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Relative permittivity, density, viscosity, refractive index and ultrasonic velocity of binary mixture of ethylene glycol monophenyl ether and 1-hexanol at different temperatures

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A B S T R A C T

Relative permittivity (ε), refractive index (n_D), density (ρ), viscosity (η), and ultrasonic velocity (u) of liquid mixtures of ethylene glycol monophenyl ether and 1-hexanol as a function of mole fraction of 1-hexanol have been measured at three different temperatures (303.15, 313.15 and 323.15 K). Various acoustical parameters viz., adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), internal pressure (π_i), and free volume (V_f) were evaluated from the experimental data. Excess dielectric, excess physico-chemical and excess acoustic parameters were calculated and fitted to the Redlich–Kister relation. The excess viscosity (η^E), excess relative permittivity (ε^E) and excess adiabatic compressibility (β^E) showed negative deviation from ideality over the entire range of concentration of 1-hexanol. Various excess parameters were qualitatively analyzed to gain some insight to the intermolecular interactions in the liquid mixture.

1. Introduction

Binary polar liquid mixtures having alcohol as one of the constituents are of considerable interest among the scientists. This is due to the fact that in such a binary liquid systems different types of molecular interactions take place. Dielectric, volumetric and ultrasonic techniques [1–4] have been tried by many researchers to gain information about inter/intra molecular interactions taking place in the variety of liquid mixtures.

One of the constituent of the binary liquid mixture under study is ethylene glycol mono-phenyl ether (EGMPE), a member of the phenyl glycol family. Phenyl glycols are self-associative and contain phenyl ring in its molecular structure. The other constituent of the binary mixture system is 1-hexanol (1-HeOH) which is also a self-associative but does not contain phenyl ring. So, it is thought that the binary liquid mixture of EGMPE and 1-HeOH will form an interesting and complex problem of liquid state physics and will provide a good scope to qualitatively analyze the physico-chemical and dielectric data to gain some insight to the intermolecular interactions in the liquid mixture. Literature survey confirms that dielectric and physico-chemical properties of EGMPE and 1-HeOH in mixed liquid state have not been studied so far.

Relative permittivity (ε), viscosity (η), density (ρ), refractive index (n_D) and ultrasonic velocity (u) for the binary mixtures of EGMPE and 1-HeOH over complete mixing range at three different temperatures (303.15, 313.15 and 323.15 K) are measured. Using measured values, excess values of the relative permittivity (ε^E), permittivity at optical frequency (ε^E_∞), viscosity (η^E), molar volume (V^E), Gibb's free energy of activation of viscous flow (ΔG^{*E}) as well as some acoustical parameters have been evaluated and fitted to the Redlich–Kister type polynomial equation [5].

2. Experimental

EGMPE (extra pure), and 1-HeOH (AR grade) were supplied by SD Fine Chem. Limited (India) and were not purified further. EGMPE was added to 1-HeOH by volume to obtain nine solutions of varying concentrations. The volume fraction was converted into mole fraction [3]. The mole fraction is accurate to 0.1%.

The values of relative permittivity, permittivity at optical frequency, density and viscosity of EGMPE, 1-HeOH and their mixtures were determined by the method explained in our earlier work [3]. The speeds of sound waves were obtained by using digital ultrasonic pulse echo velocity meter [Model no. VCT-70A, Vi Microsystems Pvt. Ltd., Chennai (India)]. Measurement accuracy of this instrument is $\pm 2\ m\ s^{-1}$. Temperature of the sample was maintained at the desired constant value using electronically operated digital constant temperature bath. [Supplied by Vi Microsystems Pvt. Ltd., Chennai (India)].

3. Data analysis

Excess values of relative permittivity (ε^E), and permittivity at optical frequency (ε^E_∞) were evaluated by the equations reported by Moumouzias et al. [4] and Sengwa and Sankhla [6] respectively.

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Table 1
Comparison of relative permittivity, permittivity at optical frequency, density and viscosity of 1-HeOH with literature data at $T = 303.15$ K.

Property	Expt.	Literature
Relative permittivity (ε)	12.80	12.11 [10]
		12.51[a] [17]
		13.03[a] [18]
Permittivity at optical freq. (ε_∞)	1.9937	1.9965 [13]
Density (ρ)/kg·m^{-3}	812.4	811.5 [11]
		812.7 [14]
		812.0 [15]
Viscosity (η)/mPa·s	3.7009	3.861 [11]
		3.769 [14]
		3.840 [16]
		3.765 [14]
Ultrasonic velocity (u)/m s^{-1}	1284.82	1287.9 [12]
		1304[a] [19]

[a] At 298.15 K.

Table 2
Relative permittivity and permittivity at optical frequency of mixtures of EGMPE + 1-HeOH as function of mole fraction (x_1) of 1-HeOH at $T = 303.15$, 313.15 and 323.15 K.

x_1	Relative permittivity (ε)			Permittivity at optical frequency (ε_∞)		
	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0.000	10.90	10.57	10.17	2.2596	2.2500	2.2404
0.100	11.03	10.63	10.20	2.2456	2.2394	2.2324
0.201	11.18	10.73	10.27	2.2325	2.2261	2.2160
0.301	11.35	10.87	10.37	2.2126	2.2043	2.1992
0.401	11.54	11.03	10.51	2.1930	2.1880	2.1810
0.501	11.73	11.21	10.66	2.1702	2.1606	2.1506
0.601	11.94	11.37	10.83	2.1370	2.1290	2.1210
0.701	12.15	11.57	11.01	2.1051	2.0999	2.0929
0.801	12.36	11.76	11.20	2.0651	2.0572	2.0502
0.900	12.58	11.96	11.40	2.0351	2.0275	2.0205
1.000	12.80	12.15	11.59	1.9937	1.9871	1.9771

Kirkwood correlation factor (g_k) as well as different acoustical parameters viz. adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), internal pressure (π_i), free volume (V_f) and their excess values have been determined from the experimental data using the standard equations [7–9].

Various parameters like molar volume, excess molar volume, excess viscosity, and excess Gibb's free energy of activation of viscous flow (ΔG^{*E}) were calculated from the measured data using the relation reported by Moumouzias et al. [4].

Variations of excess properties with concentration of 1-HeOH were expressed by Redlich–Kister [5] polynomial equation. Least square fitting procedure was carried out to determine the adjustable parameters and standard deviation (σ) [3].

4. Results and discussion

Relative permittivity (ε), permittivity at optical frequency (ε_∞), density (ρ), viscosity (η) and ultrasonic speed (u) at 303.15 K for pure 1-HeOH are compared with literature values in Table 1. They are in good agreement. Measured value of density of EGMPE is 1093.3 kg·m^{-3} at 303 K, which also is in good agreement with the reported value of 1103.41 kg·m^{-3} at 298.15 K [20]. The experimentally determined values of ε and ε_∞ of the binary mixtures as a function of mole fraction of 1-HeOH are presented in Table 2. Measured values of density, viscosity and ultrasonic velocity of the mixtures are represented in Table 3. The evaluated values of various acoustical parameters are reported in Table 4.

EGMPE and 1-HeOH have nearly equal values of dipole moment (1.5 D and 1.68 D respectively), but the relative permittivity of EGMPE (10.90 at 303.15 K) is smaller than the relative permittivity of 1-HeOH (12.80 at 303.15 K). Small difference in relative permittivity values of these two molecules is in agreement with the small difference in the molecular size (molar volume of EGMPE $\approx 1.264 \times 10^{-4}$ m^3 mol^{-1} and of 1-HeOH $\approx 1.2576 \times 10^{-4}$ m^3 mol^{-1}). Fig. 1 shows the plots of relative permittivity (ε) against mole fraction (x_1) of 1-HeOH. From the figure it can be seen that the effective permittivity of the mixture increases non-linearly with increase in concentration of 1-HeOH. Effective permittivity values of the binary mixture are smaller than that of chemically non-interacting binary liquid mixtures, this suggests that in the mixed state of EGMPE and 1-HeOH complex associates of larger size are formed. The plot shows two distinct regions in the range $0 < x_1 < 0.6$ and $0.6 < x_1 < 1$ at all the three temperatures. The boundary values of x_1 of these regions are highlighted by vertical dotted line in Fig. 1. The ε values vary linearly with x_1 in the $0.6 < x_1 < 1$ (1-HeOH rich region) but in the $0 < x_1 < 0.6$ (EGMPE rich region) non-linear behavior is observed. The linear region indicates the uniform co-operative dynamics of the EGMPE–1-HeOH structures and also suggests that the state of EGMPE and 1-HeOH molecules does not change despite the large mixing range. Nonlinear mixing range $0 < x_1 < 0.6$ confirms that the co-operative dynamics of EGMPE and 1-HeOH molecules vary within this mixing range and the structures of EGMPE and 1-HeOH are different from their pure liquid state. In the EGMPE rich region the maximum non-linearity range is up to $x_1 \approx 0.6$. This corresponds to 1:1.5 complex ratio of EGMPE–1-HeOH mixture. Two possible hydrogen bonded stable structures corresponding to 1:1.5 complex ratio of EGMPE–1-HeOH mixtures are shown in Fig. 2.

Excess relative permittivity ε^E and ε^E_∞ are plotted as a function of 1-HeOH concentration in Figs. 3 and 4 respectively. ε^E values are found negative over the entire concentration range of 1-HeOH. This clearly indicates that the interaction among the molecular species of the mixture is taking place in such a way that the effective dipole moment decreases in the mixed state and structures become more disordered. This is due to breaking of homogenous hydrogen bonded

Table 3
Density, viscosity and ultrasonic velocity of mixtures of EGMPE + 1-HeOH as function of mole fraction (x_1) of 1-HeOH at $T = 303.15$, 313.15 and 323.15 K.

x_1	Density (ρ) kg·m^{-3}			Viscosity (η) mPa·s			Ultrasonic velocity (u) m s^{-1}		
	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K	303.15 K	313.15 K	323.15 K
0.000	1093.3	1083.0	1073.9	12.8581	9.2351	5.9274	1540.72	1501.28	1466.24
0.100	1071.2	1062.9	1049.0	10.9453	7.9065	5.2855	1511.55	1467.038	1431.48
0.201	1041.4	1035.7	1024.9	9.2438	7.0052	4.8213	1479.36	1441.83	1400.19
0.301	1011.9	1010.1	999.5	8.0989	6.2388	4.3890	1449.73	1414.91	1373.41
0.401	987.3	980.9	974.9	7.2505	5.5479	3.8661	1418.75	1387.19	1348.74
0.501	964.5	954.5	946.5	6.5082	4.7643	3.5179	1385.64	1359.22	1322.86
0.601	932.7	922.5	913.8	5.6959	4.1506	3.1281	1360.74	1336.11	1300.32
0.701	903.4	890.7	886.4	4.9808	3.6046	2.7162	1338.17	1312.38	1276.48
0.801	874.0	866.2	861.1	4.3350	3.2216	2.3580	1315.59	1289.17	1248.67
0.900	849.5	843.0	831.3	3.9784	2.9810	2.1479	1293.23	1264.29	1230.69
1.000	812.4	804.4	796.6	3.7009	2.8602	2.0718	1284.82	1256.12	1218.47