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Advances in Applied Science Research, 2016, 7(2):183-187

Advances in Applied Science Research
Pelagia Research Library
ISSN: 0976-8610
CODEN (USA): AASRFC

Acoustical studies of binary (butanol+benzene), ternary (butanol+methyl benzoate+benzene) mixtures at 303 K

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ABSTRACT

The ultrasonic measurements like ultrasonic velocity, density, and viscosity of the ternary system butanol with methyl benzoate in benzene systems have been measured the whole range of mole fraction at 303K. From the measured values evaluate ultrasonic parameter such as adiabatic compressibility (β), free length (L_f), free volume (V_f) using standard relations also predict the excess parameter. The ultrasonic measurements, acoustical parameter and related excess parameter give the results of the molecular interaction between liquids. These values indicate the specific interaction of the liquid mixtures. The presence of strong dipole- dipole- type interaction was confirmed in theses system.

INTRODUCTION

The ultrasonic studies are important to understand the nature molecular interactions exist in liquid mixtures [1-3]. The molecular interactions of the liquids and liquid mixtures has been investigated through the ultrasonic measurements and related acoustical parameter. Ultrasonic velocity is related to inter molecular forces between the atoms or the molecules [3-5]. The study of molecular interaction of butanol with methyl benzoate in benzene mixtures has been important due to butanol as one of the components. A methyl benzoate highly polar liquid seems to be better among the industrial and chemical process [5-6]. The association of methyl benzoate investigated using various methods [6-10]. Our research group investigated nature of interactions are identified using various techniques including refractive index, FT-IR, dielectric measurements [11-16]. Benzene is a non-polar being aromatic and methyl benzoate also aromatic with carbonyl group act as electron donors. Though the carbonyl group is comparatively a strong proton - acceptor, the oxygen atoms in the carbonyl group can also play the important role for proton acceptor; hence butanol with its hydroxyl groups can interact with carbonyl components. The present work reports the results of ultrasonic measurements and related ultrasonic parameters at 303K in the ternary system of butanol + methyl benzoate +benzene.

MATERIALS AND METHODS

AR grade butanol , methyl benzoate and benzene liquids were used. It is purified by standard procedure with purity >99%. The ultrasonic velocities of the liquid mixtures were measured using a single crystal ultrasonic interferometer (Mittal type, Model F-80) operated at 2 MHz The temperature of the cell was controlled by circulating water through the liquid cell from thermostatically controlled constant temperature water bath. The densities of pure liquids and liquid mixtures were measured by using a 5 ml specific gravity bottle with an accuracy of ± 0.5%. The viscosities were measured using Ostwald's viscometer with an accuracy ± 0.5%. The measured valued of ultrasonic velocity, density and viscosity and related ultrasonic parameter at 303 K for the pure liquids are shown in table 1.

Table 1 The experimental values of pure liquids at 303 K

Chemical Name	Ultrasonic velocity (u) m/s	Density (ρ) Kg/m^3	Viscosity (η) Nsm^{-2}
Butanol	1233	796	0.563
Methyl benzoate	1404	1030	0.175
Benzene	1276	870	2.07

THEORY AND CALCULATIONS

From the experimental values, the acoustical parameter such as adiabatic compressibility (β), free length (L_f), and free volume (V_f), and their excess parameter have been evaluated using the following standard relations. The relations discussed given below

Adiabatic compressibility

Adiabatic compressibility has been calculated from the speed of sound (u) and density (ρ) of the medium using the relation as

$$\beta = \frac{1}{u^2\rho} \quad (1)$$

Intermolecular free length

Intermolecular free length (L_f) has been evaluated using the standard relation as:

$$L_f = K_T\beta^{1/2} \quad (2)$$

Where K_T is a temperature dependent constant known as Jacobson's constant.

Free volume (V^f)

The relation for free volume in terms of ultrasonic velocity (u) and viscosity (ρ) of the liquid as:

$$V_f = \left(\frac{M_{eff}U}{\eta K}\right)^{3/2} \quad (3)$$

Here M_{eff} is the effective molecular weight $M_{eff} = \sum m_i x_i$ which m_i and x_i are the molecular weight and mole fraction of the individual components respectively. K is a temperature independent constant which is equal to $4.28x10^9$ for all liquids.

Excess parameter

The excess parameter like ultrasonic velocity (u^E), adiabatic compressibility (β^E), intermolecular free length (L_f^E) and free volume (V^E) evaluated using relations as

$$A^E = A_{Exp} - A_{ideal} \quad (4)$$

$$A_{Ideal} = A_1X_1 + A_2X_2 \quad (5)$$

RESULTS AND DISCUSSION

Ultrasonic velocity (u), density (ρ) and viscosity (η) for the binary (Butanol with benzene) and ternary (Butanol with methyl benzoate in benzene) mixtures at 301 K are shown in table 2 to 3 also present ultrasonic parameter like adiabatic compressibility (β), intermolecular free length (L_f) and free volume (V_f) and related excess parameter (ultrasonic velocity (u^E), adiabatic compressibility (β^E), intermolecular free length (L_f^E) and free volume (V^E) . The variations of ultrasonic velocity, adiabatic compressibility, inter molecular free length and free volume with mole fractions of butanol for the binary and ternary mixtures shown in figure 1 to 4. The excess parameters like ultrasonic velocity, adiabatic compressibility, inter molecular free length and free volume plotted against mole fraction butanol given in figure 5 to 8.

In the case of binary (butanol with benzene) mixtures ultrasonic velocity and density decreases with increasing concentration of butanol also ultrasonic velocity and density decreases with increasing concentration of butanol for the ternary mixtures (butanol + methyl benzoate + benzene). Reverse trend observed in the variation of viscosity with the concentration of butanol both binary and ternary mixtures.

Further the adiabatic compressibility, free length shows reverse trend both the binary and ternary mixtures to the ultrasonic velocity as shown in figures 1 to 3. The variation of adiabatic compressibility due to change in ultrasonic velocity also interacting molecules bond broken due to the releasing dipoles of inter molecular interactions. In view of strong force of attraction between the molecules there will be an increase in cohesive force and the phenomenon

of structural changes takes place due to the existence of electrostatic field. Thus structural rearrangement of molecules results in change adiabatic compressibility thereby performance increasingly intermolecular interactions. Many researchers report the similar results in some binary and liquid mixtures [7].

Table 2 Variation of experimental values, related acoustical parameter and excess values with the concentration of butanol for the binary and ternary mixtures at 303 K

X_1	u	ρ	η	β	V_f	L_f	u^E	β^E	V_f^E	L_f^E
Butanol+ benzene										
0.1	1275	863	0.697	7.13	6.05	66.26	6	-0.08	-0.001	-0.03
0.2	1274	857	0.851	7.19	4.45	81.58	11	-0.17	-0.006	-0.06
0.3	1274	850	1.026	7.25	3.33	99.18	18	-0.27	-0.010	-0.09
0.4	1273	844	1.224	7.31	2.54	119.30	23	-0.36	-0.013	-0.13
0.5	1272	837	1.445	7.38	1.96	142.19	29	-0.44	-0.016	-0.16
0.6	1271	831	1.692	7.45	1.53	168.07	35	-0.52	-0.019	-0.19
0.7	1270	824	1.965	7.52	1.21	197.02	40	-0.60	-0.021	-0.22
0.8	1270	818	2.266	7.58	0.97	229.02	47	-0.70	-0.024	-0.26
0.9	1269	811	2.597	7.66	0.78	265.24	52	-0.77	-0.026	-0.28
Butanol+ methyl benzoate + benzene										
0.05	0.45	1337	970	0.393	5.77	5.26	30.235	4.54	-0.33	-0.02
0.10	0.40	1334	966	0.453	5.82	4.07	35.153	5.59	-0.36	-0.02
0.15	0.35	1332	962	0.518	5.86	3.19	40.473	6.66	-0.39	-0.03
0.20	0.3	1330	958	0.590	5.9	2.51	46.413	7.72	-0.42	-0.03
0.25	0.25	1328	954	0.668	5.94	1.99	52.906	8.78	-0.45	-0.03
0.30	0.20	1326	950	0.753	5.99	1.59	60.14	9.85	-0.49	-0.03
0.35	0.15	1323	946	0.844	6.04	1.27	67.97	10.92	-0.51	-0.04
0.40	0.10	1321	942	0.943	6.08	1.02	76.446	12.00	-0.55	-0.04
0.45	0.05	1319	938	1.049	6.13	0.83	85.738	13.07	-0.57	-0.04

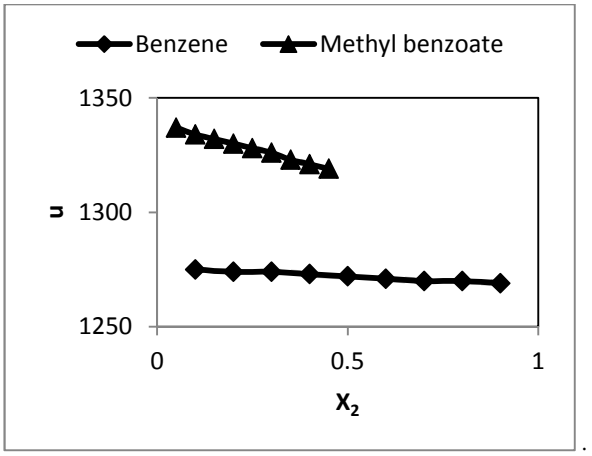

Figure 1 plots u Vs X_2

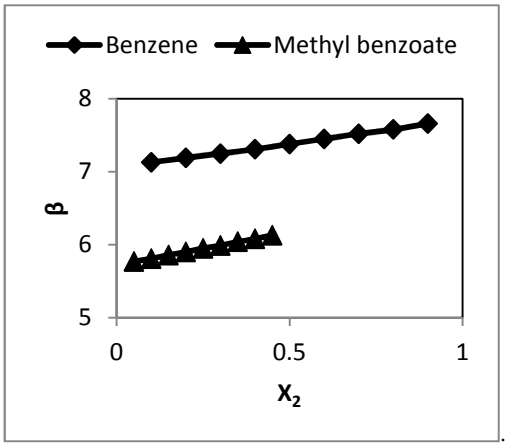

Figure 2 plots β Vs X_2

The ultrasonic velocity (u m/s), density (ρ gm/cm^3) , viscosity (η x10^{-3} Nsm^{-2}), adiabatic compressibility (β 10^{10} kg^{-1}ms^{-2}), free volume (V_f 10^{3}m^3), and inter molecular free length (L_f 10^{-10}m) and also excess values of u^E, β^E $V_f^E$and L_f^E for the butanol with benzene , butanol with methyl benzoate in benzene systems.

From tables 2, it was observed that as the concentration of butanol increases, free volume decreases due to the closed packing of molecules inside the cavity. These behaviors indicate highly associative nature between the components of liquid mixture. The magnitude of the ultrasonic parameter indicate solute – solvent interaction (butanol – benzene) smaller than the dipole – dipole (butanol – methyl benzoate). But it is essential to discuss about the excess parameters rather than the real values. They can give an idea about the nature of association or other type of interactions. The variations of excess parameters versus mole fraction of butanol have been shown in figure 5 to 8. The sign of u^E, β^E, V_f^E and L_f^E indicate weaker type (dipole- induced dipole) f interactions occurs in the binary mixtures and strong type (dipole – dipole) interactions occurs in the ternary mixtures. Many investigations suggested that the negative excess compressibility has been due to closed packed molecules and positive excess values are due to weak interaction between the unlike molecules. Similar reports were reported by many authors [14].

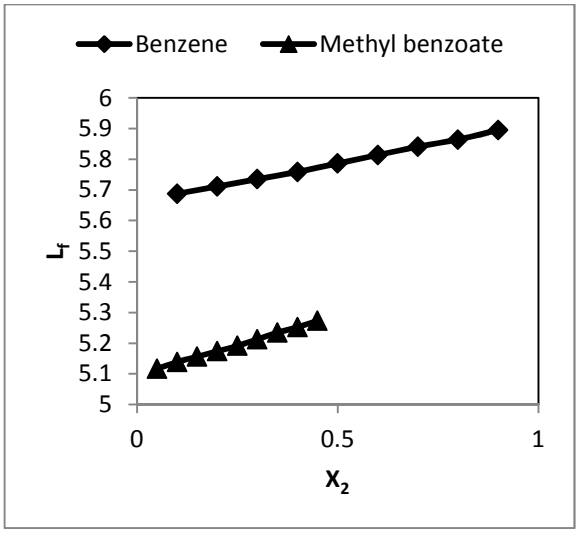

Figure 3 plots L_f Vs X_2

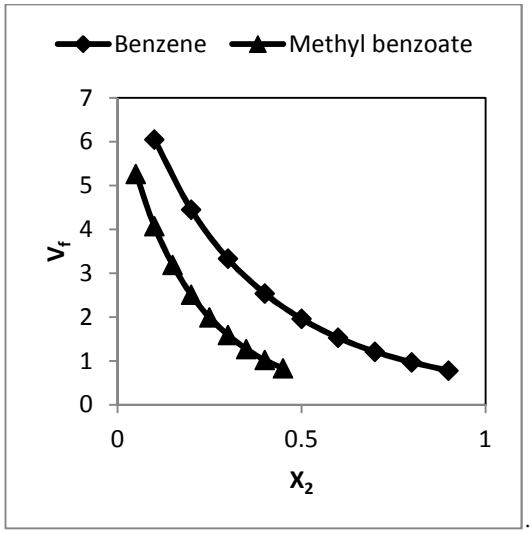

Figure 4 plots V_f Vs X_2

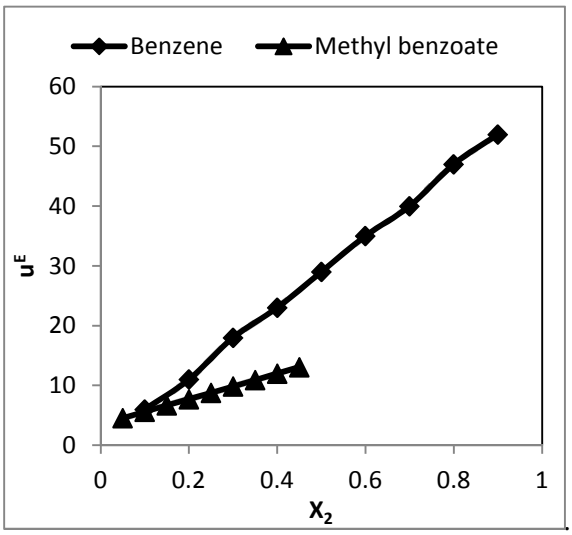

Figure 5 plots u^E Vs X_2

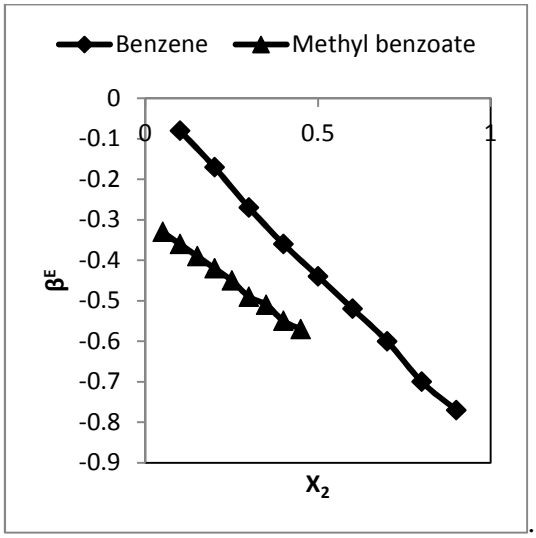

Figure 6 plots β^E Vs X_2

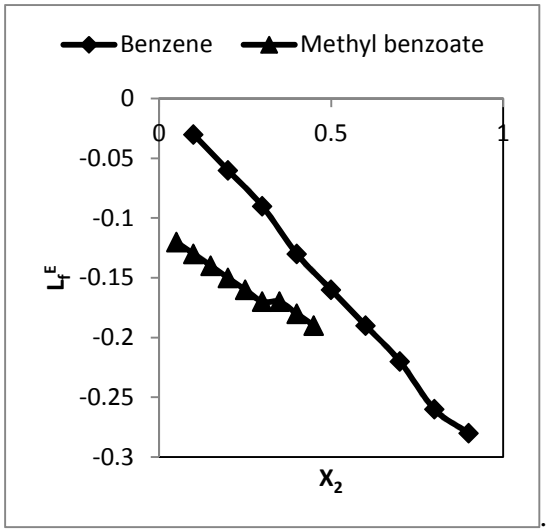

Figure 7 plots L_f^E Vs X_2

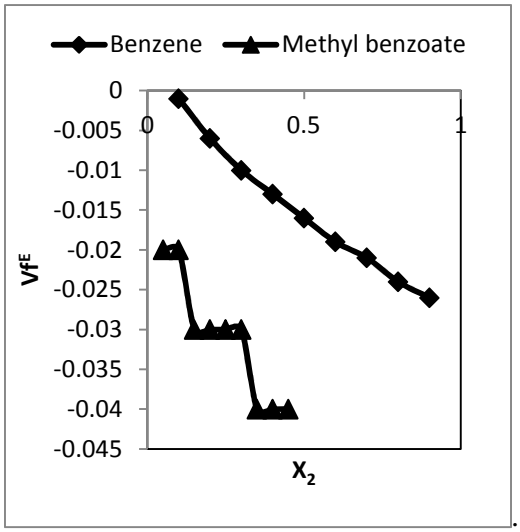

Figure 8 plots β^E Vs X_2

The value of excess inter molecular free length follows the same trend as that of excess adiabatic compressibility. The value of excess inter molecular free length are negative. The negative deviations of excess free volume have been suggested strong interaction between components confirmed.

CONCLUSION

The present report indicates that the ultrasonic parameters understand to the molecular interaction present in liquid mixtures. From Ultrasonic velocity and related acoustical parameters for binary (butanol in benzene) and ternary (butanol with methyl benzoate in benzene) mixtures by the various concentrations, it is expert that there exists a weak interaction due to dipole – induced dipole between the binary components and strong association between the ternary components due to hydrogen bonding.

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