

## **DIELECTRIC BEHAVIOURS OF PLASTICIZED PEO-LiCF<sub>3</sub>SO<sub>3</sub> ELECTROLYTES**

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### **ABSTRACT**

Films of PEO-based polymer electrolyte were prepared by the technique of solution casting. Ethylene carbonate (EC) was employed as the plasticizer and lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>) was used as the doping salt. The highest room temperature conductivity achieved in EC-plasticized system is  $2.14 \times 10^{-4} \text{ S cm}^{-1}$ . The effects of EC on the frequency-dependent dielectric properties of PEO-based electrolytes were also investigated by impedance spectroscopy, in the temperature range from 300 K to 343 K. The relaxation time for the ionic charge carriers,  $\tau$  was obtained from the variation of loss tangent,  $\tan \delta$  as a function of frequency at various temperatures for sample with highest conductivity value. The linear behaviour of temperature dependence of  $\tau$  with regression value 0.98 could be described by Arrhenius law. The activation energy for the plasticized PEO-LiCF<sub>3</sub>SO<sub>3</sub> sample was found to be 0.39 eV.

### **INTRODUCTION**

Polymeric electrolytes have attracted considerable interests during the past few years, because of their potentially wide range of applications in such fields as fuel cells, rechargeable lithium batteries, electrochromic devices and sensors [1-3]. The advantages of using these solid polymeric electrolytes (SPEs) are concentrated on their desirable characteristics: good compatibility with lithium metal; no leakage; low self-discharge in batteries; relax elastically under stress; easy processing and continuous production and so on [4-5]. However, the low ionic conductivity of SPE limits their applications. It has been recognized that the ionic transport of SPE occurs only in the amorphous polymer regions and is often governed by the segmental motion of polymer chain [6-7]. It is clear that the presence of a flexible, amorphous phase in SPE is essential for higher ionic conductivity.

In this paper, we report our research work on polyethylene oxide (PEO) as polymer electrolyte. PEO is one of the most promising solid polymer electrolytes (SPEs). However, due to poor ionic conductivity ( $\sigma = 10^{-8}$  to  $10^{-7} \text{ S cm}^{-1}$ ) of these polymer electrolytes at an ambient operating temperature, various modifications have been done. One of the modifications is through the addition of plasticizer into polymer electrolytes. In this study, we have used ethylene carbonate (EC) as a plasticizer to enhance the conductivity and also study the dielectric behavior of the prepared electrolytes by impedance spectroscopy.

## EXPERIMENTAL

All samples were prepared by the solution cast technique. PEO of molecular weight  $600,000 \text{ gmol}^{-1}$ , lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) as salt, and ethylene carbonate (EC) as a plasticizer was used. PEO was dissolved in 50 g methanol and mixed with 20 wt. %  $\text{LiCF}_3\text{SO}_3$ . After about 30 minutes, the solution were mixed with EC in ratio PEO( $\text{LiCF}_3\text{SO}_3$ ): of 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30 weight percent and stirred for about 24 hours. The solutions were then cast into Teflon petri dishes and left to dry at room temperature. The resulting films were cut in to a circle of 24 mm diameter and the thickness of every sample was measured. The samples were then kept dry in a dessicator for a week. The dried samples were then characterized by impedance spectroscopy. The electrical conductivity of the films was determined using the HIOKI 3532-50 LCR HiTESTER. The prepared films were cut into suitable sizes and sandwiched between two circular stainless steel ion-blocking electrodes. The study was carried out in the frequency range from 100 Hz to 5 MHz. The conductivity was calculated using the relation:

$$\sigma = t/AR_b \quad (1)$$

where  $\sigma$  is the conductivity,  $t$  is the thickness of film,  $A$  is the area of contact, and  $R_b$  is the bulk resistance of the sample in  $\Omega$  which is obtained from the complex impedance plot.

## RESULTS AND DISCUSSION

In PEO- $\text{LiCF}_3\text{SO}_3$  system, 30 wt. %  $\text{LiCF}_3\text{SO}_3$  added to PEO gives the highest composition of solid films that can be obtained. At higher composition of  $\text{LiCF}_3\text{SO}_3$ , films remained in a gel-like state and were mechanically unstable. The conductivities of PEO- $\text{LiCF}_3\text{SO}_3$  against the composition of  $\text{LiCF}_3\text{SO}_3$  (5 – 30 wt. %) is shown in Figure 1. The highest conductivity of PEO- $\text{LiCF}_3\text{SO}_3$  system was obtained at 20 wt. % of  $\text{LiCF}_3\text{SO}_3$ , which is  $8.64 \times 10^{-8} \text{ S/cm}$  at room temperature. This is due to the increase in the number of charge carriers and in the increase in their mobility with addition of  $\text{LiCF}_3\text{SO}_3$ . Above 20 wt. % of  $\text{LiCF}_3\text{SO}_3$  the conductivity decreases due to the presence of a large number of ions.

Figure 2 shows the conductivity versus composition of EC plasticizer (5-30 wt. %) for PEO- $\text{LiCF}_3\text{SO}_3$ -EC system. The highest conductivity obtained for this was at 20 wt. % of EC, which is  $2.14 \times 10^{-4} \text{ S/cm}$  at room temperature which is an increase of 4 orders of magnitude. This can be explained on the basis that the plasticizer interacts with the crystalline PEO rendering the complexes amorphous and hence the conductivity increases.

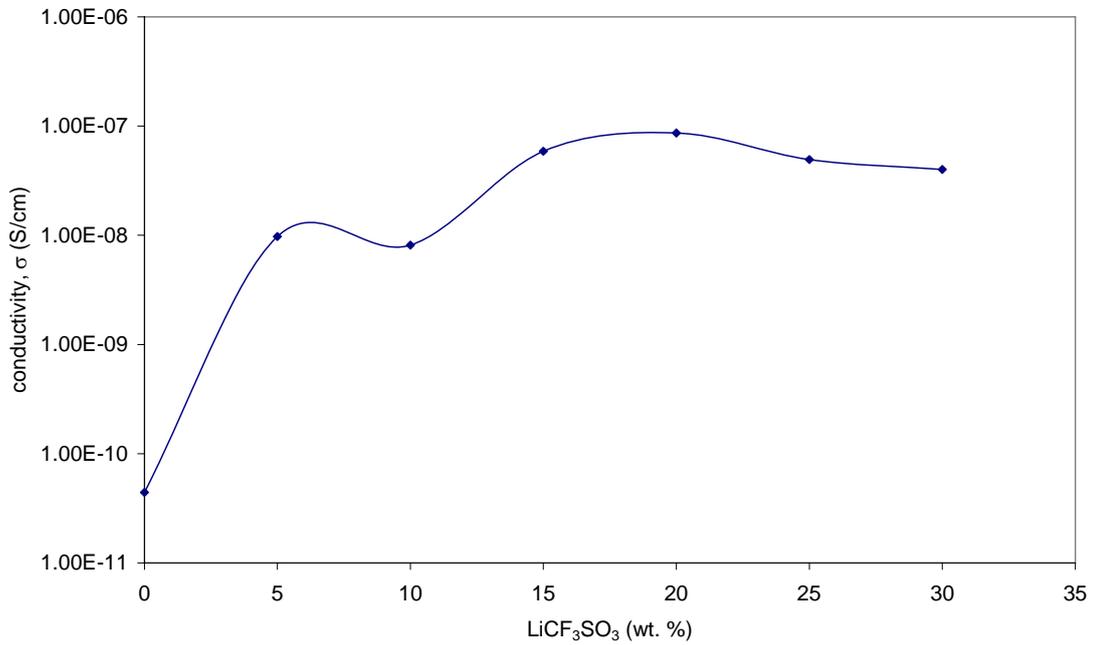


Figure 1: Variation of conductivity for PEO with different wt% LiCF<sub>3</sub>SO<sub>3</sub>

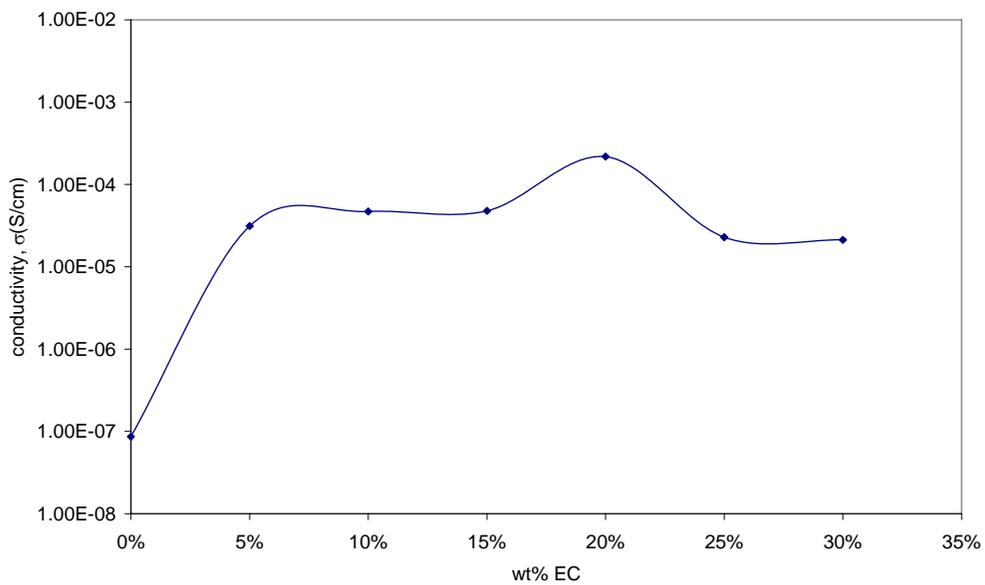


Figure 2: Variation of room temperature conductivity as a function of EC content

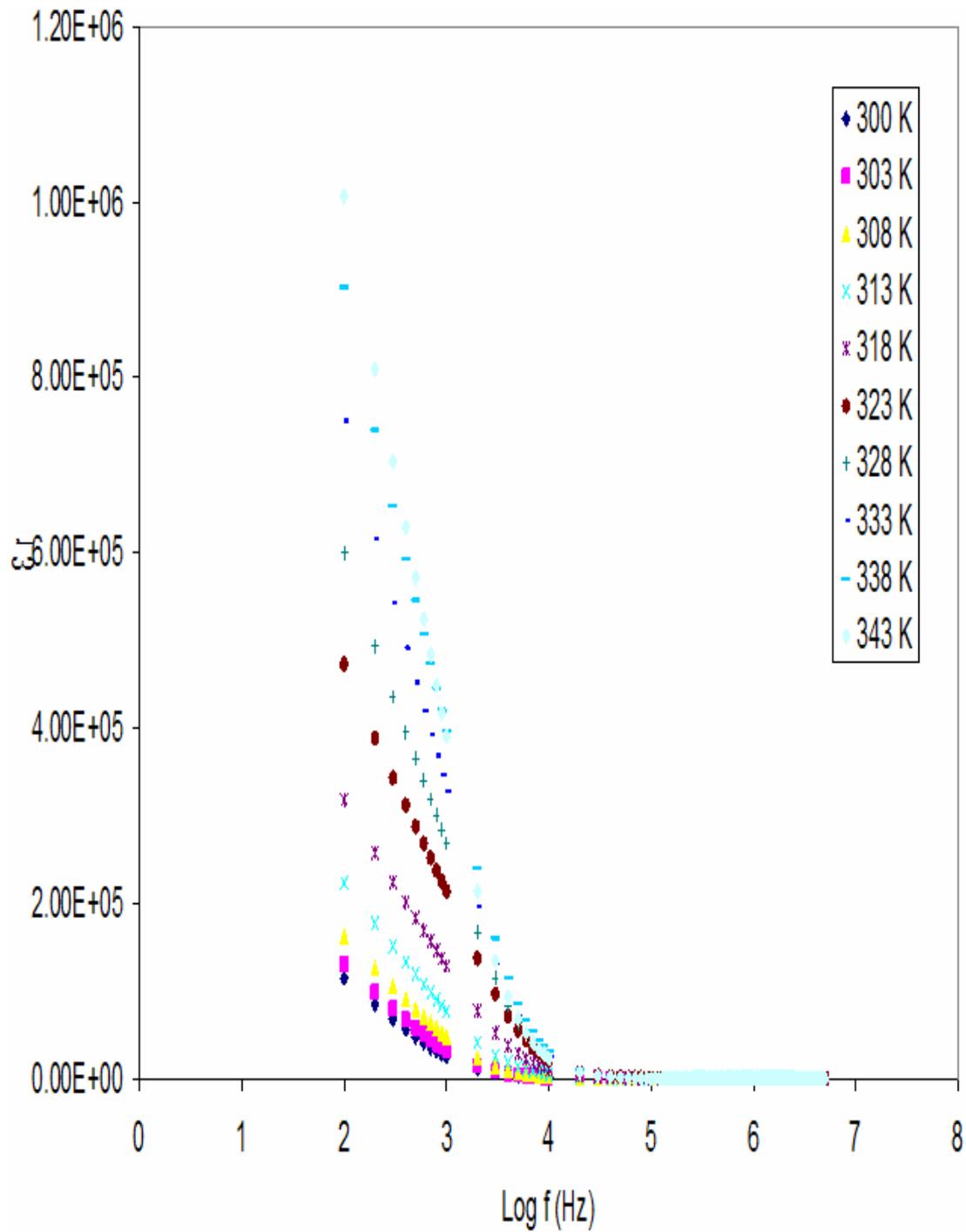


Figure 3(a): Dielectric constant versus frequency for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system at different temperature.

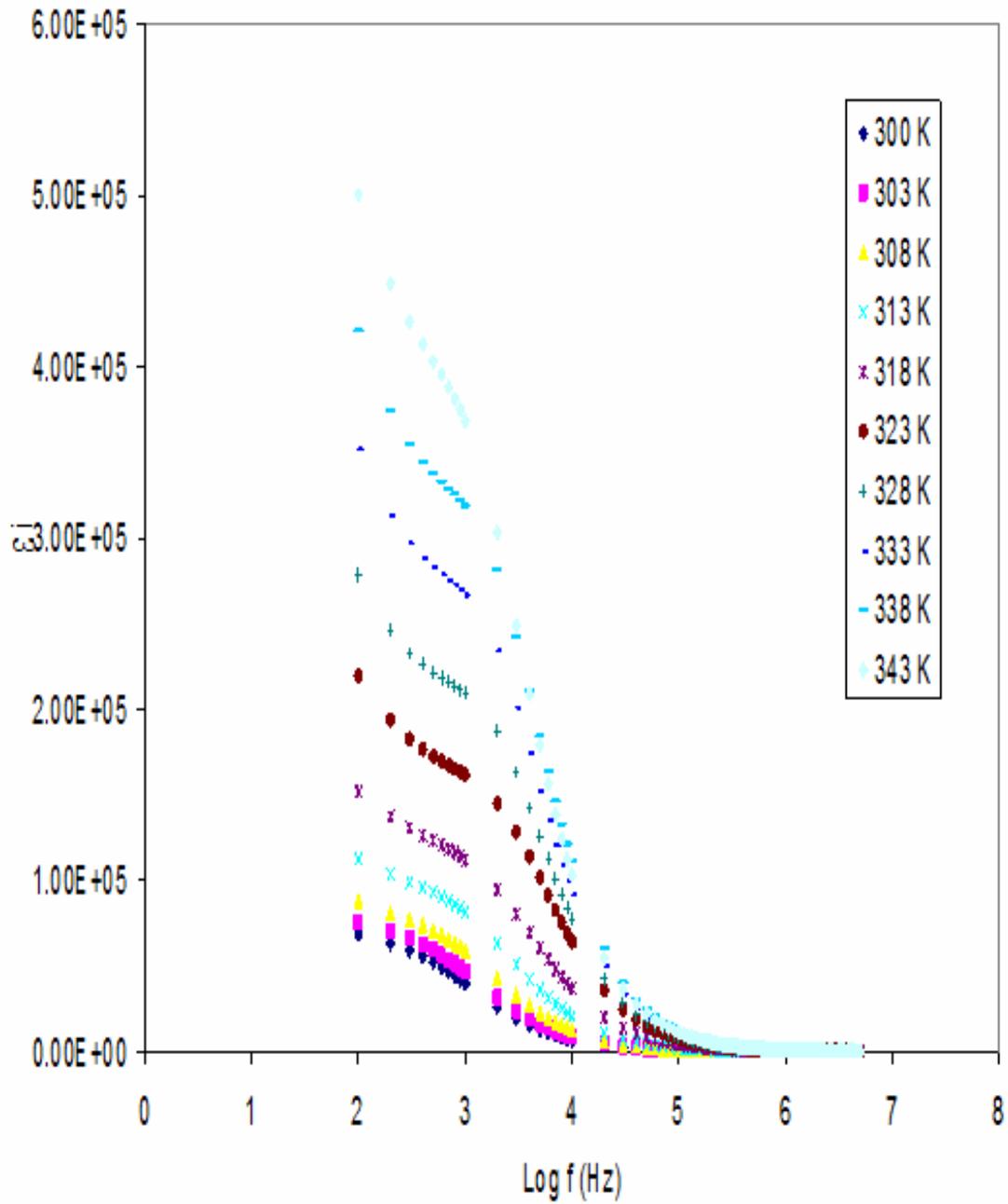


Figure 3(b): Dielectric loss versus frequency for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system at different temperature.

Figure 3 show plots of dispersion of real part and imaginary part of dielectric for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system. As can be observed from the figure 3(a) and 3(b), both the dielectric constant and dielectric loss increases as frequency decreases. The increase is more prominent towards low frequencies. The sharp increase of dielectric constant at low frequencies is due to the electrode polarization effects [8]. The polarization due to the charge accumulation decreases resulting in a decrease in the value of  $\epsilon_r$  and  $\epsilon_i$  at high frequencies. The decrease of dielectric constant with frequency shows that the system is of non-Debye type.

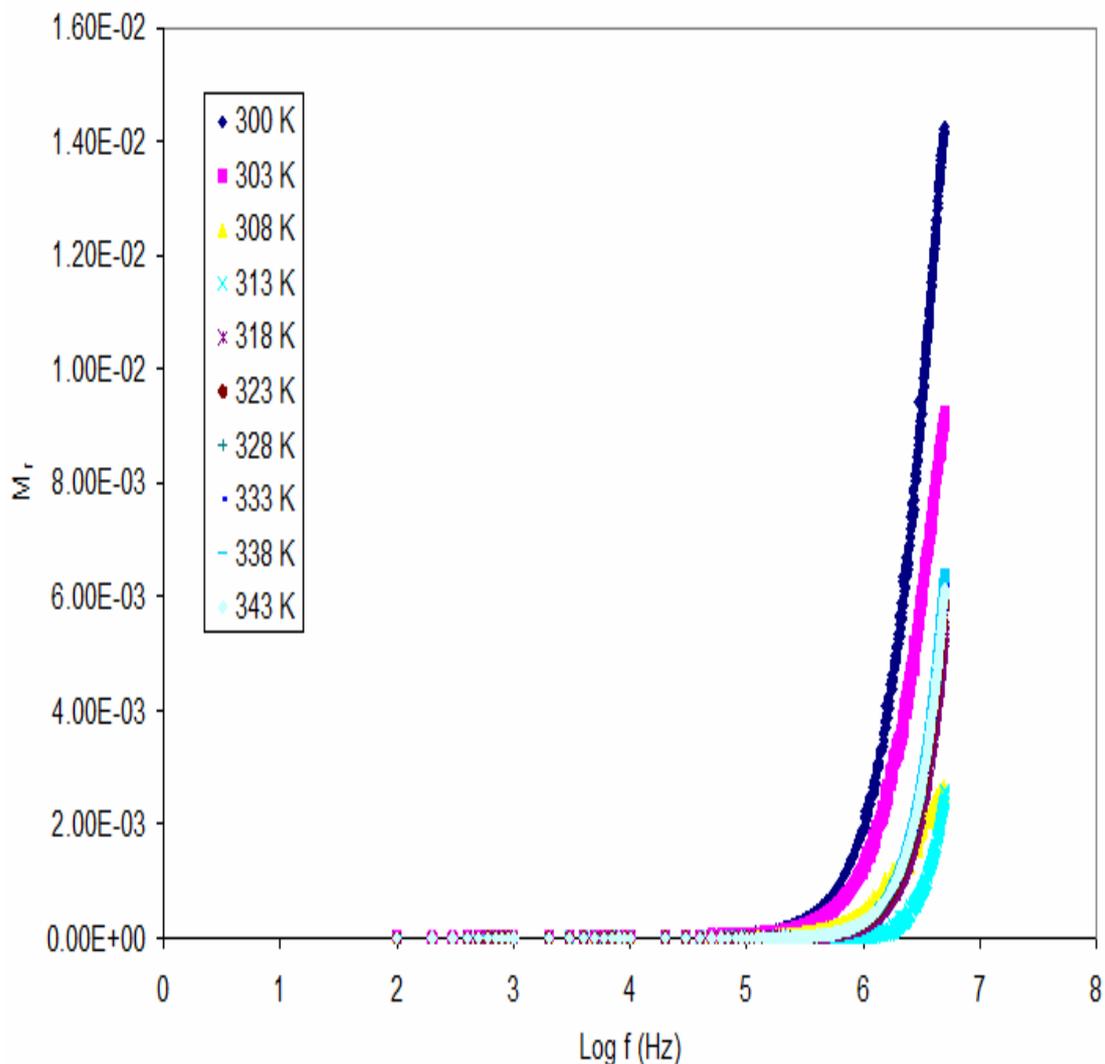


Figure 4(a): Real part of electrical modulus versus frequency for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system at different temperature.

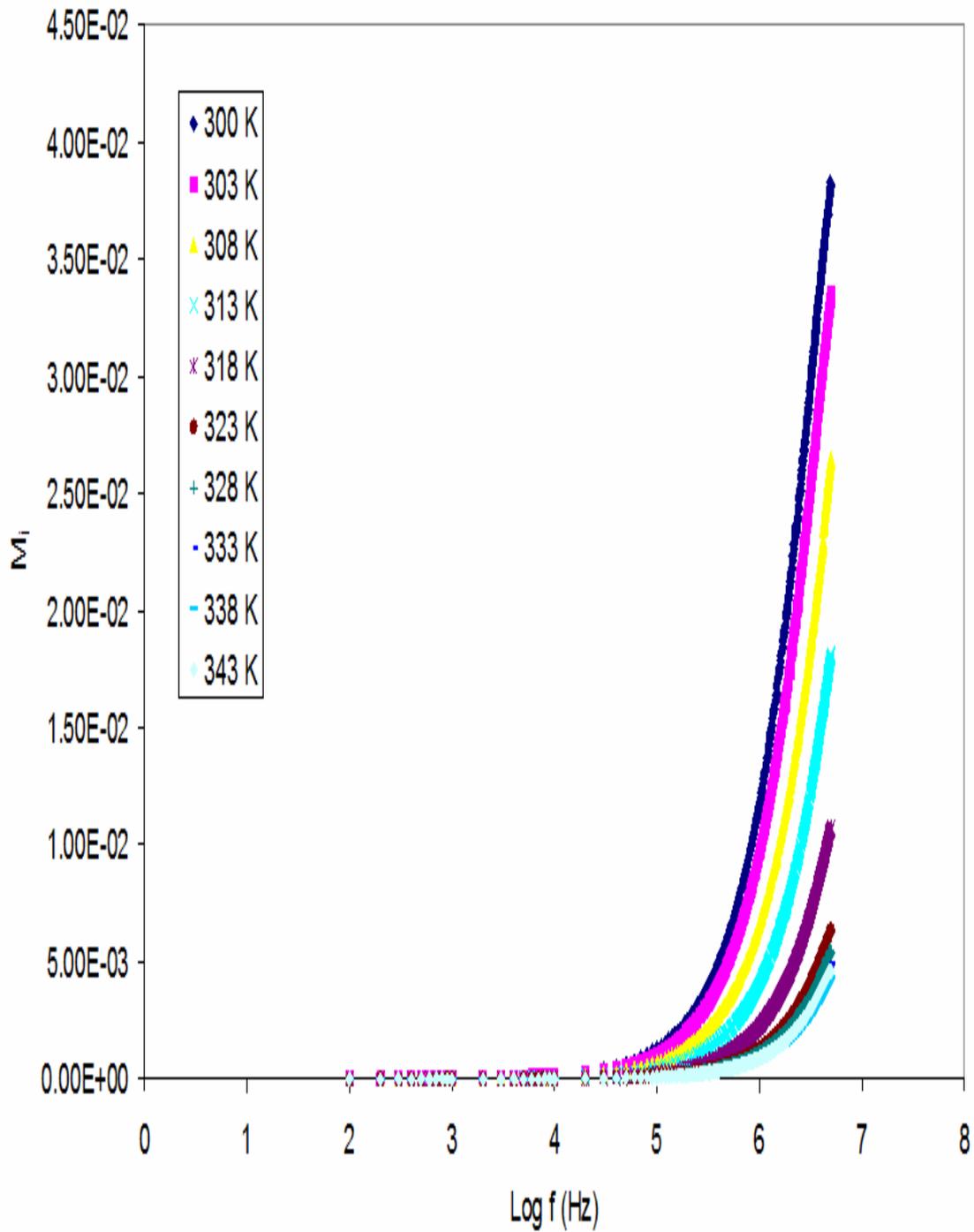


Figure 4(b): Imaginary part of electrical modulus versus frequency for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system at different temperature

Figure 4 depicts the variations of real part and imaginary part of electrical modulus for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system. The long tail present in the plot is due to the large capacitance associated with the electrodes at the low frequency region which confirms the non-Debye behavior [9-12]. Further relaxation behavior may be observed in the plot of tan δ versus frequency as shown in Figure 5.

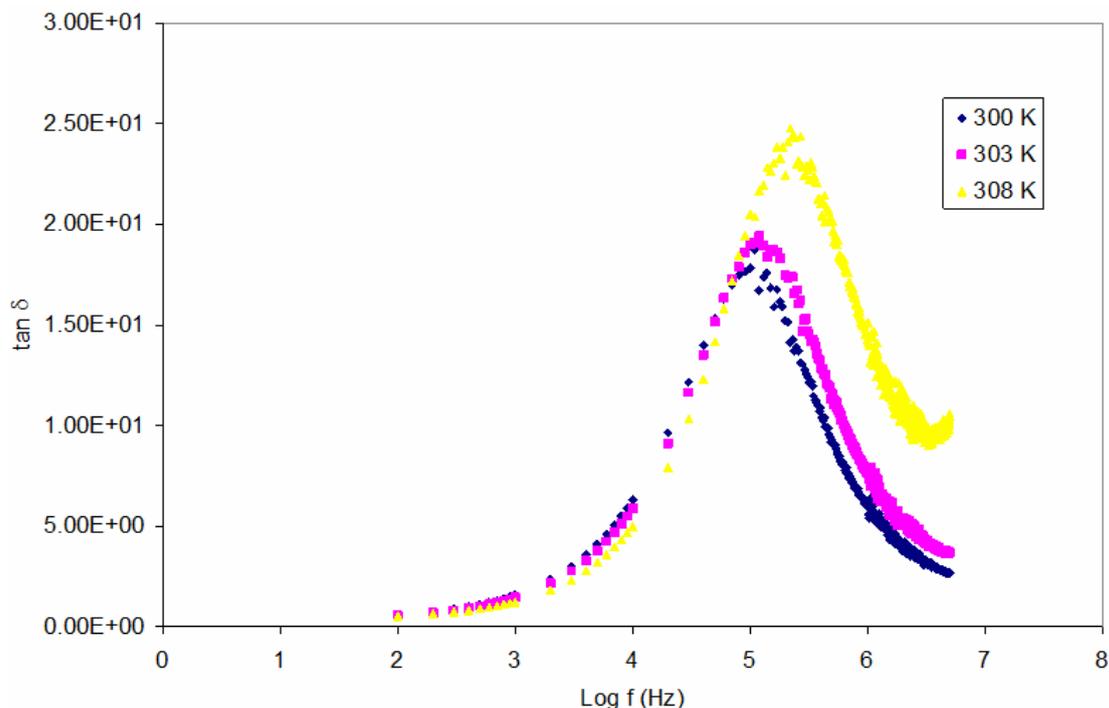


Figure 5: Variation of loss tangent ( $\tan \delta$ ) with frequency for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system at selected temperature

From the figure, it can be seen that  $\tan \delta$  increases with frequency, passes through a maximum value and thereafter decreases. The maxima of  $\tan \delta$  shift towards higher frequency and the height of the peak increases with increasing conductivity of EC. This is due to the increment in number of charge carriers for conduction which decreased the resistivity of the samples [12].

The occurrence of relaxation time,  $\tau$  can be obtained from the peak of  $\tan \delta$  using the relation:

$$\tau = 1/ \omega_{\text{peak}} \quad (2)$$

The relaxation time  $\tau$  for PEO-LiCF<sub>3</sub>SO<sub>3</sub>-EC system is listed in Table 1.

Table 1: Relaxation time at selected temperatures

Temperature (K)	$\tau$ (s)
300	$1.45 \times 10^{-6}$
303	$1.33 \times 10^{-6}$
308	$7.23 \times 10^{-7}$

As mentioned earlier, the shift of the maximum in  $\tan \delta$  towards higher frequencies at higher temperatures indicates a decrease in the value of relaxation time. The temperature dependence of relaxation time appears to be thermally activated and may be described by the Arrhenius law [13,14]:

$$\tau = \tau_o \exp (+E_d/kT) \quad (3)$$

where  $\tau_o$  is the pre exponential factor;  $E_d$  is the activation energy for the relaxation process and  $k$  is the Boltzmann constant. In order to confirm the straight line nature of this plot the regression value is usually calculated and in this case it is found to be 0.98 thus confirming its Arrhenius nature. It is also possible to calculate the value of the activation energy of the relaxation process from the slope of the plot and this is found to be 0.39 eV.

## CONCLUSION

The dielectric behaviors of the prepared samples show strong dependence on frequency and the amounts of EC. The frequency dependence of  $\epsilon_r$ ,  $\epsilon_i$ ,  $M_r$ ,  $M_i$  and  $\tan \delta$  is non-Debye type.

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