

AC impedance and dielectric spectroscopic studies of Mg²⁺ ion conducting PVA–PEG blended polymer electrolytes

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Abstract. Polyvinyl alcohol (PVA)–polyethylene glycol (PEG) based solid polymer blend electrolytes with magnesium nitrate have been prepared by the solution cast technique. Impedance spectroscopic technique has been used, to characterize these polymer electrolytes. Complex impedance analysis was used to calculate bulk resistance of the polymer electrolytes. The a.c.-impedance data reveal that the ionic conductivity of PVA–PEG–Mg(NO₃)₂ system is changed with the concentration of magnesium nitrate, maximum conductivity of 9.63×10^{-5} S/cm at room temperature was observed for the system of PVA–PEG–Mg(NO₃)₂ (35–35–30). However, ionic conductivity of the above system increased with the increase of temperature, and the highest conductivity of 1.71×10^{-3} S/cm was observed at 100°C. The effect of ionic conductivity of polymer blend electrolytes was measured by varying the temperature ranging from 303 to 373 K. The variation of imaginary and real parts of dielectric constant with frequency was studied.

Keywords. Ionic conductivity; PVA–PEG; polymer blend; Mg(NO₃)₂; dielectric constant.

1. Introduction

Polymer electrolytes have received considerable attention because of their potential applications in solid-state batteries, chemical sensors and electrochemical devices (Gray 1997; Sanchez *et al* 1998; Wang *et al* 2002). These polymer electrolytes have to satisfy several requirements, including high ionic conductivity, good mechanical properties and excellent electrochemical stability. The search for Mg²⁺ ion containing polymer electrolytes can be interesting not only for understanding the multivalent cationic conductivity mechanism in the polymer, but also due to their lower cost, and ease of handling and fabrication as thin film membranes. Several methods, such as copolymerization, plasticization, blending and addition of ceramic fillers have been used to modulate conductivity of the polymer electrolytes. Among the above, blending of polymers is a useful tool to develop new polymeric materials with improved mechanical stability. Main advantages of the blend system are simplicity of preparation and ease of control of physical properties by compositional change (Rocco *et al* 2001). Most of the studies of concentration and temperature dependence and enhancement of conductivity have been on polymers like PEO, PAN, PVA etc complexed with magnesium salts (Patric *et al* 1986; Yang *et al* 1986a, b; Huq *et al* 1987; Andrews *et al* 1988; Ramalingaiah *et al* 1996; Mitra *et al* 2001; Jaipal Reddy and Chu 2002; Perera *et al* 2004; Jeong *et al* 2006). However,

much attention has not been paid to polymer blends with magnesium salts.

In the present work, the Mg²⁺ ion conducting polymer blend electrolytes based on polyvinyl alcohol and polyethylene glycol complexed with Mg(NO₃)₂ have been prepared by solution cast technique. The polymer electrolytes have been characterized by complex impedance spectroscopic analysis in the temperature range 303–373 K.

2. Experimental

Polyvinyl alcohol (PVA) from CDH, India, having a molecular weight of 1,25,000 and polyethylene glycol (PEG) from CDH, India having a molecular weight of 4,000 were used as received. Equal quantity of PVA and PEG by weight was added to doubly distilled water with stirring the solution at room temperature to complete dissolution. Required quantity (0, 10, 20 and 30 mol %) of Mg(NO₃)₂ was also dissolved in doubly distilled water and added to the polymeric solution with continuous stirring for about 12 h. The solution was poured onto cleaned Petri dishes and evaporated slowly at room temperature under vacuum to ensure removal of the solvent traces. After drying, the films were peeled off from Petri dishes and kept in vacuum desiccators until use. The thickness of the obtained films was in the range of 80–100 μm.

When the polymer electrolyte films formed, they were placed between the blocking stainless steel electrodes of the conductivity cell with leads connected to a HIOKI 3532-50

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LCR meter interfaced to a computer for conductivity measurements. The measurements were made over a frequency range of 42 Hz to 5 MHz at different temperatures. The temperature dependent conductivity studies were carried out for PVA-PEG- x mol % $\text{Mg}(\text{NO}_3)_2$ ($x = 0, 10, 20$ and 30) polymer electrolyte films. Conductivity measurements were carried out over the same frequency range for temperatures ranging from room temperature to 373 K. The conductivity cell with connecting lead wires were placed in an oven with temperature control facilities.

3. Results and discussion

3.1 Impedance analysis

Impedance spectroscopy is a relatively new and powerful method of characterizing many of the electrical properties of electrolyte materials and their interfaces with electronically conducting electrodes. Impedance plot (plot between real and imaginary parts of impedance) for PVA-PEG- $\text{Mg}(\text{NO}_3)_2$ polymer blend electrolytes at room temperature are shown in figure 1(a, b).

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 point where the semi-circle intersects the real axis (Z') gives the value of bulk resistance (R_b). By knowing the value of bulk resistance (R_b) along with the dimensions of the sample, the conductivity of the sample has been calculated by using the relation

$$\sigma = d/R_b A,$$

where d is the thickness of the polymer electrolyte film and A the surface area of the film. It has been found that PVA-PEG- $\text{Mg}(\text{NO}_3)_2$ (35-35-30) has the highest room temperature conductivity of 9.63×10^{-5} S/cm. The conductivity values are shown in table 1.

3.2 Conductivity analysis

Figure 2 shows conductivity values of PVA-PEG- $\text{Mg}(\text{NO}_3)_2$ complexes as a function of salt concentration at 0, 10, 20 and 30 mol % in the temperature range 303-373 K.

As a general trend, in many studies for the dependence of salt concentration on the ionic conductivity in solid polymer electrolytes at low salt concentrations, the conductivity increases due to build-up of charge carriers. And at high salt concentrations, the conductivity decreases due to build-up of charge carriers offset by the retarding effect of ion cloud. In these studies, the conductivity increases with increase in magnesium salt concentration and also with temperature. The same behaviour was also observed in PVA-Cu(NO_3)₂

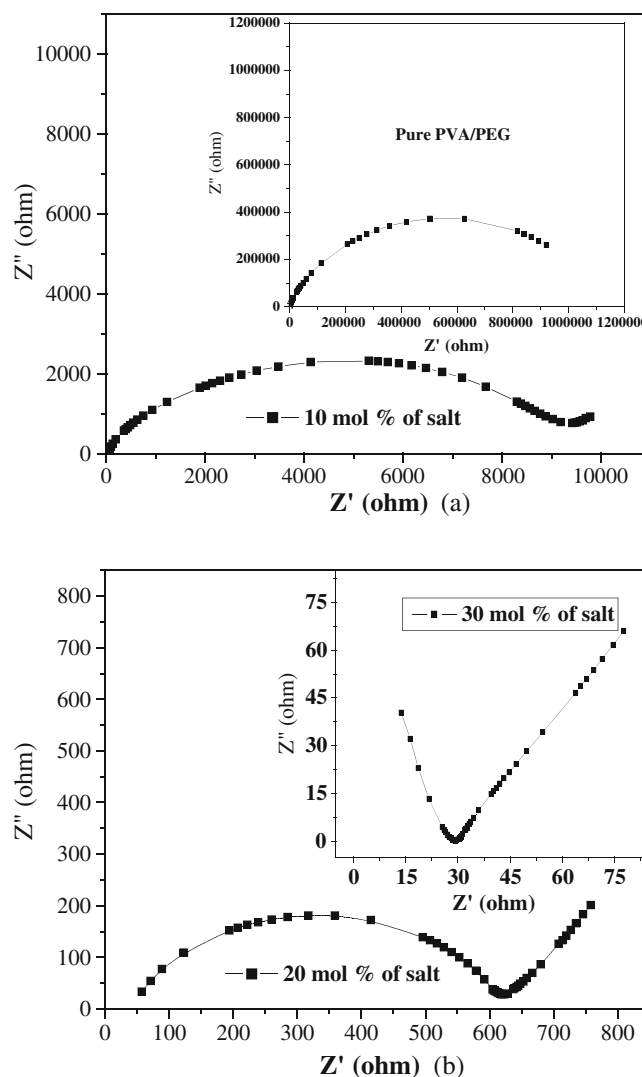


Figure 1. a-b. Impedance plots for PVA-PEG- $\text{Mg}(\text{NO}_3)_2$ doped with different concentrations of $\text{Mg}(\text{NO}_3)_2$ at 303 K.

polymer electrolytes (Ramya *et al* 2005). The maximum conductivity of 1.71×10^{-3} S/cm was obtained for the system PVA-PEG- $\text{Mg}(\text{NO}_3)_2$ (35-35-30) at 373 K. The high ionic conductivity in an electrolyte is attributed to increased ionic mobility and increased ionic charge carrier concentration.

Figure 3 shows the plot between $\log f$ and $\log \sigma$ for all the samples at room temperature. The curves consist of two different regions.

The first region observed at low frequencies corresponds to the frequency independent conductivity. This conductivity value has been assigned to the bulk conductivity of the sample. In the high frequency region, the conductivity increases with frequency. The extrapolation of the plateau region to the Y -axis gives the values of σ_{dc} . The maximum conductivity has been found to be 9.63×10^{-5} S/cm at 303 K for PVA-PEG- $\text{Mg}(\text{NO}_3)_2$ (35-35-30) polymer blend electrolyte.

The ionic conductivity of the polymer blend electrolytes have been measured by impedance spectroscopy from 303 K to 373 K. Figure 4 shows the variation of conductivity as a function of inverse temperature for the polymer electrolyte at various concentrations of $Mg(NO_3)_2$. Linear relations are observed in all polymer electrolytes and this meant that there is no phase transition in polymer matrix by the addition of salt in the temperature range studied. These results suggested that there is no dynamic conformational change in polymer matrix.

The temperature dependence of d.c. conductivity studied from conductivity spectra has been found to obey Arrhenius relation

$$\sigma = \sigma_0 \exp(-E_a/KT),$$

where σ_0 is the pre-exponential factor, E_a the activation energy and K the Boltzmann constant.

The experimental data indicate that the ionic conductivity of all the samples is enhanced with increase of temperature. When the temperature is increased, the mobility of polymer chain is enhanced, and fraction of free volume in the polymer electrolyte system increases accordingly, which facilitates the translational motion of ions. The segmental motion either allows the ions to hop from one site to another site or provides a pathway for ions to move. Hence, the ionic motion in the polymer electrolyte is due to hopping of ions from one site to another site and the dynamic segmental motion of the polymer, which leads to an increase in the ionic conductivity of the polymer electrolyte.

3.3 Dielectric analysis

Figures 5 and 6 show the plots of dielectric constant, ϵ' and dielectric loss, ϵ'' against $\log f$ of PVA-PEG- $Mg(NO_3)_2$

Table 1. Ionic conductivity values of PVA/PEG- $Mg(NO_3)_2$ polymer blend electrolytes at different temperatures.

Temperature (K)	Ionic conductivity (S/cm)			
	0 mol % of salt	10 mol % of salt	20 mol % of salt	30 mol % of salt
303	3.38×10^{-9}	3.65×10^{-7}	5.37×10^{-6}	9.63×10^{-5}
313	8.63×10^{-9}	5.42×10^{-7}	9.05×10^{-6}	1.21×10^{-4}
323	1.49×10^{-8}	9.62×10^{-7}	1.59×10^{-5}	1.90×10^{-4}
333	3.23×10^{-8}	1.78×10^{-6}	2.79×10^{-5}	3.28×10^{-4}
343	9.30×10^{-8}	2.58×10^{-6}	6.11×10^{-5}	6.15×10^{-4}
353	2.38×10^{-7}	3.04×10^{-6}	1.46×10^{-4}	8.11×10^{-4}
363	4.99×10^{-7}	6.51×10^{-6}	1.64×10^{-4}	1.17×10^{-3}
373	8.71×10^{-7}	1.32×10^{-5}	2.41×10^{-4}	1.71×10^{-3}

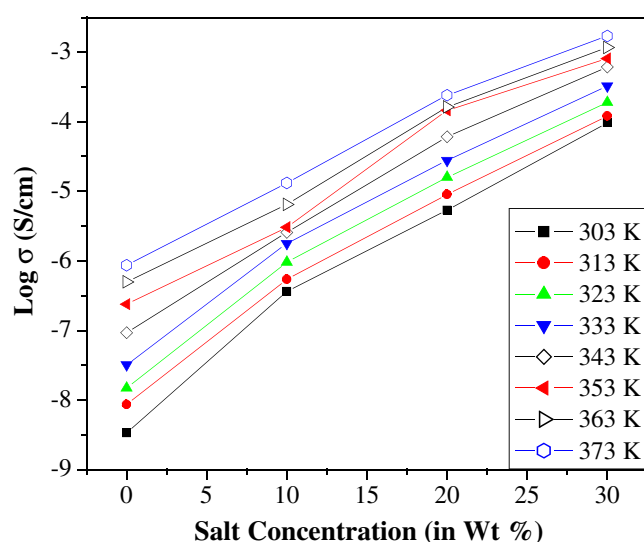


Figure 2. Composition dependence conductivity of PVA-PEG- $Mg(NO_3)_2$ system at various temperatures.

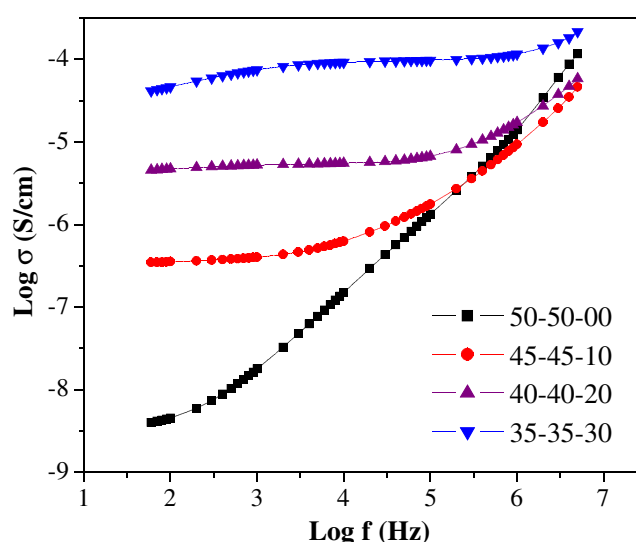


Figure 3. Conductance plot for different compositions of PVA-PEG- $Mg(NO_3)_2$ polymer electrolytes at 303 K.

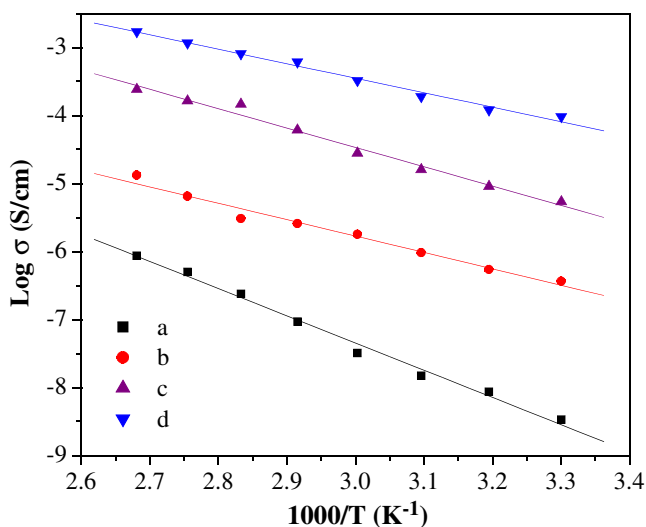


Figure 4. Temperature dependence of ionic conductivity of PVA–PEG–Mg(NO₃)₂: a. (50–50–00), b. (45–45–10), c. (40–40–20) and d. (35–35–30).

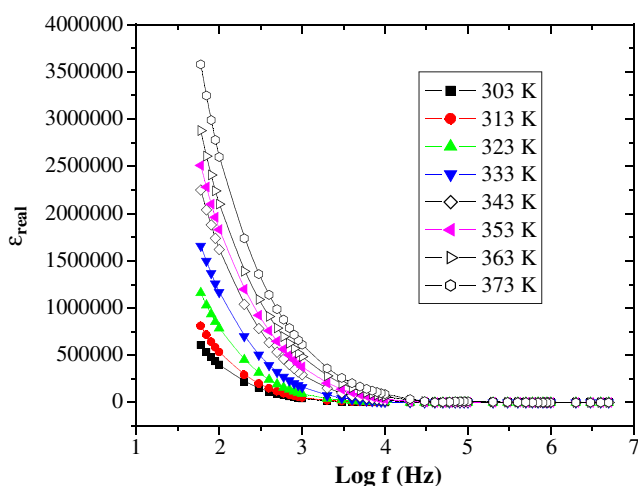


Figure 5. Typical plots of variation of real part of dielectric constant with frequency for sample 30 mol % of salt at different temperatures.

(35–35–30) at different temperatures. From the plots it is clear that the values of ϵ' and ϵ'' decreases with increasing frequency and reaches a constant value at higher frequencies. The values of ϵ' and ϵ'' are high at lower frequencies, but as the frequency of the field is increased the values begin to decrease which could be due to the dipoles not being able to follow the field variation at higher frequencies and also due to the polarization effects. The low frequency dispersion region is attributed to the 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 the field.

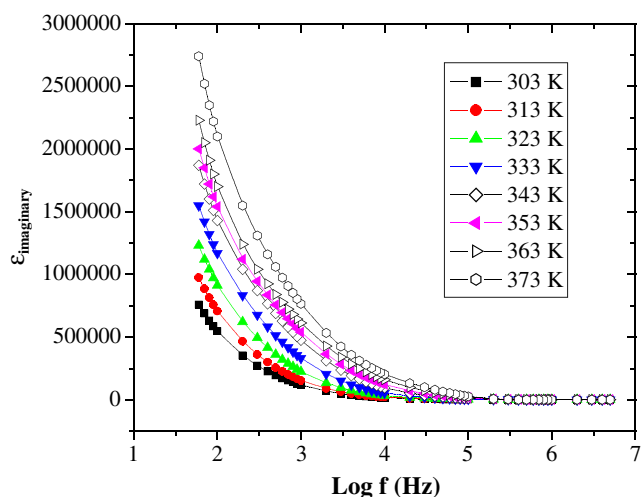


Figure 6. Typical plots of variation of imaginary part of dielectric constant with frequency for sample 30 mol % of salt at different temperatures.

The variation of dielectric permittivity with temperature is different for polar and non-polar polymers. In general, for polar polymers the dielectric permittivity increases with increasing temperature. But in case of non-polar polymers the dielectric permittivity is independent of temperature (Tareev 1979). This behaviour is typical of polar dielectrics in which the orientation of dipoles is facilitated with rising temperature and thereby the permittivity is increased.

4. Conclusions

The PVA–PEG based polymer blend electrolytes was prepared by a simple solvent casting technique. The maximum ionic conductivity of 9.63×10^{-5} S/cm is observed when the polymer blend electrolyte is complexed with 30 mol % of magnesium nitrate at room temperature. The conductance spectrum shows two distinct regions: a d.c. plateau (low frequency region) and a high frequency dispersive region. The dependence of the ionic conductivity on temperature is linear on a logarithmic scale. It obeys the Arrhenius plots of conductivity. The dielectric studies show that the polymers are polar in nature.

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