



ULTRASONIC INVESTIGATIONS IN A LIQUID MIXTURE OF ETHYLENEGLYCOL WITH n-BUTANOL

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ABSTRACT

Properties of liquid-liquid mixtures are thermodynamically very important as part of studies of thermodynamic, acoustic and transport aspects. The intermolecular forces of liquids in a mixture show a considerable effect on the physical and chemical properties. The ultrasonic studies in liquid mixtures can be helpful to study the intermolecular interaction between molecules. Here in this paper, I have taken densities, velocities and viscosities of the binary mixture (ethylene glycol with n-butanol) which have been measured for the entire range of composition at different (various) temperatures ranging from 303.15K to 318.15K and its data has been used to calculate various thermodynamic and acoustic parameters like molar volume (V_m), adiabatic compressibility (β_{ad}), inter molecular free length (L_f), acoustic impedance (Z), internal pressure (α), Enthalpy (H). The excess parameters such as excess molar volume (V_m^E), excess inter molecular free length (L_f^E), deviations in adiabatic compressibility (β_{ad}), deviations in viscosity ($\Delta\eta$) and several other parameters have also been calculated. These results have been analyzed and interpreted in terms of molecular dipole-dipole interactions. The intermolecular interactions among the components of the binary mixtures lead to the possible dipole-dipole interactions between unlike molecules. Excess molar volumes, deviation in adiabatic compressibilities and excess free length are negative in the whole composition range for all the systems at all the temperatures while viscosity deviations are positive indicating strong molecular interactions between the components. The results are discussed in the light of intermolecular interactions between the dissimilar molecules.

Keywords: Molecular interactions, hydrogen bonding, velocities, dipole-dipole interactions



1. Introduction

The intermolecular forces of liquids in a mixture show a considerable effect on the physical and chemical properties. The ultrasonic studies in liquid mixtures can be helpful in assessing degree of interaction between molecules. Ethylene glycol is an excellent aprotic solvent, completely soluble in water. The highly polar self associated Ethylene glycol (EG) is a versatile organic liquid having a special solvent power to promote a chemical reaction when used as a reaction medium. Aprotic solvent such as ethylene glycol was chosen because of its wide use in applied chemistry and participation in biological processes. Butanol (C_4H_9OH) also known as butyl alcohol is a well-known organic compound and has wide applications in chemical industry as it is used as a solvent for paint, varnish, in preserving biological specimens.

2. Experimental methods

To understand the molecular interactions in this binary system the author has taken liquid mixtures EG as a solute and Butanol as a solvent at various mole fractions and at different temperatures. Ultrasonic velocity measurements of the liquid mixtures were made using an Mittel's ultrasonic interferometer with 2 MHz cell with an accuracy of $\pm 0.02\%$... The density of all liquid mixtures were measured by employing a specific gravity bottle at 303.15K, 308.15K, 313.15K and 318.15K with an uncertainty of 0.5ml and the viscosities of liquids and liquid mixtures are measured with Ostwald's glass capillary Viscometer with an accuracy is ± 0.001 cp. All the measurements were made at all the temperatures with the help of thermostat with an accuracy of ± 0.01 K.

3. Evaluation of Thermodynamic Properties:

The binary mixtures under investigation involve butanol with ethylene glycol. In each system densities (ρ), velocities (U) and viscosities (η) of the binary mixture had been measured for the entire range of composition at four different temperatures 303.15K, 308.15K, 313.15K and 318.15K. The molar volume (V_m), adiabatic compressibility (β_{ad}), and viscosity ($\Delta\eta$), intermolecular free length (L_f) and several other parameters Rao's constant (R) and Wada's constant (W) were computed and recorded and are reported in Table 1. The excess parameters such as excess molar volume (V_m^E), excess intermolecular free length (L_f^E) and deviations in adiabatic compressibility ($\Delta\beta_{ad}$), in the entire composition range and are reported in Table 2.

**Table 1: Measured values of thermodynamic parameters at temperature 303.15K**

Mole fraction X	(U) m/s	$\rho \times 10^{-3}$ kg/m ³	η Cp	V_m cm ³ mol ⁻¹	$\beta_{ad} 10^{12}$ m ² N ⁻²	L_f 10 ⁻¹⁰ m	R	W
0.0000	1322.00	0.7865	1.8528	91.0571	83.0760	0.5749	4718	2659
0.1180	1364.25	0.7886	2.2342	92.0446	79.6164	0.5588	4669	2527
0.2273	1369.93	0.7960	2.3117	86.1972	75.7878	0.5375	4618	2514
0.3440	1372.85	0.8450	2.3332	82.4615	72.8359	0.5287	4568	2491
0.4582	1389.38	0.8639	2.3406	81.8121	69.9265	0.4834	4542	2465
0.5692	1395.76	0.8817	2.4557	80.3169	64.7358	0.4825	4529	2451
0.6380	1490.92	0.8873	2.4757	78.0838	61.9700	0.4743	4405	2425
0.7629	1493.20	0.9314	2.3192	75.0180	58.9159	0.4729	4352	2381
0.8339	1487.69	0.9343	1.8973	74.0765	55.5800	0.4684	4298	2355
0.9343	1468.62	0.9562	1.7439	72.2417	56.4196	0.4720	4235	2346
1.2000	1419.80	0.9668	1.5000	71.5360	61.0016	0.4887	4149	2295

Table 2: Excess Parameters (at 303.15K):1

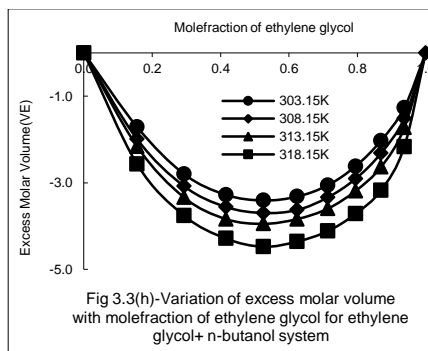
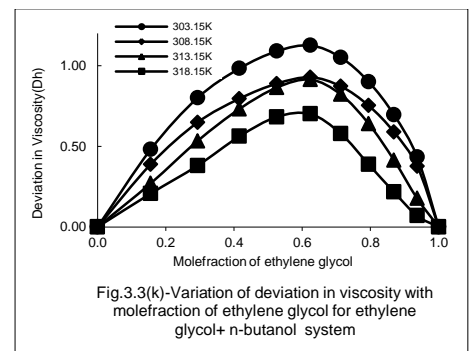
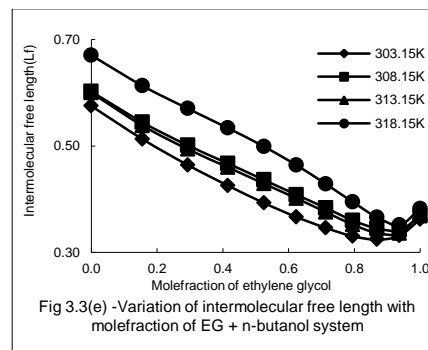
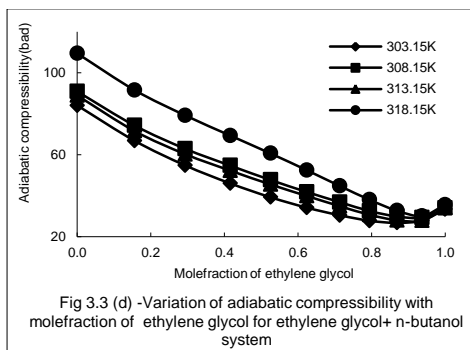
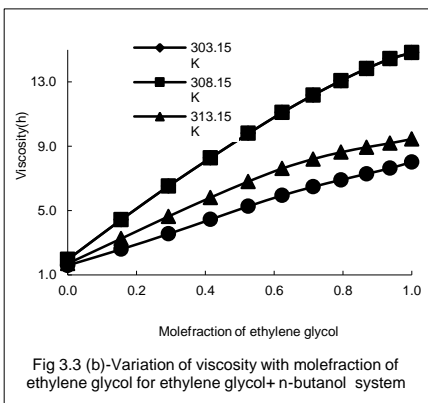
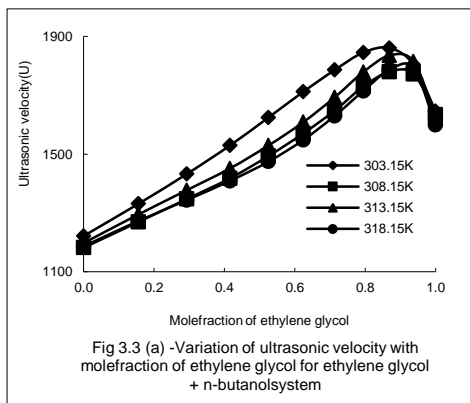
Mole fraction X	V_m^E Cm ³ mol ⁻¹	$\Delta\beta_{ad} 10^{10}$ m ² N ⁻¹	$\Delta\eta$ Cp	L_f^E 10 ⁻¹⁰ m
0.0000	0.0000	0.0000	0.0000	0.0000
0.1250	-0.4370	-4.7900	0.3450	-0.0258
0.2363	-0.8100	-7.7400	0.4340	-0.0372
0.3440	-1.0700	-10.3000	0.6950	-0.0464
0.4482	-1.3300	-11.8000	0.7200	-0.0484
0.5492	-1.4200	-13.3600	0.8140	-0.0463
0.6470	-1.4600	-12.8700	0.7850	-0.0458
0.7419	-1.1330	-10.5400	0.6730	-0.0438
0.8339	-0.8800	-8.6600	0.5300	-0.0350
0.9233	-0.4870	-5.6700	0.3950	-0.0235
1.0000	0.0000	0.0000	0.0000	0.0000

4. Results and discussions:

The results are interpreted in terms of intermolecular interactions between the components of the mixtures. The velocity and viscosity values increase with the increase in concentration of ethylene glycol. The velocity decreases with increase in temperature at any particular concentration. It is evident that molar volume, Rao's and Wada's constants decrease with increase in concentration of ethylene glycol. Both adiabatic compressibility and inter molecular free length decrease with increase in concentration of ethylene glycol and increase with increase in temperature at any particular concentration. These results are favoring inter molecular structure. The results of the variations of excess properties with the mole fraction of ethylene glycol indicate that the excess parameters such as deviation in excess molar volume, adiabatic compressibility and excess intermolecular free length are all negative in the entire composition range. But the deviation in viscosity values is positive in the entire composition range of ethylene glycol.



These variation of various parameters are plotted against the mole fraction of ethylene glycol at various temperatures and are shown below



There is a good agreement between the experimental and theoretical values of the excess parameters.



5. Conclusion:

It is concluded that increase and decrease in parameter values with the mole fraction indicates significant interactions between the mixtures. The experimental results show that the negative contributions, in general, decrease with an increase in chain length of acetates. The similar results are reported by Chauhan et al. The main property responsible for volumetric behavior is the breaking of the dipolar association. In fact, the results show that the negative contributions from the breaking of dipolar association in chemical interactions that usually predominate over positive contributions. The positive sign of $\Delta\eta$ values indicates that strong forces are predominated. The observed trend in V^E , $\Delta\beta_{ad}$ and L_f^E values suggests that stronger interactions are found in all the systems, which may also be due to structure breaking effects (steric hindrance)

The main inferences drawn are:

- The increase in mole fraction of ethylene glycol increases the net strong interactions. As the medium becomes more and more compact, the velocity continuously increases and it is observed in all the systems.
- The ultrasonic velocity values decreases with increase of temperature due to breaking of hetero and homo molecular clusters at high temperatures.
- An increase in viscosity⁴ with increase in mole fraction of ethylene glycol suggests that existing molecular interactions are increasing in magnitude.
- The minimum interaction between unlike molecules suggests that there's decrease in adiabatic compressibility and intermolecular free length with increase in mole fraction of ethylene glycol and increase with the increase in temperature.
- The negative V^E values for all the systems studied may be attributed to dipole induced-dipole interactions between the component liquids of the mixtures resulting in the formation of electron donor-acceptor reactions⁵⁻⁷.
- Weak interaction between unlike molecules gives positive excess values whereas those of dipole-dipole, dipole-induced dipole, charge transfer, and hydrogen bonding between unlike molecules gives negative excess parameters.



- The specific interaction between unlike molecules such as hydrogen bond formation and charge transfer complexes may cause for increase in viscosity⁴ in mixtures than in pure components

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