

Electrochemical Impedance study of Proton Conducting Polymer Electrolytes based on PVC Doped with Thiocyanate and Plasticized with Glycerol

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Solid polymer electrolyte (SPE) system based on poly (vinyl chloride) PVC doped with ammonium thiocyanate (NH₄SCN) salt has been prepared by solution cast techniques using glycerol as a plasticizer and THF tetra-hydro furan as a solvent. To examine the electrical properties of the electrolyte films the electrochemical impedance spectroscopy (EIS) has been used. The effect of glycerol on electrical properties and structure of the plasticized PVC-based polymer electrolyte was examined, and the various weight ratio of glycerol plasticizer (%5, %10, %15, and %20) of PVC-NH₄SCN weight is well correlated. Electrolytes are the heart of electrochemical devices and their conductivity investigation is crucial from the viewpoint of electrochemical device application. EIS electrode impedance spectroscopy was used to determine the bulk resistance R_b of the films at room temperature. The increase of the ionic conductivity with an increase in the amount of glycerol was observed through an impedance study, and the maximum ionic conductivity was 1.02512 x 10⁻⁶ S cm⁻¹ obtained from (PVC-%20 NH₄SCN-%20 glycerol) system. Dielectric relaxation studies of the polymer electrolyte film have been studied. The rise of the dielectric polarization of the films is proved by increases in a dielectric constant and dielectric loss. The peaks appeared in the imaginary part of the electric modulus reveals that ion conduction occurs through the viscoelastic relaxation dynamic. In the AC conductivity pattern plateau region ascribed to DC conductivity is appeared.

Keywords: PVC electrolyte; NH₄SCN; plasticizer; impedance study; dielectric properties

1. INTRODUCTION

In the past few years, researchers and developments have been intensively focused on solid polymer electrolytes (SPEs), that is, harmless electrolytes due to their unique application in solid-state electrochemical devices as electrolyte such as batteries [1], fuel cell, sensors, thermoelectric generator, high vacuum electrochemistry, cellular telephones, smart credit cards and so on, however, the secondary rechargeable batteries have been more considered [1-3]. Solid polymer electrolyte overcomes liquid electrolyte by high ionic conductivity, leak-proof, solvent-free characteristic and weighs less [4]. Poly (vinyl chloride) PVC based polymer electrolyte as a host polymer is one of the most favorite choices because it can be easily processed, suitable cost, it has good mechanical and thermal properties and great affinity with solvents or plasticizers [5]. The popular use of PVC polymer electrolyte is related to lone pair electrons existence at the chlorine atom and these results in dissolving of inorganic salts [6]. PVC is chosen to be a useful polymer that has special characteristics used in medical applications, for instance, cannulas, catheters, dialysis tubing, and lung bypass sets [7]. Some poly(vinyl chloride) based solid polymer electrolytes have been reported such as PVC-LiClO₄ [8], ITO/TiO₂/PVC-LiClO₄/graphite[9], PVC-LiBF₄-DBP[3], PVC-Li₂SO₄[5], PVC-LiCF₃SO₃-DMF[10], PVC based polymer electrolyte[11-13], PVC-NaClO₄ [14]. Various inorganic lithium, sodium and ammonium salts have been reported and investigated as electrical conductivity enhancer such as Li₂SO₄ [5], NaClO₄ [14], LiCF₃SO₃ LiClO₄, LiBF₄ [15], LiAsF₆, LiPF₆ [16]. some ammonium salts have been used as dopant are ammonium thiocyanate (NH₄SCN), ammonium nitrate (NH₄NO₃), ammonium iodide (NH₄I), nonetheless, ammonium thiocyanate has low lattice energy by comparison with other ammonium salts this becomes anion and cation formed more comfortably then dissolved in polar polymers [17]. Different plasticizers have been used for PVC polymer electrolyte and the result illustrates increasing conductivity and decrease the crystallization of polymers such as (EC) ethylene carbonate, (PC) propylene carbonate and (DBP) dibutyl phthalate, and (DOA) dioctyl adipate. PVC is adaptable with above plasticizers, while at the high level of plasticizers in plasticization, polymer electrolyte turns into the low mechanical property this is one of the disadvantages of plasticizers [13,16,18]. Lately, PVC as homopolymer and blended polymers of PVC based polymer electrolytes are become more popular due to having higher conductivity at ambient temperature are PVC-PEMA [19], PVC-PAN-LiTFSI [20], PVDF-PVC [21], PVA-PVC[22], PVC-PVO:KI [23], PVC-PEMA [24], PVC-PMMA [2], the highest conductivity of the above-mentioned systems is $1.30 \times 10^{-2} \text{ S cm}^{-1}$ for PVC-PVO:KI [23]. Preparing PVDF-PVC blend polymer by electrospinning had better prospect as polymer electrolyte was reported by Z. Zhong et al [25]. In the present work poly (vinyl chloride) PVC doped with 20 wt.% of ammonium thiocyanate (NH₄SCN) salt and then different amount of glycerol plasticizer was added to enhance the DC conductivity and dielectric properties.

2. EXPERIMENTAL DETAIL

2.1. Material and sample preparation

All the chemicals were purchased from commercial suppliers (Merck and Sigma-Aldrich) without further purification. Poly (vinyl chloride) PVC high molecular weight from (Sigma-Aldrich), ammonium thiocyanate (NH_4SCN 99% purity), Glycerol ($\text{C}_3\text{H}_8\text{O}_3$) %99 purity and tetra-hydro furan THF 99.9% purity from Merck have been used as a raw material for preparation of solid polymer electrolyte. For this reason, 1 g of PVC was dissolved in 50 ml of THF solution. After that the constant weight ratio 20wt.% of ammonium thiocyanate NH_4SCN was added to the solution mixture. The mixture was stirred continuously with the magnetic stirrer in order to achieve homogenous solution. Finally, various weight ratio of glycerol as a plasticizer was added to the solution. The glycerol content in the prepared samples was varied from 5 to 20 wt.%. The samples were coded as PVCG1, PVCG2, PVCG3 and PVCG4 for PVC-20% NH_4SCN 5wt.%, PVC-20% NH_4SCN 10wt.%, PVC-20% NH_4SCN 15wt.% and PVC-20% NH_4SCN 20wt.% of glycerol respectively. The solution was then poured in to different dry and clean glass petri dishes, covered with filter paper to prevent from any impurities and then allowed to evaporate slowly at ambient temperature until solvent-free PVC solid polymer electrolyte films were obtained. Table 1 summarizes the sample composition.

Table 1. The composition of PVC- NH_4SCN -glycerol systems

Sample Designation	(PVC) (1) (g)	NH_4SCN (wt.%)	Glycerol (wt.%)
PVCG1	1	20	5
PVCG2	1	20	10
PVCG3	1	20	15
PVCG4	1	20	20

2.3 Electrochemical impedance spectroscopy (EIS)

The investigation of impedance of the fabricated films was employed by means of an LCR meter (HIOKI 3531 Z Hi-tester, Japan) that was connected to a computer. The fabricated samples were cut to small circle films (diameter = 2 cm) and inserted between two electrodes of stainless steel (SS) under spring pressure to make certain an excellent contact. The measurements were employed in the frequency ranging between 50 Hz and 1 MHz at ambient temperature. The complex impedance (Z^*) real part (Z') and imaginary (Z'') part were determined and indicated as a Nyquist plot (Z' against Z''). Thus, the bulk resistance (R_b) was measured using the intersect of the Nyquist plot with the real axis.

3. RESULTS AND DISCUSSION

3.1. Impedance study

An AC-field is produced along with the polymer electrolyte when two electrodes are charged positively and negatively, which eventually makes the ions move back and forth, so the ions have the same phase as the applied voltage. The stationary polymer chains turned into polarizing chains are shown by imaginary impedance capacitor Z_i , though the movement of ions is demonstrated by real impedance Z_r [1]. The specific nature of the plasticizers can influence of the polymer chain conductivity, and ion mobility (ion and polymer-plasticizer interactions, dielectric constant and viscosity). However, the conductivity of plasticized-polymer electrolyte films is higher by comparing with none plasticized-polymer electrolyte [26]. Figure 1. Illustrate the impedance plot for solid polymer electrolytes based on (PVCG1-PVCG4) at room temperature. The charge accretion and dispersion at the electrode/electrolyte interface can be observed in the low-frequency region, and an electrical double layer capacitor EDLC is produced. However, the charge transfer process is showed by the bulk properties of the material in the high-frequency region [27]. In the PVC film interface, the influence between two blocking electrodes which showed the formation of double-layer capacitance can be denoted by an invisible spike [28]. The full semicircle for the higher amount of glycerol as a plasticizer can be seen while the semicircle for lower glycerol is smallest among all of them, in which the bulk resistance decreases as the amount of glycerol increase. Under the real axis, the center of each half-circle can be founded, which admits that the ions relaxations are non-Debye in nature [29]. The ionic conductivity of the PVC-NH₄SCN-glycerol systems is calculated by the following equation: The sample DC conductivity can be determined from the R_b value and the sample dimensions using the following equation:

$$\sigma_{dc} = \left(\frac{1}{R_b} \right) \times \left(\frac{t}{A} \right) \quad (1)$$

Where t is the thickness of the sample, R_b is the bulk resistance of the material and A is the area of the electrode [30]. The computed DC conductivities were tabulated and shown in Table 1. It's very obvious that the ionic conductivity is higher for lower bulk resistance R_b material, and the highest conductivity that is $1.02512 \times 10^{-6} \text{ S cm}^{-1}$ was found for the highest amount of glycerol (PVC-%20 NH₄SCN-%20 glycerol) system as shown in table 2.

The highest conductivity for PVC-NaI systems without plasticizer was $10^{-8} \text{ S cm}^{-1}$ reported by Muhammad, F. H., [31], and for 70%PVC-30%NH₄I-EC was $10^{-6} \text{ S cm}^{-1}$ which was studied by Elektrolit, K. [32] for PVC-LiClO₄-DEP and PVC-LiAsF₆-DBP systems the conductivity values was $10^{-7} \text{ S cm}^{-1}$ and $10^{-8} \text{ S cm}^{-1}$ respectively investigated by Stephan, A. M., and Uma, T., [33, 6], so it is clear that glycerol has better enhanced the system conductivities by comparison with DEP, DBP and EC.

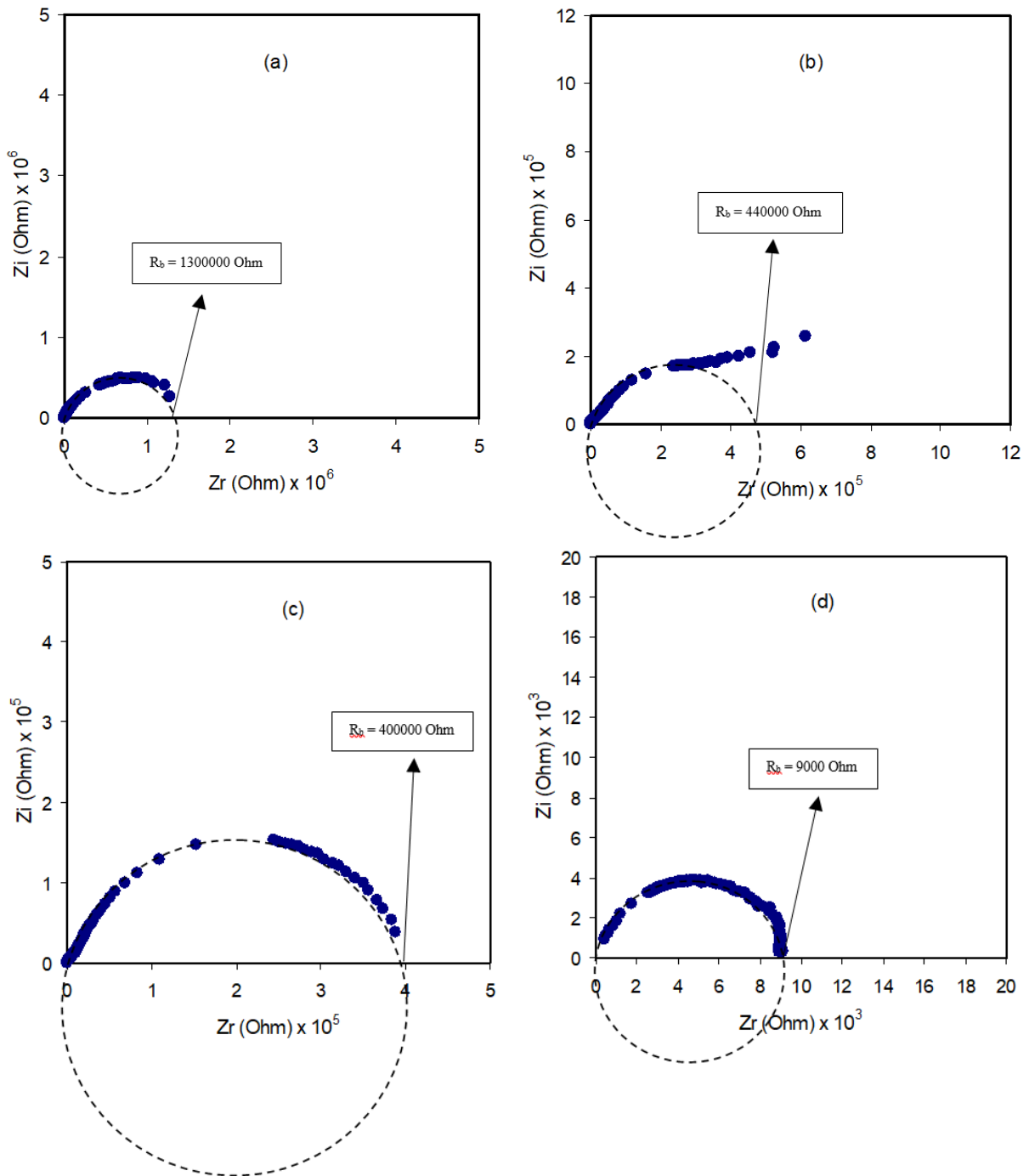


Figure 1. Impedance plots for PVC-20%NH₄SCN- (a) %5 glycerol, (b) %10 glycerol, (c) %15 glycerol, (d) %20 glycerol systems.

Table 2. the conductivity value of PVC-NH₄SCN-glycerol systems

Sample Designation	DC conductivity (S/cm)
PVCG1	7.097×10^{-9}
PVCG2	2.096×10^{-8}
PVCG3	2.306×10^{-8}
PVCG4	1.025×10^{-6}

3.2. Dielectric Properties

3.2.1. Study of dielectric constant and dielectric loss

Dielectric relaxation for any solid polymer electrolyte was studied deeply to find out the ionic transport phenomenon. Through dielectric relaxation, nature and ionic movement of polymer-plasticizer interactions can be investigated [34, 35]. relative permittivity, loss tangent, dielectric constant, microwave reflection coefficient, split post dielectric resonance technique and terahertz material are some methods for characterizing dielectric properties [35]. The dielectric constant or complex permittivity can be defined by the following equation:

$$(\epsilon^*) = \epsilon' - j\epsilon'' \quad (2)$$

Where, ϵ' is the real dielectric constant and ϵ'' is the imaginary dielectric loss which essentially demonstrated the energy loss and storage in every cycle of the applied power supply [34]. Both real and imaginary parts of complex permittivity (ϵ^*) were calculated from the impedance data (i.e., Z' and Z'') using the following equations,

$$\epsilon' = \frac{Z''}{\omega C_o (Z'^2 + Z''^2)} \quad (3)$$

$$\epsilon'' = \frac{Z'}{\omega C_o (Z'^2 + Z''^2)} \quad (4)$$

where ω is angular frequency of the applied field ($\omega=2\pi f$), ϵ' and ϵ'' are the dielectric constant and dielectric loss, respectively. C_o is the vacuum capacitance given by $\epsilon_o A/t$, where ϵ_o is a permittivity of free space, A is the electrode cross sectional area and t is the film thickness. Figure 2 and 3 refers to PVC-20% NH_4SCN salt and the various weight ratio of glycerol, it present real and imaginary part of dielectric constant (ϵ' , ϵ'') as a function of frequency at room temperature. It can be seen that the value of ϵ' rises very sharply for a higher amount of glycerol plasticizer at the low-frequency region because of the influence of space charge and electrode polarization [36]. At the electrode/electrolyte interface, the high concentration of charge carriers accumulated becomes the polarization increase in the low frequency [37]. At the higher frequency regions, it can be observed that there is no excess ion dispersion in the direction of the field because of the periodic reversal of the electric field takes place rapidly. On the other hand, both dielectric constant and dielectric loss decreased due to the declination of polarity [38].

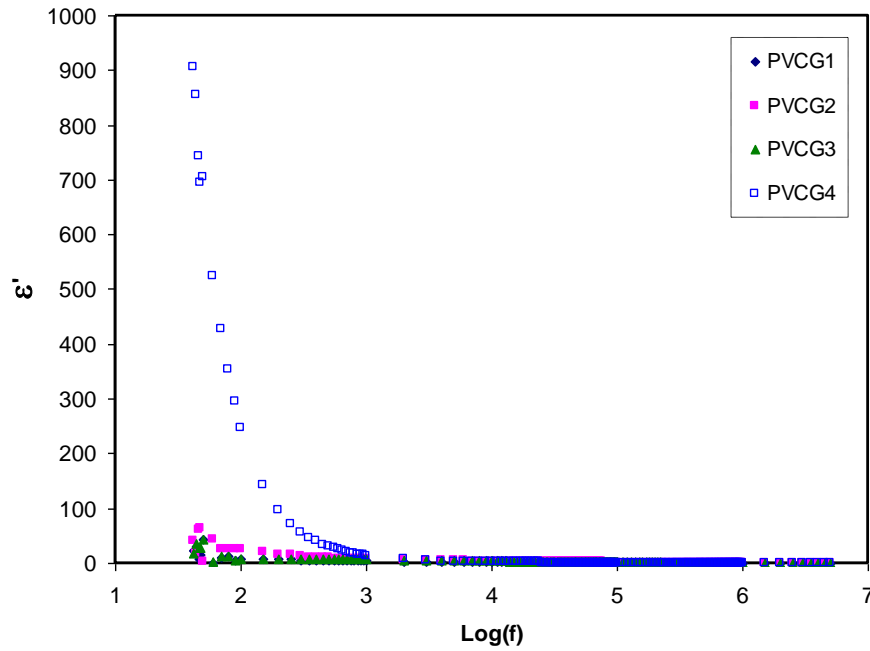


Figure 2. Dielectric constant as a function of frequency for (PVCG1-PVCG4) electrolyte systems at room temperature.

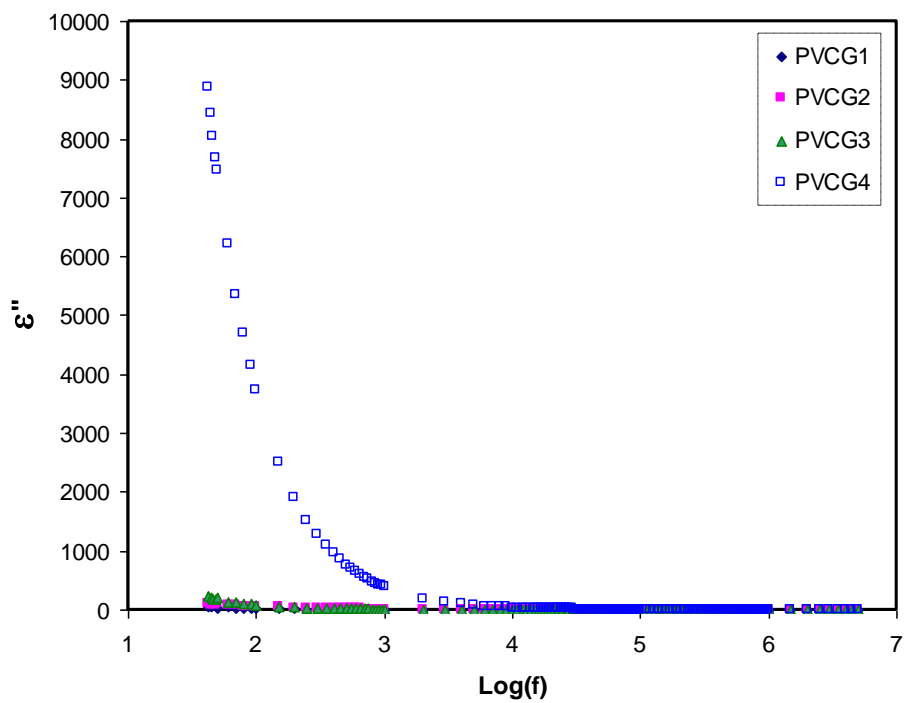


Figure 3. Dielectric loss as a function of frequency for (PVCG1-PVCG4) electrolyte systems at room temperature.

3.2.2. Tangent loss ($\tan\delta$) relaxation peak

To better understand the mechanism of ionic mobility and molecular interaction when the various weight ratio of glycerol was incorporated in PVC-20% NH_4SCN systems, the tangent loss was

performed [39]. Figure (4) shows the loss tangent spectra for the different amounts of glycerol with the PVC- NH₄SCN system as a function of frequency at ambient temperature. From the tangent loss peaks and their shift with the different weight ratios of glycerol shown the presence of dielectric relaxation process [35]. At the higher log frequency, the increase in the tangent loss is obtained. This may be due to the rise proportion of amorphous material, and the presence of dipole relaxation can be observed from the peaks [40]. It can be denoted from the plot that the electrolyte with the higher plasticizer has the shortest relaxation time [41]. The two distinguish loss tangent peaks can be seen for PVC-%20 NH₄SCN samples incorporated with 10 wt.%, 15 wt.% glycerol. However, for the samples incorporated with 20 wt.% only one loss peak noticeable at a higher frequency [42].

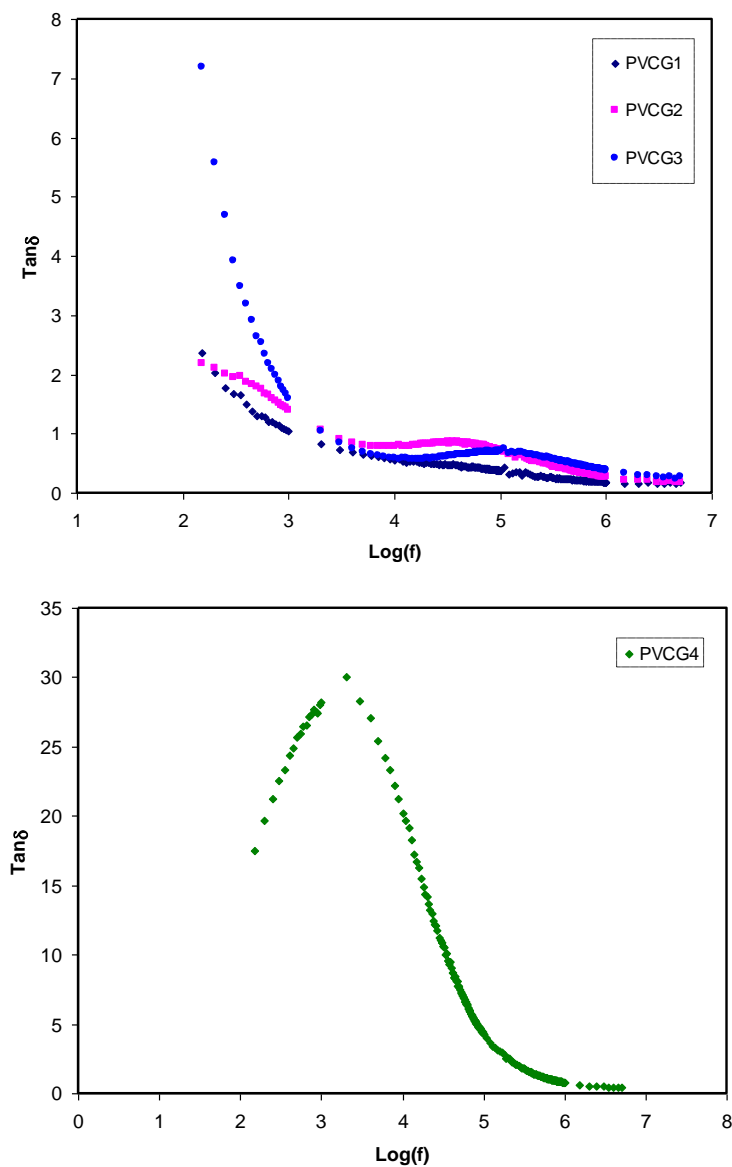


Figure 4. Loss tangent ($\tan\delta$) as a function of frequency for (PVCG1-PVCG4) electrolyte systems at room temperature.

3.2.3. Electric modulus study

Types of relaxation visco-elastic and conductivity relaxation in a polymeric material can be detected by both real and imaginary modulus due to permanent dipoles that can exist on the side chains of the polymer backbone. Hence, relaxation takes place [43]. Both real and imaginary parts of complex modulus (M^*) were calculated from the impedance data (i.e., Z' and Z'') using the following equations [44- 46],

$$M' = \frac{\epsilon'}{(\epsilon'^2 + \epsilon''^2)} = \omega C_o Z'' \tag{5}$$

$$M'' = \frac{\epsilon''}{(\epsilon'^2 + \epsilon''^2)} = \omega C_o Z' \tag{6}$$

The frequency dependence of the real part (M_r) and imaginary part (M_i) of electric modulus studied in Figures 5 and 6 respectively for PVC- NH_4SCN - glycerol polymer electrolytes as a function of frequency at room temperature. Because of the existence of the electrode polarization phenomena at the higher frequency, the values of both M_r and M_i are increased.

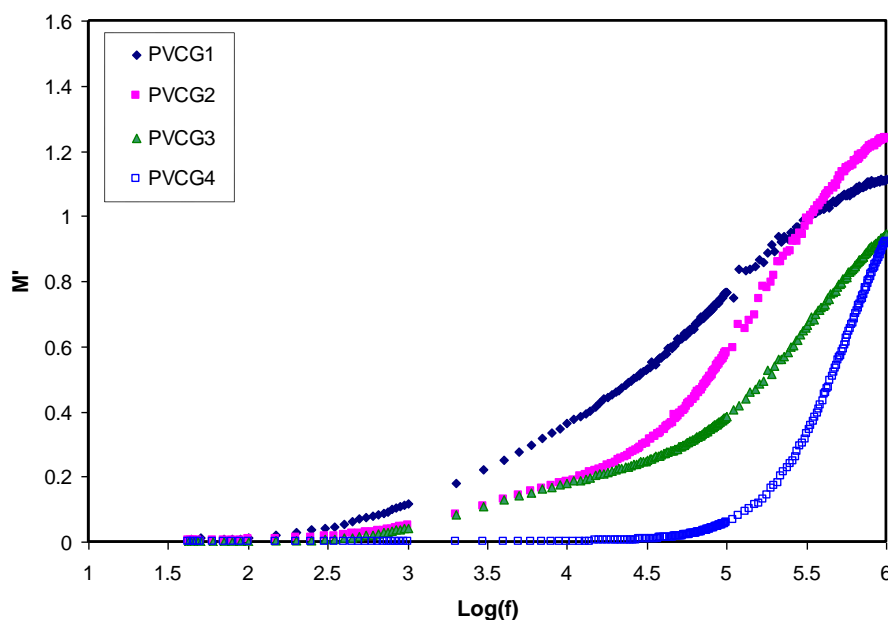


Figure 5. Variation of real modulus (M_r) as a function of frequency for (PVCG1-PVCG4) electrolyte systems at room temperature.

On the other hand, the occurrence of peaks in the modulus reveals that the PVC- NH_4SCN - glycerol polymer electrolytes are ionic conductors at a higher frequency [47, 48]. In the low-frequency regions, both M_r and M_i reach zero as shown in figures 5 and 6, in which it means the electrode polarization (EP) associated with higher capacitance value [48]. Besides, among the glycerol weight

ratio-dependent real and imaginary part of modulus spectrum demonstrated that the film with 10 wt.% of glycerol has a maximum intensity of modulus, while the film with 20 wt.% of glycerol has the lowest value of modulus and represented the high ionic conductivity than other films [49]. In the low-frequency regions, the charge of ions migrated among coordinated sites of the polymer electrolyte, so the conduction occurs in polymer electrolyte. This improves the fact that to recognize the percolation threshold phenomena, the electric module studies can be used [43].

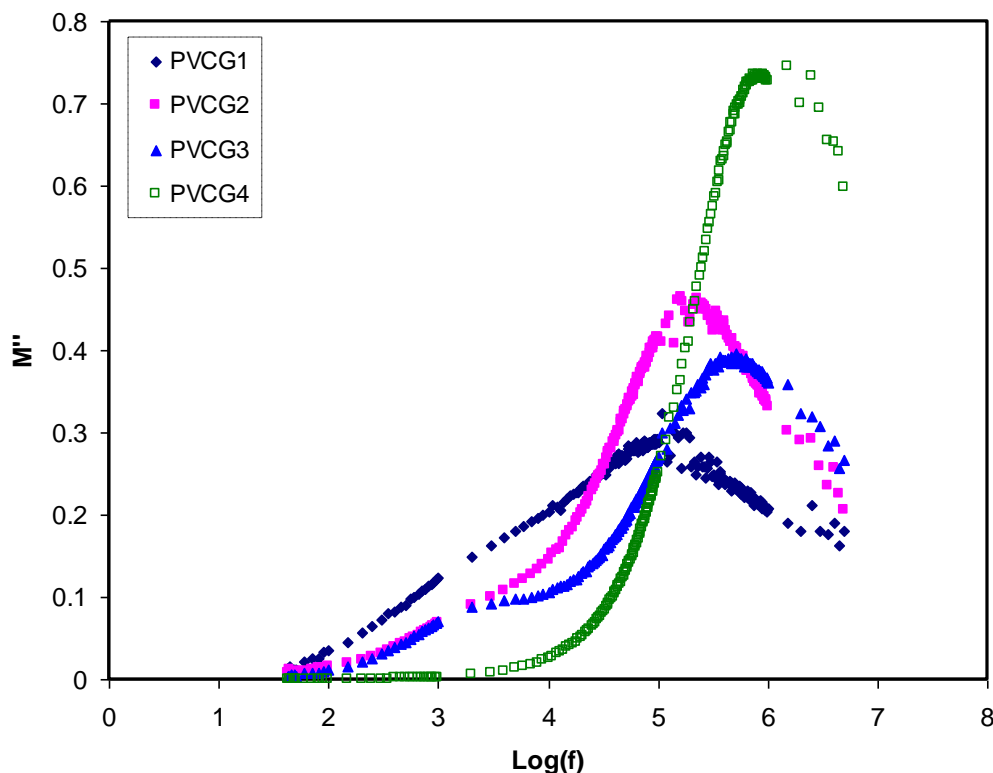


Figure 6. Variation of imaginary modulus (M_i) as a function of frequency for (PVCG1-PVCG4) electrolyte systems at room temperature.

The spectra of AC conductivity at ambient temperature for the PVC electrolyte films are indicated in Figure 7. The AC conductivities are measured by means of Eq. (7) [50-52]:

$$\sigma'_{ac} = \left[\frac{Z'}{Z'^2 + Z''^2} \right] \times \left(\frac{t}{A} \right) \tag{7}$$

It is documented that, three separate regions may possibly be recognized, first, the spike at the low frequency region, which is related to the concentration of the salt, originates from the polarization of the electrodes, second, the plateau region at the medium frequency stems from the DC conductivity at the bulk, and third, the region of high frequency, which shifts to the higher frequency when the concentration of the salt increases, arising from conductivity relaxation [51, 52]. The absence of the low frequency region in the spectra of AC is due to the fact that the spike or tail region is insignificant as shown in impedance plots (see Fig1). In earlier reports, the AC conductivity reliance on the applied electrical signal frequency was employed to be a precise technique to measure the DC conductivity

[53]. The plateau region extension to the y-axis assists to get the DC electrical conductivity. It is worth mentioning that the raise of AC conductivity with rising frequency is still noticeable at higher frequencies. In addition, the raise of AC conductivity with rising frequency indicates the reality of hopping conduction that promotes the hopping of charge carriers among the localized states [54]. Earlier report established that two phenomena can be established from the investigation of AC conductivity [40]. First, the spectra of AC conductivity can be used to measure the DC electrical conductivity. Second, the powerful relationship of AC conductivity dispersion region with the presence of semicircle at the high frequency region (see Figure 1) can be indicated from the comparison of impedance plots and AC conductivity spectra. The dispersion region of AC spectra has revealed to result from the restricted charge carriers within the samples [50, 54].

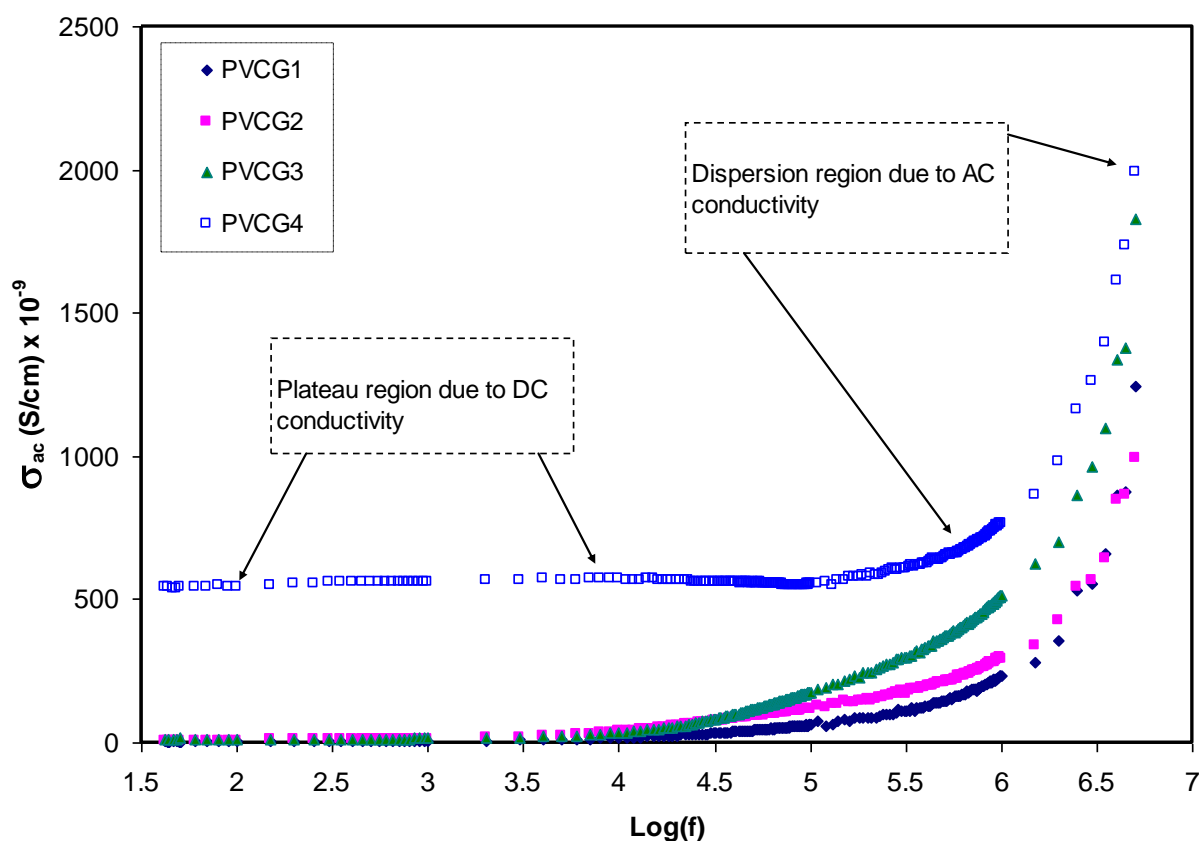


Figure 7. Variation of AC conductivity (σ_{ac}) as a function of frequency for (PVCG1-PVCG4) electrolyte systems at room temperature.

4. CONCLUSION

In the present paper, the effect of glycerol as a plasticizer in optimizing PVC based solid polymer electrolyte doped with NH_4SCN salt was prepared via solution casting method. Impedance and dielectric studies were employed to investigate the electrical properties of PVC polymer electrolyte systems at ambient temperature. It was proven that the conductivity of the systems

enhanced by increasing the amount of glycerol. Impedance study was confirmed that the ions relaxations are non-Debye in nature. To further understand the relaxation of dipoles, the dielectric studies were done in the plasticized polymer electrolyte. Through dielectric constant, it can be concluded that due to the rise of the number of charge carriers, the conductivity is increased. Dielectric modulus was studied, at a higher frequency; the presence of peaks in the modulus reveals that the polymer electrolytes are ionic conductors. Among the different weight ratios of glycerol of polymer electrolytes film, PVCG4 had the highest conductivity. Two distinct regions; namely plateau due to DC part and dispersion due to AC conductivity were observed in AC conductivity pattern.

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