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RESEARCH ARTICLE

Evaluation of Theoretical Velocities and Comparative Study of Ultrasonic Velocities in Binary Liquid Mixtures of Ethyl Lactate with Branched Alkanols at Different Temperatures

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Abstract: Theoretical velocities of binary liquid mixtures of ethyl lactate (EL) with 2-propanol (PNL), 2-butanol (BNL) and 2-methy,1-propanol (MPL), at different temperature (303.15, 308.15, 313.15 and 318.15 K) have been evaluated by using theoretical models of Nomoto (NOM), Impedance (IMP), Van Dael and Vangeel (VDV), Junjie's (JUN) and Rao's specific velocity (RAO) relations. Ultrasonic velocities and densities of these mixtures have also been measured experimentally as a function of composition of EL and temperature. The deviation in experimental values and calculated values from different theories confirms the existence of molecular interactions between molecules of the constituent liquids. 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 subjected to discussion in terms of intermolecular interactions between the component molecules in the chosen binary liquid mixtures.

Keywords: Theoretical velocities, Ultrasonic velocities, Chi-square test, Molecular interaction parameter

Introduction

In the recent years, ultrasonic studies play an important role in various organic liquid mixtures[1-4] due to the fact that the optical methods cannot identify and assess all types of interactions in the liquid mixtures having weak interactions. The physicochemical properties like adiabatic compressibility, heat capacity, coefficient of expansion may be obtained from ultrasonic velocity, density and viscosity data. The molecular interactions in pure and binary liquid mixtures can be qualitatively analyzed using ultrasonic velocity measurements which are of considerable interest in the last several years, using various theories [5-9], 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, impedance relation, Van Dael ideal mixing relation, Rao's specific velocity and Junjie's relation for the binary mixtures of several systems at various temperatures by our researchers. The results are interpreted in terms of intermolecular interactions between the binary component liquid mixtures[10-18]. In this paper, we report the experimental and theoretical ultrasonic velocities of the binary liquid mixtures of ethyl lactate with 2-propanol, 2-butanol and 2-methyl,1-propanol at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range, evaluated by using various theoretical models such as Nomoto (NOM), impedance (IMP), Van Dael and Vangeel (VDV), Junjie's (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) has also been made.

Experimental

Commercially available pure solvents were used in the present investigation EL (Merk > 99%) and PNL, BNL, MPL of AR grade procured from S.D fine chemicals (India) were purified by the standard methods described by Weissberger[19,20] and the purity of the chemicals was assessed by comparing their measured densities (ρ) and ultrasonic velocities (U) which are in good agreement with literature values. The mixtures were prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1\times 10^{-7}$ Kg and were stored in air-tight glass bottles. The uncertainty in the mole fraction was estimated to be less than $\pm 1\times 10^{-4}$. It is ensured that the components were adequately mixed before being transferred in to the apparatus. The required properties are measured within one day of the mixture preparation.

The densities, ρ, of pure liquids and their mixtures are determined for evaluating mole fractions using a $10^{-5} m^3$ Double - arm pycnometer and the values from triplicate replication at each temperature are reproducible within $2x10^{-1}$ 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 is 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 are 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. s^{-1} and an uncertainty less than ±0.1 $m.s^{-1}$. The temperature stability is maintained within ±0.01K.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

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

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 was used for evaluating the ultrasonic velocity in the liquid mixtures by the following relation:

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

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

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

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

Junjie's relation

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

$$U = \frac{\sum_{i=1}^{n} xiVi}{(\sum_{i=1}^{n} x_iM_i)^{1/2}(\sum_{i=1}^{n} x_iV_i/\rho_iu_i^2)^{1/2}} \qquad (4)$$

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)

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

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

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

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.

Molecular associations

The degree of intermolecular interaction or molecular association is given by

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

Where U_{exp} and U_{imx} are the experimental and theoretical velocities.

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) for all the three binaries ethyl lactate + 2-propanol, ethyl lactate + 2-butanol and ethyl lactate + 2-mthyl,1-propanol along with the percentage of deviations are presented in Tables 1-3 at all the four temperatures 303.15, 308.15, 313.15 and 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 + PNL)

303.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1111.3	1111.3	1111.3	1111.3	1111.3	1111.3	0.00	0.00	0.00	0.00	0.00	0.0000
0.0694	1127.2	1125.7	1124.7	1099.2	1117.2	1173.0	-0.13	-0.22	-2.49	-0.88	4.07	0.0516
0.1436	1142.8	1140.3	1138.4	1089.9	1124.8	1227.8	-0.22	-0.38	-4.63	-1.58	7.44	0.0994
0.2233	1158.0	1154.9	1152.5	1083.8	1134.0	1275.0	-0.26	-0.48	-6.40	-2.07	10.10	0.1415

Contd…..

0.3090	1173.0	1169.7	1166.9	1081.7	1145.0	1313.1	-0.28	-0.52	-7.79	-2.38	11.95	0.1760
0.4014	1187.8	1184.7	1181.6	1084.3	1158.1	1341.1	-0.26	-0.52	-8.72	-2.50	12.90	0.2001
0.5015	1202.6	1199.7	1196.7	1093.0	1173.2	1356.7	-0.24	-0.49	-9.11	-2.44	12.81	0.2106
0.6101	1217.2	1214.9	1212.2	1110.0	1190.8	1358.5	-0.19	-0.41	-8.81	-2.17	11.61	0.2026
0.7285	1231.7	1230.2	1228.1	1138.6	1211.0	1344.3	-0.12	-0.29	-7.56	-1.68	9.14	0.1702
0.8579	1246.7	1245.6	1244.4	1185.1	1234.4	1312.3	-0.09	-0.18	-4.94	-0.99	5.26	0.1067
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
308.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1106.4	1106.4	1106.4	1106.4	1106.4	1106.4	0.00	0.00	0.00	0.00	0.00	0.0000
0.0694	1120.2	1119.5	1118.6	1094.0	1111.6	1167.3	-0.06	-0.14	-2.34	-0.77	4.20	0.0485
0.1436	1134.2	1132.8	1131.1	1084.4	1118.3	1221.4	-0.12	-0.28	-4.39	-1.40	7.68	0.0940
0.2233	1147.8	1146.1	1143.8	1077.9	1126.6	1267.4	-0.14	-0.35	-6.09	-1.85	10.42	0.1339
0.3090	1160.8	1159.6	1156.9	1075.2	1136.6	1304.3	-0.10	-0.34	-7.37	-2.09	12.36	0.1656
0.4014	1174.2	1173.2	1170.3	1077.1	1148.4	1330.8	-0.09	-0.33	-8.27	-2.20	13.34	0.1884
0.5015	1187.6	1186.8	1184.0	1084.9	1162.3	1345.1	-0.06	-0.30	-8.65	-2.13	13.26	0.1982
0.6101	1200.7	1200.6	1198.1	1100.6	1178.3	1345.1	-0.01	-0.21	-8.33	-1.86	12.03	0.1901
0.7285	1214.8	1214.5	1212.6	1127.5	1196.8	1329.4	-0.03	-0.18	-7.19	-1.48	9.43	0.1609
0.8579	1228.4	1228.5	1227.4	1171.2	1218.1	1295.7	0.01	-0.08	-4.66	-0.84	5.48	0.1001
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
313.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1097.2	1097.2	1097.2	1097.2	1097.2	1097.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0694	1109.3	1109.4	1108.5	1084.7	1101.8	1157.5	0.01	-0.07	-2.22	-0.67	4.35	0.0459
0.1436	1121.4	1121.7	1120.0	1074.9	1107.9	1210.5	0.02	-0.12	-4.15	-1.20	7.95	0.0885
0.2233	1133.8	1134.0	1131.8	1068.1	1115.5	1255.5	0.02	-0.17	-5.79	-1.61	10.73	0.1268
0.3090	1145.6	1146.5	1143.9	1065.1	1124.7	1291.4	0.08	-0.15	-7.03	-1.82	12.73	0.1570
0.4014	1157.8	1159.0	1156.3	1066.5	1135.7	1316.7	0.11	-0.13	-7.89	-1.91	13.73	0.1786
0.5015	1170.2	1171.7	1169.0	1073.6	1148.5	1329.9	0.13	-0.10	-8.26	-1.85	13.65	0.1881
0.6101	1182.3	1184.4	1182.1	1088.4	1163.5	1328.9	0.18	-0.02	-7.95	-1.59	12.40	0.1801
0.7285	1195.6	1197.3	1195.4	1113.8	1180.7	1312.2	0.14	-0.01	-6.84	-1.25	9.75	0.1522
0.8579	1209.1	1210.2	1209.1	1155.4	1200.5	1277.3	0.09	0.00	-4.44	-0.71	5.64	0.0952
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
318.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1090.1	1090.1	1090.1	1090.1	1090.1	1090.1	0.00	0.00	0.00	0.00	0.00	0.0000
0.0694	1100.2	1101.1	1100.3	1077.4	1094.0	1150.1	0.09	0.01	-2.08	-0.56	4.54	0.0428
0.1436	1110.3	1112.3	1110.8	1067.3	1099.3	1202.0	0.18	0.04	-3.88	-0.99	8.26	0.0823
0.2233	1120.4	1123.5	1121.4	1060.2	1106.1	1245.8	0.27	0.09	-5.38	-1.28	11.19	0.1168
0.3090	1131.2	1134.8	1132.4	1056.6	1114.4	1280.6	0.31	0.11	-6.59	-1.49	13.21	0.1461
0.4014	1141.9	1146.1	1143.6	1057.4	1124.3	1304.7	0.37	0.15	-7.40	-1.54	14.26	0.1661
0.5015	1153.1	1157.6	1155.1	1063.8	1136.0	1316.6	0.39	0.17	-7.75	-1.48	14.18	0.1750
0.6101	1164.3	1169.1	1166.9	1077.4	1149.6	1314.1	0.41	0.22	-7.46	-1.26	12.87	0.1678
0.7285	1176.3	1180.7	1179.0	1101.3	1165.3	1296.0	0.37	0.23	-6.38	-0.93	10.18	0.1409
0.8579	1189.6	1192.3	1191.4	1140.3	1183.4	1259.9	0.23	0.15	-4.14	-0.52	5.91	0.0883
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+BNL)

x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
303.15 K												
0.0000	1145.6	1145.6	1145.6	1145.6	1145.6	1145.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0819	1159.1	1156.8	1157.4	1141.5	1150.6	1188.3	-0.20	-0.14	-1.52	-0.73	2.52	0.0311
0.1671	1171.9	1168.1	1169.2	1139.6	1156.8	1226.1	-0.32	-0.23	-2.76	-1.29	4.62	0.0576
0.2560	1184.2	1179.5	1180.9	1140.0	1164.3	1258.2	-0.39	-0.28	-3.73	-1.68	6.25	0.0790
0.3486	1196.1	1191.0	1192.5	1143.3	1173.1	1283.4	-0.43	-0.30	-4.42	-1.92	7.30	0.0945
0.4453	1207.6	1202.5	1204.1	1149.7	1183.4	1301.6	-0.42	-0.29	-4.79	-2.00	7.78	0.1032
0.5463	1219.0	1214.1	1215.6	1159.9	1195.3	1311.9	-0.40	-0.28	-4.85	-1.95	7.62	0.1044
0.6520	1229.9	1225.8	1227.1	1174.8	1208.8	1313.4	-0.34	-0.23	-4.48	-1.72	6.79	0.0961
0.7625	1241.0	1237.5	1238.5	1195.3	1224.1	1305.8	-0.28	-0.20	-3.68	-1.36	5.22	0.0779
0.8784	1251.2	1249.3	1249.9	1223.3	1241.5	1288.4	-0.15	-0.11	-2.23	-0.77	2.97	0.0461
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
308.15 K												
0.0000	1140.2	1140.2	1140.2	1140.2	1140.2	1140.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0819	1152.2	1150.2	1150.7	1135.6	1144.3	1182.3	-0.18	-0.13	-1.44	-0.68	2.61	0.0295
0.1671	1163.8	1160.2	1161.1	1133.1	1149.6	1219.2	-0.31	-0.23	-2.64	-1.22	4.76	0.0549
0.2560	1174.9	1170.3	1171.5	1132.9	1156.1	1250.2	-0.39	-0.29	-3.57	-1.60	6.41	0.0755
0.3486	1185.6	1180.4	1181.8	1135.4	1163.8	1274.3	-0.44	-0.32	-4.24	-1.84	7.48	0.0904
0.4453	1195.9	1190.6	1192.1	1140.9	1172.9	1291.3	-0.44	-0.32	-4.60	-1.92	7.97	0.0988
0.5463	1205.7	1200.9	1202.3	1150.0	1183.5	1300.1	-0.40	-0.28	-4.62	-1.84	7.83	0.0993
0.6520	1215.4	1211.2	1212.4	1163.4	1195.6	1300.1	-0.34	-0.24	-4.28	-1.63	6.97	0.0914
0.7625	1224.8	1221.6	1222.5	1182.2	1209.3	1290.8	-0.26	-0.18	-3.48	-1.26	5.39	0.0734
0.8784	1233.7	1232.1	1232.6	1207.8	1224.9	1271.7	-0.13	-0.09	-2.10	-0.71	3.08	0.0433
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
313.15 K												
0.0000	1136.2	1136.2	1136.2	1136.2	1136.2	1136.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0819	1146.5	1144.7	1145.1	1131.0	1139.3	1177.3	-0.16	-0.12	-1.35	-0.63	2.69	0.0276
0.1671	1156.8	1153.2	1154.0	1127.8	1143.5	1213.4	-0.31	-0.24	-2.51	-1.15	4.89	0.0521
0.2560	1166.4	1161.8	1162.8	1126.8	1148.8	1243.1	-0.39	-0.31	-3.39	-1.51	6.57	0.0715
0.3486	1175.4	1170.4	1171.6	1128.3	1155.3	1266.1	-0.42	-0.32	-4.01	-1.71	7.72	0.0852
0.4453	1184.3	1179.1	1180.3	1132.7	1163.0	1281.4	-0.44	-0.34	-4.36	-1.80	8.20	0.0932
0.5463	1192.7	1187.8	1189.0	1140.5	1172.0	1288.5	-0.41	-0.31	-4.38	-1.74	8.03	0.0937
0.6520	1200.6	1196.6	1197.6	1152.2	1182.4	1286.8	-0.33	-0.25	-4.03	-1.52	7.18	0.0857
0.7625	1208.4	1205.4	1206.2	1169.0	1194.3	1275.6	-0.25	-0.18	-3.26	-1.17	5.56	0.0686
0.8784	1215.8	1214.3	1214.7	1192.0	1207.9	1254.4	-0.12	-0.09	-1.96	-0.65	3.18	0.0403
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
318.15 K												
0.0000	1133.6	1133.6	1133.6	1133.6	1133.6	1133.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0819	1142.2	1140.5	1140.8	1127.7	1135.6	1173.9	-0.15	-0.12	-1.27	-0.57	2.77	0.0259
0.1671	1150.6	1147.5	1148.0	1123.7	1138.7	1208.4	-0.27	-0.22	-2.34	-1.04	5.02	0.0484

Contd...

0.2560	1158.6	1154.4	1155.2	1121.8	1142.8	1236.5	-0.36	-0.30	-3.17	-1.37	6.72	0.0666
0.3486	1166.5	1161.4	1162.3	1122.3	1147.9	1257.9	-0.43	-0.36	-3.79	-1.60	7.83	0.0803
0.4453	1173.6	1168.5	1169.3	1125.5	1154.1	1271.4	-0.44	-0.36	-4.10	-1.66	8.33	0.0873
0.5463	1180.2	1175.5	1176.4	1131.8	1161.5	1276.8	-0.39	-0.33	-4.10	-1.58	8.19	0.0874
0.6520	1186.5	1182.6	1183.4	1141.8	1170.1	1273.3	-0.33	-0.27	-3.77	-1.38	7.32	0.0798
0.7625	1192.2	1189.8	1190.3	1156.3	1180.0	1260.2	-0.20	-0.16	-3.01	-1.02	5.70	0.0630
0.8784	1197.9	1196.9	1197.2	1176.6	1191.3	1237.4	-0.08	-0.06	-1.78	-0.55	3.30	0.0366
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+MPL)

303.15 K											
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1145.6	1145.6	1145.6	1145.6	1145.6	1145.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0825	1158.9	1156.9	1157.5	1141.5	1150.6	1188.0	-0.17	-0.12	-1.50	-0.71	2.51	0.0308
0.1683	1171.8	1168.3	1169.3	1139.5	1156.9	1225.6	-0.30	-0.21	-2.75	-1.27	4.59	0.0574
0.2576	1184.5	1179.7	1181.1	1140.1	1164.4	1257.4	-0.40	-0.29	-3.75	-1.70	6.15	0.0795
0.3505	1196.6	1191.2	1192.8	1143.4	1173.3	1282.4	-0.45	-0.32	-4.45	-1.95	7.17	0.0953
0.4473	1208.3	1202.7	1204.4	1149.9	1183.6	1300.4	-0.46	-0.33	-4.83	-2.04	7.62	0.1042
0.5484	1219.6	1214.3	1215.9	1160.2	1195.5	1310.2	-0.43	-0.31	-4.87	-1.98	7.43	0.1051
0.6538	1230.6	1226.0	1227.3	1175.1	1209.0	1311.6	-0.38	-0.27	-4.51	-1.75	6.58	0.0968
0.7640	1241.0	1237.6	1238.7	1195.7	1224.4	1304.1	-0.27	-0.19	-3.65	-1.34	5.09	0.0773
0.8793	1251.2	1249.4	1250.0	1223.6	1241.7	1287.3	-0.15	-0.10	-2.21	-0.76	2.89	0.0457
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
308.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1140.2	1140.2	1140.2	1140.2	1140.2	1140.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0825	1152.1	1150.2	1150.8	1135.6	1144.3	1181.9	-0.16	-0.12	-1.43	-0.67	2.59	0.0293
0.1683	1163.9	1160.3	1161.3	1133.1	1149.7	1218.6	-0.31	-0.23	-2.65	-1.22	4.70	0.0551
0.2576	1175.2	1170.5	1171.7	1132.9	1156.2	1249.4	-0.40	-0.30	-3.60	-1.62	6.31	0.0760
0.3505	1186.1	1180.6	1182.0	1135.5	1164.0	1273.3	-0.46	-0.34	-4.27	-1.86	7.35	0.0912
0.4473	1196.5	1190.9	1192.3	1141.0	1173.1	1289.9	-0.47	-0.35	-4.64	-1.95	7.81	0.0996
0.5484	1206.4	1201.1	1202.5	1150.2	1183.7	1298.3	-0.44	-0.32	-4.66	-1.88	7.62	0.1001
0.6538	1216.0	1211.4	1212.6	1163.7	1195.8	1298.2	-0.38	-0.28	-4.30	-1.66	6.76	0.0920
0.7640	1225.1	1221.8	1222.7	1182.5	1209.5	1289.2	-0.27	-0.20	-3.48	-1.27	5.23	0.0734
0.8793	1234.1	1232.2	1232.7	1208.1	1225.1	1270.7	-0.16	-0.12	-2.11	-0.73	2.97	0.0436
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
313.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1136.2	1136.2	1136.2	1136.2	1136.2	1136.2	0.00	0.00	0.00	0.00	0.00	0.0000
0.0825	1146.5	1144.8	1145.2	1131.0	1139.3	1176.9	-0.15	-0.11	-1.36	-0.63	2.65	0.0277
0.1683	1157.0	1153.3	1154.1	1127.8	1143.5	1212.7	-0.32	-0.25	-2.53	-1.16	4.81	0.0525
0.2576	1166.9	1162.0	1163.0	1126.8	1148.9	1242.2	-0.42	-0.34	-3.44	-1.54	6.45	0.0724
0.3505	1176.3	1170.6	1171.8	1128.4	1155.4	1264.7	-0.48	-0.38	-4.07	-1.78	7.52	0.0867
0.4473	1185.3	1179.3	1180.5	1132.8	1163.1	1279.8	-0.51	-0.40	-4.43	-1.87	7.97	0.0948
0.5484	1193.7	1188.0	1189.2	1140.7	1172.2	1286.6	-0.48	-0.38	-4.44	-1.80	7.78	0.0952
0.6538	1201.6	1196.8	1197.8	1152.5	1182.6	1284.8	-0.40	-0.32	-4.09	-1.58	6.93	0.0870
0.7640	1209.2	1205.5	1206.3	1169.2	1194.5	1274.0	-0.30	-0.24	-3.30	-1.22	5.36	0.0695
0.8793	1216.6	1214.4	1214.8	1192.2	1208.0	1253.5	-0.18	-0.15	-2.01	-0.71	3.03	0.0414
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

Contd…

318.15 K												
x_1	EXP	NOM	IMP	VDV	JUN	RAO	%NOM	%IMP	%VDV	%JUN	%RAO	α
0.0000	1133.6	1133.6	1133.6	1133.6	1133.6	1133.6	0.00	0.00	0.00	0.00	0.00	0.0000
0.0825	1142.0	1140.6	1140.9	1127.7	1135.6	1173.2	-0.13	-0.10	-1.26	-0.56	2.74	0.0256
0.1683	1150.7	1147.5	1148.1	1123.7	1138.7	1207.7	-0.27	-0.22	-2.35	-1.05	4.95	0.0487
0.2576	1159.0	1154.5	1155.3	1121.8	1142.7	1235.8	-0.38	-0.32	-3.21	-1.40	6.63	0.0674
0.3505	1167.0	1161.6	1162.4	1122.3	1147.9	1256.8	-0.47	-0.39	-3.83	-1.64	7.69	0.0812
0.4473	1174.3	1168.6	1169.5	1125.6	1154.1	1270.2	-0.48	-0.41	-4.15	-1.72	8.17	0.0885
0.5484	1181.2	1175.7	1176.5	1131.9	1161.5	1275.3	-0.47	-0.40	-4.17	-1.67	7.97	0.0889
0.6538	1187.5	1182.7	1183.5	1142.0	1170.1	1271.6	-0.40	-0.34	-3.83	-1.46	7.09	0.0813
0.7640	1193.4	1189.8	1190.4	1156.6	1180.0	1258.9	-0.30	-0.25	-3.09	-1.12	5.49	0.0647
0.8793	1199.3	1197.0	1197.3	1176.7	1191.3	1236.4	-0.19	-0.17	-1.88	-0.66	3.10	0.0387
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 mixtures at 4 different temperatures system-I (EL+PNL)

		χ^2				σ				
T, K	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15	0.05	0.18	53.55	4.04	106.40	-0.018	-0.035	-0.653	-0.170	0.772
308.15	0.01	0.07	47.56	3.06	112.51	-0.006	-0.022	-0.616	-0.149	0.796
313.15	0.01	0.01	42.57	2.26	117.78	0.008	-0.008	-0.585	-0.128	0.818
318.15	0.10	0.02	36.78	1.42	125.60	0.026	0.012	-0.545	-0.102	0.848
SYSTEM-II (EL+BNL)										
		χ^2				σ				
T, K	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15	0.13	0.06	15.55	2.65	38.79	-0.029	-0.021	-0.338	-0.137	0.481
308.15	0.12	0.06	14.04	2.36	40.52	-0.029	-0.021	-0.322	-0.129	0.493
313.15	0.12	0.07	12.40	2.05	42.45	-0.028	-0.022	-0.303	-0.121	0.507
318.15	0.11	0.07	10.76	1.68	43.77	-0.027	-0.022	-0.283	-0.109	0.517
SYSTEM-III (EL+MPL)										
		χ^2				σ				
T, K	NOM	IMP	VDV	JUN	RAO	NOM	IMP	VDV	JUN	RAO
303.15	0.14	0.07	15.68	2.70	37.16	-0.030	-0.021	-0.339	-0.137	0.471
308.15	0.14	0.08	14.21	2.43	38.72	-0.031	-0.023	-0.324	-0.131	0.483
313.15	0.15	0.10	12.78	2.20	40.10	-0.033	-0.026	-0.308	-0.125	0.493
318.15	0.14	0.10	11.10	1.83	41.72	-0.031	-0.026	-0.287	-0.114	0.505

Even though, there are variations between the evaluated and experimental values for all the theoretical models, the deviations in velocities for Impedance relation (IMP) and Nomoto models (NOM) are found to be less than that of other approaches at all temperatures. The occurrence of positive deviations in all the models confirms the existence of molecular interactions due to strong hydrogen bonding interactions between the components[21]. There are larger variations in some intermediate concentration range in all the models 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 resulting in the deviations.. Therefore, it is attributed that the observed deviation of theoretical values of velocity from the experimental values arise due to the molecular interactions between the unlike molecules in the liquid mixtures. From the tables, it is observed that maximum 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. The percentage deviations in velocity are found to have both negative and positive magnitudes indicating the 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 PNL to MPL. This suggests somewhat stronger interaction of EL with PNL in comparison to other components. The negative values 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 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.

Conclusion

From the values of experimental and evaluated velocity values, it may be concluded that, the Impedance Relation followed by Nomoto relation of Ultrasonic velocity have provided results with smaller deviations. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by Impedance Relation and Nomoto relation in deriving the empirical relations have not been truly observed in the aforementioned binary liquid mixtures. However, the positive deviations of the experimental velocities from the theoretical values using all the theoretical models indicate the existence of chemical forces such as hydrogen bonding and dipole-dipole interactions between the component molecules.

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