



# Characterization of relaxation processes over static permittivity frequency regime and compliance of the Stokes-Einstein-Nernst relation in propylene carbonate



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## ABSTRACT

Complex dielectric permittivity, alternating current electrical conductivity, electric modulus and impedance spectra of propylene carbonate were investigated in the frequency range from 20 Hz to 1 MHz and temperatures from 278 K to 328 K. The values of static permittivity, Kirkwood correlation factor, ionic conductivity, electric double layers and conductivity relaxation times, and the conductivity and relaxation activation energies of the propylene carbonate were determined. The effects of ionic impurities on electrical conduction and low frequency relaxation processes in propylene carbonate were explored. It was found that the conductivity behaviour of ionic contaminants in neat liquid propylene carbonate fulfilled the Stokes-Einstein-Nernst relation for the ions movement in viscous media. These results confirm great significance in interpretation of ion-conduction mechanism in liquid and solid polymer electrolytes when propylene carbonate is used as solvent and plasticizer, respectively.

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## 1. Introduction

Highly polar liquids commonly absorb volatile ionic impurities at the stage of their synthesis and packaging [1]. The concentration of these ions is further activated in the liquids under influences of natural electromagnetic and other irradiations [1–3]. These unidentified charges strongly contributed to the dielectric behaviour of polar liquids in low frequency region (static permittivity frequency regime) [4,5]. Further, they alter the ionic conductivity (described in terms of volume conductivity) and exhibit a temperature dependent Debye-type conductivity relaxation which mainly occurs in the kilohertz to megahertz frequency range [4–9]. The conduction due to free ions contamination in polar dielectric liquids arises not only from the displacement current but also from the actual charge transport behaviour similar to the ionic conduction in liquid electrolytes. Further, the significant enhancement in electrical conduction with increase of temperature of neat polar liquids also labels them as liquid semiconductors [2,3]. Comparative study on different polar liquids has established that their ionic conductivity due to residual charges increases with the increase of static permittivity and decreases with increase of viscosity of the liquid at fixed temperature [10]. It has also been established that the temperature dependent measurements of radio frequency conductivity and viscosity of the polar liquids have correlation with their molecular reorientation dynamics [2,3]. Although, the dielectric absorption spectra in the microwave frequency

region (gigahertz frequencies) is mainly used to reveal the molecular dynamics of dipolar liquids because the ionic charge transport is not important at such high frequencies [11–13].

It is worthy here to report that the concentration of volatile ionic impurities in dipolar liquid can be reduced by its drying over a molecular sieve for several days, and then by nitrogen bubbling followed by the electro dialysis deionization process, but their effect on low frequency ionic conductivity at room temperature cannot be completely eliminated. Therefore, it is interest from technological, industrial and academic point of views to study the low frequency dielectric dispersion behaviour and the residual free ions conductivity relaxation processes in highly polar (high static permittivity) liquids, because the concentration of ions contaminants is proportional to their static permittivity [10]. Static permittivity of a dipolar solvent is a direct measure of its solvating power and it governs the electrochemical behaviour and other properties of a material prepared/synthesized with the use of such polar solvents.

Among the polar solvents, propylene carbonate (PC) is a dipolar molecular system of broad liquid range (–49 °C to 242 °C) and high polarity (static permittivity  $\epsilon_s = 64.52$  at 25 °C and dipole moment  $\mu = 4.94$  D). Due to high solvating power of PC, it is commonly used solvent in preparation of electrolytes for rechargeable lithium ion batteries [14], as a plasticizer in solid polymer electrolytes [15] and in other industrial applications [16]. In order to understand the polarity of PC solvent and its solvating power for alkali and alkaline ionic salts, the dielectric characterization of PC in its pure state and binary mixtures with other polar solvents had been long back an intense subject of investigations [17–

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21]. Characterization of molecular reorientation dynamics of PC had also been attempted from an early stage of the development of dielectric relaxation spectroscopy (DRS) [22–24]. In liquid state, the PC exhibits molecular reorientation relaxation dynamics in microwave region (relaxation peak around 4 GHz and molecular relaxation time  $\tau_D = 43$  ps, at 25 °C) [24].

Recently, low-frequency (100 Hz to 5 MHz) impedance spectroscopy of PC based diluted electrolyte solution (lithium perchlorate ( $\text{LiClO}_4$ ) mole fraction  $x_{\text{LiClO}_4} = 6 \times 10^{-5}$  dissolved in molecular sieve dried PC) has been systematically investigated over the broad temperature range (250 K to 350 K) [25]. This study concluded that the charge relaxation time of known ions ( $\text{Li}^+$  and  $\text{ClO}_4^-$ ) dissolved in PC at very low concentration (one ion per  $10^4$  molecules of PC solvent) exhibits the normal Brownian dynamics and the temperature dependent conductivity-viscosity behaviour of the electrolyte obeys the Stokes-Einstein relations. Our laboratory measurement at room temperature (298 K) revealed the dc ionic conductivity ( $\sigma_{dc}$ ) of the order of  $10^{-5} \text{ S} \cdot \text{cm}^{-1}$  due to residual charges in neat PC of purity higher than 99% and was used as received. In the above mentioned study on diluted electrolyte solution [25], authors initially dried the PC solvent over molecular sieve for several days which definitely decreased the residual ions concentration, thereby; its  $\sigma_{dc}$  value drops up to  $7.26 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ , at 298 K. In the prepared diluted electrolyte solution (PC +  $\text{LiClO}_4$ ), the  $\sigma_{dc}$  value due to known  $\text{Li}^+$   $\text{ClO}_4^-$  ions again raised up to  $1.87 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$  from its background conductivity ( $7.26 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ ), at 298 K [25]. Earlier, during static permittivity measurements on neat PC, initially, it was dried over a molecular sieve for several days and then nitrogen was bubbled through the same at 60 °C in order to reduce the concentration of volatile ions impurity [24]. The  $\sigma_{dc}$  of PC after this purification processing was reported lower than  $1 \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ , at 278 K [24]. In the low electrical conducting sample of dipolar liquid, the effect of electrode polarization (EP) and electric double layers (EDLs) dynamics in low-frequency dielectric spectra cannot be completely suppressed [26], although these residual ions had no effect on static permittivity value of a solvent if measured under dynamic electric field of 1 MHz [21,24]. The dielectric relaxation study of super cooled PC in low-frequency range (5 mHz to 5 MHz) had revealed that the EP effect and EDLs dynamics can be fully suppressed at low temperature (–100 °C to –120 °C) provided that the room temperature  $\sigma_{dc}$  value of PC was reduced up to  $10^{-13} \text{ S} \cdot \text{cm}^{-1}$  by deionized electro dialysis [23].

Therefore, the above mentioned facts clearly confirm that the ionic contaminants in liquid PC influence the low-frequency dielectric dispersion and exhibit the conductivity relaxation, whatever is the concentration of these unidentified ions. The earlier temperature dependent low-frequency impedance spectroscopic study on diluted electrolyte solution (PC +  $\text{LiClO}_4$ ) revealed that the  $\text{Li}^+$  and  $\text{ClO}_4^-$  ions have the Brownian translational diffusion and their relaxation behaviour obeys the Stokes-Einstein-Nernst model [25]. In reference to this study, the conductivity relaxation behaviour of unidentified free ions in neat PC is also needed because it is important in regards to its electrochemical applications. The  $\sigma_{dc}$  ( $1.43 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ ) of neat PC, at 298 K, which is measured in our laboratory, is found close to that of the molecular sieve dried liquid PC based diluted electrolyte solution ( $\sigma_{dc} = 1.87 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ , at 298 K) [25]. Therefore, the present work concerns the study of ionic conductivity and conductivity relaxation due to ionic contaminants in neat PC, and their comparison with the conductivity behaviour of diluted electrolyte solution [25]. The ionic conductivity in electrolyte solution is resulted by the known ions of added ionic salt ( $\text{Li}^+$   $\text{ClO}_4^-$ ) and the unidentified ionic contaminants. In order to get detailed behaviour of electrical conduction in neat PC, the spectra of all the four quantities i.e. complex dielectric function (complex permittivity)  $\epsilon^*(\omega) = \epsilon' - j\epsilon''$ , alternating current (ac) electrical conductivity  $\sigma^*(\omega) = \sigma' + j\sigma''$ , electric modulus  $M^*(\omega) = M' + jM''$  and complex impedance  $Z^*(\omega) = Z' - jZ''$  were analyzed in the frequency range from 20 Hz to 1 MHz with temperature variation. Such characterization of

dielectric and electrical properties and also the relaxation processes of neat PC have noteworthy importance in analysis and understanding of the ion-conduction mechanism in liquid and plasticized solid electrolyte materials having PC as one of the constituents because the electrical properties of electrolytes are mainly characterized over the frequency range which is used in the present study.

## 2. Experimental procedure

Propylene carbonate (PC) of purity >99% was obtained from Loba Chemie, India, and it was used as received for its dielectric and electrical characterization.

The  $\epsilon^*(\omega)$ ,  $\sigma^*(\omega)$ ,  $M^*(\omega)$  and  $Z^*(\omega)$  spectra of neat PC were carried out with the use of an Agilent technologies 4284A precision LCR meter and 16452A dielectric test fixture in the frequency range from 20 Hz to 1 MHz and in the temperature range from 278 K to 328 K. The refractive index ( $n_D$ ) of PC was measured using Abbe refractometer at sodium D-lines. The measuring cells in different equipments were thermostated using a water circulation bath in which the temperature was controlled with a Thermo-Haake DC10 controller. The measurements were performed for increasing temperature in the range  $T = 278 \text{ K}$  to 328 K.

## 3. Results and discussion

The real  $\epsilon'$  and imaginary  $\epsilon''$  parts of complex dielectric permittivity of the liquid PC were determined from the Eq. (1) [27]:

$$\epsilon^*(\omega) = \epsilon' - j\epsilon'' = \alpha \left( \frac{C_p}{C_0} - j \frac{1}{\omega C_0 R_p} \right) \quad (1)$$

where  $\omega = 2\pi f$  is the angular frequency of ac electric field,  $\alpha$  is the correction coefficient,  $C_0$  and  $C_p$  are the capacitances without and with sample, respectively, and  $R_p$  is parallel resistance with sample of the cell. Fig. 1 presents the  $\epsilon'$  and  $\epsilon''$  spectra of neat PC at different temperatures. As can be clearly seen from the  $\epsilon'$  spectra, it has two different characteristic regions over the frequency range from 20 Hz to 1 MHz which separates around 20 kHz. In low frequency region, on log-log scale, the  $\epsilon'$  values increase linearly with decrease of frequency up to 5 orders of magnitude with a slope higher than unity. The enormous increase of  $\epsilon'$  values with decrease of frequency in low frequency region is certainly from the contribution of electrode polarization (EP) effect. This effect represents the formation of electric double layers (EDLs) capacitances at interface of the dielectric material and the metallic electrode surfaces in plane geometry by accumulation of long distance drifted ions and free charges [26]. In high frequency region, there is no long range movement of free charges due to fast reversal changes developed in the applied ac field, and thus the steady state region is observed in  $\epsilon'$  spectra. At a fixed frequency, it is found that the  $\epsilon'$  values in low frequency region increase with the increase of temperature which reveals that the concentration of induced ions contributed in formation of EDLs increases with the temperature enhancement of liquid PC. The EDLs length (density of accumulated ions and charges at the interface) of the liquid dielectric material decreases gradually with increase of frequency of the stimulating electric field, and at higher frequencies, it completely diminishes [26], thereby, the  $\epsilon'(f)$  values approach to the steady state (static permittivity  $\epsilon_s$ ). The inset of figure shows the enlarged view of high frequency  $\epsilon'$  spectra. It is also observed from the  $\epsilon'(f)$  spectra that the beginning frequency of steady state shifts towards higher frequency side as the temperature of liquid PC increases.

The temperature dependent  $\epsilon_s(T)$  values of liquid PC ( $\epsilon'$  value at 1 MHz are considered as  $\epsilon_s$ ) are given in Table 1. These  $\epsilon_s(T)$  values of the investigated neat PC are found in good agreement with those of the molecular sieve dried PC [21], which confirms that the concentration of unidentified ionic contaminants does not affect the static permittivity of neat PC is also true in case of, and it is also true in case of diluted electrolyte solution as reported in recent work [25]. Low-frequency

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