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Conductivity & Dielectric Behavior of Pure & Mn^{2+} Doped Poly (Vinyl Chloride) Solid Polymer Electrolyte Films

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Abstract

Solid polymer electrolytes (SPEs) consisting of poly (vinyl chloride) complexed with $MnSO_4$ have been synthesized by solution casting method. The ionic conductivity, dielectric response of the SPE system is studied within the frequency range 100 Hz – 2 MHz. The electrical conductivity was evaluated from ac impedance spectroscopy studies in the temperature range 303-363 K and the conductivity was found to increase with increasing temperature. The maximum ionic conductivity value 1.36 $x10^{-4}$ S/cm has been observed for 5 mol% at 363 K using impedance spectroscopy technique. Dielectric relaxation studies of the polymer electrolyte have been undertaken and the results are discussed. It is observed that magnitude of dielectric permittivity is high in the lower frequency region due to electrode polarization (EP) effect.

Keywords: PVC, ac impedance, Dielectric studies

I. INTRODUCTION

Solid polymer electrolytes (SPEs) are playing a vital role in the fabrication of rechargeable batteries, electrochemical cells, supercapacitors, solar cells, and specific ion sensors [1-5]. Solid polymers have better mechanical strength than those of liquid and gel polymer electrolytes. SPE are synthesized using solution casting which facilitates fabrication in desired geometry. SPE also offers good contact between electrolyte and electrode [6-10]. The ion conducting polymer electrolytes are formed by the dissolution of alkali metal salts into the various polymer hosts. Dielectric or electrical insulating materials are understood as the materials in which electrostatic fields can persist for a long time. These materials offer a very high resistance to the passage of electric current under the action of the applied direct-current voltage and therefore sharply differ in their basic electrical properties of conductive materials. Layers of such substances are commonly inserted into capacitors to improve their performance, and the term dielectric refers specifically to this application.

The use of a dielectric in a capacitor presents several advantages. The simplest of these is that the conducting plates can be placed very close to one another without risk of contact. Also, if subjected to a very high electric field, any substance will ionize and become a conductor. Dielectrics are more resistant to ionization than air, so a capacitor containing a dielectric can be subjected to a higher voltage. Also, dielectrics increase the capacitance of the capacitor. An electric field polarizes the molecules of the dielectric producing concentrations of charge on its surfaces that create an electric field opposed (antiparallel) to that of the capacitor. Thus, a given amount of charge produces a weaker field between the plates than it would without the dielectric, which reduces the electric potential. Considered in reverse, this argument means that, with a dielectric, a given electric potential causes the capacitor to accumulate a larger charge.

Poly (vinyl chloride) (PVC) can act as a mechanical stiffener in the electrolyte due to its immiscibility with the plasticizer. Poly(vinyl chloride) (PVC) is one of the most important commercial polymers that have wide a range of applications. PVC is a linear, thermoplastic and substantially amorphous polymer, with a huge commercial interest due to the accessibility to basic raw materials and its properties. It is used as thermoplastic due to its many valuable properties like low price, good process ability, chemical resistance, good mechanical strength, thermal stability and low flammability [11].Currently, PVC is one of the world's leading synthetic polymers with global consumption of above 40 million tonnes per annum [12]. The major aim of this study is to investigate a wide range of the electrical properties of PVC films by doping with different concentrations of Mn^{2+} and at different temperatures.

II. EXPERIMENTAL PART

Poly(vinyl chloride) (PVC) has a mean relative molecular mass of about 5,34,000 g/mol. PVC polymer films doped with $MnSO_4$ in various concentrations were prepared at room temperature by solution cast method. The desired concentration of $MnSO_4$ solutions (1, 2, 3, 4 and 5 mol%) were prepared by using distilled water. 1g/mol of PVC polymer is dissolved in tetrahydrofuran (THF) separately. Different amounts of $MnSo_4$ solution (1, 2, 3, 4 and 5 mol%) was added into the polymer solution. The mixture solution was magnetically stirred for 10-12 hours to get the homogeneous mixture and then cast onto poly propylene dishes. The film was slowly evaporated at room temperature to obtain free standing polymer film at the bottom of the dishes.

In order to investigate the nature of the polymer films, the electrical conductivity of polymer complexes was performed by using Hioki 3532-50 LCR Hi-Tester interfaced to a computer in the frequency range 100 Hz -2 MHz and temperature range 303-363.

III. DIELECTRIC PROPERTIES

The study of the dielectric constant of a material gives an outline of the nature of atoms, ions and their bonding in the material. From the analysis of the dielectric constant and dielectric loss as a function of frequency and temperature, the different polarization mechanism in solids can be understood. The dielectric constant and dielectric loss of pure and $MnSO_4$ doped PVC films were determined using Multi-frequency LCR meter. Figure 1 shows the plot of the dielectric constant (ε) versus frequency at room temperature. It is seen that the value of the dielectric constant is high in the lower-frequency region and then it decreases with an increase in the frequency. The high value of the dielectric constant in the low frequency region is attributed to space charge polarization, due to the charged lattice defects [13]. Figure 1, the low value of di- electric loss at high frequency suggests that the grown crystals possess good optical quality. This parameter is of vital importance for nonlinear optical materials in their applications [14]. From the figure 2, it is observed that the value of ε'' decreases monotonically with increment in the values of frequency at room temperature. As the frequency increases further, it resulted in further decrease in ε'' and reached a constant value pertaining to higher frequencies applied to the sample up to 10^6 Hz. From this, it is evident that a large ε' values are observed at low frequencies. At these low frequencies, dipoles follow the field direction and the values of ε' are found to be very high due to the EP phenomenon [15]. At moderate frequencies, dipoles begin to lag behind the field so the values of ε' start to decrease. However, in the high-frequency range dipoles cannot orient themselves in the applied electric field direction and hence the values of ε' reach its minimum values [16]. From Figure 3, 1 mol% Mn^{2+} doped PVC electrolyte it is observed that the ε' gradually increase with temperature, which is attributed to migration and interfacial polarization of Mn^{2+}. This type of trend is observed in the polar dielectrics in which orientation of dipoles facilitated with increasing temperature and thereby the values of ε' are increased.

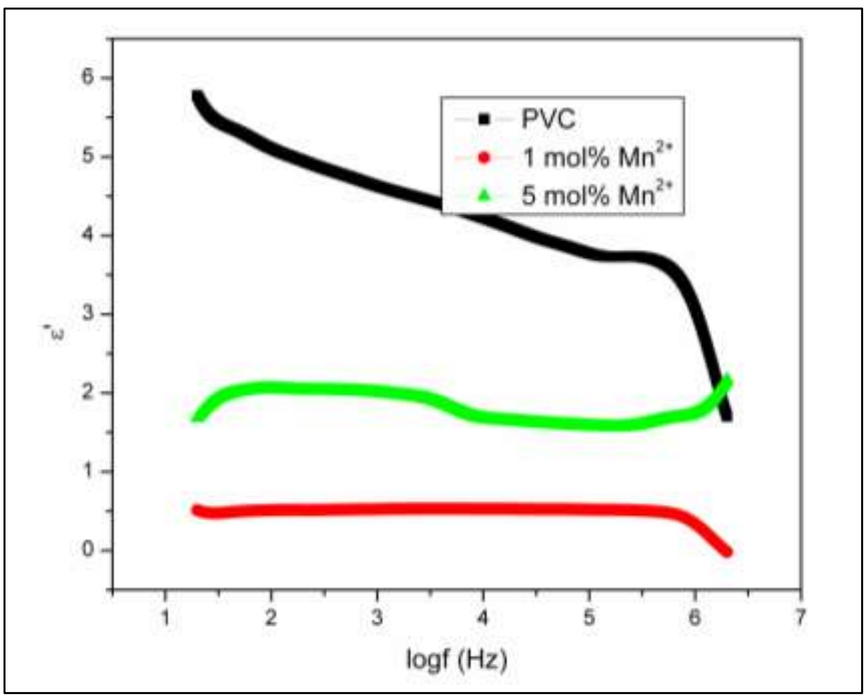

Fig. 1: Variation of real part of dielectric constant with frequency of Mn^{2+} doped PVC electrolytes at 303K

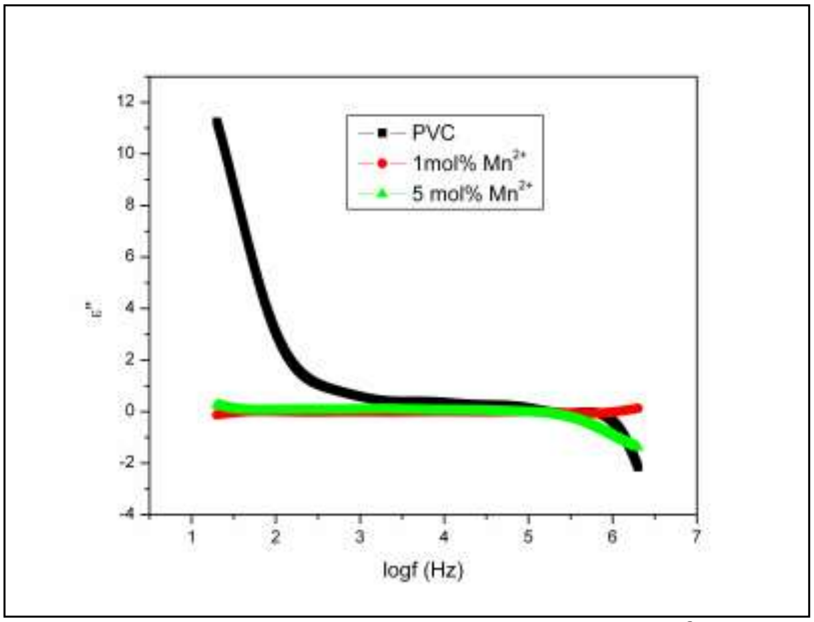

Fig. 2: Variation of Imaginary part of dielectric constant with frequency plots of Mn^{2+} doped PVC electrolytes

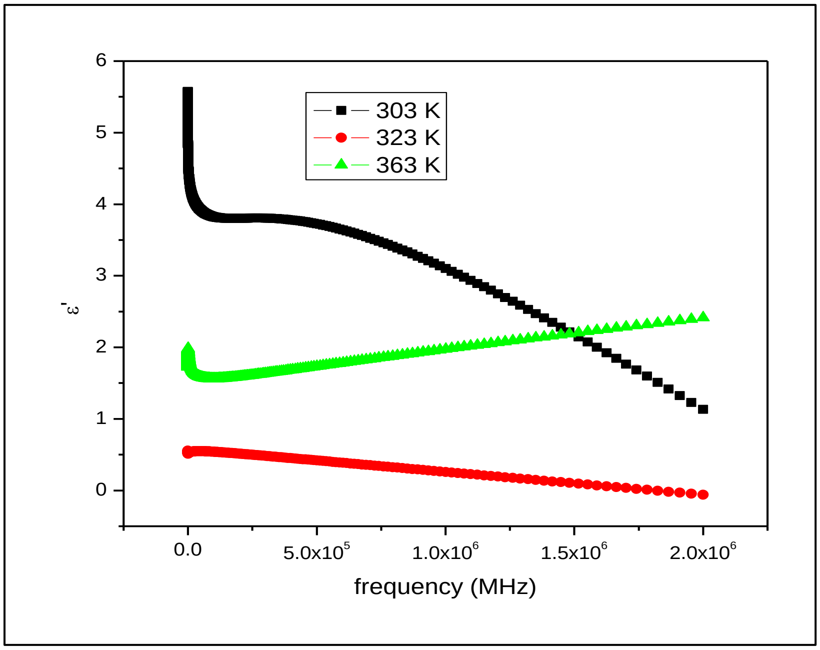

Fig. 3: Dielectric constant vs. frequency plots of 1 mol% Mn^{2+} doped PVC electrolytes at different temperatures

IV. IMPEDANCE ANALYSIS

Impedance spectroscopy is employed to establish the conduction mechanism, observing the participation of the polymeric chain, mobility and carrier generation processes. The conductivities of the polymer complexes were calculated from bulk resistance obtained by the intercepts of the typical impedance curves for room temperature. The impedance curves of PVC doped $MnSO_4$ (1 and 5 mol%) are shown in figure 4. The disappearance of the semicircle portion in the impedance curve leads to a conclusion that the current carriers are ions and this leads one to further conclude that total conductivity is mainly the result of ion conduction [17]. Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity. Hence, the increment of composition causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility. The ionic conductivity was calculated from

$$\sigma = \frac{l}{R_b A} \qquad \text{…………… (1)}$$

where l and A represents the thickness and area of the film. R_b is the bulk resistance of the electrolyte obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance.

From Figure 5, an inclined straight line in the low frequency region is due to the dominance of electrode polarization (EP) effect. The semi-circle is not observed in high frequency region. However, it is known that the region below the intercept represents the impedance due to EP effect while above the intercept gives the impedance due to bulk of the SPE. Figure 6, 5 mol% Mn^{2+} doped PVC electrolyte at 363 K shows Z′ values decreased sharply with increase in frequency and display characteristic dispersion at low frequencies.

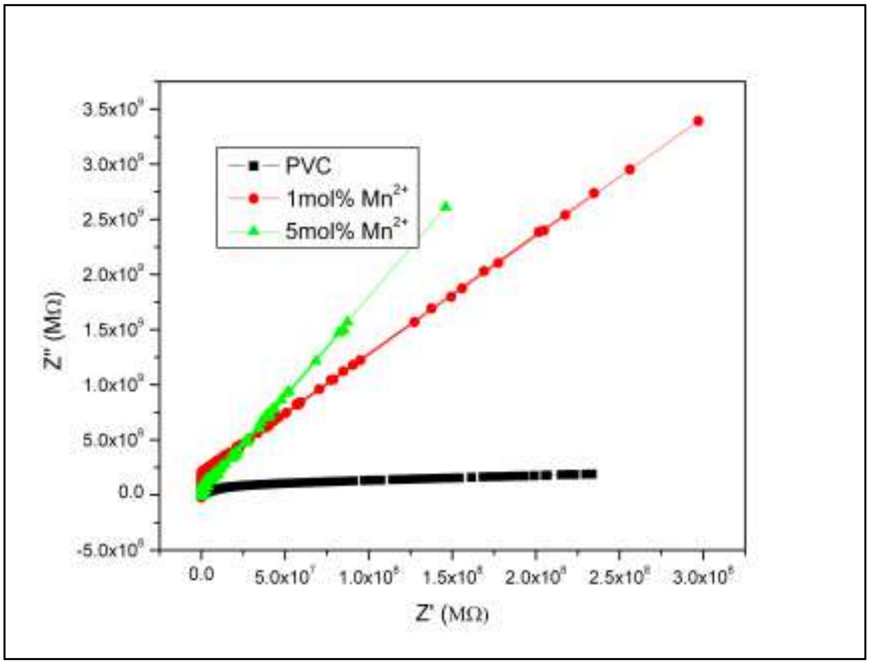

Fig. 4: Nyquist plots of Mn^{2+} doped PVC polymer electrolyte at different compositions at 303 K

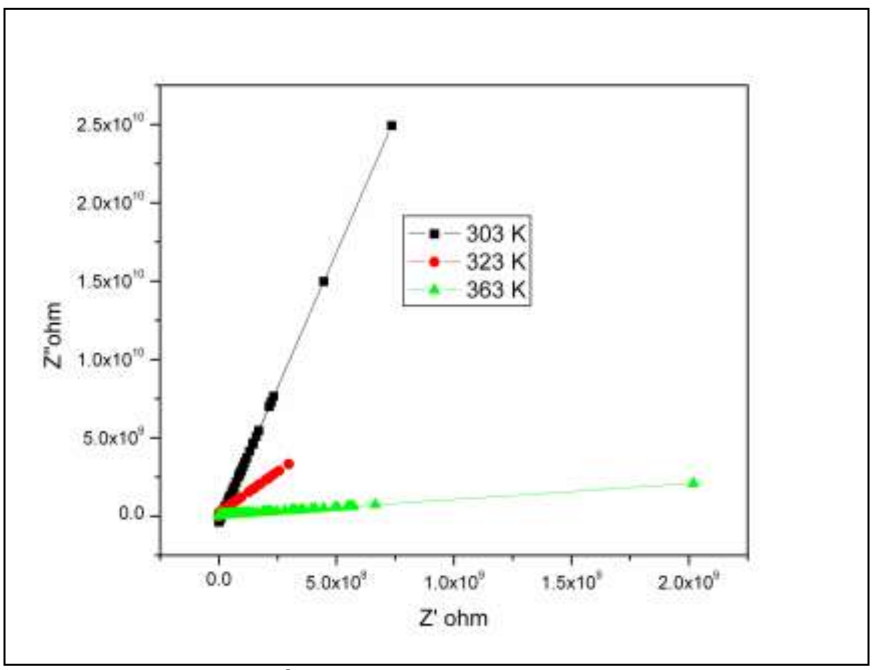

Fig. 5: Nyquist plots of Mn^{2+} doped PVC polymer electrolyte at different temperatures

From the Table 1, it is depicted that the maximum conductivity value 1.36 x 10^{-4} S/cm at 363 K is observed. The maximum conductivity 0.95 x 10^{-4} S/cm at room temperature with good mechanical stability has been observed for 5mol% Mn^{2+} system among the various compositions studied. Figure 7, shows the conductivity versus temperature inverse plots of Mn^{2+} doped PVC polymer electrolytes respectively. The Figure 7 shows that the ionic conduction in all polymer electrolyte system obeys the VTF (Vogel – Tammam- Fulcher) relation, which describes the transport properties in a viscous matrix [18]. It supports the idea that the ions move through the plasticizer rich phase, which is the conductivity medium and involves.

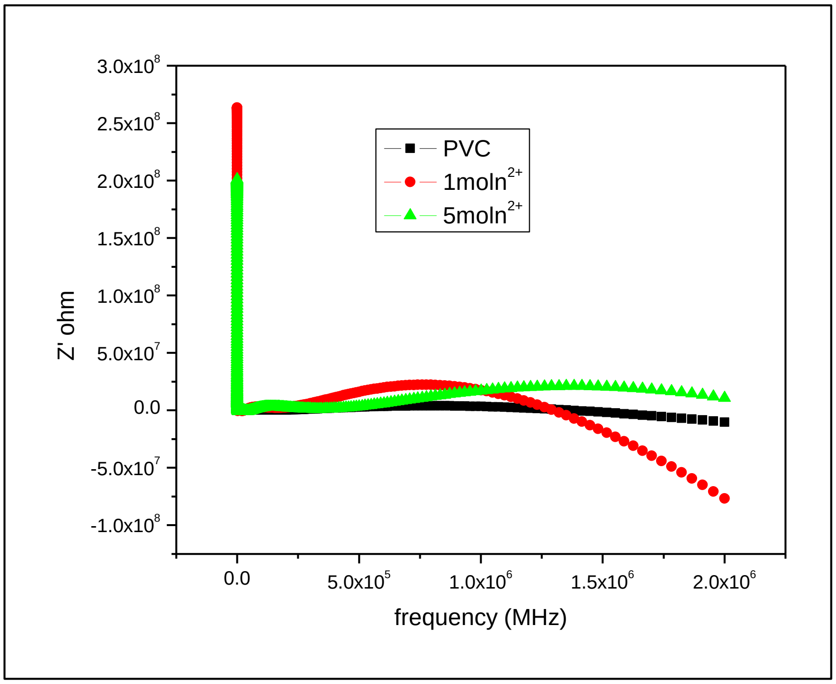

Fig. 6: Typical impedance vs. Frequency plot of $MnSO_4$ doped PVC films at 363 K

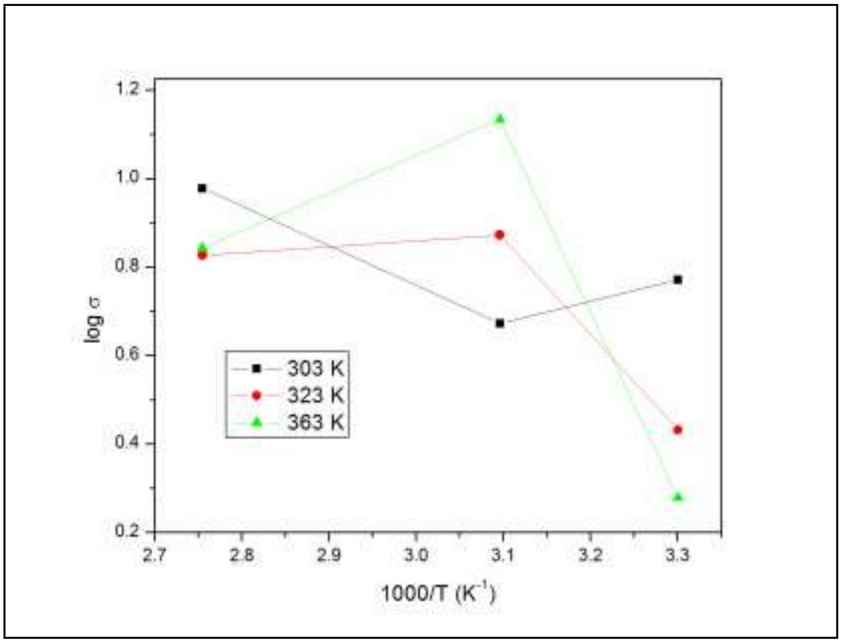

Fig. 7: Variation of ac conductivity with temperature of MnSO4 doped PVC films at different temperatures

Table – 1
Ionic conductivity values of PVC complexed with $MnSO_4$

Composition	*Ionic conductivity values of PVC doped Mn^{2+} ($*10^{-4}$ S/cm)*		
	303	*323*	*363*
Pure	*0.59*	*0.35*	*0.19*
1 mol	*0.47*	*0.62*	*1.36*
5 mol	*0.95*	*0.23*	*0.69*

V. CONCLUSIONS

PVC based polymer electrolytes were prepared by solvent cast technique. All electrolytes show appreciable conductivity even at room temperature. Maximum conductivity (1.36 x10^{-4} S/cm) at 363 K temperature with good mechanical stability has been observed for PVC doped 1mol% $Mn^{2+.}$ The maximum conductivity 0.95 x 10^{-4} S/cm at room temperature with good mechanical stability has been observed for 5mol% Mn^{2+} system among the various compositions studied. The dielectric relaxation of the samples was also discussed. Large magnitudes of values are observed in the low frequency region is due to EP effect.

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