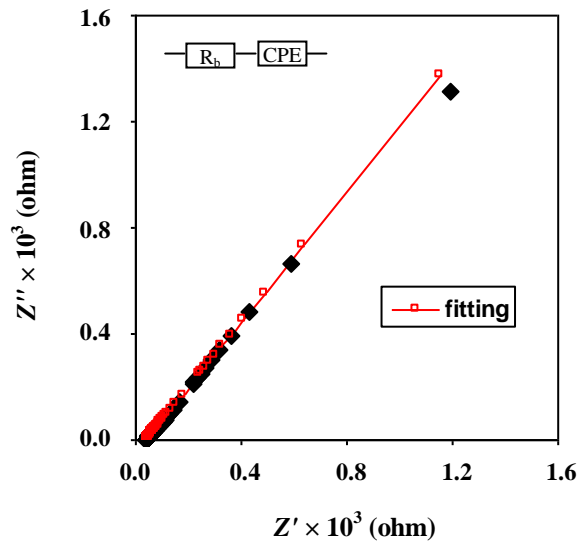


Figure 6.5: Cole-Cole plot of CIL5 electrolyte at room temperature

### 6.3 CONDUCTIVITY-TEMPERATURE RELATIONSHIP OF CHITOSAN- $\text{NH}_4\text{I}$ ELECTROLYTES

The conductivity-temperature relationship is as shown in Figure 6.6. In order to verify whether the relationship is Arrhenian or obeys the VTF rule, the data is converted into a plot of  $\ln \sigma T^{1/2}$  versus  $1000/|T-T_0|$ . This plot should exhibit a linear relationship with the appropriate  $T_0$ , the ideal glass transition temperature.  $T_0$  is usually taken to be 50 K

below the glass transition temperature,  $T_g$  [Qian *et al.*, 2002; Pas *et al.*, 2005].  $T_0$  in this work is determined by trial and error. The results is as shown in Figure 6.7.

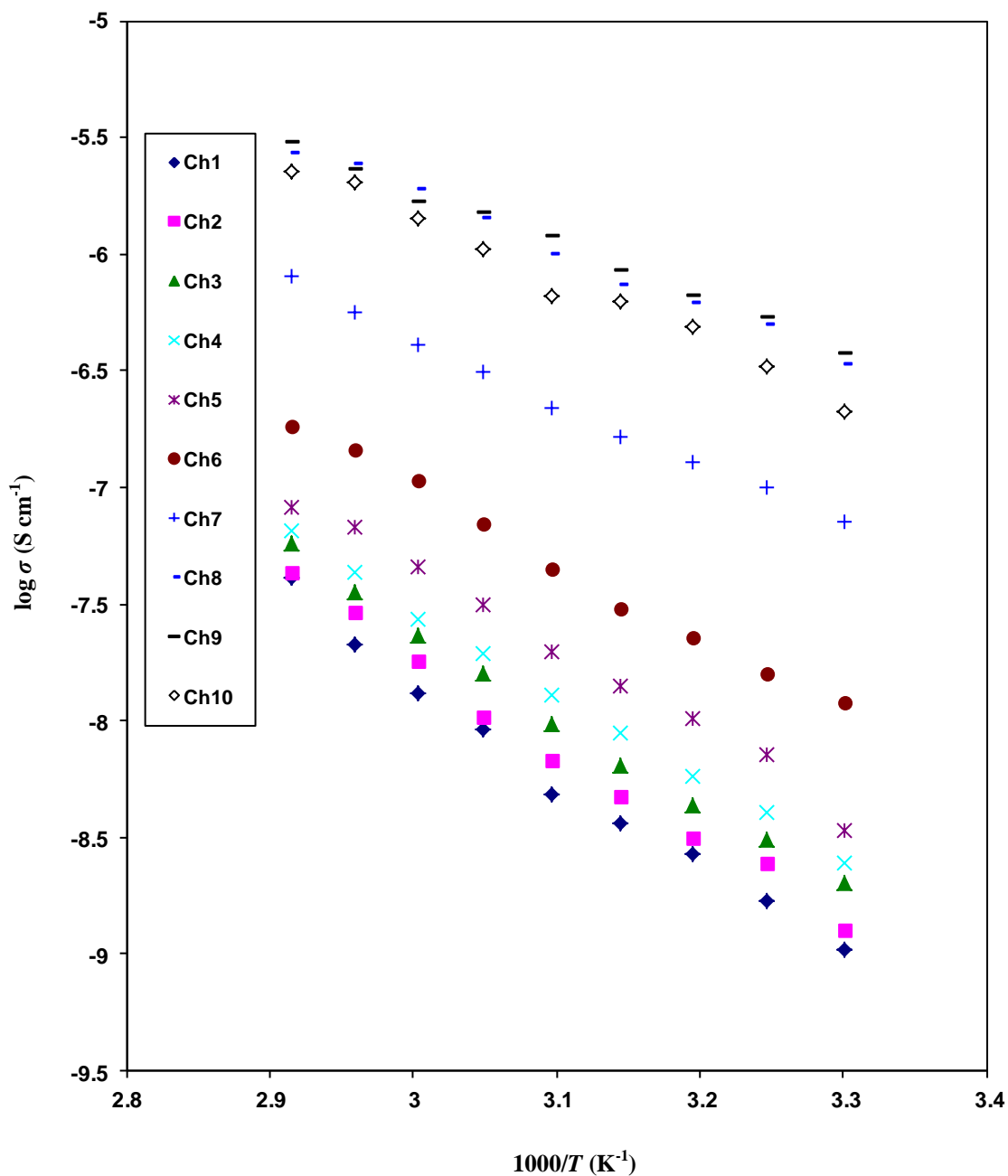


Figure 6.6: Plot  $\log \sigma$  versus  $1000/T$  for chitosan- $\text{NH}_4\text{I}$  electrolytes

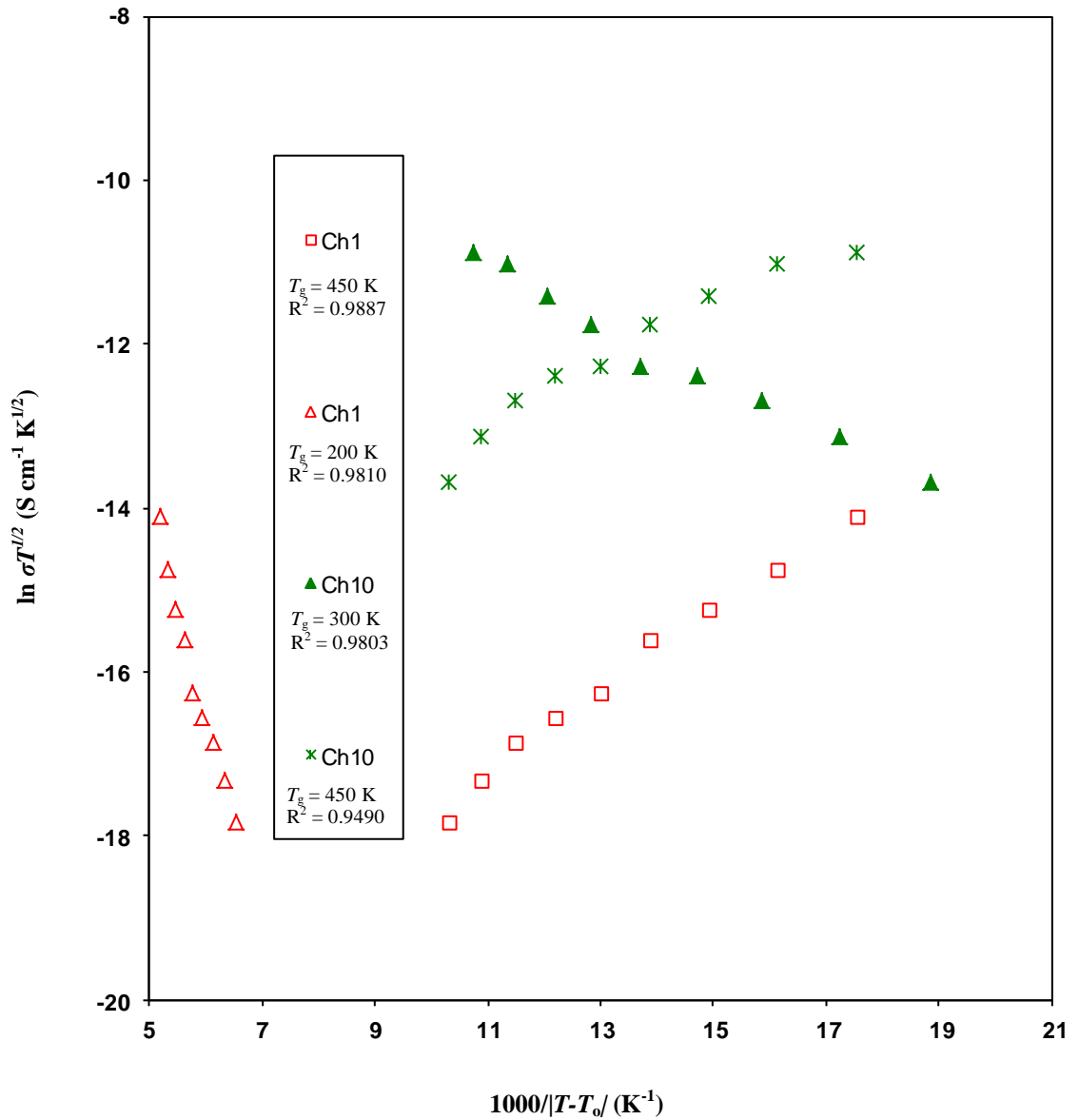


Figure 6.7: Plot  $\ln \sigma T^{1/2}$  versus  $1000/|T-T_0|$  for chitosan-NH<sub>4</sub>I electrolytes

Based on the report by Sakurai *et al.* (2000), the  $T_g$  for chitosan is about 476 K. Although there may be variations in  $T_g$  due to the chitosan source, it is still expected to be high due to the high rigidity of the glucosamine ring. From Figure 6.7, based on the data evaluated for temperatures above 300 K, the plot of  $\ln \sigma T^{1/2}$  versus  $1000/|T-T_0|$  has a positive gradient that violates VTF rule. To obtain a plot that follows VTF rule,  $T_0$  has to be of low value in order to get a linear graph that follows the VTF equation. The low

value of  $T_o$  and  $T_g$  is not justified for chitosan what more the samples contain  $\text{NH}_4\text{I}$  salt. Hence, the conductivity-temperature relationship for the chitosan- $\text{NH}_4\text{I}$  system is Arrhenian and can be represented by:

$$\sigma = \sigma_0 \exp\left(\frac{-E_A}{kT}\right) \quad (6.7)$$

Here  $\sigma_0$  is the pre-exponential factor that is dependent on the number density of mobile ions,  $E_A$  is activation energy,  $k$  is Boltzmann constant and  $T$  is absolute temperature in Kelvin. The activation energy,  $E_A$  can be obtained from the slope of  $\log \sigma$  versus  $1000/T$  graph. Activation energy is the energy required for an ion to begin movement.

At 5 wt.%  $\text{NH}_4\text{I}$  (Ch1), the room temperature conductivity is  $1.04 \times 10^{-9} \text{ S cm}^{-1}$  which increases to a maximum conductivity of  $3.7 \times 10^{-7} \text{ S cm}^{-1}$  at 45 wt.%  $\text{NH}_4\text{I}$  (Ch9). The conductivity of the Ch9 sample increases to  $3.01 \times 10^{-6} \text{ S cm}^{-1}$  at 343 K. For an increase in temperature of less than 100 K, the conductivity has increased by almost one order of magnitude. As the salt content increases, the number density of mobile ions,  $\eta$  in the electrolyte increases. From first principle, the conductivity,  $\sigma$  can be expressed as

$$\sigma = \eta e \mu \quad (6.8)$$

Here,  $e$  is electron charge and  $\mu$  is mobility of ions. It is evident that the conductivity is expected to increase when  $\eta$  and/or  $\mu$  increases. The linear variation of  $\log \sigma$  versus  $10^3/T$  plot suggests that ionic conduction is a thermally activated process. Variation of the room temperature conductivity, pre-exponential factor,  $\sigma_0$  and activation energy,  $E_A$  as a function of  $\text{NH}_4\text{I}$  content for all the chitosan- $\text{NH}_4\text{I}$  electrolytes are shown in Figure 6.8. From the figure, it can be observed that conductivity increases as salt composition increases until 45 wt.%  $\text{NH}_4\text{I}$  which can be related to the increase in the number of



mobile charge carriers [Osman *et al.*, 2001]. The highest room temperature conductivity is observed for the sample containing 45 wt.%  $\text{NH}_4\text{I}$  designated as Ch9. Above 45 wt.%  $\text{NH}_4\text{I}$ , the conductivity decreases. This can be attributed to the reassociation of the ions into neutral aggregates [Teeters *et al.*, 1996].

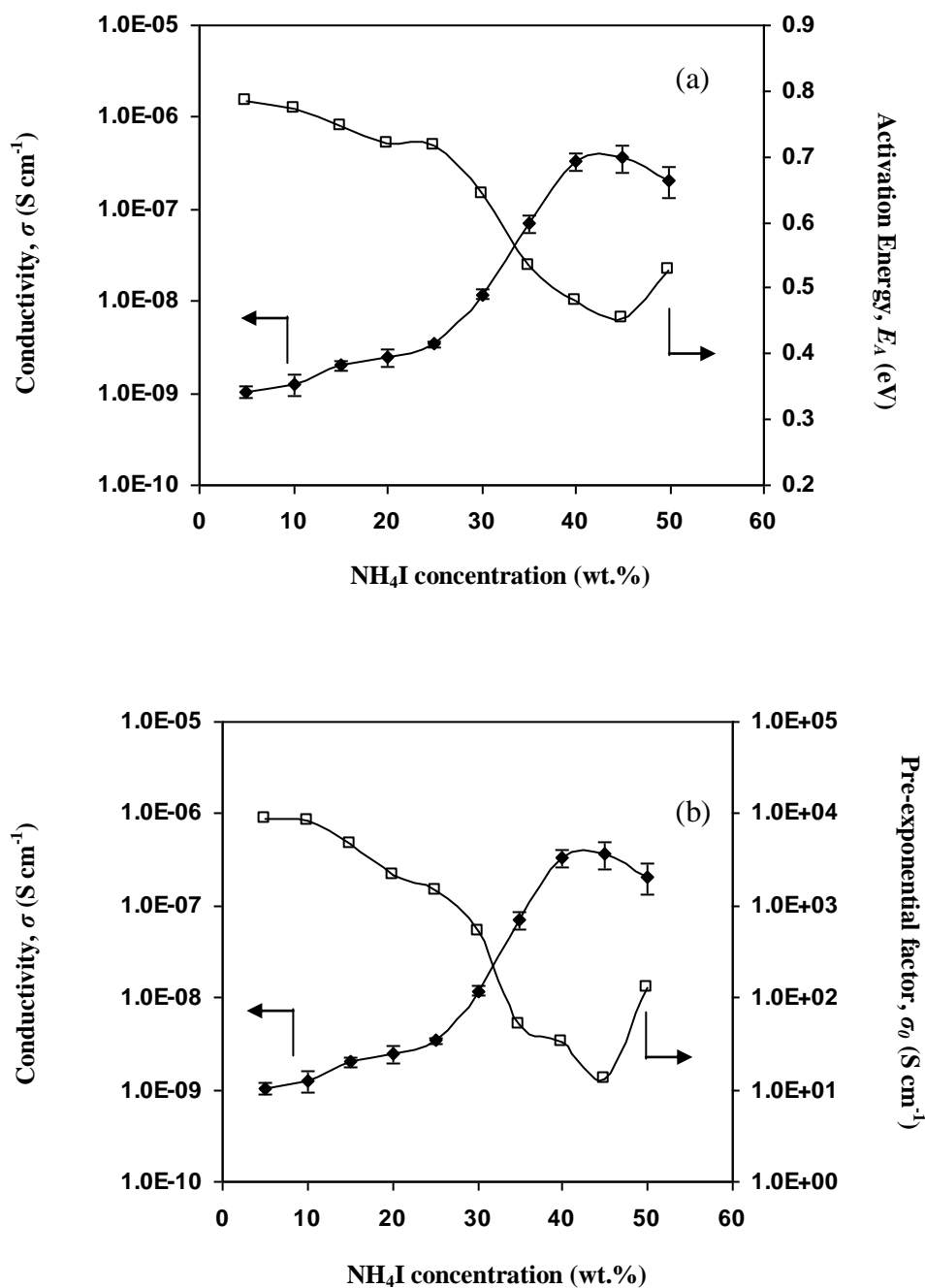


Figure 6.8: (a) The ionic conductivity at room temperature and activation energy dependence on  $\text{NH}_4\text{I}$  content (b) Conductivity and pre-exponential factor versus  $\text{NH}_4\text{I}$  content

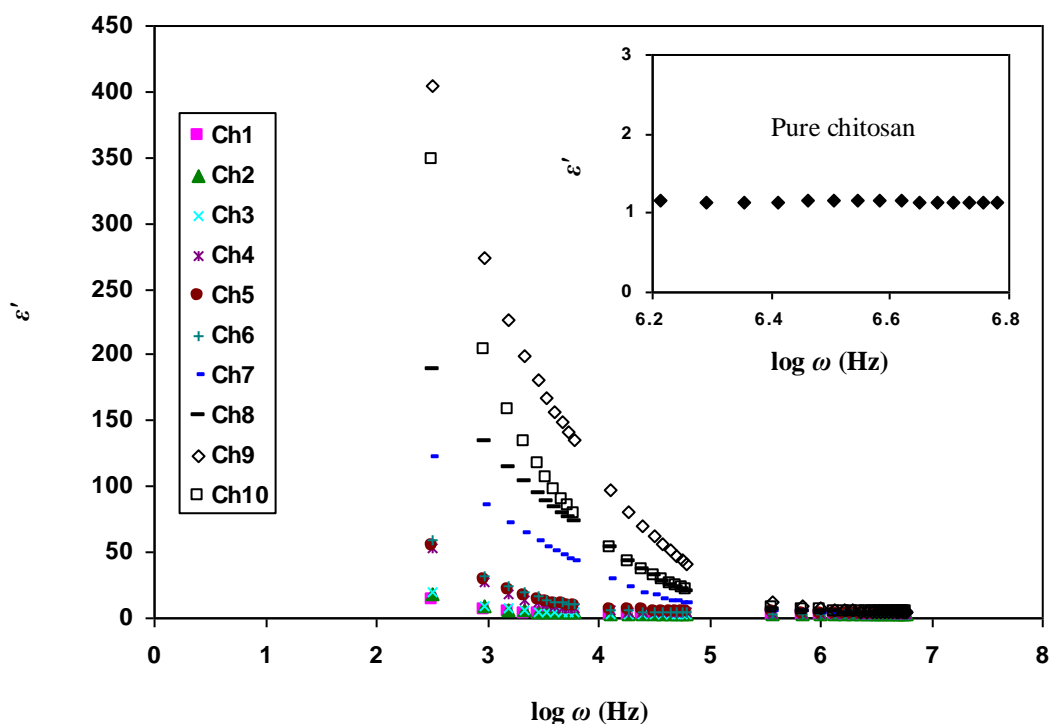
From Figure 6.8 (a), it can be observed that  $E_A$  decreases as salt content increases up to 45 wt. %. Above this composition, it slightly increases. The increase in conductivity with salt can therefore be explained in terms of the decrease in  $E_A$ . As  $E_A$  is the energy required for the ions to conduct charge, the lower the activation energy required, the faster the ion will begin conducting charge. In other words, the charge carriers become mobile more easily. This leads to conductivity increment. Hence, it can be seen that the film exhibiting the highest conductivity possesses the lowest  $E_A$  value. Table 6.1 lists the ionic conductivity at room temperature and the associated activation energy for different chitosan-NH<sub>4</sub>I electrolytes. The behavior of pre-exponential factor with NH<sub>4</sub>I concentration follows that of  $E_A$ . XRD result in chapter 5 supports Ch9 as the highest conducting since it is the most amorphous film.

**Table 6.1: Ambient temperature conductivity, pre-exponential factor and activation energy of various chitosan-NH<sub>4</sub>I electrolytes**

Electrolyte	$\sigma$ (S cm <sup>-1</sup> )	$\sigma_0$ (S cm <sup>-1</sup> )	$E_A$ (eV)
Ch0	$(8.07 \pm 0.71) \times 10^{-10}$	$13.84 \times 10^3$	0.80
Ch1	$(1.04 \pm 0.13) \times 10^{-9}$	$9.02 \times 10^3$	0.78
Ch2	$(1.26 \pm 0.33) \times 10^{-9}$	$8.57 \times 10^3$	0.77
Ch3	$(2.02 \pm 0.27) \times 10^{-9}$	$4.68 \times 10^3$	0.75
Ch4	$(2.47 \pm 0.54) \times 10^{-9}$	$2.15 \times 10^3$	0.72
Ch5	$(3.41 \pm 0.19) \times 10^{-9}$	$1.48 \times 10^3$	0.70
Ch6	$(1.19 \pm 0.16) \times 10^{-8}$	$5.39 \times 10^2$	0.64
Ch7	$(7.07 \pm 1.56) \times 10^{-8}$	$5.10 \times 10^1$	0.53
Ch8	$(3.35 \pm 0.79) \times 10^{-7}$	$3.20 \times 10^1$	0.48
Ch9	$(3.73 \pm 1.22) \times 10^{-7}$	$1.32 \times 10^1$	0.45
Ch10	$(2.09 \pm 0.79) \times 10^{-7}$	$1.30 \times 10^2$	0.53

## 6.4 DIELECTRIC STUDIES OF CHITOSAN-NH<sub>4</sub>I ELECTROLYTES

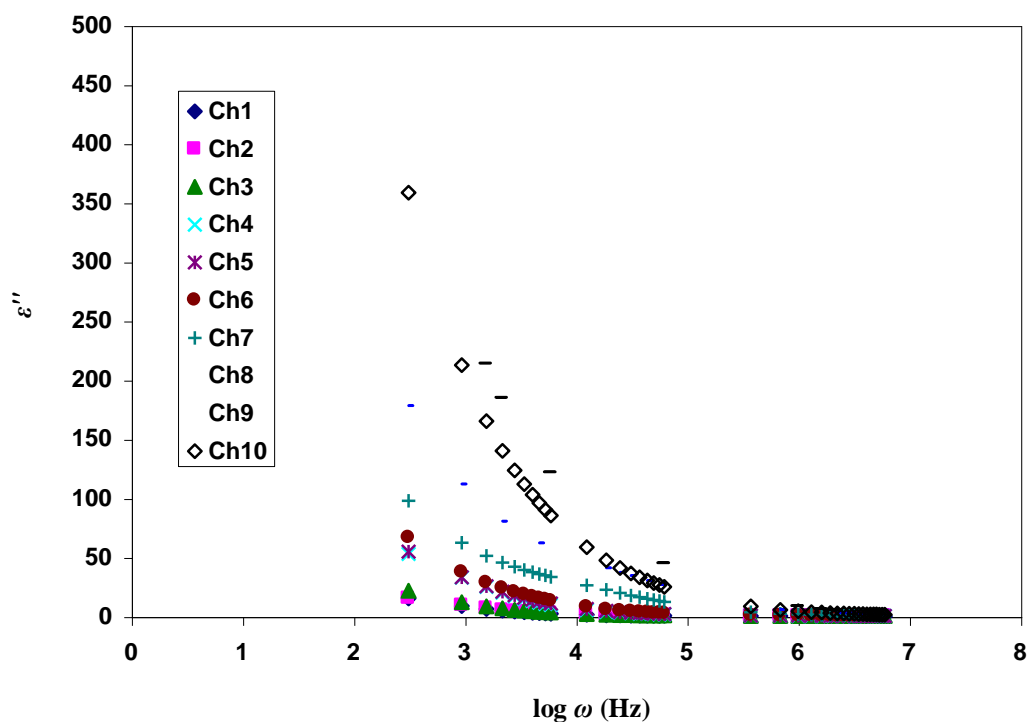
Variation of the dielectric constant with frequency at ambient temperature for all chitosan-NH<sub>4</sub>I samples is displayed in Figure 6.9. For every sample, it can be observed that  $\epsilon'$  decreases with increasing frequency. The dielectric constant of pure chitosan was estimated to be 1.1 as shown in the inset of Figure 6.9.



**Figure 6.9:** Frequency dependence on dielectric constant at room temperature for various chitosan-NH<sub>4</sub>I electrolytes

The  $\epsilon'$  versus  $\log \omega$  graph can be divided into two regions i.e. the low frequency region between 50 Hz to 500 kHz and from 500 kHz to 1 MHz, the high frequency region. The low frequency region is the space charge region and  $\epsilon'$  has high values. At such low frequency, the period of the applied electric field is very long and the ions accumulate at the electrode/electrolyte interface. It can be seen for every salt concentration, at a fixed frequency say 1 kHz,  $\epsilon'$  increases with salt content in the sample from 5 to 45 wt.% after which  $\epsilon'$  drops. This rise and fall of  $\epsilon'$  follows the conductivity trend. Figure 6.10

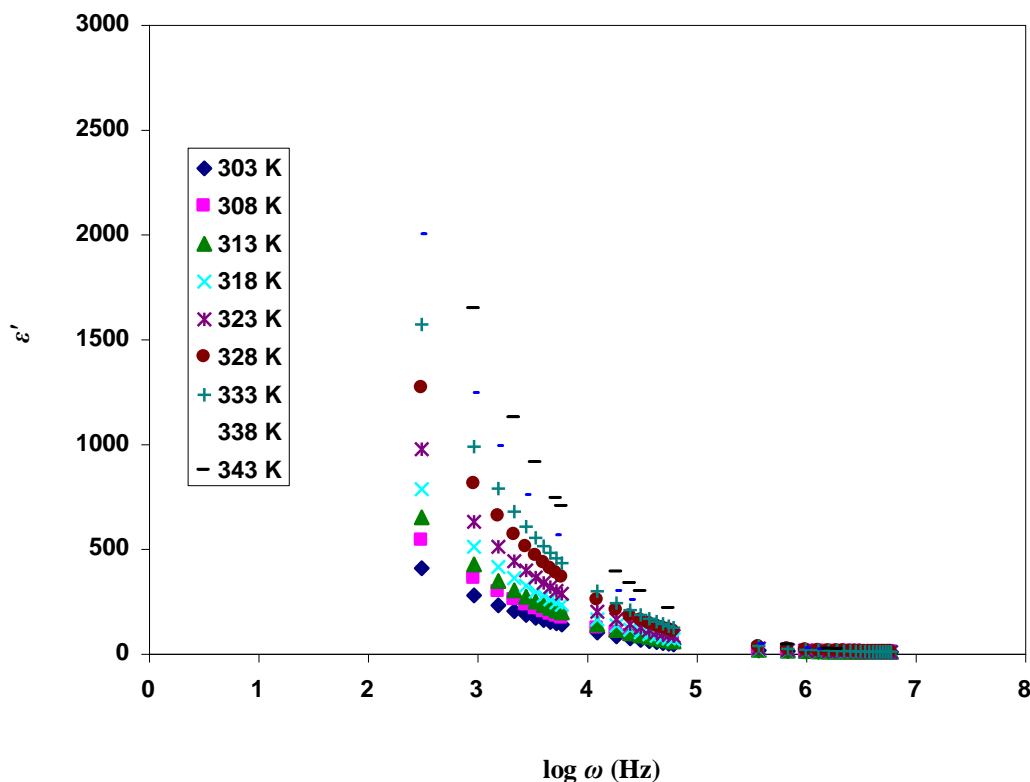
presents the variation of the imaginary part of complex permittivity i.e. dielectric loss,  $\epsilon''$  as a function of  $\log \omega$ .



**Figure 6.10: Frequency-dependent dielectric loss at room temperature for various chitosan-NH<sub>4</sub>I electrolytes**

As can be seen from the figure, dielectric loss decreases with the increase in frequency. The highest dielectric loss  $\epsilon''$  occurs at lower frequencies due to accumulation of free charges at the electrode-electrolyte interface. At high frequencies, the fast periodic reversal of the electric field results in the decrease of the excess ion diffusion in the field direction. This leads to a decrease in build-up of free charges thus decreasing  $\epsilon''$  [Vieira *et al.*, 2007].

Figure 6.11 presents the frequency variation of the real part of complex permittivity i.e. dielectric constant,  $\epsilon'$  for the highest conducting chitosan-NH<sub>4</sub>I electrolyte (Ch9) at different temperatures.



**Figure 6.11: Frequency dependence of dielectric constant at selected temperatures for Ch9 electrolyte**

The dielectric constant increases with temperature at all frequencies. In the low frequency region the increase in  $\epsilon'$  with temperature is quite significant, but in the high frequency region the increase in  $\epsilon'$  with temperature is quite significant, but in the high frequency region the increase is smaller. The increase in  $\epsilon'$  with temperature is in accordance to the increase in conductivity with temperature. It may be thought that temperature has increased the energy of the free ions leading to increased ionic mobility and this is reflected by the increase in  $\epsilon'$  and conductivity.

The graph of dielectric loss,  $\epsilon''$  with frequency as a function of  $\log \omega$  at various temperatures for the highest conducting Ch9 sample is given in Figure 6.12. The behavior of  $\epsilon''$  with frequency at different temperatures is the same as that for  $\epsilon'$

According to Saroj and Singh (2012), the increase in  $\epsilon'$  with temperature is due to the increase in amorphousness of the sample.

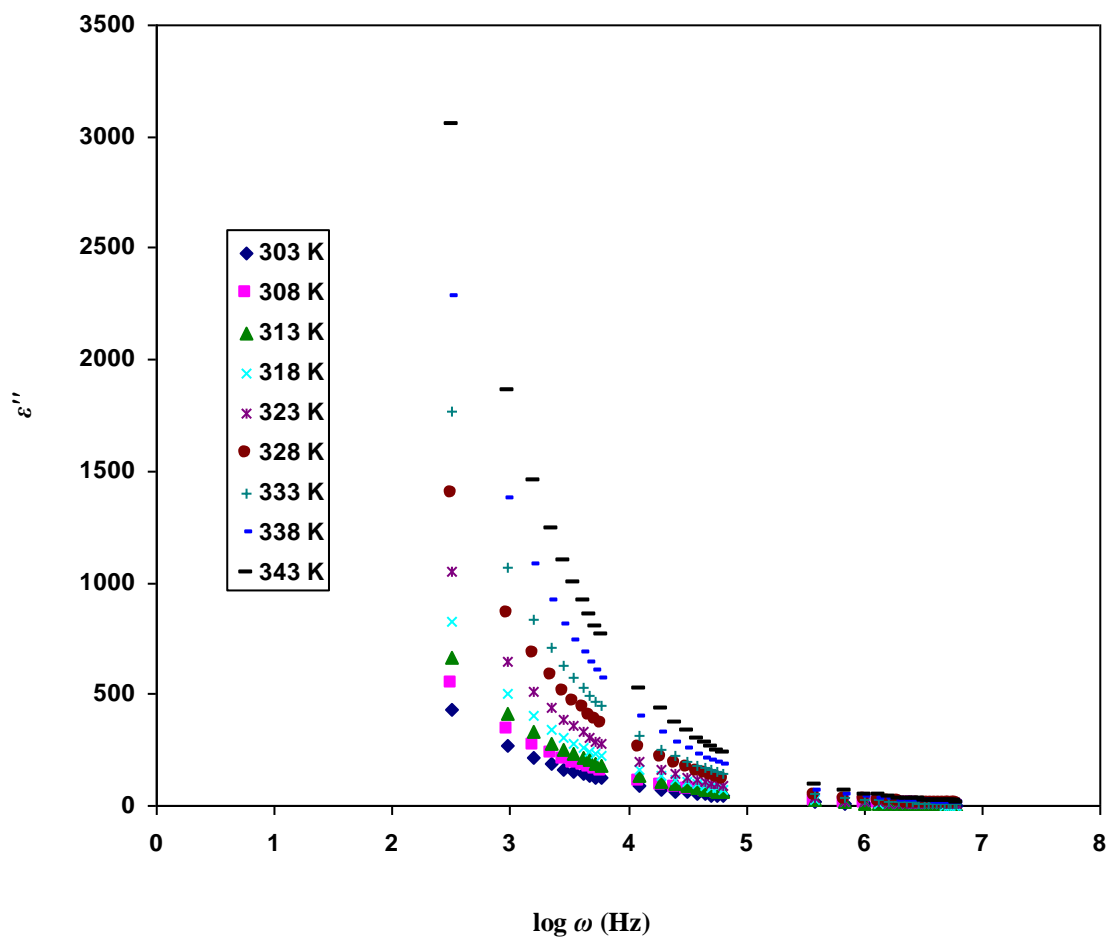


Figure 6.12: Frequency-dependent dielectric loss at selected temperatures for Ch9 electrolyte

### 6.5 CONDUCTIVITY-TEMPERATURE RELATIONSHIP OF (CHITOSAN-PVA)-NH<sub>4</sub>I ELECTROLYTES

The conductivity-temperature relationship is as shown in Figure 6.13. In order to verify whether the relationship is Arrhenian or obeys the VTF rule, the data are converted into a plot of  $\ln \sigma T^{1/2}$  versus  $1000/|T-T_0|$  which is shown in Figure 6.14.

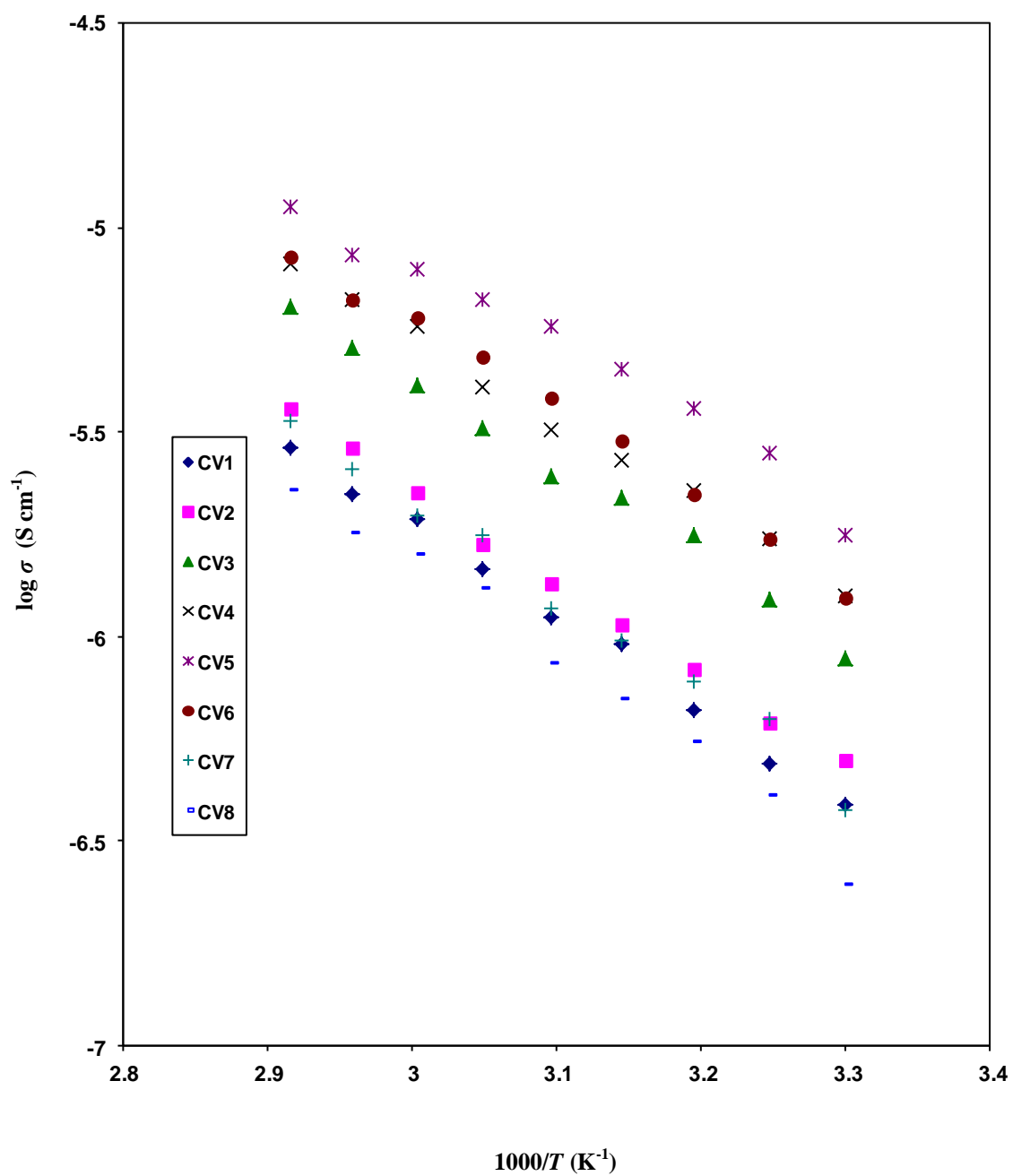


Figure 6.13: Plot  $\log \sigma$  versus  $1000/T$  for (chitosan-PVA)- $\text{NH}_4\text{I}$  electrolytes

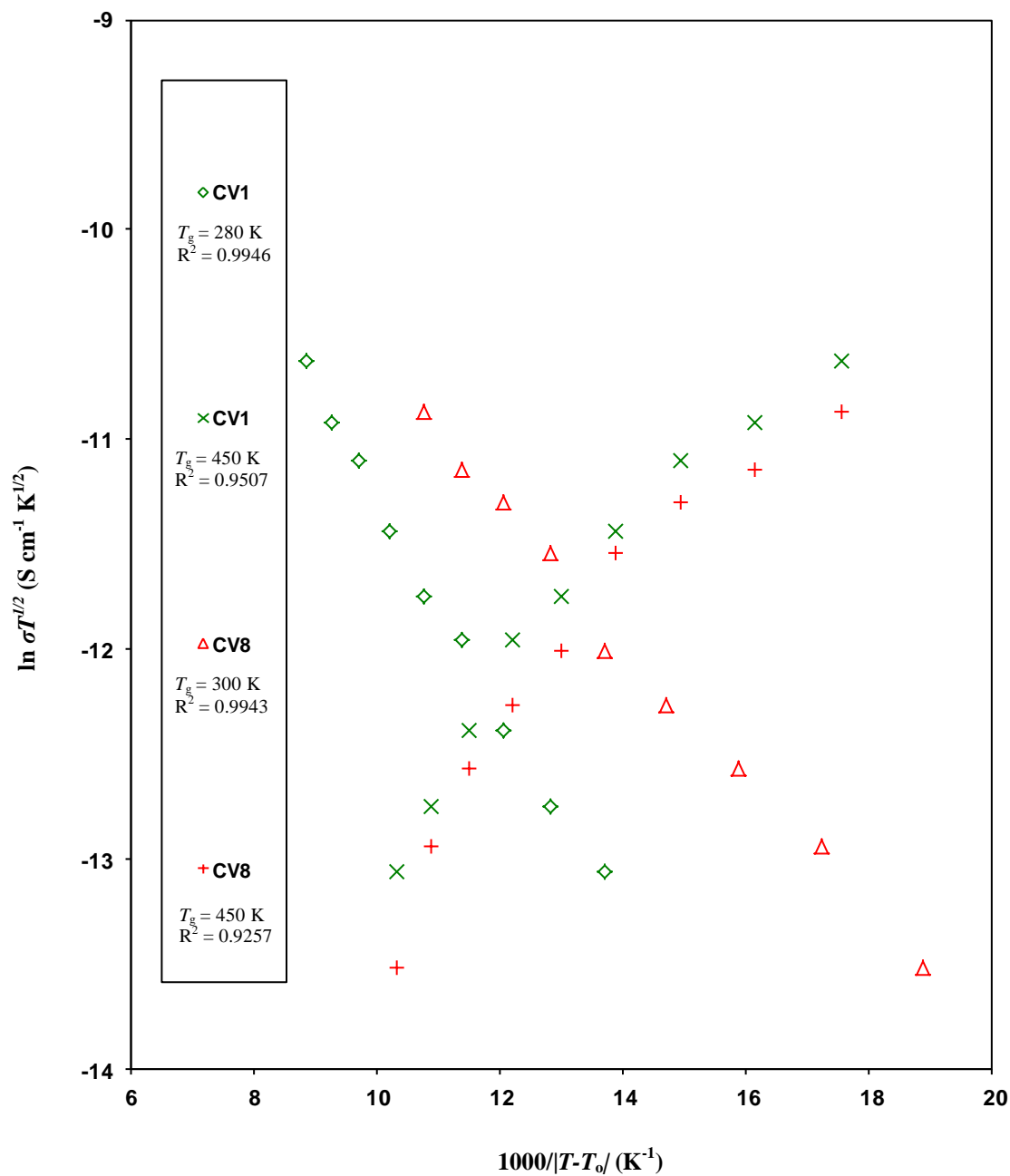


Figure 6.14: Plot  $\log \sigma T^{1/2}$  versus  $1000/|T - T_0|$  for (chitosan-PVA)- $\text{NH}_4\text{I}$  electrolytes

If for the previous sample the  $T_g$  value was based on the work of Sakurai *et al.* (2000) but for samples in this section, it is based on the works of both Sakurai *et al.* (2000) and Agrawal and Awadhia (2004) for  $T_g$  of PVA which is 363 K. Depending on the



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composition of chitosan and PVA,  $T_g$  of the blend should be between the two glass transition temperatures [Lewandowska, 2009]. Based on these reports, it can be implied that the conductivity-temperature relationship cannot follow the VTF rule.

From Figure 6.13, the ionic conductivity is observed to increase with the increase in temperature and PVA concentrations (until 27.5 wt.% PVA (CV5)) for chitosan-PVA blended systems. The increase in conductivity can be attributed to the increase in mobility of ions [Rajendran *et al.*, 2004]. This conductivity-temperature behavior of (chitosan-PVA)-NH<sub>4</sub>I electrolytes shows that conduction is a thermally activated process. The regression value,  $R^2$  for all (chitosan-PVA)-NH<sub>4</sub>I samples lies in the range of 0.98 to 1.

Figure 6.15(a) presents the activation energy (obtained from the slope of Arrhenius plot) and the conductivity of chitosan/PVA blends as a function of PVA content (expressed in terms of wt.% PVA) at a fixed salt concentration. A conductivity maximum can be observed at  $1.77 \times 10^{-6} \text{ S cm}^{-1}$  for the sample with (27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.% NH<sub>4</sub>I (CV5). Conductivity decreases when the PVA content is more than 27.5 wt. %. The increase in conductivity is attributed to the amorphousness of the samples and the decrease in conductivity is attributed to the salt recrystallizing out of the samples as can be deduced from the diffraction patterns of CV6 and CV8 samples. From Figure 6.15(a), the highest conducting sample exhibits the lowest value for activation energy. The behavior of  $\sigma_0$  with PVA concentration as shown in Figure 6.15(b) can be considered similar to the behavior of activation energy. Values of conductivity at room temperature,  $\sigma_0$  and the associated activation energy for chitosan-PVA-NH<sub>4</sub>I systems are tabulated in Table 6.2.

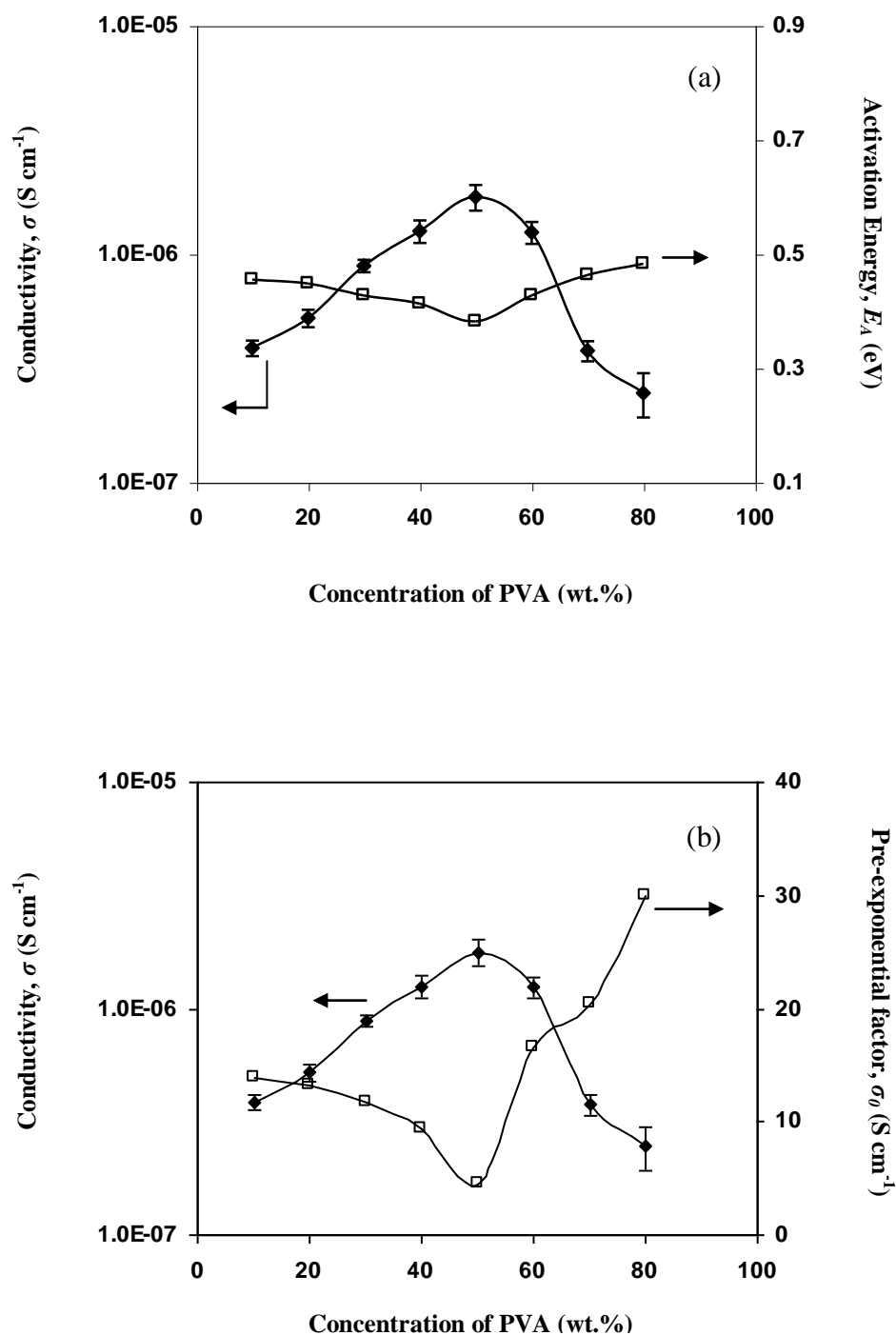


Figure 6.15: (a) The ionic conductivity at room temperature and the activation energy of chitosan-PVA-NH<sub>4</sub>I electrolytes with various concentrations of PVA (expressed as wt.% of chitosan) (b) Conductivity and pre-exponential factor versus PVA concentration

**Table 6.2: Ambient temperature conductivity, pre-exponential factor and activation energy of various (chitosan-PVA)-NH<sub>4</sub>I electrolytes**

Electrolyte	$\sigma$ (S cm <sup>-1</sup> )	$\sigma_0$ (S cm <sup>-1</sup> )	$E_A$ (eV)
CV1	$(3.87 \pm 0.31) \times 10^{-7}$	13.92	0.45
CV2	$(5.23 \pm 0.45) \times 10^{-7}$	13.24	0.45
CV3	$(8.86 \pm 0.56) \times 10^{-7}$	11.75	0.43
CV4	$(1.26 \pm 0.14) \times 10^{-6}$	9.29	0.41
CV5	$(1.77 \pm 0.23) \times 10^{-6}$	4.60	0.38
CV6	$(1.24 \pm 0.14) \times 10^{-6}$	16.50	0.43
CV7	$(3.76 \pm 0.38) \times 10^{-7}$	20.49	0.46
CV8	$(2.46 \pm 0.54) \times 10^{-7}$	30.00	0.48

## 6.6 DIELECTRIC STUDIES OF (CHITOSAN-PVA)-NH<sub>4</sub>I ELECTROLYTES

The frequency dependence on dielectric constant at ambient room temperature for various (chitosan-PVA)-NH<sub>4</sub>I electrolytes is presented in Figure 6.16. The values of  $\epsilon'$  decrease with increasing frequency similar to the electrolytes in the chitosan-NH<sub>4</sub>I systems. The dielectric constant of pure PVA was estimated as shown in the inset of Figure 6.14. It can be seen from the figure that the  $\epsilon'$  of PVA is  $\sim 2.2$ . As mentioned before, the estimated  $\epsilon'$  of chitosan is  $\sim 1.1$ . This may also explained why the chitosan-PVA based electrolytes exhibit higher conductivity than the chitosan-NH<sub>4</sub>I electrolytes. The higher dielectric constant of PVA helps in solvating a larger portion of the added salt thereby increasing the conductivity. Figure 6.17 represents the variation of dielectric loss as a function of  $\log \omega$  at ambient temperature 303 K for various (chitosan-PVA)-NH<sub>4</sub>I samples. It is noted that  $\epsilon''$  decreases with the increase in frequency for every sample and increases accordingly to the conductivity of (chitosan-PVA)-NH<sub>4</sub>I systems at a specific frequency. Hence, the highest value of dielectric loss is observed in the highest conducting sample (CV5).

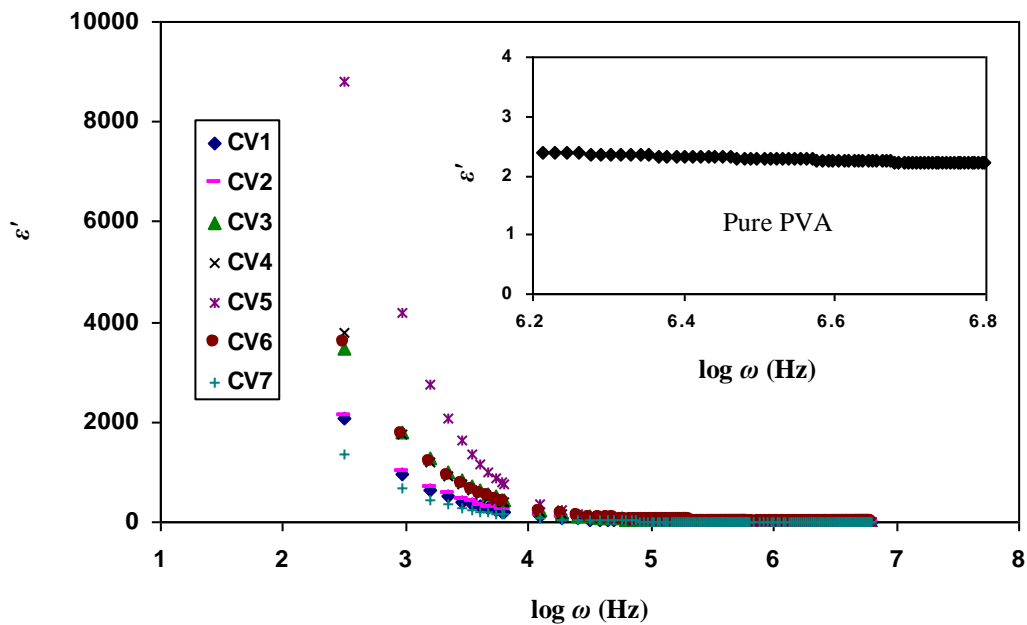


Figure 6.16: Frequency dependence on dielectric constant at room temperature for various (chitosan-PVA)- $\text{NH}_4\text{I}$  electrolytes

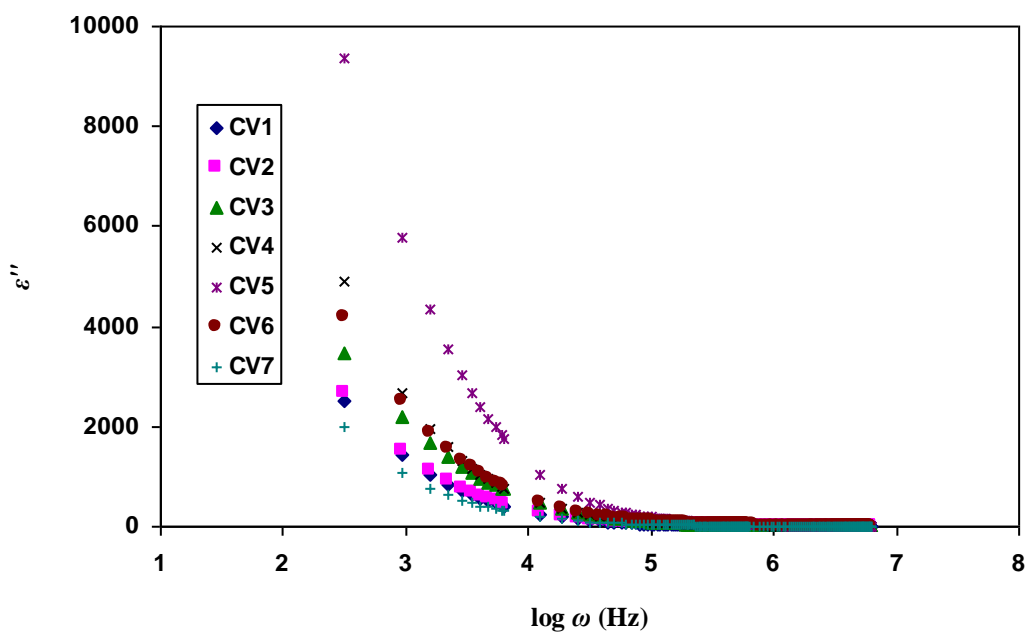


Figure 6.17: Frequency dependence on dielectric loss at room temperature for various (chitosan-PVA)- $\text{NH}_4\text{I}$  electrolytes

For CV5, the graphs of dielectric constant and dielectric loss versus frequency at selected temperatures are shown in Figures 6.18 and 6.19, respectively. The dielectric constant and dielectric loss decrease as frequency increases for all temperatures. Increase in dielectric constant and loss are observed with increase in temperature at a specific frequency.

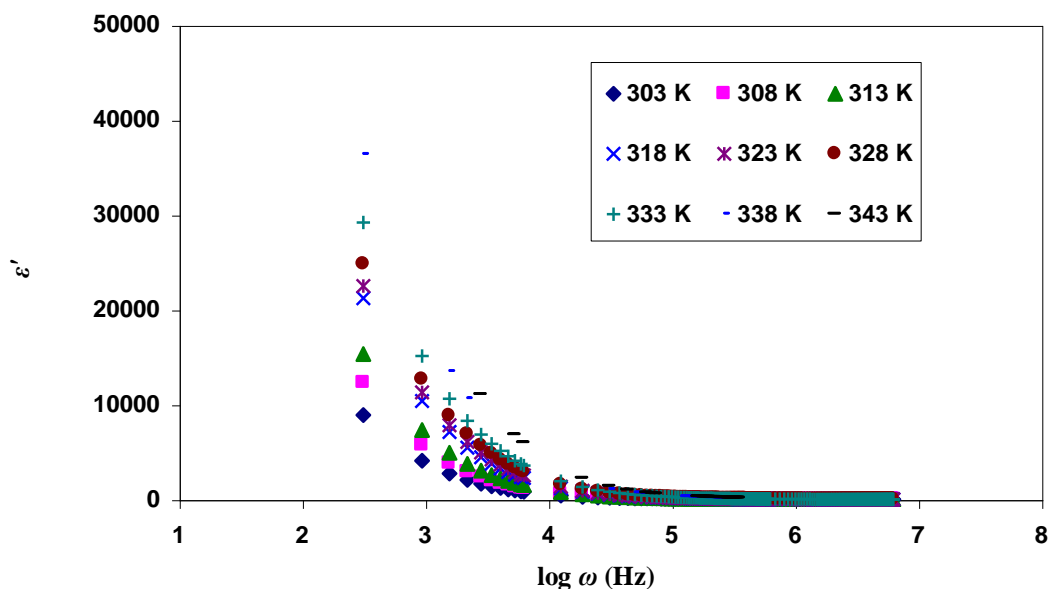


Figure 6.18: Frequency dependence on dielectric constant at selected temperatures for CV5 electrolyte

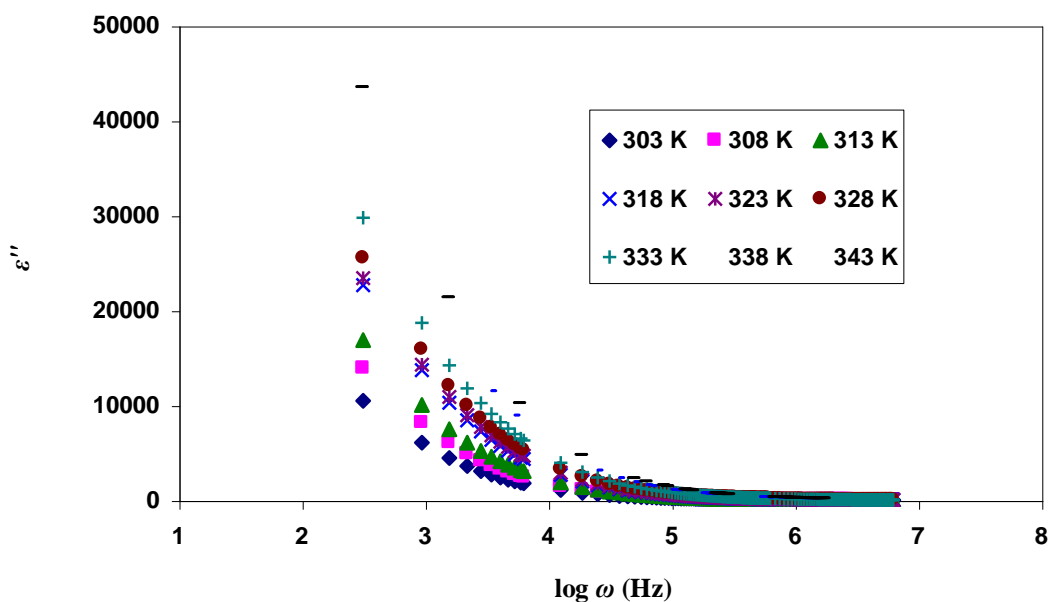


Figure 6.19: Frequency dependence on dielectric loss at selected temperatures for CV5 electrolyte

### 6.7 CONDUCTIVITY-TEMPERATURE RELATIONSHIP OF (CHITOSAN-PEO)-NH<sub>4</sub>I ELECTROLYTES

The conductivity-temperature relationship is as shown in Figure 6.20. In order to verify whether the relationship is Arrhenian or obeys the VTF rule, the data are converted into a plot of  $\ln\sigma T^{1/2}$  versus  $1000/|T-T_0|$  which is shown in Figure 6.21.

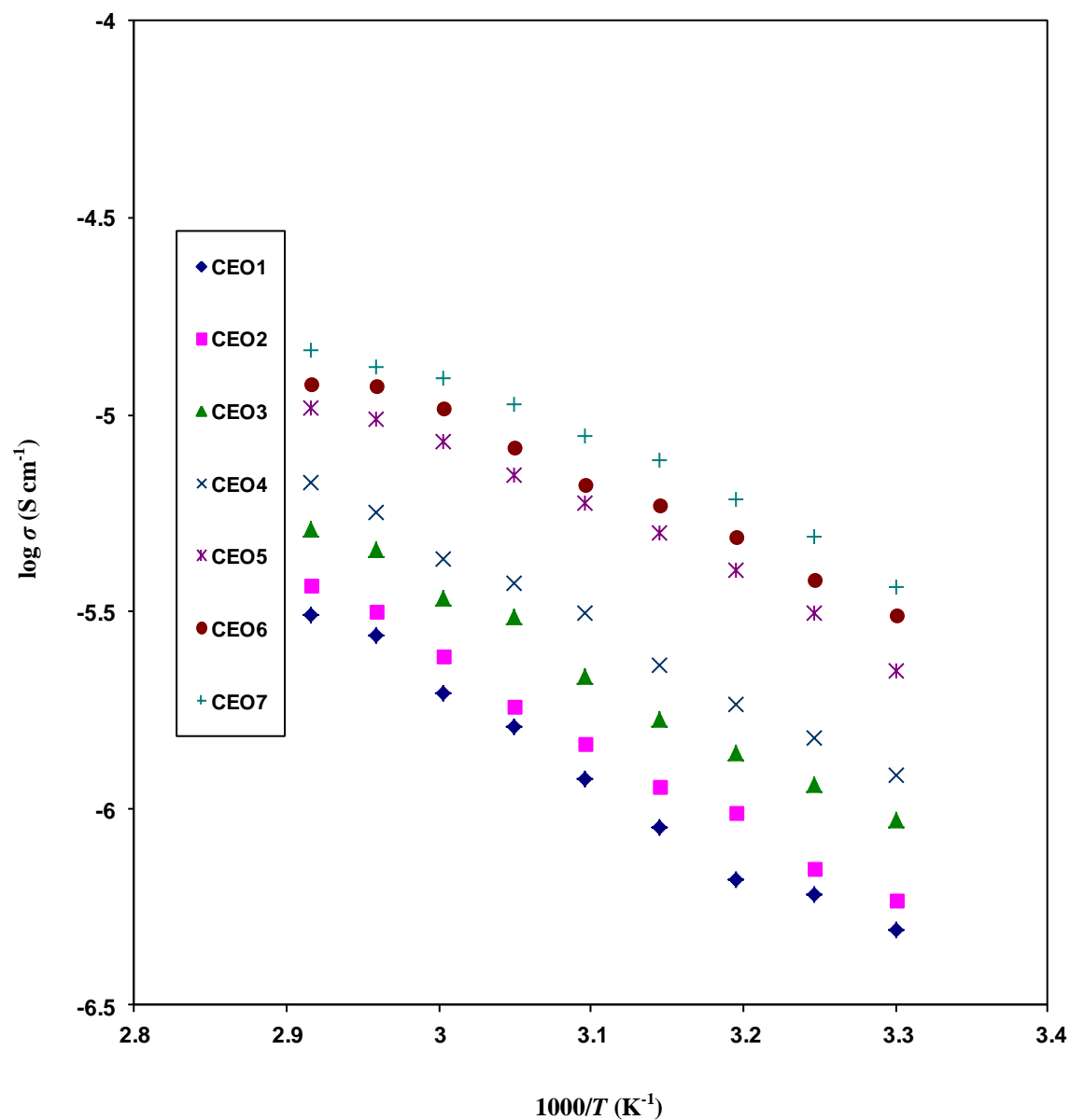


Figure 6.20: Plot  $\log \sigma$  versus  $1000/T$  for (chitosan-PEO)-NH<sub>4</sub>I electrolytes

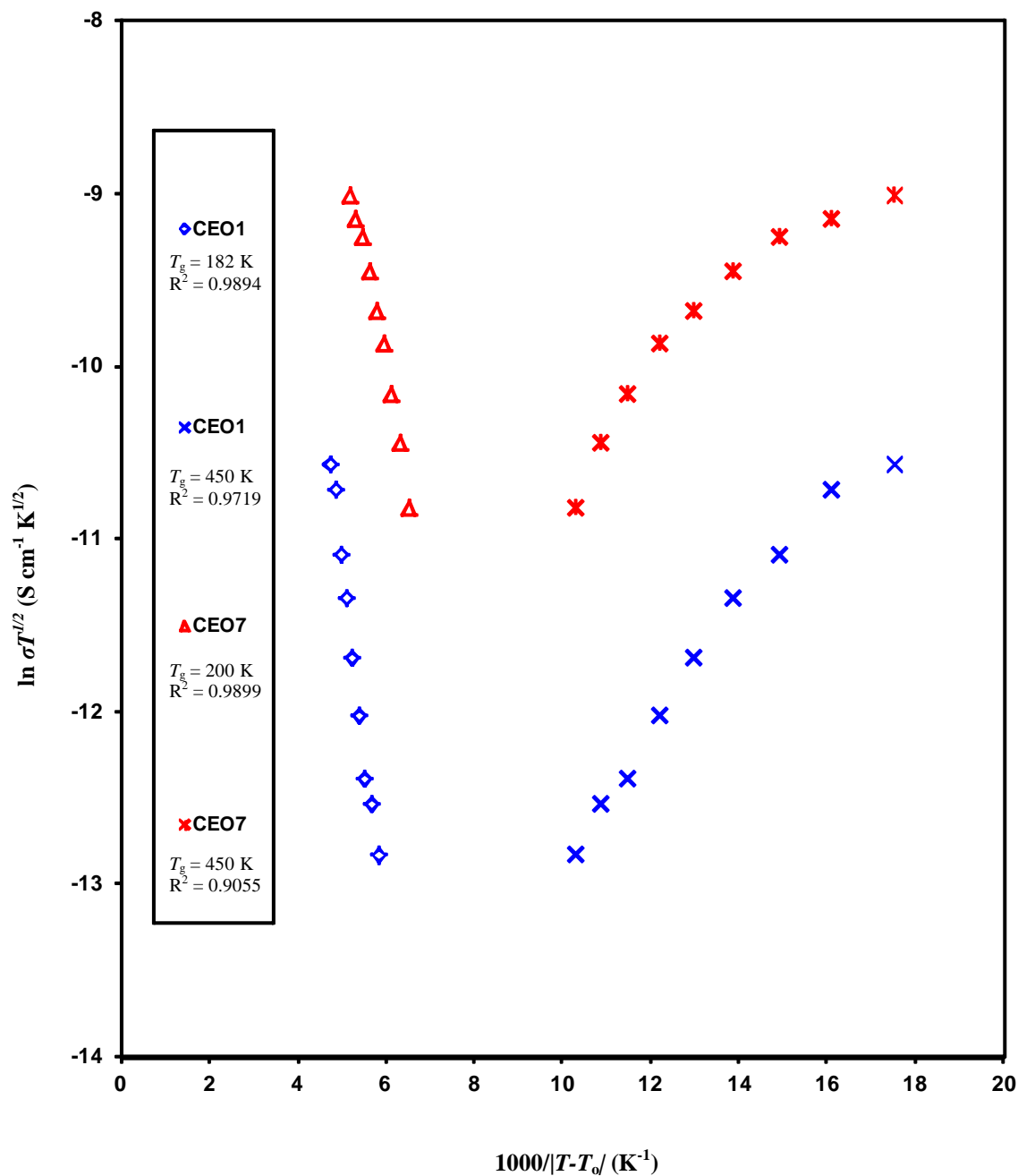
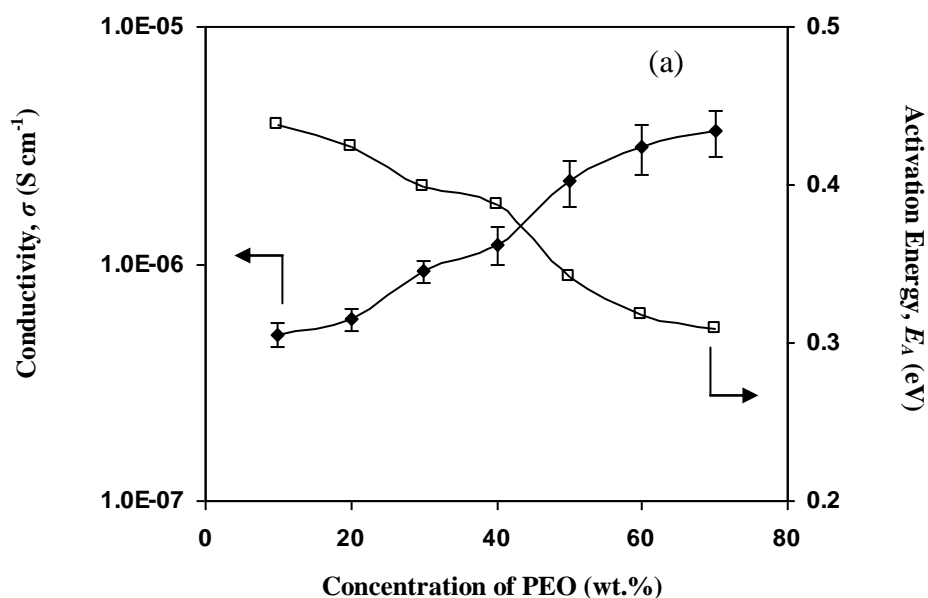


Figure 6.21: Plot  $\log \sigma T^{1/2}$  versus  $1000/|T-T_0|$  for (chitosan-PEO)- $\text{NH}_4\text{I}$  electrolytes

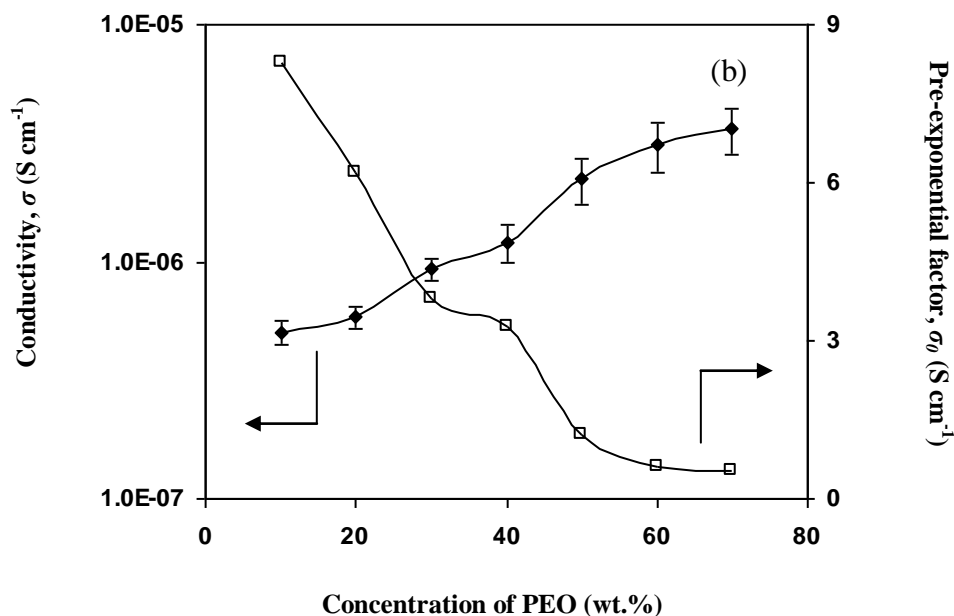
The  $T_g$  value for the (chitosan-PEO)- $\text{NH}_4\text{I}$  system was based on the work of Sakurai *et al.* (2000) and Stephan (2006) for  $T_g$  of PEO which is 209 K. From the literature, it can be understood that  $T_g$  of the blend should be between the two glass transition

temperatures [Lewandowska, 2009] based on the composition of chitosan and PEO. Based on these reports, it can be implied that the conductivity-temperature relationship of the (chitosan-PEO)-NH<sub>4</sub>I system do not follow the VTF rule.

Figure 6.20 shows the plot of  $\log \sigma$  versus  $1000/T$  for (chitosan-PEO)-NH<sub>4</sub>I electrolytes. From the figure, it can be observed that the ionic conductivity of the chitosan-PEO electrolyte blends increases with increasing temperature and PEO content. From Figure 6.20, the regression value,  $R^2$  for all (chitosan-PEO)-NH<sub>4</sub>I samples lies in the range of 0.98 to 1. This indicates that the temperature dependence on ionic conductivity of these systems obeys Arrhenius rule. The ionic conductivity at room temperature, activation energy and the pre-exponential factor,  $\sigma_0$  with different compositions of PEO expressed in terms of chitosan content (wt.%) are plotted in Figure 6.22. The activation energy of the samples was calculated from the slope of  $\log \sigma$  versus  $1000/T$  using Arrhenius equation.







**Figure 6.22:** (a) The ionic conductivity at room temperature and the activation energy of chitosan-PEO-NH<sub>4</sub>I electrolytes with various concentrations of PEO (expressed as wt.% of chitosan) (b) Conductivity and pre-exponential factor versus PEO concentration

From Table 6.1, it is known that the ionic conductivity of 55 wt.% chitosan-45 wt.% NH<sub>4</sub>I (Ch9) electrolyte without blending is  $3.73 \times 10^{-7} S\ cm^{-1}$  at room temperature. As can be seen in Figure 6.22, the conductivity increases to  $3.66 \times 10^{-6} S\ cm^{-1}$  when blending chitosan with PEO for electrolyte composition of (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH<sub>4</sub>I.

The values of room temperature conductivity and activation energy for different chitosan-PEO-NH<sub>4</sub>I systems are tabulated in Table 6.3. It can be observed that the sample designated as CEO7 exhibits the highest conductivity and the lowest  $E_A$  value.  $E_A$  of highest conducting chitosan-PEO-NH<sub>4</sub>I electrolyte is lower than that of highest conducting electrolyte containing chitosan as host and NH<sub>4</sub>I as ion supplying salt (shown in Figure 6.8). This indicates that the ions in chitosan blends system can move more easily compared to that of the single polymer host system.

**Table 6.3: Ambient temperature conductivity, pre-exponential factor and activation energy of various (chitosan-PEO)-NH<sub>4</sub>I electrolytes**

Electrolyte	$\sigma$ (S cm <sup>-1</sup> )	$\sigma_0$ (S cm <sup>-1</sup> )	$E_A$ (eV)
CEO1	$(5.06 \pm 0.57) \times 10^{-7}$	8.30	0.44
CEO2	$(5.84 \pm 0.63) \times 10^{-7}$	6.19	0.42
CEO3	$(9.29 \pm 1.02) \times 10^{-7}$	3.79	0.40
CEO4	$(1.21 \pm 0.21) \times 10^{-6}$	3.25	0.39
CEO5	$(2.24 \pm 0.50) \times 10^{-6}$	1.20	0.34
CEO6	$(3.11 \pm 0.72) \times 10^{-6}$	0.62	0.32
CEO7	$(3.66 \pm 0.80) \times 10^{-6}$	0.55	0.31

## 6.8 DIELECTRIC STUDIES OF (CHITOSAN-PEO)-NH<sub>4</sub>I ELECTROLYTES

Figure 6.23 presents the variation of dielectric constant with  $\log \omega$  at 303 K for (chitosan-PEO)-NH<sub>4</sub>I electrolytes. Decrease of  $\epsilon'$  with increasing frequency and its increment with PEO composition is true in these systems. From the figure, dielectric constant of pure PEO was estimated as  $\sim 2.8$ . The higher conductivity for this system compared to the (chitosan-PVA)-NH<sub>4</sub>I and chitosan-NH<sub>4</sub>I systems justified the higher dielectric constant of PEO.

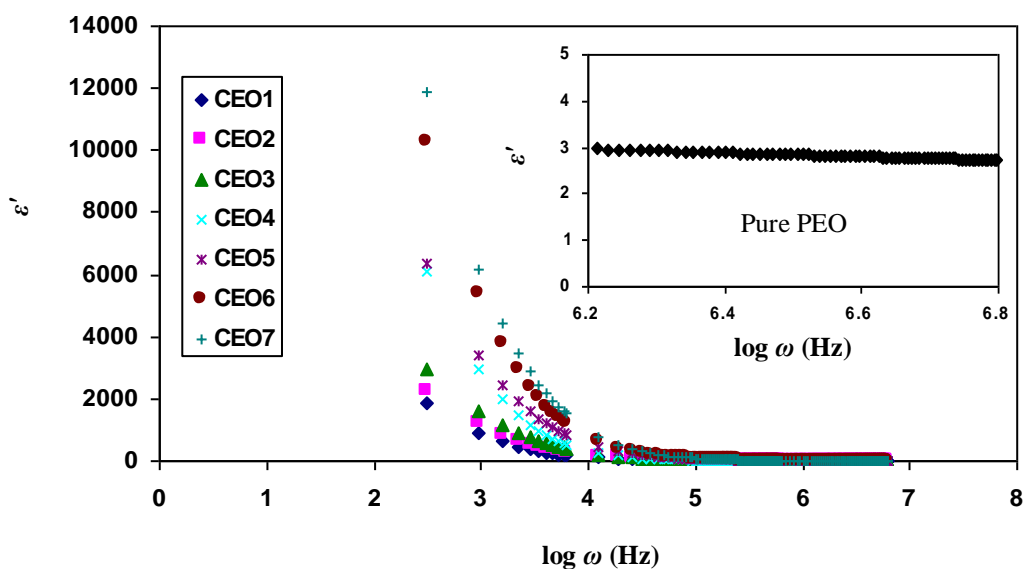
**Figure 6.23: Frequency dependence on dielectric constant at room temperature for different (chitosan-PEO)-NH<sub>4</sub>I electrolytes**

Figure 6.24 shows the variation of dielectric loss as a function of  $\log \omega$  at 303 K for various (chitosan-PEO)-NH<sub>4</sub>I electrolytes. Graphs of frequency dependence on dielectric constant and dielectric loss at various temperatures for the highest conducting (chitosan-PEO)-NH<sub>4</sub>I electrolyte with the designation CEO7 are depicted in Figures 6.25 and 6.26, respectively.

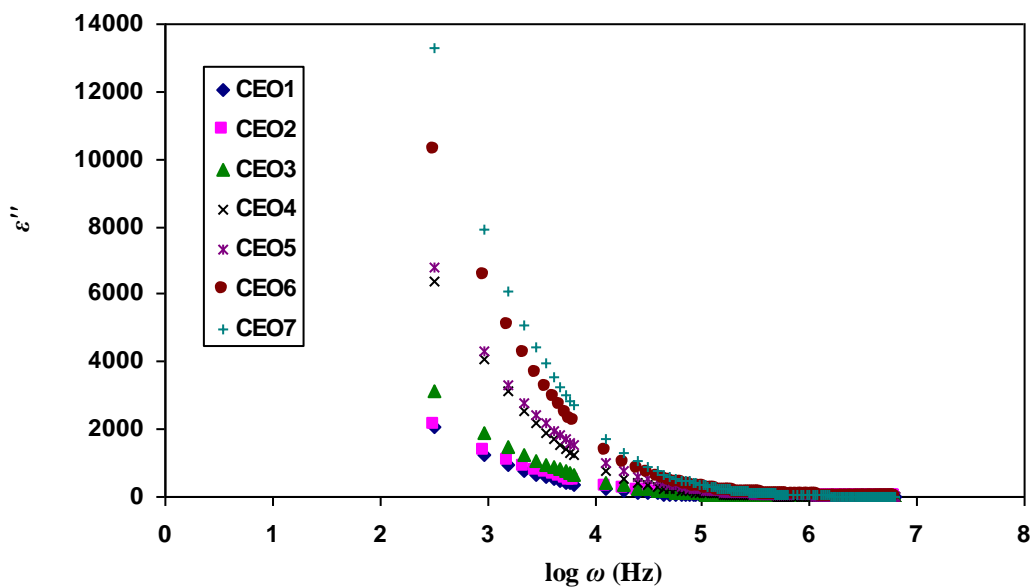


Figure 6.24: Frequency dependence on dielectric loss at room temperature for different (chitosan-PEO)-NH<sub>4</sub>I electrolytes

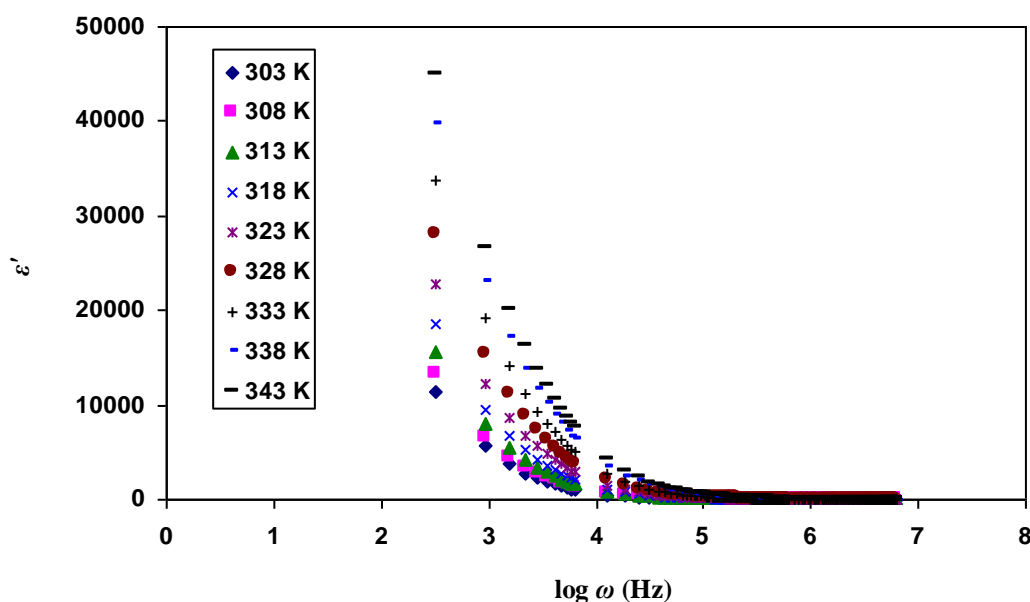


Figure 6.25: Frequency dependence on dielectric constant at selected temperatures for CEO7 electrolyte

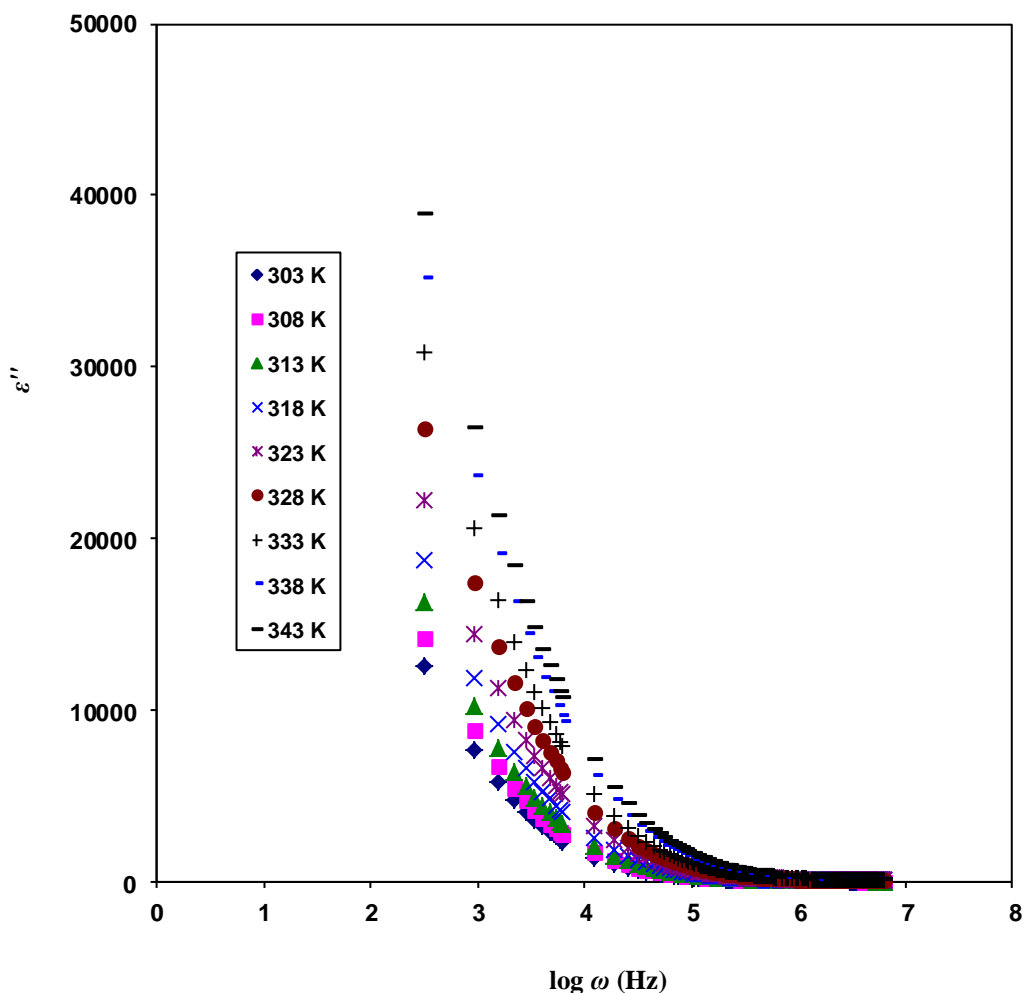


Figure 6.26: Frequency dependence on dielectric loss at selected temperatures for CEO7 electrolyte

## 6.9 CONDUCTIVITY-TEMPERATURE RELATIONSHIP OF CHITOSAN-NH<sub>4</sub>I-IL ELECTROLYTES

The conductivity-temperature relationship is as shown in Figure 6.27. In order to verify whether the relationship is Arrhenian or obeys the VTF rule, the data are converted into a plot of  $\ln \sigma T^{1/2}$  versus  $1000/|T-T_0|$  which is shown in Figure 6.28.

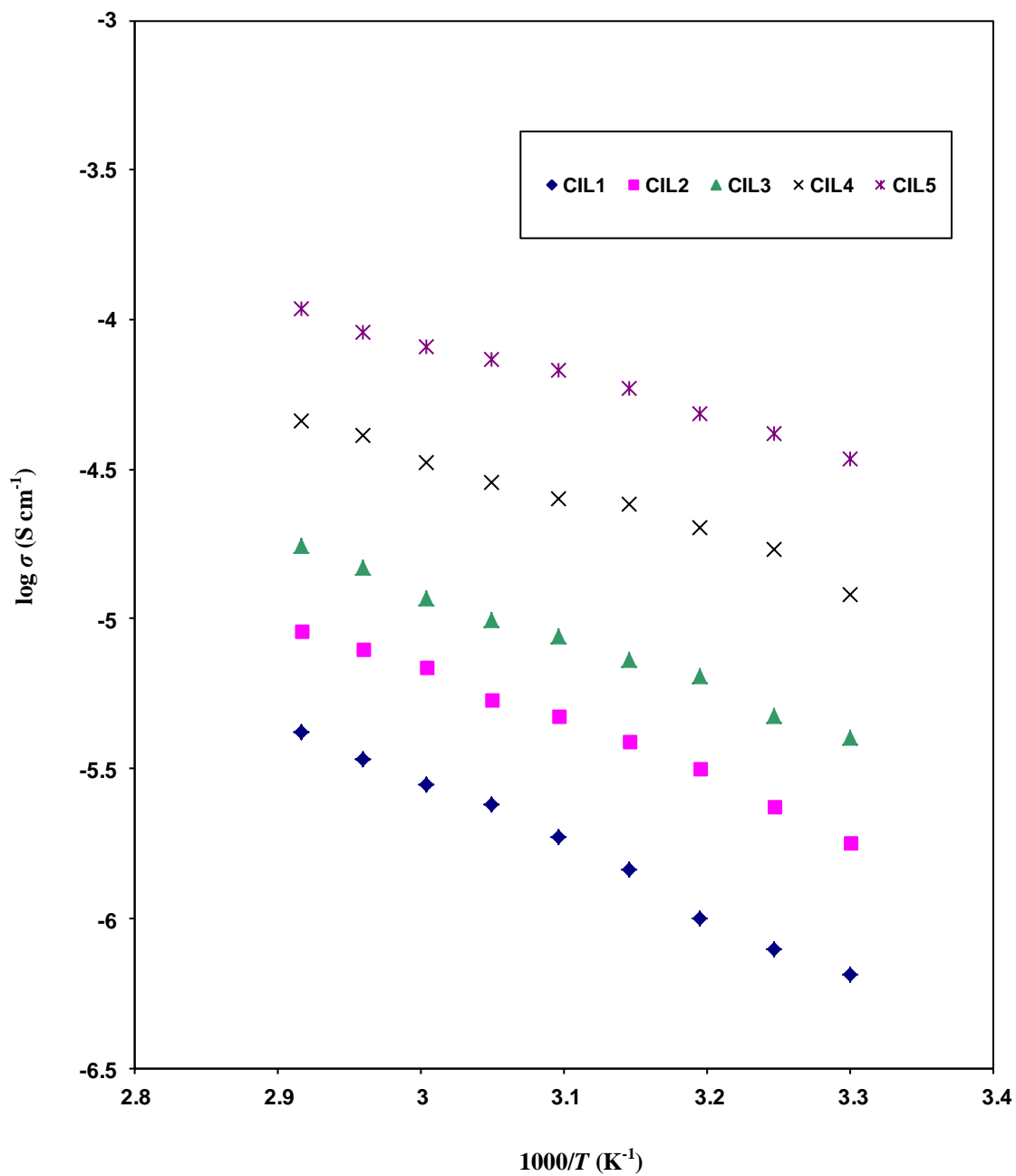


Figure 6.27: Plot  $\log \sigma$  versus  $1000/T$  for chitosan-NH<sub>4</sub>I-IL electrolytes

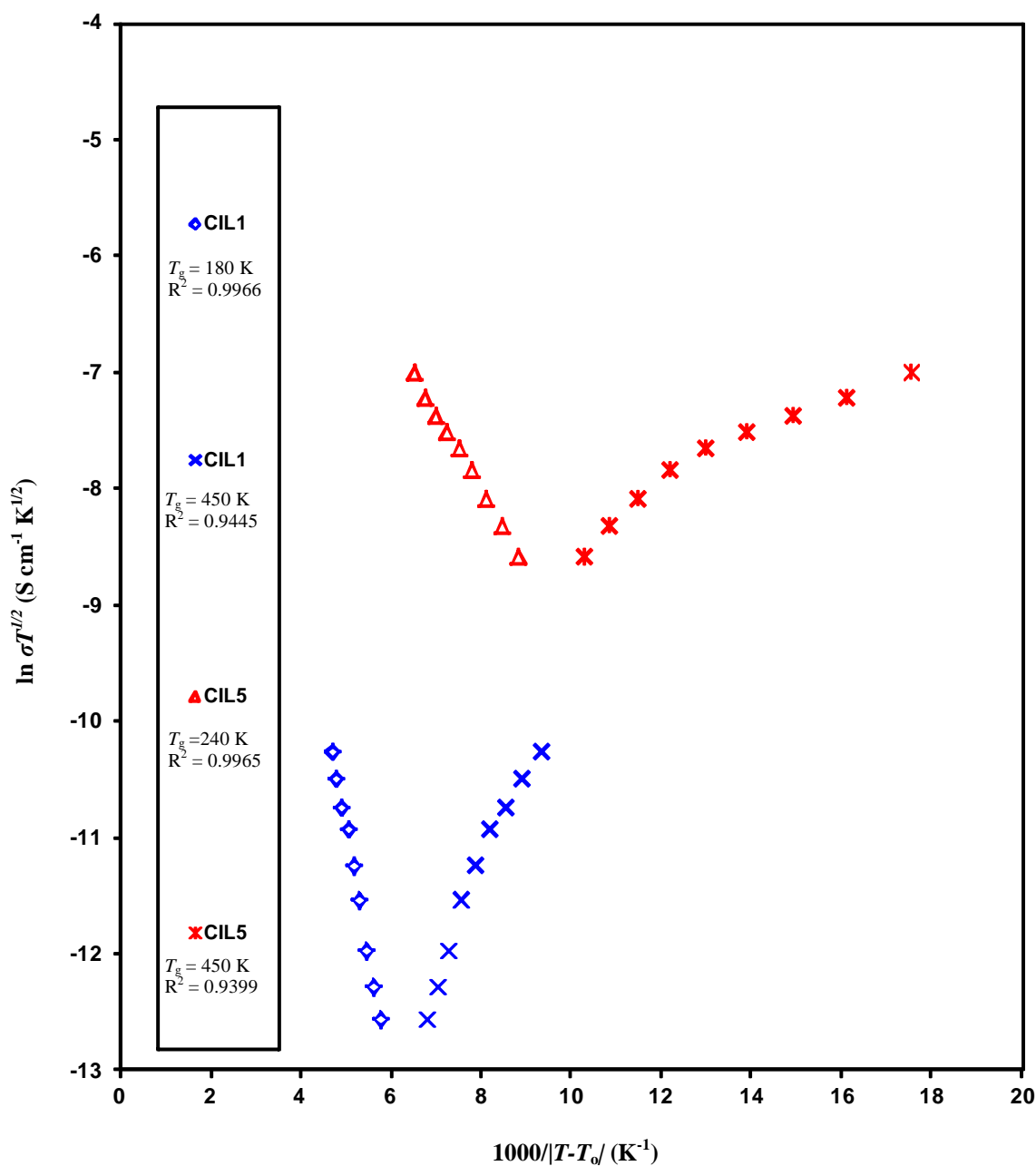


Figure 6.28: Plot  $\ln \sigma T^{1/2}$  versus  $1000/|T-T_0|$  for chitosan-NH<sub>4</sub>I-IL electrolytes

It can therefore be inferred that the VTF relationship is not relevant to the present system. Fig. 6.27 shows the plot of  $\log \sigma$  versus  $1000/T$  for chitosan-NH<sub>4</sub>I-IL electrolytes in the range between 298 K and 343 K. The increase in conductivity with temperature indicates that the ionic conduction of electrolyte is thermally activated. It can be deduced that the temperature dependence of ionic conductivity for chitosan-

$\text{NH}_4\text{I-IL}$  electrolytes also obeys Arrhenius rule and the activation energy,  $E_A$  can be obtained from the slope of the plot  $\log \sigma$  vs  $1000/T$ . Figure 6.29 depicts the variation of ambient temperature conductivity and the associated  $E_A$  and  $\sigma_0$  as a function of IL compositions.

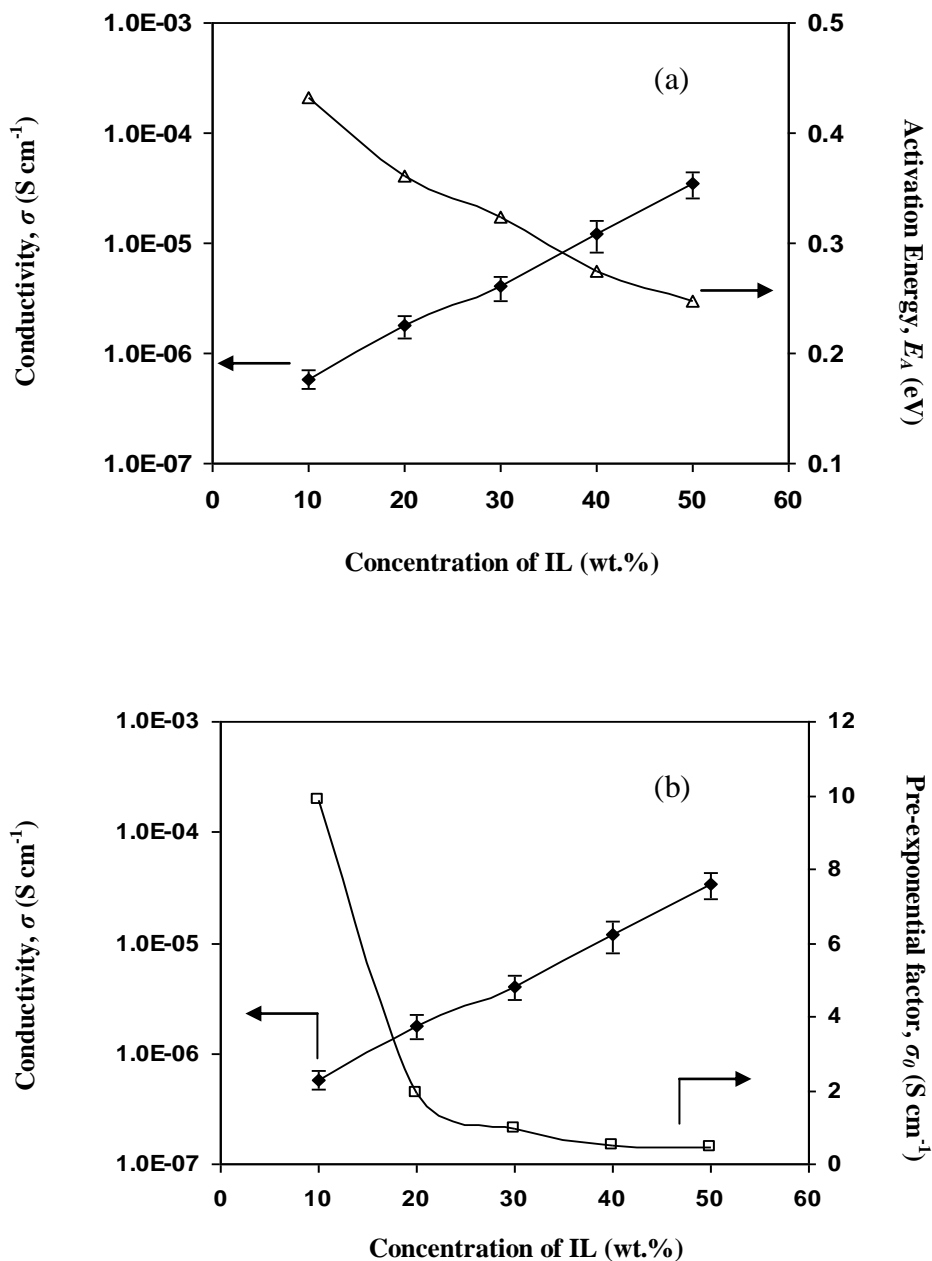


Figure 6.29: (a) The ionic conductivity at room temperature and the activation energy of chitosan- $\text{NH}_4\text{I-IL}$  electrolytes with various concentrations of IL (b) Conductivity and pre-exponential factor versus IL concentration

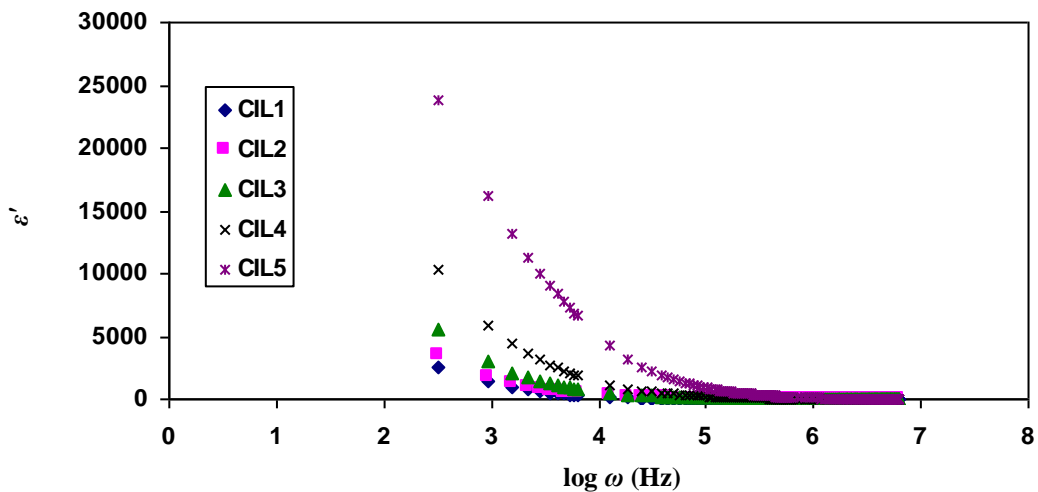
From Figure 6.29, it can be observed that the conductivity increases with increasing IL concentrations. The conductivity increases up to  $3.43 \times 10^{-5} \text{ S cm}^{-1}$  for 50 wt.% IL. An increase by two orders of magnitude is observed. The values of room temperature conductivity, pre-exponential factor and activation energy for different chitosan-NH<sub>4</sub>I-IL electrolyte are tabulated in Table 6.4.

**Table 6.4: Ambient temperature conductivity, pre-exponential factor and activation energy of various chitosan-NH<sub>4</sub>I-IL electrolytes**

Electrolyte	$\sigma \text{ (S cm}^{-1}\text{)}$	$\sigma_0 \text{ (S cm}^{-1}\text{)}$	$E_A \text{ (eV)}$
CIL1	$(6.44 \pm 1.07) \times 10^{-7}$	9.86	0.43
CIL2	$(1.78 \pm 0.43) \times 10^{-6}$	1.94	0.36
CIL3	$(4.03 \pm 1.01) \times 10^{-6}$	0.94	0.32
CIL4	$(1.20 \pm 0.39) \times 10^{-5}$	0.49	0.27
CIL5	$(3.43 \pm 0.91) \times 10^{-5}$	0.45	0.25

## 6.10 DIELECTRIC STUDIES OF CHITOSAN-NH<sub>4</sub>I-IL ELECTROLYTES

Figures 6.30 and 6.31 show the frequency variation on dielectric constant and dielectric loss for electrolytes with various IL content. It can be seen that the highest conducting sample, CIL5 gives the highest values for both dielectric constant and dielectric loss.



**Figure 6.30: Frequency dependence on dielectric constant at room temperature for different chitosan-NH<sub>4</sub>I-IL electrolytes**



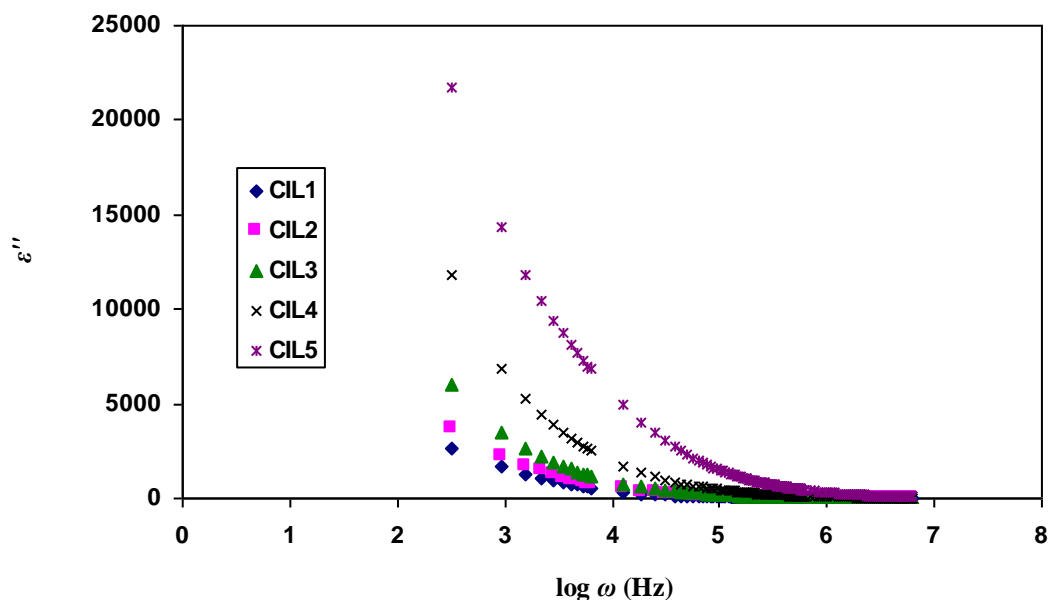


Figure 6.31: Frequency dependence on dielectric loss at room temperature for different chitosan-NH<sub>4</sub>I-IL electrolytes

The frequency dependence on dielectric constant and dielectric loss at selected temperatures for CIL5 electrolyte are depicted in Figures 6.32 and 6.33, respectively.

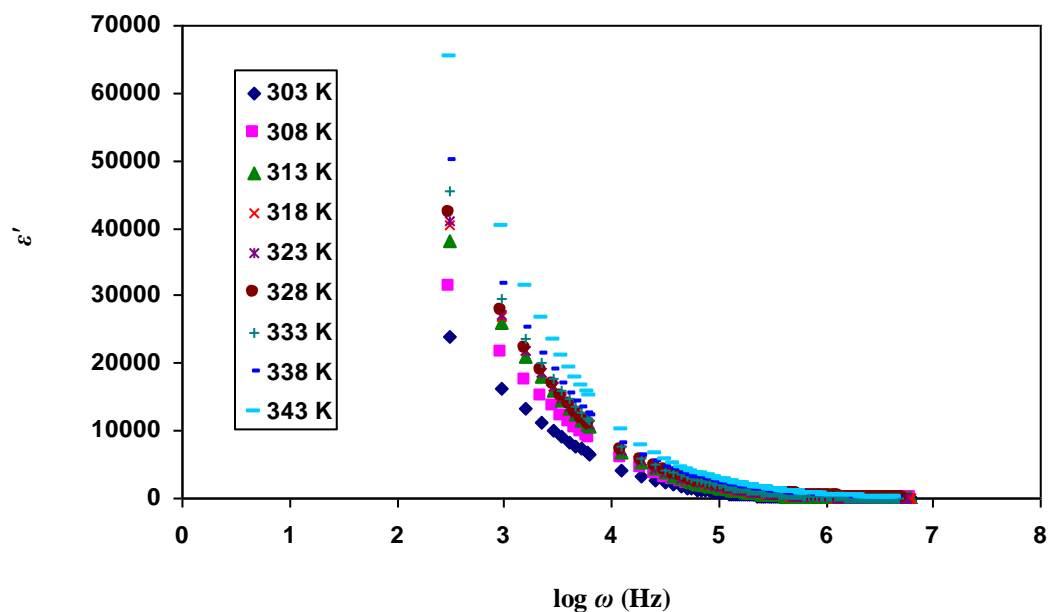


Figure 6.32: Frequency dependence on dielectric constant at selected temperatures for CIL5 electrolyte

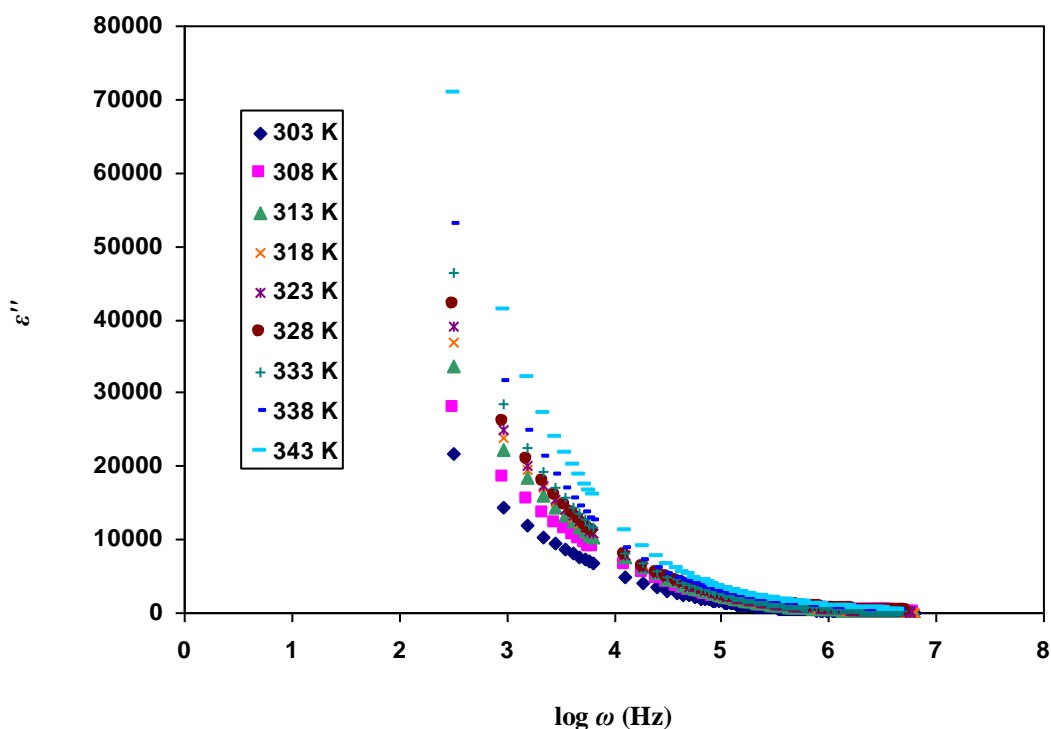


Figure 6.33: Frequency dependence on dielectric loss at selected temperatures for CIL5 electrolyte

The trend also follows the order of conductivity.

## 6.11 TRANSFERENCE NUMBER MEASUREMENTS

The polarization curve for the measurement of transference number for samples Ch9, CV5, CEO7 and CIL5 electrolytes are shown in Figure 6.34, 6.35, 6.36 and 6.37, respectively. This has been done by using DC polarization technique. The ionic and electronic transference numbers estimated from the polarization curve are  $t_{\text{ion}} = 0.85$  and  $t_e = 0.15$  for Ch9 electrolyte,  $t_{\text{ion}} = 0.91$  and  $t_e = 0.09$  for CV5 electrolyte,  $t_{\text{ion}} = 0.93$  and  $t_e = 0.07$  for CEO7 electrolyte and for CIL5 electrolyte,  $t_{\text{ion}} = 0.93$  and  $t_e = 0.07$ . This suggests that charge transport in the polymer electrolytes is mainly ions.

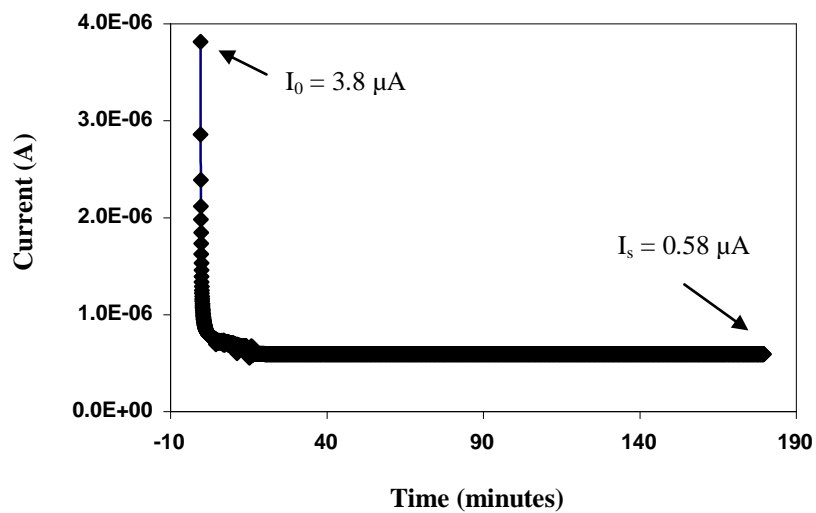


Figure 6.34: dc polarization measurement for SS/55 wt.% chitosan-45 wt.%  $\text{NH}_4\text{I}$  electrolyte/SS at room temperature

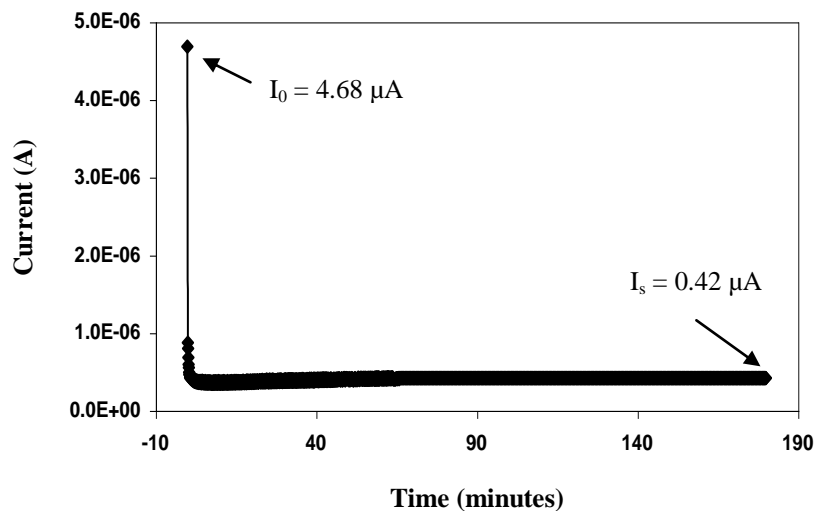


Figure 6.35: dc polarization measurement for SS/(27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.%  $\text{NH}_4\text{I}$  electrolyte/SS at room temperature

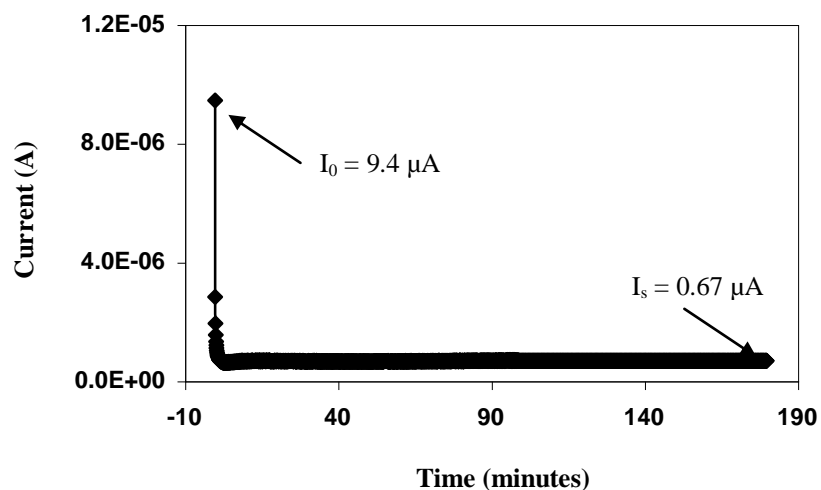


Figure 6.36: dc polarization measurement for SS/(16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.%  $\text{NH}_4\text{I}$  electrolyte/SS at room temperature

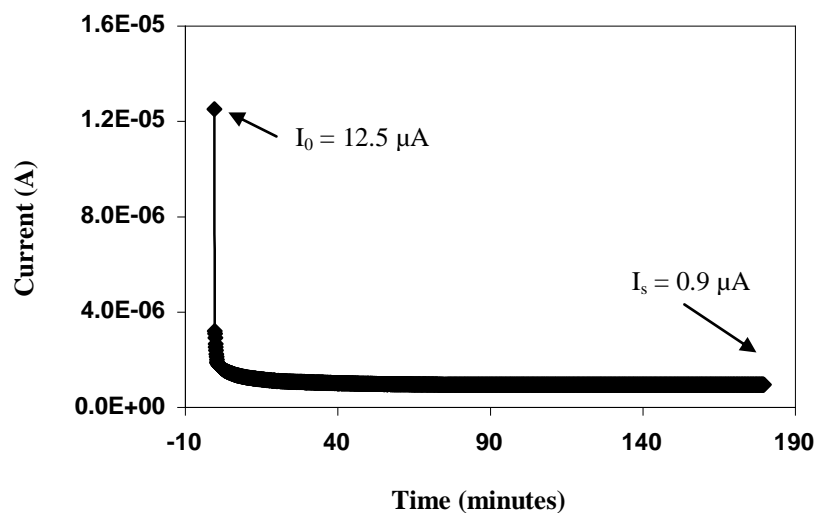


Figure 6.37: dc polarization measurement for SS/(27.5 wt.% chitosan-22.5 wt.%  $\text{NH}_4\text{I}$ -50 wt.% IL electrolyte/SS at room temperature

**6.12 SUMMARY**

The ionic conductivity of the chitosan film increases with the increase in  $\text{NH}_4\text{I}$  concentration. The highest room temperature conductivity is obtained at the value of  $3.73 \times 10^{-7} \text{ S cm}^{-1}$  for 55 wt.% chitosan-45 wt.%  $\text{NH}_4\text{I}$  electrolyte. The conductivity is further increased to  $1.77 \times 10^{-6} \text{ S cm}^{-1}$  for (27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.%  $\text{NH}_4\text{I}$  electrolyte,  $3.66 \times 10^{-6} \text{ S cm}^{-1}$  for (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.%  $\text{NH}_4\text{I}$  electrolyte and  $3.43 \times 10^{-5} \text{ S cm}^{-1}$  for 27.5 wt.% chitosan-22.5 wt.%  $\text{NH}_4\text{I}$ -50 wt.% IL electrolyte. Conductivity-temperature studies for all electrolyte systems show that the trend obeys Arrhenius rule. The lowest activation energy is obtained for the highest conducting electrolyte in all the four systems. All the dielectric constant and dielectric loss plots at room temperature and elevated temperatures show that the trend is in accordance with the conductivity for all the electrolytes. From the studies on transference number, it is known that the charge transport in all the polymer electrolytes is dominated by the ions.