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Dielectric Relaxation And Molecular Interactions Study Of Glymes In Aqueous Solutions Using TDR Technique

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ABSTRACT: *The dielectric measurement of glymes viz. Ethylene glycol dimethyl ether (EGDME) and diethylene glycol dimethyl ether (DEGDME) in aqueous solutions have been carried out in the frequency range of 10 MHz to 30 GHz using time domain technique. The measurements have been done over whole composition range of glymes and water, at temperatures 25 °C, 15 °C and 5 °C. The dielectric parameters for these glymes – water mixture have been evaluated using non linear least square method. Molecular interactions among the EGDME, DEGDME with water molecules have been discussed using parameters such as Excess dielectric permittivity, Kirkwood correlation factor and Bruggeman Factor.*

Keywords: *TDR, Glymes, Excess dielectric permittivity, Kirkwood correlation factor, Bruggeman factor.*

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I. INTRODUCTION:

Glymes viz. ethylene glycol dimethyl ether (EGDME) and diethylene glycol dimethyl ether (DEGDME) are saturated non-cyclic polyethers without any other functional group. These are completely miscible in water [1]. The chemical composition of EGDME (monoglyme) is $C_4H_{10}O_2$ and that of DEGDME (diglyme) is $C_6H_{14}O_3$. Glymes are usually stable, less toxic, environment caring than general laboratory solvents and have both hydrophilic and hydrophobic characters. Glymes have wide applications in laboratory such as organic synthesis, electrochemistry, biocatalysis, materials, Chemical Vapor Deposition (CVD) and industrial applications such as cleaning products, inks, adhesives, coatings, batteries, electronics, absorption refrigeration, heat pumps as well as pharmaceutical formulations etc [1]. Water is a strong hydrogen bonding liquid which shows highly cooperative phenomenon [2]. Therefore, the dielectric relaxation study of glymes in aqueous solutions will be interesting and useful in various applications. In literature, there is a little experimental data available regarding dielectric properties of glymes [1-6]. Iglesias et.al. have measured the permittivities and densities of glymes with n-heptane. In which, excess permittivity and its behavior with temperature and that of excess molar volume were discussed in detail [3]. Buchner et. al. studied the excess molar volumes over the whole composition range of open-chain and cyclic ethylene glycol ethers in aqueous solutions [2]. Smith et. al. extensively studied conformational, translational, rotational dynamics and thermodynamic properties of glymes in aqueous solutions through molecular dynamics simulations [7-11]. The study reveals strong hydrogen bonding interactions of glymes in aqueous solutions. The dipole-dipole interactions among the glymes – water discussed in terms of hydrophilic and hydrophobic conformers. In our previous work, the dielectric dispersions of EGDME and DEGDME with aqueous solutions were studied at low frequency range of 20 Hz to 2 MHz using Precision LCR meter [6]. In this frequency range, it is not possible to explain the dielectric relaxation process of these binary mixtures. In order to study the relaxation process among the binary mixtures of EGDME and DEGDME with water, the dielectric measurements have been carried out in the high frequency range of 10 MHz to 30 GHz using time domain technique. The dielectric parameters are evaluated using non linear least square method. Molecular interactions among the EGDME, DEGDME with water molecules have been discussed using parameters such as Excess dielectric permittivity, Kirkwood correlation factor and Bruggeman Factor.

II. EXPERIMENTAL

2.1. Materials

EGDME and DEGDME were obtained commercially from Alfa Aesar with purity 99%. The de-ionized water with HPLC grade was obtained from Fisher Scientific India Pvt Ltd. They were used without further purification. The solutions were prepared at different mole fractions of water in EGDME and DEGDME.

2.2. Measurements and Data Analysis

The Tektronix model no. DSA8200 Digital Serial Analyzer sampling mainframe along with sampling module 80E08 has been used for the dielectric measurements. A repetitive fast rising voltage pulse was fed through coaxial cable of impedance 50 ohm. DSA monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ i.e. for open end and with sample $R_x(t)$ were recorded in time window of 5 ns and digitized in 2000 points. The Fourier transformation of the pulses and data analysis were done to determine complex permittivity spectra $\varepsilon^*(\omega)$ using non linear least squares fit method and explained in detail in the literature [12-15].

III. RESULTS AND DISCUSSION

Generally, the complex permittivity spectra of binary mixtures show evidence of non-Debye type behavior. Therefore it is convenient to use other empirical models such as Cole-Cole or Cole-Davidson for fitting the spectra. After observing the Cole-Cole plots (Fig. 1 & 2), it is found that the permittivity spectra of binary mixtures of glymes – water are best fitted in Cole-Davidson (CD) model. Figs. 3 and 4 (a & b) show examples of complex permittivity spectra (dielectric permittivity and dielectric loss) for EGDME – water and DEGDME – Water mixtures at 25 °C. The complex dielectric permittivity data were fitted to a CD model using non linear least squares fit method and the dielectric relaxation parameters are evaluated. The following expression shows the CD model [16].

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

In above eq. 1 the fitting parameters ε0, ε∞, τ and β are the fitting parameters and described as static dielectric permittivity, limiting high frequency permittivity, relaxation time in ps and the asymmetric distribution parameter, respectively. β varied such that $0 \le \beta \le 1$. All these values (ε0, ε∞,τ and β) at temperature range studied here are reported in Table 1.

3.1 Dielectric Parameters:

In earlier work, the dielectric relaxations of alkoxyethanols and alkoxyethoxyethanols namely Ethylene glycol mono methyl ether [EE] and mono ethyl ether of diethylene glycol [EEE] have been studied thoroughly [17-18]. EE and EEE have similar composition to that of EGDME (C4H10O2) and DEGDME (C6H14O3) respectively. Though the chemical composition is same, there is distinct difference in the dielectric parameters. The values of static dielectric permittivity for EE = 14.45 and for EEE = 14.79 and that of EGDME = 6.37 and for DEGDME = 7.75. The values of relaxation times in ps for EE, EEE are 41.96, 53.65 respectively and that for EGDME and DEGDME are 5.08, 6.59 respectively. It suggests different structures of these molecules. Alkoxyethanols have two functional groups (oxy and hydroxyl) in the same molecules. For the glymes studied here have only one functional group (oxy) in a molecule. The dielectric parameters are very sensitive to the functional groups in a molecule. Therefore, though they have similar chemical composition, the dielectric parameters gives diverse values in pure form. Now in context of aqueous solutions of these glymes, the values of static dielectric permittivity (ε0) for glymes-water mixtures at different temperatures are plotted in Fig. 5 and 6. If the static dielectric permittivity evaluated for the binary mixtures of these systems using additive property (ideal case), the nature of the static permittivity vs. mole fraction of water should show straight line behavior [18]. But these plots exhibit non-ideal nature or piecewise linear nature. The plots for all temperatures studied here show approximately two pieces of linear regions, first $0 \le XW \le 0.6$ and second $0.6 \le XW \le 1.0$. This evidence of non linearity in dielectric permittivity values of glyme-water mixtures may be due to some molecular associations of the unlike molecules. Another dielectric parameter evaluated from fitting is the relaxation time. The relaxation time vs. XW for EGDME – water and DEGDME – water are plotted and shown in Fig. 7 and 8 respectively. Relaxation times for pure EGDME, DEGDME and water obtained here are 5.08 ps, 6.59 ps and 8.21 ps respectively. On addition of glyme in water the relaxation times for binary mixtures of glyme – water increases around XW = 0.8 and above this concentration, the relaxation times decreases and converges towards the relaxation time of glymes. This non-ideal nature of relaxation times of binary mixtures of glymes – water gives an idea about molecular association among the unlike molecules which supports our earlier discussion. Further molecular association in binary molecules is confirmed in the subsequent section using Excess dielectric permittivity, Kirkwood correlation factor and Bruggeman factor.

3.2 Excess dielectric permittivity $(\varepsilon0)E$:

The excess permittivity values provide useful information regarding the solute – solvent interactions [19-21]. The dipole – dipole interaction in a binary mixture may be explained in terms of $(\varepsilon0)E$ values. The $(\varepsilon0)E$ values may be greater than unity or less than unity. One could explain positive values of $(\varepsilon0)E$ as an increase in dipole-dipole interactions (structure enhancement) present in solvent molecules on addition of solute molecules or vice versa whereas the negative values of $(\varepsilon0)E$ could be explained as structure-breaker of solvent on addition of solute molecules.

The plots (Fig.9 and 10) present excess permittivity values for EGDME – water and DEGDME – water binary mixtures at different temperatures. The values of $(\varepsilon0)E$ for EGDME – water and DEGDME – water are in good agreement with our previous study [6]. The plots exhibit a pronounced minima and it gives negative values of $(\varepsilon0)E$ for whole concentration range. These negative $\varepsilon0E$ values for glymes – water mixtures confirm the experimental evidence of molecular interactions among the unlike molecules. The dipole-dipole interaction is such that the number of effective dipoles per unit volume gets reduced. The corresponding minima of $\varepsilon0E$ value observed at XW = 0.7 for EGDME – water and DEGDME – water at temperatures studied here except at 5 °C for EGDME –water. At 5 °C, for EGDME – water, the minimum of $\varepsilon0E$ value finds at XW = 0.8. The corresponding XW indicates formation of maximum complexes through H-bonding at this concentration.

3.3 Kirkwood correlation factor

The Kirkwood correlation factor is helpful in understanding the short range dipolar ordering in pure as well as binary form. The formulation for the same is described comprehensively in the literature [22].

At 25 ˚C the ‘g’ value of water is 2.8 which is higher than the ‘g’ value of EGDME (1.32) and DEGDME (1.58) indicates that the water has stronger parallel ordering of orientation correlation among its molecules in pure form as compared to the EGDME and DEGDME molecules in their pure form. The densities and dipole moments for evaluating the Kirkwood correlation factors are used from literature [23].

The geff values for entire concentrations and temperature range for EGDME – water and DEGDME – water are shown in Fig. 11 and Fig. 12, respectively. These binary mixture concentrations illustrate interesting results. In pure form, all these three liquids have ‘g’ values greater than unity. But on addition of water in EGDME the values ‘geff’ decreases slowly. At XW = 0.4, the value of geff lowest and it is less than unity for the temperatures 25 °C and 15 °C indicates the anti parallel dipole –dipole interactions. Above this concentration, the value of geff increases and is greater than unity suggest the parallel dipole-dipole orientation of EGDME – water mixtures. The temperature effect is observed on the values of geff for EGDME – water mixtures. The nature of curve (Fig.11) is similar for the temperatures studied here but for 5 °C, the geff remains greater than unity for whole composition range. For DEGDME – water mixtures the values of geff is less than unity for the temperatures 25 °C and 15 °C in the region 0.4 ≤ XW ≤ 0.6. Therefore in this region the hydrogen bonding interactions among the DEGDME – water is anti parallel. Above XW = 0.6, the values of ‘geff’ display monotonic increase with increasing concentration of water suggest strong parallel orientation correlation among DEGDME – water mixtures. The effect of temperature is also observed on the DEGDME – water mixtures. The nature of curve (Fig. 12) is similar for all the temperatures but for 5 °C the geff remains greater than unity for whole composition range indicates parallel orientation of dipole-dipole in DEGDME –water mixtures. .

3.4 Bruggeman Factor

According to the Bruggeman equation, it envisages a linear relationship between the Bruggeman factor (fB) and the volume fraction of solvent [24]. The experimental values of fB donot follow the linear behavior. This non linear behavior of fB values can be explained by modified Bruggeman mixture formula as earlier used [25]. In Bruggeman mixture formula, the value of ‘a’=1 means the ideal mixture with no molecular interaction between solute and solvent. Bruggeman factor (fB) for EGDME –water and DEGDME – water mixtures vs. volume fraction of water plotted in Fig. 13 and 14. Dotted line in Fig. 13 and 14 reveals ideal behavior according to Bruggeman mixture formula. But actual experimental values signify the non-ideal behavior of mixture which confirms the solute-solvent molecular interaction between glymes-water mixtures. The calculated value of ‘a’ is determined using least square fit are 2.18 and 2.04 for EGDME – water and DEGDME – water binary mixtures at 25 °C.

IV. CONCLUSIONS

The temperature dependent complex permittivity spectra of EGDME – water and DEGDME – water have been studied using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. The non-linear nature of dielectric parameters reveals molecular association in binary mixtures of these liquids. The excess dielectric permittivity, Kirkwood correlation factor and Bruggeman factor confirms the molecular interactions among the EGDME – water and DEGDME – water binary mixtures.

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Figure Captions:

Fig.1 Cole-Cole plot for EGDME – water mixtures at 25°C.

Fig.2 Cole-Cole plot for DEGDME – water mixtures at 25°C.

Fig.3 Frequency dependent complex permittivity (a. for ε' and b. for ε") of EGDME –water binary mixtures at 25°C.

Fig.4 Frequency dependent complex permittivity (a. for ε' and b. for ε") of DEGDME –water binary mixtures at 25°C.

Fig.5 Static dielectric permittivity (εo) for EGDME – water binary mixtures vs. mol. fraction of water (XW).

Fig.6 Static dielectric permittivity (εo) for DEGDME – water binary mixtures vs. mol. fraction of water (XW).

Fig.7 Relaxation time in ps. (τ) for EGDME – water binary mixtures.

Fig.8 Relaxation time in ps. (τ) for DEGDME – water binary mixtures.

Fig.9 Excess Dielectric permittivity (εoE) for various concentrations of EGDME and water at different temperatures.

Fig.10 Excess Dielectric permittivity (εoE) for various concentrations of DEGDME and water at different temperatures.

Fig.11 Kirkwood correlation factor (geff) for EGDME – water mixtures.

Fig.12 Kirkwood correlation factor (geff) for DEGDME – water mixtures.

Fig.13 Bruggeman Factor (fB) as function of volume fraction of water for EGDME – water mixtures.

Fig.14 Bruggeman Factor (fB) as function of volume fraction of water for DEGDME – water mixtures.

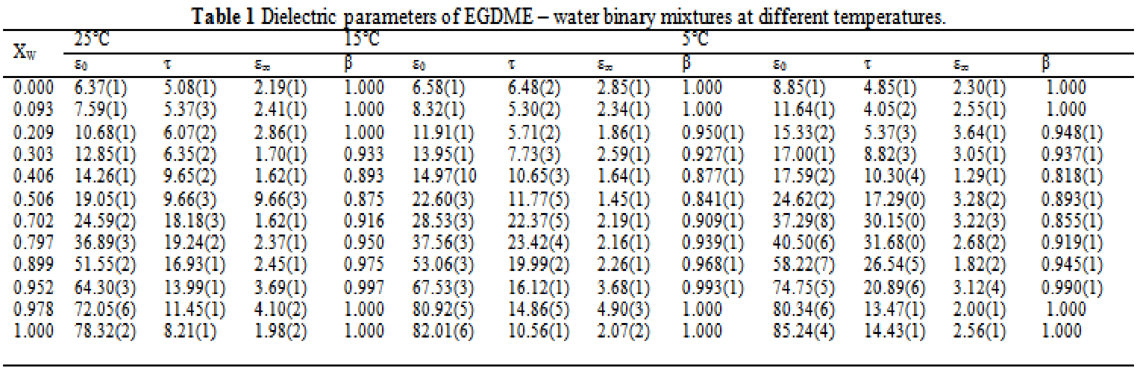


Table 1 Dielectric parameters of EGDME – water binary mixtures at different temperatures.

X_W	25°C			15°C				5°C				
	ε_0	τ	ε_∞	β	ε_0	τ	ε_∞	β	ε_0	τ	ε_∞	β
0.000	6.37(1)	5.08(1)	2.19(1)	1.000	6.58(1)	6.48(2)	2.85(1)	1.000	8.85(1)	4.85(1)	2.30(1)	1.000
0.093	7.59(1)	5.37(3)	2.41(1)	1.000	8.32(1)	5.30(2)	2.34(1)	1.000	11.64(1)	4.05(2)	2.55(1)	1.000
0.209	10.68(1)	6.07(2)	2.86(1)	1.000	11.91(1)	5.71(2)	1.86(1)	0.950(1)	15.33(2)	5.37(3)	3.64(1)	0.948(1)
0.303	12.85(1)	6.35(2)	1.70(1)	0.933	13.95(1)	7.73(3)	2.59(1)	0.927(1)	17.00(1)	8.82(3)	3.05(1)	0.937(1)
0.406	14.26(1)	9.65(2)	1.62(1)	0.893	14.97(10	10.65(3)	1.64(1)	0.877(1)	17.59(2)	10.30(4)	1.29(1)	0.818(1)
0.506	19.05(1)	9.66(3)	9.66(3)	0.875	22.60(3)	11.77(5)	1.45(1)	0.841(1)	24.62(2)	17.29(0)	3.28(2)	0.893(1)
0.702	24.59(2)	18.18(3)	1.62(1)	0.916	28.53(3)	22.37(5)	2.19(1)	0.909(1)	37.29(8)	30.15(0)	3.22(3)	0.855(1)
0.797	36.89(3)	19.24(2)	2.37(1)	0.950	37.56(3)	23.42(4)	2.16(1)	0.939(1)	40.50(6)	31.68(0)	2.68(2)	0.919(1)
0.899	51.55(2)	16.93(1)	2.45(1)	0.975	53.06(3)	19.99(2)	2.26(1)	0.968(1)	58.22(7)	26.54(5)	1.82(2)	0.945(1)
0.952	64.30(3)	13.99(1)	3.69(1)	0.997	67.53(3)	16.12(1)	3.68(1)	0.993(1)	74.75(5)	20.89(6)	3.12(4)	0.990(1)
0.978	72.05(6)	11.45(1)	4.10(2)	1.000	80.92(5)	14.86(5)	4.90(3)	1.000	80.34(6)	13.47(1)	2.00(1)	1.000
1.000	78.32(2)	8.21(1)	1.98(2)	1.000	82.01(6)	10.56(1)	2.07(2)	1.000	85.24(4)	14.43(1)	2.56(1)	1.000

Table 2 Dielectric parameters of DEGDME – water binary mixtures at different temperatures.

X_W	25°C			15°C				5°C				
	ε_0	τ	ε_∞	β	ε_0	τ	ε_∞	β	ε_0	τ	ε_∞	β
0.000	7.75(1)	6.59(2)	1.94(1)	0.936(1)	8.23(1)	7.59(2)	2.07(1)	0.936(1)	10.31(1)	7.34(3)	2.75(1)	0.874(1)
0.393	13.60(1)	13.13(5)	1.97(1)	0.857(1)	14.03(2)	14.97(5)	2.13(1)	0.848(1)	17.32(4)	18.59(13)	2.64(1)	0.764(1)
0.504	15.97(2)	14.79(5)	2.17(1)	0.856(1)	16.31(2)	16.95(7)	2.22(1)	0.839(1)	19.47(5)	23.38(17)	3.12(1)	0.766(1)
0.604	18.25(3)	17.80(7)	2.04(1)	0.860(1)	18.66(3)	20.68(7)	2.20(1)	0.853(1)	21.08(6)	30.83(25)	3.26(2)	0.787(1)
0.702	24.32(3)	21.99(6)	2.57(1)	0.890(1)	25.25(3)	26.77(9)	2.50(1)	0.871(1)	29.21(9)	42.60(34)	3.60(2)	0.806(1)
0.778	29.33(3)	23.63(6)	2.47(1)	0.895(1)	30.33(4)	`29.10(8)	2.73(1)	0.891(1)	34.47(9)	45.21(31)	3.51(2)	0.836(1)
0.854	38.50(3)	23.32(4)	2.50(1)	0.916(1)	38.71(4)	28.37(7)	2.54(1)	0.908(1)	40.37(9)	45.05(23)	3.28(1)	0.872(1)
0.918	50.96(3)	18.13(2)	2.28(1)	0.932(1)	52.21(4)	20.28(3)	2.31(1)	0.927(9)	59.47(9)	31.35(10)	2.34(3)	0.879(1)
0.946	58.74(3)	14.62(1)	1.61(1)	0.946(1)	60.70(3)	17.21(1)	2.38(1)	0.949(7)	69.73(8)	23.67(5)	3.20(3)	0.912(1)
0.968	63.57(1)	12.92(6)	2.86(4)	0.997(1)	65.57(4)	14.54(6)	2.61(4)	0.994(1)	74.30(5)	19.23(6)	1.37(4)	0.981(1)
0.985	72.20(5)	10.37(6)	3.22(4)	1.000	74.38(6)	11.55(5)	3.12(4)	1.000	83.05(6)	15.21(6)	2.80(5)	1.000
1.000	78.32(2)	8.21(1)	1.98(2)	1.000	82.01(6)	10.56(1)	2.07(2)	1.000	85.24(4)	14.43(1)	2.56(1)	1.000

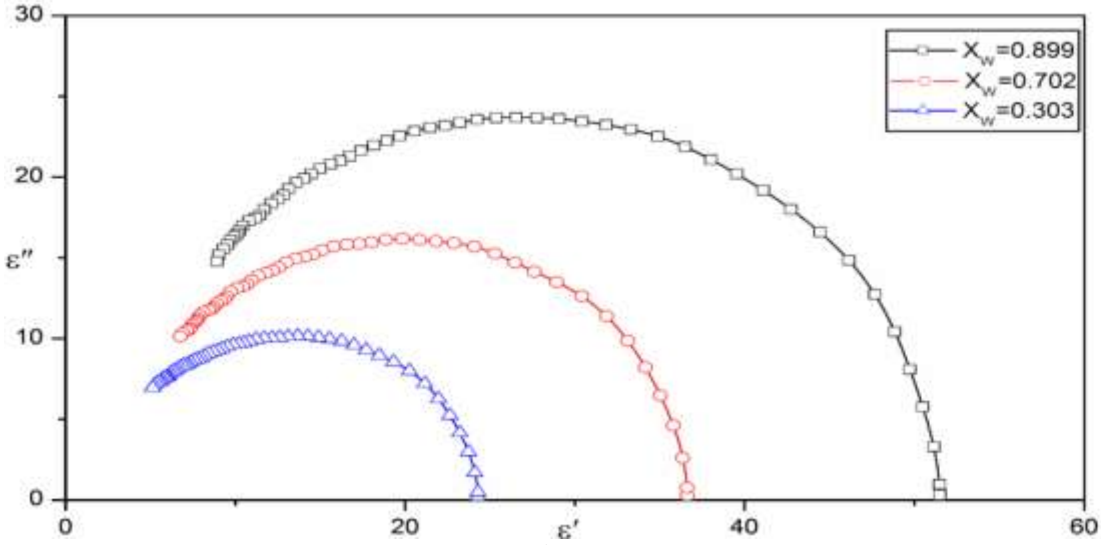
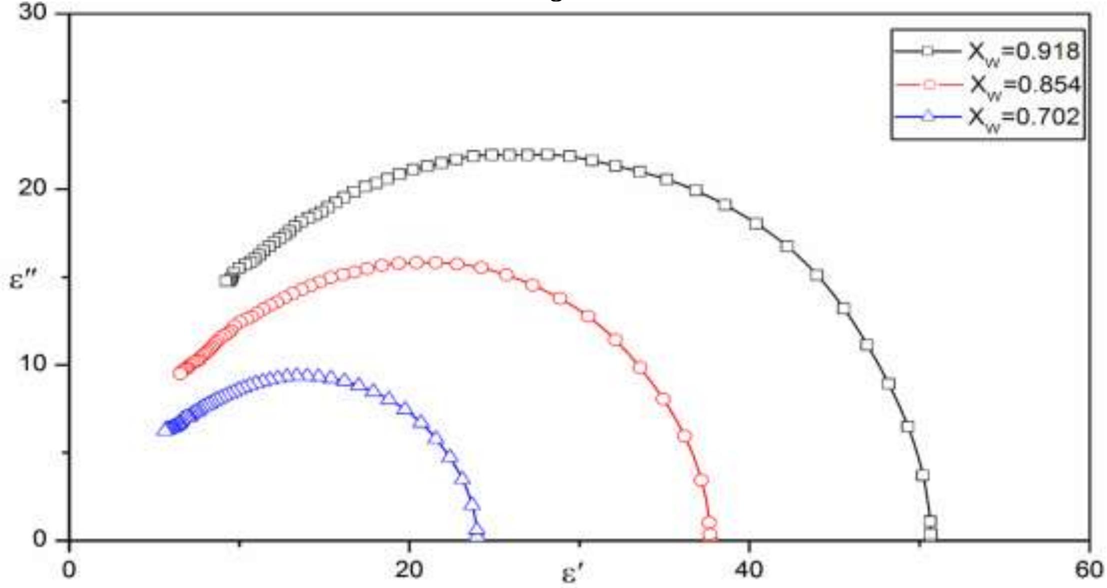


Fig.1



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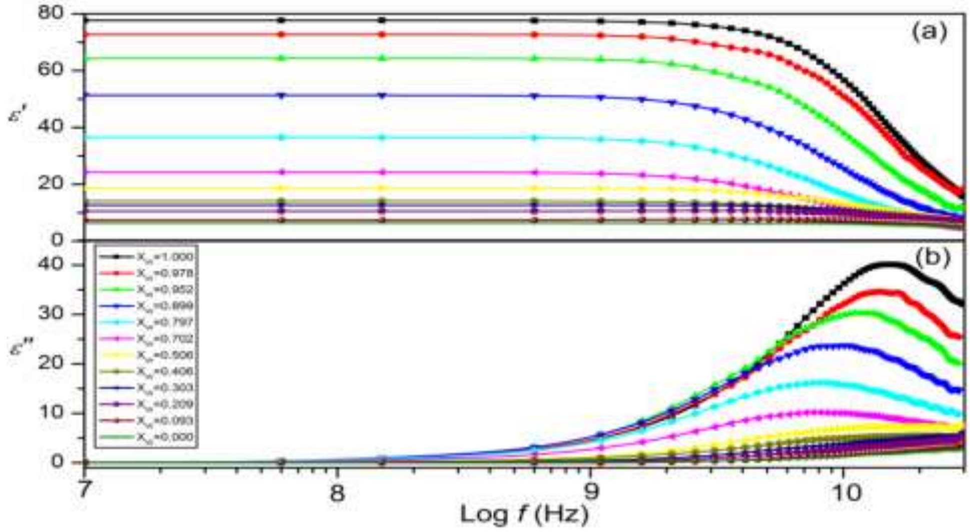
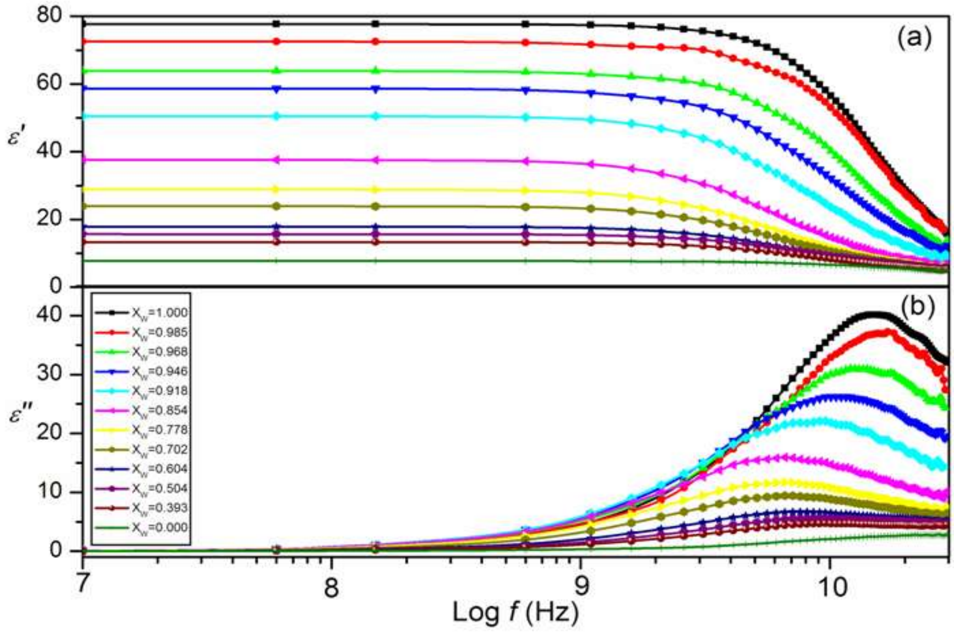


Fig.3



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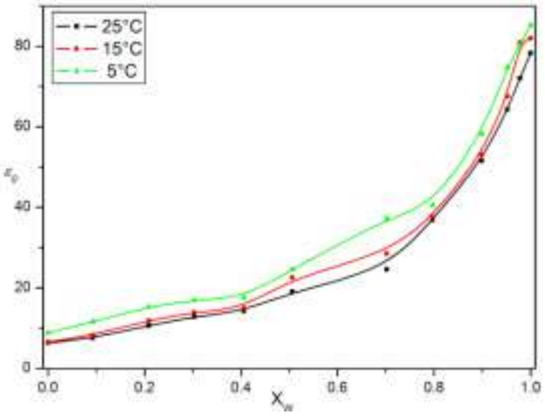

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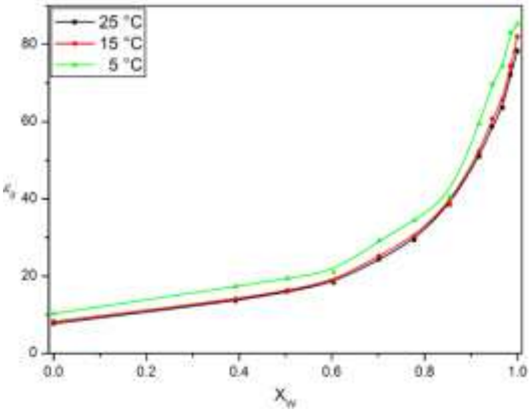

Fig.6

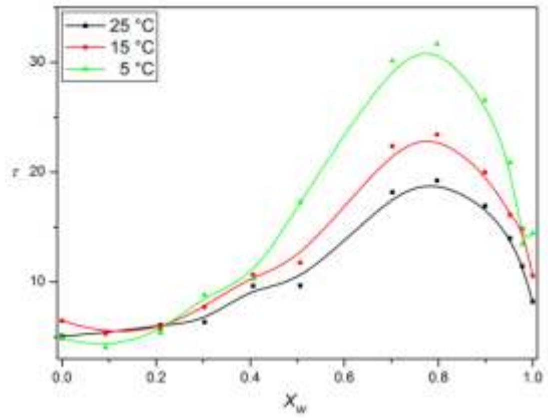

Fig.7

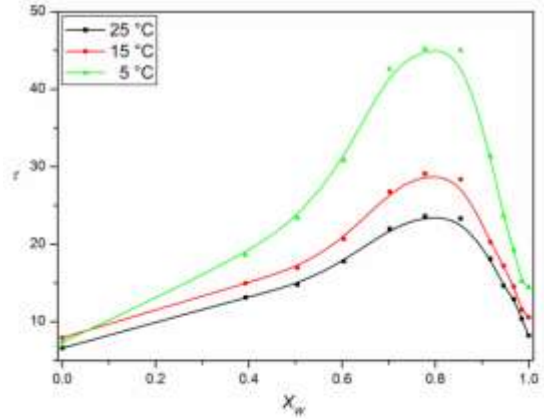

Fig.8

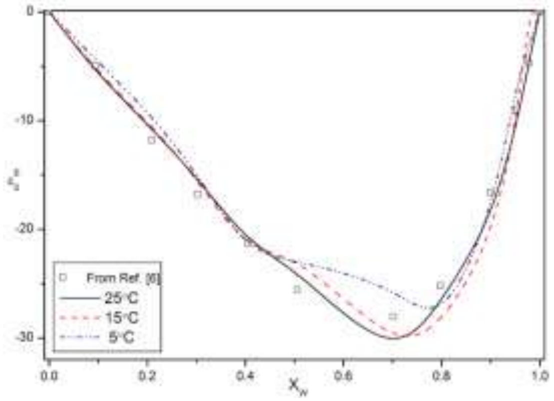

Fig.9

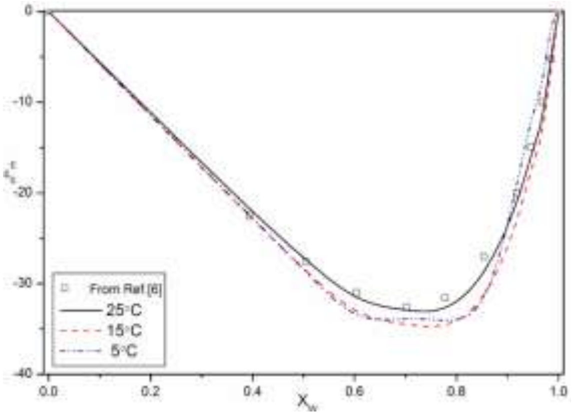

Fig.10

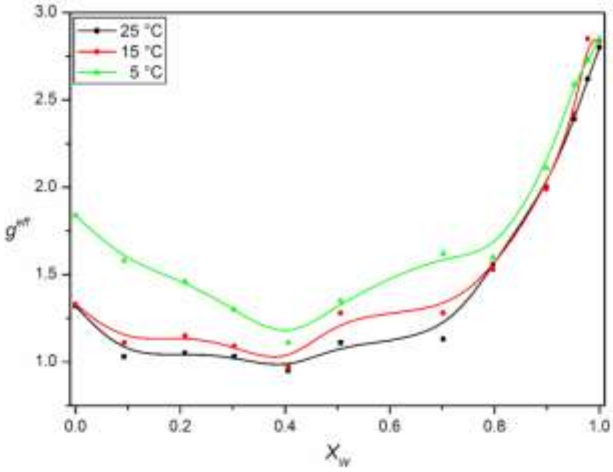

Fig.11

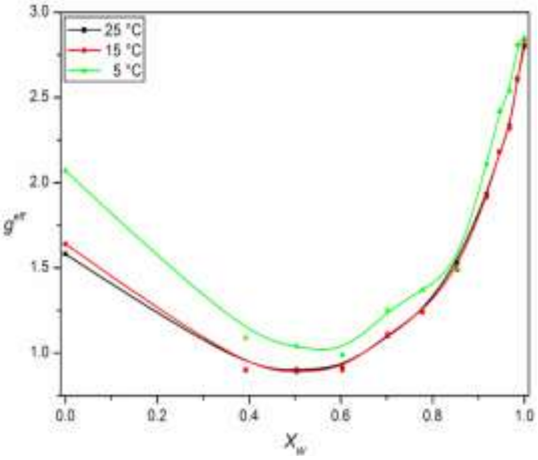

Fig.12

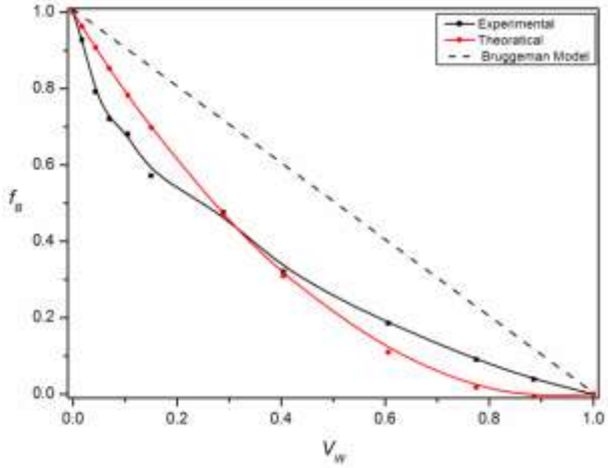

Fig.13

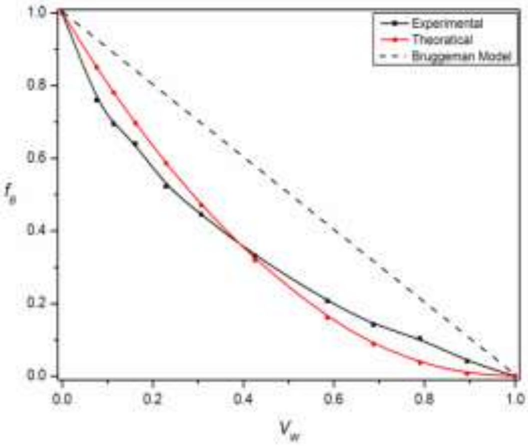

Fig.14

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