

CONDUCTIVITY STUDIES AND DIELECTRIC BEHAVIOUR OF PVDF-HFP-PVC-LiClO₄ SOLID POLYMER ELECTROLYTE

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ABSTRACT

The polymer electrolytes comprising the blend of polyvinylidene fluoride-hexafluoropropylene and polyvinyl chloride as the host polymer and lithium perchlorate as the dopant were prepared by solution casting technique. The polymer blend film containing 35 wt.% LiClO₄ exhibited the highest room temperature conductivity in the order of magnitude $\sim 10^{-4}$ S cm⁻¹. The conductivity and dielectric behavior of selected electrolytes systems were analyzed. The dielectric constant, ϵ_r and dielectric loss, ϵ_i increases with temperature in the low frequency region, but almost negligible in the high frequency region. This is due to electrode polarization effects. The real part, M_i and imaginary part, M_r electrical modulus show an increase at the high frequency end. The present of M_i peak in the plot M_i versus frequency indicates that the systems are ionic conductors. The phenomenon suggests a plurality of relaxation mechanism. The log conductivity versus 1000 reciprocal of temperature ($\log \sigma$ vs $1000/T$) plots shows regression values close to unity, indicating that the plot obeys Arrhenius relationship. The frequency dependence of conductivity follows the universal power law variation, $\sigma(\omega) \propto A\omega^s$. The plot of pre-exponent s versus temperature suggests that the conduction mechanism in the system film can be described using a Small Polaron model (SP).

INTRODUCTION

In recent years, there has been a growing demand for high energy density rechargeable solid state batteries for application in portable electronic devices. The most attractive solid state rechargeable battery is the lithium rechargeable battery using solid polymer electrolyte as the separator. This type of battery has the advantages including leakage free, high single cell voltage and has no memory effect. The use of solid polymer electrolyte also makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility. The ideal solid electrolyte for application in solid state batteries would be those with ionic conductivity of a liquid, the mechanical properties of a solid and the formability of a commodity thermoplastic [1]. In the search for such solid electrolytes, various types of ionic conducting polymer systems were studied.

A lot of effort has been done to enhance ionic conductivity of polymer electrolytes. One of the ideas is by blending of polymers. Many blend electrolyte systems have been studied and reported in the literature. Among them are PVC/PEO [2], PVAc/PMMA [3-4], PVA/PMMA [5], PVDF-PVC [6-7], PVC/PMMA [8], PVDF-co-HFP/PMMA [9],

PVDF-HFP/PAN [10], PVDF-HFP/PVAc [11], PVDF-HFP/PEG [12] and PVDF-HFP/PVK [13] blend based electrolyte systems.

In the present study, PVDF-HFP/PVC polymer blend electrolytes were prepared by incorporating LiClO₄ as the doping salt. PVDF-HFP was chosen because of its appealing properties. It has high dielectric constant, ϵ of 8.4 [9] and occurred in two phases (amorphous and crystalline). Amorphous phase enhances higher ionic conduction, meanwhile crystalline phase provides strong mechanical support in the polymer electrolyte [2, 14-15]. In order to improve the ionic conductivity, PVC was blended with PVDF-HFP. PVC was used because it contains high crystalline properties which can help in mechanical support. Furthermore PVC is inexpensive, flexible and easily available [16]. LiClO₄ was used as the doping salt because it has smaller ionic radius, smaller dissociation energy and is highly soluble in most of the ionic solvents.

EXPERIMENTAL

Sample preparation

The polymer electrolytes composed of a blend of polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) and polyvinyl chloride (PVC) (both from Aldrich) as host polymers and lithium perchlorate (LiClO₄) as doping salt were prepared by solution casting technique with Dimethylformamide (DMF) (R&M) as solvent. The mixture of polymers and doping salt in suitable amounts were stirred continuously with a magnetic stirrer for 24 hours at room temperature until a homogenous solution was obtained. The solutions were then poured into petri dishes and left to dry at room temperature to form a film. The films were kept in desiccators (vacuum) for further drying.

Conductivity measurements

To study the conductivity behaviour of the polymer electrolytes, impedance spectroscopy was performed using a HIOKI 3532-50 LCR HiTESTER. The samples were cut into a proper size and sandwiched between two stainless steel electrodes. The conductivity (σ) was calculated using the following equations,

$$\sigma = t/R_b A \quad (1)$$

where t is the thickness of the electrolyte, A is the electrolyte contact area and R_b is the bulk resistance which was obtained from the plots of imaginary impedance, Z_i against real impedance, Z_r . The impedance can be written as,

$$Z^* = Z_r + jZ_i \quad (2)$$

Using the impedance data, the dielectric constant (ϵ^*), electrical modulus (M^*) was obtained using the equations as follows:

$$\epsilon_r(\omega) = Z_i / \omega C_o (Z_r^2 + Z_i^2) \quad (3)$$

$$\varepsilon_i(\omega) = Z_r / \omega C_o (Z_r^2 + Z_i^2) \quad (4)$$

$$M_r(\omega) = \varepsilon_r / (\varepsilon_r^2 + \varepsilon_i^2) \quad (5)$$

$$M_i(\omega) = \varepsilon_i / (\varepsilon_r^2 + \varepsilon_i^2) \quad (6)$$

where ε_o is vacuum space permittivity, ε_i is the dielectric loss and ω is $2\pi f$, f is the frequency in Hz, $C_o = \varepsilon_o A/t$, A is the electrode-electrode contact area and t is thickness. A.c. conductivity is obtained by using the following equation,

$$\sigma_{ac}(\omega) = \varepsilon_o \varepsilon_i \omega \quad (7)$$

RESULTS AND DISCUSSION

Table 1 lists the composition of the polymer electrolyte systems studied in this work, their designation and room temperature ionic conductivity values. The ionic conductivity of pure PVDF-HFP/PVC electrolyte system (S0) is in the order of magnitude 10^{-11} S cm⁻¹. On addition of 5 wt.% of salt., the conductivity increases to 10^{-7} S cm⁻¹. The conductivity continuous to increase with increasing salts content. The highest conductivity is 1.05×10^{-4} S cm⁻¹ for the system containing 35 wt.% of salt (S7). The addition of more than 35 wt.% of salt diminishes the conductivity. The increase in conductivity could be due to the increase in number of charge carrier or free ions due to increasing salt concentration. The decrease in conductivity when salt concentration exceeding 35 wt.% could be due to the formation of ion pairs and aggregates. The formation of ion pairs produces neutral species and thus reduces the number of free ions. On the other hand, although ion aggregates may be charged, their mobility is impaired by their size and thus gives an adverse effect to conductivity [17].

Table 1: Composition, designation and conductivity values of PVDF-HFP/PVC blend based electrolyte systems.

Composition (wt.%)	Designation	Conductivity (S cm ⁻¹)
PVDF-HFP/PVC:LiClO ₄ (100:0)	S0	4.32×10^{-11}
PVDF-HFP/PVC: LiClO ₄ (95:5)	S1	3.59×10^{-7}
PVDF-HFP/PVC: LiClO ₄ (90:10)	S2	1.94×10^{-6}
PVDF-HFP/PVC: LiClO ₄ (85:15)	S3	4.22×10^{-6}
PVDF-HFP/PVC: LiClO ₄ (80:20)	S4	2.18×10^{-5}
PVDF-HFP/PVC: LiClO ₄ (75:25)	S5	3.05×10^{-5}
PVDF-HFP/PVC: LiClO ₄ (70:30)	S6	4.10×10^{-5}
PVDF-HFP/PVC: LiClO ₄ (65:35)	S7	1.05×10^{-4}
PVDF-HFP/PVC: LiClO ₄ (60:40)	S8	8.11×10^{-5}

Figure 1 shows the plots of log conductivity versus the inverse of temperature for the polymer electrolyte systems S3 and S7. The pattern of temperature dependent conductivity plots can be said to follow the Arrhenius behavior:

$$\sigma = \sigma_0 \exp (-E_A/kT) \quad (8)$$

where σ_0 is the pre-exponential factor, E_A is activation energy, k is Boltzmann constant and T is absolute temperature [18]. The activation energy, E_A can be calculated from the slope of the plots. The activation energy of electrolyte system S3 is 0.60 eV and for the system S7 is 0.35 eV. It can be observed that the system S7 has a higher ionic conductivity but lower activation energy compared to the system S3. The activation energy for lithium ions transport is significantly low for the blended complex with high salt concentration which was reported by Baskaran and coworkers [4]. For application in devices operating over a wide range of temperature, it is desirable to have electrolytes with uniform conductivity. Therefore, electrolyte systems with low activation energies are desirable [19-20].

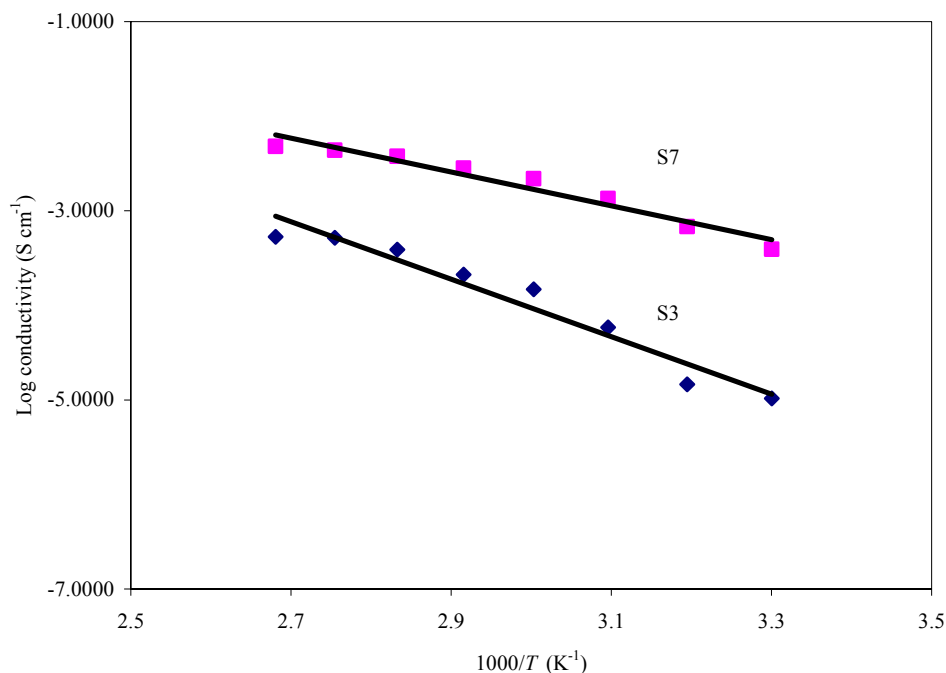


Figure 1: Log conductivity vs 1000/T for S3 and S7 electrolyte systems.

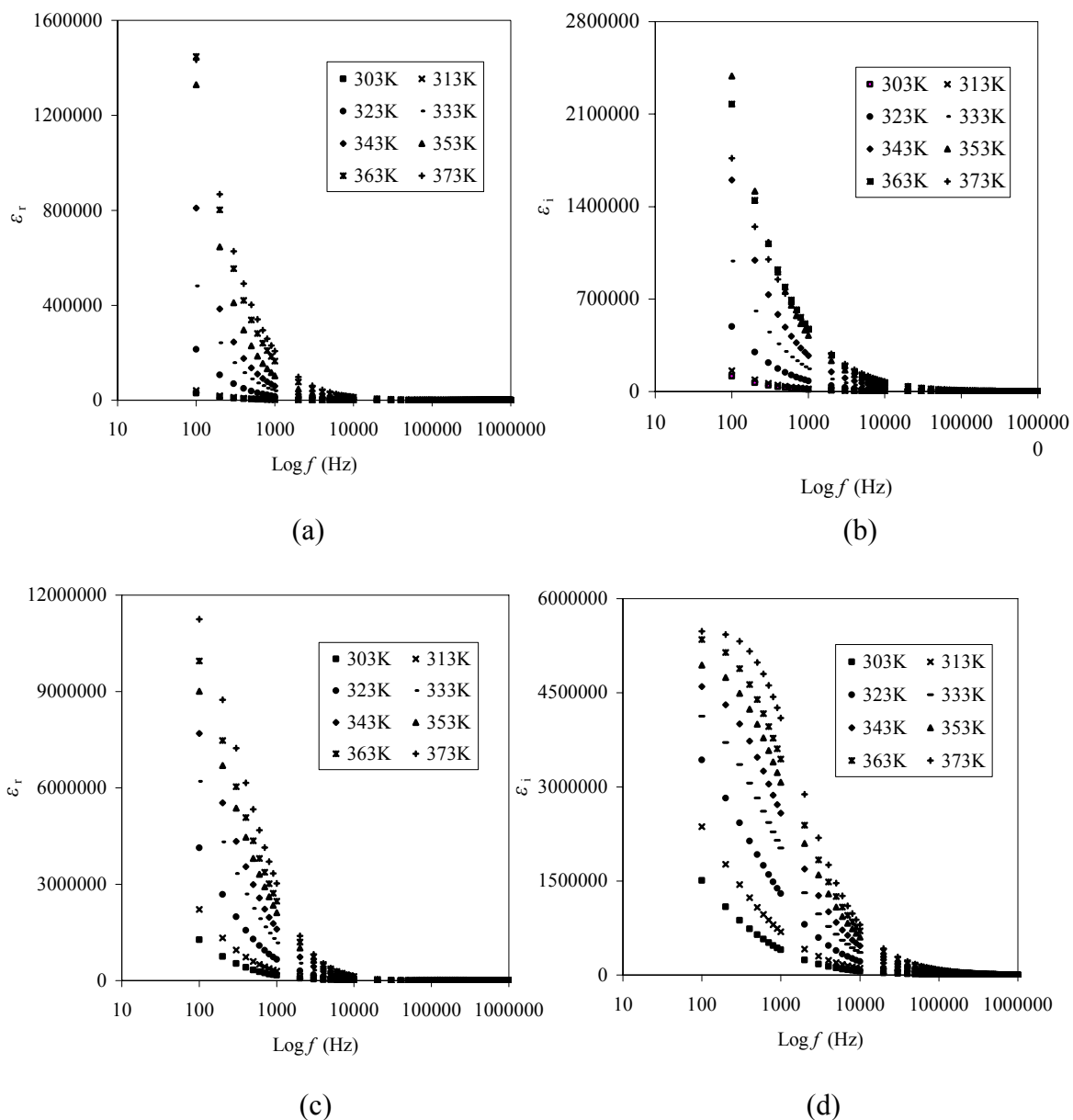


Figure 2: (a) is dielectric constant and (b) dielectric loss as a function of frequency for electrolyte system S3 and (c) dielectric constant and (d) dielectric loss for electrolyte systems S7 at various temperatures.

Analysis of frequency dependent electrical response of polymer electrolytes is a versatile approach to understand the nature of ionic transport. For this reason, the collected complex impedance for electrolyte systems S3 and S7 were analyzed using the formalisms of complex permittivity (ϵ), electrical modulus (M) and conductivity $\sigma(\omega)$.

Figures 2(a) and (b) show dielectric plots for systems S3 meanwhile (c) and (d) are the plots for S7 at various temperatures. Both the dielectric constant (ϵ_r) and dielectric loss (ϵ_i) part increase with decreasing frequency. This is attributed to the high contribution of charge accumulation at the electrode-electrolyte interface [4]. At higher frequencies the periodic reversal of the electric field occurs so fast and there is no excess ion diffusion in the direction of the field. The polarization is due to charge accumulation decreases and results in the decrease in both the dielectric constant and dielectric loss. The increase in the dielectric constant and dielectric loss with temperature can be attributed to the increase in charge carrier density due to the increase in dissociation of ion aggregates.

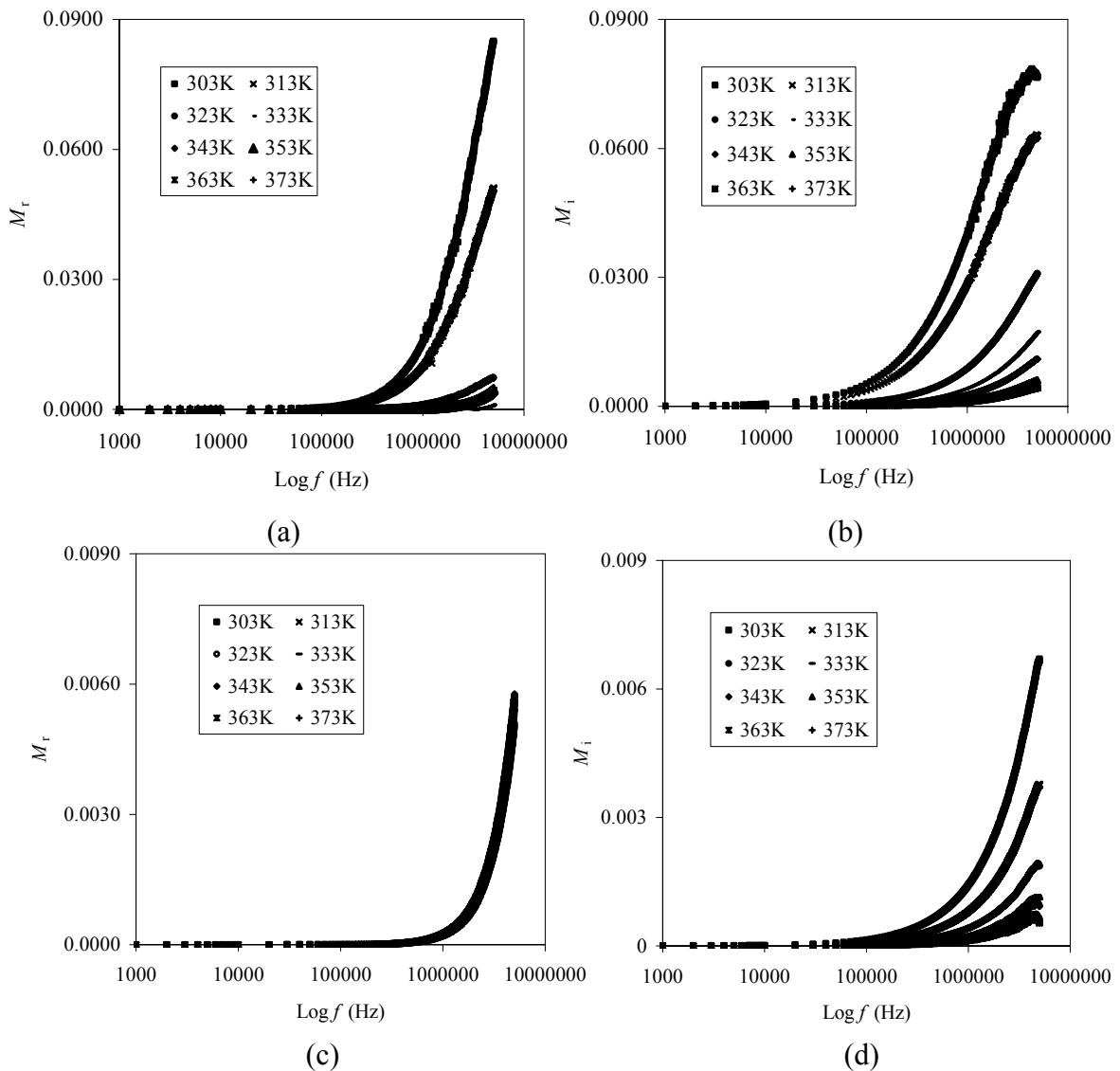


Figure 3: Frequency of (a) real part and (b) imaginary part of electrical modulus for electrolyte system S3 and (c) real part and (d) imaginary part of electrical modulus for electrolyte system S7 at various temperatures.

The variation of real part (M_r) and imaginary part (M_i) for electrical modulus with frequency are shown in Figure 3. Both M_r and M_i are observed to increase in the high frequency region. M_i peak cannot be observed well in Figure 3. However, the M_i peaks are expected to increase in height and occur at higher frequency as the temperature increases. The presence of M_i relaxation peak indicates that the electrolyte systems are ionic conductors. The values of M_r and M_i approach zero in the low frequency region. The long tail in the low frequency region observed in Figure 3(b) and (d) is due to large capacitance associated with the electrodes [21]. The angular frequency dependence of log conductivity, $\sigma_{ac}(\omega)$, for samples S3 and S7 at various temperatures, Figure 4, can be said to obey the power law [22] given by,

$$\sigma_{ac}(\omega) = A\omega^s \quad (9)$$

where A is constant at a particular temperature, ω the angular frequency ($\omega = 2\pi f$) and s is the frequency exponent (s less than unity). From the figure it can be observed that the conductivity increases as frequency increases.

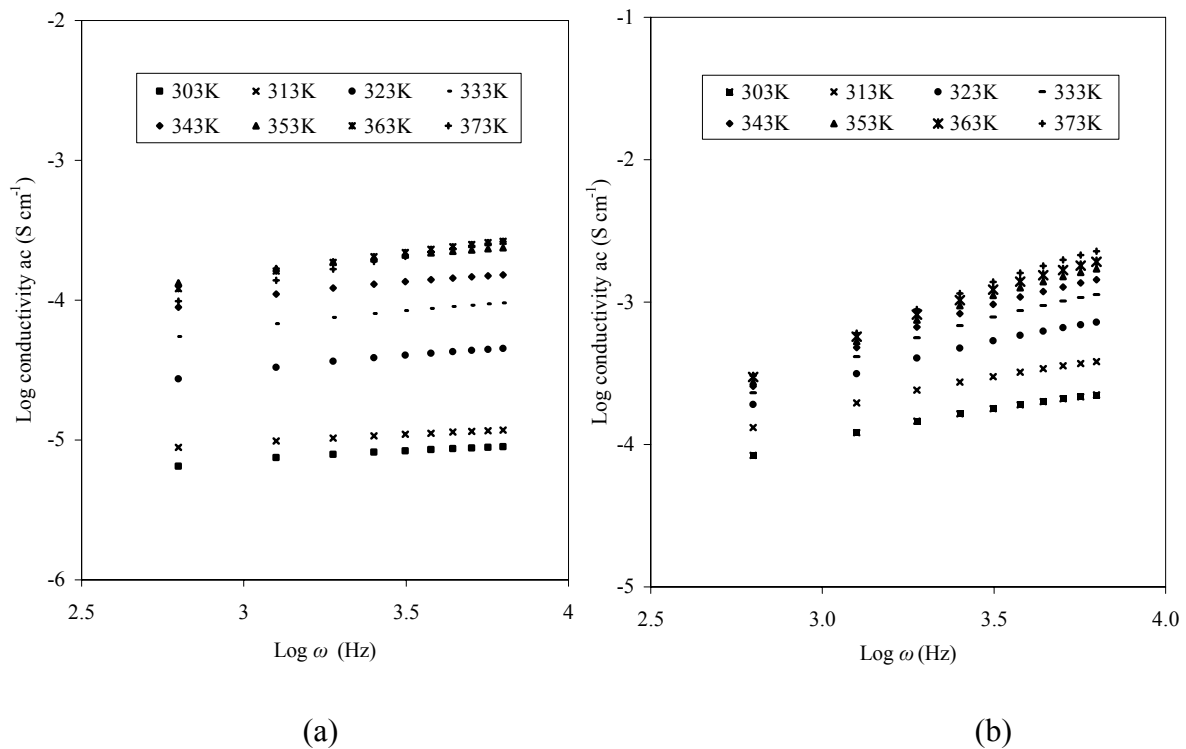


Figure 4: Frequency dependence of conductivity a.c. for electrolyte systems (a) S3 and (b) S7 at various temperatures.

The value of the frequency exponent s was obtained from the slope of graphs. The value s is in the range from 0 to 1. Figure 5 shows the variation of s with the temperature. As can be seen in the figure, the value of s for both samples increases with increasing

temperature. This indicates that the Small Polaron model can be used to describe the conduction mechanism in these electrolyte systems [23].

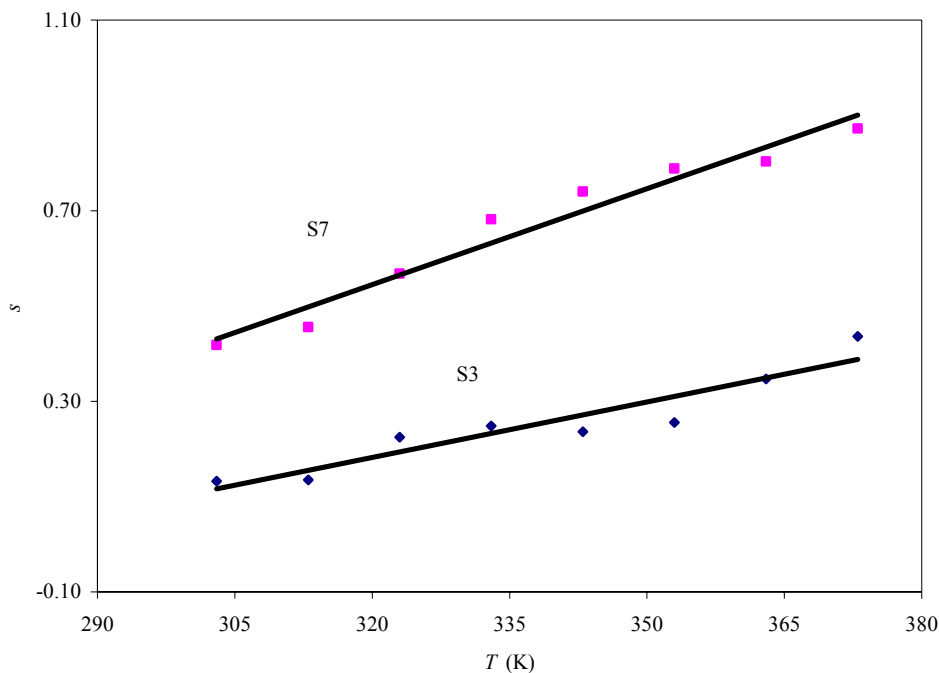


Figure 5: The variation of s with temperature for electrolyte systems S3 and S7.

CONCLUSION

The ionic conductivity of blend polymer electrolytes was determined by impedance studies. The blend polymers containing 35 wt.% LiClO_4 (S7) exhibits the highest conductivity $1.05 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The dielectric and ac conductivity of sample was studied. The activation energy values for the blend polymer electrolyte systems S3 and S7 are 0.60 and 0.35 eV respectively. The conduction mechanism in both samples follows the SP model.

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