



Dielectric and Thermodynamic Properties of 2, 3-Butanediol + 2-ethyl-1-hexanol Mixtures

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Abstract

Experimental results of dielectric investigations for binary mixtures of 2, 3-butanediol, 2, 3-BD, in 2-ethyl-1-hexanol, 2EH, were reported for various mole fractions and temperatures (298.2-308.2) K and they were used to calculate dielectric parameters such as Kirkwood correlation factor, excess permittivity and Bruggeman parameter. These parameters were used to carry out temperature dependent dielectric studies on the mixtures. The investigation showed a systematic change in dielectric parameters of the systems with the change in concentration and temperature.

Keywords: Dielectric Permittivity, Kirkwood Correlation Factor, Hetero Interaction.

Introduction

The dielectric permittivity is a macroscopic property which can play an important role in the solution properties. The value of dielectric constant is strongly related to the chemical structure of a molecule. The static dielectric provides useful information on the intermolecular interactions and molecular ordering in solutions. Therefore, by using dielectric studies on binary liquid mixtures over a range of mole fractions, it is possible to obtain valuable information regarding the nature and strength of interactions in liquid mixtures [1-3].

Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the -OH group. Diols are liquids whose molecules can strongly associate in solution. Owing to the presence of two hydroxy groups in the molecule,

butanediols are capable of forming intermolecular and intramolecular hydrogen bonds, which gives rise to a diversity of structures existing in the liquid [4-6]. Heterogeneous and homogeneous interactions in binary mixtures have been studied using dielectric measurements and reported by several investigators [7-10].

The strength of the intermolecular interactions depends on several factors including the molecular structure, temperature, solvent and other factors. In this work, we used experimental densities, refractive indices and dielectric constants of a binary polar liquid mixtures (2, 3-butanediol + 2-ethyl-1-hexanol) at various mole fractions at different temperatures to calculate some related properties and then to discuss intermolecular solute-solvent interactions between the components of the above binary system. The Kirkwood correlation factor, excess permittivity and Bruggeman parameter are determined.

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Theoretical Considerations

The modified form of the Kirkwood-Frohlich equation (Eq.1) [11–13] for mixtures of two polar liquids may be written as

$$\frac{4\pi N}{9kT} \left[\frac{\mu_1^2 \rho_1}{M_1} x_1 + \frac{\mu_2^2 \rho_2}{M_2} x_2 \right] g^{\text{eff}} = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} \quad (1)$$

where x_2 , ρ_2 , M_2 and μ_2 are the mole fraction, density, molecular weight and dipole moment of the solute (2, 3-BD), respectively; x_1 , ρ_1 , M_1 and μ_1 are the corresponding quantities of the pure solvent (2-EH); ε and n are the static permittivity and refractive index of the liquid mixtures, respectively; N is the Avogadro number and k is the Boltzmann constant. g^{eff} is the effective correlation factor for a binary mixture.

Corrective Kirkwood correlation factor, g_f , is given by:

$$\frac{4\pi N}{9kT} \left[\frac{\mu_1^2 \rho_1 g_1}{M_1} x_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} x_2 \right] g_f = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} \quad (2)$$

$$g^{\text{eff}} = g_1 \rightarrow \quad \text{if } x_2 = 0$$

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The value of g_f is unity for an ideal liquid and deviation from unity shows the existence of intermolecular interactions between compounds in the mixture.

The literature values [14] of dipole moments, μ , (dipole moments of the free molecules) of the studied compounds at different temperatures are listed in Table 1.

Interactions between the unlike molecules (heterogeneous interaction) may be obtained from the excess permittivity. The excess permittivity is defined as [15].

$$\varepsilon^E = (\varepsilon - n^2)_{12} - [(\varepsilon - n^2)_1 x_1 + (\varepsilon - n^2)_2 x_2] \quad (3)$$

where the subscripts 12, 1 and 2 denote the mixture, solvent and solute, respectively. The heterogeneous interactions between unlike molecules of the mixture may also be obtained from the modified Bruggeman equation [16]. The Bruggeman equation for a

binary mixture [17] is given by the expression.

$$f_B = \left(\frac{\varepsilon - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} \right) \left(\frac{\varepsilon_1}{\varepsilon} \right)^{\frac{1}{3}} = [1 - x_2] \quad (4)$$

where x_2 is mole fraction instead of volume fraction. For a non-linear variation of f_B with x_2 , the Bruggeman factor is modified to

$$f_B = 1 - [a - (a-1)x_2]x_2 \quad (5)$$

where “ a ” is an interaction parameter that gives information about heterogeneous interactions between molecules.

Experimental

Materials

All chemicals for the dielectric investigations were purchased in high purity (spectroscopic and HPLC grades) from Merck. Solutions of these materials were prepared by accurately weighing of appropriate amounts of the solute into 10 cm³ volumetric flasks.

Density and Refractive index measurements

The densities of the solutions were measured at different temperatures using DA-210 (Kyoto electronic) density meter, in combination with a remote measuring cell. The refractive indices of the solutions were determined at a wavelength of 589 nm using an Abbe Refractometer (Model CETI). The density meter and the refractometer were initially calibrated before being used to perform measurements. The temperature was controlled by circulation of water through a jacket surrounding the sample and was measured to an accuracy of ± 0.1 K.

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 10 kHz.

A cylindrical cell was constructed for measurements on small volumes of solutions (3 ml). A detailed description of the dielectric

cell is given Ref.18. The electrical capacitance of the empty cell was about 30 pF. The reproducibility of the air capacity after repeated heating and cooling was better than 0.02%. Due to high stability and reproducibility of the electrical capacity of cell, it was possible to obtain accurate dielectric results for solutions of the materials over a wide range of solute concentration and temperatures. The temperature of the cell could be controlled to be better than ± 0.1 K. The static permittivities of the standard liquids used to calibrate the dielectric cell.

Results and Discussion

The dielectric permittivity, ϵ_{12} , density, ρ_{12} , and refractive index, n_{12} of the 2, 3-butanediol in 2-ethyl-1-hexanol were measured at different temperatures and a range of solute mole fractions. The obtained data are summarized in Table 2 as a function of concentration.

The concentration dependence of the permittivity of solutions of 2, 3-butanediol in 2-ethyl-1 hexanol at several temperatures is shown in Fig. 1.

Values of the effective Kirkwood correlation factor of the mixture, g_{eff} , Corrective Kirkwood correlation factor, g_f , the Bruggeman factor, f_B , and the excess permittivity, ϵ^E , for 2, 3-butanediol in 2-ethyl-1-hexanol binary mixtures as a function of the mole fraction of 2, 3-butanediol, x_2 , at (298.2, 303.2 and 308.2) K are reported in Table 3.

The variations of g_f with mole fraction of 2, 3-butanediol is non-linear. This indicates a hetero interaction between the mixture components. The values of g_f are less than unity, indicating anti-parallel alignment of dipoles in the mixture. The non-linear behavior of g_f versus x_2 confirms the presence of a stronger hetero interaction (Fig. 2). This hetero interaction between the components may be due to dipole-dipole interactions and hydrogen bonding between the -OH group of 2, 3-butanediol and 2-ethyl-1-hexanol.

The ϵ^E values of the binary mixtures were calculated using Eq.3 Deviations of ϵ^E from zero are a measure of the strength of the intermolecular interactions between solute and solvent molecules in the mixture. The ϵ^E values provide the following information:

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

(b) $\epsilon^E < 0$ indicates that the two liquids interact in a manner that the total number of effective dipoles is reduced. The two liquid mixtures may form multimers, leading to the smaller dipoles.

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

The ϵ^E values of 2, 3-butanediol and 2-ethyl-1-hexanol mixtures are negative over the entire range of solute mole fractions at three temperatures. As it can be seen from Fig. 3, the ϵ^E values reach a minimum at $x_2 = 0.55$ mole fraction of 2, 3-butanediol at 298.2 K. This shows that the hetero interaction (between the -OH group of 2, 3-butanediol and 2-ethyl-1-hexanol) is at a maximum at $x_2 = 0.55$.

Interaction between the unlike molecules of the mixture may also be analyzed by Corrective Kirkwood correlation factor and modified Bruggeman equation. Fig. 4 shows the plot of the Bruggeman factor f_B versus mole fraction of 2, 3-butanediol (the mole fraction x_2 is used in place of the volume fraction). The plots for f_B also deviate from linearity, which shows the existence of intermolecular interactions between 2, 3-butanediol and 2-ethyl-1-hexanol. Deviation of the Bruggeman parameter 'a' from unity is a measure of the interaction between unlike molecules in the mixtures. The value of 'a' was determined by the least-squares method. For 2, 3-butanediol and 2-ethyl-1-hexanol, the interaction parameter 'a' was determined to be 1.327 at 298.2 K.

Conclusions

At three different temperatures from 298.2 to 318.2 K, values of the dielectric permittivity, effective Kirkwood correlation factor, the excess permittivity and the Bruggeman factor for 2, 3-butanediol were determined in 2-ethyl-1-hexanol solutions at various concentrations. Values of the static dielectric constant increase with rising concentration of 2, 3-butanediol in 2-ethyl-1-hexanol. Also, the static dielectric constant decrease with increasing temperature. Values of the excess permittivity ϵ^E and Bruggeman

factor f_B are found to depend on the concentration of the mixtures and in all of concentrations deviate from linearity. The ε^E values reach a minimum at $x_2 = 0.55$ mole

fraction of 2, 3-butanediol at 298.2 K. This shows that the hetero interaction at a maximum at this mole fraction.

Table 1. The molecular dipole moment of the investigated compounds at different temperatures.

Compound	μ (D)		
	298.2 K	303.2 K	308.2 K
2,3-butanediol	1.97	1.91	1.86
2-ethyl-1-hexanol	1.90	1.81	1.72

Table 2. Permittivity, ε_{12} , refractive index, n_{12} and density, ρ_{12} ($\text{g} \cdot \text{cm}^{-3}$), of the 2, 3- butanediol + 2-ethyl-1-hexanol binary liquid mixtures at three temperatures.

x_2	298.2 K			303.2 K			308.2 K		
	ε_{12}	n_{12}	ρ_{12}	ε_{12}	n_{12}	ρ_{12}	ε_{12}	n_{12}	ρ_{12}
0.000	7.611	1.4293	0.83062	7.135	1.4274	0.82690	6.687	1.4257	0.82310
0.100	8.083	1.4294	0.83779	7.669	1.4276	0.83511	7.246	1.4258	0.83146
0.250	9.278	1.4297	0.85438	9.048	1.428	0.85077	8.386	1.4260	0.84699
0.401	10.980	1.4301	0.87423	10.658	1.4284	0.86856	10.164	1.4264	0.86478
0.450	11.670	1.4304	0.88245	11.348	1.4286	0.87698	10.823	1.4267	0.87125
0.499	12.360	1.4308	0.89064	11.946	1.4289	0.88454	11.412	1.4270	0.88127
0.550	12.958	1.4311	0.89794	12.590	1.4292	0.89337	12.079	1.4272	0.88950
0.600	13.694	1.4314	0.90660	13.372	1.4296	0.90277	12.808	1.4275	0.89813
0.650	14.659	1.4318	0.91649	14.199	1.4299	0.91227	13.629	1.4278	0.90750
0.750	16.407	1.4324	0.93450	15.947	1.4306	0.92969	15.361	1.4286	0.92711
0.898	19.166	1.4337	0.96652	18.707	1.4319	0.96281	18.097	1.4299	0.95911
1.000	21.282	1.4348	0.99431	20.776	1.433	0.99040	20.244	1.4311	0.98615

Table 3. Effective Kirkwood correlation factor, g_{eff} , the Bruggeman factor, f_B , and the excess permittivity, ϵ^E , of the polar 2, 3- butanediol + 2-ethyl-1-hexanol binary liquid mixtures at three temperatures.

x_2	298.2 K				303.2 K				308.2 K			
	g_{eff}	g_f	f_B	ϵ^E	g_{eff}	g_f	f_B	ϵ^E	g_{eff}	g_f	f_B	ϵ^E
0.000	1.644	1.000	1.000	0.00	1.711	1.000	1.000	0.00	1.785	1.000	1.000	0.00
0.100	1.630	0.885	0.946	-0.89	1.714	0.887	0.938	-0.83	1.795	0.884	0.933	-0.80
0.250	1.720	0.824	0.822	-1.75	1.858	0.843	0.794	-1.50	1.887	0.812	0.811	-1.69
0.401	1.888	0.827	0.667	-2.11	2.019	0.834	0.649	-1.95	2.108	0.826	0.647	-1.96
0.450	1.961	0.838	0.610	-2.09	2.099	0.846	0.592	-1.92	2.188	0.836	0.592	-1.96
0.499	2.030	0.848	0.555	-2.07	2.154	0.848	0.545	-1.99	2.246	0.839	0.545	-2.04
0.550	2.075	0.848	0.510	-2.17	2.212	0.852	0.497	-2.05	2.314	0.846	0.495	-2.06
0.600	2.143	0.859	0.456	-2.12	2.294	0.867	0.440	-1.95	2.391	0.857	0.442	-2.01
0.650	2.245	0.884	0.389	-1.84	2.379	0.883	0.383	-1.80	2.482	0.874	0.385	-1.87
0.750	2.403	0.916	0.276	-1.46	2.551	0.916	0.271	-1.42	2.663	0.909	0.273	-1.49
0.898	2.632	0.963	0.114	-0.72	2.798	0.965	0.110	-0.68	2.923	0.959	0.114	-0.76
1.000	2.799	1.000	0.000	0.00	2.971	1.000	0.000	0.00	3.120	1.000	0.000	0.00

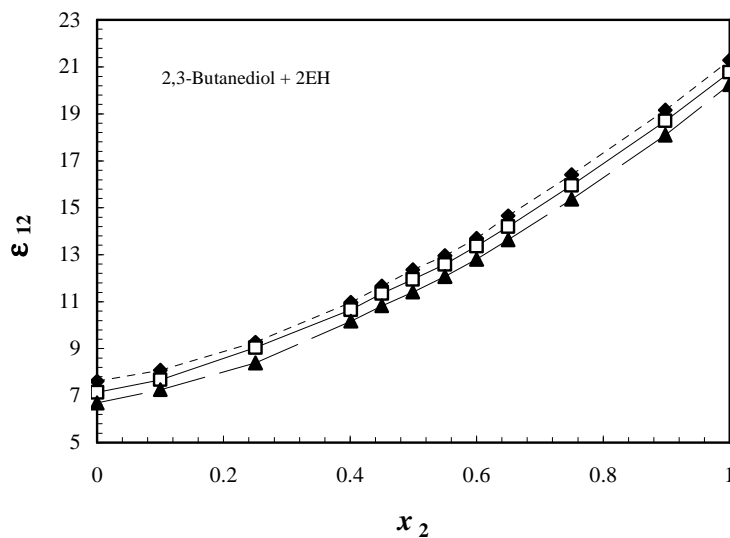


Figure 1. Dielectric permittivity of 2, 3-butanediol + 2-ethyl-1-hexanol solutions as a function of the solute mole fraction at three temperatures. 298.2 K (◆), 303.2 K (□), 308.2 K (▲).

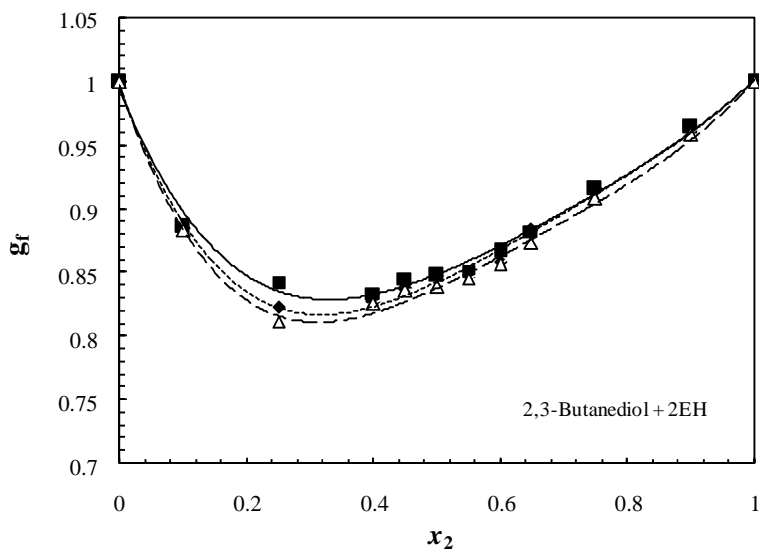


Figure 2. Corrective Kirkwood correlation factor, g_f , at three temperatures. 298.2 K (◆), 303.2 K (■), 308.2 K (Δ).

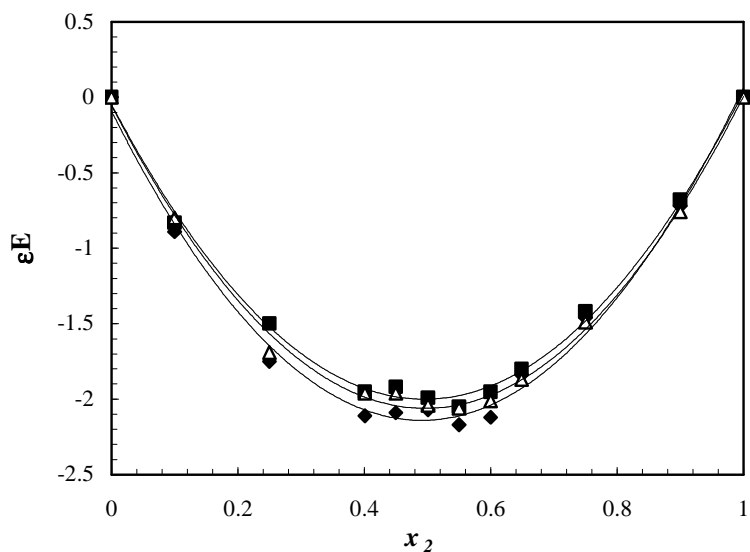


Figure 3. Excess permittivity of 2, 3-butanediol + 2-ethyl-1-hexanol mixtures at three temperatures. 298.2 K (◆), 303.2 K (■), 308.2 K (Δ).

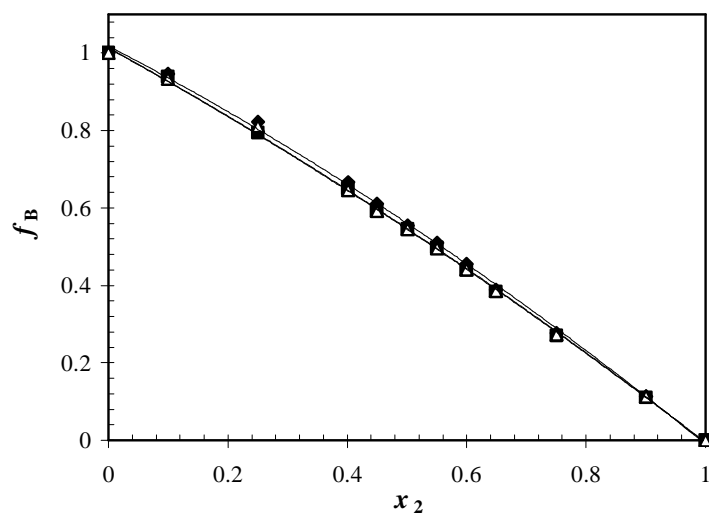


Figure 4. Bruggeman factor versus mole fraction of 2, 3-butanediol + 2-ethyl-1-hexanol mixtures at three temperatures. 298.2 K (◆), 303.2 K (■), 308.2 K (Δ).

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