

Short communication

# Vibrational, ac impedance and dielectric spectroscopic studies of poly(vinylacetate)–*N,N*–dimethylformamide–LiClO<sub>4</sub> polymer gel electrolytes

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## Abstract

Polymer electrolyte membranes that consist of poly(vinyl acetate) (PVAc) and LiClO<sub>4</sub> with different concentrations of plasticizer (*N,N*-dimethylformamide (DME)) have been prepared by a solution-casting technique. The formation of polymer-salt complexes has been confirmed by FT-IR spectral studies. Conductivity studies have been carried out using ac impedance spectroscopy in the frequency range 42 Hz–5 MHz. The influence of the addition of plasticizer (DMF) on the ionic conductivity of the PVAc–LiClO<sub>4</sub> polymer electrolyte complex has been discussed. The maximum value of bulk conductivity for PVAc(70)–DMF(20)–LiClO<sub>4</sub>(10) system is found to be  $4.2 \times 10^{-4} \text{ S cm}^{-1}$  at 303 K. The temperature dependence of the conductivity of the polymer electrolytes follows the Vogel–Tamman–Fulcher relationship. Transport properties, such as activation energy and charge carrier concentration, have been calculated from the VTF formalism. The ionic transference number of the mobile ions has been estimated by Wagner's polarization method and is found to be  $\geq 0.96$  for all the samples.

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**Keywords:** Poly(vinylacetate) based gel electrolytes; FT-IR studies; Ionic conductivity; Vogel–Tamman–Fulcher relationship; Dielectric studies; Ionic transference number

## 1. Introduction

Polymer electrolytes are of technological interest due to their possible applications in rechargeable batteries chemical sensors, fuel cells and electrochromic display devices [1,2]. The main advantages of polymer electrolytes are their good mechanical properties, the ease of fabrication of films of desirable sizes, and their ability to form good electrode–electrolyte contact. To date, several classes of polymer electrolytes have been developed and characterized. In particular, Gel Polymer Electrolytes (GPE) are reported to be suitable for electrochemical devices since their transport properties are quite exceptional and they have an ionic conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$  [3], an electrochemical stability window exceeding 4.5 V [3] and lithium-ion transference numbers averaging 0.9 [3]. These electrolytes comprise polymers such as poly(acrylonitrile) (PAN), poly(vinyl pyrrolidone) (PVP), which are plasticized with solutions of

lithium salts in organic solvents of low molecular weight for example, ethylene carbonate (EC), propylene carbonate (PC), *N,N*-dimethylformamide (DMF),  $\gamma$ -butyrolactone and their mixtures. The addition of plasticizer to the polymer electrolyte decreases the glass transition temperature of the polymer and softens the polymer backbone, which results in high segmental motion and thus increases the ionic conductivity. Further, the high dielectric constant of the plasticizer gives rise to the dissociation of salt and provides free ions. The low viscosities of these plasticizers also lead to high ionic mobility that, in turn, enhances conductivity [4]. Sung et. al [5] have investigated the ionic conductivity, electrochemical stability and interfacial properties of poly(vinyl chloride-co-vinylacetate) based gel electrolytes.

In the present study, gel polymer electrolytes are synthesized by adding 10–20 wt.% of plasticizer (DMF) to the host polymer poly(vinyl acetate) (PVAc) with constant LiClO<sub>4</sub> salt concentration. The effect of DMF in PVAc–LiClO<sub>4</sub> on Li<sup>+</sup> ionic conductivity is analyzed by using impedance and dielectric spectroscopy. Transport number measurements are performed to reveal the conducting species, and the Li<sup>+</sup> ion dynamics of the plasticized polymer electrolytes are

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Table 1  
VTF parameters and mechanical properties for (90)PVAc–DMF–LiClO<sub>4</sub>(10) electrolyte compositions

Various PVAc/DMF ratios	A (S cm <sup>-1</sup> K <sup>1/2</sup> )	Activation energy, E <sub>a</sub> (eV)	Mechanical properties
90:00	0.36	0.049	Free-standing stable films
80:10	1.71	0.048	Free-standing stable films
75:15	4.29	0.044	Free-standing less stable films
70:20	4.86	0.033	Free-standing gel films

examined. FT-IR spectral studies are carried out to confirm the polymer–plasticizer–salt complex formation.

## 2. Experimental

PVAc (Himedia) and LiClO<sub>4</sub> (Himedia) were dried by heating under vacuum at 100 °C and 120 °C for 12 h and 10 h, respectively. The plasticizer was DMF (E-Merck) and tetrahydrofuran (THF, S.d. Fine. Chem. Ltd.) was used as the solvent. Gel samples of PVAc–DMF–LiClO<sub>4</sub> in different weight ratios have been prepared by the solution-casting technique. Appropriate weights of PVAc and LiClO<sub>4</sub> (Table 1) were dissolved in THF followed by the addition of DMF. The solution was then stirred continuously until the mixture became homogeneous viscous liquid. Solutions of different compositions were poured into identical Petri glass dishes of 10 cm diameter. The films are dried in a vacuum chamber at room temperature for 24 h. The polymer films were further dried in a vacuum chamber at 60 °C for 5 h to remove any traces of solvent (THF) and then stored in sealed containers in a desiccator. Gel-like and solvent-free polymer electrolyte films with thickness of 1–2 mm were obtained. FT-IR measurements were made with a Shimadzu-8000 spectrophotometer instrument in the wave number range of 4000 to 400 cm<sup>-1</sup>. Electrolytic conductivity was determined from ac impedance measurements using a HIOKI 3532 LCR meter in the frequency range 42 Hz to 5 MHz over temperature range from 303 to 373 K. The cell arrangement used for the conductivity measurement consists of two aluminium electrodes, which act as blocking electrodes for Li<sup>+</sup> ions.

## 3. Results and discussion

### 3.1. FT-IR spectral studies

FT-IR spectroscopy is used to analyse the interactions among atoms or ions in electrolyte systems. The FT-IR spectra of pure PVAc, LiClO<sub>4</sub> and PVAc–DMF–LiClO<sub>4</sub> complexes of various compositions are shown in Fig. 1. The vibrational bands at 2923, 2865 and 1375 cm<sup>-1</sup> in the polymer complexes are ascribed to CH<sub>3</sub> asymmetric stretching,

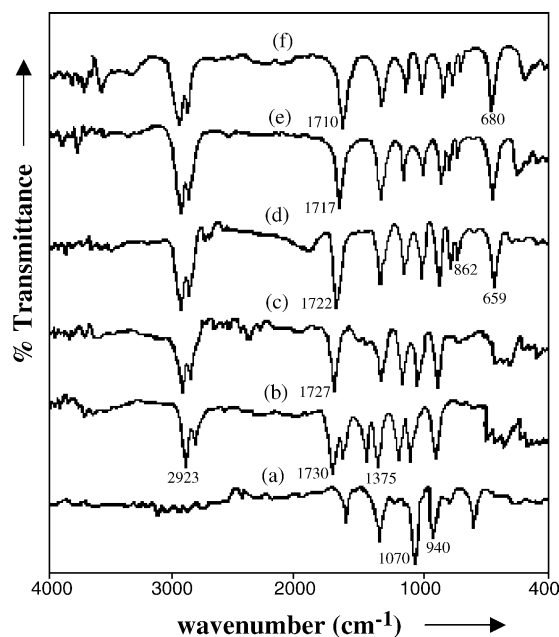


Fig. 1. FT-IR spectra of (a) LiClO<sub>4</sub> (b) pure PVAc (c) PVAc(90)–LiClO<sub>4</sub>(10), (d) PVAc(80)–DMF(10)–LiClO<sub>4</sub>(10), (e) PVAc(75)–DMF(15)–LiClO<sub>4</sub>(10), (f) PVAc(70)–DMF(20)–LiClO<sub>4</sub>(10).

symmetric stretching and symmetric bending vibrations of PVAc, respectively. The vibrational bands at 1245, 1100 and 1090 cm<sup>-1</sup> are ascribed to C–O–C symmetrical stretching, C–O and C–C stretching vibrations of PVAc, respectively. The vibrational peaks at 1620, 1320, 1070, 940 and 750 cm<sup>-1</sup> are ascribed to LiClO<sub>4</sub>.

The stretching frequency at 1730 cm<sup>-1</sup> which corresponds to C=O of pure PVAc, is shifted to (1727–1710 cm<sup>-1</sup>) in the complexes. The shift observed in the carbonyl stretching frequencies of complexes when compared to pure PVAc indicates complex formation. The addition of LiClO<sub>4</sub> causes a small decrease (5–7 cm<sup>-1</sup>) of the C–O–C stretching down to lower wave numbers due to the co-ordination of oxygen with the lithium cation which causes the change in the glass transition temperature, T<sub>g</sub>. A similar effect has been reported by Wiczorek and Stevens [6] for the polyether–poly(methyl methacrylate) based system. The O=C–N deformation mode of DMF at 659 cm<sup>-1</sup> is sensitive to the salt present in the plasticized polymer complex. The plasticizer–salt interaction takes place between the Li<sup>+</sup> of the salt and the oxygen atom of the O=C–N group of the plasticizer, which affects the stretching mode of the O=C–N group at 659 cm<sup>-1</sup>. The changes in the intensity of the band at 659 cm<sup>-1</sup> and its shift to higher wave numbers may be due to the interaction of the salt with the O=C–N group of the DMF spectrum. The same phenomenon was reported for the DMF plasticized PVdF polymer complex system by Jacob and Arof [7]. The splitting of the C–N symmetric stretching vibration of the plasticizer into a doublet at 862 and 884 cm<sup>-1</sup> is evidence of plasticizer–polymer interaction.

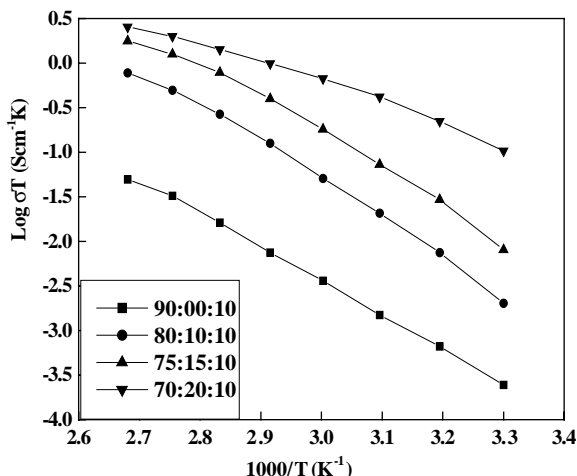


Fig. 2. Arrhenius plot for PVAc–DMF–LiClO<sub>4</sub> of various compositions.

The vibrational bands of PVAc (2923, 1375, 1090 and 940 cm<sup>-1</sup>) and LiClO<sub>4</sub> (1070 and 940 cm<sup>-1</sup>) are shifted in the polymer electrolyte complexes. The vibrational bands ascribed to PVAc (1625 and 1410 cm<sup>-1</sup>) and LiClO<sub>4</sub> (1320, 1620 and 750 cm<sup>-1</sup>) are found to be absent in the polymer complexes. The broadening and shifting of the vibrational bands that correspond to pure PVAc in the plasticized polymer electrolyte system imply weak interaction between the polymer and the salt. The above analysis establishes the formation of polymer–salt complexes.

### 3.2. Temperature dependence of ionic conductivity

The variation of ionic conductivity,  $\sigma$  with reciprocal temperature for PVAc–LiClO<sub>4</sub> based polymer electrolytes with different amounts of the plasticizer DMF is shown in Fig. 2. The curvatures of the Arrhenius-type plots indicate that the ionic conduction obeys the Vogel–Tamman–Fulcher (VTF) relation [8], which describes the transport properties in a viscous matrix. The VTF relation supports the idea that the ions move through the plasticizer-rich phase, i.e.

$$\sigma = AT^{-1/2} \exp \left[ -\frac{E_a}{k(T - T_0)} \right] \quad (1)$$

where  $A$  is a fitting constant proportional to the number of charge carriers,  $E_a$  is a second fitting constant akin to an activation energy,  $k$  is the Boltzmann constant and  $T_0$  is the equilibrium temperature of the system corresponding to zero configuration entropy [9].  $T_0$  is found to be approximately equal to  $T_g - 50$  K, where  $T_g$  represents the thermodynamic glass transition temperature of the system [10]. In order to extract the VTF parameters  $A$  and  $E_a$ , the approximate values of  $T_0$  for all the electrolytes have been found. Given that  $T_g$  is related to the electrolyte melting point  $T_m$ , i.e.  $T_g \approx 2/3 T_m$  [10,11].

$T_0$  can be approximated as  $2/3 T_m - 50$  K. In this study, the melting point ( $T_m$ ) for all the electrolytes has been found and the approximate value of  $T_0$  (i.e.  $T_g$ ) has been

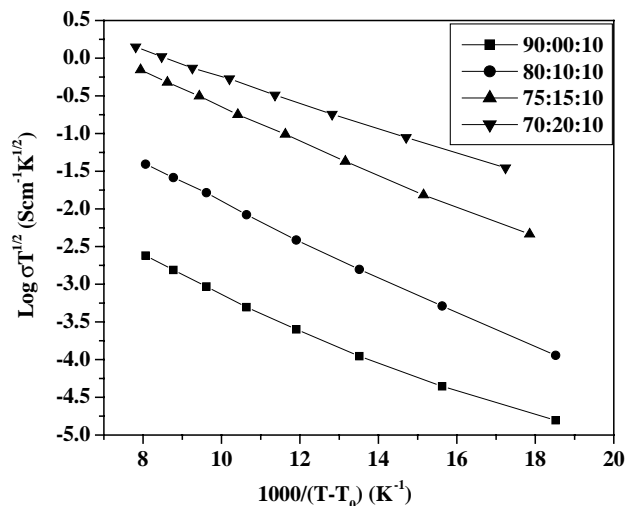


Fig. 3. VTF plots of ionic conductivity for PVAc–DMF–LiClO<sub>4</sub> gel polymer electrolytes of various compositions.

estimated. The linear relationship in the Fig. 3 confirms that the variation in conductivity with temperature follows a VTF relationship. The parameters  $A$  and  $E_a$  determined from the linear plots of  $\ln \sigma T^{1/2}$  versus  $1/(T - T_0)$  are listed in Table 1. It is seen that  $A$  rises significantly with increasing DMF concentration, which is related to the increase in number of charge carriers, on the other hand,  $E_a$  decreases probably because of a much lower electrolyte viscosity at high plasticizer concentrations which increases the ionic mobility. In polymer electrolytes, the change in conductivity with temperature has been explained [12,13] in terms of segmental motion that results in an increase in the free volume of the system that, in turn, would also facilitate the motion of ionic charge [14]. Thus, the segmental motion either permits the ions to hop from one site to another or provides a pathway for ions to move. In other words, the segmental movement of the polymer facilitates the transitional ionic motion. At high temperatures, the polymer chains acquire faster internal modes in which bond rotations produce segmental motion. This favours inter-chain and intra-chain ion movements and, accordingly, the conductivity of the polymer electrolyte becomes high [15].

The variation of activation energy and ionic conductivity with DMF content in the polymer electrolytes is presented in Fig. 4. The activation energy ( $E_a$ ) decreases with increasing DMF concentration, probably on account of lower electrolyte viscosity at high DMF content that increases the ionic mobility. The data also show that low activation energy and high ionic conductivity are features of the PVAc(70)–DMF(20)–LiClO<sub>4</sub>(10) polymer complex. This effect is due to the high charge carrier concentration in the 20 wt.% DMF ratio, regardless of the temperature. A similar effect has been reported by Renard et al. [16] for PVdF-based gel electrolytes. The VTF plots indicate that the plasticized polymer electrolytes have a higher ionic conductivity and lower activation energy compared with

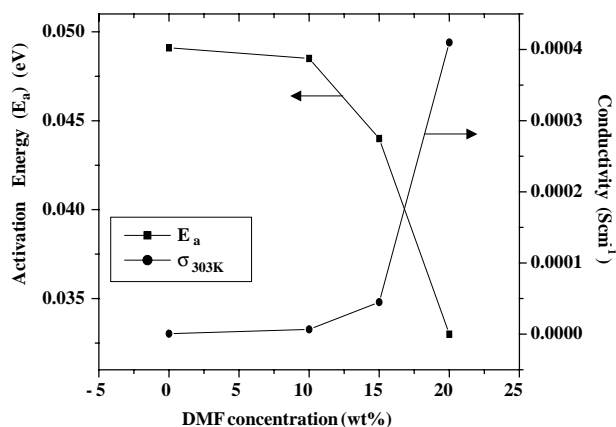


Fig. 4. Variation of conductivity and activation energy with DMF concentration.

the 90 wt.% PVAc–10 wt.%  $\text{LiClO}_4$ , solid type, polymer electrolyte.

### 3.3. Impedance analysis

Typical impedance plots ( $Z'$  versus  $Z''$ ) for all the polymer electrolytes at 303 K are given in Fig. 5. The plots show two

well-defined regions namely, a high frequency region semi-circle which is due to the bulk effect of the electrolytes and a linear region in the low-frequency range that is attributed to the effect of blocking electrodes. At low-frequency, the impedance plot should show a straight line parallel with the imaginary axis, but the double-layer at the blocking electrodes causes the curvature [17].

The low-frequency intercept on the  $Z'$  axis gives the bulk electrical resistance ( $R_b$ ) value. The bulk resistance decreases with addition of DMF in the polymer electrolyte. The improved ionic conductivity is due to enhancement of the ionic mobility and number of carrier ions, as many previous workers have already reported [18]. It is noted that the semicircle in the high frequency region gradually fades away as the content of DMF increases, and completely disappears in polymer electrolytes with more than 20 wt.% DMF. This result suggests that only the resistive component of polymer electrolyte can be considered, when the amount of the plasticizing electrolyte solution is high. Polymer electrolytes with low solvent contents can be considered as a homogeneous phase of the polymer plasticized by the aprotic solvent. In this case, the migration of ions may occur through the free volume of matrix polymer, which can be represented by a resistor. The

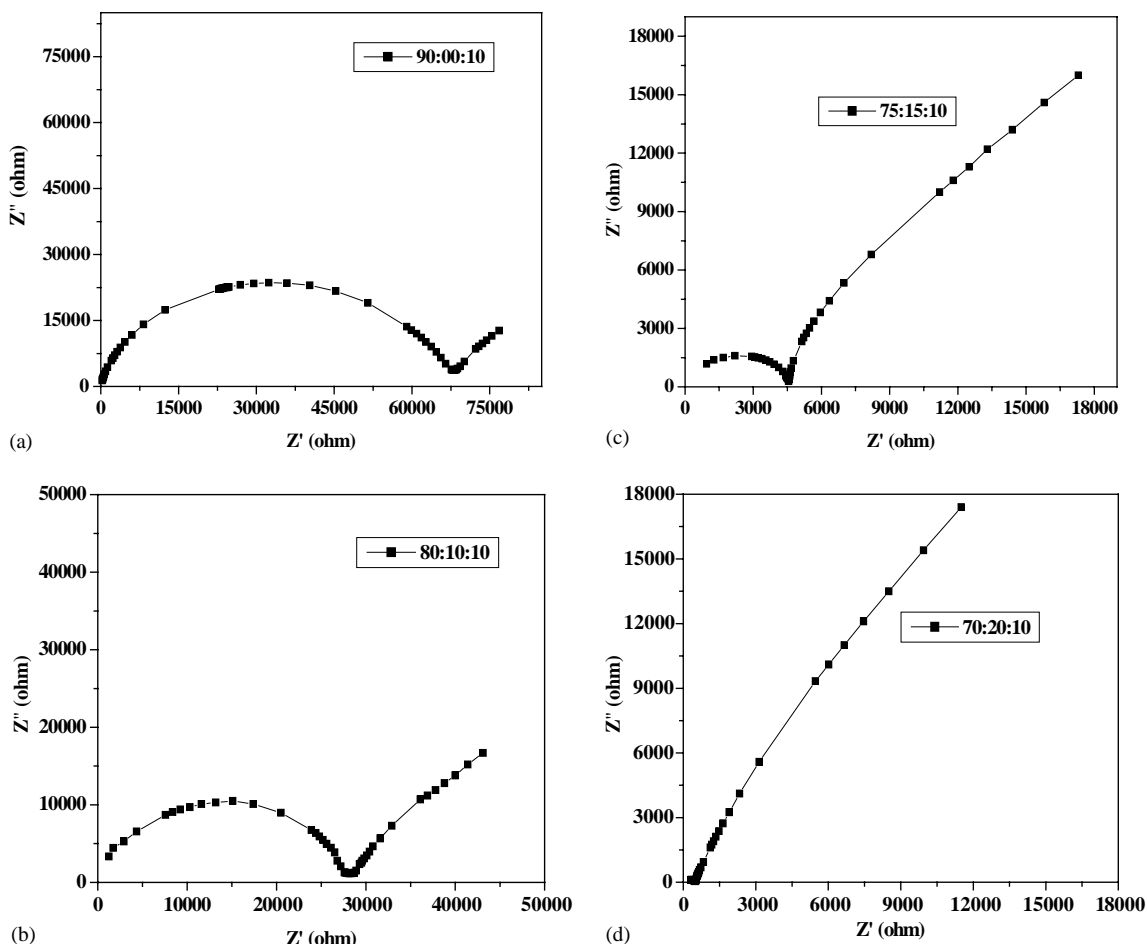


Fig. 5. Impedance plot of PVAc–DMF– $\text{LiClO}_4$  complexes at 303 K.

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, a semicircle at high frequency can be observed. As the amount of DMF increases, it is possible to construct a local effective pathway in polymer electrolytes for ionic conduction. As a result, ions can be transported quickly in the plasticizer-rich phase as the electric potential alternates between the positive electrode and the negative electrode in an ac field. Therefore, no capacitance effect occurs in polymer electrolytes with high contents of DMF.

The ionic conductivity is calculated using the equation  $\sigma = t/R_b A$ , where  $t$  is the thickness of the polymer electrolyte film and  $A$  is the surface area of the film. From the conductivity results, and from the data in Tables 1 and 2, it is clear that the addition of plasticizer has a remarkable effect on the transport properties of the electrolyte. The conductivity value of the PVAc(90)–LiClO<sub>4</sub>(10) is found to increase from  $7.6 \times 10^{-7}$  to  $4.1 \times 10^{-4}$  S cm<sup>-1</sup> on the addition of 10, 15 and 20 wt. % DMF. This result may be due to the formation of effective local pathways for ionic conduction. The addition of plasticizer also substantially reduces the  $T_g$  of the polymer, increases the segmental mobility, and thus enhances the conductivity. This enhancement of conductivity has been studied by many researchers [19,20].

### 3.4. Transference number measurements

The transference numbers corresponding to ionic ( $t_{ion}$ ) and electronic ( $t_{ele}$ ) transport has been evaluated in PVAc–DMF–LiClO<sub>4</sub> electrolyte systems by means of the Wagner polarization technique [21]. In this technique, the dc current is monitored as a function of time on application of a fixed dc voltage across the sample with blocking electrodes. The results of dc polarization measurements on the PVAc(70)–DMF(20)–LiClO<sub>4</sub>(10) electrolyte taken with aluminium blocking electrodes by applying a 1.0 V dc bias voltage at 333 K are shown in Fig. 6. The transference numbers are calculated from the polarization current versus time plot using the equations

$$t_{ion} = \frac{(I_i - I_f)}{I_i} \quad (2)$$

$$t_{ele} = \frac{I_f}{I_i} \quad (3)$$

where  $I_i$  is the initial current and  $I_f$  is the final residual current. The calculated data for the transport numbers are listed in Table 2. For all compositions of the PVAc–DMF–LiClO<sub>4</sub> electrolyte systems, the values of the ionic transference number ( $t_{ion}$ ) are in the range of 0.96–0.98. This suggests that charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from electrons.

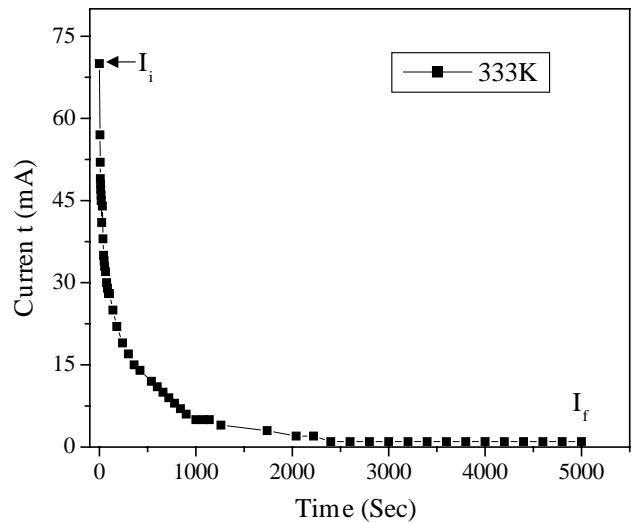


Fig. 6. Polarization current vs. time plots for PVAc(70)–DMF(20)–LiClO<sub>4</sub>(10) at 333 K.

### 3.5. Dielectric analysis

The complex permittivity ( $\epsilon$ ), or dielectric constant, of a system is defined by

$$\epsilon = \epsilon' - j\epsilon'' = \epsilon' - j \left( \frac{\sigma}{\omega\epsilon_0} \right) \quad (4)$$

where  $\epsilon'$  is real part of the dielectric constant,  $\epsilon''$  is the imaginary part of the dielectric constant of the material,  $\sigma$  is the conductivity,  $\omega$  is the angular frequency, and  $\epsilon_0$  is the permittivity of the free space. The  $\epsilon'$  versus  $\log f$  plots for all the PVAc–DMF–LiClO<sub>4</sub> gel electrolytes are given in Fig. 7. The  $\epsilon'$  values increase with the amount of DMF in the polymer electrolytes. The plasticized electrolyte exhibits a much higher  $\epsilon'$  value at room temperature. The high positive dielectric permittivity obtained in the plasticized

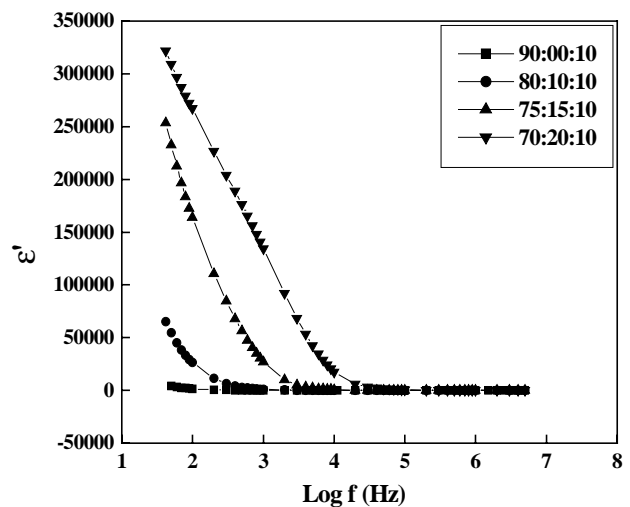


Fig. 7. Variation of  $\epsilon'$  as function of frequency for PVAc–DMF–LiClO<sub>4</sub> based electrolytes at 303 K.

Table 2  
Conductivity parameters of PVAc–DMF–LiClO<sub>4</sub> polymer complexes

PVAc–DMF–LiClO <sub>4</sub> compositions (wt.%)	Conductivity, $\sigma_b$ (S cm <sup>-1</sup> )			Transport number		Log $\epsilon'$ at 1 KHz
	303 K	333 K	373 K	$t_{ion}$	$t_{ele}$	
90:00:10	$7.6 \times 10^{-7}$	$8.1 \times 10^{-6}$	$1.3 \times 10^{-4}$	0.96	0.04	1.9
80:10:10	$6.9 \times 10^{-6}$	$1.2 \times 10^{-4}$	$3.5 \times 10^{-3}$	0.96	0.04	2.97
75:15:10	$4.5 \times 10^{-5}$	$6.2 \times 10^{-4}$	$1.4 \times 10^{-2}$	0.97	0.03	4.43
70:20:10	$4.1 \times 10^{-4}$	$3.1 \times 10^{-3}$	$1.6 \times 10^{-2}$	0.98	0.02	5.19

system can be attributed to the localization of charge carriers. The dielectric permittivity rises sharply towards low frequencies due to electrode polarization effects [22]. The low-frequency dispersion region is attributed to the contribution of charge accumulation at the electrode–electrolyte interface [23]. The higher values (Table 2) of  $\epsilon'$  for the plasticized system (higher  $\sigma$ ) are due to the enhanced charge carrier density in the space charge accumulation region, that results in an increase in the equivalent capacitance. The observed variation in  $\epsilon'$  with frequency can be attributed to the formation of a space charge region at the electrode and electrolyte interface, which is familiarly known as  $\omega^{(n-1)}$  variation or the non-Debye type of behaviour, where the space charge regions with respect to the frequency are explained in terms of ion diffusion [24]. At higher frequencies, due to high periodic reversal of the electric field at the interface, the contribution of charge carriers (ions) towards the dielectric constant decreases with increasing frequency. In addition, the polarization due to the charge accumulation decreases and results in a decrease in the value of  $\epsilon'$ .

#### 4. Conclusions

PVAc–DMF–LiClO<sub>4</sub> gel-type polymer electrolytes of 90:10, 80:10:10, 75:15:10 and 70:20:10 have been prepared by the solution-casting method. The complex formation has been confirmed by FT-IR spectral studies. Impedance spectroscopy reveals that the bulk conductivity of the electrolytes increases in the order of  $10^{-7}$  to  $10^{-4}$  S cm<sup>-1</sup> as the weight ratio of DMF increases from 10 to 20 wt.%. The temperature dependence of the ionic conductivity of the gel polymer electrolyte films appears to confirm the VTF relation. The activation energy decreases with increasing DMF concentration. Measurements of transport numbers show that the charge transport in the blended polymer electrolyte films is predominantly due to ions. The low-frequency dispersion of the dielectric

constant reveals the space charge effects that arise from the electrodes.

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