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Evaluation and comparative study of theoretical ultrasonic velocities in binary liquid mixtures of o-chloro phenol with alkoxyethanols at different temperatures and atmospheric pressure

G.R.Satyanarayana[1], K.Sujatha[2], Zareena Begum[1], C.Rambabu[1]*
[1]Department of chemistry, Acharya Nagarjuna University, A.P., (INDIA)
[2]Department of Chemistry, St.V.Depaul College, Eluru, A.P., (INDIA)
E-mail: rbchintala@gmail.com

ABSTRACT

Theoretical velocities of binary liquid mixtures of orthochlorophenol (OCP) with 2-methoxyethanol(MOE), 2-ethoxyethanol(EOE) and 2-butoxyethanol(BOE), at T = (303.15, 308.15, 313.15, 318.15) K and atmospheric pressure, have been evaluated by using Nomoto (NOM), impedance (IMP), Van Dael and Vangeel (VDV),Junjie (JUN) and Rao's specific velocity (RAO) modwls. Ultrasonic velocities and densities of these mixtures have also been measured experimentally as a function of composition of OCP and temperature. 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 investigate 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

Theoretical velocities;
Ultrasonics;
Hydrogen bonding;
Chi-square test;
Molecular interaction parameter.

INTRODUCTION

In the recent past, there is a rapid growth on ultrasonic studies in various organic liquid mixtures[1-10] due to the fact that the optical methods cannot detect and assess all types of interactions, especially weak interactions in liquid mixtures. The important physicochemical properties like adiabatic compressibility, heat capacity, coefficient of expansion and critical temperature may be obtained from ultrasonic velocity, density and viscosity data. The molecular interactions in pure and binary liquid mixtures can be analyzed using ultrasonic velocity measurements which are of considerable interest for the physicists in the last few decades[11-21]. Using various theories[22-30], ultrasonic sound velocities in liquid mixtures have been calculated and compared with experimental values.

The present work is a continuation of our research programme on a comparison of experimental ultrasonic velocity with the theoretical models of Nomoto, Van Dael ideal mixing relation, Rao's specific velocity, impedance relation and Junjie relation for the binary mixtures of several systemsat varios temperatures by Rama Rao et al[31-34]. Of these models, Nomoto relation was reported to be in good agreement with 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.

In this paper, we report the experimental and theoretical ultrasonic velocities of the binary liquid mixtures of OCP with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol at 303.15, 308.15, 313.15, 318.15K over the entire composition range, evaluated by using various theories such as Nomoto (NOM), impedance (IMP), Van Dael and Vangeel (VDV), Junjie (JUN) and Rao's specific velocity (RAO) relations. 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 reported.

EXPERIMENTAL

The commercially available pure solvents were used in the present investigation. OCP (Merk > 99%) and MOE,EOE,BOE of AR grade procured from S.D fine chemicals (India) were purified by the standard methods described by A.Weissberger[35] 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 ± 1×10^{-7} Kg and were stored in air-tight glass bottles. The uncertainty in the mole fraction was estimated to be less than ± 1×10^{-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

Nomoto theory

Nomoto's empirical formula for the sound velocity (U) in binary liquid mixtures, 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 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

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

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

Impedance relation

Using the specific acoustic impedance of the pure liquids, the ultrasonic velocity in the liquid mixtures is determined using the following relation:

$$U = \sum x_i Z_i / \sum x_i \rho_i \quad (2)$$

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

Van Dael and Vangeel relation

Van Dael and Vangeel derived the formula for ultrasonic velocity in the liquid mixtures using 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 eqns are respectively

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

and

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

Junjie relation

Junjie[26] relation for the ultrasonic velocity of the mixture in terms of the mole fraction, molecular weight and density of the mixture. Junjie's is given by

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

where the symbols have their usual meanings.

Rao's relation

Using the ratio of the temperature coefficient of velocity and expansion coefficient, Rao[13] derived a formula for ultrasonic velocity (U) given by

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

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 formulan

$$\chi 2 = \sum_{i=1} U(obs) - U(cal))2 / U(cal)) \qquad (6)$$

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 using the relation

$$SdU = 1/n \sum (U (obs) - U (cal)) / U (obs)) X100\% \qquad (7)$$

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

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

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity for the system along with theoretical values and percentage deviations for 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+MOE, OCP+EOE, OCP+BOE by the equations from respective theories are presented in TABLES 1-3 at all the 4 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.

The values of ultrasonic velocity computed by various theories along with experimental values (U) are given in TABLES 1-3. There are variations between the evaluated and experimental values. 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 tempera-

TABLE 1 : Experimental and theoretical values of velocities with their % deviations for the system OCP+MOE

AT 303.15K

x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1356	1356.0	1356.0	1356.0	1356.0	1356.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0797	1361.2	1358.5	1358.6	1343.4	1353.3	1472.0	-0.20	-0.19	-1.31	-0.58	8.14	0.0266
0.1630	1364.4	1361.1	1361.2	1333.2	1351.8	1580.3	-0.25	-0.24	-2.29	-0.93	15.82	0.0473
0.2503	1367.5	1363.6	1363.8	1325.5	1351.4	1675.0	-0.29	-0.27	-3.07	-1.18	22.49	0.0643
0.3418	1370.4	1366.1	1366.3	1320.7	1352.1	1748.9	-0.31	-0.30	-3.63	-1.33	27.62	0.0767
0.4379	1373.2	1368.7	1368.9	1318.9	1354.0	1794.2	-0.33	-0.32	-3.95	-1.40	30.66	0.0840
0.5388	1375.9	1371.2	1371.4	1320.8	1357.0	1803.0	-0.34	-0.33	-4.00	-1.37	31.05	0.0852
0.6451	1378.2	1373.7	1373.9	1326.9	1361.3	1768.9	-0.32	-0.31	-3.72	-1.23	28.35	0.0788
0.7570	1380.3	1376.3	1376.4	1338.1	1366.7	1687.0	-0.29	-0.28	-3.06	-0.98	22.22	0.0641
0.8752	1382	1378.8	1378.9	1355.7	1373.4	1556.5	-0.23	-0.22	-1.91	-0.62	12.63	0.0392
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	α
0.0000	1347.0	1347.0	1347.0	1347.0	1347.0	1347.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0797	1346.2	1348.3	1348.3	1333.9	1343.5	1466.7	0.16	0.16	-0.91	-0.20	8.95	0.0185
0.1630	1348.3	1349.6	1349.6	1323.2	1341.1	1578.6	0.10	0.10	-1.86	-0.54	17.08	0.0384
0.2503	1350.3	1350.9	1351.0	1314.8	1339.7	1676.4	0.04	0.05	-2.63	-0.78	24.15	0.0547
0.3418	1352.2	1352.2	1352.3	1309.2	1339.4	1752.3	0.00	0.01	-3.18	-0.94	29.59	0.0667
0.4379	1353.8	1353.5	1353.6	1306.6	1340.2	1798.1	-0.02	-0.02	-3.49	-1.01	32.82	0.0736
0.5388	1355.1	1354.8	1354.9	1307.3	1342.0	1805.6	-0.02	-0.02	-3.53	-0.97	33.24	0.0744
0.6451	1356.2	1356.1	1356.2	1312.1	1344.8	1767.9	-0.01	0.00	-3.25	-0.84	30.36	0.0684
0.7570	1356.9	1357.4	1357.4	1321.6	1348.8	1680.4	0.04	0.04	-2.60	-0.60	23.84	0.0541
0.8752	1357.2	1358.7	1358.7	1337.0	1353.8	1542.8	0.11	0.11	-1.49	-0.25	13.68	0.0304
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	α
0.0000	1337.0	1337.0	1337.0	1337.0	1337.0	1337.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0797	1330.1	1337.7	1337.7	1323.8	1333.1	1459.5	0.57	0.57	-0.48	0.23	9.72	0.0096
0.1630	1331.1	1338.4	1338.4	1312.8	1330.2	1574.0	0.55	0.55	-1.38	-0.06	18.25	0.0281
0.2503	1332.8	1339.1	1339.1	1304.2	1328.4	1674.2	0.47	0.48	-2.15	-0.33	25.62	0.0444
0.3418	1334.3	1339.8	1339.8	1298.2	1327.6	1751.8	0.41	0.41	-2.71	-0.50	31.29	0.0564
0.4379	1335.4	1340.5	1340.5	1295.1	1327.8	1798.4	0.38	0.38	-3.02	-0.57	34.67	0.0632
0.5388	1336.2	1341.2	1341.2	1295.3	1329.0	1805.1	0.37	0.38	-3.06	-0.54	35.10	0.0641
0.6451	1336.5	1341.9	1341.9	1299.4	1331.2	1765.3	0.40	0.41	-2.78	-0.40	32.09	0.0579
0.7570	1336.3	1342.6	1342.6	1308.1	1334.4	1674.2	0.47	0.47	-2.11	-0.14	25.29	0.0436
0.8752	1335.5	1343.3	1343.3	1322.5	1338.7	1532.0	0.58	0.59	-0.98	0.24	14.71	0.0198
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	α
0.0000	1314.0	1314.0	1314.0	1314.0	1314.0	1314.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0797	1299.0	1315.1	1315.1	1301.2	1310.6	1437.2	1.24	1.24	0.17	0.89	10.64	0.0034
0.1630	1301.9	1316.2	1316.3	1290.6	1308.2	1552.7	1.10	1.10	-0.87	0.49	19.27	0.0176
0.2503	1304.4	1317.4	1317.4	1282.4	1306.9	1654.0	0.99	1.00	-1.69	0.19	26.80	0.0346
0.3418	1306.5	1318.5	1318.5	1276.8	1306.5	1732.7	0.92	0.92	-2.27	0.00	32.62	0.0471
0.4379	1308.3	1319.6	1319.7	1274.1	1307.1	1780.1	0.86	0.87	-2.61	-0.09	36.06	0.0544
0.5388	1309.5	1320.7	1320.8	1274.7	1308.7	1787.5	0.86	0.86	-2.66	-0.06	36.50	0.0553
0.6451	1310.1	1321.8	1321.9	1279.2	1311.3	1747.8	0.90	0.90	-2.36	0.09	33.41	0.0489
0.7570	1310.0	1323.0	1323.0	1288.3	1314.9	1656.5	0.99	0.99	-1.66	0.37	26.45	0.0340
0.8752	1309.0	1324.1	1324.1	1303.1	1319.5	1513.7	1.15	1.15	-0.45	0.80	15.64	0.0090
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+EOE

x1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
						AT 303.15K						
0.0000	1316.0	1316.0	1316.0	1316.0	1316.0	1316.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0961	1327.4	1322.4	1324.3	1313.0	1314.9	1424.6	-0.37	-0.23	-1.09	-0.94	7.32	0.0221
0.1930	1337.8	1328.9	1332.1	1311.9	1315.3	1519.1	-0.67	-0.43	-1.94	-1.68	13.55	0.0400
0.2907	1347.3	1335.4	1339.5	1312.6	1317.4	1594.8	-0.88	-0.58	-2.57	-2.22	18.37	0.0535
0.3894	1355.7	1341.9	1346.4	1315.4	1321.1	1647.7	-1.02	-0.68	-2.97	-2.55	21.54	0.0622
0.4889	1363.0	1348.4	1353.0	1320.2	1326.5	1674.1	-1.07	-0.73	-3.14	-2.68	22.83	0.0658
0.5893	1369.2	1355.0	1359.3	1327.3	1333.6	1671.9	-1.04	-0.72	-3.06	-2.60	22.11	0.0641
0.6906	1374.2	1361.6	1365.2	1336.7	1342.5	1640.1	-0.92	-0.65	-2.73	-2.30	19.36	0.0569
0.7928	1377.9	1368.2	1370.9	1348.6	1353.3	1579.4	-0.71	-0.51	-2.12	-1.78	14.63	0.0438
0.8959	1380.3	1374.8	1376.3	1363.4	1366.3	1491.9	-0.40	-0.29	-1.22	-1.02	8.09	0.0249
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**	**α**
0.0000	1299.8	1299.8	1299.8	1299.8	1299.8	1299.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.0961	1310.4	1305.7	1307.4	1296.6	1298.4	1411.1	-0.35	-0.23	-1.05	-0.91	7.69	0.0214
0.1930	1320.1	1311.7	1314.6	1295.2	1298.6	1508.0	-0.63	-0.41	-1.89	-1.63	14.24	0.0388
0.2907	1328.8	1317.7	1321.4	1295.6	1300.3	1585.5	-0.84	-0.56	-2.50	-2.14	19.32	0.0519
0.3894	1336.6	1323.7	1327.8	1298.0	1303.6	1639.5	-0.97	-0.66	-2.89	-2.46	22.67	0.0603
0.4889	1343.3	1329.7	1333.9	1302.4	1308.6	1666.0	-1.02	-0.70	-3.05	-2.59	24.02	0.0638
0.5893	1349.0	1335.7	1339.6	1308.9	1315.2	1662.8	-0.98	-0.69	-2.97	-2.51	23.27	0.0622
0.6906	1353.5	1341.8	1345.1	1317.7	1323.5	1629.0	-0.87	-0.62	-2.65	-2.22	20.35	0.0551
0.7928	1356.9	1347.8	1350.3	1329.0	1333.6	1565.3	-0.67	-0.49	-2.06	-1.71	15.36	0.0425
0.8959	1359.1	1353.9	1355.3	1343.0	1345.8	1474.3	-0.38	-0.28	-1.19	-0.98	8.48	0.0241
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**	**α**
0.0000	1274.0	1274.0	1274.0	1274.0	1274.0	1274.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0961	1284.7	1280.9	1282.9	1271.5	1273.4	1392.4	-0.30	-0.15	-1.03	-0.88	8.38	0.0209
0.1930	1294.7	1287.8	1291.2	1270.8	1274.4	1496.1	-0.53	-0.27	-1.85	-1.57	15.56	0.0379
0.2907	1304.0	1294.8	1299.1	1272.1	1276.9	1579.6	-0.70	-0.37	-2.45	-2.07	21.14	0.0508
0.3894	1312.4	1301.7	1306.5	1275.3	1281.1	1638.2	-0.81	-0.45	-2.83	-2.39	24.83	0.0591
0.4889	1320.0	1308.7	1313.6	1280.5	1286.9	1667.4	-0.85	-0.48	-2.99	-2.51	26.32	0.0626
0.5893	1326.7	1315.7	1320.3	1288.0	1294.4	1664.6	-0.83	-0.48	-2.92	-2.43	25.47	0.0611
0.6906	1332.5	1322.8	1326.7	1297.8	1303.8	1629.0	-0.73	-0.44	-2.61	-2.16	22.25	0.0542
0.7928	1337.4	1329.8	1332.7	1310.2	1315.1	1561.4	-0.56	-0.35	-2.03	-1.67	16.75	0.0419
0.8959	1341.2	1336.9	1338.5	1325.5	1328.4	1464.8	-0.32	-0.20	-1.17	-0.95	9.22	0.0238
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**	**α**
0.0000	1250.2	1250.2	1250.2	1250.2	1250.2	1250.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0961	1261.0	1257.6	1259.7	1248.1	1250.1	1374.5	-0.27	-0.11	-1.02	-0.86	9.00	0.0208
0.1930	1271.2	1265.0	1268.6	1247.9	1251.6	1484.0	-0.48	-0.20	-1.83	-1.54	16.75	0.0377
0.2907	1280.7	1272.5	1277.0	1249.5	1254.7	1572.5	-0.64	-0.28	-2.43	-2.03	22.79	0.0505
0.3894	1289.4	1279.9	1285.0	1253.1	1259.3	1634.9	-0.74	-0.34	-2.81	-2.34	26.79	0.0588
0.4889	1297.5	1287.4	1292.6	1258.8	1265.6	1656.0	-0.78	-0.38	-2.98	-2.46	27.63	0.0623
0.5893	1304.7	1294.9	1299.8	1266.8	1273.6	1660.5	-0.75	-0.38	-2.91	-2.38	27.27	0.0608
0.6906	1311.2	1302.5	1306.6	1277.1	1283.5	1625.4	-0.66	-0.35	-2.60	-2.11	23.97	0.0541
0.7928	1316.8	1310.0	1313.1	1290.1	1295.2	1553.9	-0.51	-0.28	-2.03	-1.63	18.01	0.0418
0.8959	1321.4	1317.6	1319.3	1306.0	1309.1	1452.0	-0.29	-0.16	-1.17	-0.93	9.88	0.0238
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 3 : Experimental and theoretical values of velocities with their % deviations for the system OCP+BOE

						AT 303.15K						
x1	**EXP**	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**	**%NOM**	**%IMP**	**%VDV**	**%JUN**	**%RAO**	**α**
0.0000	1322.0	1322.0	1322.0	1322.0	1322.0	1322.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1256	1332.1	1327.9	1332.0	1328.0	1319.2	1388.5	-0.32	-0.01	-0.31	-0.97	4.23	0.0062
0.2442	1341.0	1333.7	1340.6	1334.1	1318.2	1438.6	-0.54	-0.03	-0.52	-1.70	7.28	0.0104
0.3565	1348.7	1339.6	1348.0	1340.1	1319.0	1473.1	-0.67	-0.05	-0.64	-2.20	9.22	0.0130
0.4628	1355.6	1345.6	1354.5	1346.1	1321.8	1492.7	-0.74	-0.08	-0.70	-2.49	10.12	0.0141
0.5638	1361.5	1351.5	1360.3	1352.1	1326.4	1499.0	-0.74	-0.09	-0.69	-2.58	10.10	0.0140
0.6597	1366.7	1357.4	1365.5	1358.1	1333.1	1493.3	-0.68	-0.09	-0.63	-2.46	9.26	0.0128
0.7510	1371.2	1363.4	1370.1	1364.0	1341.7	1477.2	-0.57	-0.08	-0.53	-2.15	7.73	0.0107
0.8379	1375.1	1369.4	1374.2	1369.8	1352.6	1452.2	-0.42	-0.07	-0.39	-1.64	5.60	0.0078
0.9208	1378.5	1375.4	1378.0	1375.6	1365.7	1419.8	-0.23	-0.04	-0.21	-0.93	2.99	0.0042
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**	**α**
0.0000	1276.0	1276.0	1276.0	1276.0	1276.0	1276.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1256	1288.1	1284.2	1290.1	1284.5	1274.9	1350.3	-0.30	0.16	-0.28	-1.02	4.83	0.0055
0.2442	1299.1	1292.5	1302.2	1293.0	1275.8	1407.2	-0.50	0.24	-0.47	-1.79	8.32	0.0094
0.3565	1309.2	1300.8	1312.8	1301.5	1278.6	1447.1	-0.64	0.28	-0.58	-2.34	10.53	0.0118
0.4628	1318.4	1309.2	1322.0	1310.0	1283.4	1470.7	-0.70	0.28	-0.63	-2.66	11.55	0.0128
0.5638	1326.8	1317.6	1330.2	1318.5	1290.2	1479.6	-0.70	0.25	-0.63	-2.76	11.51	0.0128
0.6597	1334.6	1326.0	1337.5	1326.9	1299.2	1475.3	-0.65	0.21	-0.58	-2.65	10.54	0.0117
0.7510	1341.8	1334.4	1344.0	1335.2	1310.5	1459.5	-0.55	0.16	-0.49	-2.33	8.77	0.0098
0.8379	1348.3	1342.9	1349.8	1343.6	1324.2	1433.8	-0.40	0.11	-0.35	-1.79	6.34	0.0071
0.9208	1354.4	1351.4	1355.2	1351.8	1340.6	1400.1	-0.22	0.06	-0.19	-1.02	3.38	0.0038
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**	**α**
0.0000	1269.0	1269.0	1269.0	1269.0	1269.0	1269.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1256	1280.1	1276.4	1281.6	1276.6	1267.4	1350.3	-0.29	0.12	-0.27	-0.99	5.49	0.0055
0.2442	1290.2	1283.8	1292.4	1284.2	1267.7	1412.2	-0.50	0.17	-0.46	-1.74	9.46	0.0093
0.3565	1299.3	1291.2	1301.8	1291.8	1269.9	1455.0	-0.62	0.19	-0.58	-2.26	11.98	0.0116
0.4628	1307.6	1298.7	1310.1	1299.4	1274.0	1479.3	-0.68	0.19	-0.63	-2.57	13.13	0.0127
0.5638	1315.2	1306.2	1317.4	1307.0	1280.1	1487.2	-0.69	0.17	-0.62	-2.67	13.08	0.0126
0.6597	1322.1	1313.7	1323.9	1314.5	1288.2	1480.1	-0.63	0.14	-0.57	-2.56	11.95	0.0116
0.7510	1328.3	1321.2	1329.7	1322.0	1298.5	1460.2	-0.54	0.10	-0.48	-2.25	9.93	0.0097
0.8379	1334.0	1328.8	1334.9	1329.4	1311.1	1429.6	-0.39	0.07	-0.35	-1.72	7.16	0.0070
0.9208	1339.2	1336.4	1339.7	1336.7	1326.1	1390.2	-0.21	0.03	-0.19	-0.98	3.80	0.0038
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**	**α**
0.0000	1244.0	1244.0	1244.0	1244.0	1244.0	1244.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1256	1255.2	1252.0	1257.6	1252.2	1243.1	1330.8	-0.26	0.19	-0.24	-0.97	6.02	0.0048
0.2442	1265.5	1260.0	1269.3	1260.4	1244.0	1397.0	-0.44	0.30	-0.40	-1.70	10.39	0.0081
0.3565	1275.1	1268.1	1279.5	1268.7	1246.7	1442.8	-0.55	0.35	-0.50	-2.22	13.16	0.0101
0.4628	1283.9	1276.1	1288.4	1276.9	1251.4	1469.0	-0.61	0.35	-0.55	-2.53	14.42	0.0110
0.5638	1292.1	1284.2	1296.3	1285.1	1258.1	1477.5	-0.61	0.33	-0.55	-2.63	14.35	0.0110
0.6597	1299.7	1292.4	1303.4	1293.2	1266.8	1469.9	-0.56	0.28	-0.50	-2.53	13.10	0.0101
0.7510	1306.8	1300.5	1309.7	1301.3	1277.7	1448.8	-0.48	0.22	-0.42	-2.23	10.87	0.0085
0.8379	1313.4	1308.7	1315.4	1309.3	1290.9	1416.1	-0.35	0.15	-0.31	-1.71	7.82	0.0062
0.9208	1319.5	1317.0	1320.5	1317.3	1306.6	1374.2	-0.19	0.08	-0.17	-0.97	4.15	0.0033
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 4 : Values of Chi-square and sigma relative deviation for all the binary mixtures of OCP at different temperatures

SYSTEM-I (OCP+MOE)										
	X^2					**SdU**				
T(K)	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**
303.15K	0.10	0.09	12.09	1.52	679.51	-0.026	-0.025	-0.278	-0.097	1.598
308.15K	0.01	0.01	8.86	0.66	770.34	0.004	0.004	-0.236	-0.062	1.693
313.15K	0.27	0.27	6.10	0.17	852.03	0.042	0.042	-0.191	-0.021	1.775
318.15K	1.20	1.20	4.08	0.24	910.20	0.089	0.089	-0.147	0.027	1.842
SYSTEM-II (OCP+EOE)										
	X^2					**SdU**				
T(K)	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**
303.15K	0.83	0.39	7.22	5.26	367.97	-0.071	-0.049	-0.214	-0.182	1.251
308.15K	0.74	0.36	6.71	4.82	401.15	-0.068	-0.047	-0.207	-0.175	1.306
313.15K	0.51	0.17	6.36	4.45	471.95	-0.057	-0.032	-0.204	-0.170	1.407
318.15K	0.42	0.10	6.20	4.20	531.93	-0.052	-0.025	-0.203	-0.166	1.490
SYSTEM-III (OCP+BOE)										
	X^2					**SdU**				
T(K)	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**	**NOM**	**IMP**	**VDV**	**JUN**	**RAO**
303.15K	0.40	0.01	0.35	4.86	74.18	-0.049	-0.005	-0.046	-0.175	0.615
308.15K	0.35	0.05	0.29	5.45	93.83	-0.047	0.017	-0.042	-0.188	0.693
313.15K	0.33	0.02	0.28	5.04	119.85	-0.046	0.012	-0.042	-0.181	0.778
318.15K	0.26	0.08	0.21	4.82	141.60	-0.041	0.022	-0.036	-0.179	0.845

ture 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[36]. 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 hydrogen bonding. 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 at 0.5 mole fraction of all the 3 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.

Figures 1, 2 and 3 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. It is positive for three systems and 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 stronger interactions between the mixing molecules, which increase from BOE to MOE. This suggests somewhat stronger interaction of OCP with MOE in comparison to other components. The negative values indi-

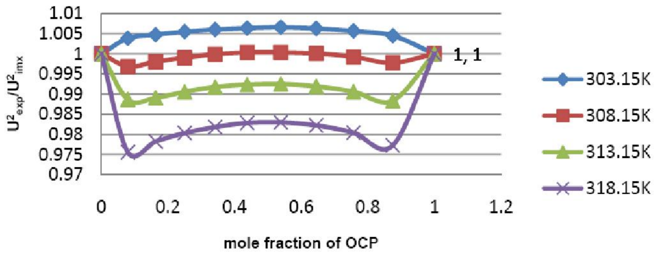

Figure 1 :Plots of $U^2_{exp}/U2_{imx}$ vs X_1 for the studied system OCP+MOE, at temperatures 303.15K, 308.15K, 313.15K,318.15K

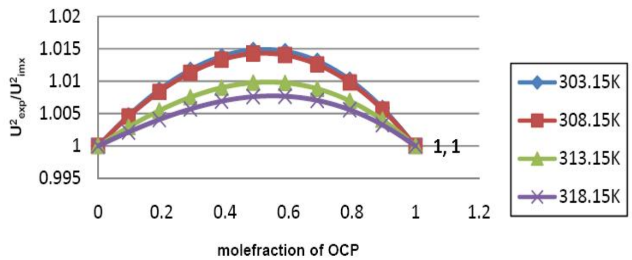

Figure 2 : Plots of U^2_{exp}/U^2_{imx} vs X_1 for the studied system OCP+EOE, at temperatures 303.15K , 308.15K, 313.15K,318.15K

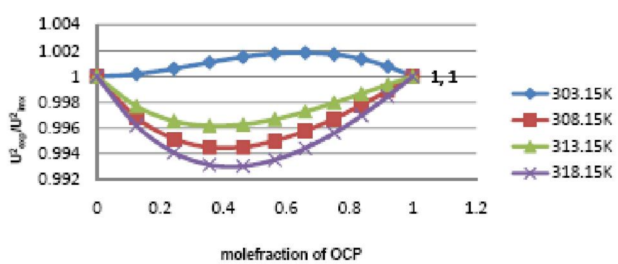

Figure 3 : Plots of U^2_{exp}/U^2_{imx} vs X_1 for the studied system OCP+BOE, at temperatures 303.15K, 308.15K, 313.15K,318.15K

cate 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 dipole-dipole interactions 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.

CONCLUSIONS

From the values of experimental and evaluated velocity values, it may be concluded that, the Nomoto's relation and Impedance relation of Ultra sound velocity have provided good results. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by Nomoto, Van Dael and Vangael 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[37].

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