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Theories of ultrasonic velocities and their application in binary liquid mixtures of o-chlorophenol with some aliphatic esters at different temperatures

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ABSTRACT

Ultrasonic velocities and densities of the binary liquid mixtures of o-chlorophenol with different aliphatic esters like methylacetate, ethylacetate and butylacetate are measured at temperatures 303.15, 308.15, 313.15 and 308.15K and atmospheric pressure. Theoretical velocities have been evaluated by using Nomoto (NOM), impedance (IMP), Van Dael and Vangeel (VDV), Junjie (JUN) and Rao's specific velocity (RAO) models. A good agreement is found between experimental and theoretical values. U^2_{exp} / U^2_{imx} *has also been evaluated for non-ideality in the mixtures. Chi-square test for the goodness of the fit is applied to understand the relative applicability of these theories to the present systems. The results are discussed in terms of intermolecular interactions between the component molecules in these binary liquid mixtures.*

Keywords: o-chlorophenol, theoretical velocities, ultrasonics, Chi-square test, interaction parameter.

INTRODUCTION

The measurement of ultrasonic velocities finds extensive applications in understanding Physico-chemical behaviour of liquid mixtures [1-3]. The molecular interactions in pure and binary liquid mixtures have been studied by measuring ultrasonic velocities by several researchers [4-12]. The theoretical values of ultrasonivc velocity have been evaluated by using Nomoto [13] , impedance relation [14], Van Deal and Vangeel ideal mix relations [15], Junjie [16] and Rao's Specific velocity relation [17] and the results are interpreted in terms of molecular interactions.The present work is a continuation of our research programme on a comparison of experimental ultrasonic velocity with various theoretical models for the binary mixtures of several systems at various temperatures [18-22].

In this paper, we report the experimental and theoretical ultrasonic velocities of the binary liquid mixtures of o-chlorophenol (OCP) with methylacetate (MA), ethylacetate (EA) and n-butylacetate (BA) evaluated by using various theories such as Nomoto, impedance relation, Van Dael and Vangeel, , Junjie's and Rao's specific velocity relation at 303.15-318.15K over entair composition range. Further, a comparative study of theoretical results with experimental values using Chi-square test and the study of molecular interactions from the deviation (**α**) in the value of U^2_{exp} / U^2_{imx} (from unity) have also been studied. Of these models, Nomoto relation and Impdance relation were reported to be in good agreement with the experimental results for the binary mixture at all temperatures under study and the results are interpreted in terms of intermolecular interactions between the binary component liquid mixtures.

MATERIALS AND METHODS

The commercially available pure solvents were used in the present investigation. OCP (Merk > 99%) and MA,EA,BA of AR grade procured from S.D fine chemicals (India) were purified by the standard methods described by A.Weissberger [23] and the purity of the chemicals was assessed by comparing their measured densities (ρ) and ultrasonic velocities (U) which were in good agreement with literature values. The mixtures were prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1\times 10^{-7}$ Kg and were stored in air-tight glass bottles. The uncertainty in the mole fraction was estimated to be less than $\pm 1\times10^{-4}$. It was ensured that the components were adequately mixed before being transferred in to the apparatus. The required properties were measured within one day of the mixture preparation.

The densities, ρ, of pure liquids and their mixtures determined using a $10^{-5}m^3$ Double - arm pycnometer, and the values from triplicate replication at each temperature are reproducible within 2 x 10^{-1}kg m^3 and the uncertainty in the measurement of density is found to be 2 parts in 10^4 parts. The reproducibility in mole fractions was within ±0.0002 Temperature control for the measurement of viscosity and density is achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ±0.01 K, using a proportional temperature controller. Adequate precautions were taken to minimize evaporation losses during the actual measurements. The ultrasonic velocity of sound (U) is measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi model F05) operating at 2 MHz. The measured speeds of sound have a precision of 0.8 m. sec^{-1} and an uncertainty less than ± 0.1 m. sec^{-1}. The temperature stability was maintained within ± 0.01K.by circulating water bath around the measuring cell through a pump.

THEORETICAL CONSIDERATIONS:

1.1 Nomoto theory : Nomoto's empirical formula is based on the assumption of the linear dependence of the molecular sound velocity on concentration and the additivity of the molar volume in the liquid mixture. The sound velocity U is given by

$$U = \left[\frac{\sum_{i=1}^{n} x_i R_i}{\sum_{i=1}^{n} x_i V_i}\right]^3$$

where the molar sound velocity $R = x_1R_1+x_2R_2.$

Hence, ultrasonic velocity (U) is given by

$$U = \left[\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right]^3 \qquad \text{..............} (1)$$

In the above equation $R_i = (M_i/\rho_i)\, U_i^{1/3} = V_i\, (U_i)^{1/3}$

1.2 Impedance relation: The specific acoustic impedance of the pure liquids are used for evaluating the ultrasonic velocity in the liquid mixtures by the following relation:

$$U= \sum x_iZ_i/\sum x_{ii} \qquad \text{.............} (2)$$

where Z_i is acoustic impedance and ρ_i is the density of the mixture.

1.3 Van Dael and Vangeel relation: Van Dael and Vangeel obtained the formula for ultrasonic velocity in the liquid mixtures adopting the adiabatic compressibilities of the pure liquids based on ideal mixing of the liquids. Van Dael and Vangeel assumed that the adiabatic compressibility (β_{ad}) of the mixture is given by

$$\beta_{ad} = \phi_A (\beta_{ad})_A + \phi_B (\beta_{ad})_B$$

and suggested the following relation for sound velocity in homogeneous liquid mixtures.

$$\beta_{ad}^{im} = \phi_A \frac{\gamma_A}{\gamma^{im}} (\beta_{ad})_A + \phi_B \frac{\gamma_B}{\gamma^{im}} (\beta_{ad})_B$$

Where ϕ and γ refer the volume function and principal specific ratio.

It holds true if the mixture is an ideal one and also $\gamma_A = \gamma_B = \gamma_{im}$. It can be transformed into a linear combination of the mole fractions if the additional assumption $v_A = v_B$ is made

$\beta_{ad}^{im} = x_A (\beta_{ad})_A + x_B (\beta_{ad})_B$

The sound velocities appropriate to the above equations are given by

$$\frac{x_A v_A + x_B v_B}{x_A M_A + x_B M_B} \frac{1}{(U^{im})^2} = \varphi_A \frac{v_A}{M_A U_A^2} + \varphi_B \frac{v_B}{M_B U_B^2}$$ and

$$\frac{1}{x_A M_A + x_B M_B} \frac{1}{(U^{im})^2} = \frac{x_A}{M_A U_A^2} + \frac{x_B}{M_B U_B^2} \qquad \text{............. (3)}$$

1.4 Junjie relation: This relation derived by Junjie for the ultrasonic velocity of the mixture in terms of the mole fraction, molecular weight and density of the mixture.

$$U = \frac{\sum_{i=1}^{n} xiVi}{(\sum_{i=1}^{n} x_i M_i)^{1/2} (\sum_{i=1}^{n} x_i V_i / \rho_i u_i^2)^{1/2}} \qquad \text{............... (4)}$$

where the symbols have their usual meanings.

1.5 Rao's relation: Using the ratio of the temperature coefficient of velocity and expansion coefficient, Rao derived a formula for ultrasonic velocity (U)

$$U = \left(\frac{R}{V}\right)^3 \qquad \text{............... (5)}$$

where V is the molar volume and R is called Rao's constant or molar sound velocity, which is constant for a liquid at a temperature.

CHI-SQUARE TEST FOR GOODNESS OF FIT:

According to Karl Pearson, Chi-square value is evaluated for the binary liquid mixtures under study using the formula

$$\chi^2 = \sum_{i=1}^{n}((U_{(obs)} - U_{(cal)})^2 / U_{(cal)}) \qquad \text{................ (6)}$$

where n is the number of data used,

and '$U_{(obs)}$ = experimental values of ultrasonic velocities

$U_{(cal)}$ = computed values of ultrasonic velocities

AVERAGE PRECENTAGE OF ERROR (SdU):

The Average percentage error is calculated by using the relation

$$SdU = 1/n\sum((U_{(obs)} - U_{(cal)}) / U_{(obs)}) \times 100\% \qquad \text{................ (7)}$$

where n is the number of data used.

$U_{(obs)}$ = experimental values of ultrasonic velocities

MOLECULAR ASSOCIATIONS:

The degree of intermolecular interaction or molecular association is given by

$$\boldsymbol{\alpha} = [U^2_{exp}/U^2_{imx}]-1 \qquad \text{.................(8)}$$

RESULTS AND DISCUSSION

The experimental ultrasonic velocities and the theoretical values evaluated by Nomoto's Relation (NOM), Impedance Relation (IMP), Vandeal Vangael Ideal Mixing Relation (VDV), Junjie's relation (JUN), Rao's specific velocity method (RAO) are compared for all the three binaries OCP+MA, OCP+EA, OCP+BA along with the percentage of deviations are presented in TABLES 1-3 at all the four temperatures 303.15, 308.15, 313.15, 318.15 K and atmospheric pressure. The validity of different theoretical formulae is checked by the chi-square test for all the mixtures at all the temperatures and the values are given in TABLE-4.

TABLE-1

EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM OCP+MA

x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
AT 303.15K												
0.0000	1132.4	1132.4	1132.4	1132.4	1132.4	1132.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.0803	1155.6	1155.8	1158.9	1128.5	1141.7	1208.4	0.02	0.28	-2.35	-1.21	4.57	0.0487
0.1641	1179.4	1179.6	1185.0	1127.9	1153.4	1281.6	0.01	0.47	-4.37	-2.21	8.66	0.0935
0.2519	1203.8	1203.7	1210.7	1131.1	1167.8	1349.8	-0.02	0.57	-6.04	-2.99	12.12	0.1328
0.3437	1228.7	1228.1	1236.1	1138.7	1185.1	1409.4	-0.05	0.60	-7.32	-3.55	14.71	0.1643
0.4399	1254.0	1252.8	1261.2	1151.7	1205.7	1457.1	-0.09	0.57	-8.15	-3.85	16.20	0.1854
0.5409	1279.5	1277.8	1285.9	1171.4	1230.1	1489.2	-0.13	0.49	-8.45	-3.86	16.38	0.1931
0.6470	1305.3	1303.2	1310.2	1199.9	1258.9	1501.3	-0.16	0.38	-8.07	-3.55	15.02	0.1834
0.7586	1331.0	1328.9	1334.3	1240.2	1293.0	1489.5	-0.15	0.25	-6.82	-2.86	11.91	0.1518
0.8761	1356.5	1355.0	1358.0	1297.6	1333.3	1450.3	-0.11	0.11	-4.34	-1.71	6.92	0.0927
1.0000	1381.4	1381.4	1381.4	1381.4	1381.4	1381.4	0.00	0.00	0.00	0.00	0.00	0.0000
AT 308.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1102.9	1102.9	1102.9	1102.9	1102.9	1102.9	0.00	0.00	0.00	0.00	0.00	0.0000
0.0803	1126.5	1126.9	1130.3	1099.5	1112.4	1184.6	0.04	0.34	-2.40	-1.25	5.17	0.0497
0.1641	1150.6	1151.4	1157.3	1099.4	1124.4	1263.6	0.06	0.58	-4.46	-2.28	9.82	0.0955
0.2519	1175.5	1176.1	1183.9	1103.0	1139.1	1337.3	0.05	0.72	-6.17	-3.10	13.76	0.1358
0.3437	1201.0	1201.3	1210.2	1111.1	1156.8	1401.7	0.03	0.77	-7.48	-3.68	16.72	0.1683
0.4399	1226.9	1226.8	1236.0	1124.5	1177.9	1453.0	-0.01	0.74	-8.34	-3.99	18.43	0.1904
0.5409	1253.3	1252.7	1261.5	1144.7	1203.0	1486.7	-0.05	0.66	-8.66	-4.01	18.63	0.1986
0.6470	1280.0	1278.9	1286.7	1173.8	1232.6	1498.3	-0.08	0.52	-8.29	-3.70	17.06	0.1890
0.7586	1306.8	1305.6	1311.4	1215.0	1267.8	1483.2	-0.09	0.4	-7.02	-2.99	13.50	0.1568
0.8761	1333.6	1332.6	1335.9	1273.8	1309.7	1437.8	-0.07	0.18	-4.48	-1.79	7.82	0.0960
1.0000	1360.0	1360.0	1360.0	1360.0	1360.0	1360.0	0.00	0.00	0.00	0.00	0.00	0.0000
AT 313.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1083.5	1083.5	1083.5	1083.5	1083.5	1083.5	0.00	0.00	0.00	0.00	0.00	0.0000
0.0803	1107.5	1107.8	1111.2	1080.3	1093.2	1169.8	0.03	0.34	-2.45	-1.29	5.62	0.0510
0.1641	1132.2	1132.6	1138.6	1080.5	1105.4	1253.3	0.03	0.56	-4.57	-2.36	10.70	0.0981
0.2519	1157.5	1157.6	1165.5	1084.3	1120.3	1331.4	0.01	0.69	-6.33	-3.21	15.02	0.1396
0.3437	1183.4	1183.1	1192.1	1092.6	1138.3	1399.5	-0.02	0.74	-7.67	-3.82	18.26	0.1732
0.4399	1209.8	1209.0	1218.3	1106.2	1159.6	1453.4	-0.07	0.71	-8.56	-4.15	20.14	0.1960
0.5409	1236.5	1235.2	1244.2	1126.7	1184.9	1488.2	-0.11	0.62	-8.89	-4.17	20.35	0.2046
0.6470	1263.5	1261.8	1269.6	1156.0	1214.9	1498.8	-0.14	0.48	-8.51	-3.85	18.62	0.1948
0.7586	1290.6	1288.8	1294.8	1197.5	1250.5	1480.5	-0.14	0.32	-7.22	-3.11	14.71	0.1616
0.8761	1317.5	1316.2	1319.6	1256.8	1292.9	1429.5	-0.10	0.15	-4.61	-1.87	8.50	0.0990
1.0000	1344.0	1344.0	1344.0	1344.0	1344.0	1344.0	0.00	0.00	0.00	0.00	0.00	0.0000
AT318.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1062.9	1062.9	1062.9	1062.9	1062.9	1062.9	0.00	0.00	0.00	0.00	0.00	0.0000
0.0803	1087.5	1087.3	1090.9	1060.0	1072.6	1153.4	-0.01	0.32	-2.53	-1.37	6.06	0.0525
0.1641	1112.6	1112.1	1118.5	1060.3	1084.7	1241.2	-0.05	0.53	-4.70	-2.51	11.56	0.1012
0.2519	1138.4	1137.3	1145.7	1064.3	1099.6	1323.4	-0.10	0.64	-6.51	-3.41	16.25	0.1441
0.3437	1164.7	1162.9	1172.5	1072.7	1117.5	1395.0	-0.15	0.67	-7.90	-4.06	19.78	0.1789
0.4399	1191.4	1188.9	1198.8	1086.5	1138.8	1451.4	-0.21	0.63	-8.81	-4.41	21.82	0.2025
0.5409	1218.4	1215.3	1224.9	1107.0	1164.2	1487.1	-0.25	0.53	-9.15	-4.45	22.06	0.2115
0.6470	1245.5	1242.2	1250.5	1136.3	1194.4	1496.7	-0.27	0.40	-8.77	-4.10	20.16	0.2014
0.7586	1272.6	1269.4	1275.7	1178.0	1230.3	1475.0	-0.25	0.25	-7.43	-3.32	15.91	0.1671
0.8761	1299.2	1297.1	1300.6	1237.5	1273.3	1418.3	-0.16	0.11	-4.75	-2.00	9.17	0.1023
1.0000	1325.2	1325.2	1325.2	1325.2	1325.2	1325.2	0.00	0.00	0.00	0.00	0.00	0.0000

TABLE-2												
EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM OCP+EA												
AT 303.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1117.3	1117.3	1117.3	1117.3	1117.3	1117.3	0.00	0.00	0.00	0.00	0.00	0.0000
0.0971	1141.8	1142.0	1152.1	1123.7	1125.6	1191.6	0.02	0.91	-1.58	-1.42	4.36	0.0324
0.1949	1166.7	1167.2	1184.6	1133.1	1136.6	1259.8	0.04	1.53	-2.88	-2.58	7.98	0.0602
0.2932	1192.0	1192.6	1214.9	1145.7	1150.7	1322.6	0.05	1.92	-3.89	-3.47	10.96	0.0826
0.3922	1217.8	1218.5	1243.2	1161.9	1168.2	1376.0	0.05	2.09	-4.59	-4.08	12.99	0.0986
0.4919	1244.0	1244.7	1269.8	1182.2	1189.4	1415.2	0.05	2.08	-4.97	-4.39	13.76	0.1073
0.5922	1270.6	1271.3	1294.8	1207.4	1215.0	1439.5	0.05	1.90	-4.98	-4.38	13.29	0.1076
0.6931	1297.7	1298.2	1318.4	1238.3	1245.7	1447.1	0.04	1.59	-4.58	-4.00	11.51	0.0983
0.7948	1325.2	1325.6	1340.6	1276.2	1282.7	1438.2	0.03	1.16	-3.70	-3.21	8.53	0.0782
0.8970	1353.1	1353.3	1361.6	1323.0	1327.2	1417.5	0.02	0.63	-2.22	-1.91	4.76	0.0459
1.0000	1381.4	1381.4	1381.4	1381.4	1381.4	1381.4	0.00	0.00	0.00	0.00	0.00	0.0000
AT 308.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1095.2	1095.2	1095.2	1095.2	1095.2	1095.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0971	1120.0	1120.0	1130.2	1101.7	1103.5	1176.5	-0.01	0.90	-1.64	-1.48	5.04	0.0335
0.1949	1145.3	1145.1	1162.7	1111.1	1114.6	1251.1	-0.01	1.52	-2.98	-2.68	9.24	0.0624
0.2932	1170.8	1170.6	1193.1	1123.8	1128.6	1316.2	-0.02	1.90	-4.02	-3.60	12.42	0.0855
0.3922	1196.8	1196.5	1221.5	1140.0	1146.0	1369.9	-0.02	2.07	-4.74	-4.24	14.46	0.1021
0.4919	1223.1	1222.8	1248.2	1160.4	1167.3	1410.0	-0.03	2.05	-5.13	-4.57	15.28	0.1111
0.5922	1249.8	1249.4	1273.3	1185.5	1192.9	1434.6	-0.03	1.88	-5.15	-4.56	14.78	0.1114
0.6931	1276.8	1276.5	1296.9	1216.4	1223.6	1442.3	-0.03	1.57	-4.73	-4.17	12.96	0.1018
0.7948	1304.3	1303.9	1319.1	1254.4	1260.7	1432.6	-0.03	1.14	-3.82	-3.34	9.84	0.0810
0.8970	1331.9	1331.8	1340.1	1301.4	1305.4	1404.9	-0.01	0.61	-2.30	-1.99	5.48	0.0475
1.0000	1360.0	1360.0	1360.0	1360.0	1360.0	1360.0	0.00	0.00	0.00	0.00	0.00	0.0000
AT 313.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1080.7	1080.7	1080.7	1080.7	1080.7	1080.7	0.00	0.00	0.00	0.00	0.00	0.0000
0.0971	1105.6	1105.3	1115.5	1087.2	1088.8	1166.9	-0.03	0.90	-1.66	-1.52	5.54	0.0341
0.1949	1130.8	1130.2	1147.9	1096.6	1099.7	1245.9	-0.06	1.51	-3.03	-2.75	10.17	0.0635
0.2932	1156.4	1155.5	1178.2	1109.2	1113.6	1314.7	-0.08	1.88	-4.09	-3.70	13.69	0.0870
0.3922	1182.3	1181.2	1206.5	1125.3	1130.8	1370.9	-0.09	2.04	-4.82	-4.35	15.95	0.1039
0.4919	1208.6	1207.4	1233.0	1145.5	1151.8	1412.2	-0.10	2.02	-5.22	-4.69	16.85	0.1131
0.5922	1235.1	1233.9	1257.9	1170.5	1177.3	1436.4	-0.10	1.85	-5.23	-4.68	16.30	0.1134
0.6931	1261.9	1260.8	1281.3	1201.2	1207.9	1442.0	-0.09	1.54	-4.81	-4.28	14.27	0.1036
0.7948	1289.0	1288.1	1303.4	1239.0	1244.7	1428.5	-0.07	1.12	-3.88	-3.44	10.82	0.0824
0.8970	1316.4	1315.8	1324.3	1285.7	1289.4	1395.5	-0.04	0.60	-2.33	-2.05	6.01	0.0483
1.0000	1344.0	1344.0	1344.0	1344.0	1344.0	1344.0	0.00	0.00	0.00	0.00	0.00	0.0000
AT 318.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1052.5	1052.5	1052.5	1052.5	1052.5	1052.5	0.00	0.00	0.00	0.00	0.00	0.0000
0.0971	1078.4	1077.8	1088.6	1059.4	1061.0	1144.1	-0.05	0.95	-1.76	-1.61	6.09	0.0361
0.1949	1104.6	1103.6	1122.2	1069.2	1072.3	1228.3	-0.09	1.59	-3.20	-2.92	11.20	0.0673
0.2932	1131.1	1129.7	1153.5	1082.3	1086.6	1301.8	-0.13	1.98	-4.32	-3.94	15.08	0.0924
0.3922	1158.0	1156.3	1182.8	1098.9	1104.4	1361.7	-0.15	2.14	-5.10	-4.63	17.59	0.1105
0.4919	1185.2	1183.4	1210.3	1119.7	1126.0	1405.5	-0.16	2.11	-5.53	-5.00	18.58	0.1204
0.5922	1212.7	1210.8	1236.1	1145.4	1152.1	1430.5	-0.16	1.92	-5.55	-5.00	17.96	0.1209
0.6931	1240.5	1238.7	1260.3	1177.1	1183.7	1435.3	-0.14	1.60	-5.11	-4.58	15.71	0.1106
0.7948	1268.5	1267.1	1283.2	1216.1	1221.8	1419.3	-0.11	1.16	-4.13	-3.68	11.88	0.0881
0.8970	1296.7	1295.9	1304.8	1264.4	1268.2	1382.1	-0.06	0.62	-2.49	-2.20	6.58	0.0517
1.0000	1325.2	1325.2	1325.2	1325.2	1325.2	1325.2	0.00	0.00	0.00	0.00	0.00	0.0000

The data reveals that the velocities computed from Nomoto's relation (NOM) and Impdance relation (IMP) exhibit more satisfactory agreement with the experimental values in the temperature range 303.15K to 318.15K than other approaches in the binary systems. It is observed that the experimental values show deviation with the theoretical values of ultrasonic velocities which confirms the existence of molecular interactions [22]. This may be due to interactions occurring between the hetero molecules of the binaries. Higher deviations are observed in Rao's specific and slight variations in Junjie's theories. There are higher variations in some intermediate concentration range suggesting the existence of strong tendency of association between component molecules as a result of dipole-dipole interactions. However, there is reasonably a good agreement between the experimental and theoretical velocities of Nomoto's relation and Impedance relation. Nomoto's theory proposes that the volume does not change upon 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 interactions are taken into account. But upon mixing, interactions between the molecules occur 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 that the molecular interactions are taking place between the unlike molecules in the liquid mixtures. From the Tables it is observed that maximum positive deviation exhibiting a minimum of approximately 0.5 mole fraction for all the three systems at all the temperatures. The ratio U^2_{exp}/U^2_{imx} is an important tool to measure the non ideality in the mixtures especially in such cases where the properties other than sound velocity are not known.

TABLE-3

EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM OCP+BA

x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
AT 303.15K												
0.0000	1165.2	1165.2	1165.2	1165.2	1165.2	1165.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1263	1192.2	1185.7	1202.4	1184.4	1170.4	1230.3	-0.54	0.86	-0.65	-1.83	3.20	0.0131
0.2454	1217.8	1206.5	1234.2	1204.2	1178.3	1284.5	-0.93	1.35	-1.11	-3.24	5.48	0.0226
0.3580	1242.0	1227.5	1261.5	1224.5	1189.1	1328.0	-1.17	1.56	-1.41	-4.26	6.92	0.0288
0.4645	1265.1	1248.7	1285.3	1245.3	1203.1	1361.1	-1.29	1.60	-1.56	-4.90	7.59	0.0320
0.5654	1286.9	1270.2	1306.2	1266.6	1220.5	1384.4	-1.30	1.49	-1.58	-5.16	7.57	0.0323
0.6612	1307.7	1292.0	1324.7	1288.5	1241.9	1398.6	-1.20	1.29	-1.47	-5.03	6.95	0.0301
0.7522	1327.5	1314.0	1341.1	1310.9	1267.7	1404.6	-1.02	1.03	-1.25	-4.50	5.81	0.0255
0.8388	1346.3	1336.2	1355.9	1333.8	1298.9	1403.1	-0.75	0.71	-0.93	-3.53	4.22	0.0188
0.9213	1364.3	1358.7	1369.3	1357.3	1336.3	1395.1	-0.41	0.37	-0.51	-2.05	2.26	0.0103
1.0000	1381.4	1381.4	1381.4	1381.4	1381.4	1381.4	0.00	0.00	0.00	0.00	0.00	0.0000
AT 308.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1149.4	1149.4	1149.4	1149.4	1149.4	1149.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.1263	1176.0	1169.4	1185.7	1168.2	1154.4	1224.4	-0.56	0.82	-0.67	-1.84	4.11	0.0135
0.2454	1201.2	1189.6	1216.6	1187.5	1162.0	1285.9	-0.96	1.28	-1.14	-3.26	7.06	0.0232
0.3580	1225.0	1210.1	1243.2	1207.3	1172.6	1334.1	-1.21	1.49	-1.44	-4.28	8.91	0.0295
0.4645	1247.5	1230.8	1266.4	1227.6	1186.2	1369.2	-1.33	1.52	-1.59	-4.91	9.76	0.0327
0.5654	1268.8	1251.7	1286.7	1248.4	1203.2	1392.0	-1.34	1.42	-1.61	-5.17	9.71	0.0329
0.6612	1289.0	1272.9	1304.7	1269.6	1224.0	1403.6	-1.24	1.22	-1.50	-5.04	8.89	0.0306
0.7522	1308.1	1294.3	1320.8	1291.4	1249.2	1404.9	-1.05	0.97	-1.27	-4.50	7.40	0.0260
0.8388	1326.3	1316.0	1335.2	1313.8	1279.5	1397.4	-0.78	0.67	-0.94	-3.53	5.36	0.0192
0.9213	1343.6	1337.9	1348.2	1336.6	1316.0	1382.0	-0.42	0.35	-0.52	-2.05	2.86	0.0104
1.0000	1360.0	1360.0	1360.0	1360.0	1360.0	1360.0	0.00	0.00	0.00	0.00	0.00	0.0000
AT 313.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1130.2	1130.2	1130.2	1130.2	1130.2	1130.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1263	1157.2	1150.5	1167.0	1149.2	1135.4	1215.4	-0.58	0.85	-0.69	-1.88	5.03	0.0140
0.2454	1182.7	1171.0	1198.4	1168.7	1143.3	1284.9	-0.99	1.33	-1.18	-3.33	8.65	0.0241
0.3580	1206.8	1191.7	1225.4	1188.7	1154.0	1338.6	-1.25	1.54	-1.50	-4.38	10.92	0.0307
0.4645	1229.6	1212.8	1248.9	1209.2	1167.8	1376.6	-1.37	1.57	-1.66	-5.03	11.95	0.0340
0.5654	1251.3	1234.0	1269.6	1230.3	1185.0	1399.9	-1.38	1.47	-1.68	-5.29	11.88	0.0344
0.6612	1271.8	1255.5	1287.9	1251.9	1206.1	1409.7	-1.28	1.27	-1.56	-5.16	10.84	0.0320
0.7522	1291.2	1277.2	1304.2	1274.1	1231.6	1407.5	-1.08	1.00	-1.33	-4.62	9.00	0.0271
0.8388	1309.7	1299.2	1318.8	1296.8	1262.4	1394.5	-0.80	0.70	-0.99	-3.62	6.47	0.0200
0.9213	1327.3	1321.5	1332.0	1320.1	1299.3	1373.0	-0.44	0.36	-0.54	-2.11	3.44	0.0109
1.0000	1344.0	1344.0	1344.0	1344.0	1344.0	1344.0	0.00	0.00	0.00	0.00	0.00	0.0000
AT 318.15K												
x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	Alpha
0.0000	1110.4	1110.4	1110.4	1110.4	1110.4	1110.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.1263	1138.0	1130.7	1147.4	1129.4	1115.7	1203.2	-0.64	0.83	-0.76	-1.96	5.73	0.0153
0.2454	1163.9	1151.3	1178.9	1148.9	1123.6	1278.7	-1.08	1.29	-1.29	-3.46	9.86	0.0263
0.3580	1188.4	1172.2	1206.1	1169.0	1134.4	1336.5	-1.37	1.49	-1.64	-4.55	12.46	0.0335
0.4645	1211.4	1193.2	1229.7	1189.6	1148.2	1376.7	-1.50	1.51	-1.81	-5.22	13.64	0.0371
0.5654	1233.2	1214.6	1250.5	1210.7	1165.5	1400.1	-1.51	1.40	-1.82	-5.49	13.54	0.0375
0.6612	1253.7	1236.2	1268.9	1232.4	1186.7	1408.5	-1.40	1.21	-1.70	-5.35	12.35	0.0348
0.7522	1273.1	1258.1	1285.2	1254.7	1212.2	1403.3	-1.18	0.95	-1.44	-4.78	10.23	0.0295
0.8388	1291.4	1280.2	1299.9	1277.6	1243.1	1386.5	-0.87	0.66	-1.07	-3.74	7.36	0.0218
0.9213	1308.8	1302.6	1313.2	1301.1	1280.2	1359.8	-0.48	0.34	-0.59	-2.18	3.90	0.0119
1.0000	1325.2	1325.2	1325.2	1325.2	1325.2	1325.2	0.00	0.00	0.00	0.00	0.00	0.0000

Figures a, b and c represent the variation of U^2_{exp}/U^2_{imx} with the mole fraction of OCP for all three binary systems studied, and the ratio of U^2_{exp}/U^2_{imx} gives an idea of extent of interaction taking place between molecules of the mixtures. The positive deviation for three systems infers strong interactions between the components. The percentage of deviation in velocity is reflecting both negative and positive magnitudes, indicating non ideal behaviour of liquid mixtures. The evaluated interaction parameters are positive for all the systems, indicating strong interactions between the mixing molecules. The negative values of interaction parameter indicates the dominance of dispersion forces arising from the breakage of hydrogen bonds in the associates. But a positive value of (α) in all the system clearly indicates the existence of strong tendency for the formation of association in mixture through strong dipole-dipole / hydrogen bonding interactions and higher values of percentage deviation indicates maximum departure of the particular theory from experiment at that particular concentration and magnitude of the chi-square value finally determines the overall validity of the theory. The chi square values along with average percentage error are given in TABLE- 4.

TABLE-4										
VALUES OF CHI-SQUARE AND SIGMA RELATIVE DEVIATION FOR ALL THE BINARY MIXTURES OF OCP AT DIFFERENT TEMPERATURES										
SYSTEM-I (OCP+MA)										
		χ^2				SdU				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.01	0.22	48.60	10.25	177.60	-0.007	0.037	-0.601	-0.266	0.942
308.15K	0.00	0.36	50.00	10.84	224.25	-0.001	0.048	-0.617	-0.277	1.052
313.15K	0.01	0.32	51.94	11.55	263.54	-0.005	0.046	-0.634	-0.288	1.135
318.15K	0.04	0.25	54.22	12.89	304.24	-0.015	0.040	-0.654	-0.307	1.215
SYSTEM-II (OCP+EA)										
		χ^2				SdU				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.00	2.90	17.05	13.24	120.36	0.004	0.136	-0.348	-0.305	0.795
308.15K	0.00	2.78	17.89	14.09	149.67	-0.002	0.134	-0.360	-0.318	0.887
313.15K	0.01	2.67	18.27	14.70	179.54	-0.007	0.132	-0.366	-0.327	0.966
318.15K	0.02	2.86	20.16	16.40	213.61	-0.010	0.138	-0.390	-0.350	1.051
SYSTEM-III (OCP+BA)										
		χ^2				SdU				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	1.16	1.67	1.72	18.65	39.38	-0.087	0.101	-0.106	-0.360	0.471
308.15K	1.23	1.48	1.76	18.46	63.83	-0.090	0.096	-0.108	-0.361	0.594
313.15K	1.28	1.57	1.89	19.10	93.88	-0.093	0.100	-0.113	-0.370	0.713
318.15K	1.51	1.42	2.20	20.23	120.05	-0.101	0.096	-0.123	-0.385	0.803

Fig (a):Plots of U^2_{exp}/U^2_{imx} vs X_1 for the studied system OCP+MA, at temperatures 303.15K , 308.15K, 313.15K,318.15K

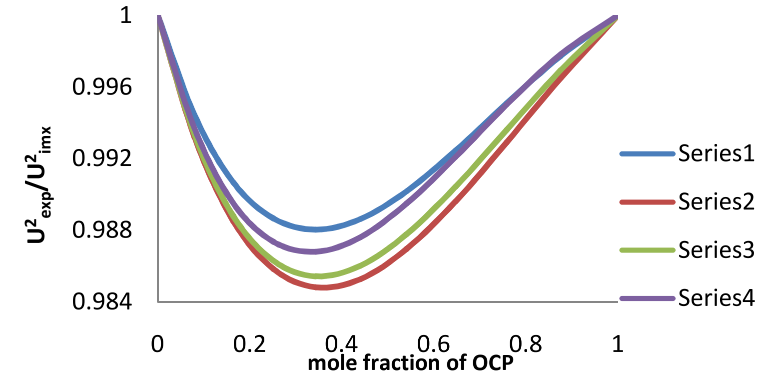
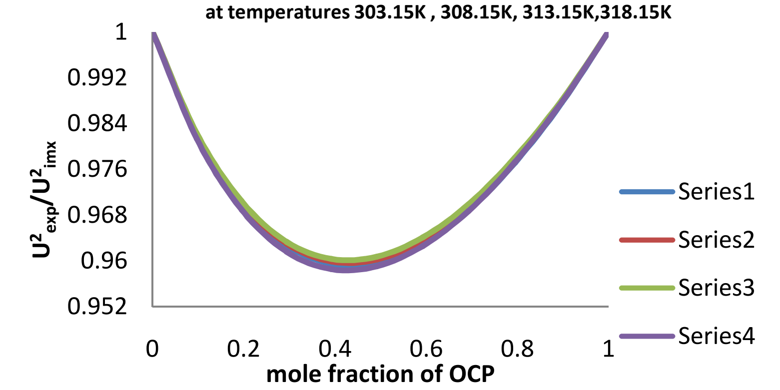
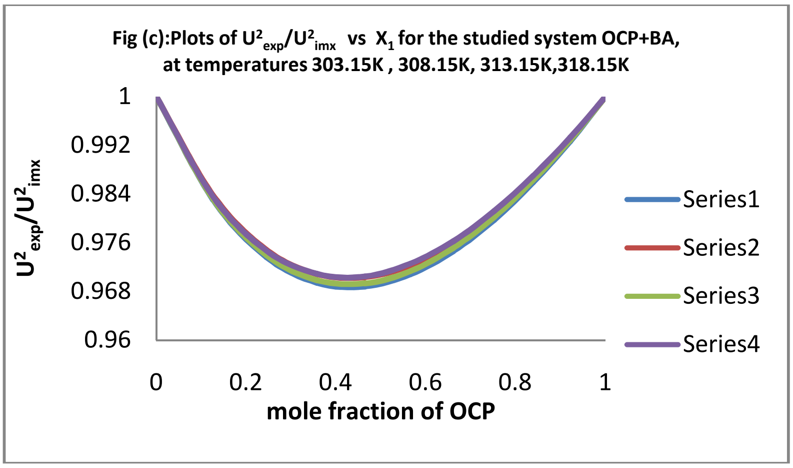


Fig (b):Plots of U2exp/U2imx vs X1 for the studied system OCP+EA, at temperatures 303.15K , 308.15K, 313.15K,318.15K





CONCLUSION

From the values of experimental and evaluated velocity values, it may be concluded that, the Nomoto's relation, Impedance relation have provided good agreement. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by Nomoto, and Impedance relation in deriving the empirical relations have been truly observed in the aforementioned binary liquid mixtures. The success of Nomoto's relation in predicting the experimental ultrasonic velocities for polar-polar liquid mixtures has also been emphasized by others [24].

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