



Analysis of Proton Conducting P(Vdcl-co-AN-co-MMA)-NH₄SCN-EC Tri Block Copolymer Electrolytes

KEYWORDS

Evaporating system; Steady state availability; Markov birth-death process, Transition diagram

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ABSTRACT

The proton conducting tri block copolymer electrolytes based on Poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate)(P(VdCl-co-AN-co-MMA)-Ammonium thio cyanate (NH₄SCN) (P(VdCl-co-AN-co-MMA):NH₄SCN) and Poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate)(P(VdCl-co-AN-co-MMA)-Ammonium thio cyanate (NH₄SCN)-Ethylene Carbonate (EC) (P(VdCl-co-AN-co-MMA):NH₄SCN:EC of different compositions were prepared by solution casting technique. Structural and surface morphological characterizations were studied by X-ray diffraction (XRD) analysis and Scanning Electron Microscopy (SEM) measurements respectively. The conductivity behaviors of copolymer-salt and copolymer-salt-plasticizer complexes were studied by employing ac impedance measurements. The highest bulk conductivity was found to be $1.32 \times 10^{-3} \text{ S cm}^{-1}$ at 303 K for the plasticized sample. The conductance, dielectric behavior and relaxation parameters of the samples have been presented and discussed.

1. Introduction

The science of polymer electrolytes has attracted ever increasing interest for the past two decades due to the potentially promising applications of such electrolytes in all solid state batteries and electrochemical devices. The study of polymer electrolytes was launched by Fenton et al in 1973 and their work inspired intense research and development on the synthesis of new polymer electrolytes [1]. Since the discovery that a number of polymer-salt complexes exhibited considerable conductivity, much research efforts have been directed to find the optimal combination of host polymer and dopant salt for fast ionic transport. Various methods have been applied to increase the conductivity of electrolytes. One of the approaches relied upon the addition of plasticizer to the polymer complex (known as Gel Polymer Electrolytes) (GPEs).

Among the polymer matrixes that has been promising for the application in GPEs, polyacrylonitrile (PAN), poly (vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA), and poly(ethylene oxide) (PEO) based polymers has been most extensively studied. The GPEs with these matrixes exhibit high ionic conductivity, usually over $10^{-3} \text{ S cm}^{-1}$ at room temperature [2].

Also works have been reported on the acrylonitrile and methylmethacrylate based copolymer electrolytes. Qizhen Xiao et al has reported on the conductivity behavior of block copolymer electrolytes based on Poly (vinylidene fluoride) (PVdF) and Poly(ethylene oxide-block-methyl methacrylate)(PEO-b-PMMA) copolymer [3]. Yu-Hao Liang et al has reported on the conductivity behavior of plasticized copolymer electrolytes based on Poly (acrylonitrile-block-ethylene glycol) (P(AN-b-EG)) copolymer [4]. Kyung-Hee Lee et al has reported the effect of silica on the electrochemical characteristics of the plasticized copolymer electrolytes based on Poly (acrylonitrile-co-methyl methacrylate) (P(AN-co-MMA)) copolymer [5]. But so far no work has been reported on the tri block copolymer electrolytes based on P(VdCl-co-AN-co-MMA).

The plasticizer EC has been selected due to its high dielectric constant (95.3) [6] which will easily dissociate the salt into ions thereby easily enhancing the conductivity. Moreover ammonium thio cyanate is a good proton donor to the polymer matrix. Herrington et al [7] have reported that ammonium salts exhibit specific conductivity which is of the 5 to 6 orders of magnitude higher than alkali salts.

In the present study the new copolymer P(VdCl-co-AN-co-MMA) has been doped with various concentrations of NH₄SCN and for the same system, the plasticizer EC has been added for various compositions and the conductivity behavior of all the copolymer complexes has been analyzed. The presence of large number of polar groups such as oxygen, nitrogen and chlorine in the copolymer (Fig.1) has been a great advantage to enhance the ionic mobility. And it is interesting to note that so far no works has been reported on this copolymer which has further enhanced the curiosity to learn about the conductivity behavior of this new tri block copolymer electrolyte.

2. Experimental Details

P(VdCl-co-AN-co-MMA) (Himedia) and NH₄SCN (Himedia) were dried by heating under vacuum at 100°C and 120°C for 12 h and 10 h, respectively and tetrahydrofuran (THF, S.d. Fine. Chem. Ltd.) was used as the solvent. Copolymer electrolytes of P(VdCl-co-AN-co-MMA):NH₄SCN and the plasticized electrolytes of P(VdCl-co-AN-co-MMA):EC:NH₄SCN in different weight ratios has been prepared by solution-casting technique. Appropriate weights of P(VdCl-co-AN-co-MMA) and NH₄SCN (Table 1) were dissolved in THF. The solution was then stirred continuously until the mixture became homogeneous viscous liquid. Similarly appropriate weights of P(VdCl-co-AN-co-MMA) and NH₄SCN (Table 1) were dissolved in THF followed by the addition of EC. The solution was then stirred continuously until the mixture became homogeneous viscous liquid. These solutions of different compositions were poured into identical Petri glass dishes of 10 cm diameter. The films were dried in a vacuum chamber at

room temperature for 24 h. The copolymer films were further dried in a vacuum chamber at 60°C for 5 h to remove any traces of solvent (THF) and was then stored in sealed containers in a desiccator. Gel-like and solvent-free polymer electrolyte films with thickness of (1–2) mm were obtained.

The Cu-K α line was used for XRD measurements by the usual θ -2 θ scan. SEM micrographs of samples were observed with a field emission scanning electron microscope (FE-SEM; JSM-6335F, JEOL Ltd.). The electrical conductivity, dielectric behavior and relaxation parameters studies were carried out on the copolymer electrolyte films by using a computer-controlled HIOKI model 3532 LCZ meter of frequency range 42 Hz–5 MHz at 303 K.

Fig. 1 Structure of Poly(vinylidene chloride-co-acrylonitrile-co-methylmethacrylate):

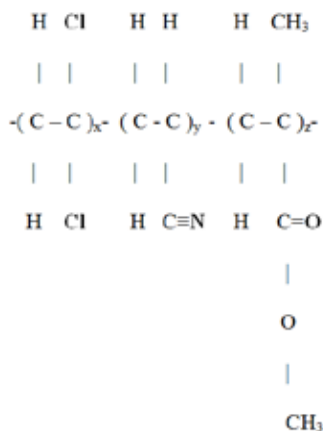


Table 1
Compositions of pure copolymer and its complexes

SAMPLE COMPOSITION	USED HEREAFTER AS
P(VdCl-co-AN-co-MMA) - Pure Copolymer	P(VdCl.)
70m% P(VdCl-co-AN-co-MMA):30m% NH ₄ SCN	70m% P(VdCl.):30m% NH ₄ SCN
50m% P(VdCl-co-AN-co-MMA):50m% NH ₄ SCN	50m% P(VdCl.):50m% NH ₄ SCN
45m% P(VdCl-co-AN-co-MMA):45m% NH ₄ SCN:10m% EC	45m% P(VdCl.):45m% NH ₄ SCN:10m% EC
25m% P(VdCl-co-AN-co-MMA):25m% NH ₄ SCN:50m% EC	25m% P(VdCl.):25m% NH ₄ SCN:50m% EC

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction analysis

XRD measurements were conducted to examine the nature of crystallinity of the copolymer electrolytes (P(VdCl.):NH₄SCN and (P(VdCl.):NH₄SCN:EC films with respect to that of pure copolymer P(VdCl.) and NH₄SCN to investigate the occurrence of complexation. XRD patterns of pure P(VdCl.), P(VdCl.):NH₄SCN complexes and P(VdCl.):NH₄SCN:EC complexes of different compositions have been depicted in Figs.2 (a-e). It was observed that the P(VdCl.) showed two broad diffraction peaks at 32.34° and 38.56° and another two sharp peaks at 24.88° and 15.8° as seen in Fig 2(a).

For the P(VdCl.):NH₄SCN complexes as shown in Fig. 2(b-c), it was found that the incorporation of NH₄SCN into the copolymer matrix has caused slight increase in the amorphous nature of the sample which was observed from the increase in broadness and decrease in intensity of the peaks with respect to that of P(VdCl.). The amorphous nature has produced greater ionic diffusivity leading to high ionic conductivity.

The diffractograms of P(VdCl.):NH₄SCN:EC complexes has

been presented in the Fig. 2 (d-e). It was observed that the broadness and the intensity of the same peaks mentioned above has been further increased and decreased respectively when compared with that of the P(VdCl.): NH₄SCN complexes which has enhanced the conductivity of the plasticized copolymer complexes.

Also it has been observed that the peaks 2 θ = 24° and 26° (JCPDS 23-0029) [8] corresponding to pure NH₄SCN were absent in the XRD patterns of P(VdCl.):NH₄SCN and P(VdCl.):NH₄SCN:EC complexes as seen from Fig. 2 (b-e).

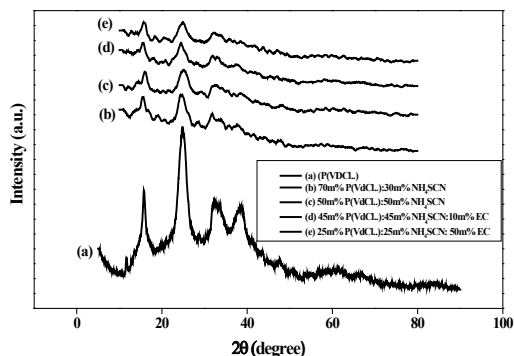


Fig. 2. XRD Diffractograms of (a). P(VdCl.), (b). 70m% P(VdCl.):30m% NH₄SCN (c). 50m% P(VdCl.):50m% NH₄SCN, (d). 45m% P(VdCl.):45m% NH₄SCN:10m% EC & (e). 25m% P(VdCl.):25m% NH₄SCN:50m% EC

3.2. Morphological Characteristics

Scanning electron micrographs (SEM) of pure P(VdCl.), P(VdCl.):NH₄SCN complexes and P(VdCl.):NH₄SCN:EC copolymer electrolytes have been shown in Figs. 3(a-e). From Fig 3(a), smooth and non porous morphology has been observed for P(VdCl.). For 70m% P(VdCl.):30m% NH₄SCN, the porosity has increased and less number of minute pores has been observed from Fig. 3(b). When the concentration of NH₄SCN has been increased to 50m%, the size and depth of these pores has been increased and appears like a hole with appreciable size as evident from Fig. 3(c) however there was no increase in the number of pores.

In the micrograph of 45m% P(VdCl.):45m%NH₄SCN:10m% EC, large number of small pores have been observed as evident from Fig. 3(d) which might be due to the addition of plasticizer EC. The pore size has slightly further increased and a small well like structure has been observed for each pores for 25m% P(VdCl.):25m% NH₄SCN:50m% EC as evident from Fig. 3(e). This large amount of pores in the porous membrane and increase in the size of the pores with small well like structure has enlarged the contact areas between copolymer and solvent such that the electrolyte solution has been well retained in the membrane by copolymer-solvent interactions which in turn has enhanced the conductivity [9]. Hence the conductivity has been more for the copolymer complex 25m% P(VdCl.):25m% NH₄SCN:50m% EC which has been in good agreement with the SEM micrographs.

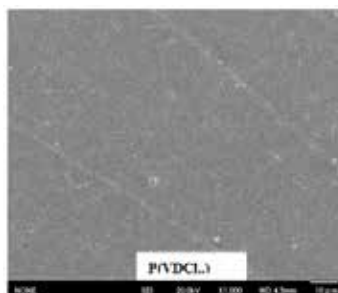


Fig. 3(a). SEM Micrograph of P(VdCl.)

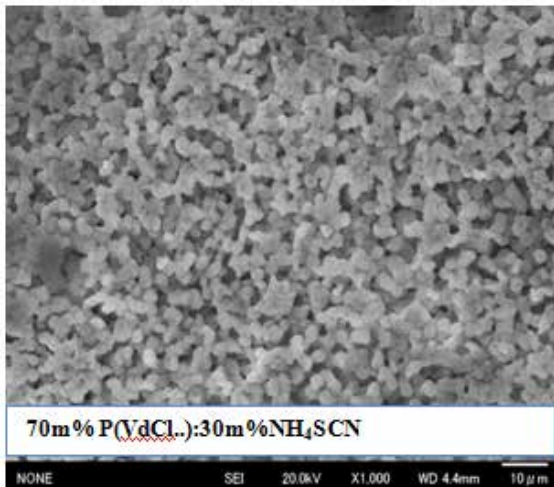


Fig. 3(b). SEM Micrograph of 70m% P(VdCl.):30m% NH₄SCN

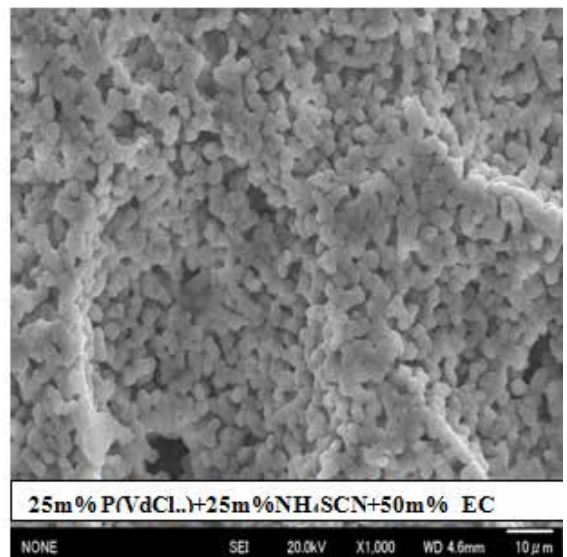


Fig. 3(e). SEM Micrograph of 25m% P(VdCl.):25m% NH₄SCN:50m% EC

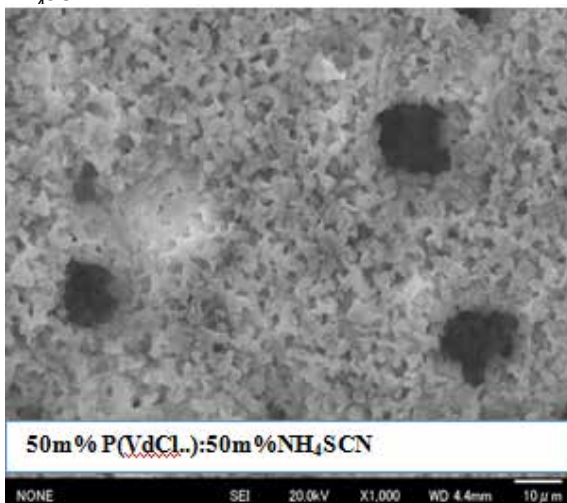


Fig. 3(c). SEM Micrograph of 50m% P(VdCl.):50m% NH₄SCN

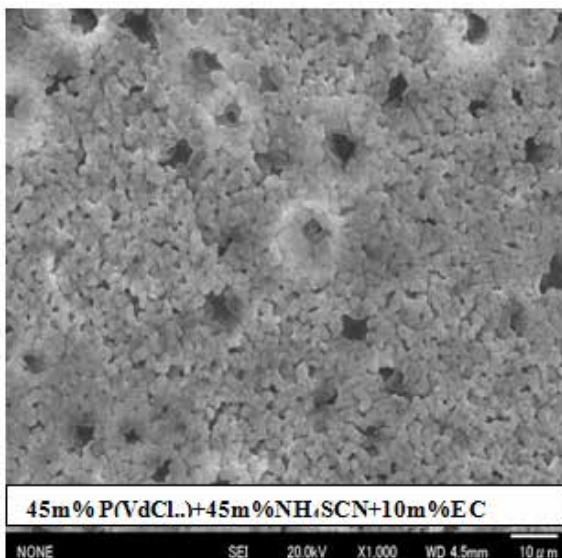


Fig. 3(d). SEM Micrograph of 45m% P(VdCl.):45m% NH₄SCN:10m% EC

AC Impedance Analysis

The ionic conductivity of the P(VdCl.):NH₄SCN systems and P(VdCl.):NH₄SCN:EC plasticized system of different compositions at 303 K was derived from the complex impedance plots and has been presented in Figs. 4(a-d). The plots consisted of a high-frequency depressed semicircle represented by a frequency-dependent capacitor C_g parallel to a bulk resistor (R_b) and a low frequency spike represented by a constant phase element CPE. The high-frequency part of impedance plots has been related to bulk relaxation processes according to Armstrong's model of solid electrolyte [10] and the low-frequency spur has been resulted from the electrode/electrolyte interfacial properties. It has been observed that the semicircle depression has decreased with increase in content of NH₄SCN as seen from Figs. 4(a-c).

The EQ software program developed by Boukamp [11, 12] has been used to extract the bulk electrical resistance (R_b) of the copolymer electrolytes from the impedance plot of the low-frequency side intercept on the Z' axis. The ionic conductivity (σ) was calculated using the equation

$$\sigma = L/R_b A \text{ (S cm}^{-1}\text{)} \text{ ----- Equation (1)}$$

where 'L' and 'A' represented the thickness of the copolymer electrolyte film surface area of the film respectively.

From the impedance spectra of 70m% P(VdCl.):30m% NH₄SCN and 50m% P(VdCl.): 50m% NH₄SCN as seen from Figs. 4(a-b), it was observed that the value of the bulk resistance has decreased with increase in NH₄SCN content due to which the ionic conductivity has been enhanced. It was seen from the Table 2 that the ionic conductivity for 70m% P(VdCl.):30m% NH₄SCN and 50m% P(VdCl.):50m% NH₄SCN was $5.94 \times 10^{-7} \text{ S cm}^{-1}$ and $2.10 \times 10^{-4} \text{ S cm}^{-1}$ respectively at 303 K. With the increase of NH₄SCN content, the conductivity has also increased due to the increase in charge carrier concentration.

Similarly from the impedance spectra of 45m% P(VdCl.):50m% NH₄SCN:10m% EC and 25m% P(VdCl.):25m% NH₄SCN:50m% EC as seen in Figs. 4(c-d), it has been observed that the semicircle slowly disappears and only the spur remains for the high concentration of the EC. Also from Table 2, the conductivity value of 45m% P(VdCl.):45m% NH₄SCN:10m% EC and 25m% P(VdCl.):25m% NH₄SCN:50m% EC was found to be 9.21 x

$10^{-4} \text{ S cm}^{-1}$ and $1.32 \times 10^{-3} \text{ S cm}^{-1}$ respectively at 303 K. There has been appreciable increase in conductivity when compared with that of the $\text{P(VdCl.)}:\text{NH}_4\text{SCN}$ system which might be due to the enhancement of the ionic mobility and number of carrier ions due to the plasticizing effect of EC [13, 14] as many previous workers had already reported.

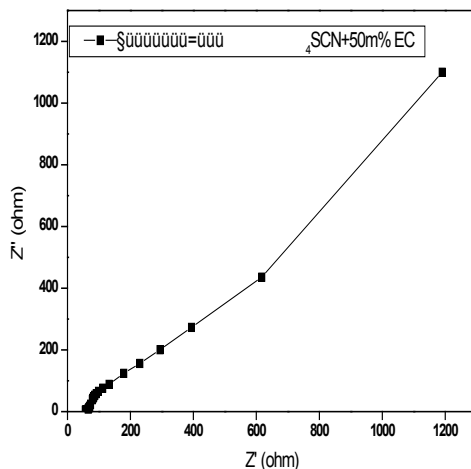
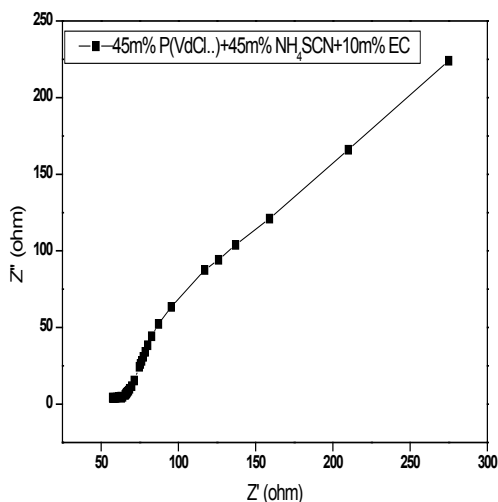
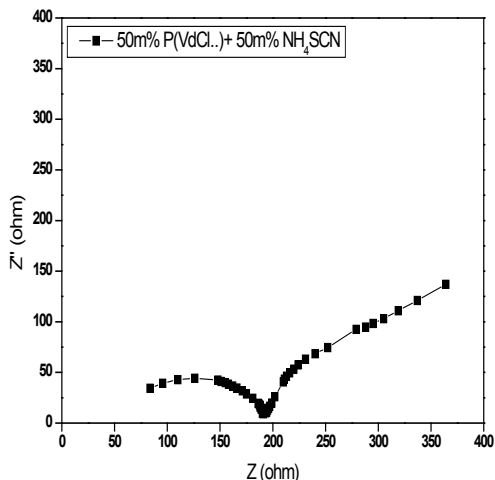
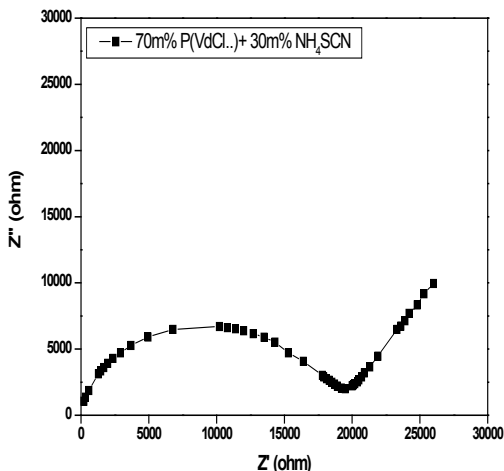


Fig. 4 Nyquist Plots of (a) 70m% P(VdCl.):30m% NH_4SCN (b). 50m% P(VdCl.):50m% NH_4SCN , (c). 45m% P(VdCl.):45m% NH_4SCN :10m% EC & (d). 25m% P(VdCl.):25m% NH_4SCN :50m% EC at 303 K

Table 2
Ionic conductivity from Nyquist plot of P(VdCl.): NH_4SCN & P(VdCl.): NH_4SCN :EC copolymer complexes

VARIOUS COMPOSITIONS OF COPOLYMER ELECTROLYTES	σ FROM NYQUIST PLOT (S cm^{-1})
70m% P(VdCl.):30m% NH_4SCN	5.94×10^{-7}
50m% P(VdCl.):50m% NH_4SCN	2.10×10^{-4}
45m% P(VdCl.):45m% NH_4SCN :10m% EC	9.21×10^{-4}
25m% P(VdCl.):25m% NH_4SCN :50m% EC	1.32×10^{-3}

Conductance Spectra Analysis

The logarithmic plots of the conductivity as a function of angular frequency for $\text{P(VdCl.)}:\text{NH}_4\text{SCN}$ & $\text{P(VdCl.)}:\text{NH}_4\text{SCN}$:EC copolymer complexes has been shown in the Fig.5. As seen from Fig. 5, the conductance spectra showed three regions, low frequency dispersion region due to the electrode polarization effects, frequency independent plateau region in the mid frequency range representing the d.c. conductivity and dispersive region at high frequencies for both the $\text{P(VdCl.)}:\text{NH}_4\text{SCN}$ & $\text{P(VdCl.)}:\text{NH}_4\text{SCN}$:EC copolymer complexes. It was seen that the conductivity values obtained from Nyquist plots and Conductance spectra were in good agreement with each other.

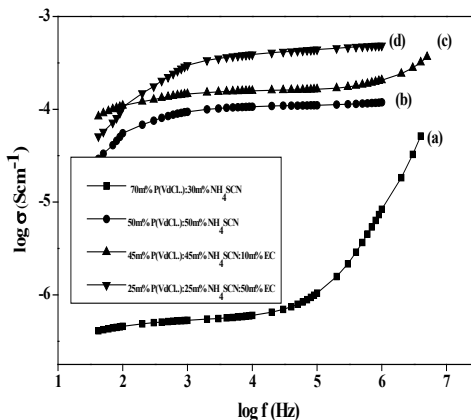


Fig. 5. Conductance Spectra of (a) 70m% P(VdCl.):30m% NH_4SCN (b). 50m% P(VdCl.):50m% NH_4SCN , (c). 45m% P(VdCl.):45m% NH_4SCN :10m% EC & (d). 25m% P(VdCl.):25m% NH_4SCN :50m% EC at 303 K

Dielectric Spectra

The complex permittivity (ϵ^*) or dielectric constant of a system has been defined defined by

$$\epsilon^* = \epsilon' - j \epsilon'' = \epsilon' - j (\sigma / \omega \epsilon_0) \text{----- Equation (2)}$$

where ϵ' , ϵ'' , σ , ω and ϵ_0 represented the real part of dielectric constant of the material, imaginary part of dielectric constant of the material, conductivity, angular frequency and permittivity of free space respectively. The Figs. 6(a) & 6(b) showed ϵ' Vs $\log f$ and ϵ'' Vs $\log f$ plots respectively for (P(VdCl.):NH₄SCN & P(VdCl.):NH₄SCN:EC copolymer complexes. It was seen from the Figs. 6(a) and 6(b) that for both the (P(VdCl.):NH₄SCN & P(VdCl.):NH₄SCN:EC systems, the dielectric permittivity has risen sharply towards low frequency which was due to the electrode polarization effects [15]. The low frequency dispersion region has been attributed to the contribution of charge accumulation at the electrode-electrolyte interface. At high frequencies, due to high periodic reversal of the field at the interface, the contribution of charge carriers (ions) towards the dielectric constant has decreased with increasing frequency. Hence ϵ' has decreased with increasing frequency.

From Fig. 6(b), it has been observed that the dielectric loss (ϵ'') became very large ($\sim 3 \times 10^6$) at lower frequencies which was due to free charge motion within the material [16]. These values do not correspond to the bulk dielectric processes but were due to the free charges build up at the interface between the material and the electrodes. At very low frequencies there was time for charges to build up at the interfaces before the field changes the direction and this has contributed to very large apparent values of ϵ'' . This phenomenon has lead to the so called "conductivity relaxation" [17].

P(VdCl.):25m% NH₄SCN:50m% EC at 303 K

Loss Tangent Spectra

The dielectric relaxation parameter of the copolymer complexes (P(VdCl.):NH₄SCN & P(VdCl.):NH₄SCN:EC) has been obtained from the plot of $\tan \delta$ as a function of frequency. The dielectric loss tangent ($\tan \delta$) has been defined by the equation

$$\tan \delta = \epsilon'' / \epsilon' \text{-----Equation (3)}$$

The variation of $\tan \delta$ with frequency has been presented in Fig. 7 for all the copolymer complexes P(VdCl.):NH₄SCN & P(VdCl.):NH₄SCN:EC at 303 K. It has been observed from Fig. 7 that for all the copolymer complexes $\tan \delta$ increases with increasing frequency, reaches a maximum and then decreases with further increase of frequency. For the maximum dielectric loss, the loss tangent peak has been described by the relation $\omega\tau = 1$ where τ and ω represented relaxation time and angular frequency of the applied electric field [18] respectively. The relaxation parameters for all the copolymer complexes at 303 K have been calculated and tabulated in Table 4.

From Table 3, it was seen that the relaxation time (τ) has decreased from 4.98×10^{-4} s for 70m% P(VdCl.):30m% NH₄SCN to 4.89×10^{-5} s for 50m% P(VdCl.):50m% NH₄SCN. The relaxation time has further decreased from 3.20×10^{-5} s for 45m% P(VdCl.):45m% NH₄SCN:10m% EC to 1.60×10^{-6} s for 25m% P(VdCl.):25m% NH₄SCN:50m% EC. This decrease in relaxation time τ has enhanced the ionic conductivity. From Table 4, it was noted that the relaxation time was lowest for 25m% P(VdCl.):25m% NH₄SCN:50m% EC and hence exhibited high ionic conductivity which was in good agreement with the results of Nyquist plots.

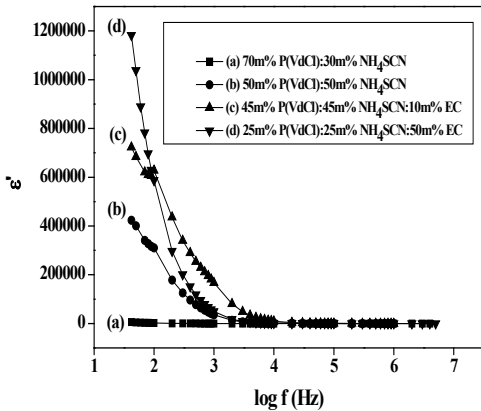


Fig. 6(a). Dielectric Spectra of (a) 70m% P(VdCl.):30m% NH₄SCN (b). 50m% P(VdCl.):50m% NH₄SCN, (c). 45m% P(VdCl.):45m% NH₄SCN:10m% EC & (d). 25m% P(VdCl.):25m% NH₄SCN:50m% EC at 303 K

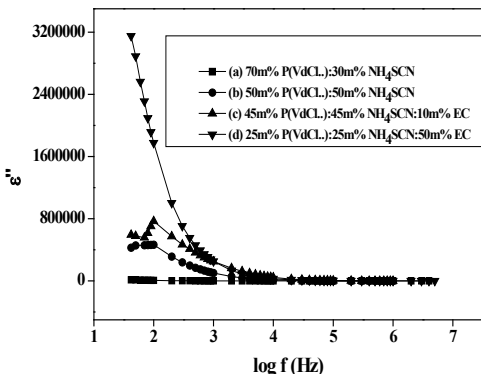


Fig. 6(b). Dielectric Spectra of (a) 70m% P(VdCl.):30m% NH₄SCN (b). 50m% P(VdCl.):50m% NH₄SCN, (c). 45m% P(VdCl.):45m% NH₄SCN:10m% EC & (d). 25m% P(VdCl.):25m% NH₄SCN:50m% EC at 303 K

Table 3
Calculated Dielectric relaxation parameters for the copolymer complexes

SAMPLE COMPOSITION	RELAXATION FREQUENCY log ω_m (Hz)	ω_m (Hz)	RELAXATION TIME τ (s)
70m% P(VdCl.):30m% NH ₄ SCN	3.30	2.01×10^3	4.98×10^{-4}
50m% P(VdCl.):50m% NH ₄ SCN	4.31	2.05×10^4	4.89×10^{-5}
45m% P(VdCl.):45m% NH ₄ SCN:10m% EC	4.50	3.13×10^4	3.20×10^{-5}
25m% P(VdCl.):25m% NH ₄ SCN:50m% EC	5.80	6.27×10^5	1.60×10^{-6}

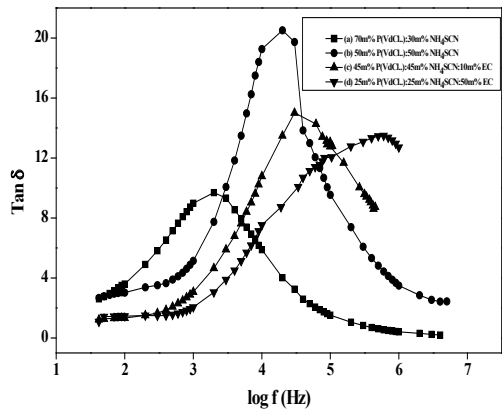


Fig. 7. Loss Tangent Spectra of (a) 70m% P(VdCl.):30m% NH₄SCN (b). 50m% P(VdCl.):50m% NH₄SCN, (c). 45m% P(VdCl.):45m% NH₄SCN:10m% EC & (d). 25m% P(VdCl.):25m% NH₄SCN:50m% EC at 303 K

4. CONCLUSION

The copolymer electrolytes of P(VdCl.):NH₄SCN and P(VdCl.):NH₄SCN:EC complexes of various compositions have been prepared by solution casting method. XRD studies revealed the increase in amorphous nature of P(VdCl.):NH₄SCN:EC thereby producing greater ionic diffusivity when compared with that of P(VdCl.):NH₄SCN complexes. The SEM micrographs have revealed the porosity and formation of pores for P(VdCl.):NH₄SCN complexes. There has been further increase in porosity, size of the pores and formation of ring like structure with small well for P(VdCl.):NH₄SCN:EC complexes.

The conductivity was found to exhibit increasing trend with

increasing concentration of NH₄SCN. In P(VdCl.):NH₄SCN systems, the maximum conductivity observed was 2.10×10^{-4} S cm⁻¹ for 50m% P(VdCl.):50m% NH₄SCN. But the highest conductivity of 1.32×10^{-3} S cm⁻¹ was observed for 25m% P(VdCl.):25m% NH₄SCN):50m% EC for the plasticized system. The low frequency dispersion of dielectric constant for both P(VdCl.):NH₄SCN and P(VdCl.):NH₄SCN:EC complexes revealed the space charge effects that have arisen from the electrodes. From the loss tangent spectra, it was found that the relaxation time (τ) was lowest for 25m% P(VdCl.):25m%NH₄SCN:50m% EC and hence exhibited highest ionic conductivity.

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