Dielectric Study on Polar Binary Mixtures of (Ester-Alcohol) at 298.2 K

A. Ghanadzadeh*, H. Ghanadzadeh, M. Alinejad
Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran

Abstract
Dielectric constant measurements were made on binary mixtures of ethyl acetate (EA) and butyl acetate (BA) with the two amyl alcohols (iso-amyl alcohol (IAA) and tert-butyl alcohol (TBA)) for various concentrations at T = 298.2 K and in a frequency of 100 kHz. In order to obtain valuable information about heterogeneous interaction (interactions between the unlike molecules), the Kirkwood correlation factor, the Bruggeman dielectric factor and the excess permittivity were calculated.

Keywords: *Dielectric Constant, Kirkwood Correlation Factor, Excess Permittivity*

1. Introduction

Dielectric studies on the binary mixtures are important for understanding the inter-molecular interactions in the mixture due to the dipole–dipole interactions and hydrogen bonding. The dielectric investigations of binary polar liquid mixtures provide valuable information regarding intermolecular interactions and the consequent structural rearrangement of molecules in solution. The heterogeneous and homogeneous interactions in binary mixtures using dielectric measurements have been studied and reported by several investigators [1-6].

Esters are an important class of industrial chemicals with many scientific and industrial applications. These compounds with a carbonyl group and linking oxygen function are hydrogen-bond acceptors. The primary use of esters is as solvents and flavoring agents in many chemical formulations. They are also used in the manufacture of many polymeric materials. Alcohols have been the subject of extensive practical and theoretical investigations in the study of intermolecular hydrogen bonding [7]. Due to the presence of –OH group in the molecule, the solution chemistry of these compounds can be strongly influenced by the intermolecular hydrogen bond formation. The aliphatic alcohols are excellent H-bond donors/ acceptors and, therefore, are strongly associated through intermolecular H-bonding.

Due to the industrial and scientific importance of the esters and alcohols,

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∗ Corresponding author: aggilani@guilan.ac.ir

significant investigations have been carried out on the dielectric measurements of these compounds and their binary mixtures by several researchers [8-10].

The investigation reported here presents a useful dielectric data for the polar binary systems of (EA + IAA), (EA + TBA), (BA + IAA), and (BA + TBA). This work is concerned with the determination of the dielectric behavior and the molecular association of the polar-polar binary mixtures of (ester-alcohol) for various mole fractions at $T = 298.2$ K.

2. Experimental
2-1. Materials
All chemicals for dielectric investigations, with high purity (spectroscopic grade) were purchased from Merck. The chemical structures of the investigated compounds are given in Table 1. Solutions of these materials were prepared by accurately weighing appropriate amounts of solute in 10 cm^3 volumetric flasks. HPLC grade cyclohexane was used as solvent for the dipole moment measurements of the compounds. HPLC grade 1,4-dioxane was used as a standard liquid for calibration of the dielectric cell.
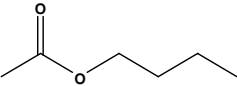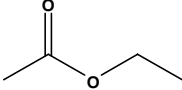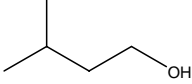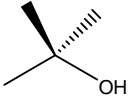
2-2. Refractive index measurements
The refractive indices of the solutions were determined at a wavelength of 589 nm using an Abbe Refractometer (Model CETI). The refractometer was initially calibrated by automatic zeroing function and then used to perform refractive index measurements at 298.2 K. The temperature of the refractometer was controlled by circulation of water and was measured to an accuracy of ±0.1 K.

2-3. Dielectric apparatus
The electrical capacitance of the dielectric cell was measured using a Wayne Kerr model 6425B Digibridge. Measurements of the capacitance required for calculating the static dielectric permittivity were performed at a frequency of 100 kHz. The samples were checked for any ionic conditions.

Table 1. Compounds used in this study.

Compound	Molecular structure	Abbreviation	Molar mass
Butyl acetate		BA	116.16
Ethyl acetate		EA	88.11
Iso amyl alcohol (3-methyl-1-butanol)		IAA	88.15
tert-butyl alcohol (2-methyl-2-propanol)		TBA	74.12

2-4. Dielectric cell

A three-terminal dielectric cell was constructed for measurements on small volumes of solutions (3 ml). The outer, inner and guard electrodes of the cell were made from stainless steel. The gap between the inner and the outer electrodes was approximately 1mm. The electrical capacitance of the empty cell was about 30 pF. The temperature of the cell could be controlled to be better than ±0.1K. The instrument was calibrated at every working temperature with air and using liquid with well-known dielectric permittivity.

3. Results and discussion

The dipole moments, μ, of EA, BA, IAA, and TBA dissolved in cyclohexane were calculated using the Guggenheim–Debye equation [11]. The expression for the dipole moment is given by

$$\mu^2 = \frac{27kT}{4\pi N_A \left(\varepsilon_1 + 2\right)\left(n_1^2 + 2\right)} \left(\frac{\Delta}{C}\right)_{C \to 0} \qquad (1)$$

Where ε_1 is the static permittivity and n_1 is the refractive index of pure non-polar solvent, k is the Boltzmann constant and N_A is Avogadro's number. The dielectric increment is given by $\Delta = \left(\varepsilon_{12} - n_{12}^2\right) - \left(\varepsilon_1 - n_1^2\right)$, where the subscript 12 denotes a property of the solution, C is the molar concentration (mol/cm^3), and $(\Delta/C)_o$ is the limiting gradient of the plot versus concentration. The permittivity and the refractive index values of these liquids were measured independently at $T = 298.2$ K.

By substituting values of $(\Delta/C)_o$ into the Guggenheim–Debye equation, dipole moments of the compounds were calculated. The results of the dipole moment measurements in cyclohexane along with the literature values [12-14] are presented in Table 2. The uncertainties in the measured refractive indices, relative permittivities, dipole moments and temperature are about ±0.0001, ±0.005, ±0.05 and ±0.1, respectively.

Table 2. The molecular dipole moments of the compounds obtained in solution in cyclohexane at $T = 298.2$ K.

Compound	$\mu_{obs.}$ (D)	μ_{Ref} (D)
Ethyl acetate	1.76	1.78
Butyl acetate	1.83	1.84
Isoamyl alcohol	1.80	1.72
Tert-butyl alcohol	1.66	1.66

The effective dipole moments, μ_{eff}, of the pure liquids can be calculated using the Kirkwood–Frohlich equation [15]

$$g\mu^2 = \frac{9kTM}{4\pi N_A d} \frac{\left(\varepsilon - n^2\right)\left(2\varepsilon + n^2\right)}{\varepsilon \left(n^2 + 2\right)^2} \qquad (2)$$

In which "g" is the Kirkwood correlation factor and is a measure of the molecular association between a reference molecule and its nearest neighbors. The departure of "g" from unity is indicative of molecular association.

The modified form of the Kirkwood equation

(2) [16] for the mixtures of two polar liquids may be written as

$$\left(\frac{\mu_1^2 d_1}{M_1} x_1 + \frac{\mu_2^2 d_2}{M_2} x_2 \right) g_{eff}$$

$$= \frac{9kT}{4\pi N_A} \frac{\left(\varepsilon - n^2 \right)\left(2\varepsilon + n^2 \right)}{\varepsilon \left(n^2 + 2 \right)^2} \qquad (3)$$

Where g_{eff} is the effective correlation factor for a binary mixture.

The values of static permittivity, ε_{12}, effective Kirkwood correlation factor of the mixture, g_{eff}, the Bruggeman factor, f_B and the excess permittivity, ε^E for the polar

binary systems of (EA + IAA) , (EA + TBA), (BA + IAA), and (BA + TBA) at T = 298.2 K are given in Tables 3 and 4. The concentration dependence of the solution permittivity of the polar binary liquid mixtures at *T* = 298.*2 K* is shown in Figs. 1 and 2. The non-linear variations of *ε12* indicate the interaction between the unlike molecules (heterogeneous interaction). The heterogeneous interaction between the ester (EA or BA) and the alcohol (IAA or TBA) could be due to the dipole-dipole interaction and hydrogen bonding between the interacting molecules.

Table 3. Permittivity, ε_{12}, refractive index, n_{12}, effective Kirkwood correlation factor, g_{eff}, the Bruggeman factor, f_B, and the excess permittivity, ε^E, of the [EA (1) + IAA (2)] and [EA (1) + TBA (2)] liquid mixture at *T* = 298.2 K.

System	X_2	ε_{12}	n_{12}	g_{eff}	g_f	ε^E	f_B
EA (1) + IAA (2)	0	6.06	1.3699	1.00	1.00	0.00	1.00
	0.09	6.22	1.3736	1.03	0.89	–0.64	0.97
	0.18	6.51	1.3763	1.11	0.83	–1.11	0.92
	0.28	6.98	1.3796	1.20	0.79	–1.57	0.86
	0.38	7.55	1.3830	1.32	0.78	–1.89	0.77
	0.47	8.26	1.3860	1.47	0.79	–1.99	0.68
	0.58	9.33	1.3902	1.70	0.82	–1.90	0.55
	0.68	10.4	1.3933	1.93	0.85	–1.72	0.43
	0.74	11.12	1.3959	2.08	0.87	–1.53	0.35
	0.80	11.85	1.3972	2.24	0.90	–1.34	0.28
	0.92	13.68	1.4018	2.62	0.96	–0.58	0.11
	1	14.97	1.4053	2.89	1.00	0.00	0.00
EA (1) + TBA (2)	0	6.06	1.3699	1.00	1.00	0.00	1.00
	0.1	6.19	1.3736	1.05	0.92	–0.46	0.97
	0.21	6.52	1.3763	1.15	0.88	–0.77	0.90
	0.31	6.91	1.3796	1.27	0.86	–0.97	0.82
	0.41	7.33	1.3830	1.40	0.85	–1.13	0.74
	0.51	7.87	1.3860	1.56	0.85	–1.18	0.63
	0.61	8.52	1.3902	1.76	0.87	–1.12	0.52
	0.71	9.19	1.3933	1.97	0.89	–1.04	0.41
	0.81	10.07	1.3972	2.24	0.93	–0.75	0.27
	0.91	10.98	1.4018	2.54	0.96	–0.43	0.13
	0.95	11.37	1.4053	2.67	0.98	–0.26	0.08
	1	11.94	1.3699	2.85	1.00	0.00	0.00

Table 4. Plot of excess permittivity of binary mixture of (●) [BA (1) + IAA (2)] and (▲) [BA (1) + TBA (2)] as a function of the alcohol mole fraction at $T = 298.2$ K.

| System	X_2	ε_{12}	n_{12}	g_{eff}	g_f	ε^E	f_B
BA (1) + IAA (2)	0	5.01	1.3926	0.92	1.00	0.00	1.00
	0.07	5.12	1.3929	0.93	0.81	-0.60	0.98
	0.12	5.28	1.3932	0.97	0.81	-0.94	0.96
	0.23	5.71	1.3947	1.06	0.73	-1.62	0.89
	0.34	6.34	1.3956	1.19	0.71	-2.10	0.80
	0.45	7.2	1.3968	1.37	0.72	-2.35	0.69
	0.55	8.18	1.3985	1.57	0.75	-2.38	0.58
	0.65	9.34	1.3997	1.81	0.79	-2.23	0.46
	0.74	10.61	1.4011	2.06	0.84	-1.86	0.35
	0.84	12.08	1.4026	2.35	0.89	-1.40	0.22
	0.92	13.53	1.4040	2.62	0.94	-0.76	0.11
	1	15.10	1.4053	2.92	1.00	0.00	0.00
BA (1) + TBA (2)	0	5.01	1.3924	0.92	1.00	0.00	1.00
	0.07	5.11	1.3916	0.94	0.90	-0.39	0.98
	0.13	5.23	1.3907	0.96	0.85	-0.68	0.95
	0.26	5.57	1.3895	1.03	0.77	-1.24	0.89
	0.37	6.08	1.3883	1.15	0.76	-1.50	0.79
	0.48	6.76	1.3877	1.30	0.78	-1.58	0.68
	0.58	7.52	1.3868	1.47	0.81	-1.52	0.56
	0.68	8.31	1.3862	1.64	0.83	-1.42	0.44
	0.77	9.18	1.3859	1.83	0.87	-1.18	0.33
	0.85	9.96	1.3856	1.99	0.90	-0.96	0.23
	0.93	11.01	1.3853	2.21	0.96	-0.46	0.11
	1	11.96	1.3850	2.41	1.00	0.00	0.00
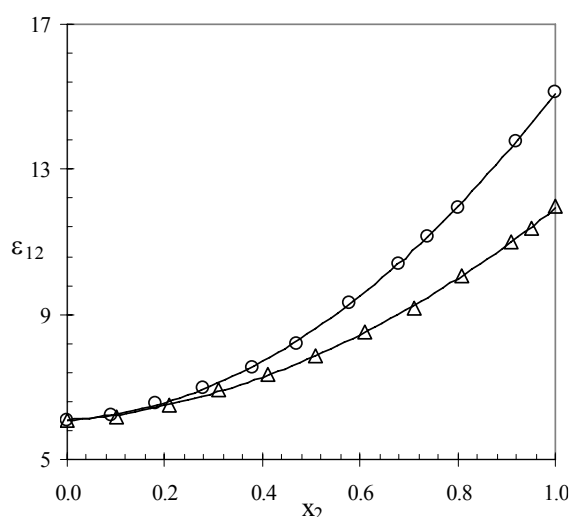
Figure 1. Plot of dielectric permittivity of binary mixture of (○) [EA (1) + IAA (2)] and (Δ) [EA (1) + TBA (2)] as a function of the alcohol mole fraction at $T = 298.2$ K.
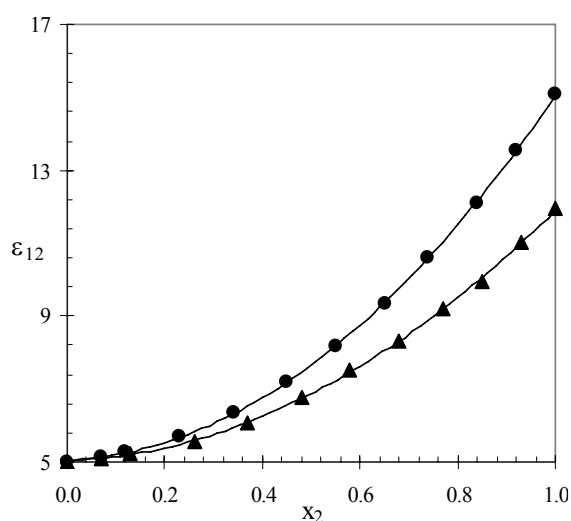

Figure 2. Plot of dielectric permittivity of binary mixture of (●) [BA (1) + IAA (2)] and (▲) [BA (1) + TBA (2)] as a function of the alcohol mole fraction at $T = 298.2$ K.

The interaction between the unlike molecules (heterogeneous interaction) may be obtained by the excess permittivity. The excess permittivity is defined as [17].

$$\varepsilon^E = \left(\varepsilon - n^2\right)_{12} - \left[\left(\varepsilon - n^2\right)_1 x_1 + \left(\varepsilon - n^2\right)_2 x_2\right] \quad (4)$$

where the subscript 12, 1 and 2 denote the mixture, solvent and solute, respectively. The excess permittivity provides qualitative information about the multimer formation in the mixture. The heterogeneous interaction between the unlike molecules of the mixture may also be obtained from the modified Bruggeman equation. The Bruggeman equation for a binary mixture is given by the expression

$$f_B = \left(\frac{\varepsilon - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right)\left(\frac{\varepsilon_1}{\varepsilon}\right)^{1/3} = \left(1 - \phi_2\right) \quad (5)$$

where ϕ_2 is volume fraction. For a non-linear variation of f_B with ϕ_2, the Bruggeman factor is modified as

$$f_B = 1 - \left[a - (a-1)\phi_2\right]\phi_2 \quad (6)$$

where "a" is the interaction parameter, which gives information about the heterogeneous interaction between the molecules. Value of "a" can be obtained by the least square fit method. Deviation of this value from zero is a measure of the strength of the intermolecular interaction between solute and solvent molecules in mixture. The ε^E values provide the following information:

(a) $\varepsilon^E = 0$ indicates that there is no interaction between unlike molecules.

(b) $\varepsilon^E < 0$ indicates that the two liquids interact in a manner in which the total

number of effective dipoles is reduced. The two liquid mixtures may form multimers, leading to the smaller dipoles.

(c) $\varepsilon^E > 0$ indicates that the unlike molecules interact in a manner that causes the effective dipoles to increase.

The ε^E values of the binary mixtures are negative over the entire range of solute mole fractions at $T = 298.2$ K. As it can be seen from Figs. 3 and 4, the ε^E values reach a minimum at $x_2 \cong 0.5$ mole fraction of IAA or TBA. This shows that the hetero interaction between the –OH group of the alcohol and $C = O$ group of the ester are at a maximum at about $x_2 = 0.5$.
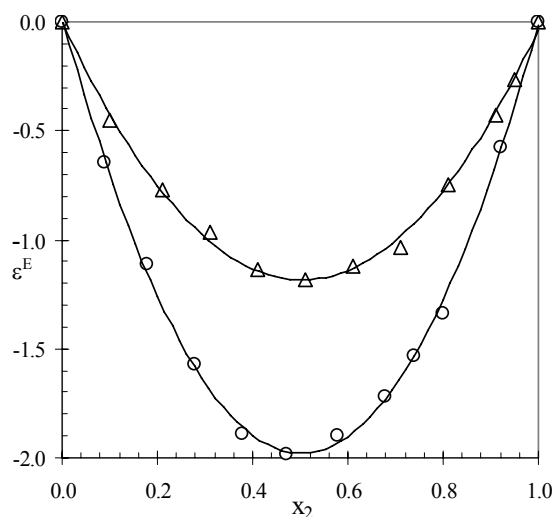

Figure 3. Plot of excess permittivity of binary mixture of (○) [EA (1) + IAA (2)] and (Δ) [EA (1) + TBA (2)] as a function of the alcohol mole fraction at $T = 298.2$ K.

The heterogeneous interaction between the unlike molecules of the mixture may also be obtained from the modified Bruggeman equation. Figs. 5 and 6 show the plot of Bruggeman factor f_B versus mole fraction of IAA or TBA (the mole fraction x_2 is used in

place of volume fraction). The plots for f_B also deviate from linearity, which shows the existence of intermolecular interaction between the ester and alcohol.
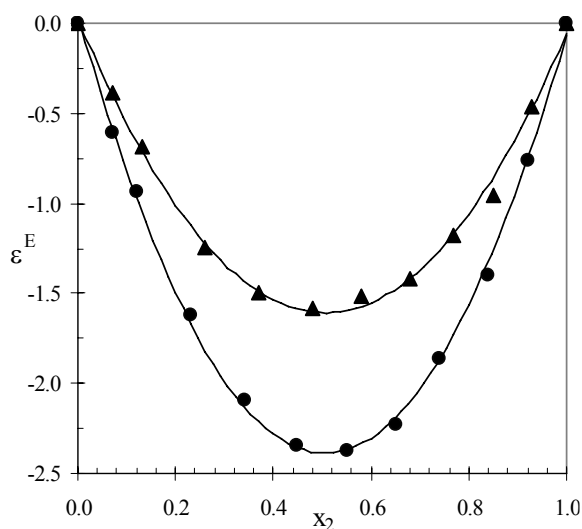

Figure 4. Plot of excess permittivity of binary mixture of (●) [BA (1) + IAA (2)] and (▲) [BA (1) + TBA (2)] as a function of the alcohol mole fraction at $T = 298.2$ K.
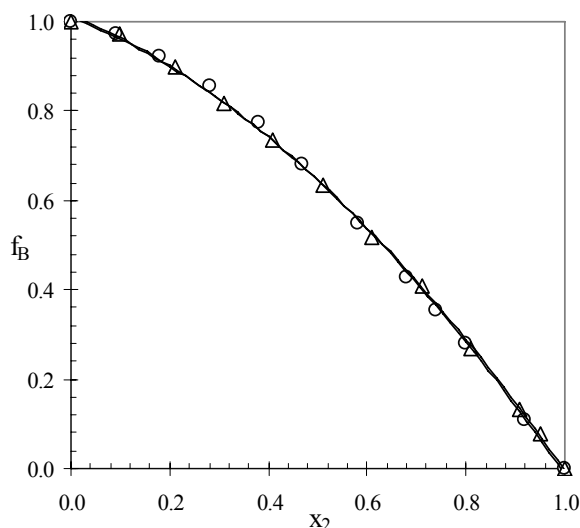

Figure 5. Plot of the Bruggeman factor for binary mixture of (○) [EA (1) + IAA (2)] and (Δ) [EA (1) + TBA (2)] as a function of the alcohol mole fraction at $T = 298.2$ K.
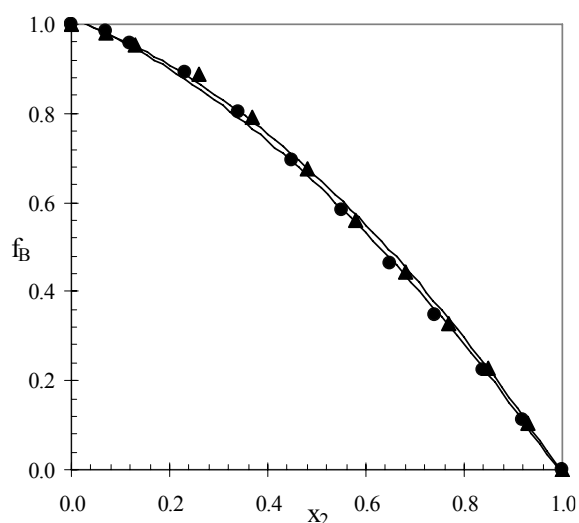
Figure 6. Plot of the Bruggeman factor for binary mixture of (●) [BA (1) + IAA (2)] and (▲) [BA (1) + TBA (2)] as a function of the alcohol mole fraction at T = 298.2 K.

4. Conclusions

The values of the dipole moment for the investigated liquids in cyclohexane solution were determined at $T = 298.2$ K. From the dielectric data, the heterogonous interactions for investigated mixtures were calculated. The effective Kirkwood correlation factor, the excess permittivity and the Bruggeman factor were reported for the binary systems of (EA + IAA), (EA + TBA), (BA + IAA), and (BA + TBA) at $T = 298.2$ K. Values of excess permittivity ε^E and Bruggeman factor f_B are found to depend on the concentration of the mixtures. For the polar-polar mixtures, the strength of the interaction between the unlike molecules reach a maximum when the composition is approximately 0.5 in ester or alcohol (i.e. $x_1 = x_2 = 0.5$).

References

[1] Smith, J. W., Electric Dipole Moments, Butterworths Publications Ltd, London, p. 369 (1955).

[2] Janini, G. M. and Katrib, A. H., "Determination of the dipole moment of polar compounds in non-polar solvents", J. Chem. Educ., 60, 1087-1088, (1983).

[3] Smyth, C. P., Molecular Interactions, Vol. II, John Wiley & Sons Ltd, New York, p. 128 (1980).

[4] Ghanadzadeh, A. and Beevers, M. S., "Effect of surface and molecular structure on the dielectric behavior in thick layers of cyanobiphenyl liquid crystals", J. Mol. Liq., 100(1), 47–57, (2002).

[5] Ghanadzadeh, A. and Beevers, M. S., "Dielectric investigations and molecular association in non-mesogenic and mesogenic solutions", J. Mol. Liq., 102(1-3), 365-377, (2003).

[6] Ghanadzadeh, A., Mamaghani, M. and Anbir, L., "Dipole moment and intermolecular association of some carbonyl compounds in non-polar solvents", J. Sol. Chem., 32(7), 625-636, (2003).

[7] Becker, U. and Stockhausen, M., "A dielectric relaxation study of some mixtures of mono and dihydric alcohols", J. Mol. Liq., 81(2), 89, (1999).

[8] Dharmalingam, K., Ramachandran, K., Sivagurunathan, P., Prabhakar Undre, B., Khirade, P. W. and Mehrotra, S. C., "Dielectric relaxation of binary mixtures of alcohols with acrylic esters", J. Appl. Polym. Sci., 107(4), 2312-2316, (2008).

[9] Sivagurunathan, P., Dharmalingam, K., Ramachandran, K., Prabhakar Undre, B., Khirade, P. W. and Mehrotra, S. C.,

"Dielectric studies on binary mixtures of ester with alcohol using time domain reflectometry", J. Mol. Liq., 133(1), 139-145, (2007).

[10] Dharmalingam, K., Ramachandran, K., Sivagurunathan, P., Prabhakar Undre, B., Khirade, P. W. and Mehrotra, S.C., "Dielectric study of Acrylate–Alcohol Mixtures Using time-domain reflectometry", Bull. Korean Chem. Soc., 27(12), 2040-2044, (2006).

[11] Guggenheim, E. A., "A proposed simplification in the procedure for computing electric dipole moments", Trans. Faraday Soc., 45, 714–719, (1949).

[12] McClellan, A. L., Tables of experimental dipole moments, W. H. Freeman & Co., San Francisco and London. (1963).

[13] Ghanadzadeh, A., Ghanadzadeh, H., Sariri R. and Ebrahimi, L., "Dielectric study of molecular association in the binary mixtures (2-ethyl-1-hexanol + alcohol) and (cyclohexane + alcohol) at 298.2 K", J. Chem. Thermodyn., 37, 357-362, (2005).

[14] Vijila, C., Ramalingam, A., Palanisamy, P. K. and Masilamani, V., "Role of dipole moment of solvents in formation and stabilization of the TICT states in Coumarin 445 under nitrogen laser excitation", Spectrochim. Acta Part A, 57, 491-497, (2001).

[15] Frohlich, H., Theory of Dielectrics, Oxford University Press, London, (1949).

[16] Pawar, V. P. and Mehrotra, S. C., "Dielectric Relaxation Study of Chloro Group with Associative Liquids. II. 1,2-Dichloroethane with Methanol, Ethanol, and 1-Propanol", J. Sol. Chem., 31(7), 577-588, (2002).

[17] Tabellout, M., Lancoleur, P., Emery, J. R., Hayward, D. and Pethrick, R. A., J. Chem. Soc., Faraday Trans. 86, 1453-1459 (1990).