



Theoretical evaluation and comparative study of ultrasonic velocities in binary liquid mixtures of o-chlorophenol with o, p-xylenes and o-chlorotoulene at different temperatures

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ABSTRACT

Ultrasonic velocities and densities of the binary liquid mixtures of o-chlorophenol with o-xylene, p-xylene and o-chlorotoulene have been measured over the entire composition range of mole fractions at a temperature range from 303.15 to 318.15 K with an interval of 5 K. The theoretical values of ultrasonic velocity were evaluated by using Nomoto (NOM), Impedance (IMP), Van Deal and Vangeel (VDV), Junjie (JUN), Rao's specific velocity (RAO) models. The results were discussed in terms of non-ideality in the mixtures, molecular interaction parameter, Relative deviation σ and Chi-square (χ^2) test for the goodness of the fit is applied to understand the applicability of these theories to the present systems.

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Introduction

The measurement of ultrasonic velocities finds extensive applications in understanding Physico-chemical behaviour of liquid mixtures [1-11]. Ultrasonic velocities of liquid mixtures containing polar and non-polar groups are of considerable importance in understanding intermolecular interaction between component molecules [12-21]. Many researchers compared the experimental values of ultrasonic velocities with theoretically evaluated values for organic liquid mixtures using different theories/ models like Nomoto [22], Impedance relation [23], Van Dael and Vangeel [24], Junjie [25] and Rao's specific velocity [26]. The present study is a continuation of our research programme on application of theoretical models of ultrasonic velocities for some liquid binaries at different temperatures [27-32].

In this paper, we report the experimental and theoretical ultrasonic velocities of o-chlorophenol with o-xylene, p-xylene and o-chlorotoulene evaluated by various theoretical models such as Nomoto (NOM), Impedance (IMP), Van Deal and Vangeel (VDV), Junjie (JUN), Rao's specific velocity (RAO) at 303.15-318.15K over the entire composition range. Relative applicability of the theories to the present systems has been checked and discussed. Further, the results were explained in terms of molecular interaction parameter, deviation in the variation of $U_{\text{exp}}^2/U_{\text{imx}}^2$, relative deviation σ and Chi-square (χ^2) test for the goodness of the fit is applied to understand the applicability of these theories for the systems studied.

Materials and Methods

The pure solvents used in the present study o-chlorophenol (OCP) (Merk >99%) and o-xylene (OXL), p-xylene (PXL) and o-chlorotoulene (OCT) from S.D fine chemicals India Ltd., were purified as described in the literature [33,34]. The density was measured with a pycnometer having a bulb volume of about 25 cm³ and an internal capillary diameter of about 1 mm. The density was then determined from the mass of the sample and the volume of pycnometer. Uncertainties in density

determinations were estimated to be within $\pm 0.0001 \text{ g cm}^{-3}$. 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 $\pm 0.1 \text{ m.sec}^{-1}$ and temperature stability was maintained within $\pm 0.01\text{K}$ by circulating water bath around the measuring cell through a pump.

Theoretical Considerations:

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

$$U = \frac{\left[\frac{\sum_{i=1}^n x_i R_i}{\sum_{i=1}^n x_i V_i} \right]^3}{\left[\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right]^3} \quad \text{..... (1)}$$

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

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:

$$U = \frac{\sum x_i Z_i}{\sum x_{ii}} \quad \text{..... (2)}$$

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

Van Dael and Vangeel relation: Van Dael and Vangeel 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

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

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

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.

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

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)

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

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

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

where n is the number of data used,

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

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

Relative percentage of error (σ):

The Average percentage error is calculated by using the relation $\sigma = 1/n \sum ((U_{(obs)} - U_{(cal)}) / U_{(obs)}) \times 100\%$ $\dots\dots\dots (7)$

where n is the number of data used.

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

Molecular Associations:

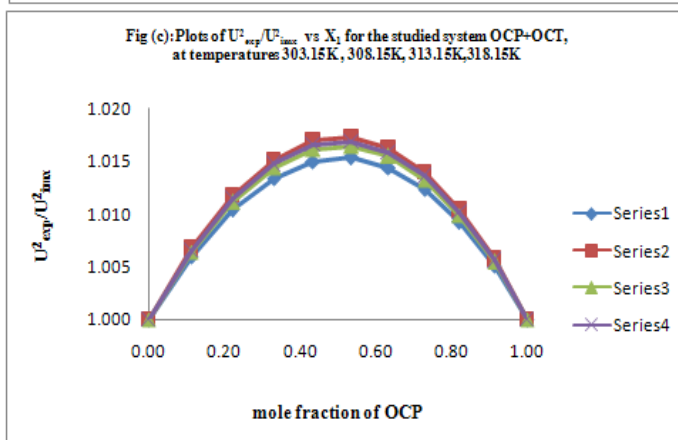
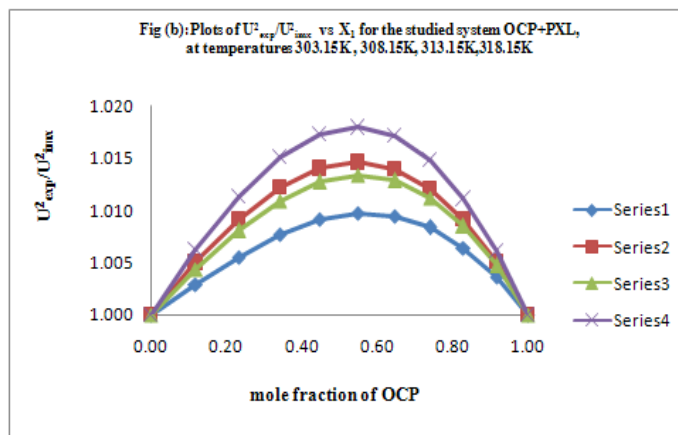
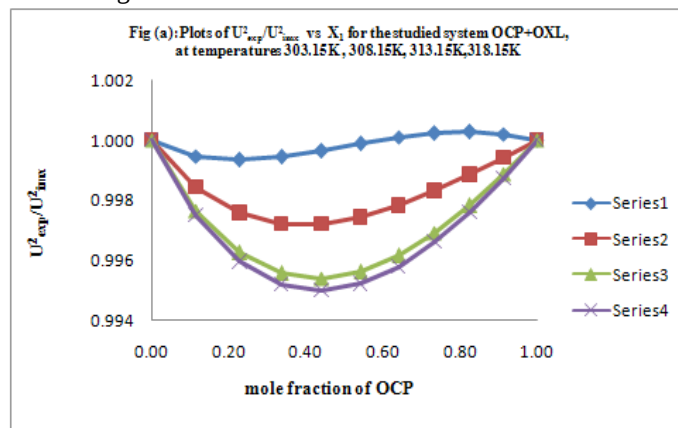
The degree of intermolecular interaction or molecular association is given by

$$\alpha = [U_{exp}^2 / U_{imx}^2] - 1 \quad \dots\dots\dots (8)$$

Results and discussion

The experimental ultrasonic velocities and the theoretical values evaluated by Nomoto's Relation (NOM), Impedance

Relation (IMP), Van Deal and Vangeel Ideal Mixing Relation (VDV), Junjie's relation (JUN), Rao's specific velocity method (RAO) are compared for all the three binaries o-chlorophenol + o-xylene, o-chlorophenol + p-xylene, o-chlorophenol + o-chlorotoulene 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.



The data reveals that the velocities computed from Nomoto's relation (NOM) and Impedance 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 [35]. This may be due to interactions occurring between the hetero molecules of the binaries. Higher deviations are observed in Rao's specific velocity method.

TABLE-1												
EXPERIMENTAL AND THEORETICAL VALUES OF VELOCITIES WITH THEIR % DEVIATIONS FOR THE SYSTEM (OCP + OXL)												
AT 303.15K												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1336.2	1336.2	1336.2	1336.2	1336.2	1336.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1168	1343.1	1340.7	1343.4	1337.9	1331.2	1383.3	-0.18	0.03	-0.38	-0.88	3.00	0.0077
0.2293	1349.3	1345.2	1349.8	1340.4	1328.3	1420.3	-0.31	0.03	-0.66	-1.56	5.26	0.0133
0.3378	1355.0	1349.7	1355.4	1343.6	1327.4	1447.3	-0.39	0.03	-0.84	-2.03	6.81	0.0170
0.4424	1360.1	1354.2	1360.3	1347.5	1328.6	1464.1	-0.44	0.02	-0.93	-2.31	7.65	0.0188
0.5434	1364.7	1358.7	1364.8	1351.9	1331.8	1471.3	-0.44	0.01	-0.94	-2.41	7.82	0.0190
0.6410	1368.8	1363.2	1368.8	1356.9	1337.1	1469.4	-0.41	0.00	-0.87	-2.31	7.35	0.0177
0.7353	1372.5	1367.7	1372.4	1362.3	1344.6	1458.7	-0.35	-0.01	-0.74	-2.03	6.28	0.0150
0.8264	1375.8	1372.3	1375.7	1368.3	1354.4	1439.9	-0.26	-0.01	-0.55	-1.56	4.65	0.0111
0.9146	1378.8	1376.8	1378.7	1374.6	1366.6	1413.9	-0.14	-0.01	-0.30	-0.88	2.55	0.0061
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1313.1	1313.1	1313.1	1313.1	1313.1	1313.1	0.00	0.00	0.00	0.00	0.00	0.0000
0.1168	1319.5	1317.8	1320.6	1315.0	1308.5	1360.7	-0.14	0.08	-0.34	-0.83	3.12	0.0069
0.2293	1325.5	1322.4	1327.1	1317.7	1306.0	1398.1	-0.23	0.12	-0.59	-1.47	5.47	0.0119
0.3378	1331.1	1327.1	1332.9	1321.1	1305.5	1425.3	-0.30	0.14	-0.75	-1.92	7.08	0.0152
0.4424	1336.2	1331.8	1338.1	1325.1	1306.9	1442.3	-0.33	0.14	-0.83	-2.19	7.94	0.0168
0.5434	1341.0	1336.5	1342.7	1329.7	1310.3	1449.6	-0.33	0.13	-0.84	-2.28	8.11	0.0170
0.6410	1345.4	1341.2	1346.8	1334.8	1315.8	1447.7	-0.31	0.11	-0.78	-2.20	7.61	0.0159
0.7353	1349.5	1345.9	1350.6	1340.4	1323.4	1437.1	-0.27	0.08	-0.67	-1.93	6.49	0.0135
0.8264	1353.2	1350.6	1354.0	1346.5	1333.2	1418.3	-0.20	0.06	-0.50	-1.48	4.81	0.0100
0.9146	1356.8	1355.3	1357.1	1353.1	1345.3	1392.4	-0.11	0.03	-0.27	-0.84	2.63	0.0055
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1295.2	1295.2	1295.2	1295.2	1295.2	1295.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1168	1301.4	1300.1	1303.0	1297.3	1291.0	1344.1	-0.11	0.12	-0.32	-0.80	3.28	0.0064
0.2293	1307.3	1304.9	1309.8	1300.2	1288.8	1382.6	-0.18	0.19	-0.54	-1.41	5.76	0.0110
0.3378	1312.9	1309.8	1315.8	1303.8	1288.6	1410.5	-0.23	0.22	-0.69	-1.85	7.44	0.0140
0.4424	1318.1	1314.7	1321.1	1308.0	1290.3	1428.0	-0.26	0.23	-0.77	-2.11	8.34	0.0155
0.5434	1323.0	1319.5	1325.9	1312.7	1294.0	1435.5	-0.26	0.22	-0.78	-2.20	8.50	0.0157
0.6410	1327.7	1324.4	1330.3	1318.1	1299.6	1433.5	-0.25	0.19	-0.73	-2.12	7.97	0.0147
0.7353	1332.1	1329.3	1334.2	1323.9	1307.3	1422.6	-0.21	0.16	-0.62	-1.86	6.79	0.0125
0.8264	1336.3	1334.2	1337.8	1330.2	1317.2	1403.4	-0.16	0.11	-0.46	-1.43	5.02	0.0092
0.9146	1340.3	1339.1	1341.0	1336.9	1329.4	1376.9	-0.09	0.06	-0.25	-0.81	2.74	0.0051
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1275.4	1275.4	1275.4	1275.4	1275.4	1275.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.1168	1281.7	1280.4	1283.3	1277.6	1271.6	1325.9	-0.10	0.13	-0.32	-0.79	3.45	0.0063
0.2293	1287.6	1285.4	1290.2	1280.6	1269.7	1365.5	-0.18	0.20	-0.54	-1.39	6.05	0.0109
0.3378	1293.2	1290.3	1296.4	1284.3	1269.7	1394.3	-0.22	0.24	-0.69	-1.82	7.81	0.0140
0.4424	1298.5	1295.3	1301.8	1288.6	1271.6	1412.2	-0.25	0.25	-0.77	-2.07	8.75	0.0155
0.5434	1303.6	1300.3	1306.7	1293.5	1275.4	1419.7	-0.25	0.24	-0.78	-2.16	8.91	0.0157
0.6410	1308.4	1305.3	1311.1	1298.9	1281.1	1417.5	-0.24	0.21	-0.72	-2.08	8.34	0.0146
0.7353	1312.9	1310.3	1315.2	1304.8	1288.9	1406.1	-0.20	0.17	-0.62	-1.83	7.10	0.0125
0.8264	1317.2	1315.2	1318.8	1311.2	1298.7	1386.3	-0.15	0.12	-0.46	-1.40	5.24	0.0092
0.9146	1321.3	1320.2	1322.1	1318.0	1310.8	1359.0	-0.08	0.06	-0.25	-0.80	2.85	0.0050
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 + PXL)												
AT 303.15K												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1289.3	1289.3	1289.3	1289.3	1289.3	1289.3	0.00	0.00	0.00	0.00	0.00	0.0000
0.1190	1306.4	1298.3	1304.6	1295.2	1286.5	1359.4	-0.62	-0.14	-0.86	-1.53	4.05	0.0174
0.2330	1321.4	1307.4	1317.8	1302.0	1286.1	1415.0	-1.06	-0.27	-1.46	-2.67	7.09	0.0299
0.3425	1334.3	1316.5	1329.3	1309.6	1288.2	1456.2	-1.34	-0.38	-1.85	-3.46	9.13	0.0381
0.4476	1345.5	1325.6	1339.4	1318.0	1292.8	1482.7	-1.47	-0.45	-2.04	-3.92	10.20	0.0421
0.5486	1354.9	1334.8	1348.4	1327.0	1300.0	1495.0	-1.48	-0.48	-2.06	-4.05	10.34	0.0424
0.6457	1362.8	1344.1	1356.4	1336.7	1309.9	1494.0	-1.37	-0.47	-1.91	-3.88	9.63	0.0394
0.7393	1369.3	1353.3	1363.6	1347.0	1322.7	1481.1	-1.16	-0.41	-1.62	-3.40	8.17	0.0333
0.8294	1374.4	1362.6	1370.1	1357.9	1338.6	1457.0	-0.86	-0.32	-1.20	-2.61	6.01	0.0245
0.9162	1378.5	1372.0	1376.0	1369.4	1358.1	1423.3	-0.47	-0.18	-0.66	-1.48	3.25	0.0133
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1274.2	1274.2	1274.2	1274.2	1274.2	1274.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1190	1291.6	1282.6	1288.4	1279.6	1271.0	1350.9	-0.70	-0.25	-0.93	-1.60	4.59	0.0189
0.2330	1306.6	1291.0	1300.7	1285.9	1270.2	1411.6	-1.19	-0.45	-1.59	-2.78	8.03	0.0325
0.3425	1319.4	1299.5	1311.5	1292.9	1271.9	1456.0	-1.51	-0.60	-2.01	-3.60	10.35	0.0414
0.4476	1330.1	1308.0	1320.9	1300.7	1276.0	1483.8	-1.66	-0.69	-2.21	-4.07	11.56	0.0457
0.5486	1338.9	1316.6	1329.3	1309.1	1282.6	1495.7	-1.67	-0.72	-2.22	-4.20	11.71	0.0460
0.6457	1346.0	1325.2	1336.7	1318.2	1291.9	1492.5	-1.55	-0.69	-2.07	-4.02	10.89	0.0426
0.7393	1351.5	1333.8	1343.4	1327.8	1304.0	1476.0	-1.31	-0.60	-1.75	-3.51	9.21	0.0360
0.8294	1355.6	1342.5	1349.5	1338.0	1319.2	1447.3	-0.97	-0.45	-1.30	-2.69	6.76	0.0264
0.9162	1358.4	1351.2	1355.0	1348.8	1337.7	1408.0	-0.53	-0.25	-0.71	-1.52	3.65	0.0143
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1251.6	1251.6	1251.6	1251.6	1251.6	1251.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.1190	1269.7	1260.6	1266.9	1257.6	1249.0	1330.6	-0.71	-0.22	-0.95	-1.63	4.80	0.0193
0.2330	1285.3	1269.7	1280.2	1264.5	1248.8	1393.3	-1.21	-0.40	-1.62	-2.84	8.41	0.0332
0.3425	1298.7	1278.9	1291.7	1272.1	1251.0	1439.4	-1.53	-0.54	-2.05	-3.67	10.83	0.0423
0.4476	1310.1	1288.0	1301.9	1280.5	1255.7	1468.4	-1.68	-0.63	-2.26	-4.15	12.08	0.0468
0.5486	1319.6	1297.2	1310.9	1289.6	1262.9	1481.0	-1.69	-0.66	-2.28	-4.29	12.23	0.0471
0.6457	1327.3	1306.5	1318.9	1299.3	1272.8	1478.2	-1.57	-0.63	-2.11	-4.11	11.36	0.0437
0.7393	1333.5	1315.8	1326.1	1309.6	1285.6	1461.6	-1.33	-0.55	-1.80	-3.60	9.60	0.0369
0.8294	1338.3	1325.2	1332.7	1320.5	1301.5	1432.5	-0.98	-0.42	-1.33	-2.75	7.04	0.0271
0.9162	1341.7	1334.6	1338.6	1332.0	1320.8	1392.7	-0.53	-0.23	-0.73	-1.56	3.80	0.0147
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1233.8	1233.8	1233.8	1233.8	1233.8	1233.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.1190	1252.9	1242.7	1249.0	1239.7	1231.2	1321.5	-0.81	-0.31	-1.05	-1.73	5.48	0.0213
0.2330	1269.2	1251.7	1262.1	1246.5	1231.1	1391.1	-1.38	-0.56	-1.79	-3.00	9.60	0.0367
0.3425	1283.0	1260.8	1273.5	1254.1	1233.3	1441.8	-1.74	-0.75	-2.26	-3.88	12.37	0.0467
0.4476	1294.6	1269.8	1283.5	1262.4	1237.9	1473.2	-1.91	-0.85	-2.49	-4.38	13.80	0.0516
0.5486	1304.0	1278.9	1292.4	1271.4	1245.0	1485.9	-1.92	-0.89	-2.50	-4.52	13.95	0.0520
0.6457	1311.5	1288.1	1300.4	1281.0	1254.8	1481.1	-1.78	-0.84	-2.32	-4.32	12.94	0.0482
0.7393	1317.2	1297.3	1307.5	1291.2	1267.4	1460.8	-1.51	-0.73	-1.97	-3.77	10.91	0.0407
0.8294	1321.3	1306.6	1314.0	1302.0	1283.1	1426.6	-1.11	-0.55	-1.46	-2.88	7.97	0.0298
0.9162	1323.9	1315.9	1319.9	1313.3	1302.2	1380.6	-0.61	-0.30	-0.80	-1.63	4.29	0.0162
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 + OCT)												
AT 303.15K												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1283.8	1283.8	1283.8	1283.8	1283.8	1283.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.1135	1300.3	1293.3	1296.5	1293.7	1290.0	1262.2	-0.54	-0.29	-0.51	-0.79	-2.93	0.0103
0.2236	1315.1	1302.9	1308.4	1303.6	1296.9	1258.5	-0.93	-0.51	-0.88	-1.38	-4.31	0.0179
0.3305	1328.3	1312.6	1319.5	1313.4	1304.6	1261.4	-1.18	-0.66	-1.12	-1.79	-5.04	0.0229
0.4344	1339.9	1322.3	1330.0	1323.2	1312.9	1267.2	-1.32	-0.74	-1.25	-2.02	-5.42	0.0255
0.5353	1350.0	1332.0	1339.8	1333.0	1322.1	1275.7	-1.34	-0.76	-1.27	-2.07	-5.51	0.0258
0.6334	1358.8	1341.8	1349.1	1342.7	1332.0	1285.8	-1.25	-0.71	-1.18	-1.97	-5.37	0.0241
0.7288	1366.2	1351.6	1357.8	1352.4	1342.9	1297.2	-1.07	-0.61	-1.01	-1.71	-5.05	0.0205
0.8217	1372.4	1361.5	1366.1	1362.1	1354.7	1311.6	-0.79	-0.46	-0.75	-1.29	-4.43	0.0152
0.9120	1377.4	1371.4	1374.0	1371.8	1367.5	1332.2	-0.44	-0.25	-0.41	-0.72	-3.29	0.0083
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1265.8	1265.8	1265.8	1265.8	1265.8	1265.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.1135	1282.3	1275.0	1278.1	1275.4	1271.8	1254.4	-0.57	-0.33	-0.54	-0.82	-2.18	0.0110
0.2236	1297.1	1284.3	1289.5	1284.9	1278.5	1253.6	-0.98	-0.58	-0.94	-1.43	-3.35	0.0190
0.3305	1310.1	1293.6	1300.3	1294.4	1285.9	1255.2	-1.25	-0.75	-1.20	-1.84	-4.19	0.0243
0.4344	1321.4	1303.0	1310.3	1303.9	1294.0	1260.2	-1.40	-0.84	-1.33	-2.08	-4.64	0.0271
0.5353	1331.2	1312.4	1319.8	1313.3	1302.8	1270.0	-1.42	-0.85	-1.35	-2.13	-4.59	0.0275
0.6334	1339.6	1321.8	1328.8	1322.7	1312.5	1280.2	-1.32	-0.80	-1.26	-2.02	-4.43	0.0257
0.7288	1346.5	1331.3	1337.2	1332.1	1322.9	1293.3	-1.13	-0.69	-1.07	-1.75	-3.95	0.0218
0.8217	1352.2	1340.8	1345.2	1341.4	1334.3	1308.3	-0.84	-0.51	-0.80	-1.32	-3.25	0.0162
0.9120	1356.7	1350.4	1352.8	1350.7	1346.6	1328.4	-0.46	-0.28	-0.44	-0.74	-2.08	0.0088
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1244.2	1244.2	1244.2	1244.2	1244.2	1244.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1135	1261.1	1253.9	1257.1	1254.2	1250.7	1241.6	-0.57	-0.32	-0.55	-0.83	-1.55	0.0110
0.2236	1276.3	1263.8	1269.3	1264.3	1257.8	1242.8	-0.98	-0.55	-0.94	-1.45	-2.62	0.0191
0.3305	1289.8	1273.6	1280.6	1274.3	1265.7	1245.0	-1.25	-0.71	-1.20	-1.87	-3.47	0.0245
0.4344	1301.7	1283.6	1291.3	1284.3	1274.3	1251.7	-1.39	-0.79	-1.33	-2.10	-3.84	0.0272
0.5353	1312.0	1293.5	1301.4	1294.3	1283.7	1261.6	-1.41	-0.81	-1.35	-2.16	-3.85	0.0276
0.6334	1321.0	1303.5	1310.9	1304.3	1293.9	1272.4	-1.32	-0.76	-1.26	-2.05	-3.68	0.0258
0.7288	1328.6	1313.6	1319.9	1314.2	1304.9	1285.7	-1.13	-0.66	-1.08	-1.78	-3.22	0.0219
0.8217	1334.9	1323.7	1328.3	1324.2	1316.9	1301.1	-0.84	-0.49	-0.80	-1.34	-2.53	0.0163
0.9120	1340.0	1333.8	1336.4	1334.1	1329.9	1321.7	-0.46	-0.27	-0.44	-0.75	-1.36	0.0089
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												
X ₁	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1228.3	1228.3	1228.3	1228.3	1228.3	1228.3	0.00	0.00	0.00	0.00	0.00	0.0000
0.1135	1244.9	1237.8	1240.9	1238.1	1234.7	1231.2	-0.57	-0.33	-0.55	-0.82	-1.10	0.0111
0.2236	1259.8	1247.4	1252.6	1247.9	1241.7	1234.3	-0.98	-0.57	-0.95	-1.43	-2.02	0.0192
0.3305	1272.9	1257.0	1263.7	1257.6	1249.4	1239.0	-1.25	-0.73	-1.20	-1.85	-2.67	0.0245
0.4344	1284.5	1266.6	1274.0	1267.3	1257.8	1246.8	-1.39	-0.82	-1.34	-2.08	-2.94	0.0273
0.5353	1294.6	1276.3	1283.8	1277.0	1266.9	1256.1	-1.41	-0.83	-1.36	-2.14	-2.97	0.0277
0.6334	1303.2	1286.0	1293.0	1286.7	1276.8	1268.3	-1.32	-0.78	-1.27	-2.03	-2.68	0.0259
0.7288	1310.5	1295.7	1301.7	1296.3	1287.5	1280.9	-1.13	-0.67	-1.08	-1.76	-2.26	0.0220
0.8217	1316.6	1305.5	1310.0	1306.0	1299.1	1294.9	-0.84	-0.50	-0.81	-1.33	-1.64	0.0163
0.9120	1321.4	1315.3	1317.8	1315.6	1311.7	1310.1	-0.46	-0.28	-0.44	-0.74	-0.86	0.0089
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 LIQUID MIXTURES OF O-CHLOROPHENOL AT DIFFERENT TEMPERATURES										
SYSTEM-I (OCP + OXL)										
χ^2					σ					
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.14	0.00	0.65	4.25	44.21	-0.029	0.001	-0.063	-0.163	0.483
308.15K	0.08	0.01	0.51	3.76	46.71	-0.022	0.009	-0.056	-0.154	0.500
313.15K	0.05	0.04	0.43	3.44	50.68	-0.017	0.015	-0.052	-0.149	0.523
318.15K	0.04	0.04	0.42	3.28	54.83	-0.017	0.016	-0.052	-0.146	0.546
SYSTEM-II (OCP + PXL)										
χ^2					σ					
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	1.60	0.16	3.09	12.01	76.60	-0.100	-0.031	-0.139	-0.279	0.627
308.15K	2.00	0.36	3.57	12.75	96.84	-0.112	-0.047	-0.151	-0.290	0.702
313.15K	2.04	0.30	3.68	13.12	104.09	-0.114	-0.043	-0.154	-0.296	0.730
318.15K	2.59	0.54	4.40	14.37	133.60	-0.130	-0.058	-0.170	-0.313	0.821
SYSTEM-III (OCP + OCT)										
χ^2					σ					
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	1.29	0.41	1.16	3.11	26.54	-0.090	-0.050	-0.085	-0.140	-0.434
308.15K	1.43	0.52	1.29	3.24	16.77	-0.095	-0.057	-0.090	-0.144	-0.340
313.15K	1.40	0.46	1.29	3.29	10.86	-0.095	-0.054	-0.091	-0.146	-0.270
318.15K	1.39	0.48	1.28	3.17	5.88	-0.095	-0.055	-0.091	-0.144	-0.196

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 $U_{\text{exp}}^2/U_{\text{imx}}^2$ 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 a, b and c represent the variation of $U_{\text{exp}}^2/U_{\text{imx}}^2$ with the mole fraction of OCP for all three binary systems studied, and the ratio of $U_{\text{exp}}^2/U_{\text{imx}}^2$ gives an idea of extent of interaction taking place between molecules of the mixtures. The positive deviation for the systems infers specific molecular 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. The positive value of (α) in all the systems clearly indicates the existence of the formation of association in mixture through dipole-dipole / dipole-induced dipole interactions/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 in sigma are given in TABLE- 4.

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 [30,31]

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