Theoretical Evaluation of Ultrasonic Velocities in the Liquid Binary System of Isomeric Xylenes with Ethyl Lactate

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Abstract: Ultrasonic velocities and densities of the binary liquid mixtures of ethyl lactate with *o*-xylene, *m*-xylene and *p*-xylene have been measured, over the entire composition range of mole fractions at different temperatures 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 are 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 was applied to understand the applicability of these theories to the present systems.

Keywords*: Ethyl lactate, Ultrasonic velocities, Chi-square test, Molecular interaction parameter

Introduction

The studies on ultrasonic velocities and their dependence on composition and temperature are of great importance in many fields of applied research and find applications in important chemical, industrial and biological processes. Ultrasonic velocities of liquid mixtures containing polar and non-polar groups are of considerable importance in understanding intermolecular interaction between component molecules[1-6]. Comparative studies on the experimental theoretical values of ultrasonic velocities for various organic liquid mixtures using different theories/ models like Nomoto[7], Impedance relation[8], Van Dael and Vangael[9], Junjie[10] and Rao's specific velocity[11] have been carried out by many researchers. The present study is a continuation of our research programme on application of theoretical models of ultrasonic velocities of liquid binaries at different temperatures[12-16].

In this paper, we report the experimental and theoretical ultrasonic velocities of ethyl lactate (EL) with *o*-xylene, *m*-xylene and *p*-xylene evaluated by various theoretical models such as Nomoto (NOM), Impedance (IMP),Van Deal and Vangeel (VDV), Junjie (JUN), Rao's

specific velocity (RAO) at 303.15-318.15 K 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.

Experimental

The pure solvents used in the present study such as ethyl lactate (EL) (Merk >99%) and *o*-xylene (OXL), *m*-xylene (MXL) and *p*-xylene (PXL)) was acquired from S.D fine chemicals India ltd and were purified as described in the literature[17,18]. 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) was 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.s^{-1} and an uncertainty less than ±0.1 m.sec^{-1} and temperature stability was maintained within ±0.01 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

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

where the molar sound velocity R = $x_1R_1+x_2R_2$. Hence, ultrasonic velocity (U) is given by

$$U = \left[\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right]^3 \tag{1}$$

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:

$$U = \sum x_i Z_i / \sum x_{ii} \tag{2}$$

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.

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

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

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

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

Junjie's 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 is given as

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

where the symbols have their usual meanings.

Rao's relation

Using the ratio of the temperature coefficient of velocity and expansion coefficient, Rao derived a formula for ultrasonic velocity (U)

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

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 formula

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

where n is the number of data used and 'U $_{(obs)}$ = experimental values of ultrasonic velocities, $U_{(cal)}$ = computed values of ultrasonic velocities

Relative percentage of error (σ)

The Average percentage error is calculated by using the relation

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

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

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

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 EL + *o*-xylene, EL + *m*-xylene, EL + *p*-xylene 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 (EL + OXL)

X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
AT 303.15 K												
0.0000	1337.8	1337.8	1337.8	1337.8	1337.8	1337.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.1051	1331.2	1330.0	1328.5	1329.2	1329.1	1345.0	-0.09	-0.20	-0.15	-0.16	1.04	0.0031
0.2090	1324.7	1322.2	1319.6	1320.8	1320.6	1349.6	-0.19	-0.38	-0.30	-0.31	1.88	0.0060
0.3117	1317.8	1314.5	1311.2	1312.6	1312.4	1351.4	-0.25	-0.50	-0.39	-0.41	2.55	0.0079
0.4133	1310.5	1306.8	1303.1	1304.7	1304.4	1349.8	-0.28	-0.57	-0.45	-0.47	3.00	0.0090
0.5138	1303.1	1299.1	1295.3	1296.9	1296.6	1344.5	-0.31	-0.60	-0.47	-0.50	3.18	0.0095
0.6132	1295.3	1291.5	1287.9	1289.4	1289.1	1334.9	-0.30	-0.57	-0.46	-0.48	3.05	0.0092
0.7115	1287.0	1283.8	1280.8	1282.1	1281.8	1319.3	-0.25	-0.48	-0.38	-0.40	2.51	0.0077
0.8087	1278.4	1276.3	1274.0	1274.9	1274.7	1300.7	-0.17	-0.34	-0.27	-0.29	1.75	0.0055
0.9049	1269.8	1268.7	1267.5	1268.0	1267.9	1280.6	-0.09	-0.18	-0.14	-0.15	0.85	0.0029
1.0000	1261.2	1261.2	1261.2	1261.2	1261.2	1261.2	0.00	0.00	0.00	0.00	0.00	0.0000
AT 308.15 K												
0.0000	1312.1	1312.1	1312.1	1312.1	1312.1	1312.1	0.00	0.00	0.00	0.00	0.00	0.0000
0.1051	1305.9	1305.0	1303.7	1304.3	1304.1	1320.3	-0.07	-0.17	-0.13	-0.14	1.10	0.0025
0.2090	1300.0	1297.9	1295.7	1296.6	1296.4	1325.4	-0.16	-0.33	-0.26	-0.28	1.96	0.0052
0.3117	1293.7	1290.9	1288.0	1289.2	1288.9	1327.9	-0.22	-0.44	-0.35	-0.37	2.64	0.0070
0.4133	1287.1	1283.9	1280.7	1282.0	1281.7	1326.9	-0.25	-0.50	-0.40	-0.42	3.09	0.0079
0.5138	1280.4	1276.9	1273.7	1275.0	1274.6	1322.2	-0.27	-0.53	-0.42	-0.45	3.27	0.0085
0.6132	1273.3	1270.0	1266.9	1268.2	1267.8	1313.1	-0.26	-0.50	-0.40	-0.43	3.12	0.0081
0.7115	1265.7	1263.1	1260.5	1261.5	1261.2	1298.3	-0.21	-0.41	-0.33	-0.35	2.58	0.0066
0.8087	1258.0	1256.2	1254.0	1255.0	1254.8	1281.1	-0.14	-0.30	-0.23	-0.25	1.84	0.0047
0.9049	1250.2	1249.4	1248.3	1248.7	1248.6	1261.8	-0.07	-0.15	-0.12	-0.13	0.93	0.0023
1.0000	1242.6	1242.6	1242.6	1242.6	1242.6	1242.6	0.00	0.00	0.00	0.00	0.00	0.0000
AT 313.15 K												
0.0000	1293.6	1293.6	1293.6	1293.6	1293.6	1293.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.1051	1287.2	1286.4	1285.1	1285.7	1285.6	1302.1	-0.06	-0.16	-0.12	-0.13	1.16	0.0024
0.2090	1281.0	1279.2	1277.0	1277.9	1277.8	1307.4	-0.14	-0.31	-0.24	-0.25	2.06	0.0048

0.3117	1274.6	1272.1	1269.3	1270.4	1270.2	1309.4	-0.20	-0.42	-0.33	-0.34	2.73	0.0066
0.4133	1267.9	1265.0	1261.8	1263.1	1262.9	1308.6	-0.23	-0.48	-0.38	-0.40	3.21	0.0075
0.5138	1261.0	1257.9	1254.7	1256.0	1255.8	1303.3	-0.24	-0.50	-0.39	-0.42	3.36	0.0079
0.6132	1253.8	1250.9	1247.9	1249.1	1248.9	1294.7	-0.23	-0.47	-0.37	-0.39	3.26	0.0075
0.7115	1246.1	1243.9	1241.4	1242.4	1242.2	1280.3	-0.17	-0.38	-0.30	-0.32	2.75	0.0060
0.8087	1238.5	1237.0	1235.1	1235.8	1235.7	1263.2	-0.12	-0.28	-0.22	-0.23	2.00	0.0043
0.9049	1230.7	1230.1	1229.0	1229.4	1229.3	1243.2	-0.05	-0.14	-0.10	-0.11	1.02	0.0021
1.0000	1223.2	1223.2	1223.2	1223.2	1223.2	1223.2	0.00	0.00	0.00	0.00	0.00	0.0000

					AT 318.15 K							
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1273.2	1273.2	1273.2	1273.2	1273.2	1273.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.1051	1266.6	1266.1	1264.9	1265.4	1265.3	1282.7	-0.04	-0.13	-0.09	-0.10	1.27	0.0019
0.2090	1260.2	1259.0	1257.0	1257.8	1257.7	1288.1	-0.09	-0.26	-0.19	-0.20	2.21	0.0038
0.3117	1253.8	1252.0	1249.4	1250.5	1250.3	1290.1	-0.14	-0.35	-0.27	-0.28	2.89	0.0053
0.4133	1247.2	1245.1	1242.1	1243.3	1243.1	1289.4	-0.17	-0.41	-0.31	-0.33	3.38	0.0063
0.5138	1240.4	1238.1	1235.1	1236.3	1236.1	1284.0	-0.18	-0.43	-0.33	-0.35	3.51	0.0066
0.6132	1233.2	1231.2	1228.4	1229.5	1229.3	1275.2	-0.16	-0.39	-0.30	-0.31	3.41	0.0059
0.7115	1225.8	1224.4	1222.0	1222.9	1222.8	1261.5	-0.12	-0.31	-0.23	-0.25	2.92	0.0047
0.8087	1218.3	1217.6	1215.8	1216.5	1216.4	1244.3	-0.06	-0.21	-0.15	-0.16	2.13	0.0030
0.9049	1211.0	1210.8	1209.8	1210.2	1210.1	1224.7	-0.01	-0.10	-0.06	-0.07	1.13	0.0013
1.0000	1204.1	1204.1	1204.1	1204.1	1204.1	1204.1	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 (EL+MXL)

					AT 303.15 K							
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1304.0	1304.0	1304.0	1304.0	1304.0	1304.0	0.00	0.00	0.00	0.00	0.00	0.0000
0.1035	1301.7	1299.8	1298.8	1299.1	1298.5	1316.0	-0.15	-0.22	-0.20	-0.25	1.10	0.0040
0.2062	1298.9	1295.6	1293.9	1294.4	1293.3	1327.8	-0.26	-0.39	-0.35	-0.43	2.23	0.0070
0.3081	1295.5	1291.4	1289.1	1289.7	1288.3	1334.7	-0.32	-0.49	-0.44	-0.56	3.03	0.0089
0.4092	1291.6	1287.1	1284.6	1285.3	1283.6	1337.4	-0.35	-0.54	-0.49	-0.62	3.54	0.0098
0.5095	1287.4	1282.8	1280.3	1281.0	1279.2	1337.1	-0.36	-0.55	-0.50	-0.63	3.86	0.0101
0.6091	1282.9	1278.5	1276.1	1276.8	1275.1	1331.8	-0.34	-0.53	-0.48	-0.61	3.82	0.0096
0.7080	1278.2	1274.2	1272.2	1272.7	1271.2	1320.0	-0.31	-0.47	-0.43	-0.55	3.27	0.0087
0.8060	1272.9	1269.9	1268.3	1268.7	1267.6	1301.6	-0.24	-0.36	-0.33	-0.42	2.26	0.0066
0.9034	1267.2	1265.5	1264.7	1264.9	1264.3	1281.5	-0.13	-0.20	-0.18	-0.23	1.13	0.0036
1.0000	1261.2	1261.2	1261.2	1261.2	1261.2	1261.2	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	1285.5	1285.5	1285.5	1285.5	1285.5	1285.5	0.00	0.00	0.00	0.00	0.00	0.0000
0.1035	1282.8	1281.3	1280.3	1280.6	1280.0	1299.0	-0.12	-0.20	-0.17	-0.22	1.26	0.0034
0.2062	1279.7	1277.1	1275.3	1275.8	1274.7	1311.4	-0.20	-0.34	-0.30	-0.39	2.48	0.0061
0.3081	1276.2	1272.9	1270.6	1271.2	1269.7	1318.1	-0.26	-0.44	-0.39	-0.51	3.28	0.0078
0.4092	1272.4	1268.6	1266.0	1266.8	1265.0	1321.0	-0.30	-0.50	-0.44	-0.58	3.82	0.0089
0.5095	1268.2	1264.3	1261.7	1262.4	1260.6	1319.9	-0.31	-0.51	-0.45	-0.60	4.07	0.0092
0.6091	1263.7	1260.0	1257.5	1258.2	1256.5	1314.3	-0.29	-0.49	-0.43	-0.57	4.01	0.0087
0.7080	1258.9	1255.7	1253.6	1254.1	1252.6	1302.5	-0.25	-0.42	-0.38	-0.50	3.46	0.0076
0.8060	1253.7	1251.3	1249.7	1250.2	1249.0	1284.5	-0.19	-0.32	-0.28	-0.38	2.46	0.0057
0.9034	1248.4	1247.0	1246.1	1246.3	1245.6	1263.7	-0.11	-0.18	-0.17	-0.22	1.23	0.0033
1.0000	1242.6	1242.6	1242.6	1242.6	1242.6	1242.6	0.00	0.00	0.00	0.00	0.00	0.0000

					AT 313.15 K							
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

0.1035	1262.9	1261.6	1260.6	1260.9	1260.3	1280.9	-0.10	-0.18	-0.16	-0.21	1.43	0.0031
0.2062	1259.5	1257.5	1255.7	1256.2	1255.0	1293.0	-0.16	-0.31	-0.26	-0.35	2.66	0.0052
0.3081	1256.0	1253.3	1250.9	1251.7	1250.1	1300.5	-0.22	-0.40	-0.35	-0.47	3.54	0.0070
0.4092	1252.2	1249.0	1246.4	1247.2	1245.4	1303.2	-0.25	-0.46	-0.40	-0.54	4.07	0.0080
0.5095	1247.9	1244.8	1242.1	1242.9	1241.0	1301.7	-0.25	-0.46	-0.40	-0.55	4.31	0.0080
0.6091	1243.5	1240.5	1238.0	1238.7	1236.9	1295.9	-0.24	-0.44	-0.38	-0.53	4.22	0.0077
0.7080	1238.8	1236.2	1234.1	1234.7	1233.1	1284.7	-0.21	-0.38	-0.33	-0.46	3.70	0.0067
0.8060	1233.8	1231.9	1230.3	1230.7	1229.5	1266.8	-0.15	-0.28	-0.25	-0.35	2.67	0.0050
0.9034	1228.6	1227.6	1226.7	1226.9	1226.2	1245.2	-0.08	-0.16	-0.14	-0.19	1.35	0.0027
1.0000	1223.2	1223.2	1223.2	1223.2	1223.2	1223.2	0.00	0.00	0.00	0.00	0.00	0.0000

AT 318.15 K												
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1244.4	1244.4	1244.4	1244.4	1244.4	1244.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.1035	1241.3	1240.5	1239.5	1239.8	1239.2	1260.2	-0.07	-0.14	-0.12	-0.17	1.52	0.0024
0.2062	1237.9	1236.5	1234.8	1235.3	1234.2	1272.8	-0.11	-0.25	-0.21	-0.30	2.82	0.0042
0.3081	1234.5	1232.5	1230.4	1231.0	1229.6	1279.7	-0.16	-0.33	-0.29	-0.40	3.66	0.0057
0.4092	1230.8	1228.5	1226.1	1226.8	1225.1	1282.5	-0.19	-0.38	-0.33	-0.46	4.20	0.0066
0.5095	1226.8	1224.5	1222.1	1222.7	1221.0	1280.9	-0.19	-0.39	-0.33	-0.47	4.41	0.0067
0.6091	1222.8	1220.4	1218.2	1218.8	1217.1	1275.5	-0.19	-0.38	-0.33	-0.47	4.31	0.0067
0.7080	1218.4	1216.4	1214.4	1214.9	1213.5	1264.7	-0.17	-0.33	-0.29	-0.40	3.80	0.0057
0.8060	1213.7	1212.3	1210.8	1211.2	1210.1	1246.6	-0.11	-0.23	-0.21	-0.30	2.71	0.0041
0.9034	1208.8	1208.2	1207.4	1207.6	1207.0	1226.4	-0.05	-0.12	-0.10	-0.15	1.45	0.0020
1.0000	1204.1	1204.1	1204.1	1204.1	1204.1	1204.1	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 (EL+PXL)

AT 303.15 K												
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1286.8	1286.8	1286.8	1286.8	1286.8	1286.8	0.00	0.00	0.00	0.00	0.00	0.0000
0.1070	1286.4	1284.2	1283.6	1283.5	1282.6	1301.7	-0.17	-0.22	-0.22	-0.29	1.19	0.0045
0.2124	1285.9	1281.6	1280.5	1280.5	1278.9	1317.8	-0.33	-0.42	-0.42	-0.55	2.48	0.0085
0.3162	1284.3	1279.1	1277.7	1277.5	1275.4	1329.8	-0.41	-0.52	-0.53	-0.69	3.55	0.0106
0.4184	1282.4	1276.5	1274.9	1274.8	1272.4	1338.2	-0.46	-0.58	-0.59	-0.78	4.35	0.0120
0.5190	1280.1	1273.9	1272.3	1272.2	1269.7	1343.2	-0.48	-0.61	-0.62	-0.81	4.93	0.0125
0.6181	1277.6	1271.4	1269.9	1269.7	1267.3	1339.1	-0.49	-0.60	-0.62	-0.81	4.82	0.0125
0.7157	1274.5	1268.8	1267.5	1267.4	1265.3	1330.4	-0.45	-0.55	-0.56	-0.72	4.38	0.0112
0.8119	1270.7	1266.3	1265.3	1265.2	1263.6	1314.8	-0.35	-0.42	-0.43	-0.56	3.47	0.0087
0.9066	1266.3	1263.7	1263.2	1263.1	1262.2	1292.7	-0.20	-0.25	-0.25	-0.32	2.09	0.0050
1.0000	1261.2	1261.2	1261.2	1261.2	1261.2	1261.2	0.00	0.00	0.00	0.00	0.00	0.0000

AT 308.15 K												
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1274.7	1274.7	1274.7	1274.7	1274.7	1274.7	0.00	0.00	0.00	0.00	0.00	0.0000
0.1070	1273.4	1271.5	1270.7	1270.8	1270.0	1289.8	-0.15	-0.21	-0.21	-0.27	1.29	0.0041
0.2124	1271.8	1268.2	1266.9	1267.0	1265.7	1305.3	-0.28	-0.39	-0.38	-0.48	2.63	0.0075
0.3162	1269.5	1265.0	1263.2	1263.5	1261.7	1315.5	-0.36	-0.49	-0.48	-0.62	3.63	0.0096
0.4184	1266.9	1261.8	1259.8	1260.0	1258.0	1323.5	-0.40	-0.56	-0.54	-0.70	4.47	0.0109
0.5190	1264.1	1258.6	1256.6	1256.8	1254.6	1327.8	-0.44	-0.59	-0.58	-0.75	5.04	0.0117
0.6181	1260.8	1255.3	1253.5	1253.7	1251.6	1322.6	-0.43	-0.58	-0.56	-0.73	4.90	0.0114
0.7157	1257.1	1252.1	1250.6	1250.7	1248.9	1313.5	-0.39	-0.52	-0.51	-0.65	4.49	0.0102
0.8119	1252.6	1248.9	1247.8	1247.9	1246.5	1297.4	-0.29	-0.38	-0.38	-0.49	3.58	0.0076
0.9066	1247.6	1245.8	1245.1	1245.2	1244.4	1275.0	-0.15	-0.20	-0.19	-0.26	2.20	0.0039
1.0000	1242.6	1242.6	1242.6	1242.6	1242.6	1242.6	0.00	0.00	0.00	0.00	0.00	0.0000

					AT 313.15 K						
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1251.1	1251.1	1251.1	1251.1	1251.1	1251.1	0.00	0.00	0.00	0.00	0.00	0.0000
0.1070	1249.8	1248.3	1247.6	1247.6	1246.8	1265.8	-0.12	-0.18	-0.17	-0.24	1.28	0.0035
0.2124	1248.4	1245.5	1244.3	1244.3	1242.9	1281.6	-0.23	-0.33	-0.33	-0.44	2.66	0.0066
0.3162	1246.5	1242.7	1241.2	1241.2	1239.4	1292.6	-0.31	-0.43	-0.43	-0.57	3.70	0.0086
0.4184	1244.4	1239.9	1238.2	1238.2	1236.1	1300.5	-0.36	-0.50	-0.50	-0.66	4.51	0.0100
0.5190	1241.9	1237.1	1235.4	1235.4	1233.2	1304.7	-0.39	-0.52	-0.53	-0.70	5.06	0.0106
0.6181	1239.1	1234.3	1232.7	1232.7	1230.6	1301.2	-0.39	-0.52	-0.52	-0.69	5.01	0.0104
0.7157	1235.8	1231.5	1230.2	1230.1	1228.3	1292.2	-0.35	-0.46	-0.46	-0.61	4.56	0.0092
0.8119	1231.8	1228.7	1227.7	1227.7	1226.3	1277.9	-0.25	-0.33	-0.33	-0.45	3.74	0.0067
0.9066	1227.5	1226.0	1225.4	1225.4	1224.6	1256.1	-0.13	-0.17	-0.17	-0.24	2.33	0.0034
1.0000	1223.2	1223.2	1223.2	1223.2	1223.2	1223.2	0.00	0.00	0.00	0.00	0.00	0.0000
					AT 318.15 K						
X_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1233.6	1233.6	1233.6	1233.6	1233.6	1233.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.1070	1232.0	1230.6	1229.9	1230.0	1229.2	1248.6	-0.11	-0.17	-0.17	-0.23	1.35	0.0033
0.2124	1230.2	1227.6	1226.4	1226.5	1225.2	1263.6	-0.21	-0.31	-0.30	-0.41	2.71	0.0060
0.3162	1228.1	1224.7	1223.1	1223.2	1221.5	1274.9	-0.28	-0.41	-0.40	-0.54	3.81	0.0080
0.4184	1225.9	1221.7	1220.0	1220.1	1218.1	1283.1	-0.34	-0.48	-0.48	-0.64	4.67	0.0096
0.5190	1223.1	1218.8	1217.0	1217.1	1215.0	1286.2	-0.35	-0.50	-0.49	-0.66	5.16	0.0099
0.6181	1220.0	1215.8	1214.1	1214.2	1212.2	1282.5	-0.34	-0.48	-0.47	-0.64	5.13	0.0095
0.7157	1216.6	1212.9	1211.5	1211.5	1209.8	1273.9	-0.31	-0.42	-0.42	-0.56	4.71	0.0084
0.8119	1212.5	1209.9	1208.9	1208.9	1207.6	1258.8	-0.21	-0.30	-0.30	-0.41	3.82	0.0059
0.9066	1208.2	1207.0	1206.4	1206.5	1205.7	1238.1	-0.10	-0.15	-0.14	-0.21	2.47	0.0029
1.0000	1204.1	1204.1	1204.1	1204.1	1204.1	1204.1	0.00	0.00	0.00	0.00	0.00	0.0000

Table 4. Values of χ^2 and σ for all values of the 3 binary mixturesat 4 different temperatures system-I (EL+OXL)

	χ^2					σ				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.06	0.24	0.15	0.16	6.47	-0.019	-0.038	-0.030	-0.032	0.193
308.15K	0.04	0.18	0.11	0.13	6.77	-0.016	-0.033	-0.026	-0.028	0.200
313.15K	0.03	0.16	0.10	0.11	7.29	-0.015	-0.031	-0.024	-0.026	0.210
318.15K	0.02	0.11	0.06	0.07	8.01	-0.010	-0.026	-0.019	-0.021	0.222
					SYSTEM-II (EL+MXL)					
	χ^2					σ				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.09	0.22	0.18	0.29	9.58	-0.025	-0.038	-0.034	-0.043	0.235
308.15K	0.06	0.18	0.14	0.24	10.81	-0.020	-0.034	-0.030	-0.040	0.252
313.15K	0.04	0.14	0.11	0.20	12.13	-0.017	-0.031	-0.027	-0.037	0.270
318.15K	0.02	0.10	0.07	0.15	12.67	-0.012	-0.026	-0.022	-0.031	0.279
					SYSTEM-III (EL+PXL)					
	χ^2					σ				
T(K)	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15K	0.17	0.27	0.28	0.48	15.61	-0.033	-0.042	-0.043	-0.056	0.301
308.15K	0.13	0.24	0.23	0.38	16.27	-0.029	-0.039	-0.038	-0.050	0.310
313.15K	0.10	0.18	0.18	0.32	16.58	-0.025	-0.034	-0.034	-0.046	0.316
318.15K	0.08	0.16	0.15	0.28	17.25	-0.023	-0.032	-0.032	-0.043	0.325

The data reveals that the velocities computed from Nomoto's relation (NOM), Impedance relation (IMP), Van Deal and Vangeel Ideal Mixing Relation (VDV) and Junjie's relation (JUN) exhibit more satisfactory agreement with the experimental values in the temperature range 303.15 K to 318.15 K than the Rao's specific velocity method (RAO). It is observed that the experimental values show deviation with the theoretical values of ultrasonic velocities which confirms the existence of molecular interactions[19]. This may be due to interactions occurring between the hetero molecules of the binaries. Higher deviations are observed in Rao's specific velocity method. 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 is observed approximately at 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 1-3 represent the variation of U^2_{exp}/U^2_{imx} with the mole fraction of EL 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. 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 and values of percentage deviation indicates the 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.
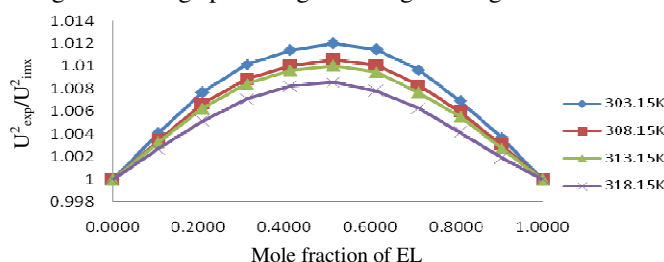

Figure 1. Plots of U^2_{exp}/U^2_{imx} *vs*. X_1 for the studied system EL+OXL, at temperatures 303.15, 308.15, 313.15 and 318.15 K
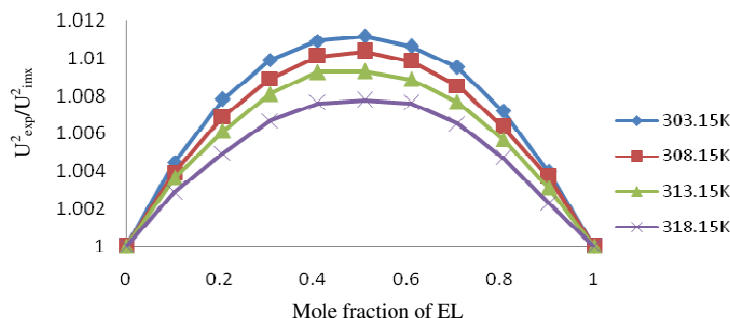
Figure 2. Plots of U^2_{exp}/U^2_{imx} *vs*. X_1 for the studied system EL+MXL, at temperatures 303.15, 308.15, 313.15 and 318.15 K

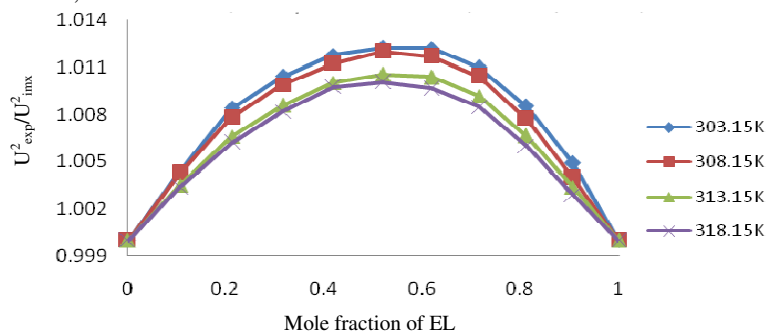**Figure 3.** Plots of U^2_{exp}/U^2_{imx} *vs*. X_1 for the studied system EL+PXL, at temperatures 303.15, 308.15, 313.15 and 318.15 K

Conclusion

From the values of experimental and evaluated velocity values, it may be concluded that, the Nomoto's relation, Impedance relation, Van Deal and Vangeel Ideal Mixing Relation, Junjie's relation have provided good agreement. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by these models 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[15].

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