CHAPTER 4

ELECTRICAL PROPERTIES
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4.1 Impedance Spectroscopy Analysis

In order to measure the highest electrical conductivity (\( \sigma \)) of the chitosan acetate-salt complexes, impedance spectroscopy was carried out.

4.2 Room Temperature Conductivity Dependence on Doping Salt Content

From impedance spectroscopy measurement, the magnitude of complex impedance and phase angle are obtained. Conductivity measurement was carried out in a dessicator to prevent the film from absorbing water vapor that can influence the conductivity value. Magnitude of the imaginary impedance was calculated from \( Z_{\sin \theta} (Z'') \) and the magnitude of the real impedance was calculated from \( Z_{\cos \theta} (Z') \). The Cole-Cole plots [61] of \(-Z'' Vs Z'\) were then plotted as shown in Figure 4.1. The shapes of the impedance plots are typical of polymer electrolytes consisting of a constant phase element (CPE) and a resistor in parallel [62-63]. A CPE is an element, the capacitance of which changes with frequency. The equivalent circuit that represents this impedance plot is shown in Figure 4.2 [64]. According to Linford [65], the second CPE (CPE 2) is possibly due to a capacitive term, which changes with frequency and would arise if air were present in the electrode gap. The first CPE is the charge transfer capacitance and the resistance represents the bulk electrolyte resistance.
Figure 4.1: Cole-Cole plot for highest conducting sample, i.e. sample containing 0.2 g silver triflate in 1.0 g chitosan + 0.4 g EC at room temperature.

Figure 4.2: Equivalent circuit representing the above Cole-Cole plot.
Figure 4.3 shows the respective complex admittance plot. The intercept of the depressed semicircle with the real admittance axis will give the inverse of the bulk resistance $1/R_b$. Here $1/R_b$ is equal to $Y'$ and it is observed that the reciprocal of the intercept value at the real admittance axis of the complex admittance plot is approximately the same value as the $R_b$ value obtained from the complex impedance plot [66]. Using equation 2.9, the electrical conductivity of the films is calculated and tabulated with other parameters in Table 4.1 below.
Table 4.1: Electrical conductivity of 1.0 g AC + 0.4 g EC at different ratios of silver triflate with contact area, $A = 1.35$ cm$^2$ and film thickness $l = 0.012$ cm at room temperature.

<table>
<thead>
<tr>
<th>Weight of dopant (g)</th>
<th>Conductivity $\sigma$ (µS cm$^{-1}$)</th>
<th>Average conductivity $\sigma$ (µS cm$^{-1}$)</th>
<th>Standard deviation $S$ (µS cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>8.76 8.92 8.91</td>
<td>8.86</td>
<td>0.09</td>
</tr>
<tr>
<td>0.2</td>
<td>10.28 10.19 10.13</td>
<td>10.20</td>
<td>0.08</td>
</tr>
<tr>
<td>0.3</td>
<td>5.99 6.10 6.15</td>
<td>6.08</td>
<td>0.08</td>
</tr>
<tr>
<td>0.4</td>
<td>3.95 3.82 3.93</td>
<td>3.90</td>
<td>0.07</td>
</tr>
<tr>
<td>0.5</td>
<td>3.25 3.39 3.41</td>
<td>3.35</td>
<td>0.09</td>
</tr>
<tr>
<td>0.6</td>
<td>3.32 3.15 3.25</td>
<td>3.24</td>
<td>0.09</td>
</tr>
<tr>
<td>0.7</td>
<td>3.28 3.12 3.19</td>
<td>3.20</td>
<td>0.08</td>
</tr>
</tbody>
</table>

From Table 4.1, it can be observed that the total conductivity of chitosan acetate-AgCF$_3$SO$_3$ system varies with the silver triflate content. The sample with the highest electrical conductivity of $1.02 \times 10^{-5}$ S cm$^{-1}$ contains 0.2 g of the silver salt. At higher (> 0.2 g salt) and lower (< 0.2 g salt) concentrations of AgCF$_3$SO$_3$, the electrical conductivity is low. The standard deviation value clearly shows that the error in the conductivity values for samples containing 0.1 g – 0.4 g of silver triflate is low. There is no overlap in conductivity values within the range specified by the standard deviation unlike for samples containing more than 0.4 g of silver triflate. Figure 4.4 shows the variation of electrical conductivity behavior that has been observed in the chitosan acetate-silver triflate system. This trend of conductivity vibration may be explained in terms of the degree of crystallinity of the sample. It well known that ionic conductivity occurs in the amorphous region of the polymer [67-68]. Hence increasing the amorphous regions will increase the electrical conductivity and increasing the crystalline regions will decrease conductivity.
Figure 4.4: Variation of electrical conductivity versus amount of dopant in the chitosan acetate-silver triflate system (The electrical conductivity of value $1.86 \times 10^{-6}$ S cm$^{-1}$ is obtained from N. M.Morni [43]).

As an alternative explanation to the increase and decrease of conductivity with salt content the phenomena of ion dissociation and associations are considered [63]. The plot of conductivity variation with salt concentration can be divided into three regions. Region I is the low salt concentration, region II is the intermediate salt regime and region III is the high salt concentration regime. In region III the values of conductivity does not decrease much with salt content. The standard deviation shows that the electrical conductivity value overlaps one another especially for salt content of 0.5 g to 0.6g. According to Mellander and Albinsson [63], an important aspect in
optimizing ionic conductivity in polymer electrolyte is ion association. It has been shown in a number of alkali triflate (such as sodium triflate and lithium triflate) salt-polymer (propylene oxide) complexes that the formation of ion-pairs and higher aggregates is common. In region I, a solution of anions and cations are formed as the salt concentration increases. The presence of EC as a plasticizer help to increase the formation of anions and cations, resulting in the increase in the number of mobile species and hence the conductivity. The rate of ion association is less than the rate of ion dissociation and therefore the conductivity increases.

The decrease in conductivity in region II could be attributed to the increase in the rate of ion association compared to the rate of ion dissociation. Also as an additional factor, the decrease in conductivity can be related to the high salt concentration affecting the mean distance between the ions and makes these ions to become closer to one another. Since the ions are so close to one another, the dissolved cation coordinating to the nitrogen in the amine group in chitosan may form transient crosslinks between the chain segments. This might explain the further decrease in segmental flexibility with increasing concentration of salts in region III. The film with such salt contents conforming to region III in the present work is not soft, but brittle and has a rough surface texture. These physical properties indirectly indicate that the high salt concentration has caused chain interlinking. Due to this interlinking, the mobility of the charge carriers is greatly reduced leading to a decrease in conductivity, $\sigma$ in region III.
4.3 Temperature-Dependence Conductivity

In order to understand the transport mechanism of the chitosan acetate-AgCF$_3$SO$_3$ system, the temperature dependence of conductivity is examined. Following the same procedure as before but varying the temperature of the samples, the bulk resistance was determined from the complex impedance plots and the respective conductivity value was calculated as before. The plot of $\ln \sigma T$ versus $10^3/T$ is as shown in Figure 4.5.

The regression value for all the graphs is between $-0.9922$ to $-0.9957$ indicating a good straight line fit of all points. Hence the conductivity-temperature relationship obeys Arrhenius rule as depicted in Figure 4.5. It can be observed that the sample with 0.2 g silver triflate as the highest electrical conductivity at all temperatures followed by the samples containing 0.1 g, 0.3 g, 0.4 g and 0.5 g silver triflate. This is in accordance with Figure 4.5. The fact that the plot of $\ln \sigma T$ versus $10^3/T$ obeys Arrhenius rule indicates that the temperature range in which the conductivity was measured is still well below the glass transition temperature. The glass transition temperature of chitosan has been reported to be 203°C (476K). If this is also true for our chitosan sample, then the addition of salt would even make the glass transition temperature higher. This is because the glass transition temperature increases with increasing salt concentration [69-70].
Figure 4.5: $\ln \sigma T$ versus $10^5/T$ plot for different weight of dopant containing 0.1, 0.2, 0.3, 0.4, and 0.5 g of silver triflate (ST) in AC + 0.4 g EC.
Therefore the free volume concept could not be used to explain the conductivity mechanism that takes place in the present investigated systems. The conducting mechanism that can be proposed is the ion hopping mechanism as in ionic crystal. Following Arrhenius rule the activation energy of the ions can be calculated from the gradient of the \( \ln \sigma T \) versus \( 10^3/T \) graph. Figure 4.6 shows the activation energy plot versus amount of dopant. It can be seen that the activation energy decreases until a dopant weight of 0.2 g after which the activation energy increases again. It can be deduced that the activation energy is lowest for the sample with the highest conductivity. Thus, in terms of activation energy, the conductivity increases with dopant salt up to an amount of 0.2 g due to the decrease in activation energy. Decrease in conductivity for dopant amount greater than 0.2 g is due to the increase in activation energy of the ions in the samples. Hence the ions migrate through the sample via some thermally activated hopping mechanism as depicted in Figure 4.7 (a) and (b). This cationic displacement along a macromolecular chain below \( T_g \) has been suggested by Soquet et. al. [18]. The increase and decrease in conductivity with doping salt content are due to the decrease and increase in activation energy of the ions respectively.
4.4 Frequency-Dependence Conductivity

Figure 4.8 shows the variation of conductivity with frequency for chitosan acetate-silver triflate system. It can be observed that above 100 kHz conductivity increases at a faster rate than at frequencies below 100 kHz. Once again the trend follows that of Figure 4.4. The small dispersion between conductivity and frequency below 100 kHz could be attributed to space charge effect. Space charge contribution could be explained as follows. At very low frequencies, say 1 kHz, the reversal of the electric field or the alternating voltage may occur at a very slow rate. Hence the charged species will be accumulated at the electrode-electrolyte interface for a much longer time. There will be less mobile ions in the bulk of the material and hence the
conductivity will be low at low frequencies. As the frequency increases, the reversal of the electric field occurs at a faster rate and the charge conducting species could not accumulate at the electrode-electrolyte interface for long. Hence the number of mobile charge carriers in the bulk of the material will increase, leading to an increase in conductivity. At 100 kHz when the electric field makes a change in direction once every 10 μs the number of accumulated charged species at the electrode-electrolyte interface becomes even less. With further increase in frequency the dispersion between conductivity and frequency increases. The large dispersion between conductivity and frequency above 100 kHz could also be attributed to relaxation effects due to the presence of water. If water is present in the sample, a hump should exist between 100-10000 kHz [71-73], we will confirm the presence of water by transforming the impedance date into the permittivity formalism.

Figure 4.9 shows the conductivity-frequency dispersion from room temperature up to 363 K. It can be observed that the conductivity increases with frequency and with temperature. Below the knee frequency, i.e. the frequency at which conductivity increases at a faster rate, the conductivity value is almost constant except at 363 K. At 313 K to 353 K the conductivity seems to obey Johnscher’s dispersion law, \( \sigma(\omega) = \sigma(0) + A\sigma(\omega)^n \). Here \( \sigma(0) \) is the dc conductivity and \( A \) and \( n \) are constants. It can be inferred that \( \sigma(0) \) is very small at room temperature and is about 3 μS cm\(^{-1}\) at 353 K (obtained by extrapolating the plot to zero frequency).
Figure 4.7: (a) and (b) show the schematic representation of a cationic displacement along a macromolecular chain below $T_g$. 
Figure 4.8: Room temperature conductivity-frequency dependence for chitosan acetate-silver triflate system.
Figure 4.9: Conductivity-frequency dispersion at ambient and elevated temperatures for the highest conducting film of chitosan acetate-silver triflate system.
4.5 Complex Permittivity

The dielectric loss (imaginary part of complex permittivity) is shown to vary with frequency, Figure 4.10. It can be observed that the dielectric loss increases with decreasing frequency and with increasing temperature. This is again attributed to the space charge effect due to the accumulation of charges at the electrode-electrolyte interface. As the electric field changes direction very rapidly as frequency increases the charges are prevented from accumulation at the interface for a long time. Hence, there are more mobile species in the bulk rather than at the interface at high frequency. Thus the dielectric loss decreases but the conductivity increases with increasing frequency. This result is consistent with the result shown in Figures 4.8 and 4.9. Since there is no hump observed between 100 to 10000 kHz, it is anticipated that the relaxation effect of water does not contribute significantly to the sharp rise in conductivity at frequencies above 100 kHz. The decrease in accumulation of charges at the electrode-electrolyte interface is more significant factor to be considered.
Figure 4.10: Dielectric loss versus frequency at ambient and elevated temperatures for the highest conducting film of chitosan acetate-silver triflate system.
4.6 Complex Electrical Modulus

The spectrum of the complex electric modulus formalism has the advantage whereby the space charge effects very seldom mask the feature of the spectra. A highly capacitive phenomenon is suppressed in modulus formalism. The spectra of the modulus formalism show peaks that are related to the ionic conductivity and the peak shifts toward higher frequency with increasing conductivity of the sample. Figure 4.11 and 4.12 show the real and imaginary parts of the complex formalism.

It can be observed that at frequencies below 10 kHz, the real and imaginary parts taper to very low values. Since $M$ is inversely proportional to $\varepsilon$, and $\varepsilon$ is proportional to capacitance C, the low values of the real and imaginary parts of complex modulus indicate highly capacitive phenomena. It can be observed from Figure 4.12 that the value of $M''$ increases at a decreasing rate implying a peak appearance at frequencies above 1 MHz. Figure 4.13 shows the imaginary modulus spectra at different temperatures for the highest conductivity sample. Here the peaks are clearly observed and the peaks are located at higher frequencies as the temperature increases. The occurrence of these peaks at higher frequency as the temperature increases implies shorter relaxation times as conductivity increases. The increase in conductivity with temperature is also illustrated by the $\ln \sigma T$ Vs $10^3/T$ plots of Figure 4.4. According to Mellander and Albinson [63], the peak shows that the sample is an ionic conductor.
Figure 4.11: Real electric modulus versus frequency with dopant contents for chitosan acetate-silver triflate system. Notice the suppression of highly capacitive phenomena at frequencies below 100 kHz.
Figure 4.12: Imaginary electric modulus versus frequency for different dopant contents for chitosan acetate-silver triflate system. Possible conductivity relaxation peaks at higher frequencies could not be observed due to the limited frequency range available with the instrument. The highly capacitive phenomena are once again suppressed at low frequencies.
Figure 4.13: $M''$ (imaginary electric modulus) versus frequency for highest conducting sample containing 0.2 g of salt in chitosan acetate-silver triflate system at different temperatures. It is to be noticed that the conducting relaxation peaks is shifted to higher frequencies as the conducting increases with temperature.
4.7 Transference Number Measurement

In order to confirm whether the samples are ionic or electronic conductors, transference number measurement was carried out using dc polarization technique [74]. Using the circuit as described in chapter 2, the polarization current was collected until it is saturated. Figure 4.14 shows the experimental result of the transference number measurement.

From the plots it can be observed that the current decay profile is somewhat exponential. The values of transference number were obtained by normalizing the polarization current with the initial current at time zero. The current at saturation is the electronic current. The electronic transference number for the film with the highest electrical conductivity i.e. sample with 0.2 g of silver triflate is 0.05. Hence the ionic transference number is 0.95 and the sample is an ionic conductor. It can be observed that all the samples are ionic conductors. These results confirm those of complex electric modulus which infer that the relaxation peaks indicate that the samples are ionic conductors. However it is difficult to determine whether the major species is the cation or the anion. In polymers both cation and anion are mobile. From literature cationic transference number $t_{Ag}$ has been reported as 0.027 for PEO-Ag salt sample with O/Ag ratio of 8.8 [75]. From this, it can be inferred that the major conducting species in the present study could be CF$_3$SO$_3^-$ anions.
Figure 4.14: Polarization current versus time graph obtained for transference number experiment of the chitosan acetate-silver triflate system.
4.8 Transient Ionic Current (TIC)

Transient ionic current experiment can be directed to determine ionic mobility [76-77]. This technique can be employed to demonstrate the role played by mobile ions in ionic/superionic systems. Figure 4.15 shows the depolarization curve, which upon decay exhibits two peaks. It is expected that the first peak is due to Ag⁺ and the second peak is due to CF₃SO₃⁻. From equation (3.13) the mobility of Ag⁺ ion is 2.67 X 10⁻⁴ cm²/Vs and that of the CF₃SO₃⁻ ion is 1.96 X 10⁻⁴ cm²/Vs. The mobility for both ions are almost similar as expected.

![Current mA vs Time/scan graph](image)

- Time/scan = 1.0 cm/s
- Voltage scan = 0.01 mV/cm
- Resistance, R = 3.3 kΩ
- Voltage applied, V = 0.5 V
- Sample thickness, d = 0.014 cm

- \( \tau_{Ag^+} = 1.5 \text{ s} \)
- \( \tau_{CF3SO3^-} = 2.0 \text{ s} \)
- \( \mu_{Ag} = 2.67 \times 10^{-4} \text{ cm}^2/\text{V-s} \)
- \( \mu_{CF3SO3} = 1.96 \times 10^{-4} \text{ cm}^2/\text{V-s} \)

Figure 4.15: The polarization curve for the highest conducting silver triflate film at room temperature.
4.9 Summary

The sample with the highest electrical conductivity contains 0.2 g of silver triflate salt. Conductivity-temperature studies indicate that ionic conductivity occurs by way of some thermally activated mechanism. From conductivity-temperature studies the samples with high conductivity has low activation energies and vice-versa. The dc conductivity, which according to Johnscher exists in all materials, is of the order $\mu$S cm$^{-1}$. Transference number measurement confirms that the samples are ionic conductors. Transient ionic current measurement shows that the anion and cation have almost the same mobility. It is now important to know whether complexation between the salt and polymer matrix has taken place. We will now look into results obtained from XRD, FTIR, XPS and SEM.