

CHAPTER 5**ELECTRICAL STUDIES OF CHITOSAN-NH₄SCN COMPLEXES CHITOSAN-NH₄SCN COMPOSITES****5.1 Introduction**

In the present study, impedance spectroscopy is employed to investigate the electrical properties of chitosan-NH₄SCN complexes and chitosan-NH₄SCN-Al₂TiO₅ composite polymer electrolyte. The effect of filler on the dielectric of chitosan complexes will be studied and presented in this chapter.

5.2 Conductivity studies of chitosan-NH₄SCN samples

The ionic conductivity in a polymer is generally linked to the number of ions and the mobility of conducting species in the polymer complexes. Fig. 5.1 shows the variation of room temperature conductivity as a function of NH₄SCN concentration (in wt. %). It can be observed that the conductivity of the sample increases as the concentration of NH₄SCN increased and reaches a maximum at $1.38 \times 10^{-4} \text{ S cm}^{-1}$ for 40 wt. % of NH₄SCN. This could probably be due to the dissociation of salt into ions as concentrations of salt increases leading to an increase in H⁺ concentration. Thus, the increase in conductivity with salt concentration may be attributed to the increase in number of charge carriers [Majid and Arof, 2007].

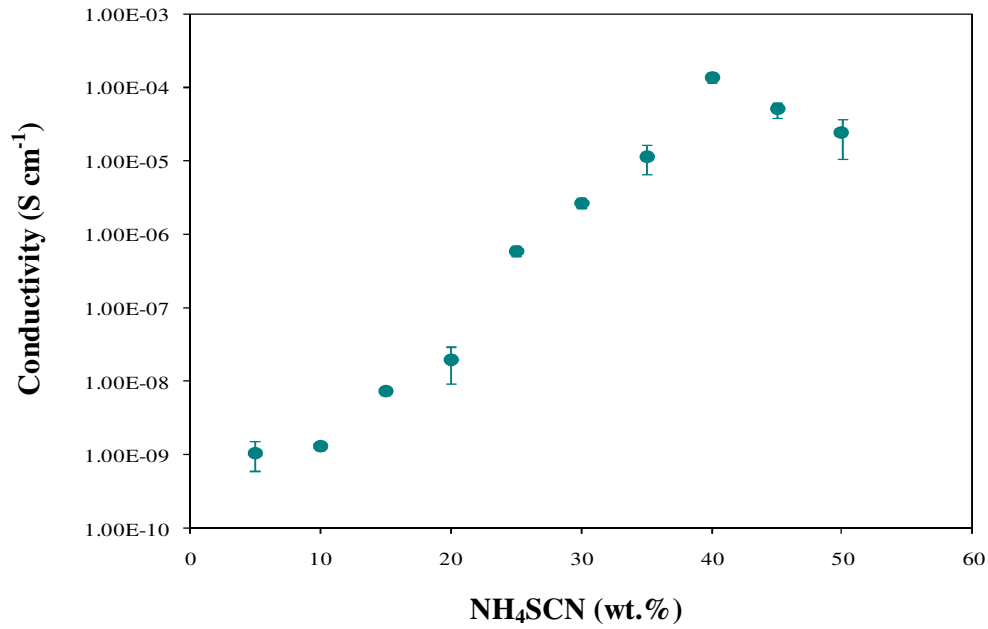


Fig. 5.1: Room temperature conductivity of NH₄SCN concentration (wt. %)

The conductivity begins to decrease with further addition of salt beyond 40 wt. %. This could be due to the formation of neutral ion pairs at higher salt concentrations, which reduces the effective number of free ions for conduction, thus resulting in the decline of conductivity [Ramya et al., 2006]. The values of the conductivity for the samples under investigations are tabulated in Table 5.1.

Table 5.1: Conductivity of the polymer electrolyte with respect to the NH₄SCN concentration

No.	NH ₄ SCN (wt. %)	Conductivity (S cm ⁻¹)
1	5	1.07 × 10 ⁻⁹
2	10	1.30 × 10 ⁻⁹
3	15	7.27 × 10 ⁻⁹

Table 5.1 continued.....

4	20	2.00×10^{-8}
5	25	6.25×10^{-7}
6	30	2.66×10^{-6}
7	35	1.15×10^{-5}
8	40	1.38×10^{-4}
9	45	5.09×10^{-5}
10	50	2.44×10^{-5}

5.3 Conductivity – Temperature dependence in the chitosan-NH₄SCN system

Fig. 5.2 shows the plots of log conductivity versus $10^3/T$ for highest conducting sample i.e. 60 wt.% chitosan – 40 wt.% NH₄SCN. The conductivity of chitosan-based electrolyte system increases with temperature, as observed from Fig. 5.2. Temperature helps to dissociate undissolved salt into ions or neutral ion-pair into ions thus increase the number of mobile charge carriers. Also, temperature can increase mobility of the ion. Since $\sigma = \eta q\mu$, where η is the number density of mobile ions, q is the electronic charge and μ is mobility of ionic species. So, if η and μ increase, conductivity will increase.

Regression values for the plot is 0.9809, which suggests that the points lie on a straight line and obey Arrhenius Law. From the plot of log σ versus $1,000/T$, the activation energy was calculated using the Arrhenius equation:

$$\sigma = \sigma_0 \exp (-E_a / kT) \quad (5.1)$$

where σ_0 is the pre-exponential factor; E_a is the activation energy; T is the absolute temperature and k is the Boltzmann's constant. Activation energy for 60 wt.% chitosan – 40 wt.% NH_4SCN sample is 0.096 eV.

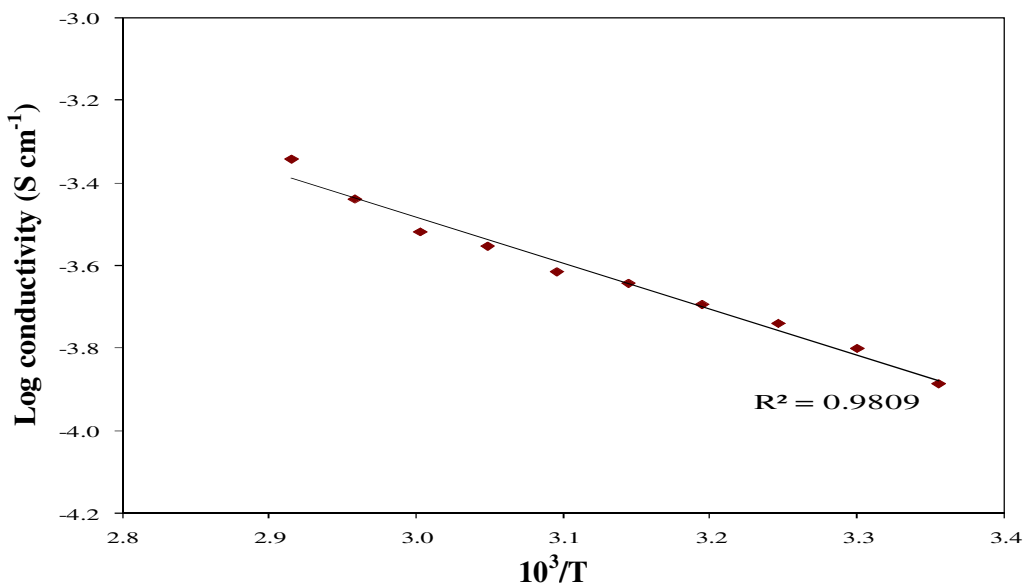


Fig. 5.2: Arrhenius plot for highest conducting sample in chitosan- NH_4SCN

5.4 Conductivity studies of chitosan- NH_4SCN - Al_2TiO_5 samples

In this section, the effect of Al_2TiO_5 on conductivity of the chitosan-salt complexes was investigated. The ammonium thiocyanate (NH_4SCN) salt was chosen as the proton supplier and its amount was fixed at 40 wt.%, since 60 wt.% chitosan – 40 wt.% NH_4SCN is the highest conducting sample with activation energy, 0.096 eV. Fig. 5.3 depicts the impedance plots for chitosan- NH_4SCN - Al_2TiO_5 at room temperature.

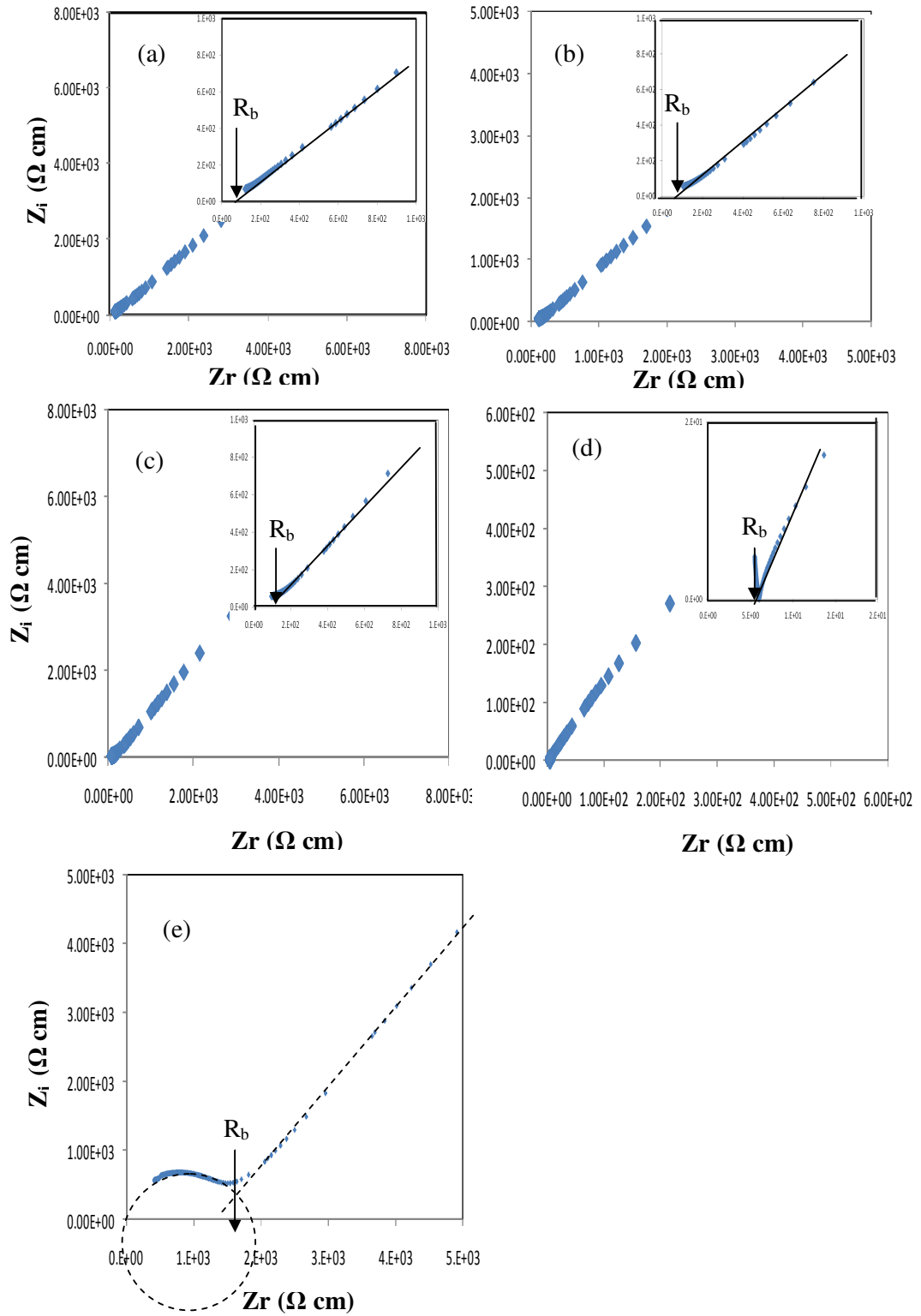


Fig. 5.3: Cole-Cole plot for the sample of chitosan -NH₄SCN- Al₂TiO₅ system with different wt.% of (a) 1 wt. % (b) 2 wt. % (c) 4 wt. % (d) 5 wt. % and (e) 7 wt. % Al₂TiO₅.

The Cole-Cole plots of the composite membrane shows a spike at low frequency region implying that the material is very capacitive implying that it is a good dielectric material. The low frequency of the spike is attributed to the effect of blocking electrodes [Selvasekarapandian et al., 2005]. At low frequency region, the Cole-Cole plot must show a straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes inclination [Kim et al., 1999]. It can be observed that the Cole-Cole plot for the sample containing 7 wt.% Al_2TiO_5 consists of a spike at low frequencies and a partial semicircle at the high frequency side. The centre of the semicircle is below the real impedance axis implying that the ions have different relaxation times [Selvasekarapandian et al., 2005].

Fig 5.4 shows the variation of room temperature (25 °C) conductivity as a function of Al_2TiO_5 (in wt.%) in the chitosan- NH_4SCN system.

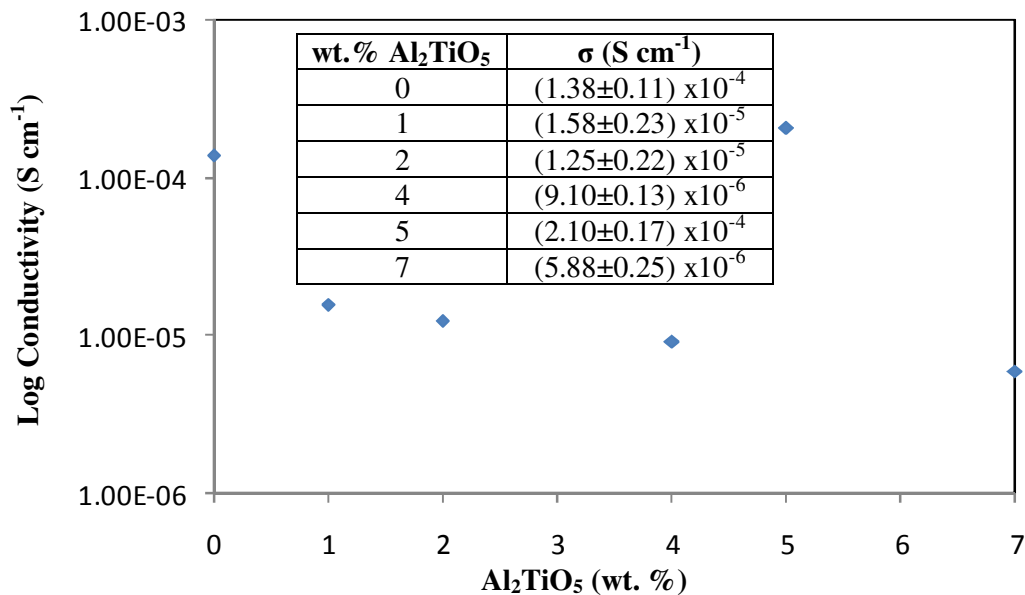


Fig. 5.4: Conductivity versus amount of Al_2TiO_5 dopant in the chitosan- NH_4SCN film.

As Al_2TiO_5 has been introduced into the chitosan- NH_4SCN system, the conductivity decreased from 1.38×10^{-4} to $1.25 \times 10^{-5} \text{ S cm}^{-1}$. The conductivity decreased, because

the fillers tend to impede ionic movement by acting as an insulator. In this region, the insulating effect of Al_2TiO_5 is effective [Park et al., 2003].

After addition of more than wt.% Al_2TiO_5 to the system, the conductivity found to increase and passes a maximum value of $2.10 \times 10^{-4} \text{ S cm}^{-1}$ at 5 wt.% Al_2TiO_5 . The increase in conductivity is possibly due to Al_2TiO_5 acting as transit site for ions to hop. The surface of hydroxides of the Al_2TiO_5 particles can form transit sites due to Lewis acid-base interaction. Further addition of Al_2TiO_5 , reveals in conductivity decrease again to $2.45 \times 10^{-6} \text{ S cm}^{-1}$ at 7 wt.% Al_2TiO_5 . The decrease observed at high filler concentration could be related with the blocking effect of the dopant in the conductivity pathway [Tambelli et al., 2002]. Table 5.2 shows the variation of conductivity of chitosan- NH_4SCN with Al_2TiO_5 content.

Table 5.2: Conductivity of the polymer electrolyte with respect to the Al_2TiO_5 concentration

No.	Al_2TiO_5 (wt. %)	Conductivity (Scm^{-1})
1	1	1.58×10^{-5}
2	2	1.25×10^{-5}
3	4	9.10×10^{-6}
4	5	2.10×10^{-4}
5	7	5.88×10^{-6}

5.5 Conductivity –Temperature Relationship of chitosan acetate salt complexes containing aluminum titanate.

Fig. 5.5 shows the plot of log conductivity versus $10^3/T$ for samples containing 5 wt. % Al_2TiO_5 in chitosan acetate- NH_4SCN with temperature ranging from 25 °C to 80 °C. The linear relationship reveals that the temperature dependence of conductivity follows Arrhenius law, suggesting that the conductivity is thermally activated. The activation energy, E_a of this system was obtained from the slope of the plot and the value is 0.091 eV. The activation energy is slightly lower than that for the chitosan- NH_4SCN samples and this is justified by the small increment in conductivity.

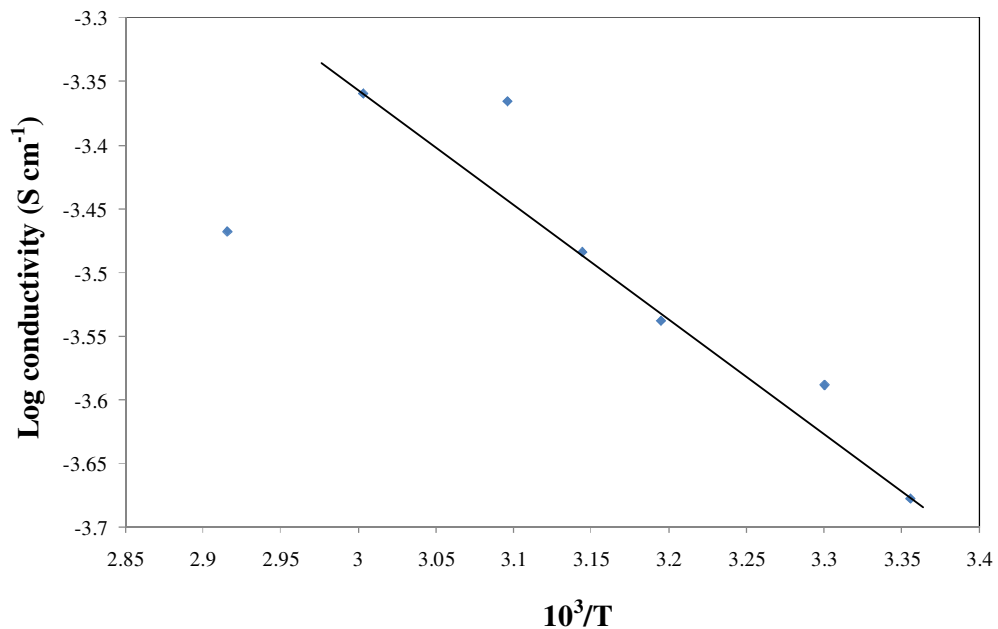


Fig. 5.5: Arrhenius plot for different weights of Al_2TiO_5 dopant in chitosan acetate- NH_4SCN film (room temperature to 80 °C)

5.6 Dielectric behavior of chitosan acetate- NH_4SCN - Al_2TiO_5 complexes

Impedance spectroscopy measurements are often performed to determine the bulk conductivity of a sample. Additional information on the material can be obtained

from a dielectric analysis, where measurements are performed over a wide frequency range. One advantage of dielectric study is that it helps in understanding the conductive behaviour of polymer electrolyte. Fig. 5.6 shows the dielectric constant variations with log frequency for different contents of Al_2TiO_5 . The dielectric constant plays a fundamental role in the ability of a polymer to dissociate salts [Wintersgill and Fontanella, 1987]. The values of dielectric constant, ϵ_r of the system decrease with increasing frequency. Decline in values of ϵ_r with frequency could be attributed to the motion of ionic charge carriers within the material. At low frequencies, there is charge buildup at the interface between the material and the electrode with electrode polarization phenomena making a significant contribution. With increasing frequency, there is insufficient time for buildup of the charges in the bulk at the boundaries of the conducting paths [Mishra and Rao, 1998].

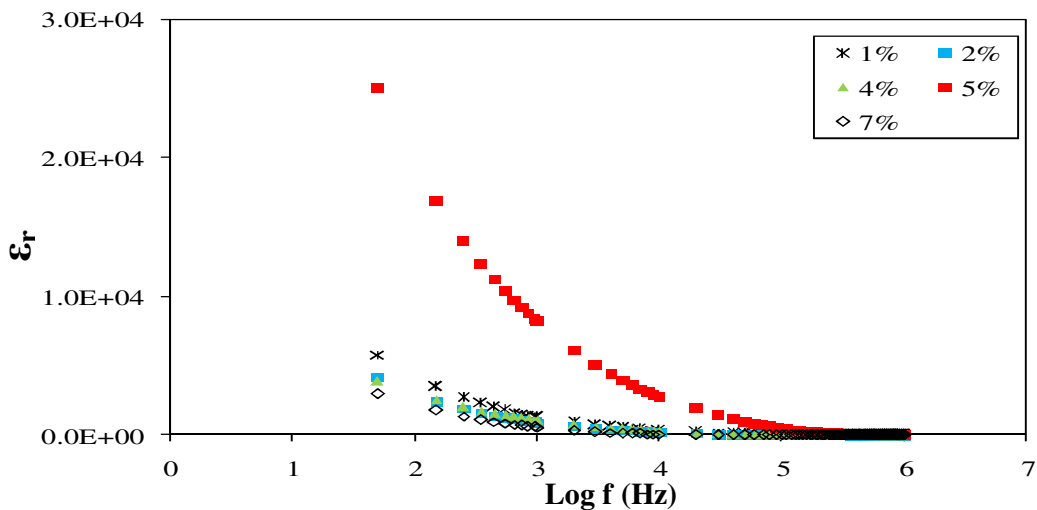


Fig. 5.6: Dielectric constant versus log frequency for chitosan- NH_4SCN complexes with different concentrations Al_2TiO_5 .

Fig. 5.7 shows the dielectric constant with log frequency for the highest conducting sample at different temperatures. The dielectric constant are observed to increase with temperature suggesting an increase in the number charge carriers. Thus, increment in conductivity with temperature could be attributed to the greater number of charge carriers when temperature rises.

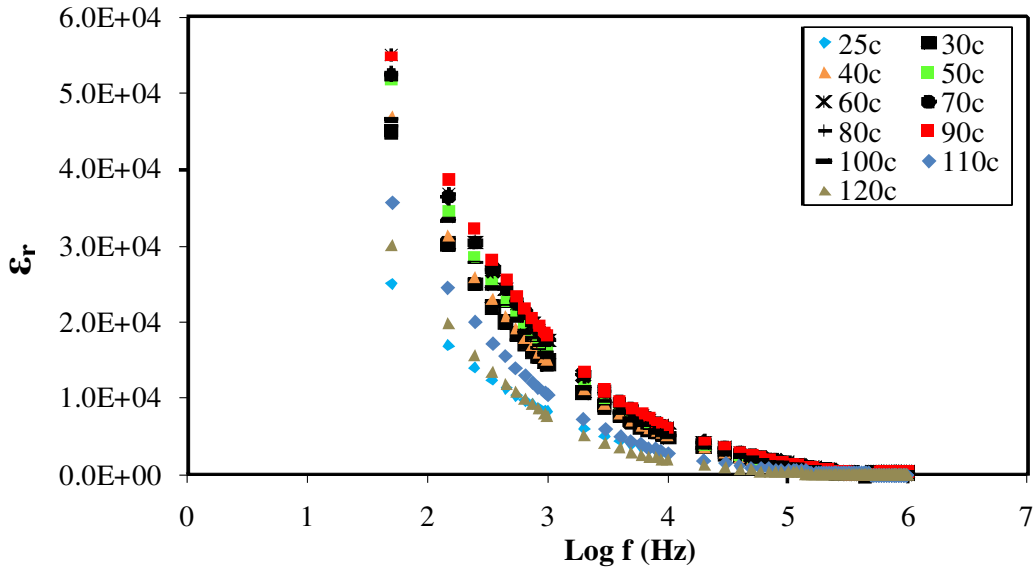


Fig. 5.7: Dielectric constant versus log frequency for the highest conducting chitosan- $\text{NH}_4\text{SCN-Al}_2\text{TiO}_5$ film at various temperature.

Fig. 5.8 shows the dielectric loss variations with frequency for different contents of Al_2TiO_5 filler samples. In order to verify the presence of residual water, the impedance data was transposed into real and imaginary permittivity data. According to Wintersgill and Fontanella (1987), the dielectric loss probes a wide variety of phenomena along with any relaxation which may be present in the material. It is therefore expected that if water is present, a relaxation peak can be observed in the dielectric loss-frequency plots.

Information on relaxing dipoles in the sample may be obtained from an analysis of the complex permittivity since the appearance of a peak in the imaginary part of the permittivity indicates that the energy is absorbed by dipoles in the sample. The relaxation frequency and the strength of the relaxation are characteristics of the relaxing dipoles [Mellander et al., 1996].

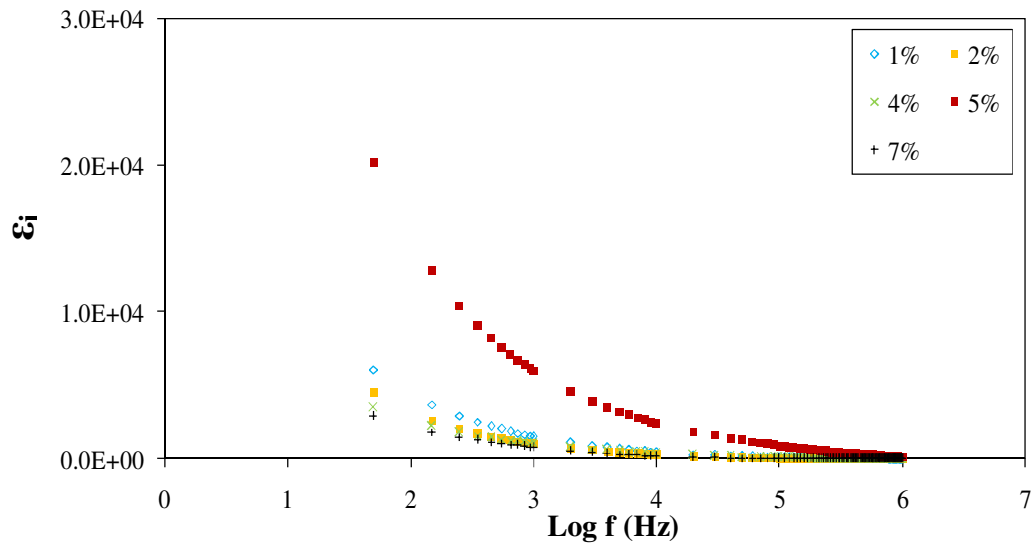


Fig. 5.8: Dielectric loss versus log frequency for chitosan-NH₄SCN complexes with different concentrations of Al₂TiO₅

Fig. 5.9 represents the temperature variation of dielectric loss of the highest conducting sample. Since no significant relaxation peak is observed in Fig. 5.8 and 5.9, it is therefore inferred that residual water does not contribute towards the electrical conductivity of chitosan-NH₄SCN-Al₂TiO₅ sample.

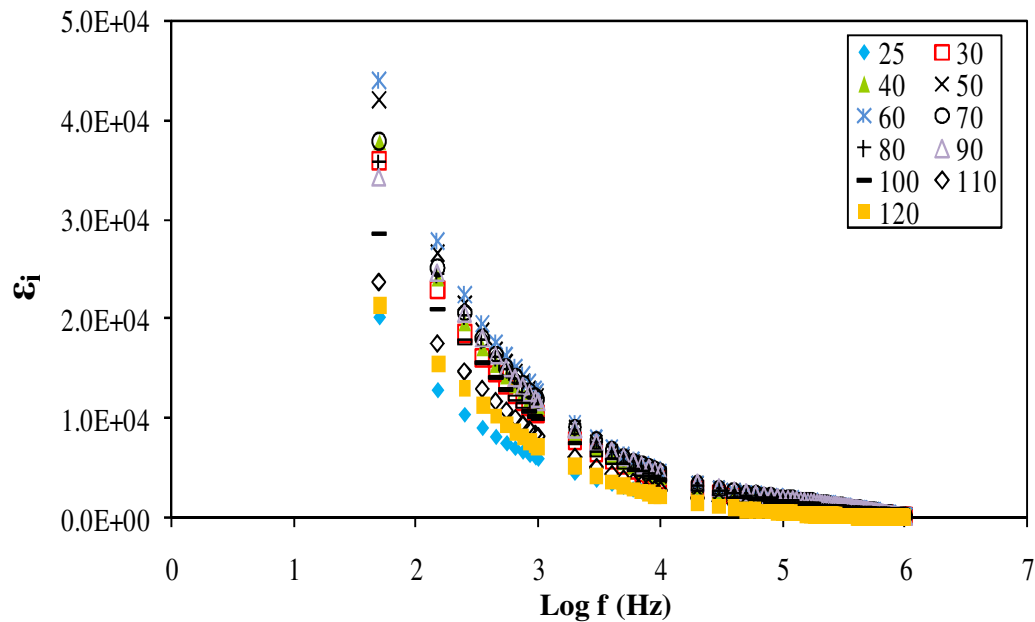


Fig. 5.9: Dielectric loss versus log frequency for the highest conducting chitosan-NH₄SCN-Al₂TiO₅ film at various temperature.

Fig. 5.10 shows the real part of the electric modulus for the chitosan-NH₄SCN-Al₂TiO₅ complexes. The value of real part of electrical modulus at room temperature in the low frequency regime, is in the vicinity of zero, implying the removal of electrode polarization phenomena [Dutta et al., 2002; Nobre and Lanfredi, 2003].

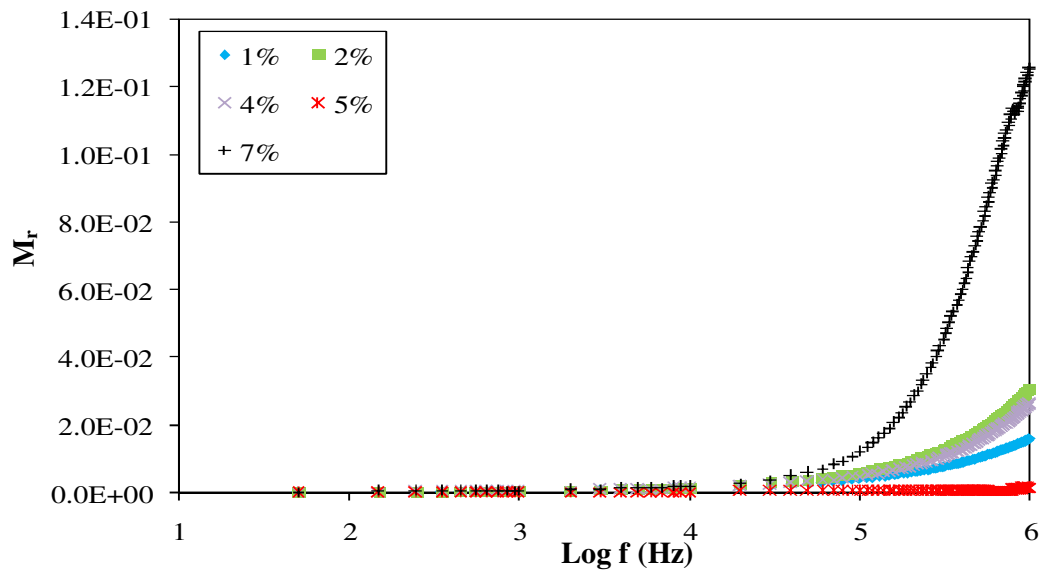


Fig. 5.10: Real part of electric modulus versus log frequency for chitosan-NH₄SCN complexes with different concentrations of Al₂TiO₅.

Fig 5.11 displays the real part of the modulus formalism of the highest conducting sample at different temperatures. The incidence of dispersion in M_r is clearly observed. The real part of modulus show an increase with increasing frequency. At low frequency, the real part of modulus approach to zero indicating the fact that the material is very capacitive.

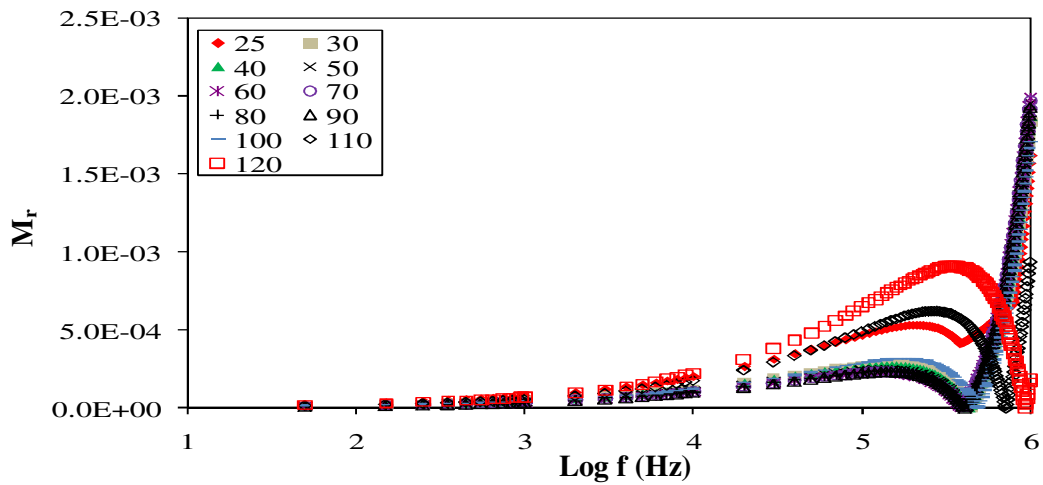


Fig. 5.11: Real part of electric modulus versus log frequency for the highest conducting chitosan-NH₄SCN-Al₂TiO₅ film at various temperature.

Fig. 5.12 presents the imaginary parts of the electric modulus for the chitosan-NH₄SCN-Al₂TiO₅ complexes.

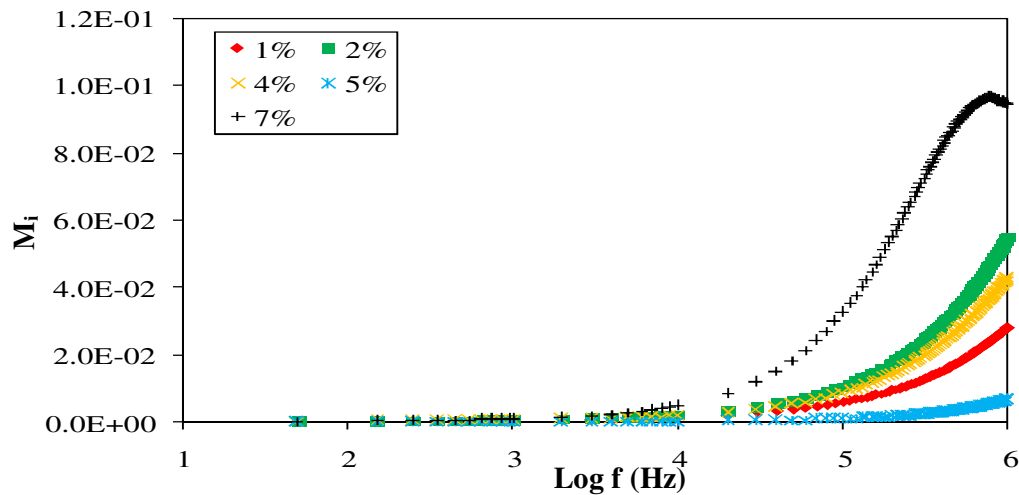


Fig. 5.12: Imaginary part of electric modulus versus log frequency for chitosan-NH₄SCN complexes with different concentrations of Al₂TiO₅.

The presence of a peak in the sample with 7 wt.% Al₂TiO₅ indicates that the sample is an ionic conductor [Mellander, 1996]. Fig. 5.13 displays the imaginary parts of electric modulus formalism of the highest conducting sample at different temperatures.

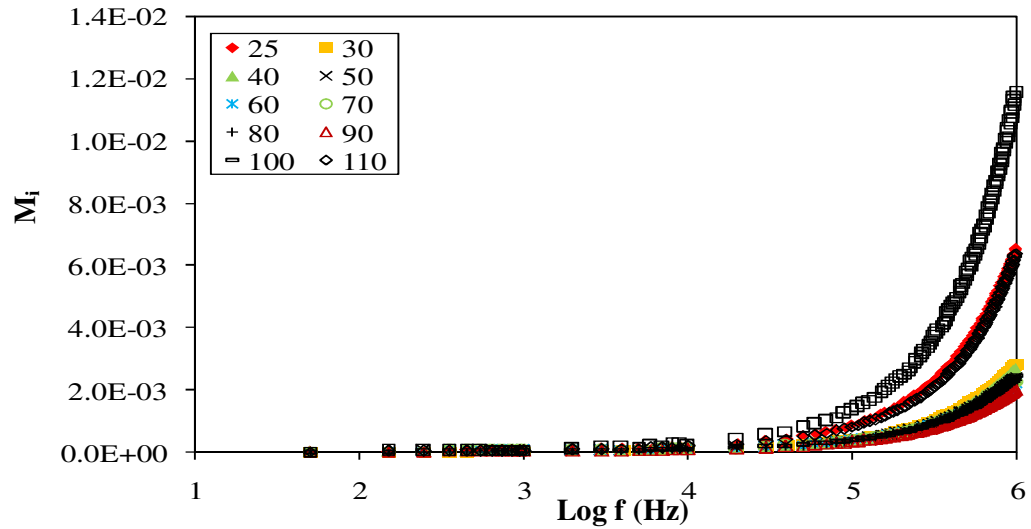


Fig. 5.13: Imaginary part of electric modulus versus log frequency for the highest conducting chitosan-NH₄SCN-Al₂TiO₅ film at different temperatures.

5.7 Summary

The chitosan-NH₄SCN-Al₂TiO₅ composite polymer electrolyte has been prepared. The effect of filler on the dielectric of this chitosan complexes has been presented. Studies on the dielectric behavior of chitosan complexes clearly showed that the values of dielectric parameters are strongly dependent on the frequency, temperature as well as the conductivity of sample. Conductivity enhancement in the present electrolyte system could be attributed from the increase in the number of free ions. The chitosan-NH₄SCN-Al₂TiO₅ shows high room temperature conductivity of $2.10 \times 10^{-4} \text{ S cm}^{-1}$.