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Structural, vibrational, thermal, and conductivity studies on proton-conducting polymer electrolyte based on poly (N-vinylpyrrolidone)

N. Vijaya · Subramanian Selvasekarapandian · G. Hirankumar \cdot S. Karthikeyan \cdot H. Nithya \cdot C. S. Ramya · M. Prabu

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Abstract The proton-conducting polymer electrolytes based on poly (N-vinylpyrrolidone) (PVP), doped with ammonium chloride ($NH₄Cl$) in different molar ratios, have been prepared by solution-casting technique using distilled water as solvent. The increase in amorphous nature of the polymer electrolytes has been confirmed by XRD analysis. The FTIR analysis confirms the complex formation of the polymer with the salt. A shift in glass transition temperature (T_g) of the PVP/NH4Cl electrolytes has been observed from the DSC thermograms which indicates the interaction between the polymer and the salt. From the AC impedance spectroscopic analysis, the ionic conductivity of 15 mol% NH4Cl-doped PVP polymer complex has been found to be maximum of the order of 2.51×10^{-5} Scm⁻¹ at room temperature. The dependence of T_g and conductivity upon salt concentration has been discussed. The linear variation of the proton conductivity of the polymer electrolytes with increasing temperature suggests the Arrhenius type thermally activated process. The activation energy calculated from the Arrhenius

N. Vijaya Department of Physics, S.F.R. College for Women, Sivakasi 626 123 Tamil Nadu, India

S. Selvasekarapandian $(\boxtimes) \cdot G$. Hirankumar \cdot S. Karthikeyan \cdot M. Prabu

Department of Physics, Kalasalingam University, Krishnankoil 626 190 Tamil Nadu, India e-mail: sekarapandian@rediffmail.com

H. Nithya Physics Division, BU-DRDO-Bharathiar University, Coimbatore 641 046 Tamil Nadu, India

C. S. Ramya Physics Division, Bharathiar University, Coimbatore 641 046 Tamil Nadu, India

plot for all compositions of PVP doped with NH4Cl has been found to vary from 0.49 to 0.92 eV. The dielectric loss curves for the sample 85 mol% PVP:15 mol% NH4Cl reveal the lowfrequency β relaxation peak pronounced at high temperature, and it may be caused by side group dipoles. The relaxation parameters of the electrolytes have been obtained by the study of Tanδ as a function of frequency.

Keywords Poly (N-vinylpyrrolidone) . Proton conductor. XRD . FTIR . DSC . Impedance spectroscopy . Relaxation

Abbreviations

- PEI Poly ethylene imide
- PAA Polyacrylic acid

Introduction

Solid polymer electrolytes have been extensively studied in recent years as they find technological applications in solidstate ionic devices due to their dimensionality, easy processability, flexibility, electrochemical stability, safety, and long life [\[1](#page-8-0)]. Among all solid polymer electrolytes, proton-conducting polymer electrolytes are of particular interest in view of their wide ranging applications in electrochemical devices such as electrochromic devices, super capacitors, fuel cells [\[2](#page-8-0)–[4](#page-8-0)], etc. One of the main objectives in polymer research is the development of polymeric system with high ionic conductivity at ambient temperature with good mechanical strength and thermal properties. Ionic conductivity of polymer electrolytes has been attributed to amorphous phases which can be achieved by several different techniques. One method to obtain the

amorphous phase is by dissolving inorganic acids or salts in suitable polymer matrix.

Proton-conducting polymer electrolytes could be prepared by complexation of various inorganic acids or salts with suitable polymer matrices. A lot of work on inorganic acids doped proton-conducting polymer electrolytes based on PVA, PEO, PEI, PAA, PVP [\[5](#page-8-0)–[12](#page-8-0)] has been found in literature. Ammonium salts have been reported as good donors of proton to the polymer matrix. Literature survey reveals that there are a few reports concerning the polymer electrolytes based on ammonium salts with PVA [\[13](#page-8-0)], PAA [\[14](#page-8-0)], PEO [[15\]](#page-8-0), etc., as host polymers. Very little work on the synthesis and characterization of ammonium salts doped proton-conducting polymer electrolytes based on PVP has been reported [\[16](#page-8-0)–[18](#page-8-0)]. Hence, an attempt has been made to develop and characterize a new proton-conducting polymer electrolyte based on poly (N-vinylpyrrolidone) (PVP) doped with ammonium chloride ($NH₄Cl$).

PVP is a biocompatible polymer used as a blood plasma expander for trauma victims. It is an amorphous polymer having high T_g (86 °C) due to the presence of the rigid pyrrolidone group. Addition of salts with a conducting species as silver and potassium to PVP has a marked influence on conductivity of the polymer [\[19,](#page-8-0) [20](#page-8-0)]. It has been reported as the best candidate for the application of humidity sensor in the presence of iodine and cobalt [\[21\]](#page-8-0). In the present work, NH4Cl-doped PVP polymer electrolytes have been prepared and characterized by various experimental techniques such as XRD, FTIR, DSC, and AC impedance spectroscopy.

Experimental details

The polymer PVP of average molecular weight, $M_{\rm w}$ of 40,000 (S d fine chemicals) and NH4Cl (Spectrum) were used in the present work. The polymer electrolytes PVP doped with NH4Cl in different molar ratios such as (100:0), (95:5), (90:10), (85:15), (80:20), and (75:25) were prepared by solution-casting technique using distilled water as solvent. Aqueous solutions of PVP and NH₄Cl were stirred continuously with a magnetic stirrer for several hours to obtain a homogeneous solution. The solution was then cast in propylene Petri dishes, and the samples were vacuum dried. Thick films of thickness of 220–330 μm were obtained.

X-ray diffraction patterns of the prepared samples were recorded at room temperature on a Philips X' Pert PRO diffractometer using CuKα radiation. FTIR spectra were recorded for the proton-conducting polymer electrolyte films in the range of 400–4,000 cm⁻¹ at room temperature using a SHIMADZU-IR Affinity-1 Spectrometer. DSC thermo grams were obtained using NETZSCH DSC 204F1 at a heating rate of 2 K/min under liquid nitrogen atmosphere in the temperature range −50 to 250 °C. Electrical measurements were performed on the polymer electrolyte films in the frequency range 42 Hz–1 MHz over the temperature range 303–343 K by sandwiching them between aluminum blocking electrodes using HIOKI 3532 LCZ meter interfaced with a computer.

Results and discussions

X-ray diffraction analysis

X-ray diffraction (XRD) studies have been carried out to investigate the occurrence of complex formation between the polymer and the salt and the degree of crystallinity of the polymer complex. Figure 1 depicts the XRD patterns of pure PVP and PVP doped with NH4Cl in different molar ratios. A broad diffraction peak around 22.7° observed from Fig. 1 can be associated with pure PVP. The broadness of this peak increases, and its relative intensity slightly decreases with increase of NH4Cl concentration which may be due to increase of amorphous nature of PVP with addition of salt. This result can be interpreted in terms of the Hodge et al. [\[22\]](#page-8-0) criterion which establishes a correlation between the intensity of the peak and the degree of crystallinity. Peaks corresponding to pure NH4Cl have been found to be absent in the salt-doped polymer complexes (90:10) and (85:15) indicating the complete dissociation of salt in the polymer matrix. However, in (80:20) polymer complex, the peaks $2\theta = 23.05^\circ$, 32.82° , 47° , 58.35° (JCPDS file no. 34–0710) corresponding to pure NH₄Cl have been observed which indicates the presence of some undissociated salt in that polymer complex.

Fourier transform infrared analysis

Fourier transform infrared (FTIR) spectroscopy is a versatile tool to analyze the polymeric materials since it provides

Fig. 1 XRD pattern of pure PVP and PVP doped with different NH4Cl concentrations

information about the interaction between the polymer and the ions. Figure 2 shows the FTIR spectra of pure PVP and PVP doped with NH4Cl in different molar ratio.

The vibrational frequencies observed in the FTIR spectra of polymer electrolytes are given in Table 1. The bands at 2,135, 1,703, 1,429, 933, and 844 cm⁻¹ have been assigned to C–N stretching, C=O stretching, CH₂ wagging, C–C bonding, and $CH₂$ bending vibrations of pure PVP, respectively. The bands at 2,135 and 1,703 cm⁻¹ in pure PVP have been shifted to 2,137 and 1,701 cm^{-1} , respectively, in 95 mol% PVP:5 mol% NH₄Cl polymer electrolyte. The band at 1,429 cm⁻¹ has been shifted to 1,425 cm⁻¹ in 95 mol% PVP:5 mol% NH4Cl polymer electrolyte and 1433 cm⁻¹ in 85 mol% PVP: 15 mol% NH₄Cl polymer electrolyte. The bands at 933 and 844 cm^{-1} have been shifted to 935 and 848 cm⁻¹ in the 85 mol% PVP:15 mol% NH4Cl. These changes confirm the complex formation between the polymer and the salt.

Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) analysis has been done to correlate the glass transition temperature with the amorphousity and the ionic conductivity of the polymer electrolytes. The DSC thermograms for different molar ratios of PVP/NH4Cl polymer electrolytes have been shown in Fig. 3. It is already reported that the glass transition temperature, T_g of the pure PVP is 359 K [\[23](#page-8-0)]. The DSC scans recorded for the prepared samples reveal an endothermic step-like change around 340 K corresponding to the glass transition temperature of the polymer electrolytes. It has been observed that the T_g of polymer electrolytes decreases with the increase in concentration of NH4Cl salt up to 15 mol%. This may be due to the softening of the complexation by the salt (plasticization of the electrolyte with addition of salt) which enhances the proton transport.

Fig. 2 FTIR spectra of pure PVP, 95 mol% PVP–5 mol% NH_4Cl and 85 mol% PVP–15 mol% NH4Cl

Table 1 Vibration frequencies observed in the FTIR spectra of PVP: NH4Cl polymer electrolytes

(cm^{-1}) Pure PVP	Wave number Composition $(mol\%)$		
	95 PVP:5NH ₄ C1	85PVP:15NH ₄ C1	Assignment
2,135	2,137	2,135	C-N Stretching
1,703	1,701	1,703	$C=O$ Stretching
1,429	1,425	1,433	CH ₂ Wagging
933	933	935	$C-C$ Bonding
844	844	848	$CH2$ Bending

However, for greater concentrations, the T_g has been found to increase which may be due to the presence of some undissociated salt in the host polymer matrices.

The polymer complex with 85 mol% PVP and 15 mol% NH₄Cl has been found to have a low T_g of 332 K. The low glass transition temperature causes the higher segmental motion of the polymer electrolyte. The T_g values of polymer electrolytes with different compositions are tabu-lated in Table [2](#page-3-0). This observed shift in $T_{\rm g}$ values of the polymer electrolytes in DSC thermograms indicates the interaction between the polymer and the salt.

Impedance analysis

Electrical characterization of all the prepared polymer samples has been performed using AC impedance spectroscopy technique. Figure [4a](#page-3-0) shows the complex impedance plots of PVP/NH4Cl polymer electrolytes with different concentrations of NH4Cl at 303 K. Each plot consists of a highfrequency semicircle and a low-frequency spike. The semicircle may be due to the bulk effect of the electrolyte and the spike may be due to the effect of the blocking electrodes. The bulk resistance (R_b) of the polymer electro-

Fig. 3 DSC thermograms of PVP–NH₄Cl polymer electrolytes with different concentrations

lytes has been calculated by the EQ software from the intercept of the high-frequency semicircle or the lowfrequency spike on the real impedance (Z') axis.

Fig. 4 a Complex impedance plots of PVP–NH₄Cl polymer electrolytes with different concentrations at 303 K. b Complex impedance plot of 15 mol% NH4Cl-doped PVP polymer electrolyte at different temperatures

Table 3 Ionic conductivity values of PVP-NH₄Cl polymer electrolytes from the impedance plots at different temperature

Temp (K)	Conductivity $\sigma_{\rm dc}$ (Scm ⁻¹)				
	90:10	85:15	80:20	75:25	
303	2.0×10^{-7}	2.51×10^{-5}	1.23×10^{-6}	6.68×10^{-7}	
313	1.06×10^{-6}	5.21×10^{-5}	4.19×10^{-6}	3.26×10^{-6}	
323	3.92×10^{-6}	9.38×10^{-5}	1.36×10^{-5}	1.18×10^{-5}	
333	9.87×10^{-6}	1.59×10^{-4}	3.47×10^{-5}	2.66×10^{-5}	
343	2.2×10^{-5}	3.17×10^{-4}	7.33×10^{-5}	6.39×10^{-5}	

The ionic conductivity (σ) of the polymer electrolytes can be calculated using the equation,

$$
\sigma = \frac{l}{AR_{\rm b}}
$$

where l and A are the thickness and area of the polymer electrolyte, respectively. The highest ionic conductivity at ambient temperature has been found to be 2.51×10^{-5} Scm⁻¹ for the15 mol% salt-doped polymer electrolyte. The dc conductivity values for all compositions of PVP–NH4Cl polymer electrolytes at different temperatures are presented in Table 3. It is observed that as the temperature increases, the ionic conductivity of the polymer electrolyte increases for all compositions.

Figure 4b represents the complex impedance plot of the highest conductivity sample at different temperatures. It has been observed that as the temperature increases, the diameter of the semicircle decreases implying the decrease in bulk resistance. At higher temperatures, the semicircle disappears indicating the prevailing of the resistive component of the electrolyte system [\[24](#page-8-0)]. The ionic conductivity of the polymer electrolyte increases with the increase of temperature which can easily be understood on the basis of the ionic transport mechanism of solid polymer electrolytes. When the temperature is increased, the ionic mobility of the

Fig. 5 Variation of conductivity and glass transition temperature as a function of salt concentration

Fig. 6 Temperature dependence of ionic conductivity of PVP/NH4Cl polymer electrolytes with different concentrations

polymer chain is enhanced and the fraction of free volume in a solid polymer electrolyte increases accordingly, which leads to an increase in the ionic conductivity of the polymer electrolyte [[25\]](#page-8-0). In addition, the mobility of charge carriers increases with increase of temperature resulting in an increase in the ionic conductivity at higher temperatures.

Concentration-dependent conductivity

Figure [5](#page-3-0) presents the variation of room temperature conductivity and glass transition temperature as a function of salt concentration. It has also been observed that the ionic conductivity increases with the increase of salt concentration up to 15 mol% and decreases at higher salt concentrations. The increase in the conductivity with increasing salt concentration may be due to the increase in the number of mobile charge carriers and increase in the amorphous nature of the polymer electrolyte, which is consistent with XRD analysis. The decrease in conductivity at higher salt concentrations can be attributed to either incomplete dissociation of salt or the formation of ion multiples [[26](#page-8-0)]. The highest conductivity for 15 mol% salt-doped system is consistent with the DSC results.

Temperature-dependent conductivity

The temperature dependence of proton conductivity for all the prepared PVP/NH4Cl polymer electrolytes over the

temperature range 303–353 K is shown in Fig. 6. It is seen that the conductivity increases linearly with increase of temperature for all compositions of polymer complexes. The polymer complex doped with 15 mol% NH4Cl salt exhibits the highest ionic conductivity. The dc conductivity values follow the Arrhenius type thermally activated process given by the relation,

$$
\sigma = (\sigma_{0/T}) \exp(-Ea/kT)
$$

where σ_0 is the pre-exponential factor, Ea the activation energy, and k the Boltzmann constant.

The activation energy for all the prepared polymer electrolytes is calculated by linear fit of the Arrhenius plot. The ionic conductivity and the activation energy values have been tabulated in Table 4. The activation energy decreases with increase in salt concentration. This is due to the increase in amorphous nature of the polymer electrolyte with addition of salt that facilitates the ionic motion in the polymer network. At higher salt concentrations, the activation energy increases due to aggregation of ions, leading to the formation of ion clusters, thus decreasing the number of mobile charge carriers. The activation energy is found to be low of the order of 0.49 eV for the highest conductivity sample.

Conductance spectra analysis

Figure [7a,](#page-5-0) b show the frequency dependence of the conductivity for all compositions of PVP/NH4Cl polymer electrolytes at room temperature and for 15 mol% NH4Cldoped PVP polymer electrolyte at different temperatures. Each plot shows three regions—low-frequency dispersion region due to the space-charge polarization at the blocking electrodes, frequency-independent plateau region representing the dc conductivity (σ_{dc}) of the polymer complex, and highfrequency dispersion region corresponding to bulk relaxation phenomenon. The $\sigma_{\rm dc}$ values can be calculated by extrapolating the plateau region to $\log \sigma$ axis.

As the frequency decreases, more and more charge accumulation occurs at the electrode–electrolyte interface which leads to a decrease in number of mobile ions and hence a decrease in conductivity at low frequency. In high-

Table 4 Conductivity and activation energy of PVP– NH4Cl polymer electrolytes

for all compositions of PVP/ NH4Cl polymer electrolytes at 303 K. b Conductance spectra for 15 mol% NH4Cl-doped polymer electrolyte at various temperatures. c Jonscher's power law graph

frequency region, the mobility of charge carriers is high, and hence, the conductivity increases with frequency [\[27](#page-8-0)]. It is also seen that the dc conductivity increases with increase of temperature suggesting that the free volume around the polymer chain causes the mobility of ions and polymer segments [[18\]](#page-8-0).

The ac conductivity obeys Jonscher's power law [[28\]](#page-8-0) represented by

$$
\sigma_{ac}(\omega) = (\sigma_{dc}) + A\omega^{\alpha}
$$

Fig. 8 a–b Variation of ε' and ε″ as functions of frequency for all PVP–NH4Cl polymer electrolytes at 303 K

where α is the power law exponent, A is the temperaturedependent parameter, and σ_{dc} is the dc conductivity. According to jump relaxation model [[29\]](#page-8-0), α is given by

$$
\alpha = \frac{\text{back hop rate}}{\text{Site relaxation time}}
$$

If α <1, i.e., the backward hopping is slower than the site relaxation time, then the charge carriers have translational motion. If $\alpha > 1$, the backward hopping is faster than the site relaxation time.

The α values have been calculated by fitting the conductivity spectra with Jonscher's power law equation using non-linear least squares fitting procedure and are tabulated in Table [4.](#page-4-0) The Jonscher's power law graph is shown in Fig. [7c](#page-5-0). The α values have been found to be less than 1 for 10,15, and 20 mol% salt-doped samples which may be due to the presence of free site for next hop, and the backward motion is slower due to less columbic interaction between the ions. For 25 mol% salt-added sample, α is greater than one which may be either due to the presence of a bad site for next hop or columbic repulsion between the ions. A low value of α is obtained for 15 mol% salt-doped PVP polymer electrolyte. This indicates that the number of free sites available for hopping of ions in this composition is larger than that for the other compositions which results in an increase in the ionic conductivity. This is consistent with the result that the 15 mol% salt-doped PVP polymer electrolyte has the highest ionic conductivity.

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Dielectric spectra analysis

The dielectric behavior of any polymeric system may be described by the real and imaginary parts of the complex permittivity, ε^* which is defined by the relation,

$$
\varepsilon^* = \varepsilon'(\omega) - j\varepsilon''(\omega) = -j/\omega C_0 Z^*
$$

where the real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ components are the storage (dielectric constant) and loss of energy (dielectric loss) in each cycle of the applied electric field [[30](#page-8-0)]. Figure [8a](#page-5-0), b shows the variation of ε' as a function of frequency for all NH4Cl-doped PVP polymer electrolytes at 303 K and Fig. 9a, b represents the frequency dependence of $\varepsilon'(\omega)$ and ε'' for 85 mol% PVP:15 mol% NH4Cl at different temperatures.

As seen from the above figures, the dielectric constant ε' (5) values are very high at low frequencies and decrease with increase of frequency and become constant at higher frequencies. The high value of $\varepsilon'(\omega)$ is due to the presence

Fig. 10 a Variation of Tan δ as a function of frequency for all compositions of PVP/NH₄Cl polymer electrolytes. b for 15 mol% NH4Cl-doped polymer electrolytes

Table 5 Dielectric relaxation parameters for all compositions of PVP/NH4Cl polymer electrolytes

75:25 3.08 3.08 1.20×10^3 8.33×10^{-4}

of space-charge effects, which is contributed by the accumulation of charge carriers near the electrodes [[31,](#page-8-0) [32\]](#page-8-0). At higher frequencies, the periodic reversal of the electric field is in such a way that there is no excess ion diffusion in the field direction resulting in the decrease in dielectric constant [[33](#page-8-0)]. A high dielectric constant has been found for 15 mol% NH4Cl-doped polymer electrolyte. The large value of ε " is also due to the motion of free-charge carrier within the material.

The frequency dependence of ε " for 85 mol% PVP:15 mol% NH4Cl at different temperatures clearly shows the low frequency β relaxation peak which is pronounced at higher temperatures. This may be caused by side group dipoles and the nearest part of the backbone [\[34](#page-8-0)]. It is also observed that the dielectric constant and dielectric loss increase with increase of temperature. This is because as temperature increases, the degree of salt dissociation and redissociation of ion aggregates increases, resulting in the increase in the number of free ions or charge carrier density.

Loss tangent spectra

The dielectric relaxation parameter of the polymer electrolytes can be obtained from the study of Tanδ as a function of frequency. The dielectric loss tangent, Tanδ can be defined by the equation Tan $\delta = \varepsilon''/\varepsilon'$. The variation of Tan δ with frequency for all the prepared PVP/NH_4Cl polymer complexes at 303 K is presented in Fig. [10a.](#page-6-0) It has been observed that Tanδ increases with increasing frequency and reaches a maximum. Then it decreases for further increase of frequency. For maximum dielectric loss at a particular temperature, the loss tangent peak is described by the relation $\omega \tau = 1$ where τ is the relaxation time and ω is the angular frequency of the applied electric field. The relaxation parameters are calculated for all the prepared polymer electrolytes at 303 K and are tabulated in Table 5. A low relaxation time, different temperatures is obtained for 15 mol% salt-doped polymer electrolyte which is consistent with the conductivity analysis which shows higher conductivity for 15 mol% salt-doped polymer electrolyte.

The variation of Tanδ as a function of frequency for 15 mol% NH4Cl-doped PVP polymer sample at various temperatures presented in Fig. [10b](#page-6-0) shows an asymmetric peak. As the temperature increases, the charge carrier has been thermally activated and the loss tangent peak shifts towards higher frequency. This indicates that the relaxation time decreases with increase of temperature. The relaxation parameter for 85 mol% PVP:15 mol% NH4Cl polymer electrolytes at various temperatures are tabulated in Table 6. It is seen that the relaxation time τ decreases with increase of temperature which results in an increase in the ionic conductivity.

Conclusion

PVP-based proton-conducting polymer electrolytes with ammonium chloride in different molar ratios have been prepared by solution-casting technique using distilled water as solvent. The XRD analysis reveals the increase in amorphous nature of the polymer electrolytes. The FTIR analysis confirms the complex formation between the polymer and the salt. The thermal analysis shows a low glass transition temperature for 15 mol% NH_4Cl -doped PVP polymer electrolyte. From the conductivity analysis, it has been observed that the 15 mol% NH₄Cl-doped PVP

polymer complex has the highest conductivity of the order of 2.51×10^{-5} Scm⁻¹ at ambient temperature. The influence of the salt concentration on T_g and conductivity has been discussed. The activation energy estimated from the Arrhenius plot has been found to be 0.49 eV for 15 mol% salt-doped PVP polymer electrolyte. The dielectric loss curves for the sample 85 mol% PVP:15 mol% NH_4Cl reveal the low-frequency β relaxation peak pronounced at high temperature, and it may be caused by side group dipoles and the nearest part of the backbone. The relaxation parameters of the electrolytes have been obtained by the study of Tanδ as a function of frequency.

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