MICROWAVE DIELECTRIC RELAXATION STUDY OF BINARY MIXTURES OF POLYETHYLENE GLYCOL MONOMETHYLETHER-WATER

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Abstract
The dielectric measurement of binary mixtures of polyethylene glycol monomethylether (PEGME) [Molecular Weight(M.W.): 550] in aqueous solutions over whole concentration range and at temperatures 25˚C, 15˚C and 5˚C carried out using time domain reflectometry (TDR) technique in the frequency range of 10 MHz to 30 GHz. The dielectric spectra obtained from the measurement have been fitted to Cole-Davidson model using non linear least square fit method in order to evaluate the dielectric parameters such as the static dielectric constant and relaxation time for the mixtures. The non linear behavior of dielectric parameters suggest intermolecular interaction among the unlike molecules. Excess properties and Bruggeman factor confirms the contribution of hydrogen bonding interactions among the solute-solvent mixtures.

Keywords: Complex permittivity, Dielectric Relaxation, Time Domain Reflectometry.

I. INTRODUCTION

The study of dielectric absorption (constant) and dispersion spectra (dielectric loss) of binary liquid mixture provides information regarding molecular interaction through hydrogen bonding in the solute-solvent mixture [1]. The dielectric relaxation spectroscopy technique (DRS) is applied to the systems in which hydrogen bonds play an important role such as aqueous solutions [2]. The PEGME [$CH_3(OCH_2CH_2)_nOH$] is polymer with ‘n’ indicating average number of oxyethylene group. PEGME’s are also known as methoxy polyethylene glycols are addition of polymers of ethylene oxide and methanol. They are used in surfactants, polyester and polyurethane based paints. In literature the dielectric studies of polymers [3-5] are extensively carried out by various researchers but the dielectric study PEGME’s are scarce.

Recently, we have studied dielectric and electrical characterization over the frequency range 20 Hz to 2 MHz of binary mixture PEGME 350 in aqueous solution [6]. In present work, the complex permittivity spectra of PEGME550 with water over whole concentration range have been measured using time domain technique in the frequency range of 10MHz to 30GHz at different temperatures (25˚C, 15˚C and 5˚C). The dielectric parameters have been evaluated using non linear least square fit method. Molecular interactions among the polymers in presence of aqueous solutions have been discussed using excess properties.

II. EXPERIMENTAL DETAILS

A. Materials

PEGME550 was obtained from Alfa Aesar with purity 99% and Water with HPLC grade made by Qualigens. They were used without further purification. The solutions were prepared at different weight percentage of PEGME550 in water.

B. Measurements and data analysis

The measurements of complex permittivity spectra in the frequency range of 10 MHz to 30 GHz have been carried out by the time domain reflectometry technique. For the measurements, Tektronix model number DSA8200 digital serial analyzer with sampling module 80E08 has been used. The detailed data analysis to obtain the complex permittivity spectra ε*(ω) and the dielectric parameters using nonlinear least squares fit method have been discussed in our previous work [7]. Fig. 1 shows frequency dependent dielectric permittivity spectra for PEGME550–water mixtures at 25°C.

III. RESULTS AND DISCUSSIONS

A. Study of dielectric parameters

The complex permittivity is given as □*(ω) = □'(ω) – j□"(ω) where, □'(ω) and □"(ω) are the dielectric permittivity and dielectric loss respectively. The complex permittivity □* (ω) data were fitted by the non-linear least squares method to the Cole-Davidson model [8]

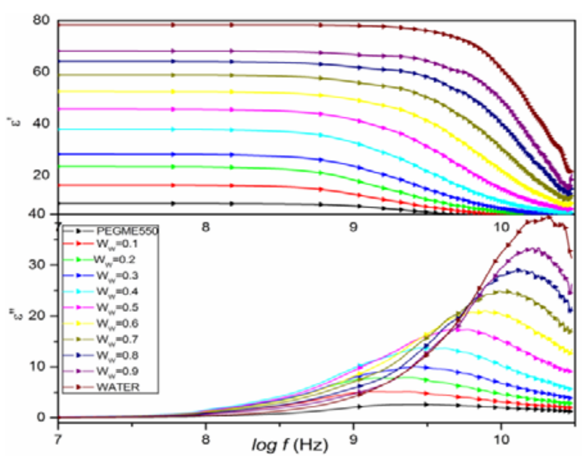

Fig. 1 Frequency dependent dielectric permittivity (ε′) and dielectric loss (ε″) for PEGME 550-water over entire concentrations at 25˚C.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(j\omega\tau)]^\beta} \qquad (1)$$

where □* (ω) is complex permittivity at an angular frequency ω, ε_0 is the static dielectric constant, ε_∞ is permittivity at high frequency, τ is the dielectric relaxation time and β is an asymmetric relaxation fitting parameter and are tabulated in Table 1. Refractive indices (n_D) of those binary mixtures have been measured by Abbe's refractometer with an accuracy $\pm 5\times10^{-4}$ and are reported in Table 1. Dielectric permittivity values of binary mixtures of PEGME 550-water against the mole fraction of water is plotted in Fig. 2.

Here, on increasing the amount of water in the mixture, as the concentration of PEGME 550 increases in water, the values of static dielectric permittivity suddenly drops from pure water around $X_W \approx 0.9$. Further increase in concentration of PEGME, the value of ε_0 very slowly decreases. Fig.3 shows the relaxation time (τ in pico-second) values of binary mixtures of PEGME 550-water against the mole fraction of water. It supports our earlier discussion, the relaxation times of binary mixtures also show non linear nature, it may possible due to certain intermolecular interactions among the solute and solvent molecules. Also the non linearity in dielectric parameters is a function of temperature and it increases with decrease in temperatures.

B. Excess dielectric permittivity

The contribution of hydrogen bonds to the dielectric properties of the mixture can be studied in terms of the excess dielectric permittivity. The excess dielectric permittivity (ε_0^E) values for the PEGME 550-water binary mixtures are obtained using formulation earlier used in the literature [9-12]. It gives qualitative information about multimers formation in the binary mixtures. In Fig. 4 the excess dielectric values are negative for entire concentrations.

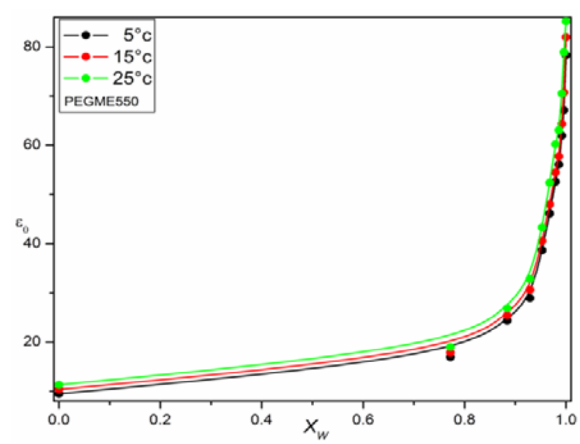

Fig. 2 Dielectric permittivity (ε_0) Vs. mole fraction of water (X_W) for PEGME550- water mixtures.

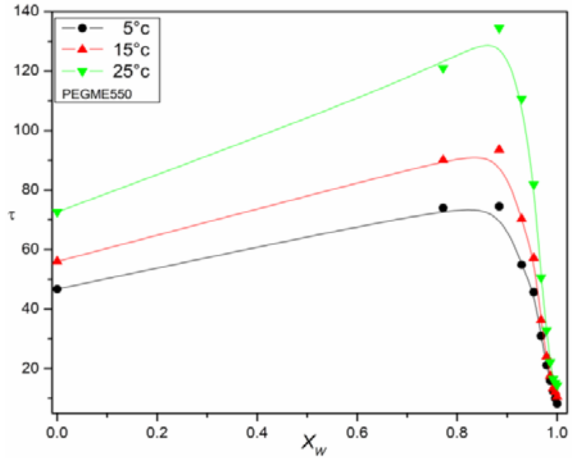

Fig. 3 Relaxation time (τ) in ps. Vs. mole fraction of water (X_W) for PEGME550-water mixtures.

These negative ε_0^E values show the experimental evidence of molecular interaction among PEGEME 550 and water molecules. This information may be endorsed as the formation of complex structure in PEGME's–water through H-bonds such that the effective dipole moment get reduced. The plot exhibit pronounced minima around X_W=0.8 which suggests the stoichiometric ratio of complex structure, water:PEGME is 4:1. Fig.5 shows the plot of excess permittivity at high frequency (ε_∞^E). Dielectric permittivity at high frequency of binary mixtures is determined from the square of refractive index (n_D). The values of ε_∞^E give information about the magnitude of electronic polarization in binary mixtures. From Fig.5 the values of $\varepsilon_\infty^E > 0$ for entire binary mixtures studied here suggests that there is a net increase in the magnitude of the electronic polarization due to H-bond interactions between PEGME 550 and water molecules in these binary systems.

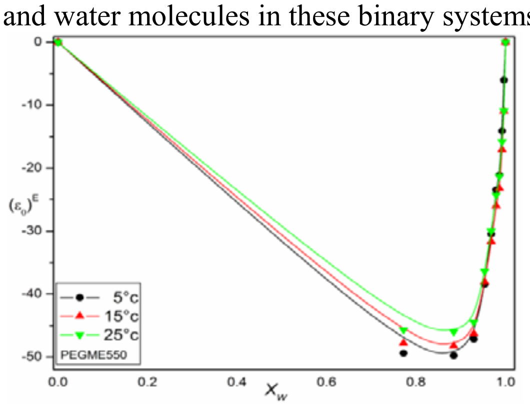

Fig. 4 Excess dielectric permittivity (ε_0^E) Vs. mole fraction of water at various temperatures for PEGME550- water mixtures.

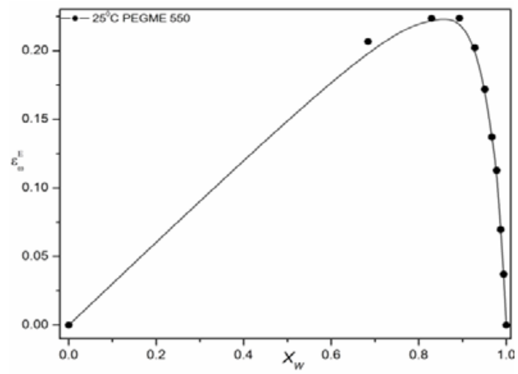

Fig. 5 Excess dielectric permittivity at high frequency (ε_∞^E) Vs. mole fraction of water at 25°C PEGME550-WATER.

IV. CONCLUSIONS

The dielectric relaxation study of PEGME550 in aqueous solutions has been studied using time domain technique in the frequency range of 10 MHz to 30 GHz. The dielectric parameters studied here exhibit non linear behavior attributed as hetero molecular interactions among the polymer–water molecules through hydrogen bonding. The intermolecular interactions among these unlike molecules are confirmed by the excess dielectric parameters. The negative values of excess dielectric values suggest that the hydrogen bonding interactions among the PEGME's-water mixtures such that the effective dipole moments get reduced.

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