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Electrical Conduction and Dielectric Relaxation Phenomena of PVA Based Polymer Electrolyte Films

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Conducting polymer electrolyte (CPE) films based on poly(vinyl alcohol) (PVA) complexed with NaI salt were prepared by a solution cast technique. The structural properties of these electrolyte films were examined by XRD studies. The XRD results revealed that the amorphous domains of PVA polymer matrix were increased with the increase of NaI salt concentration. The glass transition temperature (T_g) of these systems was determined by DSC thermograms. Electrical conductivity was measured in the temperature range of 303-373 K and the conductivity was found to increase with the increase of dopant concentration, as well as temperature. The activation energy values were 0.478, 0.351, 0.319 and 0.284 eV for pure and 10%, 20% and 30% NaI complexed PVA films, respectively. The dielectric constant (ε') was found to increase with the increase of temperature and decrease with the increase of frequency. Dielectric relaxation phenomenon was observed in the dielectric loss spectra and is attributed to the orientation of polar groups.

Keywords: CPEs, XRD, DSC, impedance dielectric properties

1 Introduction

Solid electrolyte materials attracted growing interest in recent years because of their potential application at ambient temperature in ionic devices such as polymer batteries, super capacitors and fuel cells. Ion conduction is an important characteristic in developing these materials. The advantage of polymer electrolytes over other solid electrolytes are unique mechanical and electrical properties; ease of fabrication into films of desirable sizes, and interactions to strengthen the electrode–electrolyte contact. Designed synthesis of a novel polymer electrolyte exhibiting high ionic conductivity, good electrochemical stability and mechanical strength, is highly desired and has been a vital part in the effort to create a new generation of polymer ion batteries. However, the early widely studied poly(ethylene oxide) (PEO)-based electrolytes usually exhibited very low ionic conductivity of the order of 10^{-7} $S{\cdot}cm^{-1}$, mainly because of high crystallinity and poor motion performance of the PEO backbones. PEO is a Lewis base and can accommodate only cations. The cations are solvated by the polar groups on the polymer chain (the ether oxygen), whereas the anions interact weakly (1). As the Li cations strongly coordinate with the polymer, they are not as mobile as free anions. This feature contributes to a buildup of salt concentration gradients and electrode polarization. In addition, the formation of associated ions decreases the number of charge carriers and can further decrease conductivity. Therefore, efforts have been made to improve the performance of the existing polymer electrolytes and to find new electrolytes with better mechanical and electrochemical properties. Poly(vinyl alcohol) is a polymer with carbon chain back bone with hydroxyl groups attached to the methane carbon. These OH-groups can be a source of hydrogen bonding and hence, assist in the formation of polymer electrolytes (2). A few attempts have been made with sodium salt. Apart from the scientific interest, the use of sodium has more advantages over lithium counter parts. Sodium is available in abundance at a cheaper cost than lithium. The softness of sodium metal is expected to promote good contact with the components in solid state ionic devices (3).

From the fundamental point of view, dielectric relaxation spectroscopy has been widely used to realize the microscopic dynamical relaxation process in complicated systems. The study of dielectric properties in solid polymer electrolytes is a powerful approach to obtain information about the characteristics of ionic and molecular interactions. The dielectric parameters associated with relaxation process are of particular significance in ion conducting polymers where the dielectric constant plays a fundamental role which shows the ability of the polymer material to dissolve salts. The frequency dependent conductivity and

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*Address correspondence to: P. Balaji Bhargav, Department of Physics, S. V. University, Tirupati-517 502, India. E-mail: balu_phy@yahoo.com dielectric relaxation are both sensitive to the motion of charged species and dipoles of the polymer electrolyte. The dielectric properties of the polymer electrolytes are strongly influenced by the nature of additives and temperature. E.L Shahawy et al. (4) studied the dielectric properties of cobalt doped poly(vinyl alcohol) polymer electrolytes. Dielectric measurements were performed at various temperatures and frequencies in order to investigate the effect of $CoCl_2$ doping on the relative permittivity (ϵ') and dielectric loss factor (tan δ) of the polymer. Ramya et al. (5) studied the dielectric relaxations of PVP-NH_4SCN solid polymer electrolytes. In their studies, the dielectric loss spectrum exhibited two relaxations, α and β. Ahmed et al. (6) studied the effect of dopant concentration on the electrical properties of PVA. They observed that the dielectric constant decreased with increasing frequency due to a rapid variation of the field accompanied with the applied frequency, as well as the disordering of the segmental parts of the polymer chain. Mohamed (7) studied the conductivity and dielectric constant of poly(vinyl alcohol) (PVA) doped $MnSO_4$ solid polymer electrolyte films. Feng et al. (8) studied the dielectric properties of Ag-PVA nanocomposites. The resistivity at room and low temperatures and breakdown field strength of samples were investigated. The results show that dielectric properties of composite change while the Ag content or distributing state changes. Subba Reddy et al. (9) studied the dielectric properties of (PVP+PEO) based polymer electrolytes. The decrease in dielectric permittivity was observed with increasing frequency and an increase in dielectric permittivity with increasing temperature was also observed. In the present investigations, studies have been made on the dielectric properties of sodium iodide doped poly(vinyl alcohol) (PVA) polymer electrolyte films in the 303-373 K temperature range and in the 100 Hz-1 MHz frequency range.

2 Experimental

Films of pure PVA and various compositions of complexed films of PVA with NaI salt were prepared at weight percent ratios (90:10), (80:20) and (70:30) by a solution cast technique using triple distilled water as solvent. The solutions were stirred continuously for 10–12 h to get a homogenous mixture and then cast on to polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was vacuum dried thoroughly.

In order to investigate the nature of these polymer electrolyte films, X-ray diffraction studies were carried out using a HLG4/B-PC X-ray diffractometer with CuKα radiation and Graphite monochromator at room temperature. For characterization of obtained films by differential scanning calorimetry (DSC), small fragments of the samples were encapsulated in pans and thermograms were recorded with a NETZSCH DSC 204 in the temperature range 50–100°C using aluminum as reference material. Dielectric and impedance measurements were carried out in the temperature range 303-373 K using HIOKI 3520-01 LCR Hitester over a frequency range of 100 Hz–1 MHz. The instrument was interfaced to a computer for data collection.

3 Results and Discussion

3.1 XRD Studies

X-ray diffraction patterns of pure poly(vinyl alcohol) (PVA), NaI complexed poly(vinyl alcohol) (PVA) and pure NaI salts were shown in Figure 1. It is clear from the figure that, the pure poly(vinyl alcohol) (PVA) shows a characteristic peak for an orthorhombic lattice centered at 20^0 indicating its semi-crystalline nature (10,11). The intensity of this peak decreased with the increase of NaI content. This could be due to the disruption of the PVA crystalline structure by NaI salt. No peaks pertaining to sodium iodide salt appeared in the complexes, which indicate the complete dissolution of salt in the polymer matrices. Hodge et al. (12) established a correlation between the intensity of the peak and degree of crystallinity. They observed that the intensity of XRD pattern decreases as the amorphous nature increases with the addition of dopant.

The diffraction peaks are less intense in NaI complexed PVA films when compared to the pure PVA films. This shows a decrease in the degree of crystallanity of polymer after the addition of NaI. No sharp peaks are observed for higher concentrations of NaI salt in the polymer,

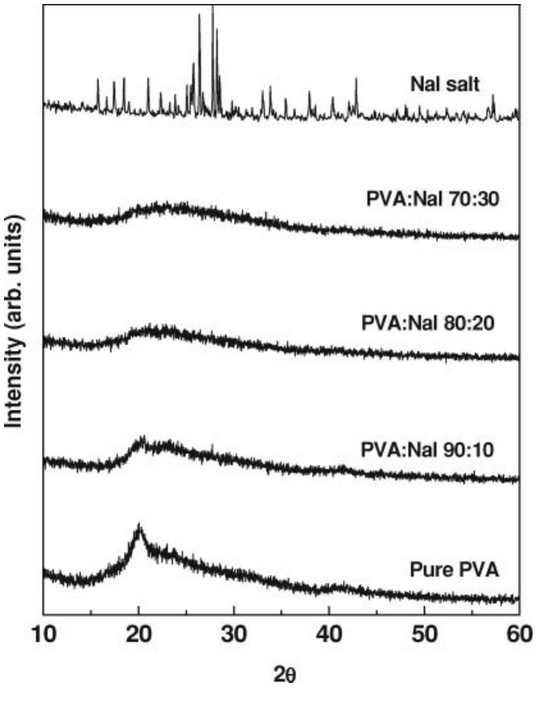

Fig. 1. XRD pattern of pure and NaI doped PVA polymer electrolyte films.

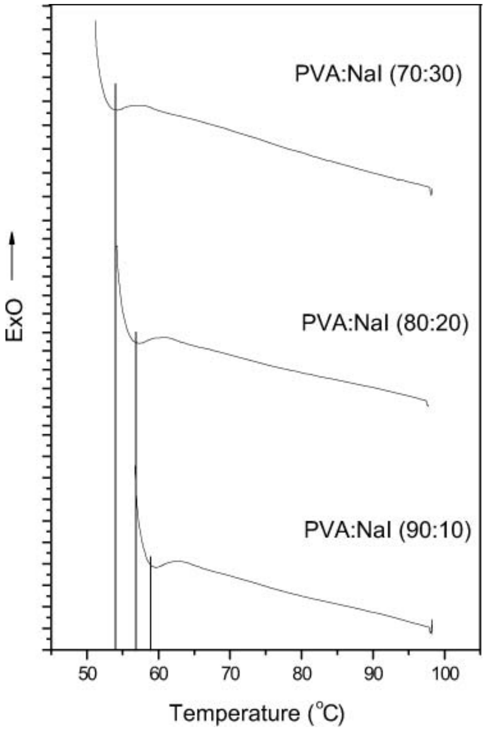

Fig. 2. DSC thermograms of pure and NaI doped PVA polymer electrolyte films.

suggesting the dominant presence of amorphous phase (13). This amorphous nature results in greater ionic diffusivity with high ionic conductivity, which can be obtained in amorphous polymers that have a flexible back bone (14).

3.2 DSC Studies

Figure 2 shows the typical plots of DSC curves of pure poly(vinyl alcohol) (PVA) and NaI complexed PVA polymer electrolyte films, respectively. The glass transition temperature for pure PVA is around 77°C. The addition of salt drastically affects the glass transition temperature of these polymer electrolyte films. By the incorporation of salt into the polymer matrix, the glass transition temperature shifts towards the lower temperature region in these polymer electrolyte system. The values of Tg for NaI doped PVA polymer electrolyte films is listed in Table 1. This decrease in glass transition temperature may be due to disruption of the polymer chain by the incorporation of dopant in to the polymer. This disruption of polymer chain will decrease the crystallinity of these electrolyte systems, which is also confirmed by XRD studies.

3.3 Electrical Studies

Table 1. Values of glass transition temperature (Tg) of PVA: NaI polymer electrolyte films at different compositions

Polymer electrolyte	$T_g^{\circ}C$
Pure PVA	77.0
(PVA:Nal)(90:10)	58.0
(PVA:Nal)(80:20)	56.0
(PVA:Nal)(70:30)	54.5

The real part of Impedance (Z′) and imaginary part of impedance (Z″) of pure PVA and various compositions of complexed films with NaI salts with weight ratios (90:10), (80:20) and (70:30) were evaluated using the relations:

$$Z = Z' - j\,Z'' = \frac{D}{\omega C} - \frac{j}{\omega C} \tag{1}$$

Where D is the dissipation factor (or) loss tangent, ω is the angular frequency and C is the capacitance of the film. Figure 3 shows the typical real (Z′) and imaginary (Z″) parts of the impedance data plotted in complex impedance plane pure, as well as NaI (70:30) doped polymer electrolyte films at different temperatures. All the impedance plots show typical impedance behavior being a semicircular portion at high frequencies followed by a spike (residual tail) at low frequencies. These results suggest that the migration of ions may occur through the free volume of matrix polymer, which can be represented by a resistor. The immobile polymer chains, on the other hand, become polarized in the alternating field, and can therefore be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, and therefore, the portion of the semicircle can be observed at high frequencies. It is noted that the semicircle observed at high frequencies completely disappears at high temperatures. This result suggests that, only the resistive component of polymer electrolyte prevails, when the amount of plasticizing solution is high (5).

The high frequency region semicircle which is due to the bulk effect of the electrolytes and the linear region in the low

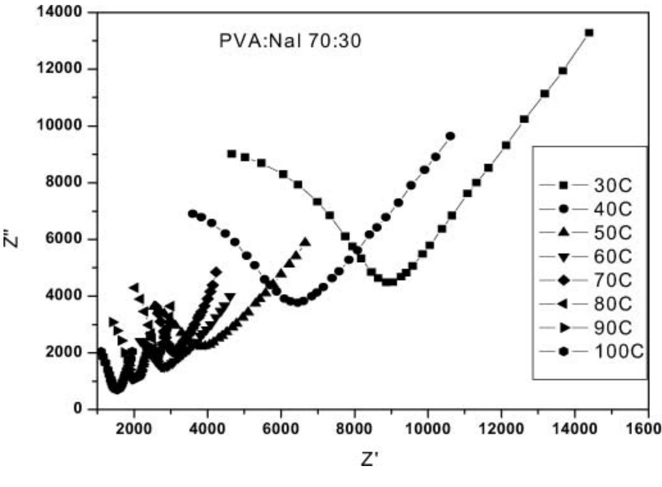

Fig. 3. Cole-Cole plot for PVA:NaI (70:30) polymer electrolyte at different temperatures in degree centigrade.

frequency range that is attributed to the effect of the blocking electrodes. In an ideal case at low frequency, the complex impedance plots should show the straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature (15,16). The bulk electrical resistance (R_b) of the material is obtained from the Cole-Cole plots with the intercept of the high frequency side on the X-axis. The bulk resistance decreases with increasing temperature. The decrease in resistance of the polymer electrolyte is due to the enhancement of the ionic mobility and the number of carrier ions with temperature (16). The migration of ions may occur through the free volume of polymer matrix, which can be represented by a resistor. The immobile polymer chains become polarized in the alternating field, which can be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel and therefore, the semicircle at high frequency can be observed in all the samples.

The conductivity of the polymer electrolyte was calculated from the measured resistance, area and thickness of the polymer film, according to the formula:

$$\sigma = L/R_b A$$

Where L is the thickness (cm) of the polymer electrolyte, A is the area of the blocking electrode (cm^2), and R_b is the bulk resistance of PVA: NaI polymer electrolyte. It was observed that the conductivity was found to increase with the increase of temperature. This can be explained on the basis of the free volume model (17) and Hopping of charge carriers between the localized states (18). Since poly(vinyl alcohol) is a linear polymer with carbon chain as the back bone, the polymer chains which are less entangled are capable of causing electrical conductivity. Further PVA being a polar polymer, ionizes the NaI salt into anions and cations under the influence of the applied electric field and temperature. These ions hop between the localized states and cause the enhanced conductivity. Further, when the temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur (19). Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence, the conductivity. The increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility. Figure 4 shows the variation of log (σ) with inverse absolute temperature for various PVA: NaI complexes. The amorphous nature also provides a bigger free volume in the polymer electrolyte system upon increasing temperature (20).

The activation energies were calculated from log σ vs. 1000/T (Fig. 4) plots using the following Arrhenius equation:

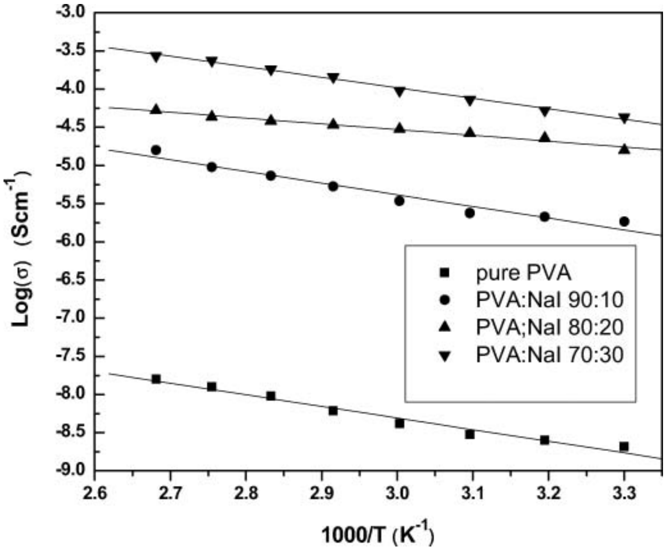

Fig. 4. Temperature dependent conductivity of PVA: NaI polymer electrolyte films at different weight percent ratios.

$$\sigma_{ac} = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

Where σ_0 is a constant, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. The activation energy values were 0.478, 0.351, 0.319 and 0.284 eV for pure and 10%, 20% and 30% NaI complexed PVA films, respectively. The low activation energy for sodium ion transport is due to the dominant presence of an amorphous nature of polymer electrolyte that facilitates the fast Na^+ ion motion in the polymer network. Similar behavior was observed in many other polymer electrolyte films (18, 21).

3.4 Dielectric Properties

3.4.1. *Frequency and temperature dependent dielectric permittivity*

Figure 5 shows the variation of dielectric permittivity (ε^1) with frequency of NaI doped poly(vinyl alcohol) (PVA) (80:20) at different temperatures. From the plots it is clear that the dielectric permittivity decreased monotonically with increasing frequency and attains a constant value at higher frequencies. Similar behavior was also observed in a number of polymers (4, 22). Verifying the fact that for polar materials, the initial value of dielectric permittivity is high, but as the frequency of the field is raised, this value begins to drop, which could be due the dipoles not able to follow the field variations at high frequencies (23) and also due to the polarization effects (17). The low frequency dispersion region is attributed to the contribution of charge accumulation at the electrode-electrolyte interface. At higher frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of

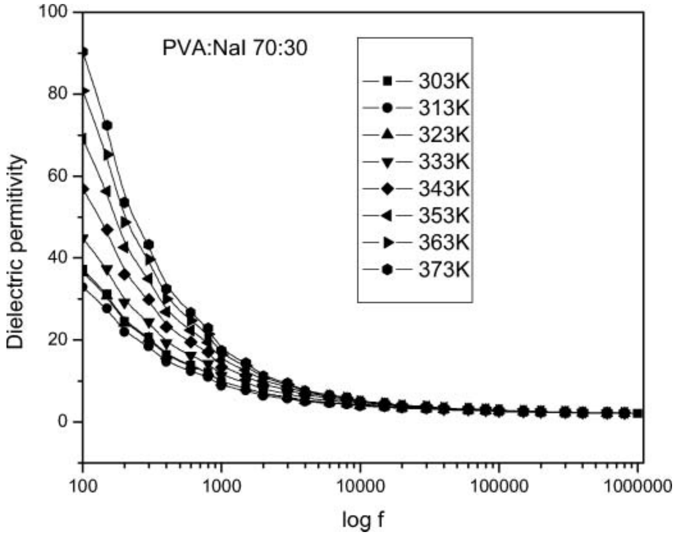

Fig. 5. Plots of ε' vs. log f of PVA: NaI polymer electrolyte films at different temperatures.

the field. Hence, ε^1decreases with increasing frequency in all the samples of PVA polymer electrolytes.

From Figure 6, it is clear that the dielectric permittivity is found to increase with increasing temperature for all the samples of PVA polymer electrolytes. The variation of ε^1 with temperature is different for non-polar polymer and polar polymers. In general for non-polar polymers the ε^1 is independent of temperature; but in the case of strong polar polymers the dielectric permittivity increases as the temperature increases (23). In polar polymers, orientation of diploes is facilitated with rising temperature and thereby the permittivity increases.

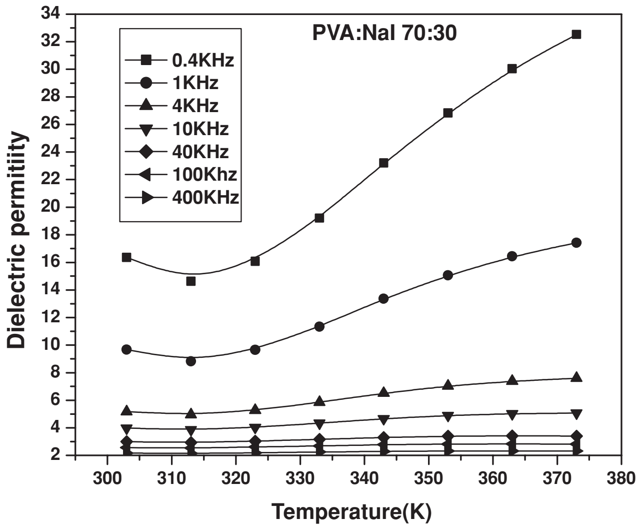

Fig. 6. Plots of ε' vs. temperatures of PVA: NaI polymer electrolyte films at different frequencies.

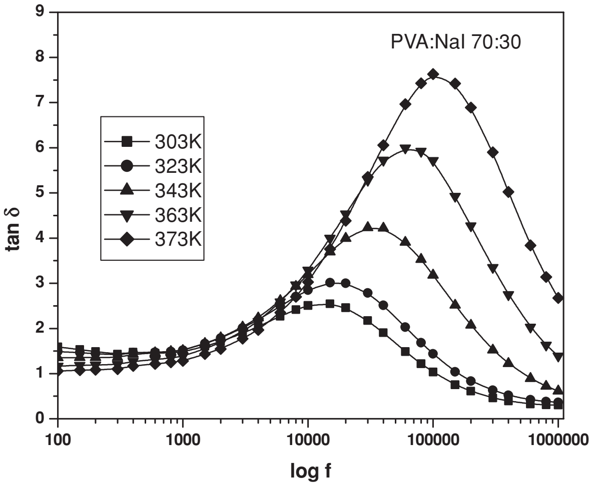

Fig. 7. Plots of tan δ vs. log f of PVA: NaI polymer electrolyte systems at different temperatures.

3.4.2. *Frequency and temperature dependent dielectric loss (tan δ)*

Figure 7 shows the variation of dielectric loss with frequency at different temperatures. In the case of pure PVA, tan δ was found to decrease with the increase of frequency and no relaxation peak was observed. But the addition of salt made significant changes on the polymer chain. In the case of salt complexed films, the tan δ was found to increase with frequency at different temperatures, passed through a maximum value and thereafter decreased. The large dielectric loss at lower frequency is due to free charge build up at the interface between the electrolyte and the electrodes (15). At higher frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of the dielectric loss. Furthermore, the frequency corresponding to maximum loss was found to shift to higher frequencies with an increase in temperature. The loss peaks and their shifts with temperature suggest a dielectric relaxation process. A similar type of behavior was observed by many researchers (4, 16, 22). This behavior suggests that the system can be represented by a parallel RC element (24). R is related to the temperature by the equation $R = Ro \exp(E_r/KT)$ where E_r is the activation energy. From this relation, it is clear that R will decrease with an increase in temperature. Hence, the tan δ shifts to the higher frequencies with increasing temperature.

Activation energy was calculated from the frequency corresponding to tan δ maximum and reciprocal of temperature and is shown in Figure 8 The data in log f_{max} vs. 1000/T fits into the equation satisfying Debye process, in which the relation f_{max} given by:

$$f_{max} = fo \exp(-E_a/kT)$$

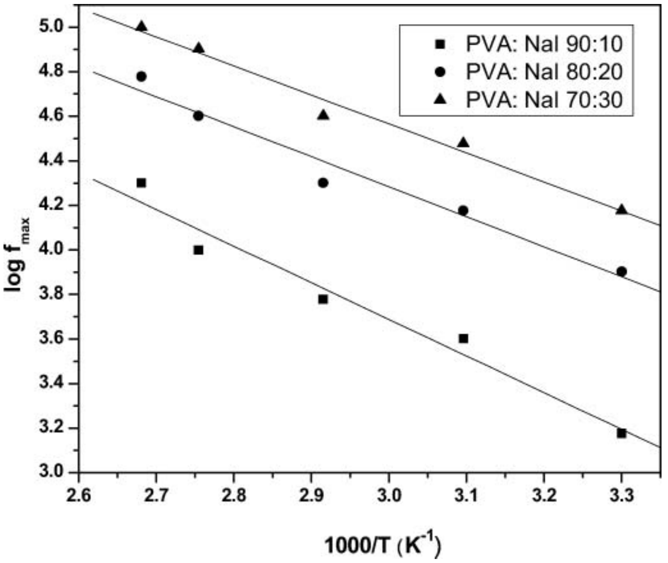

Fig. 8. Variation of log f_{max} with 1000/T at different compositions of PVA: NaI polymer electrolyte films.

Where f_{max} is the frequency relaxation peak, f_o is a constant, K Boltzmann constant, E_a is the activation energy of migration mobile ions and T is the absolute temperature. The relaxation times were found to decrease with the increase in temperature as well as composition. This decrease in relaxation time with increase in temperature may be attributed to the increase in mobility of ions in the polymer matrix. The activation energy values were 0.362, 0.336 and 0.297 eV for 10%, 20%and 30% NaI complexed films respectively and are in good agreement with the values obtained from impedance studies. Similar type of behavior was observed by many researchers (4, 16).

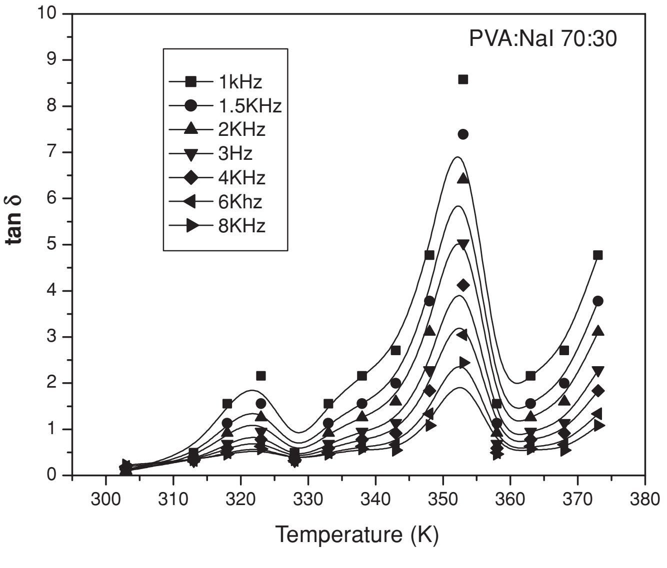

Fig. 9. Plots of tan δ vs. temperatures of PVA: NaI polymer electrolyte systems at different frequencies.

The variation tan δ with temperature at different frequencies is as shown in Figure 9. In the case of pure PVA, no relaxation peaks were observed in the present temperature and frequency range. But the addition of dopant made significant changes in the dielectric relaxation process of these polymer electrolyte films as observed in the tan δ vs. temperature plots. From the plots, it is clear that a loss peaks was observed at a temperature around 353K (above the T_g) and around 323K (below T_g). In general, polymers possess three dielectric relaxations. α, β and γ in decreasing order of temperature. The relaxation peak which occurred above T_g in the present investigations may be attributed to α-relaxation and the peak observed below T_g is attributed to β-relaxation, which may be due to the orientation of the polar groups present in the side group of the polymer. This type of relaxation is called a dipolar group relaxation (23). In the amorphous regions, the chains are irregular and entangled, whereas in crystalline regions, the chain is regularly arranged. Hence, it is very easy to move the molecular chains in the amorphous state rather than the crystalline state. The molecular packing in the amorphous state is weak and so density is smaller than that of crystalline regions. Thus, the chains in the amorphous phase are more flexible and are capable of orienting themselves relatively more easily and rapidly. The dipoles CH_2 in the side chain of the polymer will orient themselves with certain frequencies governed by the elastic restoring force which binds the dipoles to their equilibrium positions and the rotational frictional forces exerted by neighboring dipoles. In the amorphous phase, dipolar molecules should be able to orient from one equilibrium position to another relatively more easily and will contribute to absorption over a wide frequency or temperature. Since (PVA:NaI) polymer is a mixture of semi-crystalline and amorphous in nature, the dipolar molecules should be able to orient from one position to another more easily and will contribute to absorption over a wide frequency and temperature range (19, 25).

4 Conclusions

The complexation of the salt with the polymer is confirmed by XRD studies. The glass transition temperature of these electrolyte films was determined through DSC studies. The conductivity was found to increase with the increase of temperature as well as dopant concentration. The increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility. The dielectric constant was found to increase with the increase of temperature and decrease with the increase of frequency. In polar polymers, orientation of diploes is facilitated with rising temperature and thereby the permittivity increases. Dielectric spectrum shows two relaxations, occurred above T_g in the present investigations may be attributed to α–relaxation and the peak observed below T_g is attributed to β-relaxation, which may be due to the orientation of the polar groups present in the side group of the polymer.

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