

Laser Raman and conductivity studies of plasticized polymer electrolyte P(ECH-EO):propylenecarbonate: γ -butyrolactone:LiClO₄

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Abstract The plasticized polymer electrolytes composed of poly(epichlorohydrin-ethyleneoxide) (P(ECH-EO)) as host polymer, lithium perchlorate (LiClO₄) as salt, γ -butyrolactone (γ -BL), and propylene carbonate (PC) as plasticizer have been prepared by simple solution casting technique. The effect of mixture of plasticizers γ -BL and PC on conductivity of the polymer electrolyte P(ECH-EO):LiClO₄ has been studied. The band at 457 cm⁻¹ in the Raman spectra of plasticized polymer electrolyte is attributed to both the ring twisting mode of PC and the perchlorate ν_2 (ClO₄⁻) bending. The maximum conductivity value is observed to be 4.5×10^{-4} S cm⁻¹ at 303 K for 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ electrolyte system. In the present investigation, an attempt has been made to correlate the Raman and conductivity data.

Keywords Raman analysis · Ac impedance · Poly (epichlorohydrin-ethyleneoxide) · Dielectric analysis

Introduction

Polymer electrolytes have been the focus of research due to their application in electrochemical devices such as rechargeable batteries, supercapacitors, fuel cell, electrochromic devices, etc. [1]. In polymer electrolyte, the ionic motion is mainly due to the dissolved ionic species (cation and anion) in the polymer matrix. The aim of most research is focused on the enhancement of ionic conductivity. Various investigations have been performed to improve the ionic conductivity by blending of polymers [2, 3], insertion of

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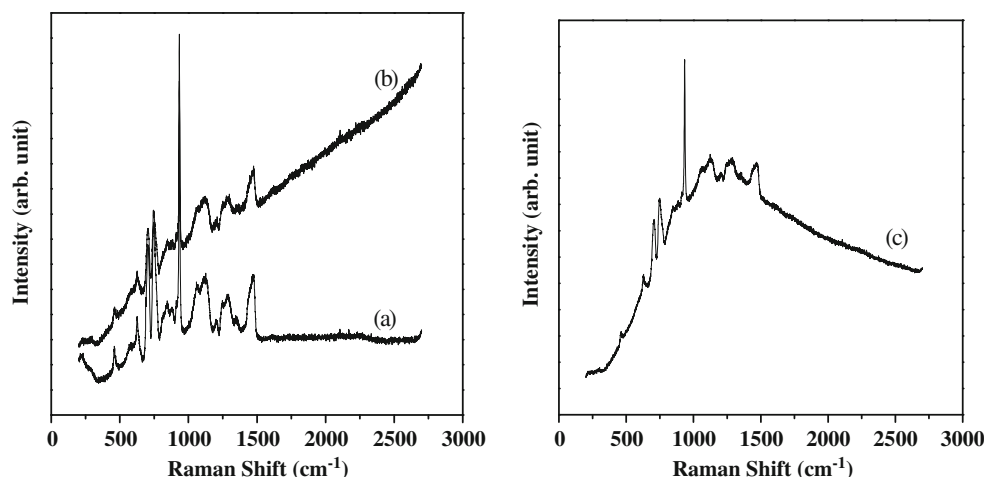
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Fig. 1 Raman spectra of (a) 70P (ECH-EO):5PC:10 γ -BL:15LiClO₄, (b) 65P(ECH-EO):10PC:10 γ -BL:15LiClO₄, and (c) 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ in the region 200–2,700 cm⁻¹



ceramic fillers [4], and plasticization [5, 6]. In application view of polymer electrolytes, plasticized polymer electrolyte which exhibits high ionic conductivity at ambient temperature is found to be a good candidate in electrochemical devices such as lithium ion rechargeable battery, sensors, electrochromic devices, etc.

The importance of lithium ion-conducting polymer electrolyte in lithium rechargeable batteries has attracted much attention of researchers in this field and some of the characteristics of lithium battery such as life time, specific power, and good performance at low temperatures are largely dependent on the formulation of the electrolyte, which is generally composed of a mixture of solvent/plasticizer and a lithium salt. Military and space applications in particular require batteries which can operate at negative temperatures, generally down to 233 K [7]. To maintain the electrolyte in a liquid state at low temperatures, solvent mixtures exhibiting low eutectic point are useful. Hence, the use of the multi plasticizers has been exploited in the present work to

improve the ionic conductivity of the polymer electrolyte and find its application in lithium rechargeable battery to work over wide range of temperature.

After Wright's [8] discovery of ionic conductivity in alkali metal salt complexes in poly(ethylene oxide) (PEO) in 1973, large efforts are being devoted on PEO-based electrolyte systems. However, the low ionic conductivity of the solvent-free PEO-based electrolyte limits its application in lithium ion battery to operate at room temperature. Conductivity $>10^{-4}$ S cm⁻¹ is approached only at above the melting point of PEO (higher than 70 °C) when the polymer is in amorphous state [9]. In order to attain high ionic conductivity at room temperature, Silva et al. [10, 11] studied different class of polyethers, the halogenated polyether, and suggested that the copolymer and the terpolymer of epichlorohydrin can be used as solid state polymeric electrolytes for devices to be operated at temperatures up to ca. 250 °C in ambient atmospheres. Munichandraiah et al. [12] have reported the ionic conductivity of hydrin:poly(ethylene

Fig. 2 Raman spectra of (a) 70P(ECH-EO):5PC:10 γ -BL:15LiClO₄, (b) 65P(ECH-EO):10PC:10 γ -BL:15LiClO₄, and (c) 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ in the region 2,700–3,200 cm⁻¹

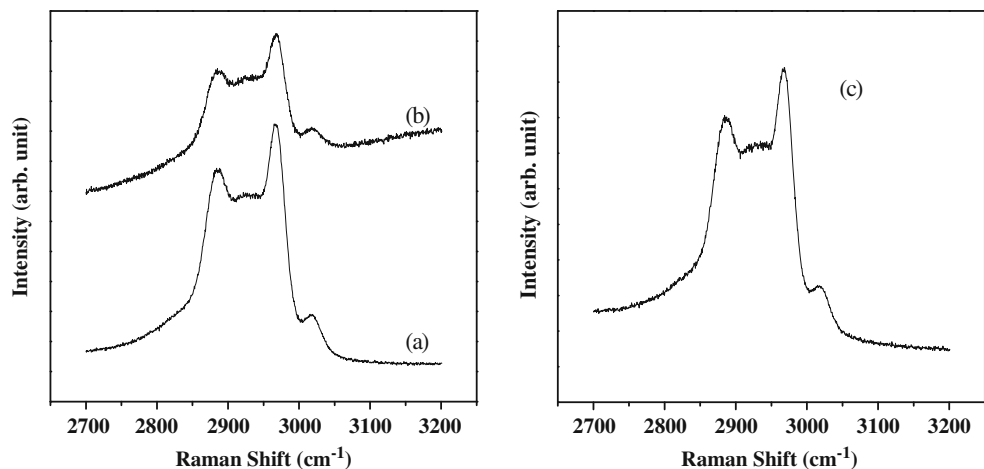
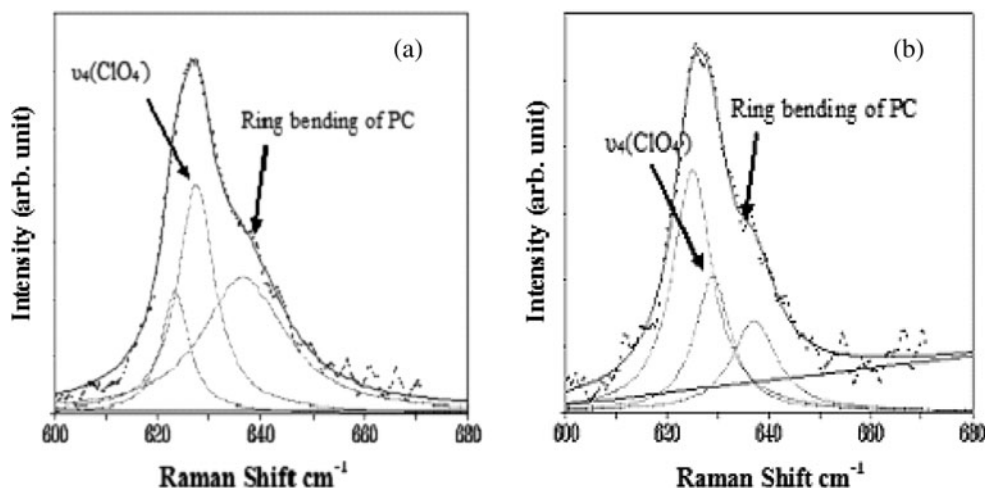


Fig. 3 PC ring bending of (a) 70P(ECH-EO):5PC:10 γ -BL:15LiClO₄ and (b) 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄



glycol) complexed with LiBF₄ to be 10⁻⁵ S cm⁻¹. Kohjiya et al. [13] studied the effect of EO unit on ionic conductivity and the lithium perchlorate (LiClO₄) concentration on the ionic conductivity. Charmette et al. [14] have studied a series of poly(ethylene oxide-co-epichlorohydrin) (P(EO/EP)) and confirmed the polymeric membrane as a suitable candidate for CO₂ separation. To the best of our knowledge, only very few reports were there on plasticized polymer electrolyte based on poly(epichlorohydrin-ethyleneoxide) (P(ECH-EO)) polymer. Hence, in our previous report, the optimization of solid polymer electrolyte (P(ECH-EO):LiClO₄) [15] and γ -butyrolactone (γ -BL) plasticized polymer electrolyte [16] have been carried out and found that γ -BL plasticized polymer electrolyte with the composition 70 mol% P(ECH-EO):15 mol% γ -BL:15 mol% LiClO₄ has the highest conductivity ($\sigma=1.3 \times 10^{-4}$ S cm⁻¹ at 303 K). However, in the present work, the multi plasticizers propylene carbonate (PC) and γ -BL has been introduced to

the solid polymer electrolyte P(ECH-EO):LiClO₄ to enhance the ionic conductivity. The ion-ion and ion-polymer interaction on plasticized polymer electrolyte has been studied by Raman analysis and also an attempt has been made to correlate Raman analysis with the conductivity.

Experimental

Preparation of plasticized polymer electrolyte

P(ECH-EO) (ECH 64% and EO 36%) and lithium perchlorate (Hi-media) are dried under vacuum. γ -BL and PC were used as plasticizer and acetone as solvent. The plasticized polymer electrolyte of various compositions has been prepared by solution casting technique. The polymer electrolyte with various ratio of polymer to salt (70P(ECH-EO):15LiClO₄, 65P(ECH-EO):15LiClO₄ and 60P(ECH-EO):15LiClO₄) is dissolved in

Fig. 4 $\nu_1(\text{ClO}_4)$ of (a) 70P(ECH-EO):5PC:10 γ -BL:15LiClO₄ and (b) 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄

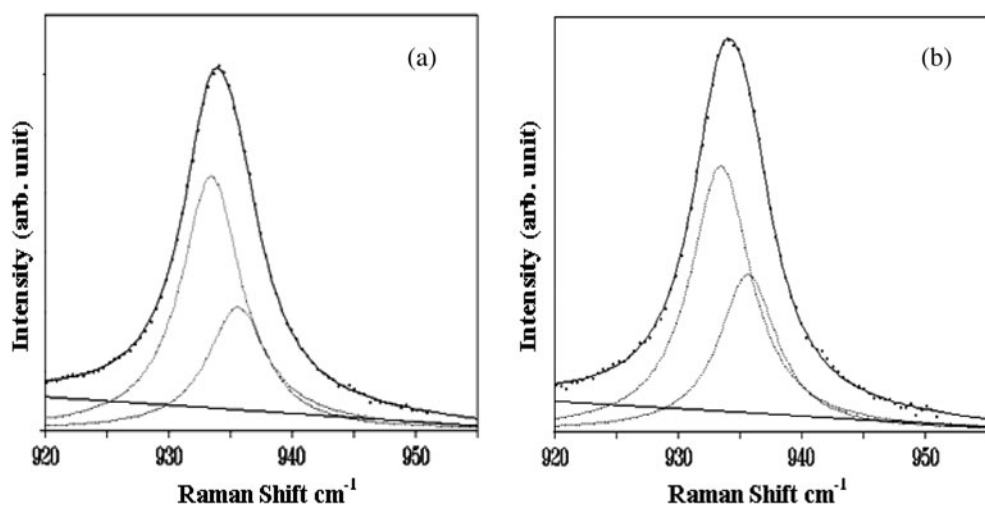


Table 1 Deconvoluted results of $\nu_1(\text{ClO}_4^-)$ stretching vibration in plasticized polymer electrolyte

Polymer electrolyte	$\nu_1(\text{ClO}_4^-)$ stretching (cm^{-1})	Half width (cm^{-1})	Peak assignment
PC/ γ -BL			
70P(ECH-EO):5PC:10 γ -BL:15LiClO ₄	933	2.94	Free ion
	936	2.92	Contact ion pair
65P(ECH-EO):10PC:10 γ -BL:15LiClO ₄	933	2.99	Free ion
	936	2.74	Contact ion pair
60P(ECH-EO):15PC:10 γ -BL:15LiClO ₄	933	2.97	Free ion
	936	2.82	Contact ion pair

the solvent acetone to get a homogeneous solution. The plasticizers, PC and γ -BL, of different compositions have been added to the polymer–salt solution. The viscous mixtures of polymer–salt–plasticizer were then allowed to stir continuously for 12 h to get homogeneous solution. The solutions are then poured on the glass petri dish and allowed to dry under vacuum at 313 K to get mechanically stable thin films of thickness 0.06 cm. The different compositions of mixed plasticized polymer electrolytes investigated are as follows:

Plasticizer: PC/ γ -BL

- 70P(ECH-EO):5PC:10 γ -BL:15LiClO₄
- 65P(ECH-EO):10PC:10 γ -BL:15LiClO₄
- 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄

Experimental techniques

The prepared polymer electrolytes were then characterized by various experimental techniques. Ion–ion interaction between the polymer and the dopant has been studied by Raman spectroscopy using Horiba Jobin Yvon LabRam Raman Spectrometer in the range 200–4,000 cm^{-1} . The data were recorded by focusing the laser through microscope. An argon ion laser of wavelength 514 nm operated at 300 mW was used to excite the sample. Conductivity measurements have been carried out using HIOKI 3532 LCZ meter in the frequency range of 42 Hz–1 MHz by sandwiching the plasticized polymer electrolyte between two aluminum electrodes (blocking electrodes).

Results and discussion

Raman analysis

Figure 1a–c and Fig. 2a–c show the laser Raman spectra of 70P(ECH-EO):5PC:10 γ -BL:15LiClO₄, 65P(ECH-EO):10PC:10 γ -BL:15LiClO₄ and 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ plasticized polymer electrolyte complexes in various frequency windows. The peaks observed at 1,114 and 705 cm^{-1} are ascribed to C–O–C

symmetric stretching and C–Cl stretching vibrations of 80P(ECH-EO):5 γ -BL:15LiClO₄ plasticized polymer electrolyte, respectively. There is a slight shift in the C–O–C stretching and C–Cl stretching towards lower wavenumbers 1,114–1,110 cm^{-1} and 605–700 cm^{-1} respectively indicating the interaction of Li⁺ ion with chlorine and ether oxygen of P(ECH-EO) in the plasticized polymer electrolyte. The intensity of C–O–C symmetric stretching and C–Cl stretching vibration gradually decreases with the addition of PC which indicates that PC enhances the weak interaction between the Li⁺ ions and the ether oxygen and chloromethylene of P(ECH-EO). As a result of this weak interactions, the interaction between the ClO₄[−] ion and ether oxygen carbons of P(ECH-EO) becomes significant. These interactions may be explained by the weakening of C–O and C–Cl bond, caused by decrease in electronic density due to the O–Li⁺ and Cl–Li⁺ interaction.

The first significant change in the observed Raman spectra is an increase in the full width at half-maximum (FWHM) of the band at 457 cm^{-1} , which is attributed to both the ring twisting mode of PC and the perchlorate $\nu_2(\text{ClO}_4^-)$ bending band. The increase in intensity of the 629 cm^{-1} band assigned to the vibration $\nu_4(\text{ClO}_4^-)$ is also observed. At the same time, the appearance of the shoulder

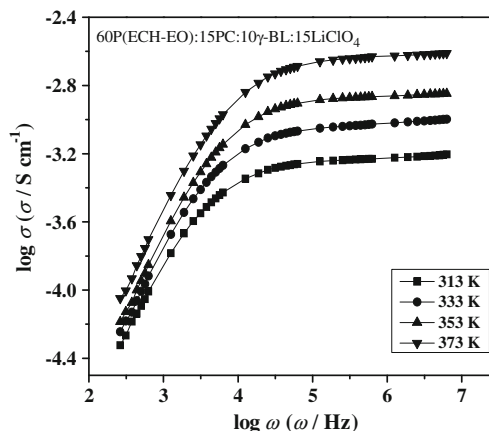


Fig. 5 Conductance spectra of 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ at different temperatures

Table 2 Variation of conductivity at different temperature for the plasticized polymer electrolyte

Polymer electrolyte	Conductivity (S cm ⁻¹)			Activation energy (eV)
	303 K	333 K	363 K	
PC/γBL				
70P(ECH-EO):5PC:10γ-BL:15LiClO ₄	1.5 × 10 ⁻⁴	3.7 × 10 ⁻⁴	9.8 × 10 ⁻⁴	0.13
65P(ECH-EO):10PC:10γ-BL:15LiClO ₄	2.9 × 10 ⁻⁴	7.9 × 10 ⁻⁴	1.4 × 10 ⁻³	0.12
60P(ECH-EO):15PC:10γ-BL:15LiClO ₄	4.5 × 10 ⁻⁴	9.4 × 10 ⁻⁴	1.7 × 10 ⁻³	0.10

peak at 633 cm⁻¹ (Fig. 3a, b) corresponds to the coupled ring bending mode and CH₂ twisting of PC [17]. The significant change in the FWHM of this band evidences that the addition of PC perturbs lithium perchlorate in the polymer electrolyte matrix.

The Raman analysis of perchlorate anion involves the identification of different species: (a) free perchlorate anion (i.e., ClO₄⁻), (b) contact ion pairs (i.e., Li⁺-ClO₄⁻), and (c) multiple ion aggregates (i.e., (Li⁺-ClO₄⁻)_n). Curve fitting within the perchlorate anion band has also been used to identify free ClO₄⁻ and contact ion pairs. The spectral locations of the curve-fitted bands were in agreement with free ClO₄⁻ (933 cm⁻¹) and contact ion pairs (938 cm⁻¹). For all the compositions of P(ECH-EO):γ-BL:PC:LiClO₄ system, only two Lorentzian bands centered at 933 and 937 cm⁻¹ were required to completely deconvolute the envelope of ClO₄⁻ as shown in Fig. 4a, b. The results are tabulated in Table 1 and it is observed that the addition of PC restricts the formation of multiple ion aggregates in the PC/γ-BL plasticized polymer electrolyte system. In the present work, the concentration of γ-BL and LiClO₄ was kept constant and the concentration of plasticizer PC was increased, when PC is introduced to the γ-BL plasticized polymer electrolyte system, some of the Li⁺ cations which have been interacting with the γ-BL plasticizer can now interact with PC molecules, which restricts the formation of ion aggregates and results in the increase of free ions and plasticizers (γ-BL and PC) for higher content PC. Hence,

when the plasticizer PC with high dielectric constant is added to the γ-BL plasticized polymer electrolyte, the number of free ions increases which result in the enhancement of ionic conductivity.

The observed vibrational bands in the 2,850–3,100 cm⁻¹ region corresponding to the C–H stretching modes are unaffected by the addition of plasticizer. In conclusion, the Raman studies show that the vibrational band shape of the hydrogen–carbon stretching modes in the region 2,800–3,200 cm⁻¹ do not change even at the highest concentration of PC, indicating that the solvent–ion interaction is highly localized on the polar groups of the polymer. It can also be said that there is no hydrogen bonding between the perchlorate anion oxygen and hydrogen of the solvent molecules [18]. This is supported by the fact that hydrogen–carbon modes, in the region 1,200–1,300 cm⁻¹, remain unaffected by increase in PC concentration.

Conductance spectra analysis

To get a complete knowledge of the relaxation processes, the conductivity of the mixed plasticized polymer electrolytes are analyzed with respect to the frequency. The logarithmic plots of conductivity variation as a function of frequency for plasticized polymer electrolytes giving the highest conductivity 60P(ECH-EO):15PC:10γ-BL:15LiClO₄ at different temperatures are shown in Fig. 5.

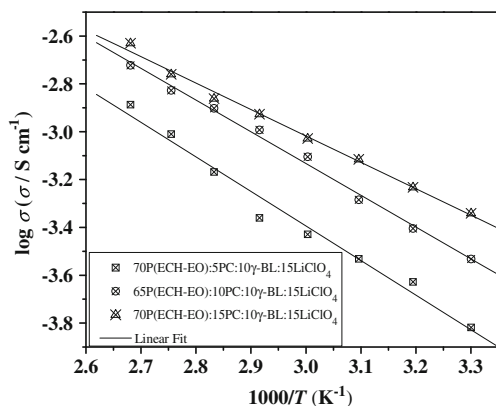


Fig. 6 Arrhenius plot of PC plasticized polymer electrolyte

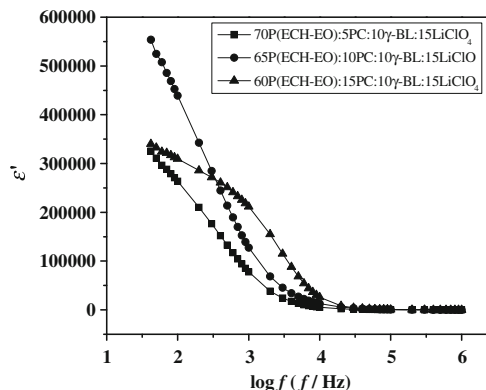


Fig. 7 Dielectric constant spectra of plasticized polymer electrolyte of different compositions of PC at 303 K

At lower frequencies, the conductivity is found to increase with increase in temperature. This low frequency spike is due to the interfacial dispersion or the space charge polarization. A frequency-independent conductivity plateau is observed in the mid-frequency region. The plateau characterizes the conduction, which is caused mainly by the hopping motion of the mobile ions and extrapolations determine the dc value of conductivity and are tabulated in Table 2. The high frequency behavior is attributed to the relaxation of the mobile ion hopping which is due to the Coulomb interactions of the charge carriers and the disorder within the structure. The conductivity dispersion is found to be less predominant at lower temperatures, and as the temperature increases, the frequency at which the dispersion becomes prominent shifts to higher frequency region. In other words, the bulk relaxation shifts to higher frequencies with increase in temperature [19].

Temperature-dependent conductivity

The temperature-dependent ionic conductivity measurements are carried out to analyze the mechanism of ionic conduction in polymer electrolyte membranes. It is observed that the temperature (T) dependence of conductivity (σ) obeys Arrhenius relationship [20].

$$\sigma = \sigma_0 \exp(-E_a/KT) \quad (1)$$

where E_a is activation energy, K is Boltzmann constant, and σ_0 is pre-exponential factor. The σ values of the mixed plasticized polymer electrolyte of P(ECH-EO):PC: γ -BL:LiClO₄ polymer electrolyte are used to construct $\log \sigma$ versus $1/T$ plots as shown in Fig. 6. It is noted that the linearity of the plot suggests the validity of the Arrhenius equation (Eq. 1) for the plasticized polymer electrolyte systems. Using the value of the slope and Eq. 1, E_a values are calculated and are tabulated in Table 2. It is found that the value of E_a decreases with the increase in PC concentration. The very low value of activation energy for the high conductivity polymer electrolytes 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ ($\sigma=4.5 \times 10^{-4}$ S cm⁻¹) suggests that the ionic conduction is facile in plasticized polymer electrolyte.

Dielectric analysis

The complex permittivity (ϵ^*) or dielectric constant of the a system is defined by

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2)$$

where ϵ' is the real part of the dielectric constant and ϵ'' is imaginary part of dielectric constant of the material. Figure 7 shows the ϵ' versus $\log f$ for different composition of P(ECH-EO):PC: γ -BL:LiClO₄ at 303 K. It is found that the

dielectric constant increases with increase in PC concentration. Similar result has been earlier by Baskaran et al. [3] for the DMF plasticized PVAc:LiClO₄ polymer electrolyte. The low frequency dispersion region is attributed to the contribution of charge accumulation at the electrode–electrolyte interface [21]. At higher frequency, due to high periodic reversal of the field at the interface, the contribution of charge carriers (ions) towards the dielectric constant decreases with increasing frequency.

The higher values of ϵ' for 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ systems are due to the enhanced charge carrier density at the space charge accumulation region, resulting in an increase in the equivalent capacitance. At higher frequencies, the periodic reversal of electric field occurs so fast and there is no excess ion diffusion in the direction of the applied field. The polarization due to the charge accumulation at the electrodes decreases, leading to the decrease in the value of ϵ' .

Conclusion

Plasticized polymer electrolytes P(ECH-EO):PC: γ -BL:LiClO₄ of various compositions have been prepared by solution casting technique. The curve fitting analysis of the $\nu_1(\text{ClO}_4^-)$ stretching in Raman spectra of both the plasticized polymer electrolyte system indicates the presence of “free anions” and “contact ion pairs”. The Raman data have been correlated with the conductivity of the polymer electrolytes. It is depicted from the impedance spectroscopic analysis that the 60P(ECH-EO):15PC:10 γ -BL:15LiClO₄ electrolyte system exhibits maximum conductivity value of 4.5×10^{-4} S cm⁻¹ at 303 K which reveals that the plasticized polymer electrolyte can be a candidate for the lithium ion rechargeable battery.

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