

Vibrational and impedance spectroscopic analysis of poly(vinyl alcohol)-based solid polymer electrolytes

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Abstract Solid polymer electrolytes based on poly(vinyl alcohol) (PVA) doped with NH_4Br have been prepared by the solution-casting method. The complex formation between the polymer and the salt has been confirmed by Fourier transform infrared spectroscopy. The highest conductivity at 303 K has been found to be of the order of 10^{-4} Scm^{-1} for 25 mol% NH_4Br -doped PVA system. The ionic transference number of polymer electrolyte has been estimated by Wagner's polarization method, and the results reveal that the conducting species are predominantly ions.

Keywords Poly(vinyl alcohol) · FTIR · Wagner's polarization · Impedance spectroscopy

Introduction

Ionically conducting polymers have been of considerable interest because of their potential application as a solid polymer electrolyte. The solid polymer electrolytes have attracted great scientific interest during the last two decades because of their advantages such as high energy density, electrochemical stability, and easy handling [1]. In the present study, poly(vinyl alcohol) (PVA) doped with different molar concentrations of ammonium bromide (NH_4Br) have been prepared by the solution-casting method, and polymer electrolytes have been subjected into different experimental

analysis. The polymer–salt interactions have been analyzed by Fourier transform infrared (FTIR) spectroscopy. The ionic transference number of polymer system has been estimated by Wagner's polarization method.

Experimental details

The polymer PVA (S.d.Fine) of average molecular weight of 125,000 and the salt NH_4Br (LOBA Chemie) were used as the raw material in this study. Dimethyl sulfoxide (DMSO) was used as the solvent. Separate solutions of PVA and NH_4Br in DMSO were prepared and subsequently mixed in incremental proportions in steps of five resulting in a series of transparent solutions ranging in PVA/ NH_4Br ratios of 95:5 to 65:35 by mol%. The solution was then casted in glass Petri dishes, and the samples were subjected to an extended drying period in a vacuum chamber before analysis until complete solvent removal takes place. Thick films of thickness in micrometer range were obtained.

The FTIR spectrum exhibited by the polymer electrolyte was recorded using a JASCO Spectrophotometer in the frequency range of 600 to $4,000 \text{ cm}^{-1}$. Electrical measurements were performed on a HIOKI make LCZ meter (model 3532) in the wave number ranging from 42 Hz–5 MHz at various temperatures ranging from 303 to 343 K using stainless steel as the blocking electrode.

Results and discussion

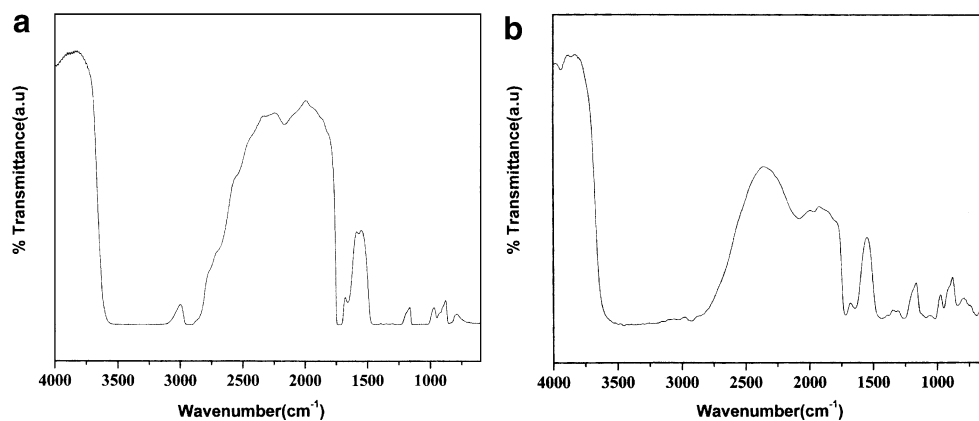
FTIR analysis

FTIR spectroscopy has been used to analyze the interactions among atoms or ions in electrolyte systems. These

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Fig. 1 FTIR spectrum PVA: **a** NH₄Br a 100:0 mol%, **b** 65:35 mol%



interactions can induce changes in the vibrational modes of PVA. The FT-IR spectrum of pure PVA and PVA doped with 35 mol% NH₄Br are as shown in Fig. 1a and b. The band observed at 2,925 cm⁻¹ for pure PVA is attributed to CH₂ asymmetric stretching vibration, and it shifts to higher wave number at 2,937 cm⁻¹ in the salt-doped system (Fig. 1b). The band observed at 1,724 and 1,659 cm⁻¹ are attributed to C=O stretching and C–O stretching of pure PVA, respectively (in Fig. 1a), and these bands are found to be displaced to lower wave numbers 1,719 and 1,646 cm⁻¹, respectively. Furthermore, a vibrational peak observed at 852 cm⁻¹ corresponding to C–H rocking of pure PVA is found to be shifted to 850 cm⁻¹. The above results confirm the complex formation between the polymer (PVA) and the salt (NH₄Br).

Transference number measurement

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport number have been evaluated in PVA–NH₄Br electrolyte systems using Wagner's polarization technique [2]. In this technique, the dc current is monitored as a function of time on the application of fixed dc voltage across the sample with blocking electrodes. The results of dc polarization measurements on the 25 mol% NH₄Br electrolyte taken with silver electrodes by applying 0.843 V dc bias voltage (at 303 K) are shown in Fig. 2. The transference numbers are calculated from the polarization current vs time plot using the equations:

$$t_{ion} = (I_i - I_f)/I_i$$

$$t_{ele} = I_f/I_i$$

where I_i is the initial current and I_f is the final residual current. The ionic transference number (t_{ion}) for all the compositions of the PVA–NH₄Br electrolyte systems are found to be in the range of 0.93–0.96. This suggests that the charge transport in these electrolyte films is predominantly ions.

Impedance analysis

Figure 3a shows the impedance plot for different mole ratios of PVA–NH₄Br polymer electrolyte system at ambient temperature (303 K). The complex impedance plots show two well-defined regions: the semicircle observed in the high frequency region, which is due to the bulk effect of the electrolytes, and the linear region, which in the low frequency range is attributed to the effect of the blocking electrodes. The bulk electrical resistance (R_b) of the polymer electrolytes has been extracted by the Z-view software from the low frequency intercept of the semicircle on the Z' axis. The ionic conductivity is calculated using the equation $\sigma = d/R_b A$, where d is the thickness of the polymer electrolyte film and A the surface area of the film. It has been found that 25 mol% NH₄Br-doped PVA has the highest ambient temperature conductivity of 5.7×10^{-4} S cm⁻¹. Figure 3b represents the impedance plot for the highest conductivity sample. The absence of the high-frequency semicircle in Fig. 3b

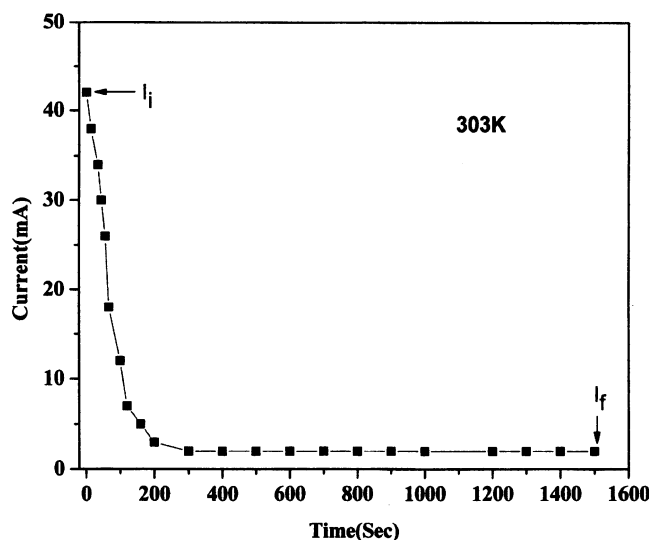


Fig. 2 Polarization current as a function of time for 75 mol% PVA/ 25 mol% NH₄Br

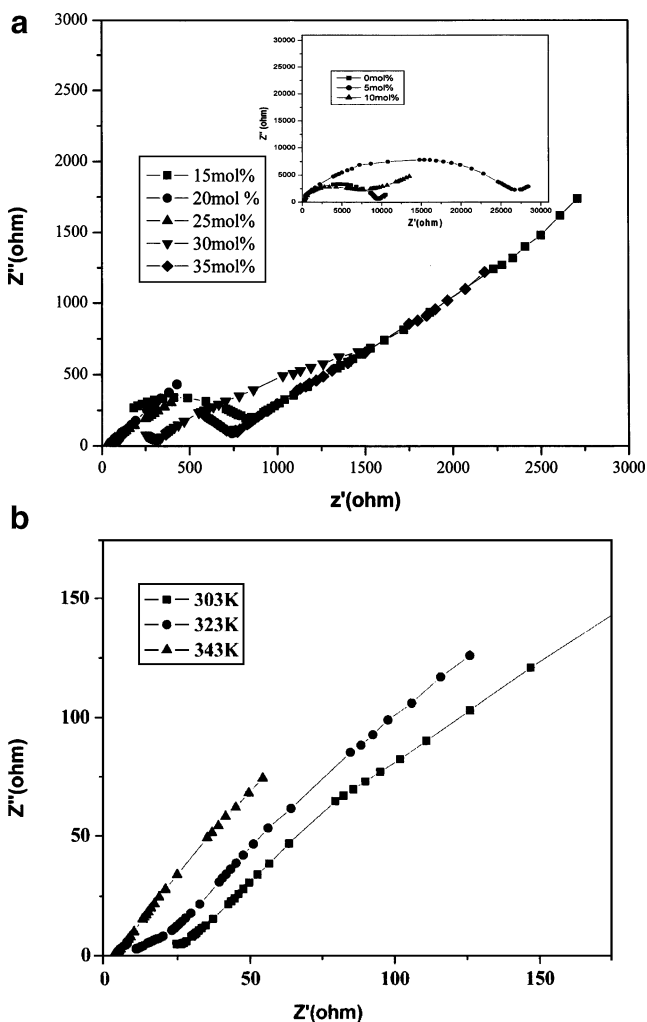


Fig. 3 **a** Impedance plots for PVA: NH₄Br doped with different concentrations of NH₄Br at 303 K. **b** Impedance plots for 75 mol PVA/25 mol%NH₄Br-doped PVA at different temperatures

indicates that the total conductivity is mainly the result of ion conduction [3].

Temperature dependence of ionic conductivity

Figure 4 shows the temperature dependence of ionic conductivity for the PVA–NH₄Br complexes. A series of straight lines with different slopes are obtained for PVA–NH₄Br samples containing different concentrations of doped salt. These results suggest that Arrhenius phenomenological relationship can be used to describe the conductivity behavior for the PVA–NH₄Br system:

$$\sigma = A \exp [-E_a/KT]$$

where E_a is the activation energy, K is Boltzman constant, and T is the temperature. The Arrhenius form is employed when the ions are decoupled from the polymer host and activated hopping is required for ionic transport.

The experimental data in Fig. 3 indicate that the conductivity of all the samples apparently is enhanced with increasing temperature. This can be easily understood on the basis of the ionic-transport mechanism of solid polymer electrolytes. When the temperature is increased, mobility of polymer chains 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 solid polymer electrolytes [4]. Furthermore, the number of charge carriers increases with increasing temperature. This is favorable to a high ionic conductivity at higher temperatures.

Concentration dependence of ionic conductivity

Conductivity is related to the number of charge carriers (n_i) and their mobility (μ_i) according to the following equation:

$$\sigma = \sum n_i q_i \mu_i$$

where q_i is the charge on each charge carrier. The variation of logarithm conductivity of PVA with the salt concentration is as shown in the Fig. 5.

Three characteristic regions can be easily distinguished. The initial low concentration region (I) in which a decrease in conductivity is observed has been ascribed to ion pair formation [5]. The subsequent linear region (II) showing an increase in conductivity beyond the minimum(at about 25 mol%), could be a result of triple ion formation or a redissociation effect [5]. The final high salt concentration region (III) in which a decrease in conductivity is observed may be due to a rapid increase in viscosity [6] or the formation of higher-order ion aggregates. The high ionic conductivity at ambient temperature is found to be $5.7 \times 10^{-4} \text{ S cm}^{-1}$ for 25 mol% NH₄Br-doped PVA.

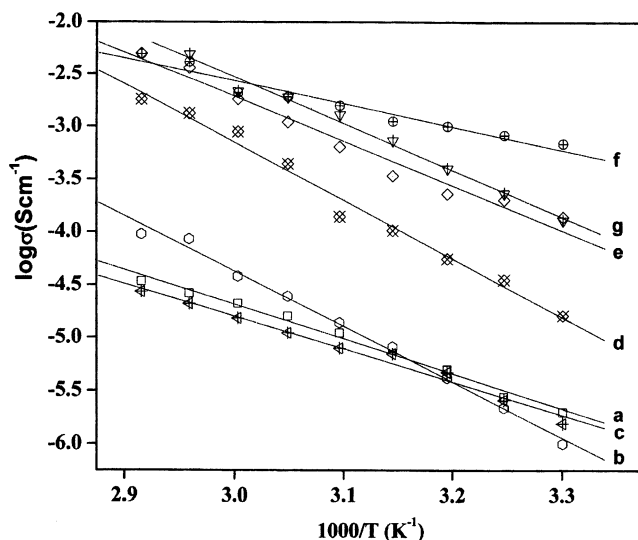


Fig. 4 Temperature dependence of ionic conductivity of PVA: NH₄Br a 100:00, b 95:05, c 90:10, d 85:15, e 80:20, f 75:25, g 70:30

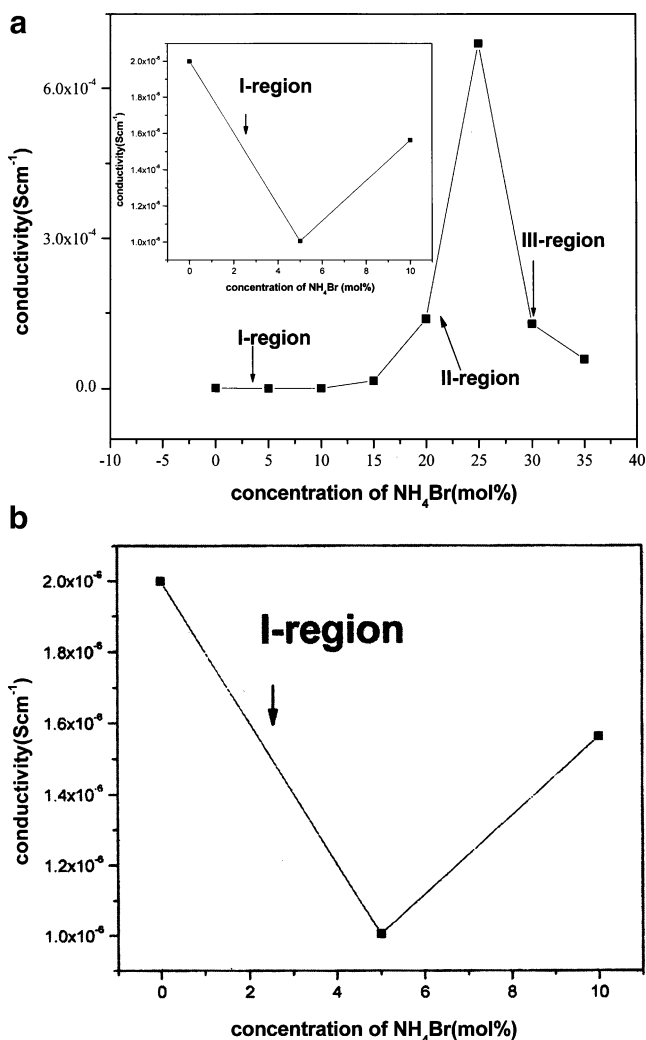


Fig. 5 Variation of ionic conductivity as a function of NH₄Br concentration

Dielectric analysis

The dielectric response is generally described by the complex permittivity:

$$\epsilon^* = \epsilon'(\omega) - \epsilon''(\omega)$$

Where real $\epsilon'(\omega)$ and imaginary $\epsilon''(\omega)$ components are the storage and loss of energy in each cycle of the applied electric field. Figure 6a and b represents the frequency dependence of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ for PVA doped with NH₄Br with different concentrations at 303 K. From the figures, it is clear that the values of $\epsilon'(\omega)$ are very high at low frequency. Such high value of dielectric permittivity at low frequencies has been explained by the presence of space charge effects, which is contributed by the accumulation of charge carriers near the electrodes [7, 8]. At higher frequencies, $\epsilon'(\omega)$ has been found to be relatively constant with frequency. This is because periodic reversal of the

field takes place so rapidly that the charge carriers will hardly be able to orient themselves in the field direction resulting in the decrease in dielectric constant [9]. The large value of $\epsilon''(\omega)$ is also due to the motion of free charge carrier within the material.

Summary and conclusion

PVA-based polymer electrolytes with different compositions of ammonium bromide have been prepared using the solution-casting technique. The complexation behavior between the polymer and the salt has been confirmed by FTIR analysis. The ionic conductivities of the electrolytes have been measured by the ac impedance technique at different temperatures. The influence of salt the concentra-

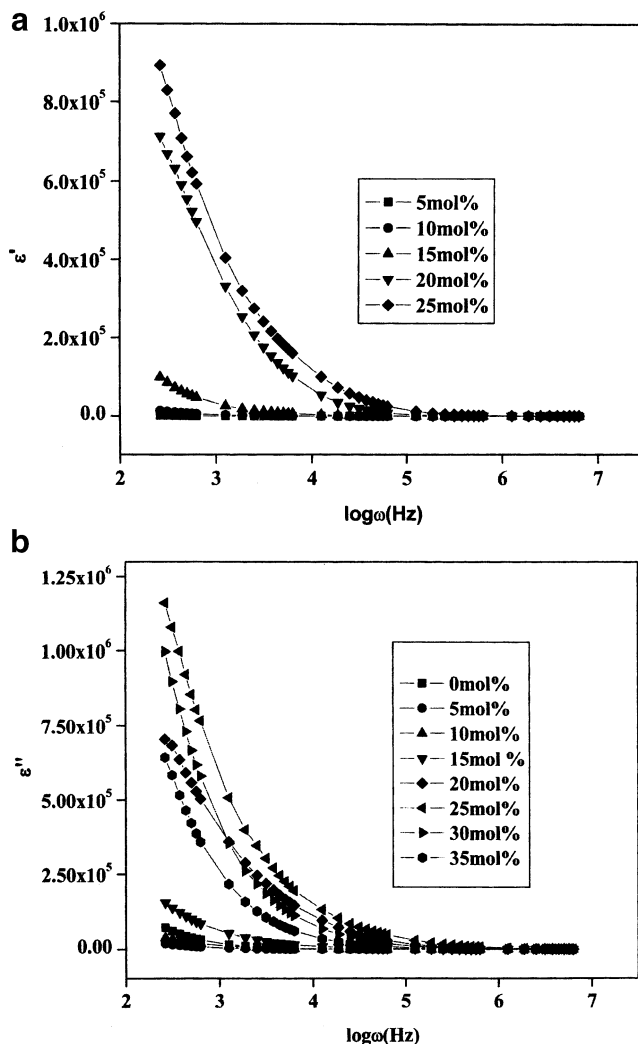


Fig. 6 Frequency dependence of a real part $\epsilon'(\omega)$ and b imaginary part $\epsilon''(\omega)$ of dielectric permittivity for different mol% NH₄Br-doped PVA

tion on the polymer has been discussed. The maximum conductivity value ($5.7 \times 10^{-4} \text{ S cm}^{-1}$) is obtained for the polymer complex with 25 mol% NH_4Br .

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