

Dielectric relaxation and related studies of 4-ethylphenol–methanol mixtures using time domain reflectometry

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Abstract. The dielectric relaxation studies of 4-ethylphenol–methanol mixtures have been carried out at various temperatures ranging from 10°C to 40°C using time domain reflectometry in the frequency range 10 MHz to 10 GHz. The relaxation mechanism in these systems is explained by Cole–Davidson model. The excess dielectric parameters, Kirkwood correlation factor and activation energy have been calculated and discussed with respect to molecular arrangements, and microdynamics of the binary mixture composed of both the associative type of liquids.

Keywords. Permittivity; microwaves; relaxation times; 4n-ethylphenol; methanol; binary mixtures.

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1. Introduction

Several workers have reported [1–4] dielectric relaxation studies of pure alcohols and their aqueous solutions to understand hydrogen bond structure in these systems. It is generally observed that hydrogen bond is a strong intermolecular interaction which causes a significant effect upon the structure, thermodynamic properties and macroscopic dielectric properties of the solutions of polar liquids. As noticed by Gestblom and Sjoblom [5] small-chain alcohols like methanol behave in a different way from long-chain alcohols as the former is characterized by faster relaxation and low activation energy whereas the latter by slower relaxation and high activation energy. The dielectric studies of aqueous methanol show ideal mixture behaviour due to the similar self association patterns of the two components. But not much work has been done on the alkyl phenol-methanol systems where the alkyl phenols are characterized by high relaxation time and activation energy but lower macroscopic permittivity compared to methanol. Such studies are expected to yield information about the structural behaviour or self association pattern and intermolecular interactions in the mixture. In view of this we have taken up the dielectric relaxation studies of different *n*-alkylphenols-methanol mixtures using time domain reflectometry (TDR) technique.

The objective of the paper is to study the dielectric relaxation in 4-ethylphenol

(4EP)–methanol (MtOH.) mixtures over entire range of concentration at four different temperatures from 10°C to 40°C using TDR. The excess dielectric properties, thermodynamic properties and Kirkwood correlation factor have been calculated and the results discussed.

2. Experimental details

4-Ethylphenol of 99% purity (Aldrich) and methanol of spectroscopic grade purity obtained commercially were used without further purification. The mixtures were prepared at various volume percentages of 4EP in MtOH in steps of 10 (before mixing) at room temperature.

The complex permittivity spectra were studied using time domain reflectometry (TDR) method as described in [6–8]. The Tektronix 7854 sampling oscilloscope with 7S12 TDR unit has been used. A fast rising step voltage pulse of 200 mV with 25 ps rise time and repetitive frequency of 1 kHz generated by a tunnel diode was propagated through a co-axial line system. The sample was placed at the end of co-axial line in standard military application (SMA) coaxial cell of 3.5 mm outer diameter and 1.35 mm effective pin length. The change in the pulse after reflection from the sample placed in the cell was monitored. In our experiment time window of 5 ns was used. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitized into 1024 points and transferred to PC/XT through GPIB. Temperature of the sample was controlled electronically within $\pm 0.2^\circ\text{C}$.

Processing of data yielded complex reflection coefficient spectra $\rho^*(\omega)$ over a frequency range of 10 MHz to 10 GHz [6, 7]. The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the least squares fit method of calibration used for HMPA-Water mixture [8, 9]. A typical reflection coefficient spectrum $\rho^*(\omega)$ (before calibration) and complex dielectric spectrum $\epsilon^*(\omega)$ (after calibration) are shown in figure 1. The discontinuity at 2 GHz and 6 GHz in

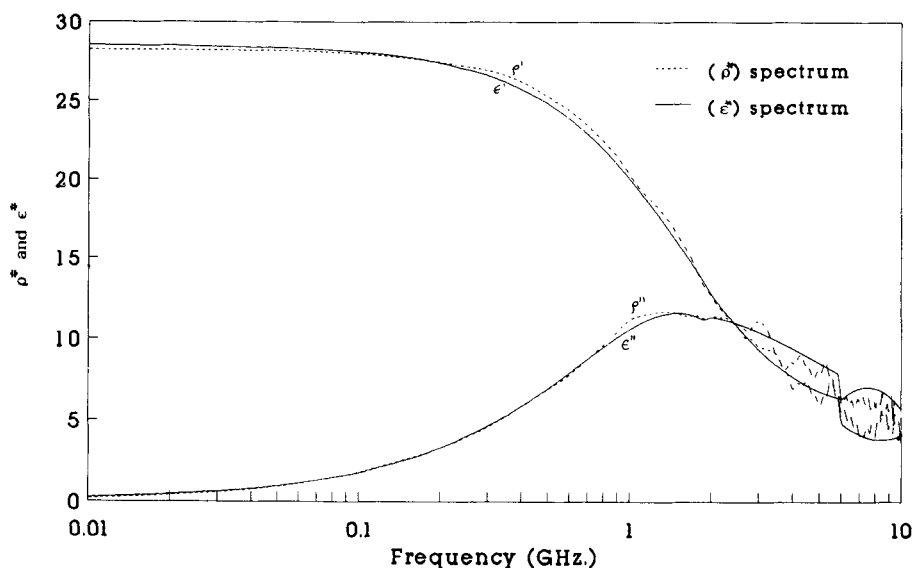


Figure 1. The reflection coefficient spectrum- (ρ^*) and corrected dielectric spectrum (ϵ^*) for a 4-ethylphenol-methanol mixture.

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the $\epsilon^*(\omega)$ spectrum is due to the numerical error caused by dividing the spectrum into three parts to achieve better accuracy in calibration [8].

3. Results and discussions

The Cole–Davidson equation was used in the least squares fit method as follows,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{(1 + j\omega\tau)^\beta} \quad (1)$$

when ϵ_s is the static dielectric constant ϵ_∞ , the high frequency dielectric constant τ the relaxation time and β the Cole-Davidson distribution parameter. Values of ϵ_s , τ and β as a function of 4EP concentration in MtOH at four different temperatures studied are given in table 1 and a graphical representation of ϵ_s and τ is given in figures 2(a) and 2(b) respectively. The values of ϵ_s of the mixture decrease from corresponding value of MtOH to that of pure 4EP whereas τ increases from that of

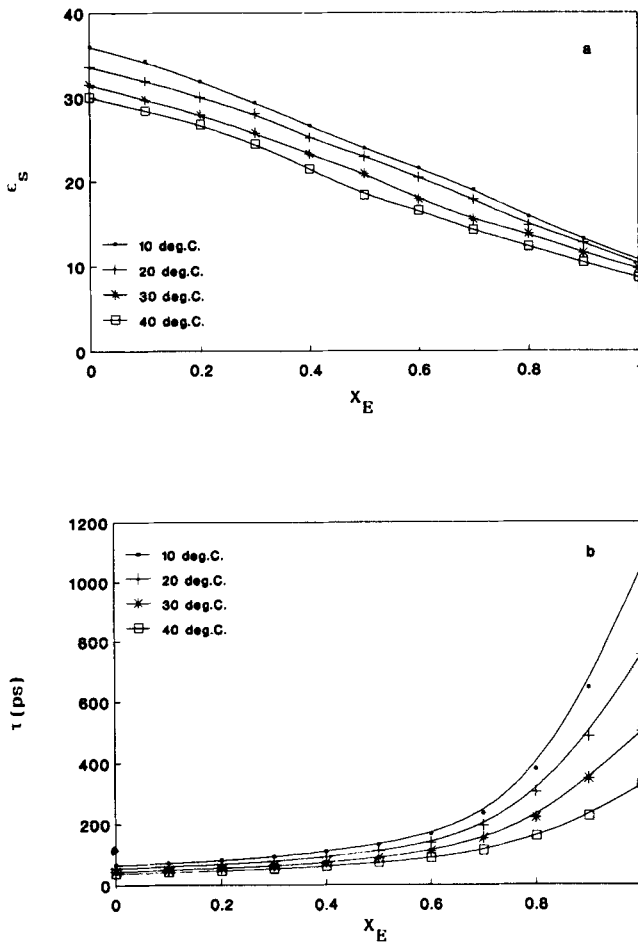


Figure 2. Variation of (a) static dielectric constant- (ϵ_s) and (b) relaxation time- (τ) with volume fraction of 4-ethylphenol (X_E) in methanol at various temperatures.

Table 1. Variation of dielectric parameters for 4-ethylphenol-methanol mixture.

Vol.% 4EP	ϵ_s	τ (ps)	β
10°C			
00	35.72(12)	66.0 (9)	0.948(3)
10	34.67(12)	71.7(11)	0.954(5)
20	32.04(10)	80.7(13)	0.931(3)
30	29.11(10)	93.2(16)	0.907(2)
40	26.09(11)	109.3(19)	0.914(2)
50	23.30 (9)	132.6(24)	0.881(2)
60	20.67 (9)	167.5(31)	0.903(2)
70	18.12 (8)	235.1(39)	0.942(3)
80	15.67 (8)	379.1(40)	0.921(3)
90	13.87 (6)	646.5(48)	0.904(2)
100	12.14 (5)	1045.4(56)	0.896(2)
20°C			
00	33.68(10)	55.8 (6)	0.936(7)
10	32.17 (9)	60.7 (8)	0.904(3)
20	29.72 (8)	68.1 (9)	0.903(3)
30	26.91 (9)	78.4(11)	0.886(2)
40	23.97 (9)	91.6(15)	0.875(2)
50	21.29 (7)	110.6(18)	0.951(6)
60	18.63 (6)	137.7(25)	0.945(5)
70	16.09 (6)	195.1(30)	0.933(3)
80	14.17 (5)	304.7(37)	0.987(8)
90	12.06 (4)	485.4(42)	0.885(3)
100	10.51 (4)	754.1(53)	0.906(3)
30°C			
00	31.53 (9)	45.3 (4)	0.951(5)
10	29.74(7)	49.3 (5)	0.948(4)
20	27.53(7)	55.3 (6)	0.936(4)
30	24.87(6)	65.3 (8)	0.955(6)
40	22.15(5)	73.9(12)	0.941(3)
50	19.53(5)	88.2(15)	0.929(3)
60	17.13(5)	111.5(18)	0.925(2)
70	14.82(3)	152.8(25)	0.908(2)
80	12.73(3)	222.0(30)	0.952(6)
90	11.01(3)	348.4(37)	0.913(3)
100	9.56(3)	502.0(45)	0.902(2)
40°C			
00	29.96 (8)	38.4 (4)	0.938(4)
10	28.08(8)	41.6 (5)	0.941(5)
20	25.92(7)	46.6 (5)	0.926(3)
30	23.33(7)	53.2 (6)	0.951(5)
40	20.73(5)	61.5 (7)	0.936(3)
50	18.27(5)	72.8(10)	0.918(2)
60	16.07(4)	88.0(13)	0.878(2)
70	13.93(4)	112.6(17)	0.893(2)
80	11.90(3)	159.3(23)	0.906(2)
90	10.23(3)	225.4(30)	0.933(4)
100	8.91(3)	328.6(35)	0.925(4)

Numbers in parentheses denote uncertainty in last significant digit obtained by least squares fit method. e.g. 8.91 (3) means 8.91 ± 0.03 , 328.6(35) means 328.6 ± 3.5 .

MtOH to 4EP. τ increases sharply in the higher concentration of 4EP. Similar trend has been observed in our study on 4n-propylphenol-methanol [10] mixtures where τ is found to be more than in 4EP-MtOH mixtures at all concentrations and temperatures.

The contributions of nonlinear effects due to solute-solvent interactions can be studied by the excess dielectric properties. The excess permittivity ϵ_s^E and excess inverse relaxation time $(1/\tau)^E$ are determined using the following equations:

$$\epsilon_s^E = [\epsilon_{sm} - \epsilon_{\infty m}] - [(\epsilon_{sM} - \epsilon_{\infty M})X_M + (\epsilon_{sE} - \epsilon_{\infty E})X_E] \quad (2)$$

$$[1/\tau]^E = [1/\tau]_m - [(1/\tau)_M X_M + (1/\tau)_E X_E] \quad (3)$$

where subscripts m, M, E correspond to the mixture, MtOH and 4n-ethylphenol respectively and X_M and X_E represent the weight fractions of the two components of the mixture. The variation of ϵ_s^E and $(1/\tau)^E$ with X_E (weight fraction of 4EP) for various temperatures are shown in figures 3(a) and 3(b) respectively. For the mixtures $\epsilon_{\infty m}$

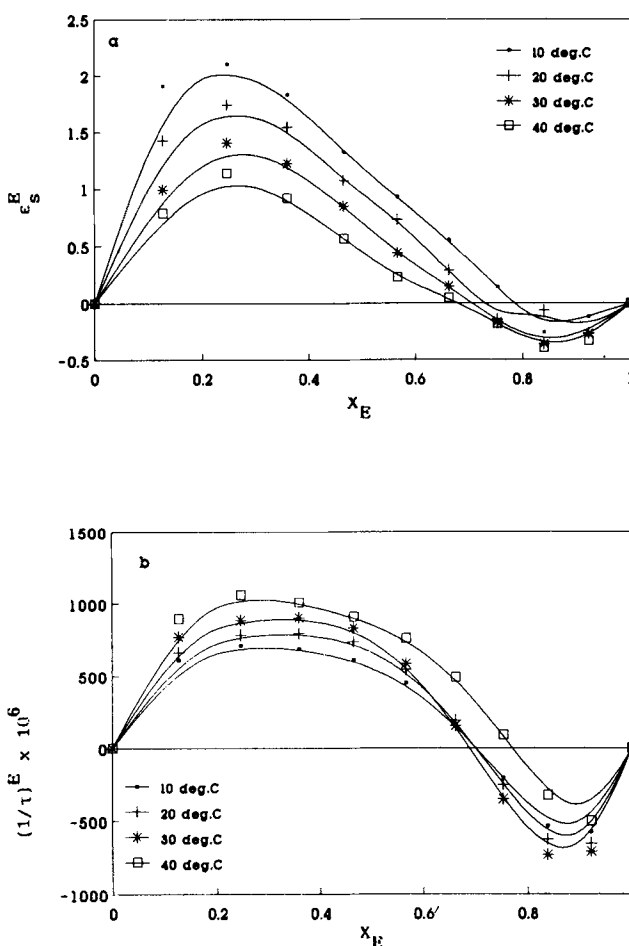


Figure 3. The excess dielectric permittivity- ϵ_s^E and excess inverse relaxation time- $(1/\tau)^E$ for 4-ethylphenol-methanol mixture as a function of weight fraction of 4-ethylphenol (X_E) at different temperatures.

values are calculated from the corresponding values $\epsilon_{\infty E}$ and $\epsilon_{\infty M}$ of the two components using additive rule.

The above models give a good qualitative account to study the solute-solvent interactions. The negative excess ϵ_s^E is associated with either the disappearance of the polymeric forms, leaving behind the dimers and monomers, or alternatively the creation of new structures of the type depicted above which have essentially zero dipole moment. Either way the net effect is that the permittivity drops below its additive value. The positive values of ϵ_s^E is interpreted as a formation of monomer structure, whereas the negative ϵ_s^E implies the formation of multimer structure. The negative excess inverse relaxation time $(1/\tau)^E$ means the creation of an environment such that the solute molecules rotate more slowly in the mixture.

The experimental values of both the excess parameters are fitted to the Redlick-Kister [11, 12] equation,

$$A^E = (X_1 X_2) \sum_j B_j (X_1 - X_2)^j \quad (4)$$

where A is any physical parameter and X_1 and X_2 are the concentrations of the two components. The coefficients B_j 's for $j=0$ to 4 are given in table 2 along with the standard deviation σ . By using these B_j values, A^E values calculated are used as guidelines to draw smooth curves in figures 3(a) and 3(b).

The excess dielectric constant ϵ_s^E is found to be positive over a wide range of concentration except for small negative values in the higher concentration region of 4EP. The ϵ_s^E is maximum around 20% of 4EP in MtOH at all temperatures. The positive ϵ_s^E values suggest that the effective number of dipoles in the mixture might be greater than their corresponding average number in their pure forms probably by creation of monomers.

$(1/\tau)^E$ values are found to be positive in the MtOH-rich region but negative in the 4EP-rich region [figure 3(b)]. The sign inversion of $(1/\tau)^E$ takes place around 70% of 4EP in MtOH. This indicates that the addition of MtOH to 4EP has created a

Table 2. Coefficients B_j 's and standard deviation σ of Redlick-Kister equation. Excess permittivity

$t(^{\circ}C)$	B_0	B_1	B_2	B_3	B_4	σ
10	4.92	8.65	3.01	7.47	3.78	0.08
20	3.67	8.90	2.94	1.91	-0.17	0.10
30	2.86	8.19	2.79	-0.05	-4.51	0.04
40	1.81	6.72	4.94	0.75	-8.60	0.04

Inverse relaxation time

$t(^{\circ}C)$	$B_0 \times 10^3$	$B_1 \times 10^3$	$B_2 \times 10^3$	$B_3 \times 10^3$	$B_4 \times 10^3$	$\sigma \times 10^3$
10	2.28	2.83	-3.37	8.09	-1.21	0.05
20	2.76	3.24	-5.23	8.95	0.01	0.10
30	3.09	4.18	-7.14	9.41	2.65	0.06
40	3.48	2.61	-0.49	9.99	-3.79	0.09

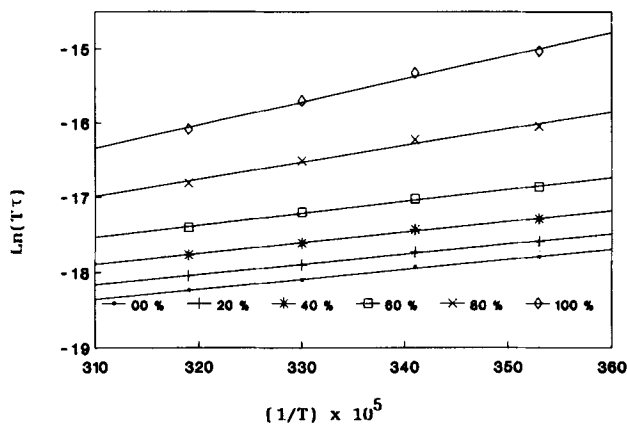


Figure 4. $\text{Ln}(T\tau)$ vs $1/T$ for 4-ethylphenol + methanol mixtures at various volume percentages of 4-ethylphenol.

hindering field such that the effective dipoles rotate slowly in the 4EP-rich region whereas in the MtOH-rich region the effective dipoles rotate faster. This variation of $(1/\tau)^E$ reflects the state of microdynamics of the system under study.

The thermodynamic parameters like molar enthalpy of activation ΔH^* and molar entropy of activation ΔS^* are determined from Eyring's rate equation [13] (eq. 5) utilizing least squares fit method.

$$\tau = \frac{h}{KT} \exp(\Delta H^* - T\Delta S^*)/RT. \quad (5)$$

The variation of $\ln(T\tau)$ with $(1/T)$ for some of the compositions of the mixture is shown in figure 4 and a good linear fitting was observed in all the cases. The results of ΔH^* and ΔS^* for various volume percentages of 4EP in MtOH are given in table 3.

Table 3. Variation of ΔH^* and ΔS^* for 4-ethylphenol + methanol solution.

Vol.% 4EP	ΔH^* kJ/mol	ΔS^* J/mol/K
00	11.03 (49)	-10.67
10	11.68 (52)	-11.25
20	11.19 (49)	-11.79
30	11.42 (42)	-12.18
40	11.81 (52)	-12.13
50	11.41 (59)	-11.65
60	13.28 (79)	-10.45
70	15.41 (173)	-5.62
80	18.95 (181)	2.48
90	23.15 (227)	12.90
100	26.03 (174)	19.10

Numbers in the parentheses indicate errors in the last significant digit.

There is no significant variation in ΔH^* in the MtOH-rich region but it sharply increases above 70% of 4EP in MtOH and in the same concentration region of 4EP $(1/\tau)^E$ is observed to be negative. From this table it can also be noticed that for more than 80% volume fraction of 4EP, ΔS^* is observed to be positive. But as suggested by Hill *et al* [14] no much significance can be attached to these values in view of the absence of higher accuracy.

The Kirkwood correlation factor g [15] explains the orientation of the electric dipoles in the polar liquids and it is given by the equation,

$$\frac{4\pi N\mu^2\rho}{9KTM}g = \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \quad (6)$$

The two modified forms of the above equation normally used to study the orientation of the electric dipoles in the binary mixture [16, 17] are as follows,

$$\frac{4\pi N}{9kT} \left(\frac{\mu_M^2\rho_M}{M_M} X_M + \frac{\mu_E^2\rho_E}{M_E} X_E \right) g_{\text{eff}} = \frac{(\epsilon_{\text{sm}} - \epsilon_{\infty\text{m}})(2\epsilon_{\text{sm}} + \epsilon_{\infty\text{m}})}{[\epsilon_{\text{sm}}(\epsilon_{\infty\text{m}} + 2)]^2} \quad (7)$$

where g_{eff} is Kirkwood correlation factor for a binary mixture, X_M and X_E represent volume fraction of MtOH and 4EP respectively. The value of g_{eff} varies between g_M

Table 4. The Kirkwood factors g_{eff} and g_f for 4-ethylphenol + methanol mixtures.

Vol.% 4EP	g_{eff}		g_f	
	10°C		20°C	
00	3.22 (19)	1.000 (61)	3.14 (19)	1.000 (61)
10	3.20 (19)	1.017 (62)	3.06 (19)	1.004 (61)
20	3.03 (18)	0.991 (60)	2.90 (18)	0.980 (60)
30	2.81 (17)	0.957 (58)	2.69 (16)	0.946 (58)
40	2.61 (16)	0.920 (56)	2.47 (15)	0.907 (55)
50	2.41 (15)	0.892 (54)	2.27 (14)	0.877 (54)
60	2.22 (14)	0.871 (53)	2.06 (13)	0.851 (52)
	2.02 (13)	0.856 (53)	1.85 (11)	0.829 (51)
				0.850 (53)

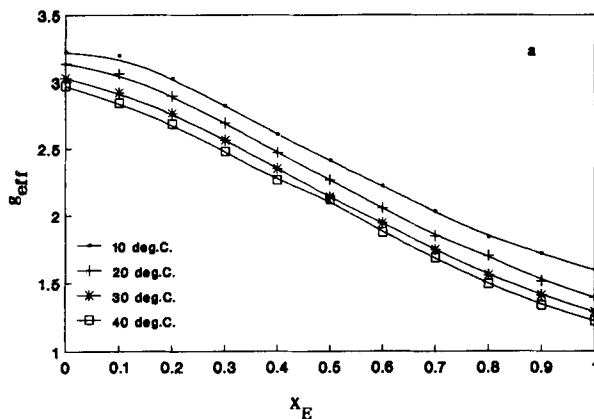
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and g_E . The second form is

$$\frac{4\pi N}{9kT} \left(\frac{\mu_M^2 \rho_M g_M}{M_M} X_M + \frac{\mu_E^2 \rho_E g_E}{M_E} X_E \right) g_f = \frac{(\epsilon_{sm} - \epsilon_{\infty m})(2\epsilon_{sm} + \epsilon_{\infty m})}{\epsilon_{sm}(\epsilon_{\infty m} + 2)^2} \quad (8)$$

where g_M and g_E are the Kirkwood correlation factors of pure MtOH and 4EP respectively, and are assumed to be affected by an amount g_f in the mixture. The value of g_f is unity for an ideal mixture and deviation from unity may indicate interaction between the two components of the mixture.

The values of g_{eff} and g_f for various compositions of the mixture are given in table 4 and are represented graphically in figures 5(a) and 5(b) respectively. The dipole moments of 4EP and MtOH are taken as 1.98 D (calculated from vector method) and 1.69 D respectively. Kirkwood correlation factor g_{eff} decreases from g of MtOH to that of pure 4EP and g of both the components is more than unity i.e. ($g_M > g_E > 1.0$) at all temperatures. This confirms the associative nature of both alcohols and phenols with parallel orientations of their electric dipoles. The extent of parallel orientation decreases with concentration of 4EP. From table 4 and figure 5(b) it is observed that



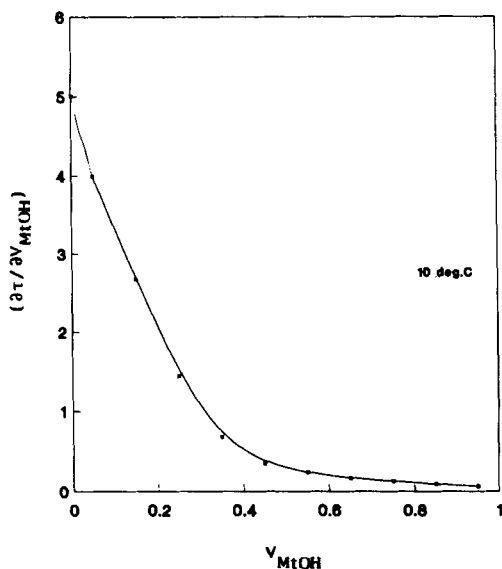


Figure 6. The variation of $(\partial\tau/\partial V_{MtOH})$ as a function of volume fraction of methanol (V_{MtOH}) for 4-ethylphenol + methanol mixture.

g_f values are less than unity for all compositions and at all temperatures and maximum deviation from unity is observed around 75% of 4EP at all temperatures. This may indicate strong interactions between the molecules of the two components.

In view of the results discussed in the above paragraphs, high relaxation time- τ , negative $(1/\tau)^E$ and high activation energy- ΔH^* in the 4EP-rich region indicate that the effective dipoles in the system may be interacting in such a way that they possess limited ability to reorient. Although both the components of the mixture are associative in nature but the high frequency relaxation of MtOH and low frequency relaxation of 4EP may indicate that the self associating patterns in the two components are totally different. The quantitative trends of the several parameters cited above suggest multimeric structure in the 4EP which breaks down effectively by the addition of MtOH. From figure 6 one can understand the effect of addition of MtOH on the relaxation time in terms of $(\partial\tau/\partial V_{MtOH})$, the sharp increase in this parameter as (V_{MtOH}) tends to zero indicate strong initial interactions between the molecules of the two components. Similar kind of observation was made by Gestblom and Sjoblom [3, 5] for aqueous solutions of higher alcohols.

According to Bruggeman, static dielectric constants of the mixture and components of the binary mixture can be related to the volume fraction of the solute (4EP in our case) by the following equation [19, 20], assuming an ideal mixture behaviour,

$$f_B = \left[\frac{\epsilon_{sm} - \epsilon_{sE}}{\epsilon_{sM} - \epsilon_{sE}} \right] \left[\frac{\epsilon_{sM}}{\epsilon_{sm}} \right]^{1/3} = (1 - X_E) \quad (9)$$

yielding a linear relationship between Bruggeman factor- f_B and X_E . However, in the present case experimental values of f_B are found to deviate from the linear relationship (figure 7). Several similar observations have been reported [16, 20]. To fit the experimental data the above equation is modified [16] as follows,

$$f_B = 1 - [a - (a - 1)X_E]X_E \quad (10)$$

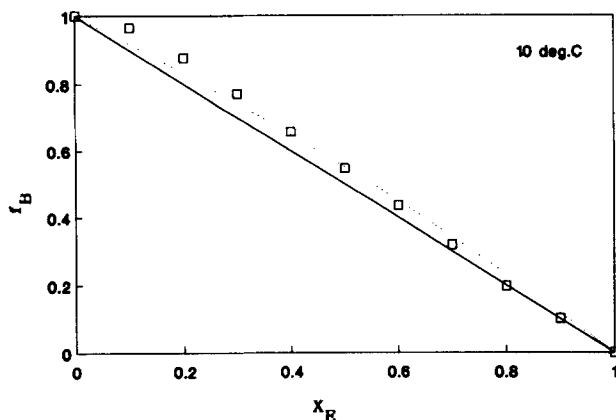


Figure 7. The Bruggeman plot for 4-ethylphenol + methanol mixtures. Open square solid line and dotted curve represent experimental points, original and modified Bruggeman equations respectively.

where a is a numerical fitting parameter and $a = 1$ for an ideal mixture. The values of a are found to be 0.792, 0.820, 0.856 and 0.885 for 10°, 20°, 30° and 40°C respectively. It is found that, the value of a tends to increase towards unity as temperature increases. The value of $a < 1$ indicates that the effective volume fraction of 4EP in MtOH has increased by a factor $[a - (a - 1)X_E]$. From figure 7, it can be seen that, the modified Bruggeman equation fits better with the experimental values of f_B than the original Bruggeman equation.

4. Conclusion

Dielectric relaxation parameters, thermodynamic parameters and Kirkwood correlation factor have been reported for 4n-ethylphenol-methanol mixtures for various temperatures and concentrations. These studies suggest that multimeric structure in the 4EP breaks down effectively in the presence of MtOH. The dielectric behaviour of this binary mixture may be better explained by modified Bruggeman equation.

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