Dielectric dispersion study of binary mixtures of methyl ethers with water at 298.15 K using frequency domain technique

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A precision LCR meter along with a liquid dielectric cell have been used to measure the capacitance and resistance of the binary mixtures of methyl ethers with water at 298.15 K in the frequency range of 20 Hz to 2 MHz. The measured values are used to compute the complex dielectric permittivity $\varepsilon^*(\omega)$. The parameters like complex electrical modulus $M^*(\omega)$, complex electrical conductivity $\sigma^*(\omega)$ and loss tangent (tan δ) are obtained from the complex dielectric permittivity values of the samples. The values of excess dielectric permittivity of the samples are calculated using the respective static dielectric permittivity values. The refractive indices of all the samples were measured using Abbe's refractometer at 298.15 K. All these parameters are used to gain insight into the concentration dependent variation in dielectric and electrical properties of the binary mixtures. A dominance of electrode polarization effect in the lower frequency region is observed for all the samples studied here.

1 Introduction

Glymes have both hydrophilic and hydrophobic characteristics. They are also thermally and chemically stable, and can even form complexes with ions. Therefore, glymes have numerous laboratory as well as industrial applications[1]. In earlier work the dielectric relaxation properties of glymes namely ethylene glycol monomethyl ether (EGDME) and ethylene glycol dimethyl ether (DEGDME) were studied at two different frequency ranges using Agilent precision LCR meter (20 Hz to 2MHz) and using time domain reflectometry (10MHz to 30GHz)[2,3]. The dielectric and electric parameters obtained from the measurement were used to explain the various relaxation processes in the binary mixtures of the glymes with water. The inter-molecular interaction among the aqueous solutions of glycol ethers have been discussed using excess dielectric properties which suggest the reduction in effective dipole per unit volume in aqueous solutions of glycol ethers[2,3]. Triethylene glycol monomethyl ether (TEGMME) with structural formula $CH_3(OCH_2CH_2)_3OH$ is known as methoxytriglycol and triethylene glycol dimethyl ether (TEGDME)

with structural formula $CH_3(OCH_2CH_2)_3OCH_3$ is known as triglyme. In literature, molecular interactions among the TEGMME – water have been studied using some physico- chemical properties[4] but the dielectric study of TEGMME and TEGDME in aqueous solutions is scarce. Therefore, in present work the dielectric measurements of these liquids in aqueous solutions over complete composition range have been carried out using frequency domain technique. Dielectric and electrical characteristics like complex dielectric permittivity $\varepsilon^*(\omega)$, complex electrical modulus $M^*(\omega)$, complex electrical conductivity $\sigma^*(\omega)$ and loss tangent (tan δ) are obtained from the measured data. The hetero molecular interactions among the glymes - water binary mixture are discussed in terms of excess properties.

2 Materials and Methods

Triethylene glycol monomethyl ether (TEGMME) (95%) and triethylene glycol dimethyl ether (TEGDME) (99%) were procured from Sigma-Aldrich (India) and Alfa Aesar (India), respectively. HPLC grade de-ionized water was purchased from Fisher Scientific India Pvt. Ltd. and it is used without further purification. Aqueous binary mixtures were prepared by taking different weight fractions of

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TEGMME (W_M) and TEGDME (W_D) in water. The Shimadzu make digital analytical balance with an accuracy of ± 0.001 g was used for the weight measurements. The dielectric measurements of all the liquid samples were performed at 298.15 K in the frequency range of 20 Hz to 2 MHz by using Agilent make (E4980A) precision LCR meter with liquid dielectric test fixture (16452 A)[5]. The refractive indices of the samples were measured by Abbe's refractometer with an accuracy of ± 0.0001. The permittivity at optical frequency is obtained by squaring the refractive index value.

3 Results and Discussion

3.1 Representation of dielectric spectra

The variations in real part $\varepsilon'(\omega)$ of dielectric permittivity spectra for TEGMME + Water and TEGDME + Water binary mixtures are show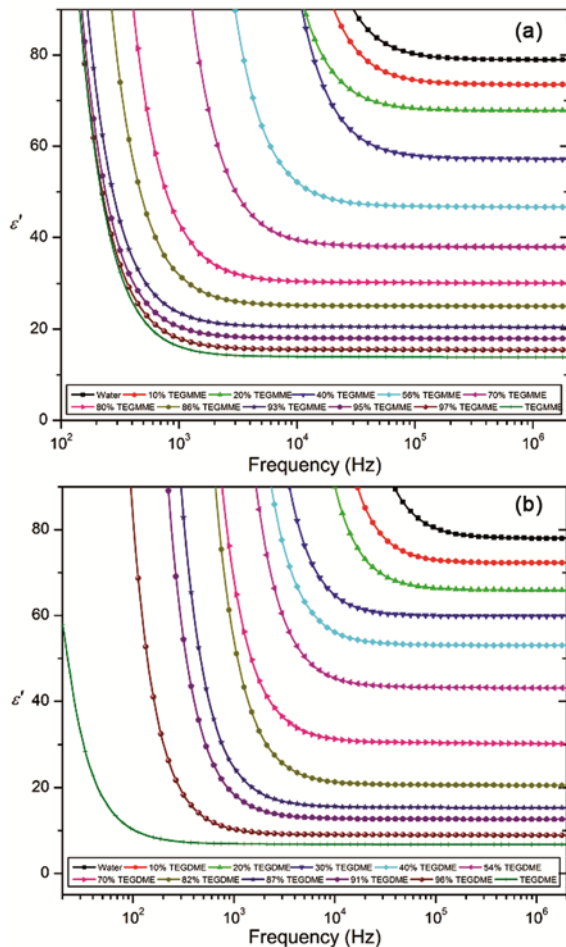n in Fig. 1 (a,b). It can be seen that in the low frequency region, ε' value increases with decrease in the frequency. This is due to the electrode polarization (EP) effect. The EP effect takes place due to formation of electric double layers (EDL) at electrode-dielectric material interface by movement of ions present in the dielectric material[6]. The EDL capacitance influences the signal at lower frequencies and covers the relaxation of the bulk sample. The frequency at which the ε' value becomes frequency independent increases with increase in the concentration of water in the binary mixtures (Fig. 1 (a) & (b). Thus, the EP effect is increasing with increase in the quantity of water in the binary mixtures. This is due to the presence of more ionic impurities in water since water is more polar as compared to TEGMME and TEGDME.

The dielectric loss $\varepsilon''(\omega)$ spectra for TEGMME and TEGDME in water are shown in Fig. 2 (a,b). It is noticed that in both the cases the dielectric loss falls
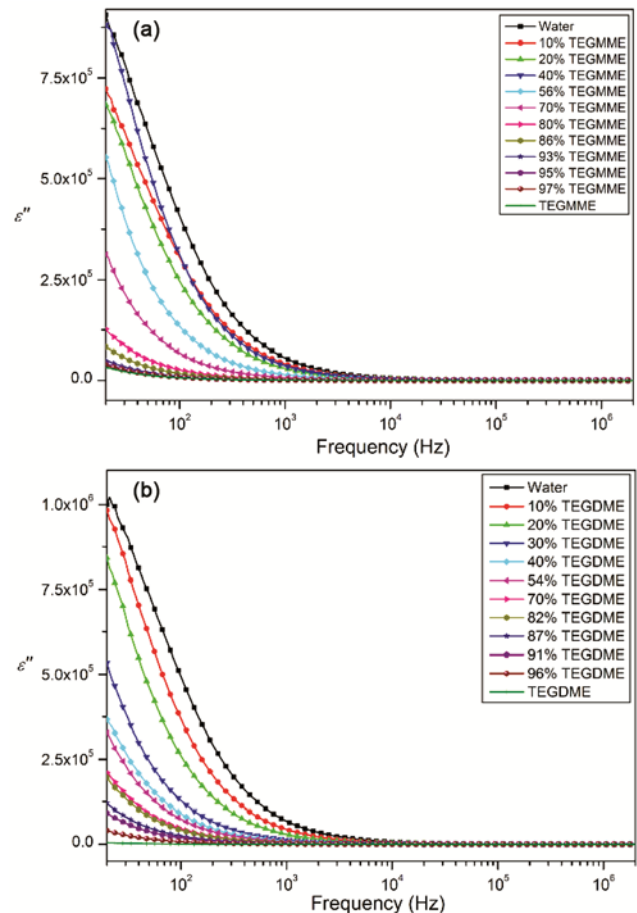

Fig. 1 — (a) and (b) shows the frequency dependent spectra of the real part ε' of the relative dielectric function $\varepsilon^*(\omega)$ for TEGMME-Water and TEGDME–Water binary mixtures respectively.

Fig. 2 — Spectra of the imaginary part $\varepsilon''(\omega)$ of the relative dielectric function $\varepsilon^*(\omega)$ for (a) TEGMME-Water and (b) TEGDME–Water binary mixtures.

rapidly with frequency up to 10^4 Hz and then it decreases slowly. Also, the dielectric loss is higher for the samples with higher concentrations of water. This is so because water is highly polar and polar liquids absorb ionic impurities in their production stage[7,8]. The ionic impurities cause the ionic conduction loss at lower frequencies which is responsible for the higher values of ε''.

The frequency dependent loss tangent tan δ (= $\varepsilon''/\varepsilon'$) spectra for TEGMME + Water and TEGDME + Water are shown in Fig. 3 (a, b). In the loss tangent spectra, the conductivity effect is suppressed and the relaxation peaks are observed. The EP relaxation frequency f_{EP} corresponding to the tan δ peak is the frequency which separates the EP phenomena from the bulk material[9]. It can be observed in Fig. 3 (a, b) that the tan δ peaks shift towards lower frequency with the increase in the
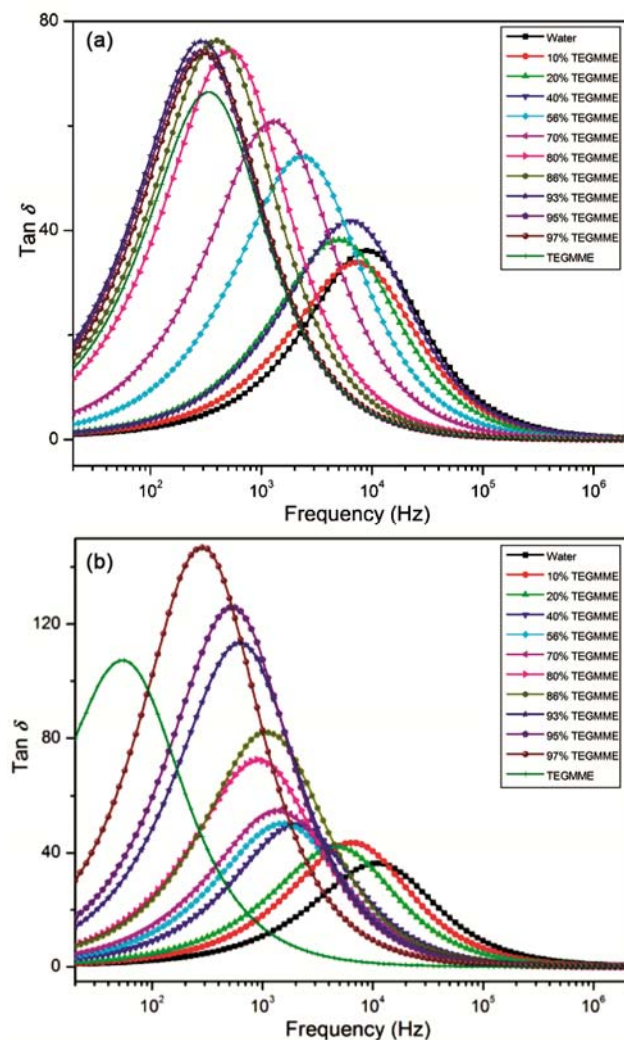
weight percent of methyl ethers in the binary mixtures. The EP relaxation time can be calculated as $\tau_{EP} = (1/2\pi f_{EP})^9$. The dielectric loss spectra shown in Fig. 2 (a, b) reveal that the dielectric loss is very high in the low frequency region due to ionic conduction process. The electric Modulus $M*(\omega) = 1/\varepsilon^*(\omega)$ is useful to explore it further. Generally, for a pure conduction process relaxation peak would be observed only in the imaginary part $M''(\omega)$ of $M*(\omega)$ spectra but not in the $\varepsilon''(\omega)$ spectra. However, in a dielectric relaxation process, the peaks would be seen in both the spectra. Thus the dielectric relaxation process can be distinguished from the localized conduction process by comparing the $M''(\omega)$ and $\varepsilon''(\omega)$ plots[10]. Also, the real part $M'(\omega)$ of $M*(\omega)$ spectra hides the space charge effect seen in the dielectric spectra[8].

Figure 4 (a, b) presents the spectra of $M'(\omega)$ for TEGMME + Water and TEGDME + Water

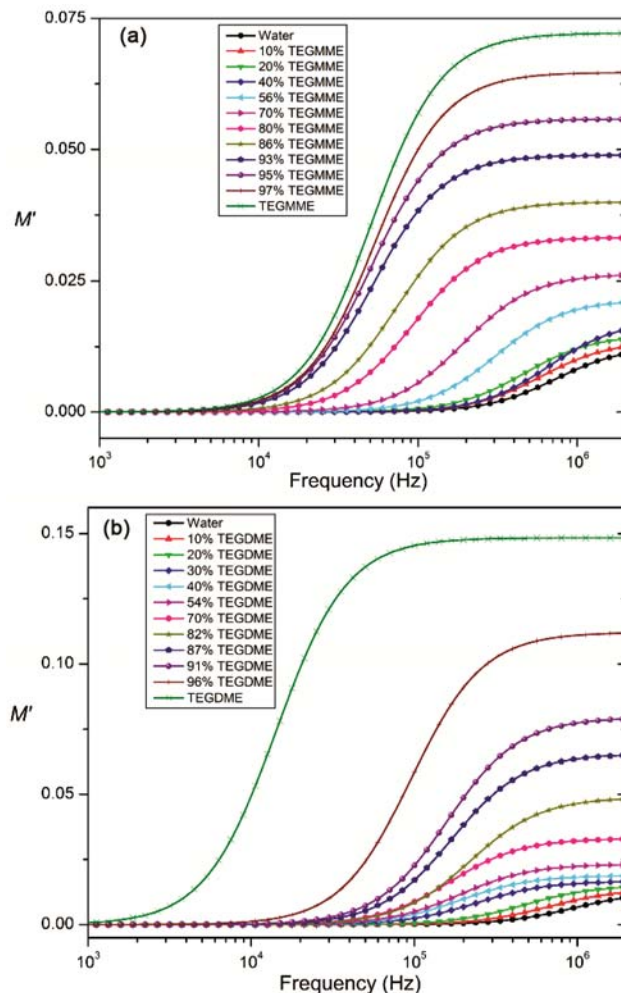Fig. 3 — Spectra of dielectric loss tan δ for (a) TEGMME-Water and (b) TEGDME–Water binary mixtures.

Fig. 4 — Spectra of the real part $M'(\omega)$ of the complex electric modulus $M*(\omega)$ for (a) TEGMME-Water and (b) TEGDME–Water binary mixtures.

respectively. It is observed in both the cases that M' approaches to zero at lower frequencies. This confirms the presence of EP at lower frequencies. A large dispersion can be seen in the ionic conduction region above f_{EP} for both the systems studied here. The values of $M'(\omega)$ increases with increase in the frequency and attains a constant level in the MHz range. These are maximum for the methyl ethers and minimum for water. This confirms the presence of fewer amounts of ionic impurities in the methyl ethers as compared to water. The spectra of imaginary part $M''(\omega)$ of $M^*(\omega)$ are shown in Fig. 5 (a, b). The peaks are observed for all the samples studied here. $M''(\omega)$ peaks shifts towards lower frequency with increase in weight percent of methyl ether. The frequency f_σ corresponding to peak value of M'' can be used

to evaluate the ionic conductivity relaxation time τ_σ ($= 1/2\pi f_\sigma$) [8].

3.2 Complex conductivity

The real part of the AC conductivity spectra of the binary mixtures of water with TEGMME and TEGDME are shown in Fig. 6 (a, b). The frequency independent plateau corresponds to the ionic or dc electrical conductivity. The dc electrical conductivity is high in water rich region while it goes on decreasing with increase in the weight fraction of methyl ethers in water. Thus, the methyl ethers contain less mobile charge carriers as compared to water.

3.3 Dielectric parameters

The measured values of static permittivity ($\varepsilon_0 =$ steady state value of ε') for pure liquids are in the order of Water ($\varepsilon_0 = 78.05$) > TEGMME ($\varepsilon_0 = 13.85$)
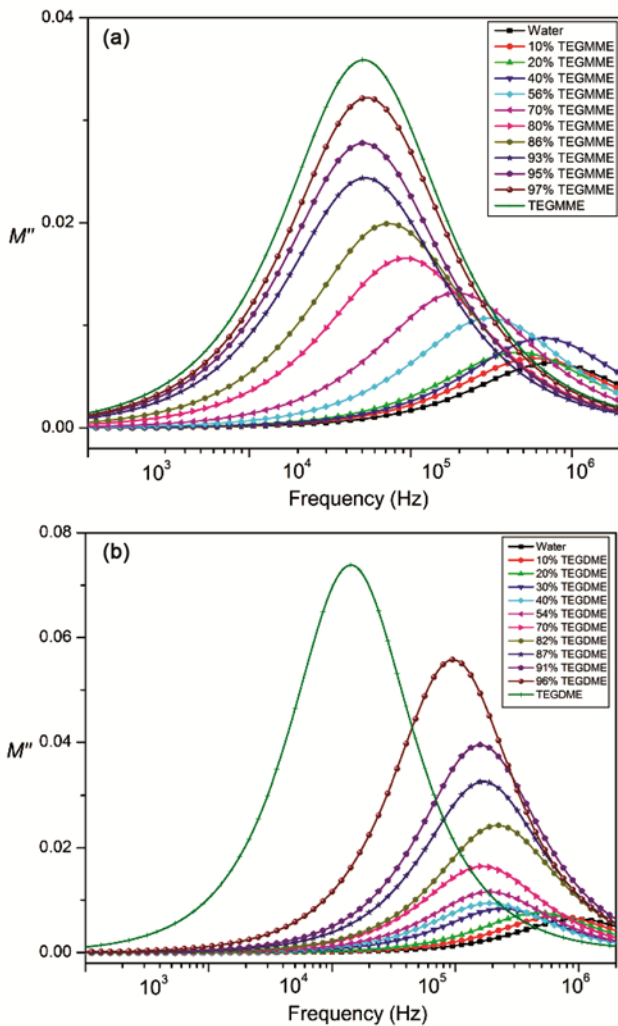

Fig. 5 — Spectra of the imaginary part $M''(\omega)$ of the complex electric modulus $M^*(\omega)$ for (a) TEGMME-Water and (b) TEGDME–Water binary mixtures.
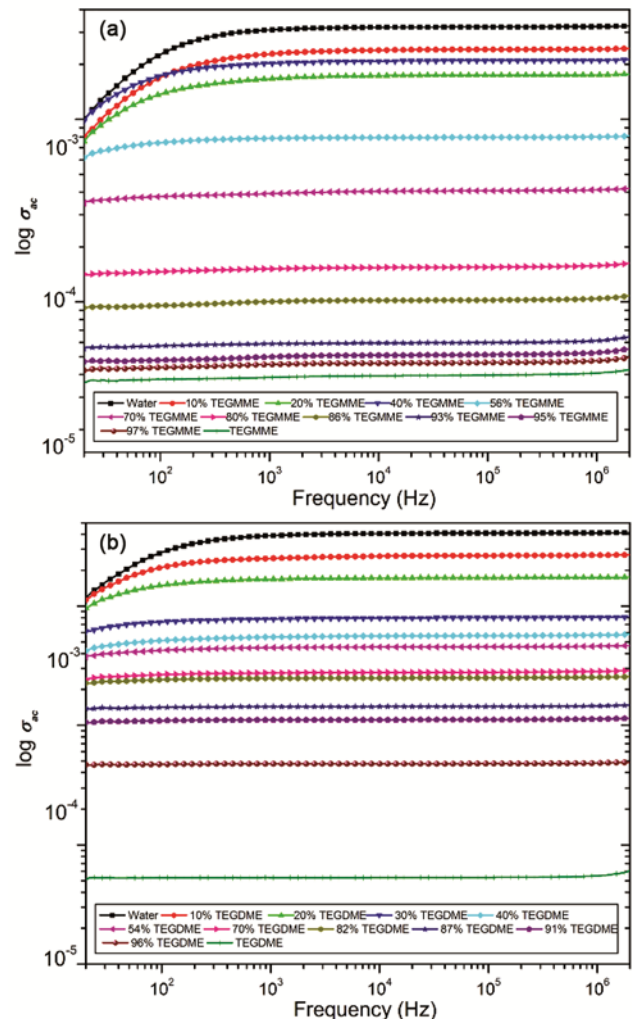
Fig. 6 — The ac conductivity spectra for (a) TEGMME-Water and (b) TEGDME–Water binary mixtures.

> TEGDME (ε_0 = 6.74). There is a large difference in the values of static permittivity of the mixture constituents of the binary mixtures studied here. Thus, the internal field of the systems would be greatly perturbed as water is added in the pure liquids. The effect of increase in chain length can also be studied from literature values and it is observed that the ε_0 values for ethylene glycol monomethyl ether [EGMME (ε_0=17.80)] > diethylene glycol monomethyl ether [DEGMME (ε_0=16.35)] > triethylene glycol monomethyl ether [TEGMME (ε_0=13.85)] > triethylene glycol dimethyl ether [TEGDME (ε_0=6.74)][11,12]. When the chemical composition of DEGMME is compared with EGMME, there is additional two CH_2 (hydrophobic) and one -O- (hydrophilic) molecule. Similar difference is seen in TEGMME in comparison with DEGMME. Generally, the increase in chain length reduces ε_0 values significantly but here the difference in ε_0 values is not much notable. This may be due to the balancing situation of hydrophobic as well as hydrophilic sites with increase in chain length of these molecules. Again if the ε_0 values of TEGMME and TEGDME are observed there is significant difference. This can be explained in similar manner as previous, in the chemical composition of TEGDME there is only one additional CH_2 group and number of -O- are same. The effect of increase in hydrophobic as well hydrophilic sites on dielectric permittivity values can be clearly studied from above observations. The values of static permittivity for all concentrations of the methyl ethers in water are plotted against the mole fraction of water (X_W) in the respective binary mixtures as shown in Fig. 7. It can be seen that the ε_0 values for both the systems increases slowly in the water deficit region (X_W < 0.6). But in the water rich region, there is an exponential increase in the permittivity of the binary mixtures. The non-linearity of the plots shows deviation from the ideal behavior. From Fig. 7, the non linearity in the curve is greater for TEGDME than TEGMME. In other words, it can be stated as the non linearity increases with increase in chain length. This is due to interactions in the constituent (glyme – water) molecules of the binary mixtures. Initially, when the water molecules are added to the pure methyl ethers, some of the bonds may broken and the free molecules then tend to form complexes with the hetero molecules through hydrogen bonding.

The excess dielectric constant (ε_0^E) values provide the experimental evidence of hydrogen bond formation between the solute and the solvent molecules of a binary mixture. The formulation to evaluate ε_0^E is discussed in numerous papers[11-16]. Using the same method, the ε_0^E values for the TEGMME + Water and TEGDME + Water binary mixtures are evaluated and plotted in Fig. 8. It can be seen that the ε_0^E values are negative for all concentrations of TEGMME + Water and TEGDME + Water binary mixtures. This confirms the formation
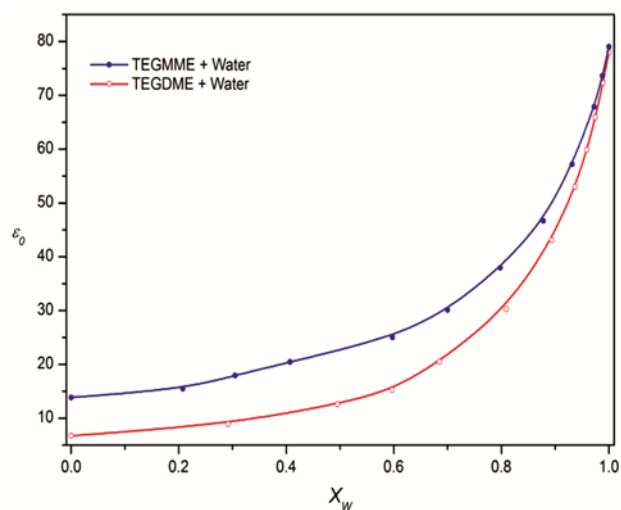
Fig. 7 — Plots of static dielectric constant ε_0 vs. mole fraction of water X_W for binary mixtures of TEGMME and TEGDME with water.
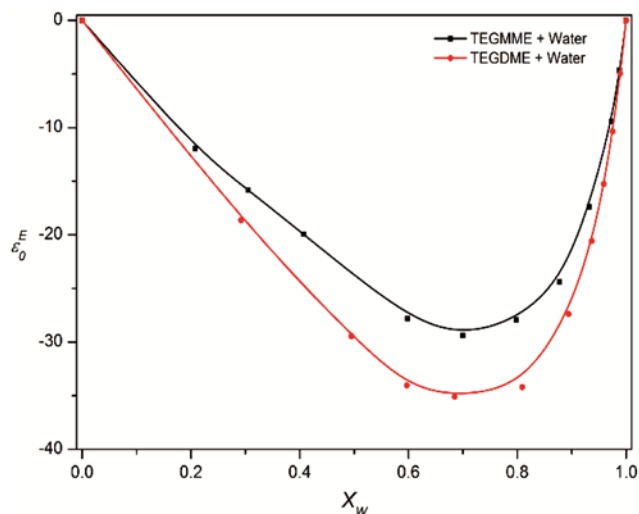
Fig. 8 — Plots of excess dielectric constant ε_0^E vs. mole fraction of water X_W for binary mixtures of TEGMME and TEGDME with water.
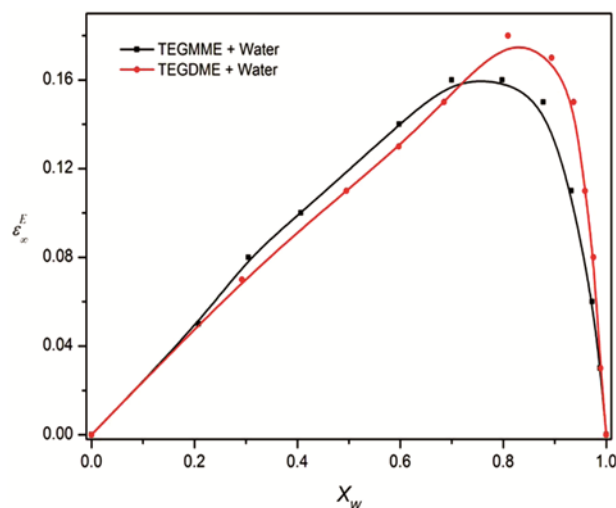
Fig. 9 — Plots of high frequency excess dielectric constant ε_∞^E vs. mole fraction of water X_W for binary mixtures of TEGMME and TEGDME with water.

of H-bonded complex between the hetero molecules of the studied mixtures with an increase in anti-parallel alignment of dipoles. Further the H-bond interaction between the unlike molecules increases initially with increase in X_W. It becomes maximum when $X_W \approx 0.7$ and then goes on decreasing. The negative peak of ε_0^E gives information about the formation of maximum complexes through H-bonding at this concentration. The peak of ε_0^E for TEGDME + Water mixture is higher as compared to the TEGMME + Water mixture. It suggests that the H-bonds are stronger between TEGDME and Water molecules than TEGMME and Water molecules. The $X_W \approx 0.7$ corresponding to the negative peak of ε_0^E value provides the stoichiometric ratio of stable complex structure. The ratio for methyl ether : water mixtures studied here is 1:2.3.

The electronic polarization of molecules is affected due to external electric field and H-bond interactions. The effect of H-bonding on electronic polarization can be recognized from the refractive index measurements[17]. The excess dielectric constant at high frequency ε_∞^E values give information about the electronic polarization in binary mixtures[17,18]. The ε_∞ values can be calculated by using the refractive index of the mixtures ($\varepsilon_\infty = n^2$). The refractive index of pure TEGDME (1.4195 at 298.15 K) is in good agreement with its literature value (1.4224 at 293.15 K)[19]. Figure 9 shows the variations in ε_∞^E values of the methyl ethers with the mole fraction X_W of water. It is observed that $\varepsilon_\infty^E > 0$ for the binary

mixtures of methyl ethers with water. This confirms that there is a considerable effect on electronic polarization due to H-bond formation between the methyl ether and water molecules. The peaks in ε_∞^E values can be observed for $0.7 < X_W < 0.8$. The hydrogen bond formation is highest in this range. Also, the peaks in ε_∞^E values are in the order of TEMME < TEGDME.

4 Conclusions

The concentration dependent dielectric and electrical properties of TEGMME, TEGDME and their binary mixtures with water have been studied in the frequency range 20 Hz to 2 MHz at 298.15 K. The electrode polarization phenomenon is observed in low frequency region. The dielectric loss is very high at the lower frequencies. It takes place due presence of ionic impurities in the liquids. The dielectric loss increases with increase in concentration of water in the binary mixtures. The non linear behavior of dielectric permittivity values of the binary mixtures gives an idea about certain molecular interaction. The intermolecular interaction in methyl ethers –water molecules have been described by excess properties.

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