

## Structural study of aqueous solutions of tetrahydrofuran and acetone mixtures using dielectric relaxation technique

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**Abstract.** The complex permittivity, static dielectric constant and relaxation time for tetrahydrofuran-water and acetone-water mixtures have been determined at 0°, 10°, 25° and 35°C using time domain reflectometry technique (TDR). The behaviour of relaxation time of the mixture shows a maxima for the mixture with 30% of water by volume. This suggests that the tendency to form cluster between water and solute molecule is maximum for this mixture. The excess permittivity for both tetrahydrofuran-water mixture and acetone-water mixtures, are found to be negative. The Kirkwood correlation factor has been determined at various concentrations of water. Static dielectric constant for the mixtures have been fitted well with the modified Bruggeman model. The values of the Bruggeman parameter  $a$  for tetrahydrofuran is found to be more than the corresponding value for acetone.

**Keywords.** Dielectrics; microwaves; tetrahydrofuran; acetone; excess permittivity; Kirkwood factor.

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### 1. Introduction

Considerable dielectric relaxation study have been done in aqueous solutions such as dimethylsulfoxide-water [1], *N,N*-dimethylformamide-water [2], *N,N*-dimethylacetamide-water [3], hexamethylphosphoramide-water [4] and acetonitrile-water [5] mixtures. For the systems studied it has been observed that the value of the relaxation time shows a maxima by addition of water in solutes. This has given the information about solute-solvent interaction, molecule packing of hydration shell to the solute molecules and molecular volume size. Tetrahydrofuran and acetone [6] are interesting systems because they are completely miscible in water and are of different structural types.

Recently, nuclear magnetic resonance (NMR) relaxation in tetrahydrofuran-water and acetone-water mixtures were studied [7], by using NMR technique at various composition of tetrahydrofuran and acetone in water solutions. The proton relaxation time rates as a function of water composition in tetrahydrofuran and acetone were observed at maximum concentration 0.8 mole fraction of water. It is interesting to compare the results with the results of dielectrics.

In this work, the dielectric relaxation of tetrahydrofuran-water and acetone-water mixtures with varying concentrations (0–100%) is reported over the frequency range 10 MHz–10 GHz by using the TDR technique. The dielectric parameters, excess dielectric permittivity, the Kirkwood correlation parameters and the Bruggeman factor have also been determined for these systems.

## 2. Experimental

### *Materials*

Tetrahydrofuran (THF) and acetone (ACT) of spectroscopic grade were obtained commercially and used without further purification. The water used in the preparation of the mixtures was obtained by double distillation procedure and deionized before use. The mixtures of various compositions (0 to 100%) were prepared by volume before mixing.

### *Apparatus*

The complex permittivity spectra was studied using (TDR) method [8,9]. The detail of the experimental method are described earlier [8,9]. The Tektronix 7854 sampling oscilloscope with 7S12 TDR unit has been used. A fast rising step voltage pulse of 25 psec rise time generated by a tunnel diode was propagated through a coaxial line system. The sample was placed at the end of coaxial line in standard military application (SMA) coaxial cell of 3.5 mm outer diameter and 0.486 mm effective pin length. All measurements were done under open load condition. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, time window of 5 ns was used. The reflected pulse without sample and with the sample were digitized in 1024 points and transferred to computer through GPIB (general purpose interface bus).

The Fourier transformation was done to yield the complex reflection coefficient spectra  $\rho^*(\omega)$  over the frequency range 10 MHz to 10 GHz. The complex permittivity spectra  $\varepsilon^*(\omega)$  was determined from the  $\rho^*(\omega)$  by applying the least squares fit method as described in our earlier publication [4].

## 3. Results and discussion

The static dielectric constant ( $\varepsilon_0$ ) and relaxation time ( $\tau$ ) have been determined by fitting the complex permittivity spectra  $\varepsilon^*(\omega)$  with the Debye equation,

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

with  $\varepsilon_0$ ,  $\tau$  as fitting parameters in (1). Since the permittivity spectra in the present study is in the frequency range of 10 MHz to 10 GHz, the  $\varepsilon_\infty$  in (1) as determined from this study is just a fitting parameter, which does not correspond to the permittivity at high frequency, related to vibrational and electronic motions. It was found to be a reasonable satisfactory procedure to keep the value of  $\varepsilon_\infty$  as a fixed parameter (3.5), for the determination of  $\varepsilon_0$  and  $\tau$  [4].

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**Table 1.** Dielectric parameters for acetone-water mixture.

Vol % of acetone	0°C		10°C	
	$\epsilon_0$	$\tau$ (ps)	$\epsilon_0$	$\tau$ (ps)
100	29.9(5)	6.2(4)	21.6(1)	4.2(3)
90	31.5(1)	11.4(1)	26.8(1)	7.4(3)
80	37.6(2)	15.5(5)	33.9(1)	10.1(4)
70	42.1(4)	18.3(10)	41.7(7)	14.0(16)
60	42.0(1)	16.9(2)	45.0(2)	13.2(2)
50	52.3(11)	17.7(16)	51.3(9)	12.0(14)
40	67.2(11)	27.9(19)	58.0(15)	17.3(3)
30	70.0(2)	21.2(4)	69.6(5)	14.8(7)
20	77.0(6)	21.1(3)	75.4(1)	15.4(6)
10	80.0(5)	17.3(6)	77.2(6)	11.8(7)
0	87.9	17.7	83.9	12.9
	25°C		35°C	
100	20.8(1)	3.4(5)	18.9(5)	2.9(5)
90	25.8(1)	7.3(4)	25.5(1)	4.8(3)
80	31.0(2)	8.6(3)	31.0(1)	7.5(4)
70	40.0(4)	10.1(6)	35.8(3)	9.1(9)
60	44.5(3)	11.9(6)	44.0(5)	10.8(9)
50	51.6(7)	10.8(10)	49.1(7)	9.3(11)
40	57.3(3)	11.8(5)	54.7(2)	10.7(4)
30	62.5(9)	10.7(12)	61.4(1)	9.4(10)
20	69.1(3)	12.2(4)	66.1(2)	9.5(8)
10	75.4(8)	10.2(6)	66.1(6)	9.5(9)
0	78.3	8.2	75.0	6.5

Numbers in brackets denote uncertainties in the last significant digit as obtained by the least squares fit method, e.g. 29.5(5) means  $29.5 \pm 0.5$ . The realistic error in  $\epsilon_0$  and  $\tau$  is estimated to be about 2% of their values.

**Table 2.** Dielectric parameters for tetrahydrofuran-water mixture.

Vol % of THF	10°C		25°C		35°C	
	$\epsilon_0$	$\tau$ (ps)	$\epsilon_0$	$\tau$ (ps)	$\epsilon_0$	$\tau$ (ps)
100	10.4(2)	5.3(2)	6.7(1)	4.0(1)	6.0(3)	3.2(4)
90	15.0(1)	14.3(2)	17.9(2)	13.2(1)	17.4(1)	11.8(3)
80	23.6(1)	18.6(1)	20.5(4)	15.5(2)	23.7(1)	14.8(4)
70	34.1(1)	24.3(3)	35.4(1)	17.4(2)	30.7(1)	14.9(2)
60	45.7(1)	26.4(2)	40.9(1)	17.0(4)	40.2(1)	14.5(3)
50	53.8(1)	25.9(2)	54.6(2)	15.6(4)	50.8(3)	14.6(8)
40	59.1(1)	24.1(2)	54.9(2)	14.8(5)	50.9(3)	13.0(7)
30	65.0(2)	21.5(3)	64.9(1)	14.0(2)	63.8(1)	9.8(2)
20	70.6(4)	17.9(6)	73.1(1)	12.6(1)	68.7(1)	9.4(2)
10	80.6(6)	15.2(7)	76.4(2)	10.6(2)	72.5(1)	7.3(1)
0	83.9	12.9	78.3	8.2	75.0	6.5

The values obtained are given in tables 1 and 2, respectively for ACT-water and THF-water mixtures. It can be seen from tables 1 and 2 that the relaxation time increases with water concentration in the mixtures. The maximum relaxation time were observed at 30% of water in both THF and ACT mixtures. Similar behaviour were observed for proton relaxation rates by NMR relaxation technique for both THF and ACT systems in water mixtures [7]. This maxima behaviour may be because the water molecule with solute molecules in the mixture creates a cluster structure such that both THF and ACT molecules rotate slower in the mixture.

The excess permittivity  $\epsilon_0^E$  and the excess inverse of the relaxation time  $1/\tau^E$  for THF and ACT in water mixtures are determined using the following equations as follows [2]

$$\epsilon_0^E = (\epsilon_0 - \epsilon_\infty)_M - ((\epsilon_0 - \epsilon_\infty)_W X_m + (\epsilon_0 - \epsilon_\infty)_S (1 - X_m)) \quad (2a)$$

$$1/\tau^E = (1/\tau)_M - [(1/\tau)_W X_m + (1/\tau)_S (1 - X_m)] \quad (2b)$$

where subscript M, W, and S correspond to the mixture, water and solute, respectively, and  $X_m$  is mole fractions of water in solute.

The viscosity data is taken from the references [10, 11]. The excess viscosity  $\eta^E$  are determined using the equation

$$\eta^E = \eta_M - ((\eta_W * X_m) + (\eta_S * (1 - X_m))). \quad (3)$$

The variation of  $\epsilon_0^E$ ,  $1/\tau^E$  (in GHz),  $\eta^E$  (in cP) with mole fraction of water ( $X_m$ ) in ACT and THF are shown in figures 1(a, b, c) and 2(a, b, c) respectively. The excess dielectric constant and inverse of relaxation time for both THF-water and ACT-water mixtures show negative behaviour. This shows that the oxygen in both THF and acetone helps in formation of hydrogen bonding in the mixtures. The corresponding plots of excess viscosity show positive behaviour. In both mixtures, the maxima is found to be in water-rich region. The molecular interaction responsible for viscous motions seems to be different from the interactions responsible for dielectric behaviour.

The Kirkwood correlation factor  $g$  provides information regarding the structural information of molecules in the polar liquids. The value of  $g$  in a pure liquid can be obtained by the following equation [12, 13]

$$\frac{4\pi N \mu^2 \rho}{9kTM} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (4)$$

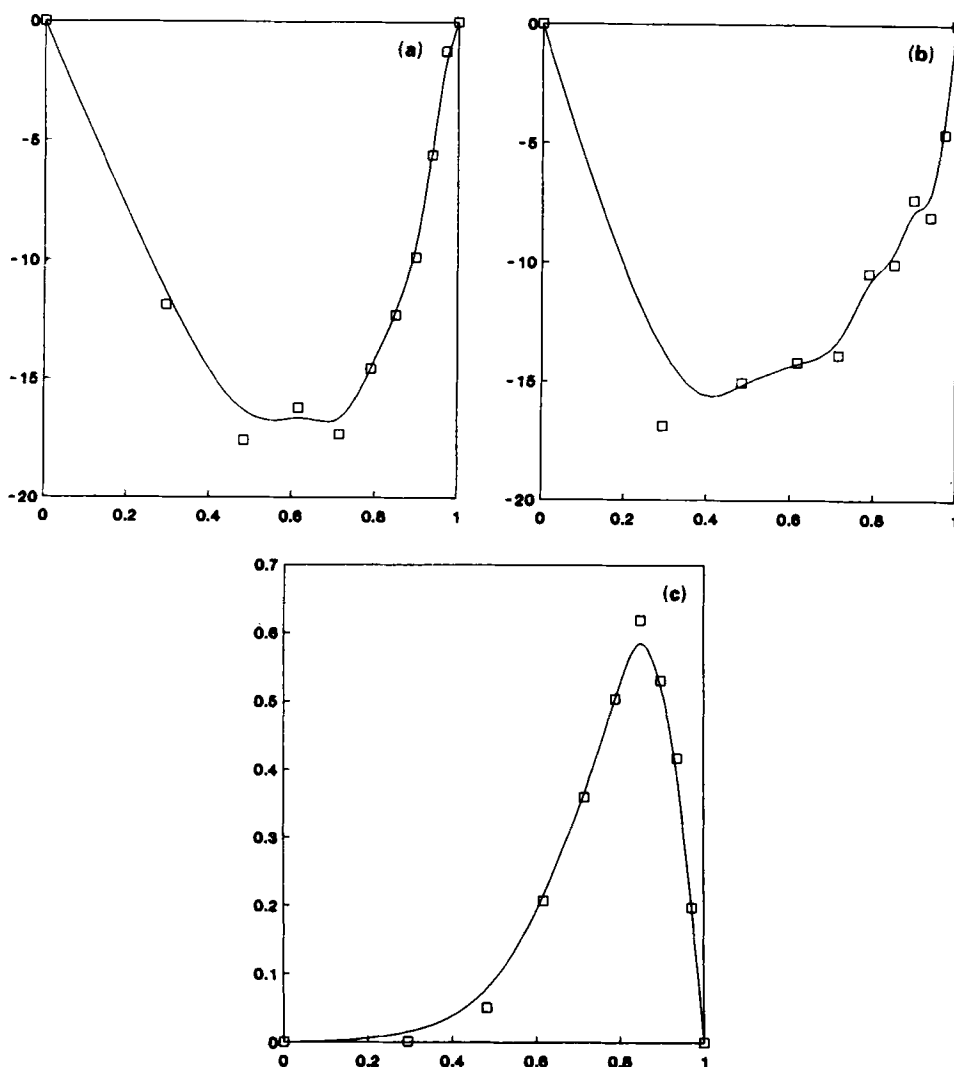
where  $\mu$ ,  $\rho$  and  $M$  correspond to the dipole moment in gas phase, density and molecular weight respectively,  $k$  is the Boltzmann constant and  $N$  is the Avogadro number.

The modified form of (4) is used to study the orientation of the electric dipoles in the binary mixtures as follows [2-4]

$$\frac{4\pi N}{9kT} \left[ \frac{\mu_W^2 \rho_W}{M_W} V_W + \frac{\mu_S^2 \rho_S}{M_S} (1 - V_W) \right] g_{\text{eff}} = \frac{(\epsilon_0 - \epsilon_\infty)_M (2\epsilon_0 + \epsilon_\infty)_M}{\epsilon_{0m} (\epsilon_{\infty m} + 2)^2} \quad (5)$$

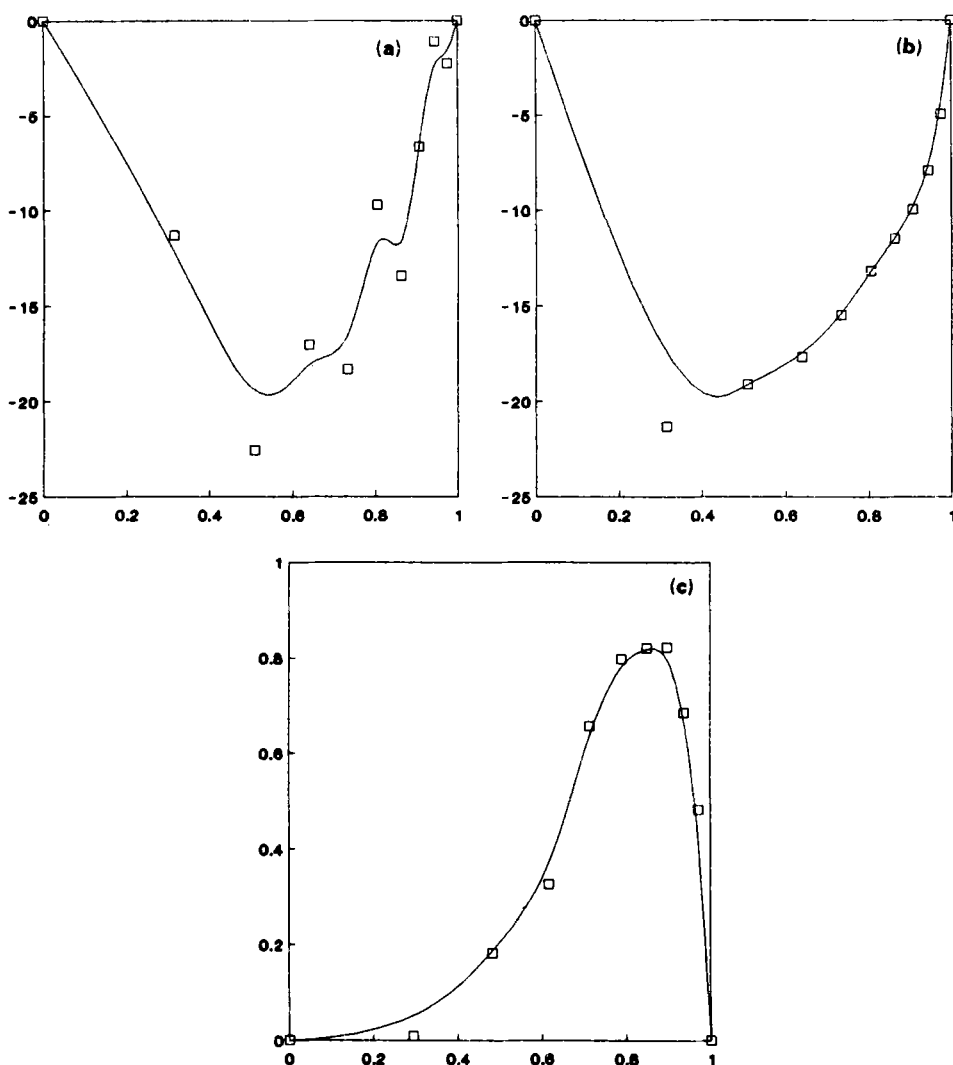
where  $g_{\text{eff}}$  is Kirkwood correlation factor for binary mixture,  $V_W$  represent the volume fraction of water in solute.  $\epsilon_{0m}$  and  $\epsilon_{\infty m}$  are the static dielectric constant and dielectric constant at high frequency, respectively. To calculate the  $g_{\text{eff}}$  we have taken  $\mu = 1.83, 1.63$  and  $2.8$  D, for water [14], THF [15] and ACT [16], respectively. The values of densities are 0.8892 and 0.7899 for THF [16] and ACT [16], respectively

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**Figure 1.** The (a) excess dielectric permittivity ( $\epsilon_0^E$ ), (b) excess relaxation time ( $1/\tau^E$ ) in GHz and (c) excess viscosity ( $\eta^E$ ) in (cP) versus mole fraction of water  $X_m$  in acetone at 25°C: ( $\square$ ) Experimental values. The solid line describes the best possible curve as obtained by the commercial (Harvard) graphic software.

at 25°C. The  $\epsilon_\infty$  values are taken as the square of the refractive index data [16] for THF and ACT. The values of  $g_{eff}$  for THF and ACT in water mixtures are given in table 3. Errors are also estimated in these values by assuming 2% error in values of permittivity. The values of the excess dielectric parameter  $\epsilon^E$  decreases rapidly near the dilute region of solute molecules. It has also been observed that in this region, the relaxation time increases rapidly with the solute concentration. This suggests the formation of cage-type structure around solute molecules. This causes the slower



**Figure 2.** The (a) excess dielectric permittivity ( $\epsilon_0^E$ ), (b) excess relaxation time ( $1/\tau^E$ ) in (GHz) and (c) excess viscosity ( $\eta^E$ ) (in cP) versus mole fraction of water  $X_m$  in tetrahydrofuran at 25°C: ( $\square$ ) Experimental values. The solid line describes the best possible curve as obtained by the commercial (Harvard) graphic software.

relaxation and lower values of orientational polarization. As the number of solute molecules increases, there are not enough water molecules available to form the cage-type structure.

The Kirkwood correlation factor for THF and ACT are smaller than the corresponding values in water. The static dielectric constant of  $\epsilon_{0m}$ ,  $\epsilon_{0w}$  and  $\epsilon_{0s}$  of the mixture, water and solute can be related with the Bruggeman mixture formula [17, 18] with volume fraction of  $X$  of water. The Bruggeman's mixture formula is given by the

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**Table 3.** The Kirkwood correlation factor for THF and ACT in water mixtures at 25°C.

Vol % of solute in water	$g_{\text{eff}}$	
	THF	ACT
100	1.17(7)	1.02(6)
90	1.37(8)	2.17(13)
80	1.55(9)	2.00(11)
70	1.90(11)	2.72(16)
60	2.00(12)	2.65(16)
50	2.20(13)	3.07(18)
40	2.32(14)	2.71(16)
30	2.41(14)	2.87(17)
20	2.54(15)	2.92(17)
10	2.65(15)	2.79(16)
0	2.67(16)	2.67(16)

expression [17, 18]

$$f_{\text{BM}} = \frac{(\epsilon_{0\text{m}} - \epsilon_{0\text{w}})}{(\epsilon_{0\text{s}} - \epsilon_{0\text{w}})} \left( \frac{\epsilon_{0\text{s}}}{\epsilon_{0\text{m}}} \right)^{1/3} = 1 - X. \quad (6)$$

The experimental data does not show the linear relation between  $f_{\text{BM}}$  and  $X$ . The experimental data is well fitted to the modified Bruggeman equation as follows [2]

$$f_{\text{BM}} = 1 - (aX - (1 - a)X^2) \quad (7)$$

where  $a$  is an arbitrary parameter,  $a = 1$  correspond to Bruggeman equation (6). The values of  $a$  have been determined by the least squares fit method. The values of  $a$  for THF-water and ACT-water mixtures are determined to be 2.30 and 1.57, respectively.

### 4. Conclusion

The dielectric relaxation parameters, excess dielectric constant, the Kirkwood correlation factor and Bruggeman factor have been reported for THF-water and ACT-water mixtures for various temperatures. The experimental dielectric relaxation data contains valuable information regarding solute-solvent interactions in the mixures. By using recently developed theories [19, 20], one may get the quantitative information about solute-solvent interactions.

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