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Thermodynamic and theoretical evaluation of binary liquid mixtures using ultrasonic NDE

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ABSTRACT

Ultrasonic velocities, densities and viscosities of the binary liquid mixtures, butan-2-one with benzene and butan-2-one with carbon tetrachloride at 308 K by applying 2 MHz frequency over the entire mole fraction range. A detailed ultrasonic speed study on the binary liquid mixtures using thermodynamically derived acoustical parameters like free length, molecular interaction parameter, molar cohesive energy and internal pressure shows the extent of intermolecular interactions. Comparing the experimental values with theoretically evaluated ultrasonic velocities from Nomoto relation, Van Deal and Vangeel relation, Junjee relation and ideal mixing relation with different mole fraction range shows the interaction between the unlike molecules. Validity and application of these theories were correlated.

Keywords: Butan-2-one, Acoustical parameters, intermolecular interactions, Nomoto

1. INTRODUCTION

The technology that we use should not affect future needs of the generation. While purchasing the objects like fruits, vegetables, pots, we pat the object and hear the sound; it is nothing but acoustic evaluation [1]. The same concept is applied in predicting the intermolecular interaction using ultrasound NDE techniques. Ultrasonic speed method shows the physico-chemical behaviour of the binary and ternary liquid mixtures. It helps in predicting the type of intermolecular interaction between the molecules.

The ketone molecules undergo dipole-dipole interaction among themselves due to the presence of carbonyl group. So they have higher boiling points than their isomers. Benzene and carbon tetrachloride have the greater tendency to dissolve the maximum number of solutes compared with the other solvents [2]. Butan-2-one, benzene and carbon tetrachloride were chosen for the present work, because it is routinely used in bounteous industrial processes like degreasing, cleaning, fluid extraction and preparation of chemicals. Ultrasonic velocities, densities and viscosities of the two binary systems, butan-2-one + benzene and butan-2-one + carbon tetrachloride have been measured at 308 K for the whole mole fraction range.

2. EXPERIMENTAL METHODOLOGY

2.1 Materials and procedure

The chemicals butan-2-one (SDFCL - 99% purity), benzene (Reachem- 99.5% purity) and carbon tetrachloride (reachem-99.5%purity) used in the current work were decontaminated using standard methods [3]. Before preceding the experiment liquids, the instrument is tested with the reference liquids such as triply distilled water [4].

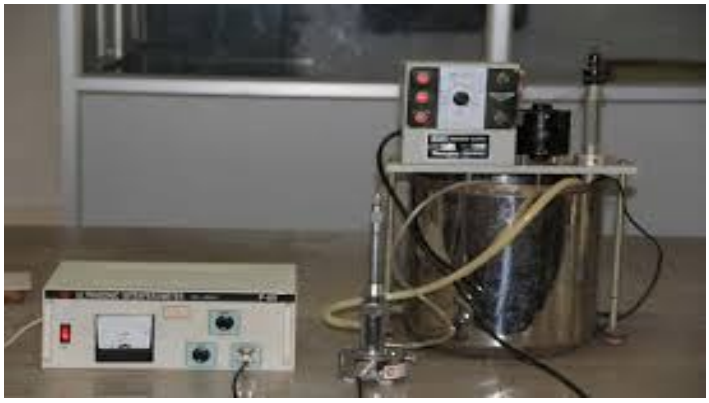

Figure 1 Thermostated Ultrasonic Interferometer equipment

Piezoelectric single quartz crystal of the interferometer undergoes vibration due to the mechanical jerk created by the reflector plate which in turn attached with the micrometre reading gives the distance travelled by the acoustic waves. Using the measured wavelength data, ultrasonic velocities of the liquids were calculated. The ultrasonic velocities of the pure components and freshly prepared binary liquid mixtures of the two systems were measured using ultrasonic interferometer (2 MHz frequency) (shown in fig.1) with thermostatically controlled water bath maintained at the temperature 308 K for the entire mole fraction range. Densities of the pure and experimental liquid mixtures have been measured using specific gravity bottle of 10 ml capacity. Ostwald viscometer (20 ml) is used to determine the flow time of the experimental liquids. The flow time is identified using digital stop watch which is used to evaluate viscosities of the liquid mixtures. An exhaustive literary survey reflects that the present task has not been done earlier.

2.2 Formulae

From the ultrasonic velocities (u), densities (ρ) and viscosities (η) of the binary liquid mixtures butan-2-one + benzene and butan-2-one + carbon tetrachloride and their pure components, thermoacoustic parameters and theoretical models have been calculated.

The acoustic parameters such as free length, molecular interaction parameter, molar cohesive energy and internal pressure can be obtained by using the following equation.

2.2.1 Free length

According to Jacobson [5], the free length (L_f) of the liquid mixtures were calculated as

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

where **β** is the adiabatic compressibility, **K** is the temperature independent constant.

2.2.2 Molecular interaction parameter

Molecular interaction parameter (χ) [6] is calculated as

$$\chi = (u^2_{exp} / u^2_{ideal}) - 1 \quad (2)$$

Where $\mathbf{u}_{exp}$ is the experimental velocity, $\mathbf{u}_{ideal}$ stands for ideal mixing velocity.

2.2.3 Molar cohesive energy

Cohesive forces (MCE) between the liquid mixtures is derived as

$$MCE = \pi_i * V_m \quad (3)$$

where $\mathbf{V_m}$ represents the molar volume of the liquid mixtures.

2.2.4 Internal pressure

The internal pressure (π_i) reflects the attractive and repulsive forces between the two different components. Suryanarayana derived the following equation,

$$\pi_i = bRT [K\eta / u]^{1/2} [\rho^{2/3} / M_{eff}^{7/6}] \quad (4)$$

where ***b*** stands for cubic packing factor, R is the gas constant, $\mathbf{M}_{eff}$ is the effective molecular weight of the solutions.

Of the bounteous theoretical models, few theoretical concepts have been correlated with the experimental ultrasonic velocity values of the liquid – liquid mixtures.

2.2.5 Nomoto relation

Nomoto [7] postulated the following model for evaluating the speeds of the binary liquid mixture theoretically as,

$$U_{mix} = [(x_1R_1 + x_2R_2) / (x_1V_1 + x_2V_2)]^3 \quad (5)$$

where $\mathbf{x_1}$, $\mathbf{x_2}$ stands for the mole fractions, $\mathbf{R_1}$ & $\mathbf{R_2}$ are Rao's constant, $\mathbf{V_1}$ & $\mathbf{V_2}$ are the molar volumes for the respective components 1 & 2.

2.2.6 Van Dael and Vangeel relation

Overcoming the Van Dael and Vangeel relation [8] using specific heat ratios, Van Dael derived the following relation for the velocity of the liquid mixtures,

$$[1/x_1M_1 + x_2M_2](1/U^2_{mix}) = x_1/(M_1u_1^2) + x_2/(M_2u_2^2) \quad (6)$$

where $\mathbf{M_1}$ & $\mathbf{M_2}$, $\mathbf{u_1}$ & $\mathbf{u_2}$ - the molecular weight and ultrasonic velocities of the components 1& 2 respectively.

2.2.7 Junjee relation

Zhang Junjee derived a theoretical calculation for the ultrasonic velocity of the liquid mixtures as follows,

$$U_{mix} = (x_1V_1 + x_2V_2) / \{[(x_1M_1 + x_2M_2)^{1/2}][(x_1V_1 / \rho_1u_1^2) + (x_2V_2 / \rho_2u_2^2)]\} \quad (7)$$

where ρ_1, ρ_2 stand for the densities of the components 1& 2.

2.2.8 Ideal mixing relation

The velocity calculation for the ideal mixing theory is given as,

$$U_{mix} = x_1 u_1 + x_2 u_2 \quad (8)$$

3. RESULTS AND DISCUSSION

3.1 Thermoacoustic parameters

Acoustic parameters like free length (L_f), molecular interaction parameter (χ), molar cohesive energy (MCE) and internal pressure (π_i) have been measured using ultrasonic velocities, densities and viscosities of the two liquid binary systems, butan-2-one + benzene and butan-2-one + carbon tetrachloride at 308 K along with mole fraction are cited in Table 3.1.1.

The ultrasonic velocity of the butan-2-one + benzene decreases with increase in the concentration of butan-2-one whereas reverse trend has been seen in the case of butan-2-one + carbon tetrachloride (in Fig. 2). The system I is in agreement with Eyring and Kincaid [10], this is mainly due to the resonant π –electron cloud of the benzene ring get easily attracted by carbonyl group of the butan-2-one molecule compared with the σ –electrons of the carbon tetrachloride molecules. This indicates the structure breaking tendency of the benzene molecules. The non- linear variation of ultrasonic velocity [11] in CCl_4 system attributes the cluster formation due to the denser carbon tetrachloride molecules. The free length is the distance acquired by the components in the liquid mixture. The variation of free length over the entire mole fraction range for the two liquid systems in Fig. 3 implicates a reverse trend with the velocity data. The higher positive magnitude of the carbon tetrachloride system shows the weaker interactions compared with the benzene systems. Benzene have maximum bonds with more electrons brings the atom closer and attracts the unlike components strongly. Decrease in the number of benzene molecules in the system I with increasing concentration shows the specific interaction as proposed by Eyring and Kincaid, and many other analysts [10], [11].

Table 3.1.1: Experimental and calculated Values of Ultrasonic Velocity (u), Density (ρ), Viscosity (η) Free Length (L_f), Interaction Parameter (χ), Molar cohesive energy (MCE) and Internal Pressure (π_i) a for various mole fractions of the two binary liquid systems- Butan-2-one + Benzene and Butan-2-one + carbon tetrachloride at 308 K.

mole fraction x_{C4H8O}	**u** m s^{-1}	**ρ** kg m^{-3}	**η** Pa s	**L_f** A^0	**χ**	**MCE** 10^3 k J mol^{-1}	**π_i** 10^5 Pascal
System I-Butan-2-one + Benzene							
0.0992	1261.20	837.80	223.36	0.5479	0.0327	724.70	783.28
0.1985	1252.40	832.70	217.18	0.5534	0.0329	719.49	778.90
0.2981	1243.20	823.60	210.03	0.5606	0.0325	713.70	770.17
0.3978	1235.80	814.15	205.08	0.5672	0.0352	711.01	764.45
0.4977	1221.20	808.70	200.94	0.5759	0.0258	710.52	764.87
0.5978	1214.00	802.70	197.31	0.5815	0.0288	708.85	763.51
0.6981	1201.20	796.70	193.82	0.5899	0.0223	709.01	764.15
0.7985	1192.20	789.85	190.74	0.5969	0.0223	709.02	763.81
0.8992	1176.80	781.00	187.45	0.6081	0.0113	711.09	763.75
1.0000	1161.25	775.20	182.60	0.6186	0.0000	709.26	762.47
System II-Butan-2-one + Carbon tetrachloride							
0.1071	912.80	1453.00	362.55	0.5748	0.0311	813.71	815.03
0.2126	930.20	1382.10	342.29	0.5783	0.0007	804.56	814.95
0.3164	951.00	1311.20	322.30	0.5808	-0.0195	794.25	813.82
0.4186	978.44	1233.35	301.51	0.5820	-0.0241	781.71	806.02
0.5192	1003.00	1155.50	281.28	0.5866	-0.0330	771.21	799.99
0.6183	1026.50	1081.00	262.10	0.5926	-0.0426	761.94	797.36
0.7159	1048.80	1008.50	243.55	0.6005	-0.0530	753.66	797.36
0.8120	1137.26	929.10	221.61	0.5770	0.0573	719.77	764.54
0.9067	1148.20	849.70	200.02	0.5976	0.0255	713.36	760.23

1.0000	1161.25	775.20	182.60	0.6186	0.0000	709.26	762.47

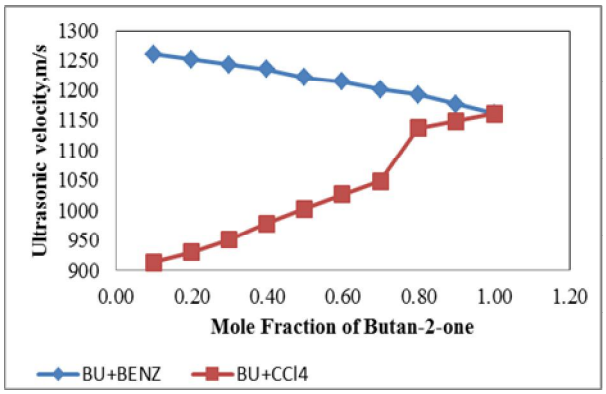

Figure 2 u - mole fraction of Butan-2-one

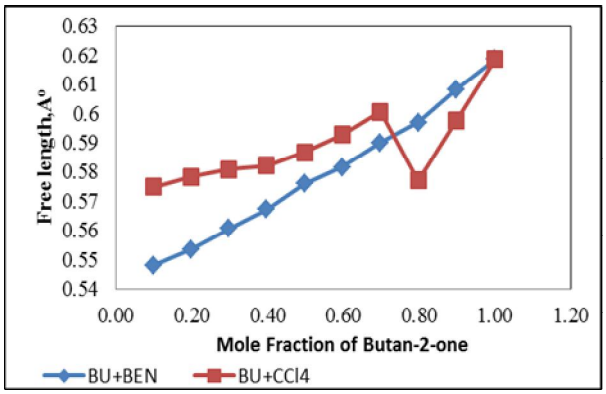

Figure 3 L_f - mole fraction of Butan-2-one

The nature of the intermolecular interaction is envisioned by manipulating the interaction parameter [12],[13].The positive values for the benzene systems throughout the mole fraction range (fig. 4) indicates the strong dipole – induced dipole interaction preceding the CCl4 systems. Aromatic molecules incomparably have lower energy than similar non- aromatic molecules, it agglomerates to gain aromaticity. As a result, the cohesive energy values [14] of the system I is lesser than system II. The large charge density of CCl_4 molecules undergoes weaker interaction with the increasing butan-2-one molecules as shown in fig 5.

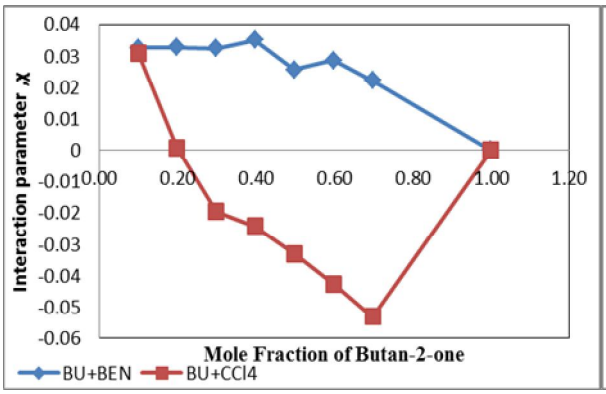

Figure 4 χ - mole fraction of Butan-2-one

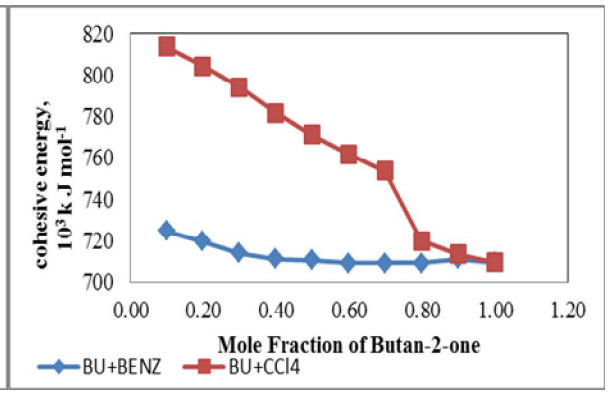

Figure 5 MCE - mole fraction of Butan-2-one

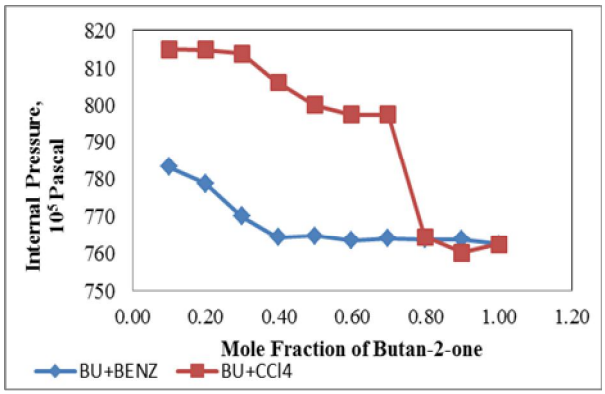

Figure 6 π_i - mole fraction of Butan-2-one

Internal pressure [15] is the sum of all the forces operating in the molecules. Internal pressure decreases with increasing concentration of the solute molecules in both the binary systems shows interaction between the unlike components (as cited in fig. 6). In both the systems, the interaction becomes weaker at higher concentration is due to the electrostriction nature of the solute – solvent molecules [16], [17].

3.2 Theoretical models

The experimental ultrasonic velocities are used to evaluate the empirical, semi empirical, statistical models such as Nomoto relation, Van Dael and Vangeel relation, Junjee relation and Ideal mixing relation at 308 K at the concentration ranges from 0.1-1.0 mole fractions are listed in Table 3.1.2.

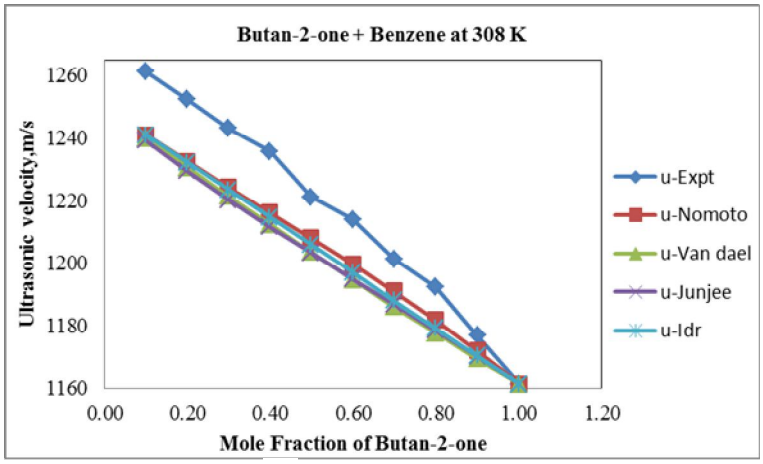

Figure 7 (a) u - mole fraction of Butan-2-one

Fig. 7(a) correlates the relation between the various theoretical models for the binary liquid system, butan-2-one + benzene. Among the calculated theoretical velocity values, Nomoto and ideal mixing relation is in agreement compared with other theories.

Table 3.1.2: Experimental and theoretical ultrasonic velocity values using Nomoto relation, Van Dael and Vangeel relation, Junjee relation and Ideal mixing relation.

mole fraction x_{C4H8O}	U^{EXP}	U^{NOMOTO}	$U^{VAN\ DAEL}$	U^{JUNJEE}	U^{IDR}
System I-Butan-2-one + Benzene					
0.0992	1261.20	1241.05	1240.17	1239.23	1241.09
0.1985	1252.40	1232.55	1230.67	1229.40	1232.28
0.2981	1243.20	1224.27	1221.37	1220.21	1223.46
0.3978	1235.80	1216.08	1212.25	1211.48	1214.62
0.4977	1221.20	1207.87	1203.33	1203.08	1205.77
0.5978	1214.00	1199.51	1194.58	1194.86	1196.90
0.6981	1201.20	1190.87	1186.00	1186.71	1188.01
0.7985	1192.20	1181.76	1177.59	1178.49	1179.11
0.8992	1176.80	1171.98	1169.34	1170.05	1170.19
1.0000	1161.25	1161.25	1161.25	1161.25	1161.25
System II-Butan-2-one + Carbon tetrachloride					
0.1071	912.80	893.63	888.73	884.74	898.91
0.2126	930.20	919.39	911.30	902.93	929.89
0.3164	951.00	945.07	935.30	922.29	960.40
0.4186	978.44	971.04	960.87	943.26	990.42
0.5192	1003.00	997.69	988.21	966.41	1019.99
0.6183	1026.50	1025.48	1017.56	992.53	1049.10
0.7159	1048.80	1054.95	1049.17	1022.78	1077.78
0.8120	1137.26	1086.77	1083.39	1058.85	1106.02
0.9067	1148.20	1121.82	1120.58	1103.47	1133.84

1.0000	1161.25	1161.25	1161.25	1161.25	1161.25

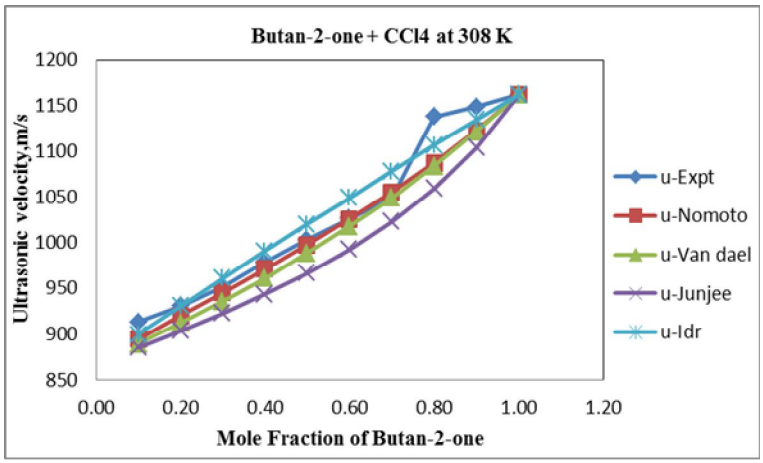

Figure 7 (b) u - mole fraction of Butan-2-one

Fig. 7(b) represents the theoretical velocity values for the butan-2-one and carbon tetrachloride systems. Nomoto and Van dael and Vangeel expressions are well suited empirical theories for the CCl_4 systems. Thus the calculated ultrasonic theoretical values reflect the intermolecular interaction between the liquid-liquid mixtures [18], [19], [20].

4. CONCLUSION

The thermoacoustic parameters like free length (L_f), molecular interaction parameter (χ), molar cohesive energy (MCE) and internal pressure (π_i) and the theoretical models using Nomoto relation, Van Dael and Vangeel relation, Junjee relation and Ideal mixing relation at 308 K at all the concentration ranges confirm the dipole-induced dipole interactions and dispersive forces between the polar butan-2-one and non- polar benzene, carbon tetrachloride liquid systems. Of the two binary mixtures, Butan-2-one and Benzene interacts stronger than the Butan-2-one and CCl_4. The ultrasonic velocity theoretical models also depicts the agglomeration of the unlike molecules. Nomoto empirical relation preponderates the other theoretical models in both the binary liquid systems.

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