



# Journal of Applied Sciences

ISSN 1812-5654

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## Acoustic and Thermodynamic Properties of Binary Liquid Mixtures of Acetophenone and Benzene

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**Abstract:** Densities and ultrasonic velocity of binary mixtures of acetophenone with benzene at 303.15, 313.15 and 323.15 K were measured over the entire composition range. From these experimental data, the internal pressure ( $\pi_i$ ), free volume ( $V_f$ ), Gibb's free energy ( $G^E$ ), viscous relaxation time ( $\tau$ ) were calculated. Also, the excess internal pressure ( $\pi_i$ ) and ultrasonic velocity ( $U^E$ ) and excess free volume were calculated. Ultrasonic velocities theoretically evaluated using Nomoto's relation, Rao's specific sound velocity relation and Junjie's equation are compared with experimental values to check applicability of these equations to the systems studied. The relative merits of these theories and relations were discussed.

**Key words:** Ultrasonic velocity, density, internal pressure, free volume, gibb's free energy, binary liquid mixture, acetophenone, benzene

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### INTRODUCTION

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. Ultrasonic velocities of the liquid mixtures consisting of polar and non-polar (Mehra and Pancholi, 2007) components are of considerable importance in understanding intermolecular interaction between component molecules and find applications in several industrial and technological processes (Pal and Kumar, 2004; Rao *et al.*, 2005). Ultrasonic velocity measurements have been employed extensively to detect and assess weak and strong molecular interactions in binary mixtures, because mixed solvents find practical applications in many chemical and industrial processes. Increasing use of benzene and acetophenone in many industrial processes have greatly stimulated the need for extensive information on the acoustic and transport properties of these liquids and their mixtures. The parameters such as ultrasonic velocity ( $u$ ), density ( $\rho$ ) and derived parameters such as internal pressure ( $\pi_i$ ), free volume ( $V_f$ ) viscous relaxation time ( $\tau$ ) provide better insight into intermolecular interactions. The investigation is carried out to study of molecular interactions in the binary liquid mixtures of acetophenone-benzene. Several researchers (Savaroglu and Aral, 2004; Sundharam and Palaniappan, 2005)

carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto, Vandael and Vangeel and Rao's specific velocity and interpreted the results in terms of molecular interactions. The sound velocity in binary liquid mixtures from various theoretical models has been compared in the present paper. An attempt has been made to compare the merits of the existing relations in binary liquid mixtures. The ultrasonic velocities of the binary liquid mixtures of acetophenone and benzene at 303.15, 313.15 and 323.15 K over the entire range have been theoretically evaluated by using various theories and compared with experimental values.

### MATERIALS AND METHODS

The chemicals used were of analytical reagent grade obtained from loba chemicals. All the components were dried over anhydrous calcium chloride and fractionally distilled (Oswal and Patel, 1995). Binary solutions were prepared on percentage basis (v/v) by dissolving known volume of acetophenone in appropriate volume of benzene and measuring their masses on a Shimadzu Corporation Japan Type BL 2205 electronic balance accurate to 0.01 g. The possible uncertainty in the mole

fraction was estimated to be less than  $\pm 0.0001$ . The densities were determined by using bicapillary pycnometer as described (Mehdihasan-Ujjan *et al.*, 1995) and calibrated with deionised double distilled water with  $0.9960 \times 10^3 \text{ kg m}^{-3}$  as its density at temperature 303 K. The pycnometer filled with air bubble free experimental liquids was kept in a transparent walled water bath to attain thermal equilibrium. The positions of the liquid level in the two arms were recorded with a help of travelling microscope which could read to 0.01 mm. The precision density measurements were within  $\pm 0.0003 \text{ g cm}^{-3}$ . Speed of sound was measured by using a variable path, single crystal interferometer (Mittal Enterprises, New Delhi). The interferometer was calibrated using toluene. The interferometer cell was filled with the test liquid and water was circulated around the measuring cell from a thermostat. The uncertainty was estimated to be  $0.1 \text{ m sec}^{-1}$ . All measurements were made in a thermostatically controlled water bath with temperature accuracy of  $\pm 0.1^\circ\text{C}$ .

**Theory:** Using experimentally measured values of ultrasonic velocity ( $u$ ) and density ( $\rho$ ) the following acoustic and thermodynamic parameters are evaluated (Subha *et al.*, 2004; Riggio *et al.*, 1986; Mehra and Pancholi, 2007; Mehra *et al.*, 2001). The internal pressure for pure liquids and their binary liquid mixtures are calculated using the suryanarayana relation as given as:

$$\pi_i = b R T [K\zeta/u]^{1/2} [\rho^{2/3}/M_{\text{eff}}^{7/6}] \quad (1)$$

where,  $b$  stands for cubic packing which is assumed to be 2 for liquids,  $K$  is dimensionless constant which is independent of temperature and nature of liquids and its value is  $4.28 \times 10^9$ ,  $R$  is gas constant,  $T$  is absolute temperature and  $M_{\text{eff}}$  is effective molecular weight  $M_{\text{eff}} = X_1M_1 + X_2M_2$

Excess Gibb's free energy of activation of viscous flow for binary liquid mixtures are obtained by using following expression:

$$G^E = RT [\ln\zeta_{\text{mix}} V_{\text{mix}} - X_1 \ln\zeta_1 V_1 - X_2 \ln\zeta_2 V_2] \quad (2)$$

The free volume is given by  $V_f = [M_{\text{eff}}u/K\zeta]^{3/2} \quad (3)$

Viscous relaxation time  $\tau = 4\zeta/3\rho u^2 \quad (4)$

The volume fraction of pure components  $\Phi_i$ , was calculated from the individual pure molar volumes ( $V_i$ ), with the relationship:

$$\Phi_i = X_i V_i / (\sum X_i V_i) \quad (5)$$

On assuming additivity of molar sound velocity Nomoto (1958) established the following equation for sound velocity:

$$U_N = [\sum(x_i R_i) / \sum(x_i V_i)]^3 \quad (6)$$

where,  $x_i$  is the molefraction,  $R_i = u_i V_i^{1/3}$  the sound velocity,  $V_i$  the molar volume and  $u_i$  is the sound velocity of the  $i$ th component. Junjie's equation is given by:

$$U_{\text{Jun}} = [\sum x_i V_i / (\sum x_i M_i)^{1/2}] [\sum(x_i V_i / \rho_i u_i^2)]^{-1/2} \quad (7)$$

Rao's (specific sound velocity) relation (Gokhale and Bhagavat, 1989) is given by:

$$U_R = (\sum x_i r_i \rho)^3 \quad (8)$$

where,  $r_i = u_i^{1/3} / \rho_i$  is the Rao's specific sound velocity of the  $i$ th component of the mixture.

## RESULTS AND DISCUSSION

Table 1 summarizes the comparison of density ( $\rho$ ) and ultrasonic velocity ( $u$ ) data for pure liquids (acetophenone and benzene) at 303.15 K with the literature. The calculated quantities of internal pressure ( $\pi_i$ ), excess gibbs energy ( $G^E$ ), free volume ( $V_f$ ) and viscous relaxation time ( $\tau$ ) of acetophenone and benzene system over the entire composition range at 303.15 K, 313.15 K and 323.15 K have been presented in Table 2.

Excess internal pressure ( $\pi_i^E$ ), excess velocity ( $U^E$ ) and excess free volume ( $V_f^E$ ) were calculated from the experimental results by the following equations, respectively:

$$\pi_i^E = \pi_{\text{im}} - (x_1 \pi_{i1} + x_2 \pi_{i2}) \quad (9)$$

$$U^E = U_M - (x_1 U_1 + x_2 U_2) \quad (10)$$

$$V_f^E = V_{\text{M}} - (x_1 V_{f1} + x_2 V_{f2}) \quad (11)$$

where,  $X_1$  and  $X_2$  are mole fractions,  $\pi_{i1}$  and  $\pi_{i2}$  are the internal pressures,  $U_1$  and  $U_2$  are the velocities and  $V_{f1}$  and

Table 1: Comparison of experimental density and sound of velocity of pure liquids with literature values at 303.15 K

	Liquid	Experimental	Literature
Density ( $\rho$ ) ( $\text{g cm}^{-3}$ )	Acetophenone	1.0198	1.0194
	Benzene	0.8624	0.8657
Sound of velocity ( $\text{m sec}^{-1}$ )	Acetophenone	1401	1391
	Benzene	1280	1285

Table 2: Experimental parameters ( $\rho$ ,  $u$ ), derived parameters (internal pressure, Gibb's free energy, free volume, relaxation time) for acetophenone + benzene system at 303.15, 313.15 and 323.15 K

Mole fraction of acetophenone	$\rho$ g cm <sup>-3</sup>	U msec <sup>-1</sup>	Internal pressure x10 <sup>8</sup> pascal	Gibb's free energy J mol <sup>-1</sup>	Free volume cm <sup>3</sup> mol <sup>-1</sup>	Viscous relaxation time x10 <sup>-7</sup> sec
303.15 K						
0.00000	0.8674	1280	1.2589	0	0.00794	5.4997
0.07791	0.8826	1292	1.3000	190.377	0.00687	6.1417
0.15975	0.8978	1304	1.3291	322.915	0.00613	6.7345
0.24581	0.9131	1316	1.3483	407.620	0.00558	7.2816
0.33642	0.9283	1328	1.3591	451.000	0.00517	7.7864
0.43198	0.9436	1340	1.3627	457.324	0.00487	8.2518
0.53288	0.9588	1352	1.3600	429.474	0.00464	8.6807
0.63958	0.9740	1364	1.3518	369.214	0.00447	9.0756
0.75260	0.9893	1376	1.3388	277.472	0.00434	9.4389
0.87252	1.0045	1388	1.3215	154.510	0.00425	9.7728
1.00000	1.0198	1401	1.2999	0	0.00420	10.06
313.15 K						
0.00000	0.84531	1251	1.2149	0	0.00925	5.2157
0.07791	0.86193	1265	1.2526	188.186	0.00808	5.7690
0.15975	0.87856	1279	1.2793	319.681	0.00725	6.2722
0.24581	0.89519	1293	1.2968	403.996	0.00664	6.7295
0.33642	0.91182	1307	1.3065	447.396	0.00619	7.1447
0.43198	0.92845	1321	1.3094	454.011	0.00586	7.5213
0.53288	0.94508	1335	1.3063	426.637	0.00560	7.8625
0.63958	0.96171	1349	1.2982	366.981	0.00542	8.1710
0.75260	0.97834	1363	1.2854	275.938	0.00528	8.4497
0.87252	0.99497	1377	1.2686	153.745	0.00520	8.7007
1.00000	1.01162	1391	1.2483	0	0.00514	8.9262
323.15 K						
0.00000	0.8198	1229	1.1188	0	0.01114	4.8355
0.07791	0.8377	1243.5	1.1712	242.218	0.00933	5.4830
0.15975	0.8556	1256	1.2111	406.290	0.00810	6.0886
0.24581	0.8735	1268.5	1.2400	507.774	0.00724	6.6404
0.33642	0.8914	1281.5	1.2593	557.092	0.00661	7.1375
0.43198	0.9093	1295	1.2705	560.821	0.00615	7.5833
0.53288	0.9271	1308	1.2750	523.343	0.00580	7.9929
0.63958	0.9450	1321	1.2735	447.400	0.00554	8.3642
0.75260	0.9629	1333	1.2672	334.553	0.00534	8.7135
0.87252	0.9808	1346	1.2558	185.460	0.00521	9.0176
1.00000	0.9987	1358	1.2407	0	0.00511	9.3058

$V_{E2}$  are the free volumes of component 1 and 2 respectively. The subscript M represents mixture properties. The variations of  $\pi_i^E$ ,  $U^E$ ,  $G^E$  and  $V_f^E$  with the molefraction of acetophenone at 303.15, 313.15 and 323.15 K are presented in Fig. 1-4.

The excess values of thermo physical properties and thermo acoustical parameters of binary liquid mixtures are fitted to a Redlich-Kister (Redlich and Kister, 1948) equation of the type:

$$Y = x_1 x_2 \sum A_i (x_1 - x_2)^i \tag{12}$$

where, Y represents excess internal pressure, excess free volume the corresponding equation. Coefficients  $A_i$  were obtained by fitting equation to experimental values using a least square regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (S). S was calculated using the relation:

$$S(Y) = [\sum (A_{exp} - A_{cal})^2 / (N-n)]^{1/2} \tag{13}$$

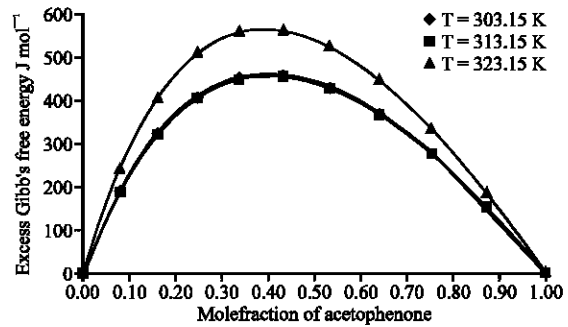


Fig. 1: Excess Gibb's energy of activation of flow for acetophenone (1) + benzene (2) at different temperatures

where, N represents the number of experimental data points and n is the number of coefficients. It is found that for the solution of the seventh degree polynomial, the agreement between the experimental values and the calculated values is satisfactory. The coefficients and standard deviations of Redlich-Kister polynomial equation are presented in Table 3.

Table 3: Redlich-Kister constants for excess internal pressure and excess Gibb's free energy of Acetophenone - benzene at 303.15, 313.15 and 323.15 K

Redlich-Kister Constants for excess internal pressure								
Temperature	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	S%
303.15 K	0.3448	-0.0725	-0.4209	-0.5665	1.9607	0.6335	-1.8881	0.5361
313.15 K	0.3207	-0.0674	-0.3903	-0.5316	1.8086	0.5940	-1.7356	0.4983
323.15 K	0.3963	-0.0848	-0.4566	-0.6352	2.1554	0.7139	-2.0911	0.5990
Redlich-Kister Constants for excess free volume								
Temperature	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	S%
303.15 K	-0.0058	0.0012	0.0086	0.0144	-0.0424	-0.0154	0.0395	0.3140
313.15 K	-0.0065	0.0013	0.0095	0.0157	-0.0465	-0.0169	0.0433	0.0134
323.15 K	-0.0095	0.0020	0.0146	0.0261	-0.0732	-0.0279	0.0680	0.0215

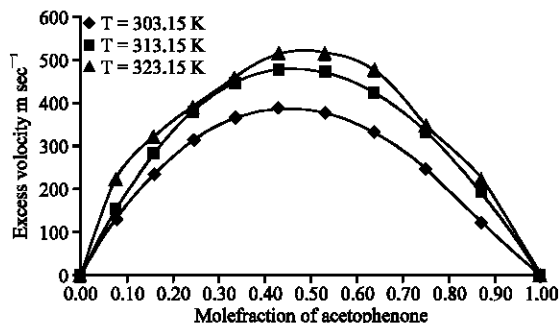


Fig. 2: Excess Velocity for acetophenone (1) + benzene (2) at different temperatures

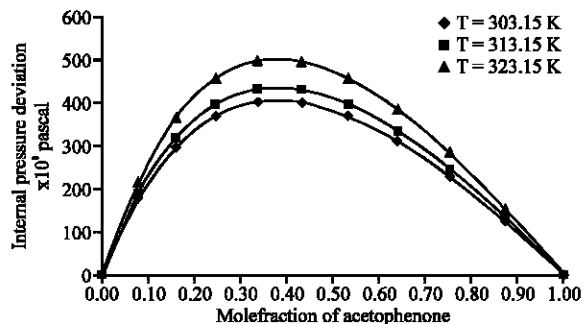


Fig. 3: Deviation of internal pressure for acetophenone (1) + benzene (2) at different temperatures

The excess Gibb's free energy of activation of viscous flow,  $\Delta G^{*E}$  is positive over the entire mole fraction range for the binary mixtures at different temperatures in Fig. 1. The sign of the values of  $\Delta G^{*E}$  can be considered as a reliable criterion for detecting or excluding the presence of interaction between unlike molecules. The positive  $\Delta G^{*E}$  values are also indicative of the strong molecular interaction between acetophenone and benzene. A detailed observation shows that the deviations of ultrasonic velocity of a mixture show increasing trend when mole fraction and temperature increases. It may be noted that such values are due to the electronic perturbation of the individual molecules during mixing and therefore depend very much on the nature of the mixing molecules. The internal pressure deviations are negative over the entire composition range of mixtures.

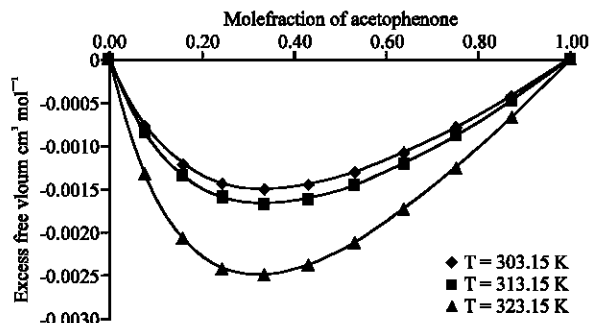


Fig. 4: Excess free volume for acetophenone (1) + benzene (2) at different temperatures

The excess free volumes are negative over the entire composition range of mixtures (Fort and Moore, 1965; Mehra *et al.*, 2001). This suggests that the component molecules are closer together in the liquid mixture than in the pure liquids forming the mixture, indicating that strong attractive interactions between component molecules such as hydrogen bonding, dipole-dipole interactions and other specific interactions between unlike molecules are operative in the system.

The experimental and theoretical velocities calculated by using the Eq. 6-8 are presented in Table 4. The validity of different theoretical formulae is checked by percentage deviation for all the mixtures at all the temperatures and is given in Table 4. The limitations and approximation incorporated in these theories are responsible for the deviations of theoretical from experimental values. In Nomoto's theory, no interaction between components of liquid mixtures has been taken into account as it is supposed that the volume does not change on mixing. Similarly the assumption for the formation of ideal mixing relation is that, the ratios of specific heats of ideal mixtures and the volumes are equal by not taking into the consideration of molecular interactions. Various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions are operative due to interactions when two liquids are mixed. This is in good agreement with the conclusions drawn by Padey *et al.* (1999) Thus the observed deviation of theoretical values of velocity from

Table 4: Values of ultrasonic velocity calculated from Nomoto, Junjie's and Rao's relations along with experimental ultrasonic velocity and percentage error for acetophenone +benzene at 303.15, 313.15 and 323.15 K

Mole fraction of (x1) acetophenone	U <sub>exp</sub> m sec <sup>-1</sup>	Nomoto	Junjie's	Rao's	Deviation (%)		
					Nomoto	Junjie's	Rao's
303.15 K							
0.00000	1280	1280	1280	1280	0	0	0
0.07791	1292	1291.7356	1287.6914	1289.1665	0.02046	0.33348	0.21931
0.15975	1304	1303.5522	1296.2027	1298.8424	0.03434	0.59795	0.39552
0.24581	1316	1315.4485	1305.5794	1309.0694	0.04191	0.79184	0.52664
0.33642	1328	1327.4242	1315.8742	1319.8949	0.04335	0.91308	0.61032
0.43198	1340	1339.4834	1327.1515	1331.3763	0.03855	0.95884	0.64355
0.53288	1352	1351.6232	1339.4781	1343.5714	0.02786	0.92617	0.62341
0.63958	1364	1363.8441	1352.9335	1356.5483	0.01143	0.81133	0.54631
0.75260	1376	1376.1469	1367.6091	1370.3846	-0.01068	0.60980	0.40809
0.87252	1388	1388.5321	1383.6100	1385.1682	-0.03834	0.31628	0.20402
1.00000	1401	1401	1401	1401	0	0	0
313.15 K							
0.00000	1251	1251	1251	1251	0	0	0
0.07791	1265	1264.3286	1259.2768	1261.5536	0.05307	0.45242	0.27244
0.15975	1279	1277.7753	1268.5682	1272.7033	0.09575	0.81562	0.49231
0.24581	1293	1291.3740	1278.9404	1284.4986	0.12575	1.08736	0.65749
0.33642	1307	1305.1259	1290.4775	1296.9960	0.14339	1.26415	0.76541
0.43198	1321	1319.0369	1303.2813	1310.2637	0.14861	1.34131	0.81274
0.53288	1335	1333.1055	1317.4629	1324.3707	0.14191	1.31363	0.79620
0.63958	1349	1347.3336	1333.1550	1339.3984	0.12353	1.17457	0.71176
0.75260	1363	1361.7238	1350.5138	1355.4397	0.09363	0.91608	0.55468
0.87252	1377	1376.2783	1369.7226	1372.5998	0.05240	0.52849	0.31954
1.00000	1391	1391	1391	1391	0	0	0
323.15 K							
0.00000	1229	1229	1229	1229	0.00000	0.00000	0.00000
0.07791	1243.5	1241.0823	1235.9608	1238.7435	0.19442	0.60628	0.382504
0.15975	1256	1253.3372	1243.9560	1249.0339	0.21200	0.95891	0.554624
0.24581	1268.5	1265.7678	1253.0627	1259.9162	0.21538	1.21697	0.676688
0.33642	1281.5	1278.3767	1263.3718	1271.4419	0.24372	1.41461	0.784865
0.43198	1295	1291.1712	1274.9933	1283.6732	0.29566	1.54492	0.874650
0.53288	1308	1304.1512	1288.0496	1296.6729	0.29424	1.52526	0.865980
0.63958	1321	1317.3203	1302.6872	1310.5151	0.27855	1.38628	0.793709
0.75260	1333	1330.6827	1319.0802	1325.2841	0.17384	1.04424	0.578831
0.87252	1346	1344.2420	1337.4349	1341.0758	0.13061	0.63633	0.365839
1.00000	1358	1358	1358	1358	0.00000	0.00000	0.00000

the experimental values shows that the molecular interactions is taking place between the unlike molecules in the liquid mixture. There is a good agreement between experimental and theoretical values in Nomoto's relation followed by Rao's specific velocity method whereas higher deviations are observed in Junjie's relations at all the temperatures.

### CONCLUSION

Experimental data of the density and speed of sound of acetophenone and benzene mixtures have been measured over the entire composition range at 303.15, 313.15 and 323.15 k. It has been observed that positive deviations for excess velocity, excess internal pressure, excess Gibbs energy where as negative deviations were observed for excess free volume at 303.15, 313.15 and 323.15 k. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of intermolecular interactions in the systems

studied. It may be concluded that out of three theories and relations, Nomoto's relation is best suited for the binary mixture of acetophenone +benzene at 303.15, 313.15 and 323.15 k.

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