



Experimental and Theoretical Studies of Ultrasonic Velocity in Binary Liquid Mixtures of Methyl Benzoate at Different Temperatures

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ABSTRACT

Ultrasonic velocities of binary liquid mixtures of methyl benzoate with 1-octanol are measured using ultrasonic interferometer at 303.15K, 308.15K, 313.15K and 318.15K over the entire range of composition. Theoretical values of ultrasonic velocity have been evaluated at the four temperatures using Nomoto's relation, Ideal mixture relation, Impedance relation, Rao's specific velocity relation and Junjie's method. Theoretical values are compared with the experimental values and U_{exp}^2/U_{imx}^2 is evaluated for non-ideality in the mixtures. A good agreement has been found between experimental and theoretical values of ultrasonic velocity. The relative applicability of these theories to the present systems has been checked and discussed. The results are explained in terms of molecular interactions occurring in these binary liquid mixtures.

Key words: Ultrasonic velocity, Methyl benzoate, 1-Octanol, molecular interactions, Theoretical models.

INTRODUCTION

Measurement of Ultrasonic velocity gives the valuable information about physicochemical behavior of binary liquid mixtures and in understanding nature of interactions in liquids and liquid mixtures [1-6]. Several researchers [7-10] carried out ultrasonic investigations on liquid mixtures and correlated the experimental results of ultrasonic velocity with theoretical relations of Nomoto [11], Van dael and Vangeel [12], impedance relation [13], Rao's specific velocity [14] and Junjie [15] relations and the results are interpreted in terms of molecular interactions. This investigation presents the evaluation of ultrasonic velocity using Nomoto's relation, ideal mixture relation, impedance relation, Rao's specific velocity relation and Junjie's relation for methyl benzoate with 1-octanol and are compared with the experimental values over the entire range of composition at four different temperatures 303.15K, 308.15K, 313.15K and 318.15K. Molecular interactions in binary mixtures are studied based on the deviation in the values of U_{exp}^2/U_{IMR}^2 .

EXPERIMENTAL SECTION

The chemicals methyl benzoate and 1-octanol of 99% pure, AR grade were supplied by SDFCL, Mumbai. The chemicals were purified by standard procedure [16]. Job's method of continuous variation was used to prepare the mixtures of required proportions. The prepared mixtures were preserved in well-stoppered conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India; Model: F-80X). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of $\pm 0.5\%$. Weights

were measured with an electronic balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1mg. An average of 4-5 measurements was taken for each sample.

THEORY

The following theories/relations are used for the prediction of ultrasonic velocity in the binary liquid mixtures.

Nomoto's relation, U_{NOM}

Nomoto established an empirical relation for ultrasonic velocity in binary liquid mixtures as

$$U_{\text{NOM}} = [(x_1 R_1 + x_2 R_2) / (x_1 V_1 + x_2 V_2)]^3 \quad (1)$$

Where R is molar sound velocity, $R_1 = (M_1/\rho_1) (U_1)^{1/3}$ and $R_2 = (M_2/\rho_2) (U_2)^{1/3}$

x_1 and x_2 are the mole fractions of 1st and 2nd components of the liquid mixture and

V is molar volume, $V_1 = M_1/\rho_1$, $V_2 = M_2/\rho_2$.

Van Dael and Vangeel Ideal Mixture relation, U_{IMR}

Van Dael and Vangeel (1969) suggested the following relation for the measurement of velocity of sound

$$U_{\text{IMR}} = [(x_1/M_1 U_1^2 + x_2/M_2 U_2^2)]^{-1/2} [1/(x_1 M_1 + x_2 M_2)]^{1/2} \quad (2)$$

Where U_{IMR} is the ideal mixture ultrasonic velocity in liquid mixture. U_1 and U_2 are ultrasonic velocities of individual compounds.

Impedance relation, U_{IR}

The product of ultrasonic velocity (U) and density (ρ) of the mixture is termed as acoustic impedance (Z) of the mixture. Hence the sound velocity in the mixture can be predicted from the knowledge of acoustic impedance and the density of the pure components.

$$U_{\text{IR}} = \sum x_i Z_i / \sum x_i \rho_i \quad (3)$$

Where x_i is the mole fraction, ρ_i the density of the mixture and Z_i is the acoustic impedance.

Rao's specific sound velocity, U_{R}

$$U_{\text{R}} = (\sum x_i r_i \rho_i)^3 \quad (4)$$

Where x_i is the mole fraction, U_i is the ultrasonic velocity, ρ_i the density of the mixture and r_i is the Rao's specific sound velocity = $U_i^{1/3} / \rho_i$.

Jungie's relation, U_{JR}

$$U_{\text{JR}} = [(x_1 V_1 + x_2 V_2) / (x_1 M_1 + x_2 M_2)]^{1/2} [(x_1 V_1 / \rho_1 U_1^2 + x_2 V_2 / \rho_2 U_2^2)]^{-1/2} \quad (5)$$

Where M_1 , M_2 are molecular weights of constituent components, ρ_1 and ρ_2 are the densities of constituent components.

RESULTS AND DISCUSSION

Ultrasonic velocity and density for the pure components methyl benzoate and 1-octanol at different temperatures 303.15K, 308.15K, 313.15K and 318.15K are given in Table 1.

The experimental values along with the values calculated theoretically using Nomoto's relation, Ideal mixture relation, impedance relation, Rao's specific sound velocity relation, and Jungie's relation for the system methyl benzoate + 1-Octanol at different temperatures 303.15K, 308.15K, 313.15K and 318.15K and are given in the Tables 2.

It can be seen from Table 2 that the theoretical values of ultrasonic velocity calculated by using various theories show deviation from experimental values. The limitations and approximation incorporated in these theories are

responsible for the deviations of theoretical values from experimental values. In Nomoto's theory, it is supposed that the volume does not change on mixing. But on mixing two liquids, the interaction between the molecules of the two liquids takes place because of the presence of various types of forces such as hydrogen bonding, dipole-dipole, dispersive forces, charge transfer and dipole-induced dipole interactions. The deviations of experimental values from theoretical values calculated using Van Dael and Vangeel equation might be due to the compressibility of the component liquids in the present mixture. The deviations of experimental values and values calculated from impedance relation and Rao's relation imply non-additivity of acoustic impedance and Rao's velocity in the liquid mixture. Large deviations are observed in case of Junjie's relation. Thus, the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interactions are taking place [17-20] between the unlike molecules in the liquid mixture.

Table-1 Ultrasonic velocity and density for pure components methyl benzoate and 1-octanol at 303.15K, 308.15K, 313.15K and 318.15K.

Component	303.15K		308.15K	
	Density ρ (kg/m ³)	Velocity u (m/s)	Density ρ (kg/m ³)	Velocity u (m/s)
Methyl benzoate	1087.5	1404	1085.9	1376.84
1-octanol	803.03	1365	801.6	1326.31
Component	313.15K		318.15K	
	Density ρ (kg/m ³)	Velocity u (m/s)	Density ρ (kg/m ³)	Velocity u (m/s)
Methyl benzoate	1084.1	1367.36	1083.8	1348.42
1-octanol	800.00	1303.33	798.1	1291.57

On increasing the temperature, the ultrasonic velocity values decrease in the binary liquid mixture. This is probably due to the fact that the thermal energy activates the molecule, which would increase the rate of association of unlike molecules [21]. Similar kinds of results were obtained by earlier workers [22-24].

The ratio $U_{\text{exp}}^2/U_{\text{IMR}}^2$ is used to measure the non-ideality in liquid mixtures, especially in those cases where the properties other than sound velocity are not known. Plots of $U_{\text{exp}}^2/U_{\text{IMR}}^2$ against mole fraction of methyl benzoate + 1-octanol system at different temperatures are given in Fig.1. It is observed from figure that, the value of $U_{\text{exp}}^2/U_{\text{IMR}}^2$ is maximum at the mole fraction of 0.1 for the system at the temperatures 303.15K and 318.15K.

Fig.1 Variation of $U_{\text{exp}}^2/U_{\text{IMR}}^2$ for Methyl benzoate + 1-octanol system.

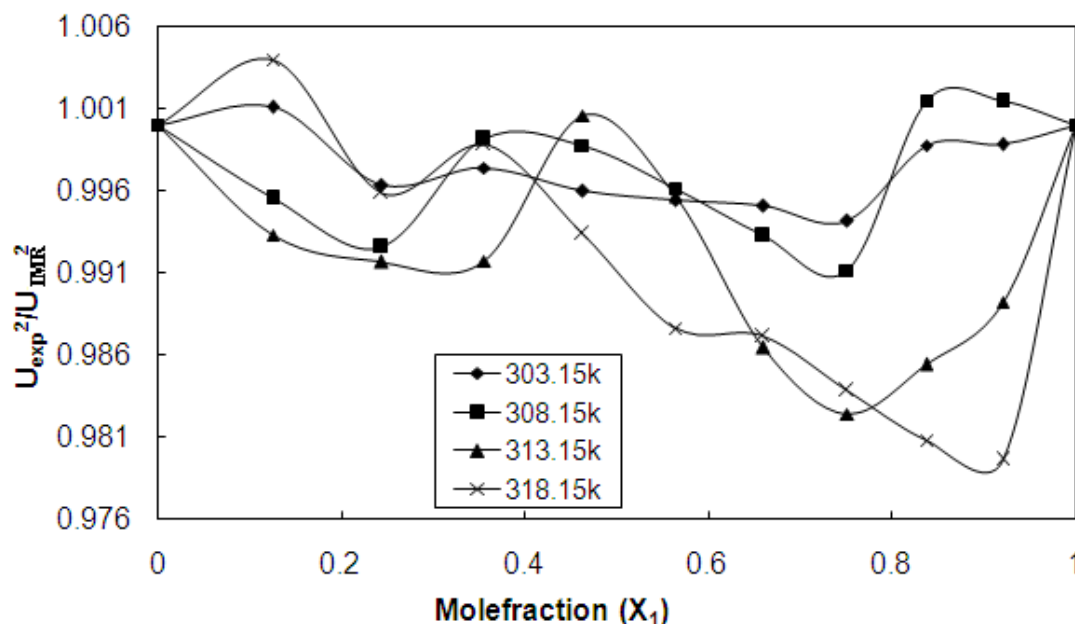


Table-2 Experimental and theoretical values of velocities (m.s^{-1}) in methyl benzoate +1-octanol system at different temperatures

X_1	U_{exp}	U_{NOM}	U_{IMR}	U_{IR}	U_{R}	U_{JR}
303.15 K						
0.0000	1365.00	1365.00	1365.00	1365.00	1365.00	1365.00
0.1258	1370.52	1368.87	1369.77	1371.36	1369.87	1362.17
0.2446	1371.80	1372.74	1374.31	1376.89	1374.47	1360.81
0.3570	1376.84	1376.62	1378.63	1381.74	1378.84	1360.90
0.4634	1380.00	1380.51	1382.75	1386.02	1382.98	1362.44
0.5643	1383.52	1384.41	1386.69	1389.84	1386.92	1365.44
0.6602	1387.05	1388.31	1390.46	1393.26	1390.67	1369.93
0.7514	1390.00	1392.22	1394.06	1396.34	1394.24	1375.97
0.8382	1396.66	1396.14	1397.51	1399.14	1397.64	1383.60
0.9210	1400.00	1400.07	1400.82	1401.68	1400.89	1392.91
1.0000	1404.00	1404.00	1404.00	1404.00	1404.00	1404.00
308.15 K						
0.0000	1326.31	1326.31	1326.31	1326.31	1326.31	1326.31
0.1258	1329.47	1331.31	1332.46	1334.55	1332.60	1324.43
0.2446	1333.33	1336.31	1338.32	1341.72	1338.55	1324.02
0.3570	1343.33	1341.33	1343.91	1348.00	1344.20	1325.09
0.4634	1348.42	1346.37	1349.25	1353.55	1349.57	1327.64
0.5643	1351.76	1351.41	1354.35	1358.50	1354.67	1331.71
0.6602	1354.66	1356.47	1359.24	1362.93	1359.53	1337.33
0.7514	1357.89	1361.55	1363.92	1366.92	1364.16	1344.57
0.8382	1369.41	1366.63	1368.40	1370.54	1368.58	1353.49
0.9210	1373.68	1371.73	1372.71	1373.83	1372.80	1364.21
1.0000	1376.84	1376.84	1376.84	1376.84	1376.84	1376.84
313.15 K						
0.0000	1303.33	1303.33	1303.33	1303.33	1303.33	1303.33
0.1258	1306.66	1309.64	1311.05	1313.78	1311.27	1302.43
0.2446	1312.94	1315.97	1318.43	1322.86	1318.80	1303.05
0.3570	1320.00	1322.32	1325.49	1330.82	1325.95	1305.20
0.4634	1332.63	1328.69	1332.24	1337.86	1332.75	1308.90
0.5643	1335.78	1335.08	1338.71	1344.12	1339.21	1314.19
0.6602	1335.78	1341.49	1344.91	1349.74	1345.37	1321.13
0.7514	1338.94	1347.93	1350.86	1354.79	1351.25	1329.81
0.8382	1346.66	1354.38	1356.58	1359.38	1356.86	1340.32
0.9210	1354.73	1360.86	1362.07	1363.55	1362.23	1352.78
1.0000	1367.36	1367.36	1367.36	1367.36	1367.36	1367.36
318.15 K						
0.0000	1291.57	1291.57	1291.57	1291.57	1291.57	1291.57
0.1258	1301.05	1297.17	1298.46	1300.86	1298.63	1290.16
0.2446	1302.35	1302.78	1305.03	1308.93	1305.33	1290.23
0.3570	1310.52	1308.42	1311.31	1316.01	1311.68	1291.80
0.4634	1312.94	1314.08	1317.31	1322.25	1317.71	1294.88
0.5643	1314.86	1319.75	1323.05	1327.82	1323.45	1299.51
0.6602	1320.00	1325.45	1328.55	1332.80	1328.92	1305.74
0.7514	1323.00	1331.16	1333.82	1337.28	1334.13	1313.64
0.8382	1326.00	1336.89	1338.89	1341.35	1339.11	1323.31
0.9210	1330.00	1342.65	1343.75	1345.04	1343.87	1334.85
1.0000	1348.42	1348.42	1348.42	1348.42	1348.42	1348.42

CONCLUSION

Theoretical evaluations of ultrasonic velocities in binary liquid mixtures are determined, and the validity of different theories is checked. The study gives quite satisfactory results with all the theories and it is observed that out of all the theories Nomoto's theory gives best results followed by ideal mixture relation and Rao's theory in all the systems studied due to the closeness in values obtained with respect to the experiment. The observed deviation of theoretical values of velocity from experimental values is attributed to the presence of intermolecular interactions in the systems studied.

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