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Theories of ultrasonic velocities and their application in the binary liquid mixtures of ethyl benzoate with 2-alkoxyethanols at different temperatures

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ABSTRACT

Ultrasonic velocities and densities of the binary liquid mixtures of ethyl benzoate with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol 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's (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.

Keywords: *Ethylbenzoate, ultrasonic velocities, Chi-square test, molecular interaction parameter.*

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's [25] and Rao's specific velocity [26]. The present study is a continuation of our research programme on the 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 ethyl benzoate with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol evaluated by various theoretical models such as Nomoto (NOM), Impedance (IMP),Van Deal and Vangeel (VDV), Junjie's (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^2_{exp}/U^2_{imx}, 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.

MATERIALS AND METHODS

The solvents used in the present study ethyl benzoate (EB) (Merk >99%) and 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE) and 2-butoxyethanol (BOE) are obtained from S.D fine chemicals India Ltd. They were purified as described in the literature [33,34]. The density was measured with a pycnometer having a bulb volume of about 25 cm^3 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 ± 0.0001 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 ± 0.1 $m.sec^{-1}$ and 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:

$U= \sum x_iZ_i/\sum x_{ii}$ .... (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

$$\frac{x_Av_A + x_Bv_B}{x_AM_A + x_BM_B}\frac{1}{(U^{im})^2} = \varphi_A \frac{v_A}{M_AU_A^2} + \varphi_B \frac{v_B}{M_BU_B^2} \qquad \text{and}$$

$$\frac{1}{x_AM_A + x_BM_B}\frac{1}{(U^{im})^2} = \frac{x_A}{M_AU_A^2} + \frac{x_B}{M_BU_B^2} \qquad \text{.............. (3)}$$

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.

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

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

Relative percentage of error (σ):
The Average percentage error is calculated by using the relation

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

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), 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 ethyl benzoate + MOE, ethyl benzoate+ EOE, ethyl benzoate + BOE 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 (EB + MOE)

AT 303.15K

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1324	1324.0	1324.0	1324.0	1324.0	1324.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.0578	1326.358	1326.2	1325.4	1307.7	1325.6	1350.0	-0.01	-0.07	-1.41	-0.06	1.79	0.0288
0.1212	1328.824	1328.4	1326.9	1292.8	1327.3	1373.1	-0.03	-0.14	-2.71	-0.12	3.33	0.0566
0.1913	1331.342	1330.6	1328.5	1279.6	1329.1	1394.4	-0.05	-0.21	-3.88	-0.17	4.74	0.0824
0.2689	1333.9	1332.9	1330.4	1268.9	1331.1	1411.6	-0.08	-0.27	-4.88	-0.21	5.83	0.1051
0.3556	1336.48	1335.1	1332.3	1261.2	1333.3	1423.1	-0.11	-0.31	-5.63	-0.24	6.48	0.1230
0.4529	1339.038	1337.3	1334.5	1257.7	1335.6	1428.8	-0.13	-0.34	-6.07	-0.26	6.70	0.1335
0.5629	1341.456	1339.5	1337.0	1260.2	1338.0	1428.6	-0.14	-0.34	-6.05	-0.26	6.50	0.1330
0.6882	1343.612	1341.7	1339.7	1271.7	1340.6	1419.4	-0.14	-0.29	-5.35	-0.23	5.64	0.1164
0.8324	1345.302	1344.0	1342.7	1297.0	1343.3	1394.2	-0.10	-0.19	-3.59	-0.15	3.64	0.0758
1.0000	1346.2	1346.2	1346.2	1346.2	1346.2	1346.2	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	1314.6	1314.6	1314.6	1314.6	1314.6	1314.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0578	1316.5	1316.3	1315.7	1298.3	1315.7	1345.1	-0.02	-0.06	-1.39	-0.06	2.17	0.0283
0.1212	1318.5	1318.0	1316.9	1283.3	1317.0	1369.7	-0.03	-0.12	-2.67	-0.11	3.88	0.0556
0.1913	1320.5	1319.8	1318.1	1270.1	1318.4	1389.9	-0.06	-0.18	-3.82	-0.16	5.25	0.0810
0.2689	1322.6	1321.5	1319.5	1259.2	1319.9	1407.7	-0.08	-0.23	-4.79	-0.20	6.44	0.1033
0.3556	1324.6	1323.2	1321.1	1251.3	1321.6	1421.6	-0.11	-0.27	-5.54	-0.23	7.32	0.1207
0.4529	1326.6	1325.0	1322.8	1247.5	1323.4	1427.2	-0.13	-0.29	-5.97	-0.25	7.58	0.1309
0.5629	1328.5	1326.7	1324.7	1249.6	1325.3	1427.3	-0.14	-0.29	-5.94	-0.24	7.43	0.1303
0.6882	1330.1	1328.4	1326.8	1260.3	1327.4	1416.0	-0.13	-0.25	-5.25	-0.21	6.45	0.1139
0.8324	1331.4	1330.2	1329.2	1284.6	1329.6	1386.6	-0.09	-0.16	-3.51	-0.14	4.15	0.0742
1.0000	1331.9	1331.9	1331.9	1331.9	1331.9	1331.9	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	1291.2	1291.2	1291.2	1291.2	1291.2	1291.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0578	1293.5	1293.7	1292.8	1275.4	1293.0	1321.5	0.02	-0.05	-1.40	-0.04	2.17	0.0286
0.1212	1295.8	1296.1	1294.4	1260.9	1295.0	1349.4	0.02	-0.11	-2.69	-0.07	4.13	0.0561
0.1913	1298.3	1298.6	1296.3	1248.3	1297.0	1370.8	0.02	-0.15	-3.85	-0.10	5.58	0.0818
0.2689	1300.9	1301.1	1298.3	1237.9	1299.3	1390.1	0.02	-0.20	-4.84	-0.12	6.86	0.1043
0.3556	1303.5	1303.6	1300.5	1230.6	1301.7	1405.2	0.01	-0.23	-5.59	-0.14	7.81	0.1220
0.4529	1306.2	1306.0	1303.0	1227.4	1304.2	1415.9	-0.01	-0.25	-6.03	-0.15	8.40	0.1325
0.5629	1308.9	1308.5	1305.7	1230.2	1306.9	1418.0	-0.03	-0.25	-6.02	-0.15	8.33	0.1321
0.6882	1311.5	1311.0	1308.7	1241.7	1309.8	1406.4	-0.04	-0.22	-5.32	-0.13	7.23	0.1156
0.8324	1314.0	1313.5	1312.1	1267.0	1312.8	1375.0	-0.03	-0.14	-3.57	-0.09	4.65	0.0754
1.0000	1316.0	1316.0	1316.0	1316.0	1316.0	1316.0	0.00	0.00	0.00	0.00	0.00	0.0000

AT318.15K

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1282.6	1282.6	1282.6	1282.6	1282.6	1282.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0578	1284.0	1284.2	1283.6	1266.6	1283.6	1313.8	0.02	-0.03	-1.36	-0.03	2.32	0.0277
0.1212	1285.8	1285.8	1284.7	1252.0	1284.8	1340.0	0.00	-0.09	-2.63	-0.07	4.22	0.0547
0.1913	1287.8	1287.5	1285.9	1239.1	1286.2	1364.7	-0.03	-0.15	-3.78	-0.13	5.97	0.0802
0.2689	1289.7	1289.1	1287.3	1228.4	1287.6	1382.9	-0.04	-0.19	-4.75	-0.16	7.23	0.1022
0.3556	1291.5	1290.8	1288.7	1220.7	1289.2	1399.0	-0.06	-0.22	-5.49	-0.18	8.32	0.1194
0.4529	1293.4	1292.4	1290.4	1217.0	1290.9	1410.2	-0.07	-0.23	-5.91	-0.19	9.03	0.1295
0.5629	1295.2	1294.1	1292.2	1219.0	1292.7	1411.3	-0.09	-0.23	-5.88	-0.19	8.97	0.1290
0.6882	1296.8	1295.7	1294.2	1229.4	1294.7	1397.6	-0.09	-0.20	-5.20	-0.16	7.77	0.1127
0.8324	1298.1	1297.4	1296.4	1253.0	1296.8	1362.9	-0.06	-0.13	-3.48	-0.11	4.99	0.0734
1.0000	1299.0	1299.0	1299.0	1299.0	1299.0	1299.0	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 (EB + EOE)

AT 303.15K

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1306.1	1306.1	1306.1	1306.1	1306.1	1306.1	0.00	0.00	0.00	0.00	0.00	0.0000
0.0701	1310.1	1310.1	1309.2	1296.6	1308.7	1331.6	0.00	-0.06	-1.03	-0.11	1.64	0.0210
0.1450	1314.2	1314.1	1312.5	1288.5	1311.5	1353.9	-0.01	-0.12	-1.95	-0.20	3.02	0.0402
0.2252	1318.3	1318.0	1316.0	1282.4	1314.7	1374.5	-0.02	-0.17	-2.73	-0.27	4.26	0.0568
0.3113	1322.5	1322.0	1319.7	1278.3	1318.2	1390.6	-0.03	-0.21	-3.34	-0.33	5.15	0.0703
0.4041	1326.7	1326.0	1323.5	1277.0	1322.0	1402.4	-0.05	-0.24	-3.75	-0.36	5.70	0.0794
0.5043	1330.9	1330.1	1327.5	1279.0	1326.1	1409.8	-0.07	-0.25	-3.90	-0.36	5.93	0.0829
0.6128	1335.0	1334.1	1331.8	1285.2	1330.6	1410.1	-0.07	-0.24	-3.74	-0.33	5.62	0.0791
0.7307	1339.1	1338.1	1336.3	1296.9	1335.5	1401.3	-0.07	-0.20	-3.15	-0.27	4.64	0.0660
0.8592	1342.8	1342.2	1341.1	1316.2	1340.6	1380.9	-0.05	-0.13	-1.98	-0.16	2.83	0.0408
1.0000	1346.2	1346.2	1346.2	1346.2	1346.2	1346.2	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	1290.4	1290.4	1290.4	1290.4	1290.4	1290.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.0701	1294.2	1294.5	1293.7	1281.0	1293.1	1318.2	0.02	-0.05	-1.02	-0.09	1.85	0.0207
0.1450	1298.2	1298.6	1297.1	1273.2	1296.1	1341.6	0.04	-0.08	-1.92	-0.16	3.34	0.0396
0.2252	1302.2	1302.8	1300.6	1267.2	1299.5	1362.5	0.04	-0.12	-2.69	-0.21	4.63	0.0560
0.3113	1306.4	1306.9	1304.4	1263.3	1303.1	1379.4	0.04	-0.15	-3.29	-0.25	5.59	0.0693
0.4041	1310.6	1311.1	1308.4	1262.1	1307.0	1392.8	0.04	-0.17	-3.70	-0.27	6.27	0.0782
0.5043	1314.9	1315.2	1312.6	1264.2	1311.3	1400.6	0.03	-0.18	-3.85	-0.27	6.52	0.0817
0.6128	1319.2	1319.4	1317.0	1270.6	1315.9	1400.8	0.01	-0.17	-3.69	-0.25	6.18	0.0781
0.7307	1323.6	1323.5	1321.7	1282.4	1320.9	1391.1	0.00	-0.14	-3.11	-0.20	5.10	0.0651
0.8592	1327.8	1327.7	1326.6	1301.9	1326.2	1369.1	-0.01	-0.09	-1.95	-0.12	3.11	0.0403
1.0000	1331.9	1331.9	1331.9	1331.9	1331.9	1331.9	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	1277.6	1277.6	1277.6	1277.6	1277.6	1277.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0701	1281.0	1281.4	1280.6	1268.2	1280.0	1306.8	0.03	-0.03	-1.00	-0.08	2.01	0.0203
0.1450	1284.5	1285.2	1283.8	1260.4	1282.8	1331.3	0.05	-0.06	-1.88	-0.14	3.64	0.0387
0.2252	1288.2	1289.0	1287.1	1254.3	1285.8	1352.8	0.07	-0.08	-2.63	-0.19	5.02	0.0548
0.3113	1292.0	1292.9	1290.6	1250.3	1289.1	1370.5	0.07	-0.11	-3.22	-0.22	6.08	0.0677
0.4041	1295.8	1296.7	1294.3	1248.9	1292.8	1384.7	0.07	-0.12	-3.62	-0.23	6.86	0.0765
0.5043	1299.8	1300.5	1298.1	1250.8	1296.7	1392.5	0.06	-0.13	-3.77	-0.23	7.14	0.0799
0.6128	1303.8	1304.4	1302.2	1256.8	1301.0	1391.9	0.05	-0.12	-3.61	-0.21	6.76	0.0763
0.7307	1307.9	1308.3	1306.6	1268.2	1305.7	1380.9	0.03	-0.10	-3.04	-0.17	5.58	0.0636
0.8592	1312.0	1312.1	1311.1	1286.9	1310.7	1356.5	0.01	-0.06	-1.91	-0.10	3.39	0.0393
1.0000	1316.0	1316.0	1316.0	1316.0	1316.0	1316.0	0.00	0.00	0.00	0.00	0.00	0.0000

AT 318.15K

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1254.2	1254.2	1254.2	1254.2	1254.2	1254.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0701	1257.9	1258.7	1257.8	1245.3	1257.2	1285.1	0.06	-0.01	-1.00	-0.05	2.17	0.0203
0.1450	1261.7	1263.1	1261.4	1237.9	1260.5	1310.9	0.11	-0.02	-1.89	-0.10	3.90	0.0389
0.2252	1265.7	1267.6	1265.3	1232.3	1264.1	1333.4	0.14	-0.03	-2.64	-0.13	5.34	0.0550
0.3113	1269.9	1272.0	1269.4	1228.8	1268.0	1353.9	0.17	-0.04	-3.24	-0.15	6.61	0.0680
0.4041	1274.3	1276.5	1273.7	1227.9	1272.3	1369.3	0.17	-0.05	-3.64	-0.16	7.45	0.0769
0.5043	1278.8	1281.0	1278.2	1230.3	1276.9	1378.1	0.17	-0.05	-3.79	-0.15	7.76	0.0804
0.6128	1283.6	1285.5	1282.9	1237.0	1281.9	1378.0	0.14	-0.05	-3.64	-0.14	7.35	0.0769
0.7307	1288.6	1290.0	1288.0	1249.1	1287.2	1366.7	0.11	-0.04	-3.06	-0.11	6.07	0.0642
0.8592	1293.7	1294.5	1293.3	1268.7	1292.9	1341.4	0.06	-0.03	-1.93	-0.06	3.69	0.0398
1.0000	1299.0	1299.0	1299.0	1299.0	1299.0	1299.0	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 (EB + BOE)

AT 303.15K

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1290.2	1290.2	1290.2	1290.2	1290.2	1290.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0923	1295.5	1295.7	1296.1	1291.0	1293.5	1310.1	0.02	0.05	-0.35	-0.16	1.13	0.0070
0.1863	1300.4	1301.3	1302.0	1292.7	1297.2	1327.7	0.07	0.12	-0.60	-0.24	2.10	0.0120
0.2818	1305.5	1306.8	1307.8	1295.2	1301.5	1342.4	0.10	0.17	-0.79	-0.31	2.83	0.0159
0.3790	1310.5	1312.4	1313.5	1298.8	1306.2	1354.1	0.15	0.23	-0.89	-0.33	3.33	0.0181
0.4780	1315.9	1318.0	1319.1	1303.4	1311.4	1362.5	0.16	0.24	-0.95	-0.34	3.54	0.0192
0.5787	1321.7	1323.6	1324.6	1309.2	1317.2	1367.5	0.14	0.22	-0.94	-0.34	3.46	0.0191
0.6812	1327.6	1329.2	1330.1	1316.3	1323.6	1368.5	0.12	0.19	-0.85	-0.30	3.08	0.0173
0.7855	1333.8	1334.9	1335.6	1324.7	1330.5	1365.4	0.08	0.13	-0.69	-0.25	2.37	0.0138
0.8918	1340.0	1340.5	1340.9	1334.6	1338.0	1358.1	0.04	0.07	-0.40	-0.15	1.35	0.0081
1.0000	1346.2	1346.2	1346.2	1346.2	1346.2	1346.2	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	1254.4	1254.4	1254.4	1254.4	1254.4	1254.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.0923	1260.8	1262.0	1262.6	1256.7	1259.3	1276.5	0.10	0.14	-0.33	-0.12	1.24	0.0066
0.1863	1267.4	1269.6	1270.7	1259.9	1264.7	1296.2	0.18	0.26	-0.59	-0.21	2.27	0.0120
0.2818	1274.4	1277.3	1278.7	1264.1	1270.8	1313.1	0.23	0.34	-0.81	-0.28	3.04	0.0164
0.3790	1281.6	1285.0	1286.6	1269.5	1277.4	1327.0	0.27	0.39	-0.95	-0.33	3.54	0.0192
0.4780	1289.0	1292.7	1294.4	1276.0	1284.7	1337.7	0.29	0.42	-1.01	-0.33	3.78	0.0204
0.5787	1296.9	1300.5	1302.1	1283.9	1292.7	1344.8	0.28	0.40	-1.00	-0.33	3.70	0.0203
0.6812	1305.3	1308.3	1309.7	1293.3	1301.3	1348.0	0.23	0.34	-0.92	-0.31	3.27	0.0187
0.7855	1313.9	1316.1	1317.2	1304.3	1310.7	1347.1	0.17	0.25	-0.73	-0.24	2.53	0.0148
0.8918	1322.9	1324.0	1324.6	1317.0	1320.9	1341.8	0.08	0.13	-0.44	-0.15	1.43	0.0089
1.0000	1331.9	1331.9	1331.9	1331.9	1331.9	1331.9	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	1249.3	1249.3	1249.3	1249.3	1249.3	1249.3	0.00	0.00	0.00	0.00	0.00	0.0000
0.0923	1254.1	1255.8	1256.4	1250.9	1253.3	1271.4	0.14	0.18	-0.26	-0.06	1.38	0.0052
0.1863	1259.6	1262.4	1263.3	1253.3	1257.9	1291.0	0.22	0.30	-0.50	-0.13	2.49	0.0100
0.2818	1265.5	1269.0	1270.2	1256.8	1263.0	1307.5	0.28	0.37	-0.69	-0.19	3.32	0.0139
0.3790	1271.5	1275.7	1277.0	1261.3	1268.7	1320.8	0.33	0.43	-0.80	-0.22	3.88	0.0163
0.4780	1277.9	1282.3	1283.7	1266.9	1275.0	1330.6	0.35	0.46	-0.86	-0.23	4.12	0.0175
0.5787	1284.6	1289.0	1290.4	1273.7	1281.9	1336.6	0.34	0.45	-0.85	-0.21	4.05	0.0172
0.6812	1291.6	1295.7	1296.9	1281.9	1289.4	1338.3	0.32	0.41	-0.75	-0.17	3.61	0.0152
0.7855	1299.2	1302.4	1303.3	1291.5	1297.5	1335.6	0.25	0.32	-0.59	-0.13	2.80	0.0119
0.8918	1307.7	1309.2	1309.7	1302.8	1306.4	1328.2	0.12	0.15	-0.37	-0.10	1.57	0.0075
1.0000	1316.0	1316.0	1316.0	1316.0	1316.0	1316.0	0.00	0.00	0.00	0.00	0.00	0.0000

AT 318.15K

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1238.2	1238.2	1238.2	1238.2	1238.2	1238.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0923	1242.2	1244.2	1244.6	1239.4	1241.8	1260.8	0.16	0.20	-0.22	-0.03	1.50	0.0045
0.1863	1247.0	1250.2	1251.0	1241.5	1246.0	1280.6	0.26	0.32	-0.44	-0.08	2.69	0.0089
0.2818	1252.2	1256.2	1257.3	1244.5	1250.6	1297.2	0.32	0.41	-0.61	-0.13	3.59	0.0124
0.3790	1257.6	1262.3	1263.5	1248.5	1255.7	1310.3	0.37	0.47	-0.72	-0.15	4.19	0.0146
0.4780	1263.4	1268.3	1269.6	1253.6	1261.4	1319.7	0.39	0.49	-0.77	-0.15	4.46	0.0157
0.5787	1269.4	1274.4	1275.6	1259.9	1267.7	1325.0	0.40	0.49	-0.75	-0.13	4.38	0.0152
0.6812	1275.8	1280.5	1281.6	1267.4	1274.6	1325.8	0.37	0.45	-0.66	-0.10	3.92	0.0133
0.7855	1282.7	1286.7	1287.5	1276.3	1282.1	1321.9	0.31	0.37	-0.50	-0.05	3.05	0.0101
0.8918	1290.3	1292.8	1293.3	1286.8	1290.2	1313.0	0.20	0.23	-0.27	-0.01	1.76	0.0055
1.0000	1299.0	1299.0	1299.0	1299.0	1299.0	1299.0	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 EB AT DIFFERENT TEMPERATURES

SYSTEM-I (EB+MOE)

	χ^2					SdU				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.012	0.078	26.106	0.047	32.771	-0.008	-0.022	-0.416	-0.017	0.423
308.15K	0.011	0.057	24.948	0.042	41.623	-0.008	-0.019	-0.409	-0.016	0.477
313.15K	0.001	0.041	25.133	0.016	48.943	0.001	-0.016	-0.414	-0.010	0.517
318.15K	0.004	0.036	23.841	0.024	55.281	-0.004	-0.015	-0.404	-0.012	0.549

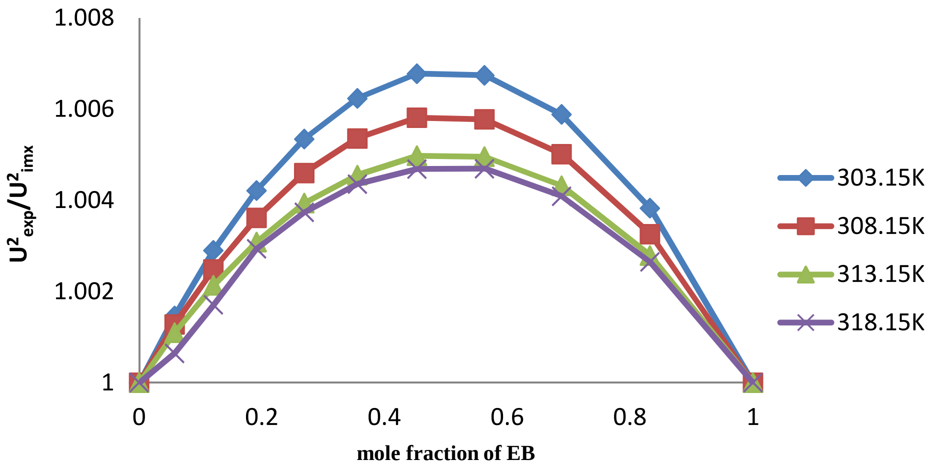
SYSTEM-II (EB+EOE)

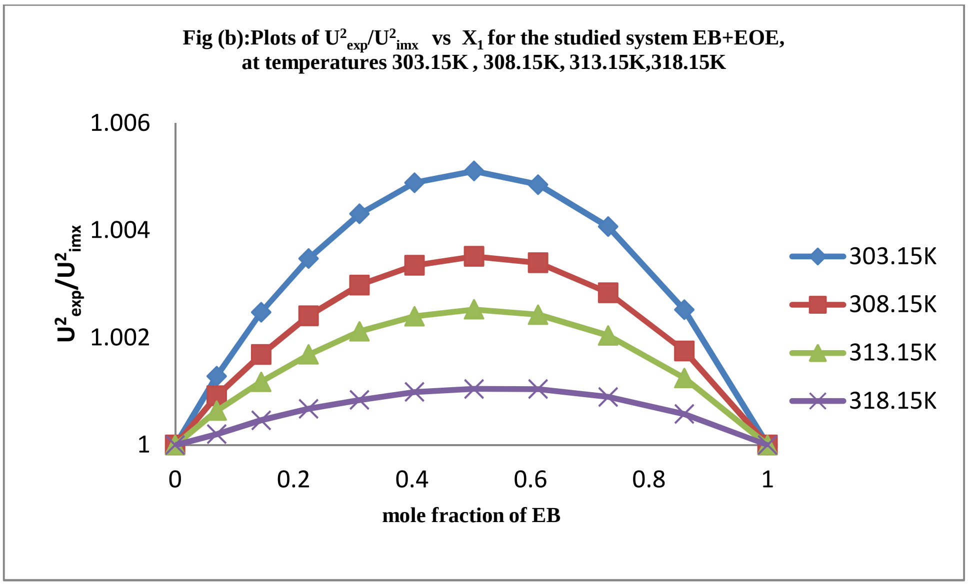
	χ^2					SdU				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.003	0.045	10.700	0.093	24.640	-0.004	-0.016	-0.264	-0.024	0.370
308.15K	0.001	0.021	10.291	0.053	29.283	0.002	-0.011	-0.260	-0.018	0.405
313.15K	0.003	0.011	9.747	0.039	34.492	0.004	-0.008	-0.255	-0.016	0.440
318.15K	0.020	0.002	9.705	0.017	39.895	0.011	-0.003	-0.256	-0.010	0.474

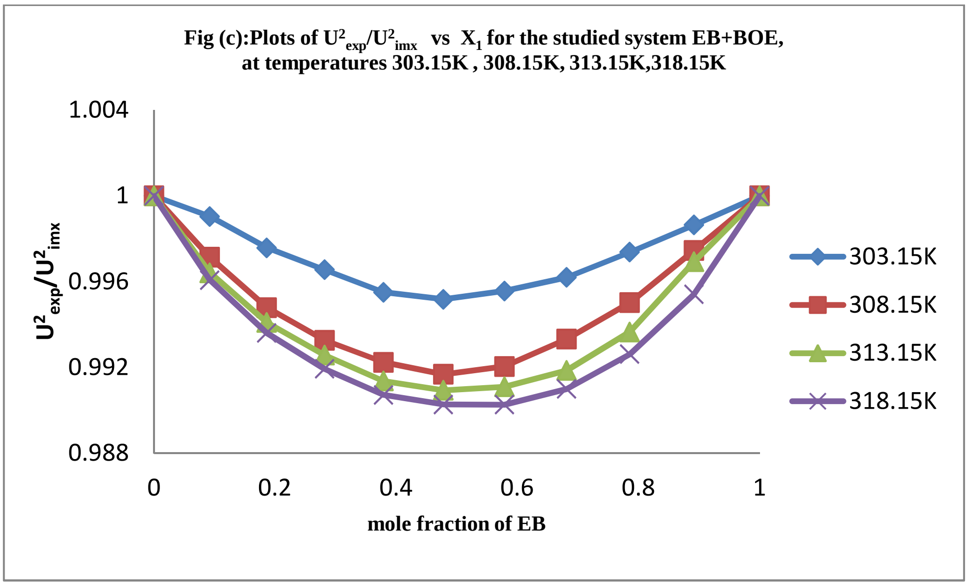
SYSTEM-III (EB+BOE)

	χ^2					SdU				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.014	0.035	0.663	0.091	8.726	0.009	0.014	-0.065	-0.024	0.226
308.15K	0.053	0.114	0.724	0.082	9.752	0.018	0.027	-0.068	-0.023	0.241
313.15K	0.085	0.147	0.505	0.033	11.630	0.023	0.031	-0.057	-0.015	0.263
318.15K	0.115	0.177	0.387	0.013	13.505	0.028	0.034	-0.050	-0.008	0.285

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







The data reveals that the velocities computed from Nomoto's relation (NOM) and Impedance relation (IMP) and Junjie's relation (JUN) exhibit more satisfactory agreement with the experimental values in the temperature range 303.15K - 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 [35-38]. This may be due to interactions occurring between the hetero molecules of the binaries. Higher deviations are observed in Van Dael and Vangeel and Rao's specific velocity methods. 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 Impedance relation and Junjie's relation. Nomoto's theory proposes that the volume does not change upon mixing of solvents. 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 all 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.

Figures a, b and **c** represent the variation of U^2_{exp}/U^2_{imx} with the mole fraction of ethyl benzoate 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 the 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 indicate 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 / 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 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 and Junjie's relation have provided good agreement. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by Nomoto, Impedance relation and Junjie's 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.

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