

# Structural and Ion Transport Studies in $(100-x)\text{PVdF} + x\text{NH}_4\text{SCN}$ Gel Electrolyte

Kamlesh Pandey<sup>1</sup>, Mrigank Mauli Dwivedi<sup>1</sup>, Nidhi Asthana<sup>1</sup>, Markandey Singh<sup>2</sup>, Shanker Lal Agrawal<sup>2</sup>

<sup>1</sup>National Centre of Experimental Mineralogy and Petrology, University of Allahabad, Allahabad, India; <sup>2</sup>Department of Physics, A.P.S. University, Rewa, India.  
E-mail: [kp542831@gmail.com](mailto:kp542831@gmail.com)

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## ABSTRACT

*In order to obtain highly conductive polymer gel electrolytes for electrochemical devices, Poly (vinylidene fluoride) (PVdF) based gel electrolytes, namely,  $(100-x)\text{PVdF} + x\text{NH}_4\text{SCN}$  electrolyte system has been synthesized by solution cast technique and characterized by XRD, DSC, IR, SEM and electrical measurements. IR study of gel electrolytes shows interaction of PVdF matrix and dopant salt with prominence of  $\alpha$ -phase. This result is also well supported by XRD and DSC studies. The electrolytes are electrochemically stable within  $\pm 1.5$  V. The optimum bulk electrical conductivity for  $90\text{PVdF} + 10\text{NH}_4\text{SCN}$  electrolyte has been found to be  $\sim 2.5 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ . Dielectric relaxation behavior shows low frequency dispersion and  $\alpha_c$ -related relaxation peak is observed in loss spectra. Polarization behavior of gel electrolyte shows ionic nature of charge transport ( $T_{\text{ion}} > 0.90$ ). The temperature dependent conductivity shows VTF behavior.*

**Keywords:** Poly (Vinylidene Fluoride), Gel Electrolyte, Ion Transport, Dielectric Relaxation, Structural Studies

## 1. Introduction

Gel polymer electrolytes have high technical interest in fabrication of electrochemical devices. Since the first report of high conductivity in gel polymer electrolytes (GPEs), these materials which have both solid and liquid like properties, have been introduced as a novel electrolyte material in the field of electrochemical device applications [1,2]. In GPEs, the polymer matrix is swelled in solvents containing ions and so can be thought of as a non-aqueous liquid electrolyte immobilized by a polymer matrix. The solvent helps in the dissolution of salt and provides the medium for ion conduction. In recent years, polymers such as polyvinyl alcohol (PVA) poly (vinylidene fluoride) (PVdF), Poly ethylene glycol (PEG), poly(vinyl chloride) (PVC), poly(acrylonitrile) (PAN), poly(vinyl pyrrolidone) (PVP) and poly(vinyl sulfone) (PVS) have been prominently used in development of GPEs [3-6]. These electrolytes have been found to possess ionic conductivity, electrochemical stability and transport properties similar to their liquid counter parts along with better dynamical properties suitable for electrochemical applications. Among the listed polymeric hosts, Poly (vinylidene fluoride) has been intensely investigated because of its interesting ferroelectric proper-

ties and technological applications. PVdF is a commercially available fluoropolymer with low surface energy and good physical, chemical, and mechanical properties. Therefore, it is reasonable to expect that the PVdF membrane with a porous surface structure should have enhanced hydrophobicity. It can exist in several crystalline phases with  $\alpha$  and  $\beta$  -phases being most common [7-9]. Further, PVdF is of semicrystalline polymer and the electrolytes based on PVdF are expected to have high anodic stabilities due to strong electron withdrawing functional groups. In PVdF based gel electrolytes, high permittivity and relatively low dissipation factor of PVdF assist in higher ionization of salts providing higher concentration of charge carriers [10] and thus rendering high electrical conductivity. Besides, PVdF is also very attractive polymer exhibiting piezoelectric and pyroelectric characteristics that have been exploited in the development of electrochemical devices [11-14]. However, properties of electrolyte films strongly depend on the crystallinity and morphology. Both these factors suffer significant variations when the material undergoes thermal and mechanical treatments.

In the view of above, a detailed experimental study (structural, thermal and electrical) on poly (vinylidene

fluoride) (PVdF) based gel polymer electrolytes with ammonium thiocyanate salt have been carried out in this investigation.

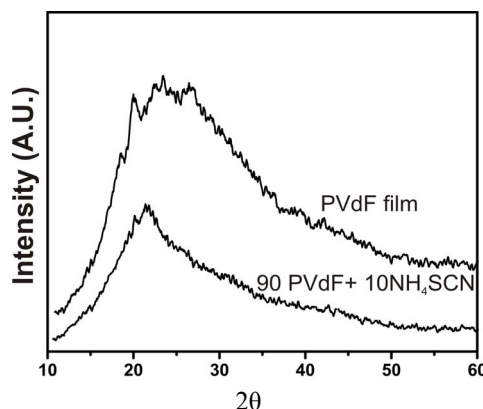
## 2. Experimental

Poly (vinylidene fluoride) (PVdF; Aldrich sigma) with an average molecular weight of  $(\sim 5.34 \times 10^5)$  and Ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ; Rankem India) were used for the preparation of polymer electrolyte.  $\text{NH}_4\text{SCN}$  salt was used after drying at  $70^\circ\text{C}$  under vacuum for 24 h and PVdF without any further purification. Distilled Tetrahydrofuran (THF) and Dimethylsulphoxide (DMSO) in a suitable ratio were used as solvent. The dissolved polymer and salt solutions were mixed together and the resulting solution was stirred continuously to obtain a homogenous mixture. The polymer solution was allowed to evaporate at  $35^\circ\text{C}$  till the achievement of gelly state. Then it was poured on a clean glass mould. Thin films thus obtained were subjected to SEM (JEOL JXA-8100) measurement for the film morphology studies while FTIR (Perkin-Elmer) and XRD (Phillips Expert model) using  $\text{Cu K}_\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ), in the Bragg's angle range ( $2\theta = 15^\circ - 60^\circ$ ) were carried out to investigate the complexation behavior. Thermal behavior of GPEs was studied by differential scanning calorimetry (DSC) (model NETZSCH DSC 200F3) in the temperature range  $25^\circ\text{C} - 150^\circ\text{C}$ . The electrical conductivity was measured from impedance plots at different temperature using LCZ meter (Hioki LCR 5322 Japan) in the frequency range 40 - 100 kHz with the signal amplitude of 20 mV. The cyclic voltammetry has been performed for the Pt/gel polymer electrolytes/Pt cell with scan rate of 0.1 V/s for fifty cycles to affirm excellent reversibility of the electrolyte. Dielectric data were extracted from cole-cole plot.

## 3. Results and Discussion

The X-diffraction pattern of pure PVdF and gel electrolyte system, namely, 90PVdF +  $10\text{NH}_4\text{SCN}$  are shown in **Figure 1**. In pure PVdF, three intense characteristic peaks located at  $19.6^\circ$  (110),  $23.5^\circ$  (200) and  $26.6^\circ$  (021) along with one small peak at  $18^\circ$  are observed. All the three major peaks correspond to orthorhombic  $\alpha$ -phase of PVdF. Few dull reflections appearing near these intense peaks show the possibility of formation of  $\gamma$ -crystals in PVdF simultaneously. The formation of different phases ( $\alpha$ -,  $\beta$  and  $\gamma$ - etc.) mostly depends upon the film formation condition and techniques. The PVdF film prepared by solution cast technique at room temperature in THF or /and DMSO show prominence of  $\alpha$  and  $\gamma$  crystallinity [15].

In 90PVdF +  $10\text{NH}_4\text{SCN}$  polymer electrolyte film, diffraction peak at  $2\theta = 18^\circ$  and  $19.6^\circ$  in pure polymer merged in a single peak with downsizing of intensities,

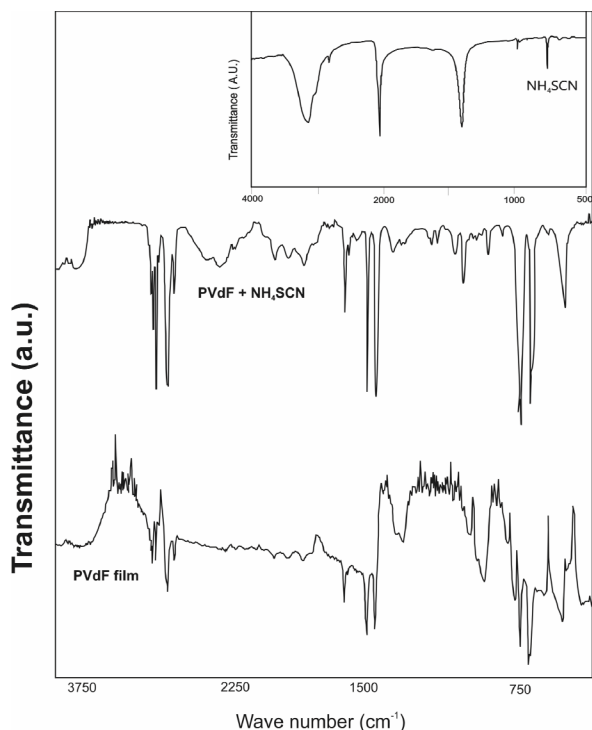


**Figure 1.** XRD curve for PVdF film and (90PVdF +  $10\text{NH}_4\text{SCN}$ ) gel electrolytes.

alongwith its shifting towards high  $2\theta$  values ( $20.1^\circ$ ). Further peak at  $26.4^\circ$  in pure PVdF completely disappeared after the complexation of salt with polymer. Similar result have been reported by Park *et al.* [16] for PVdF based system. XRD pattern of electrolyte did not reveal any peak corresponding to  $\text{NH}_4\text{SCN}$  salt, thereby indicating absence of uncomplexed salt in polymer electrolyte film. The decrease in peak intensity but increase in peak area reveals that the sample with 10 wt% salt composition is highly amorphous and thus expected to cause higher conductivity. These observations apparently show, that polymer undergoes significant structural reorganization upon addition of salt.

The IR spectrum of pristine PVdF and (90PVdF +  $10\text{NH}_4\text{SCN}$ ) films are shown in **Figure 2**. Pertinent peaks were analyzed and have been summarized in **Table 1**. Pristine PVdF is characterized by the presence of vibrational bands at  $612$  &  $763 \text{ cm}^{-1}$  and related to  $\text{CF}_2$  with skeleton bending respectively. Presence of peaks at  $532$ ,  $1210$ ,  $1383$ ,  $1432 \text{ cm}^{-1}$  show dominance of crystalline  $\alpha$ -phase in PVdF film. This spectrum also exhibits moderately intense band at  $840$  and  $510 \text{ cm}^{-1}$  indicating the existence of  $\beta$  form of polymer film [17]. Similarly, presence of  $\gamma$ -phase (in trace) is indicated by appearance of  $1234 \text{ cm}^{-1}$  absorption peak. In PVdF film, peak at  $840 \text{ cm}^{-1}$  is always visible and its intensity is not much affected by the sample preparation condition and thus can be used as an internal reference for evaluation of the fraction of  $\alpha$  and  $\beta$ -phase in the film. Another important feature in PVdF film is the presence of  $\text{CH}_2$  group  $3020 \text{ cm}^{-1}$  ( $\nu_s \text{ CH}_2$ ) and symmetric vibration at  $2970 \text{ cm}^{-1}$  ( $\nu_s \text{ CH}_2$ ). Symmetric vibrations are weaker than asymmetric vibrations since the former leads to less change in dipole moment.

In 90 PVdF +  $10\text{NH}_4\text{SCN}$  gel electrolyte system, these peaks are slightly shifted to lower wave number side along with change in intensity. The intense and broad absorption peak related to  $\text{CH}_2$  rocking vibration at  $874$



**Figure 2. Infrared spectrum of PVdF film and (90PVdF + 10NH<sub>4</sub>SCN) gel electrolytes. NH<sub>4</sub>SCN IR spectrum is shown in inset.**

cm<sup>-1</sup> in pure PVdF weakens significantly after complexation with NH<sub>4</sub>SCN, possibly due to replacement of fluorine atoms with SCN<sup>-</sup>. Few peaks (706, 1024 and 1310 cm<sup>-1</sup>) related to DMSO are also visible in pure as well as gel polymer film. The absorption peak at 677

cm<sup>-1</sup> show the presence of head to head and tail to tail configuration but the intensity of this peak enhances after the addition of salt, indicating strong salt polymer interaction. Addition of NH<sub>4</sub>SCN gives few new peaks at 2000 - 2200 cm<sup>-1</sup> which indicate formation of PVdF-NH<sub>4</sub>SCN crystalline complex [18,19]. These new peaks are ascribable to the contact ion pair and solvent separated dimer. It also enhances intensity of peaks at 1500 cm<sup>-1</sup> & 1470 cm<sup>-1</sup> and reduces/vanishes the intensity of 1860 cm<sup>-1</sup> and 1286 cm<sup>-1</sup> absorption peaks.

The SEM image of different PVdF + NH<sub>4</sub>SCN gel electrolyte systems were recorded (**Figure 3**) to assess the morphology of gel electrolyte. In pure PVdF film (**Figure 3(a)**), several pores with a lamellar distribution of poly crystalline domain and traces of two polymorphic phases ( $\alpha$  and  $\beta$ ) are observed and reported elsewhere [20]. The addition of salt drastically changes the PVdF micro structure. It clearly shows bimodal morphology with modified crystalline domain. The addition of salt (NH<sub>4</sub>SCN) connects these pores to each other due to, induced delay in phase relation or lower surface energy. In films containing 10% of salt, smooth and better structure was obtained. At very high content of salt, pore disappear giving rise to smooth morphology of films. The disappearance of porosity and enhancement of grains are advantageous for interfacial contact between the polymer and salt. This connectivity of the pores is favorable for the transportation of proton and thus enhancement of ionic conductivity [21].

In **Figure 4**, DSC curve of pure PVdF film and (90PVdF + 10NH<sub>4</sub>SCN) electrolyte film are given. In

**Table 1. Peak position and their assignment for PVdF and 90PVdF+ 10NH<sub>4</sub> SCN electrolytes.**

Peak Positions (cm <sup>-1</sup> )		Assignments
Pure PVDF	Pure PVdF + NH <sub>4</sub> SCN	
510	-	$\beta$ -phase of PVdF
532	532	$\alpha$ -phase
612	-	$\alpha$ -phase of PVdF (mixed mode of CF <sub>2</sub> )
706	706	$\nu_{as}$ (S=O) of DMSO
763	764	$\alpha$ -phase (rocking vibration)
860	848	$\beta$ -phase (out of phase combination)
	988	$\alpha$ -phase
1024	1024	$\nu_{as}$ (C=S) of DMSO
1210	-	$\alpha$ -phase of PVdF
1234	-	$\alpha$ -phase of PVdF
1286	1268	$\beta$ -phase
1310	1310	DMSO in liquid state
1383	1336	$\alpha$ -phase
1431	1428	$\beta$ -phase, in plane bending or scissoring
1839	-	Pure PVDF
2000 - 2200	2000 - 2200 (intense & sharp)	Characteristic peaks of NH <sub>4</sub> SCN
2910	2910	CH <sub>2</sub> Asymmetric stretching
3020	3020	CH <sub>2</sub> Symmetric stretching
3250	3280	N-H stretching
3600	3600	-OH bending

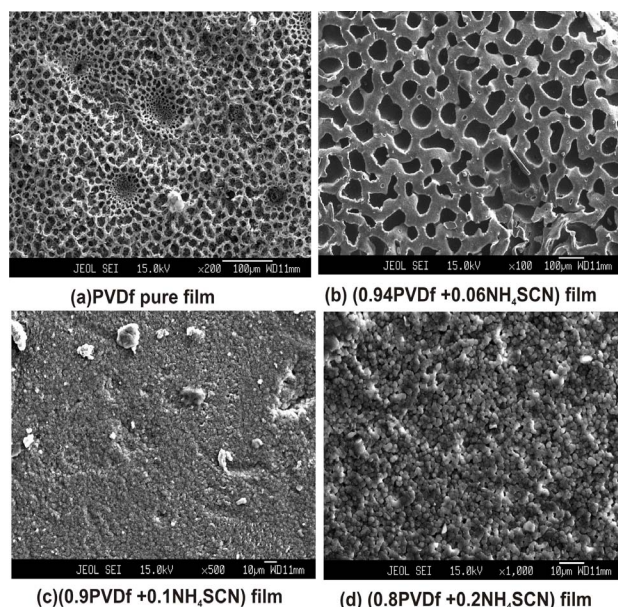


Figure 3. SEM Image of different PGE systems.

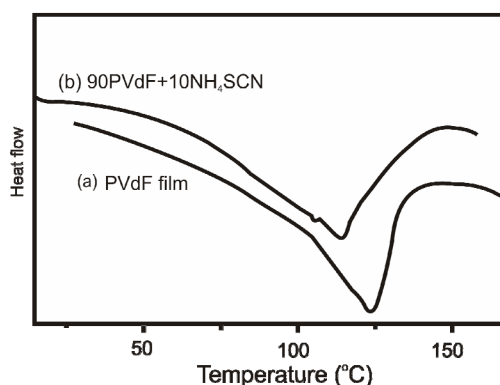


Figure 4. DSC Pattern of (a) PVdF and (b) (90PVdF + 10NH<sub>4</sub>SCN) film.

pure PVdF three strong endothermic peaks at 168°C, 172°C and 192°C have been reported and correlated to  $\alpha$  (165°C - 170°C),  $\beta$  (172°C - 177°C) and  $\gamma$  (187°C - 192°C) phases of PVdF respectively [22]. Besides a small and broad endothermic peak close to 128°C has also been reported and associated to  $\alpha$ -phase/ $\alpha$ -relaxation peak of poly (vinylidene fluoride). Appearance of 128°C endothermic peak in present investigation affirms the reported result. Other peaks could not be traced due to the range of thermal scan being limited to 150°C. In electrolyte system we observe shifting of this peak towards lower temperature (113°C). The decrease in  $T_g$  of GPE, increases the amorphousness of the electrolyte material. DSC profile of electrolyte did not reveal any characteristic endothermic transition of NH<sub>4</sub>SCN, to suggest complete absorption of salt in polymer. The position of relaxation peak after complexation shifts 15° toward lower

side (decrease from 128°C to 113°C) of NH<sub>4</sub>SCN related  $T_m$  in DSC profile indicates high compatibility of PVdF network with NH<sub>4</sub>SCN and also validates the presence of  $\alpha$ -phase dominantly as explained in XRD and IR studies.

Electrochemical stability window of a given polymer electrolyte system is determined by linear sweep voltammetry with an inert electrode (Pt- in present case) in the electrolyte sample. **Figure 5** shows, typical current / voltage curves of Pt /  $(100-x)$  PVdF +  $x\text{NH}_4\text{SCN}$  / Pt cell at a scan rate of 0.1 mV/s for different electrolyte compositions. It is apparent from the figure that GPE containing 10 wt% NH<sub>4</sub>SCN is highly stable (curve). To ascertain this fact the plot was expanded (inset of figure). In this curve a loop is visible which is related to oxidation reduction process of the electrolyte. The onset current in the anodic high voltage range is assumed to result from a decomposition process associated with electrode and this onset voltage is taken as upper limit of the electrolyte stability range. This voltage is generally located as the point of intersection of the extrapolated linear current in high voltage region with voltage axis. For all electrolyte system the current response is better in  $\pm 1.5$  volt. This implies that there is no decomposition of any components in this potential region.

Another important parameter in electrolyte performance is the ionic transference number and usually polymer electrolytes, have the value less than unity. The current vs. time graph of 90PVdF + 10NH<sub>4</sub>SCN is shown in **Figure 6**. The ionic transference number evaluated by Wagner's method of polarization for the best conducting electrolyte is 0.9. This indicates charge transport essentially through ion viz. proton in present case.

**Figure 7** shows the variation of bulk electrical conductivity with salt composition in  $[(100-x)\text{PVdF} + x\text{NH}_4\text{SCN}]$  system. Addition of NH<sub>4</sub>SCN increases the

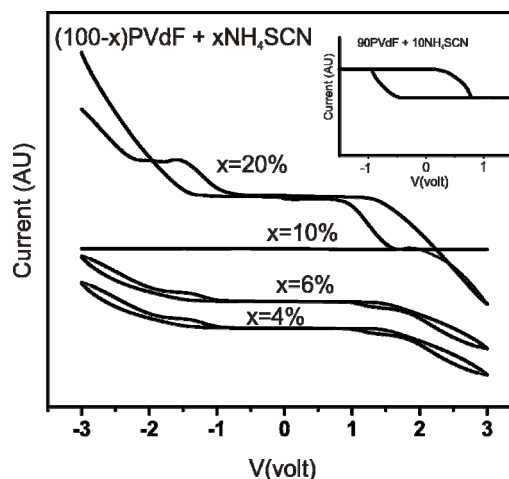


Figure 5. Variation of current with applied potential for  $[(100-x)\text{PVdF} + x\text{NH}_4\text{SCN}]$  gel electrolyte system.



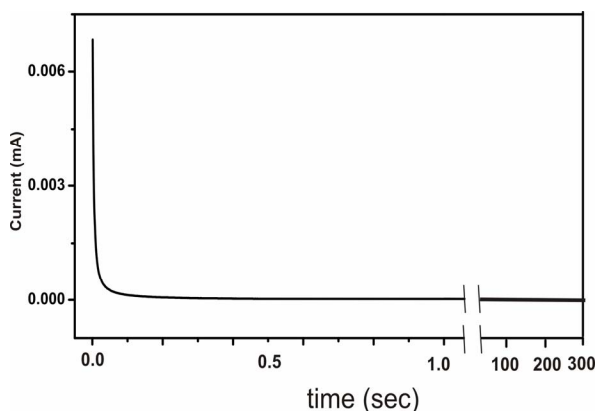


Figure 6. Variation of current with time for (90PVdF + 10NH<sub>4</sub>SCN) film system.

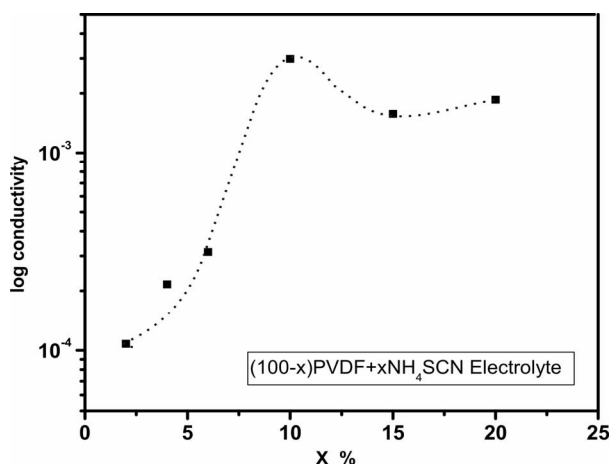


Figure 7. Variation of bulk electrical conductivity for [(100-x)PVdF + xNH<sub>4</sub>SCN] gel electrolyte system.

conductivity of PVdF film by more than two orders of magnitude, attains a maximum and then starts decreasing. The increase in conductivity can be attributed to the increase in numbers of transporting ions or ion-ion interaction and some amount of liquid trapped within polymer matrix. Initially as concentration of salt increases free ion concentration augment leading to increase in electrical conductivity. Another possible reason for increase in conductivity is the presence of trapped liquid within the pores of polymer matrix [23]. As evidenced in XRD and IR studies, the interaction between salt with fluorine group in PVdF matrix is likely to enhance the conductivity of gel electrolyte. As the concentration of salt increases significantly, the mutual distance between ions decreases until ion-ion interaction become significant. Therefore, for higher concentration (beyond 10 wt% salt), the stronger is ion-ion interaction which results in the change of free ions to ion pair or the formation of higher aggregates. Consequently, the ionic conductivity decreases as a result of decrease of mobility and as well as

number of charge carriers.

Frequency dependent conductivity of (100-x)PVdF + xNH<sub>4</sub>SCN (where  $x = 2, 4, 6, 10, 15, 20$ ) is shown in Figure 8. The a.c. conductivity of gel electrolyte has been evaluated using the relation

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta \quad (1)$$

where  $\epsilon_0$  is the vacuum permittivity and  $\omega$  is the angular frequency. Conductivity initially increases with frequency up to 1 KHz and thereafter tends to attain a plateau in all compositions. The initial increase in conductivity with frequency is due to relaxation effect of the polymer.

The frequency independent behavior of conductivity in high frequency region has been reported in other polymeric electrolytes [24] and has been well explained by Ramesh and Arof [25].

Figure 9 shows the change of bulk conductivity (evaluated by cole-cole plot) with temperature for 90PVdF + 10NH<sub>4</sub>SCN system. Temperature dependent conductivity shows the non linear increase in conductivity with temperature up to 340 K. Above 340 K, the gel-

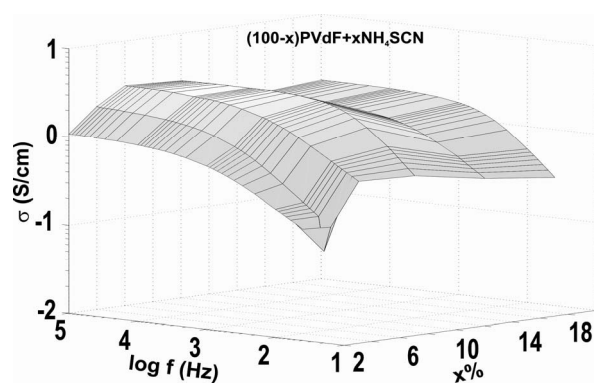


Figure 8. Variation of a.c. conductivity with frequency for (100-x) PVdF + xNH<sub>4</sub>SCN films.

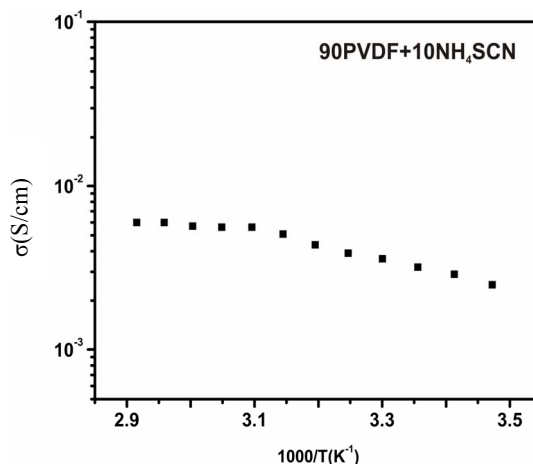


Figure 9. Variation of conductivity with temperature for (90PVdF + 10NH<sub>4</sub>SCN) polymer gel electrolyte.

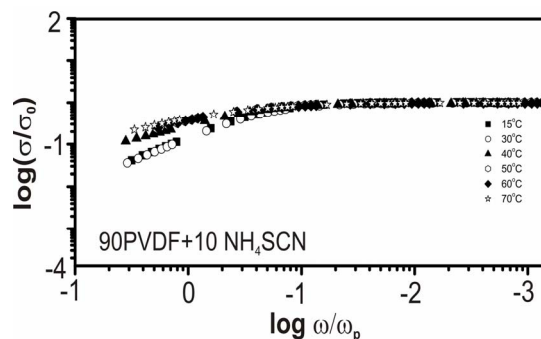
electrolyte shows a sudden change of slope in conductivity response. Positive curvature in curve indicates that ionic conduction obeys the Vogel–Tamman–Fulcher (VTF) relation-ship which describes the transport properties in viscous matrix and mathematically represented as.

$$\sigma(T) = AT^{1/2} \exp [-B / k_B (T - T_0)] \quad (2)$$

where A is the constant proportional to the number of charge carriers, B the pseudo-activation energy related to polymer segmental motion,  $k_B$  the Boltzmann constant and  $T_0$  is a reference temperature associated with ideal  $T_g$ . The motion is strongly decoupled from the segmental motion of the polymer backbone, thus finally demonstrating that the ionic transport in the gel membranes occurs mainly within the liquid solvent. The curvature at 70°C, is possibly due to transition of polymorphic phase ( $-\alpha_c$  phase) in poly (vinylidene fluoride). Such features are generally observed for highly amorphous polymeric system. The  $\alpha_c$  relaxation may have an important implication in determining the viscoelastic properties of polymeric systems. The conductivity behavior below 70°C, may be due to beginning of some crystallization process occurring due to some orientation induced stretching in electrolyte film [26]. The increase in conductivity with temperature is interpreted as hopping mechanism between coordinated sites, local structural relaxation and segmental motion of the polymer. As the amorphous region progressively increases, however, the polymer chain acquires faster internal motion and bond rotations (segmental motions). This in turn favors the hopping of inter-chain and intra-chain movement and ionic conductivity of polymer electrolyte becomes high.

To understand the relaxation dynamics in terms of conductivity spectra at different temperature, the conductivity is scaled using Ghosh's scaling method [27]. In this scaling process the a. c. conductivity is scaled by dc conductivity  $\sigma_{dc}$ , while the frequency axis is scaled by the hopping frequency  $\omega_p$  at different temperature. From **Figure 10**, it is clear that conductivity spectra for different temperature merge on a single master curve for the polymer electrolyte 90PVdF + 10NH<sub>4</sub>SCN system. This suggests the temperature independent relaxation dynamics at higher frequencies. In the low frequency region spectra of various compositions are not superimposed on a single curve which implies that the relaxation dynamics is composition dependent.

In case of polar polymers, the dielectric constant begins to drop at a certain frequency. This decrease with frequency is attributed to electrical relaxation or inability of dipole to rotate rapidly to follow the applied field. In low frequency region, ions aggregation at interface lead to a net polarization which allows formation of space charge region at electrode–electrolyte interface. **Figure**

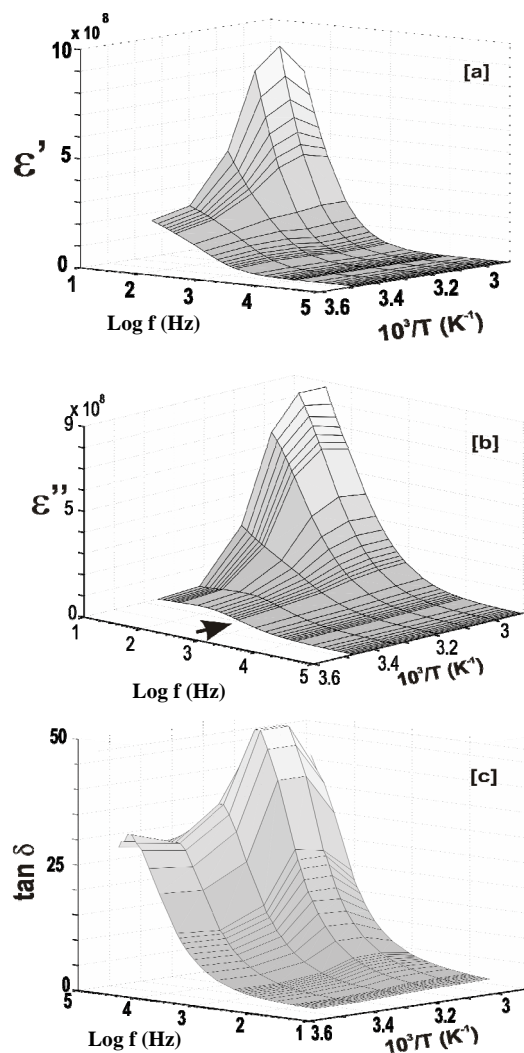


**Figure 10.** Plot of scaled conductivity with normalized frequency (90PVdF + 10NH<sub>4</sub>SCN) system.

**11(a)** and **Figure 11(b)** shows the variation of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of (90PVdF + 10NH<sub>4</sub>SCN) electrolyte system as a function of frequency for different temperatures. Strong frequency dispersion in dielectric constant and dielectric loss was recorded in lower frequency region followed by frequency independent behavior at higher frequencies (above 10 KHz) in case of polymer electrolyte as well. The dielectric constant and loss value initially increases with temperature upto 70°C and then starts decreasing. The decrease in dielectric constant beyond 70°C could be due to onset of some crystallization processes as observed by Gregorio and Cestari [26].

Thin polymers are known to be mixture of amorphous and crystalline region [28]. The amorphous regions are the area in which chains are irregular and entangled, whereas, in crystalline region chains are regularly folded or orderly arranged. In the crystalline areas, because of presence of hindering structural units (due to greater density of the region) the polymeric chains move with great difficulty than in the amorphous region. The hindrance can be assumed to possess a certain potential energy. When the polymer is heated the movement of main chain sets in, and maximizes at  $T_g$ , with losses corresponding to  $\alpha$ -relaxation. This relaxation corresponding to  $T_g$ , may also be understood by free volume theory, according to which the molecular mobility depends mainly on free volume. The dielectric dispersion appearing at higher temperature is generally connected to the ordinary motion of the molecules from one quasi stable position to the another around the skeletal bond involving large scale conformational rearrangement of the main chain, and is known as primary dispersion region or the  $\alpha$ -relaxation. The low temperature dielectric dispersion is attributed to the dielectric response of the side group which is considered to be more mobile or the small displacement of the dipoles near the frozen—in position and known as secondary dispersion region.

The variation of  $\tan \delta$  with frequency at different tem-



**Figure 11.** Variation of different dielectric parameters with frequency and temperature.

perature is shown in **Figure 11(c)**. The higher value of tangent loss can be attributed to segmental diffusion motion in amorphous region. At 70°C a relaxation process is observed in temperature dependant  $\tan \delta$  curve. This is similar to dielectric loss and labeled as  $\alpha$  or  $\alpha_c$  and can be associated to motion within crystalline region [29]. It should be noticed that this relaxation is not clearly observed as a peak in **Figure 11(b)**.

#### 4. Conclusions

The study of structural, thermal and electrical properties of gel polymer electrolyte based on PVdF-NH<sub>4</sub>SCN results a significant improvement of stability and ionic conductivity which are useful in application in electrochemical devices. XRD investigation show the increase in amorphous behavior and dominance of  $\alpha$ -phase as explained in XRD and IR studies. SEM studies show that

several pores with a lamellar distribution of poly crystalline domain with traces of two polymorphic phases ( $\alpha$  &  $\beta$ ) and the addition of salt drastically changes the PVdF micro structure. Electrical conductivity of GPEs shows the VTF nature. In dielectric studies of electrolyte system  $\alpha_c$ -relaxation peak has been observed.

#### 5. Acknowledgements

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