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Comparative Study of Experimental and Theoretical Ultrasonic Velocities in Binary Mixtures of Cyclohexanone with Aliphatic Esters at Different Temperatures

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ABSTRACT

Ultrasonic velocity evaluated by various theoretical relations viz., Nomoto, Free Length Theory (FLT), Van deal and Vangeel ideal mixing relation (IMR), Impedance Dependence Relation (IDR), and Junjie in three binary liquid mixtures of cyclohexanone as a common component with aliphatic esters (isopropyl acetate, isobutyl acetate and isoamyl acetate) at 303, 308, 313 and 318K over the entire composition range. An attempt has been made to compare the merits of the relations and the relative applicability of these theories to the present systems have been checked and discussed. The results are explained in terms of intermolecular interactions occurring in these binary systems. The deviation in the variation of U^2_{exp} / U^2_{imx} from unity has also been evaluated for explaining the non-ideality in the mixtures.

***Keywords*:** ultrasonic velocity; binary liquid mixture; aliphatic esters; intermolecular interaction

1. INTRODUCTION

Ultrasonic velocity is one of the important parameters, frequently used to investigate intermolecular interactions in binary liquid mixtures[1-4]. Theoretical evaluation of ultrasonic velocity in binary liquid mixtures and its correlation to study molecular interaction has been successfully done in recent years. Ultrasonic velocities of liquid mixtures are of considerable importance in understanding intermolecular interaction between component molecules, and they find applications in several industrial and technological processes. Ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interactions, present in binary liquid mixtures[5,6]. More over the measurement of ultrasonic velocity gives the valuable information about the physico-chemical behaviour of the liquid mixtures such as molecular association and dissociation. Several relations, semi-empirical formula and theories are available for the theoretical computation of ultrasonic velocity in liquid and liquid mixtures[7-15]. Using the theories available in literature, ultrasonic velocities in liquid mixtures have been calculated and compared with those obtained experimentally. The comparison of theoretical ultrasonic velocities with those obtained

experimentally reveals the nature of interactions between the component molecules in the mixtures.

The aim of the present investigation is to compare the ultrasonic sound velocity in six binary liquid mixtures from various theoretical relations of Nomoto, Free Length Theory (FLT), Van deal and Vangeel ideal mixing relation (IMR), Impedance Dependence Relation (IDR), and Junjie. An attempt has been made to compare the merits of the relations for the binary liquid mixtures investigated at four different temperatures. The relative applicability of these theories to the present systems have been checked and discussed. The results are explained in terms of intermolecular interactions occurring in these binary systems. The deviation in the variation of U^2_{exp} / U^2_{imx} from unity has also been evaluated for explaining the non-ideality the mixtures.

2. EXPERIMENTAL

Three liquid mixtures taken for study are:

System-1: Cyclohexanone + Isopropyl Acetate (CY + IPA)
System-2: Cyclohexanone + Isobutyl Acetate (CY + IBA)
System-3: Cyclohexanone + Isoamyl Acetate (CY + IAA)

All the chemicals used in the present research work are analytical reagent (AR) of minimum assay of 99.9% obtained from E-Merck, Germany and Sd. Fine Chemicals, India, which were used without further purification. The liquid mixtures were prepared by mixing calculated amount of pure liquids. The ultrasonic velocities in the liquid mixtures were measured using a single crystal variable path interferometer operating at a frequency of 2MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of ± 0.1%. The temperature during the experiment was controlled by circulating water around the liquid cell from the thermostatically controlled adequately stirred water bath (accurately ± 0.1 ºC). The densities of pure liquids and liquid mixtures were determined from the weight measurements using 10 ml specific gravity bottle by the standard procedure with an accuracy of ±0.1kg m^{-3}.

3. THEORETICAL ASPECTS

3. 1 Nomoto's Relation

Rao found experimentally that[7], for pure liquids, the ratio of temperature coefficients of sound velocity U and molar volume remains almost constant:

$$\frac{\left(\frac{1}{U}\right)\left(\frac{dU}{dT}\right)}{\left(\frac{1}{V}\right)\left(\frac{dV}{dT}\right)} = -3$$

Where T is the absolute temperature. On Integrating this equation we get

$$VU^{1/3} = cons\tan t = \frac{M}{\rho U^{1/3}} = R$$

Where M is molecular weight and ρ is density. The constant R is called the molar sound velocity or Rao's constant. It was found to be additive i.e., it can be calculated as a sum of increments from the atoms or atom groups in the molecule and from the chemical bonds.

On assuming the additivity of molar sound velocity (R) and no volume change on mixing, Nomoto established the following relation for a liquid mixture

$$R = \frac{M}{\rho U^{1/3}}$$

Where U and ρ are determined experimentally and M is the mean molecular weight in a binary liquid mixture

$$M = \left(X_1 M_1 + X_2 M_2\right)$$

Where X_1 and X_2 are the mole fractions and M_1 and M_2 are molecular weights of constituent components respectively. Simple theoretical treatment gives the following relation

$$U_{Nomoto} = \left[\frac{\left(X_1 R_1 + X_2 R_2\right)}{\left(X_1 V_1 + X_2 V_2\right)}\right]^3 \qquad (1)$$

3. 2. Relation based on Free Length Theory

Jacobson[9] deduce an empirical relation for ultrasonic velocity (U_{FLT}) making use of intermolecular free length (L_f) and density (ρ) as

$$U_{FLT} = \left[\frac{K}{L_{f_{mix}} \rho_{\exp}^{1/2}}\right] \qquad (2)$$

Where K is temperature dependent called Jacobson's constant and the value of K at the working temperatures of the experiment were calculated (MKS units) and they are given below

Temp (K)	303	308	313	318
Value of K	2.075×10^{-6}	2.095×10^{-6}	2.115×10^{-6}	2.135×10^{-6}

3. 3. Ideal Mixing Relation based on the Van Deal and Vangeel Theory

Van Deal and Vangeel [10,54] proposed the ideal mixing theory in the light of assumptions made by Blandamer and Wadding [55], yield the following relation for adiabatic compressibility $(\beta_{ad})_{imix}$

$$(\beta_{ad})_{imix} = \Phi_1 \frac{\gamma_1}{\gamma_{imix}}(\beta_{ad})_1 + \Phi_2 \frac{\gamma_2}{\gamma_{imix}}(\beta_{ad})_2$$

Where Φ_1 and Φ_2 volume fractions of the liquids 1 and 2, γ_1 and γ_2 are the ratios of specific heats of the respective liquids. This relation holds good if the mixture is ideal and if $\gamma_{1=}\ \gamma_{2=}\ \gamma_{imix}$. Using the additional assumption that $V_1=V_2$ the above equation can be transformed into a linear combination of mole fraction X_1 and X_2,

$$(\beta_{ad})_{imix} = X_1(\beta_{ad})_1 + X_2(\beta_{ad})_2$$

On the basis of this equation, Van Deal and Vangeel obtained the relation for ultrasonic velocity in liquid mixtures as

$$U_{IMR} = \left[\frac{1}{X_1M_1 + X_2M_2}\right]^{\frac{1}{2}} \left[\frac{X_1}{M_1U_1^2} + \frac{X_2}{M_2U_2^2}\right]^{\frac{-1}{2}} \qquad (3)$$

Where U_1 and U_2 are the ultrasonic velocities of the pure liquid components.

3. 4. Impedance Dependence Relation

The ultrasonic velocity can be evaluated by the Impedance Dependence Relation[11] of the following form

$$U_{IDR} = \frac{X_1Z_1 + X_2Z_2}{X_1\rho_1 + X_2\rho_2} \qquad (4)$$

Where X_1 and X_2 are the mole fractions, ρ_1 and ρ_2 are the densities and Z_1 and Z_2 are the acoustic impedances of the liquid components.

3. 5. Junjie's Relation

Junjie's Relation[12] for ultrasonic velocity is given by

$$U_{Junjie} = \left[\frac{X_1V_1 + X_2V_2}{(X_1M_1 + X_2M_2)^{1/2}}\right]\left[\frac{X_1V_1}{\rho_1U_1^2} + \frac{X_2V_2}{\rho_2U_2^2}\right]^{-1/2} \qquad (5)$$

Where, 1 & 2 represents the first and second component of the liquid mixture and the other symbols have their usual meanings.

3. 6. Percentage Deviation

The percentage deviation is calculated from the relation

$$PercentageDeviation = \sum \frac{\left(U_{mix(obs)} - U_{mix(cal)}\right)}{U_{mix(obs)}} X100 \qquad (6)$$

Here, $U_{mix(obs)}$ is experimental value of ultrasonic velocity and $U_{mix(cal)}$ is computed value of ultrasonic velocity. The worst-case error is the maximum value of deviation of the theoretical values from experimental values of ultrasonic velocity.

3. 7. Degree of interaction, α

The deviation of the ratio U^2_{exp} / U^2_{imx} from unity is called degree of interaction, α.

4. RESULT AND DISCUSSION

The theoretical relations used to calculate ultrasonic velocity in all the above liquid mixtures are (i) Nomoto's relation, (ii) Free Length Theory, (iii) Van Deal and Vangeel Ideal Mixture Relation, (IMR) (iv) Impedance Dependence Relation (IDR) and (v) Junjie's Relation at the temperatures 303, 308, 313 and 318K and the values along with the experimental values are given in the Tables from 1.1 to 1.3. Also the validity of different theoretical formulae is checked by percentage deviation for all the mixtures and at all the temperatures are shown.

It is observed from the tabulated values that the theoretical values of ultrasonic velocities evaluated by the above mentioned relations show deviations from the experimental values. The reason for the deviation maybe the limitations and approximations incorporated in these theories. The effect of volume change due to mixing was not considered in the Nomoto's relation. That is interaction between the molecules was not taken into account. In Free Length theory, it was assumed that the molecules are of spherical shape but it is not true at all times. In the case of Ideal mixing relation, it was assumed that, the ratio of specific heats and volumes are equal. Again no molecular interactions were considered.

Upon mixing two liquids, the interaction between the molecules of the two liquids take place because of the presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced-dipole interactions. Thus, the observed deviation of theoretical values of velocity from the experimental values shows the molecular interactions between the unlike molecules in the liquid mixture.

4. 1. Cyclohexanone + Isopropyl acetate (CY + IPA)

Tables 1. show that there is a slight deviation between experimental and theoretical values calculated by Junjie's relation, followed by ideal mixing relation and Nomoto's relation. More over the deviation in values evaluated by Junjie's relation increases with increase in temperature except at 308 K, at the same time the deviations observed for the values evaluated by other theories are continuously increase with increase in temperature. However, Junjie's relation provides the best result than the other relations., where as a large deviations are observed in Free length theory and Impedance dependence relation.

4. 2. Cyclohexanone + Isobutyl acetate (CY + IBA)

A close look at Table 2 reveals that a very slight deviation for the values obtained by Junjie's relation, increase with increase in temperature.

Table 1. Experimental and Theoretical values of Ultrasonic velocityand Percentage of Deviation at different temperatures for the binary liquid mixture- I (Cyclohexanone + Isopropyl acetate).

Mole fraction of CY	Exp. Velocity	Theoritical velocity					Percentage Deviation					$\frac{U^2}{U^2_{imx}}$
X_1	U_{exp}	U_{Nom}	U_{FLT}	U_{IMR}	U_{IDR}	U_{Junjie}	U_{Nom}	U_{FLT}	U_{IMR}	U_{IDR}	U_{Jun}	
303K												
0.0000	1096.9	1096.9	1096.9	1096.9	1096.9	1096.9	0.00	0.0	0.00	0.00	0.00	1.0000
0.1123	1108.9	1125.6	1092.4	1125.6	1134.7	1116.8	1.48	-1.5	1.48	2.28	0.71	0.9704
0.2218	1123.9	1154.9	1091.3	1154.9	1170.9	1138.4	2.69	-2.9	2.69	4.01	1.28	0.9469
0.3284	1141.1	1184.8	1092.3	1184.7	1205.4	1161.9	3.69	-4.4	3.68	5.34	1.79	0.9275
0.4321	1159.1	1215.1	1094.9	1215.1	1238.3	1187.6	4.61	-5.8	4.60	6.40	2.40	0.9099
0.5329	1192.2	1245.9	1115.5	1245.8	1269.7	1215.6	4.31	-6.8	4.30	6.10	1.92	0.9156
0.6312	1230.8	1277.3	1146.4	1277.2	1299.8	1246.4	3.64	-7.3	3.63	5.31	1.25	0.9286
0.7270	1270.8	1309.2	1185.4	1309.1	1328.6	1280.4	2.93	-7.1	2.92	4.35	0.75	0.9423
0.8202	1313.2	1341.5	1236.3	1341.4	1356.1	1318.1	2.11	-6.2	2.10	3.16	0.37	0.9583
0.9113	1359.1	1374.5	1306.4	1374.4	1382.6	1360.4	1.12	-4.0	1.11	1.70	0.10	0.9777
1.0000	1408.0	1408.0	1408.0	1408.0	1408.0	1408.0	0.00	0.0	0.00	0.00	0.00	1.0000
308K												
0.0000	1058.8	1058.8	1058.8	1058.8	1058.8	1058.8	0.00	0.00	0.00	0.00	0.00	1.0000
0.1123	1072.1	1087.1	1057.5	1087.1	1096.3	1078.2	1.38	-1.3	1.38	2.21	0.57	0.9725
0.2218	1085.5	1116.1	1057.5	1116.0	1132.2	1099.4	2.74	-2.6	2.73	4.12	1.27	0.9460
0.3284	1101.5	1145.5	1060.2	1145.4	1166.4	1122.5	3.84	-3.8	3.83	5.56	1.87	0.9246
0.4321	1120.8	1175.5	1067.2	1175.4	1199.0	1147.7	4.66	-5.0	4.64	6.52	2.34	0.9092
0.5329	1151.9	1206.0	1087.4	1205.8	1230.1	1175.3	4.49	-5.9	4.47	6.35	1.99	0.9124
0.6312	1188.9	1237.1	1118.3	1236.9	1259.8	1205.8	3.89	-6.3	3.88	5.63	1.40	0.9238
0.7270	1228.6	1268.7	1157.3	1268.5	1288.3	1239.5	3.16	-6.1	3.14	4.63	0.88	0.9380
0.8202	1272.4	1300.8	1209.5	1300.6	1315.5	1277.0	2.18	-5.1	2.17	3.28	0.36	0.9570
0.9113	1318.8	1333.5	1277.7	1333.4	1341.7	1319.1	1.10	-3.2	1.09	1.70	0.02	0.9781
0.0000	1366.8	1366.8	1366.8	1366.8	1366.8	1366.8	0.00	0.00	0.00	0.00	0.00	1.0000
313K												
0.0000	1037.9	1037.9	1037.9	1037.9	1037.9	1037.9	0.00	0.0	0.00	0.00	0.00	1.0000
0.1123	1048.2	1066.1	1037.1	1066.1	1075.7	1057.1	1.38	-1.3	1.38	2.21	0.57	0.9725
0.2218	1061.2	1095.0	1038.3	1095.0	1111.8	1078.0	2.74	-2.6	2.73	4.12	1.22	0.9460
0.3284	1077.2	1124.5	1043.1	1124.5	1146.1	1100.9	3.84	-3.8	3.83	5.56	1.81	0.9246
0.4321	1096.4	1154.6	1051.0	1154.5	1178.8	1126.0	4.66	-5.0	4.64	6.52	2.34	0.9092
0.5329	1128.5	1185.1	1072.4	1185.0	1210.0	1153.5	4.49	-5.9	4.47	6.35	1.92	0.9124
0.6312	1165.6	1216.3	1103.0	1216.1	1239.8	1183.9	3.89	-6.3	3.88	5.63	1.48	0.9238
0.7270	1205.2	1248.0	1140.1	1247.8	1268.3	1217.8	3.16	-6.1	3.14	4.63	0.83	0.9380
0.8202	1249.6	1280.3	1191.4	1280.1	1295.6	1255.6	2.18	-5.1	2.17	3.28	0.36	0.9570
0.9113	1295.6	1313.2	1256.6	1313.1	1321.7	1298.3	1.10	-3.2	1.09	1.70	0.02	0.9781
1.0000	1346.8	1346.8	1346.8	1346.8	1346.8	1346.8	0.00	0.0	0.00	0.00	0.00	1.0000
318K												
0.0000	1019.0	1019.0	1019.0	1019.0	1019.0	1019.0	0.00	0.0	0.00	0.00	0.00	1.0000
0.1123	1026.6	1047.1	1017.2	1047.2	1057.0	1037.8	1.68	-1.0	1.68	2.56	0.84	0.9665
0.2218	1038.8	1075.9	1019.0	1076.0	1093.3	1058.5	3.09	-2.2	3.09	4.55	1.56	0.9391
0.3284	1055.8	1105.3	1024.5	1105.4	1127.8	1081.1	4.21	-3.2	4.20	6.01	2.15	0.9176
0.4321	1074.8	1135.3	1032.4	1135.4	1160.6	1106.0	5.04	-4.3	5.03	6.99	2.62	0.9018
0.5329	1107.1	1165.9	1054.4	1166.0	1191.8	1133.4	4.77	-5.2	4.76	6.74	2.16	0.9068
0.6312	1143.8	1197.1	1084.9	1197.1	1221.6	1163.8	4.16	-5.6	4.15	5.99	1.55	0.9185
0.7270	1184.1	1229.0	1122.7	1229.0	1250.1	1197.7	3.43	-5.7	3.42	4.98	1.03	0.9327
0.8202	1228.4	1261.4	1173.6	1261.4	1277.3	1235.8	2.40	-4.8	2.38	3.55	0.48	0.9527
0.9113	1276.2	1294.6	1239.5	1294.6	1303.4	1279.0	1.34	-3.1	1.33	1.97	0.21	0.9733
1.0000	1328.4	1328.4	1328.4	1328.4	1328.4	1328.4	0.00	0.0	0.00	0.00	0.00	1.0000

Table 2. Experimental and Theoretical values of Ultrasonic velocityand Percentage of Deviation at different temperatures for the binary liquid mixture- II (Cyclohexanone + Isobutyl acetate).

Mole fraction of CY	Exp. Velocity	Theoritical velocity					Percentage Deviation					$\frac{U^2}{U^2_{imx}}$
X_1	U_{exp}	U_{Nom}	U_{FLT}	U_{IMR}	U_{IDR}	U_{Junjie}	U_{Nom}	U_{FLT}	U_{IMR}	U_{IDR}	U_{Jun}	
303K												
0.0000	1134.8	1134.8	1134.8	1134.8	1134.8	1134.8	0.00	0.00	0.00	0.00	0.00	1.0000
0.1259	1152.6	1160.3	1135.7	1164.1	1172.1	1153.0	0.66	-1.4	0.99	1.66	0.03	0.9802
0.2452	1169.2	1186.3	1136.8	1193.1	1206.6	1172.7	1.44	-2.8	2.00	3.10	0.30	0.9602
0.3579	1185.6	1212.6	1138.7	1221.1	1238.5	1194.0	2.23	-4.1	2.91	4.27	0.70	0.9426
0.4642	1201.7	1239.3	1138.7	1249.5	1268.0	1216.9	3.03	-5.5	3.83	5.22	1.25	0.9248
0.5652	1219.6	1266.5	1144.5	1277.1	1295.4	1242.0	3.70	-6.5	4.50	5.85	1.80	0.9119
0.6610	1256.4	1294.0	1175.0	1304.4	1321.0	1269.2	2.90	-6.9	3.68	4.89	1.01	0.9277
0.7521	1296.1	1321.9	1216.4	1331.0	1344.9	1299.0	1.95	-6.5	2.62	3.63	0.22	0.9481
0.8389	1333.9	1350.2	1265.0	1356.4	1367.2	1331.7	1.20	-5.4	1.65	2.44	-0.1	0.9670
0.9213	1371.1	1378.9	1328.1	1382.6	1388.2	1367.9	0.56	-3.2	0.83	1.23	-0.2	0.9833
1.0000	1408.0	1408.0	1408.0	1408.0	1408.0	1408.0	0.00	0.00	0.00	0.00	0.00	1.0000
308K												
0.0000	1104.3	1104.3	1104.3	1104.3	1104.3	1104.3	0.00	0.00	0.00	0.00	0.00	1.0000
0.1259	1120.4	1128.8	1105.4	1132.5	1140.1	1121.9	0.74	-1.3	1.07	1.72	0.13	0.9786
0.2452	1134.8	1153.8	1107.0	1160.4	1173.2	1140.9	1.65	-2.5	2.20	3.27	0.53	0.9563
0.3579	1148.6	1179.2	1108.6	1187.3	1203.8	1161.4	2.59	-3.6	3.25	4.59	1.10	0.9358
0.4642	1162.5	1204.8	1110.0	1214.6	1232.2	1183.5	3.51	-4.7	4.29	5.65	1.78	0.9159
0.5652	1181.4	1230.9	1120.4	1241.0	1258.6	1207.6	4.02	-5.4	4.80	6.13	2.17	0.9061
0.6610	1213.8	1257.4	1146.1	1267.3	1283.2	1233.8	3.46	-5.8	4.22	5.40	1.62	0.9172
0.7521	1251.8	1284.2	1184.5	1292.9	1306.1	1262.5	2.52	-5.6	3.18	4.16	0.84	0.9373
0.8389	1290.6	1311.3	1229.6	1317.2	1327.6	1293.8	1.58	-4.9	2.02	2.79	0.25	0.9599
0.9213	1329.8	1338.8	1290.2	1342.5	1347.8	1328.4	0.67	-3.0	0.94	1.33	-0.1	0.9811
1.0000	1366.8	1366.8	1366.8	1366.8	1366.8	1366.8	0.00	0.00	0.00	0.00	0.00	1.0000
313K												
0.0000	1087.0	1087.0	1087.0	1087.0	1087.0	1087.0	0.00	0.00	0.00	0.00	0.00	1.0000
0.1259	1097.2	1111.1	1087.4	1114.9	1122.6	1104.0	1.25	-0.8	1.59	2.26	0.62	0.9684
0.2452	1110.2	1135.7	1088.4	1142.5	1155.6	1122.6	2.24	-2.0	2.82	3.93	1.10	0.9442
0.3579	1125.2	1160.7	1091.4	1169.1	1186.0	1142.6	3.06	-3.0	3.75	5.12	1.53	0.9262
0.4642	1140.4	1186.0	1094.6	1196.1	1214.0	1164.4	3.85	-4.1	4.66	6.06	2.06	0.9089
0.5652	1158.5	1211.8	1105.0	1222.3	1240.1	1188.1	4.40	-4.8	5.22	6.58	2.49	0.8982
0.6610	1190.0	1238.0	1128.8	1248.3	1264.4	1214.0	3.88	-5.4	4.67	5.88	1.97	0.9086
0.7521	1226.2	1264.6	1162.8	1273.6	1287.1	1242.4	3.03	-5.4	3.72	4.73	1.30	0.9268
0.8389	1265.6	1291.5	1208.0	1297.7	1308.2	1273.6	2.01	-4.7	2.47	3.26	0.63	0.9510
0.9213	1306.6	1318.9	1267.6	1322.7	1328.1	1308.2	0.93	-3.0	1.22	1.62	0.12	0.9757
1.0000	1346.8	1346.8	1346.8	1346.8	1346.8	1346.8	0.00	0.00	0.00	0.00	0.00	1.0000
318K												
0.0000	1069.4	1069.4	1069.4	1069.4	1069.4	1069.4	0.00	0.00	0.00	0.00	0.00	1.0000
0.1259	1078.6	1093.2	1068.8	1097.2	1105.2	1086.0	1.34	-0.9	1.69	2.40	0.68	0.9663
0.2452	1089.8	1117.6	1070.4	1124.6	1138.2	1104.1	2.49	-1.8	3.10	4.25	1.30	0.9389
0.3579	1101.8	1142.4	1073.3	1151.2	1168.5	1123.8	3.55	-2.6	4.29	5.71	1.96	0.9159
0.4642	1117.8	1167.6	1078.1	1178.1	1196.5	1145.3	4.26	-3.6	5.12	6.58	2.40	0.9001
0.5652	1136.1	1193.3	1087.7	1204.2	1222.5	1168.7	4.79	-4.4	5.66	7.07	2.79	0.8899
0.6610	1163.8	1219.4	1107.2	1230.1	1246.7	1194.5	4.56	-5.1	5.39	6.65	2.57	0.8949
0.7521	1201.1	1246.0	1141.4	1255.4	1269.2	1222.9	3.60	-5.2	4.32	5.37	1.78	0.9153
0.8389	1241.4	1272.9	1185.0	1279.4	1290.2	1254.2	2.48	-4.7	2.97	3.78	1.02	0.9413
0.9213	1282.2	1300.4	1244.7	1304.3	1309.9	1289.2	1.40	-3.0	1.70	2.11	0.54	0.9662
1.0000	1328.4	1328.4	1328.4	1328.4	1328.4	1328.4	0.00	0.00	0.00	0.00	0.00	1.0000

Table 3. Experimental and Theoretical values of Ultrasonic velocityand Percentage of Deviation at different temperatures for the binary liquid mixture- II (Cyclohexanone + Isoamyl acetate)

Mole fraction of CY	Exp. Velocity	Theoritical velocity					Percentage Deviation					$\frac{U^2}{U^2_{imx}}$
X_1	U_{exp}	U_{Nom}	U_{FLT}	U_{IMR}	U_{IDR}	U_{Junjie}	U_{Nom}	U_{FLT}	U_{IMR}	U_{IDR}	U_{Jun}	
303K												
0.0000	1172.4	1172.4	1172.4	1172.4	1172.4	1172.4	0.00	0.00	0.00	0.00	0.00	1.0000
0.1389	1191.9	1194.6	1176.5	1196.5	1207.8	1188.7	0.22	-1.3	0.38	1.31	-0.2	0.9922
0.2667	1211.4	1217.2	1181.2	1220.7	1239.6	1206.4	0.47	-2.5	0.76	2.27	-0.4	0.9847
0.3842	1230.8	1240.0	1187.1	1244.8	1268.1	1225.3	0.74	-3.6	1.12	2.94	-0.4	0.9775
0.4923	1251.2	1263.1	1197.9	1268.7	1293.8	1245.5	0.94	-4.4	1.38	3.29	-0.4	0.9725
0.5928	1275.1	1286.6	1217.1	1292.5	1317.2	1267.4	0.89	-4.7	1.35	3.20	-0.6	0.9731
0.6859	1301.9	1310.3	1241.1	1316.1	1338.6	1291.1	0.64	-4.8	1.08	2.74	-0.8	0.9784
0.7725	1328.8	1334.2	1271.1	1339.4	1358.1	1316.6	0.41	-4.5	0.79	2.16	-0.9	0.9840
0.8536	1355.2	1358.6	1307.1	1362.6	1376.1	1344.5	0.25	-3.6	0.54	1.52	-0.7	0.9890
0.9292	1381.8	1383.1	1353.3	1385.4	1392.7	1374.8	0.09	-2.1	0.26	0.78	-0.5	0.9947
1.0000	1408.0	1408.0	1408.0	1408.0	1408.0	1408.0	0.00	0.00	0.00	0.00	0.00	1.0000
308K												
0.0000	1155.6	1155.6	1155.6	1155.6	1155.6	1155.6	0.00	0.00	0.00	0.00	0.00	1.0000
0.1389	1168.6	1175.5	1156.5	1176.6	1187.4	1170.4	0.59	-1.0	0.68	1.58	0.16	0.9863
0.2667	1184.1	1195.8	1157.4	1197.9	1215.9	1186.4	0.98	-2.3	1.15	2.61	0.20	0.9769
0.3842	1200.4	1216.4	1161.9	1219.3	1241.5	1203.5	1.31	-3.3	1.55	3.31	0.26	0.9691
0.4923	1218.0	1237.1	1168.4	1240.7	1264.5	1221.8	1.54	-4.2	1.83	3.68	0.31	0.9637
0.5928	1239.6	1258.1	1184.3	1262.1	1285.5	1241.6	1.47	-4.6	1.78	3.57	0.16	0.9646
0.6859	1264.0	1279.3	1205.2	1283.3	1304.6	1262.8	1.20	-4.8	1.50	3.11	-0.1	0.9700
0.7725	1288.8	1300.8	1231.7	1304.4	1322.1	1285.7	0.92	-4.6	1.20	2.52	-0.2	0.9761
0.8536	1314.2	1322.6	1266.5	1325.4	1338.2	1310.6	0.63	-3.7	0.85	1.80	-0.2	0.9830
0.9292	1340.0	1344.6	1310.0	1346.8	1353.1	1337.5	0.34	-2.2	0.46	0.96	-0.1	0.9907
1.0000	1366.8	1366.8	1366.8	1366.8	1366.8	1366.8	0.00	0.00	0.00	0.00	0.00	1.0000
313K												
0.0000	1137.6	1137.6	1137.6	1137.6	1137.6	1137.6	0.00	0.00	0.00	0.00	0.00	1.0000
0.1389	1147.2	1157.3	1135.1	1158.4	1169.1	1152.2	0.87	-1.0	0.97	1.87	0.43	0.9806
0.2667	1161.2	1177.4	1134.5	1179.6	1197.4	1167.9	1.37	-2.3	1.56	3.02	0.58	0.9689
0.3842	1177.2	1197.7	1136.1	1200.8	1222.8	1184.8	1.71	-3.6	1.96	3.73	0.64	0.9610
0.4923	1195.4	1218.2	1142.7	1221.9	1245.6	1202.9	1.87	-4.6	2.17	4.03	0.62	0.9569
0.5928	1216.5	1239.0	1156.3	1243.1	1266.4	1222.4	1.81	-5.2	2.14	3.94	0.48	0.9575
0.6859	1240.0	1260.0	1175.8	1264.2	1285.3	1243.4	1.59	-5.4	1.91	3.53	0.27	0.9620
0.7725	1264.2	1281.3	1203.2	1285.1	1302.6	1266.1	1.33	-5.0	1.62	2.95	0.15	0.9677
0.8536	1289.6	1302.9	1237.0	1305.9	1318.6	1290.8	1.02	-4.2	1.24	2.20	0.09	0.9751
0.9292	1316.6	1324.7	1283.0	1326.4	1333.2	1317.6	0.61	-2.6	0.74	1.25	0.07	0.9851
1.0000	1346.8	1346.8	1346.8	1346.8	1346.8	1346.8	0.00	0.00	0.00	0.00	0.00	1.0000
318K												
0.0000	1112.0	1112.0	1112.0	1112.0	1112.0	1112.0	0.00	0.00	0.00	0.00	0.00	1.0000
0.1389	1119.6	1132.2	1106.9	1133.9	1144.7	1126.8	1.12	-1.1	1.26	2.19	0.64	0.9748
0.2667	1133.8	1152.9	1106.9	1156.0	1174.0	1142.8	1.66	-2.4	1.92	3.43	0.78	0.9618
0.3842	1150.8	1173.8	1109.4	1178.1	1200.3	1160.0	1.96	-3.7	2.32	4.13	0.79	0.9540
0.4923	1169.8	1195.0	1117.5	1200.0	1224.0	1178.5	2.11	-4.6	2.52	4.42	0.73	0.9501
0.5928	1192.1	1216.5	1131.7	1221.9	1245.5	1198.5	2.00	-5.3	2.44	4.28	0.54	0.9516
0.6859	1215.8	1238.3	1150.5	1243.6	1265.0	1220.2	1.81	-5.6	2.24	3.89	0.36	0.9556
0.7725	1241.1	1260.3	1177.5	1265.1	1282.9	1243.8	1.52	-5.3	1.90	3.25	0.21	0.9623
0.8536	1267.4	1282.8	1211.2	1286.5	1299.3	1269.5	1.20	-4.6	1.48	2.45	0.16	0.9704
0.9292	1296.2	1305.4	1260.9	1307.5	1314.4	1297.6	0.70	-2.7	0.87	1.38	0.10	0.9826
1.0000	1328.4	1328.4	1328.4	1328.4	1328.4	1328.4	0.00	0.00	0.00	0.00	0.00	1.0000

The deviation in values calculated by Nomoto's relation and Ideal mixing relation follows the deviation of the values obtained by Junjie's relation.

The evaluated values by the mentioned theories have a little more deviation at middle concentrations is observed. For this binary mixture also larger deviations are observed for the values obtained by Free length theory and Impedance dependence relation. In this case, the Junjie's relation provides more appropriate result than the other relations.

4. 3. Cyclohexanone + Isoamyl acetate (CY + IAA)

A perusal of Table 3 indicate that the values calculated on the basis of Junjie's relation agree closely with the experimental values. Here the deviations are negative at 303K and at higher concentrations at 308k, the deviations are positive at the other two temperatures. The values predicted by FLT and IDR show an appreciable deviation from the experimental values and the deviations are also large and negative in the case of FLT, where as positive in case of IDR values. The values evaluated by Nomoto's relation give a close approximation after the values obtained by Junjie's relation. The values obtained by IMR relation follow the values obtained by Junjie's relation and Nomoto's relation respectively. The percentage deviations are positive for the values obtained by both Nomoto and IMR relations.

Velocities were determined on the basis of different theories and relations are discussed by other researchers earlier[13-16] and the validity of different theoretical formulae is checked by percentage deviation at different temperatures. As per the earlier studies, the limitations and approximations incorporated in these theories are responsible for the deviations between theoretical and experimental values.

In the present study, in the three binary mixtures viz., cyclohexanone with aliphatic esters, the velocities predicted by the Junjie's relation are in better agreement than the other relations. When two liquids are mixed various types of forces play a vital role due to interactions. Thus, the observed deviations between theoretical and experimental values of velocity shows that there is molecular interaction between the unlike molecules in the liquid mixture. The FLT assumes that molecules are rigid spheres with no interaction between them and it is not valid in all the cases. Hence the deviation from the experimental ultrasonic velocity values is maximum in the FLT. It is assumed that all the molecules are spherical in shape, which is not true every time. According to Nomoto's theory, it is assumed that the volume does not change on mixing. Therefore, no interaction between the components of liquid mixtures has been taken into account. Similarly, the assumption for the formation of ideal mixing relation is that, the ratios of specific heats of ideal mixtures and the volumes are also equal. Again, no molecular interaction is taken into account. But on mixing two liquids, the interaction takes place because of various forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. Thus the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture

The deviation of the ratio U^2_{exp} / U^2_{imx} from unity (degree of interaction, α) and its variation as a function of mole fraction of cyclohexanone is a direct measure of the non-ideality of the system as a consequence of association or other type of interactions. The positive values of α in all the system clearly indicate the existence of tendency for the formation of association in mixture through hydrogen bonded complexes[17,18]. Figs. 1, 2 and 3 represent the variation of U^2_{exp} / U^2_{imx} with mole fraction of cyclohexanone. It is observed that the curves are similar in all the three systems with minimum approximately at 0.5 mole fraction of cyclohexanone at all temperatures. They decrease with increase in temperature.

The trend of the curves reveal a fact that the mixtures tend move towards ideality up to the middle mole fraction of cyclohexanone.

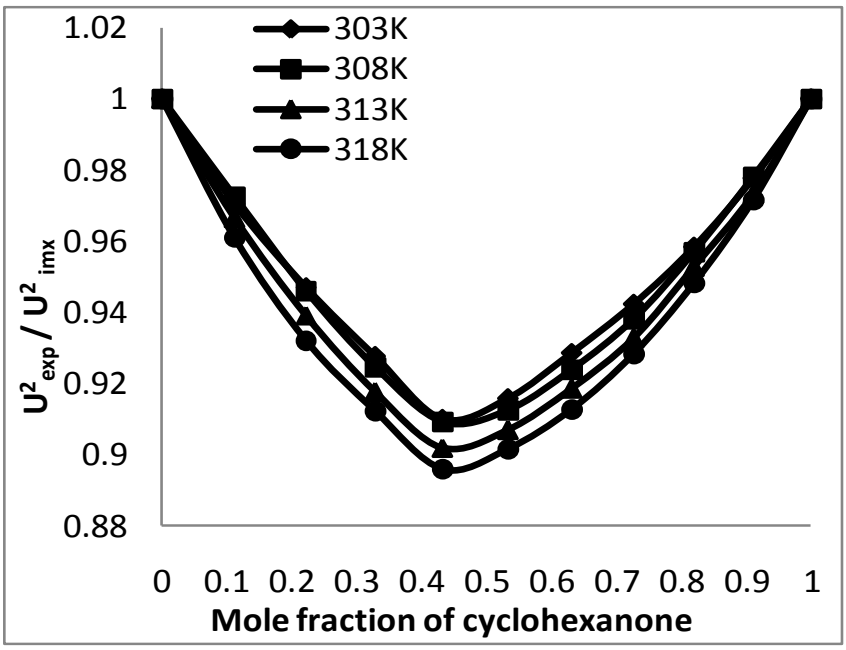

Figure 1. variation of U^2_{exp} / U^2_{imx} with mole fraction of cyclohexanone for CY+IPA

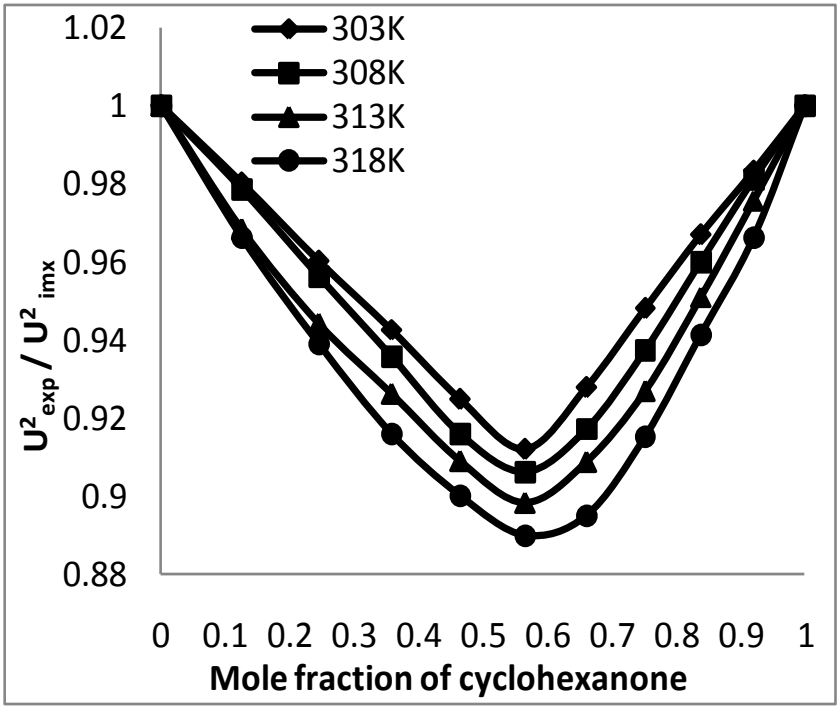

Figure 2. variation of U^2_{exp} / U^2_{imx} with mole fraction of cyclohexanone for CY+IBA.

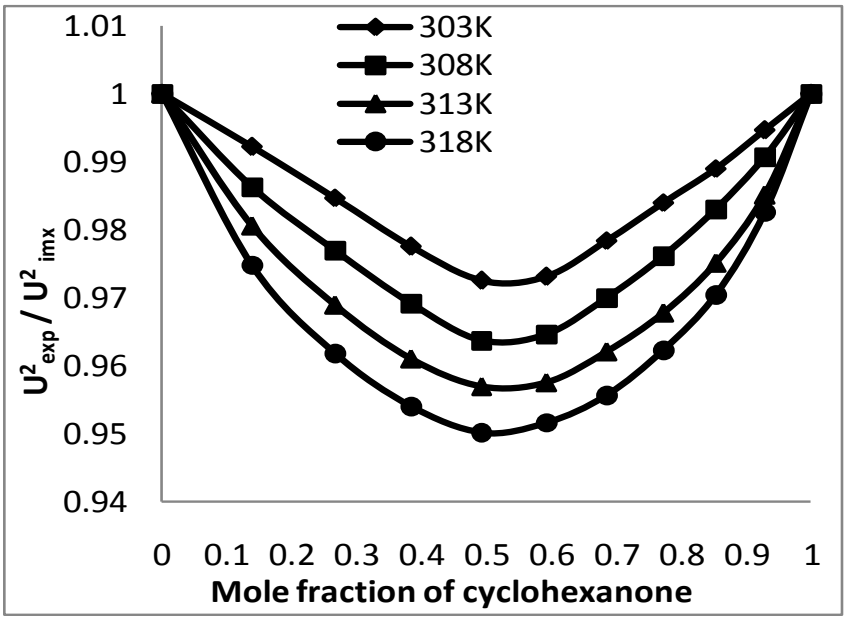

Figure 3. variation of U^2_{exp} / U^2_{imx} with mole fraction of cyclohexanone for CY+IAA.

5. CONCLUSION

In the binary liquid mixtures, Cyclohexanone + Isopropyl acetate, Cyclohexanone + Isobutyl acetate, Cyclohexanone + Isoamyl acetate it is observed that there is a close agreement between experimental and theoretical values calculated by Junjie's relation, followed by Ideal Mixing Relation and Nomoto's relation.It may be concluded that out of the five theories and relations discussed above, the Junjie's relation, Impedance Dependence Relation and Nomoto's relation for estimation of velocities show good agreement with the respective measured values of ultrasonic velocity.

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Biography

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