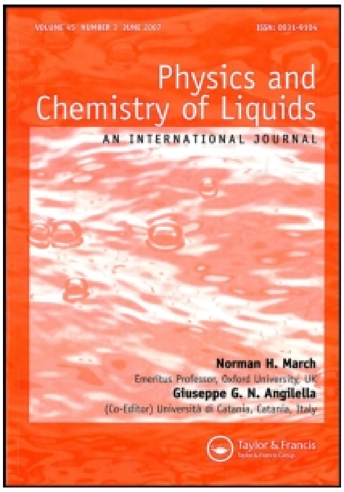

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Acoustic, viscometric and optical properties of binary mixtures of tetrahydrofuran with 1-propanol and 2-propanol

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Acoustic, viscometric and optical properties of binary mixtures of tetrahydrofuran with 1-propanol and 2-propanol

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The values estimated from various mixing rules for the ultrasonic velocity, viscosity and refractive index have been compared with the respective values measured earlier at 293, 303, and 313 K over the entire mole fraction range of two binary mixtures of tetrahydrofuran (THF) with 1-propanol (1-p) and 2-propanol (2-p). There is an excellent agreement between the experimental values of ultrasonic velocity and of refractive index with the respective values obtained from the mixing rules. The mixing rules for viscosity provide values agreeing broadly with those obtained from experimental measurements. The relative merits and interrelations of these mixing rules are discussed.

Keywords: Tetrahydrofuran; Propanol; Mixing rules; Ultrasonic velocity; Viscosity; Refractive index

1. Introduction

Theoretical knowledge concerning the mixing properties of liquids is of importance in many engineering design processes associated with chemical, petrochemical, and pharmaceutical industries and therefore attracts a lot of attention from the scientific community [1–6]. A number of empirical, semi-empirical, and statistical-mechanical theories already exist which provide mixing rules for theoretically predicting the ultrasonic velocity (u), viscosity (η), and refractive index (n) of liquid mixtures with different components and compositions. From the values of these parameters, a number of other related thermo-dynamic parameters [7–17] can be calculated for a given liquid mixture. Studying the thermodynamic parameters associated with the mixtures helps us to gain better understanding of various intermolecular interactions, taking place within these mixtures, as well as of the transport properties of the mixtures under different physicochemical conditions [7–17]. This in turn helps in bringing out the facts which can have positive implications for both industry as well as the theory building process.

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Thus, we can verify and modify the already existing theories and formulations [8,13–18] or can lay a solid groundwork for the emergence of new theories and formulations of various physicochemical phenomena associated with liquid mixtures.

In our effort towards a systematic investigation of the acoustic, viscometric, and optical properties of binary liquid mixtures, we earlier reported [19,20] ultrasonic velocity (u), refractive index (n), and the excess values of isentropic compressibility (β_S^E), viscosity (η^E), internal pressure (π_i^E), molar volume (V_m^E), and energy of activation for viscous flow (ΔG^E) for tetrahydrofuran (THF) + 1-propanol (1-p) and THF + 2-propanol (2-p) mixtures at the atmospheric pressure and 293, and 313 K temperatures over the whole composition range. The choice of the component liquids was based on the facts that THF is frequently utilized as a solvent in many pharmaceutical synthetic procedures because of its broad solvency for polar and non-polar compounds. THF is particularly capable of dissolving many ionic species and organometallics, which are commonly used in specialty syntheses. THF solvents can be used to join rigid plastic pipes and in compounded cements for leather, plastic sheet film extrusions, and for moulded plastic parts assemblies. The combined advantages of rapid solvent activity, minimum gelation, and lower relative viscosities for resin solutions, make THF an attractive solvent choice. While 1-p and 2-p are used in the synthesis of many organic compounds and as coupling and dispersing agents in the chemical, pharmaceutical, and household industries, as carrier and extraction solvent for natural products, such as flavourings, vegetable oils, resins, waxes, and gums, and as a solvent for synthetic polymers, such as polyvinyl butyral, cellulose esters, lacquers, and PVC adhesives.

As an extension of earlier studies for examining the validity of various mixing rules for predicting the values of u, η, and n for multicomponent liquid mixtures we have investigated four mixing rules [17,18], viz., van Dael and Vangeel's relation, Nomoto's relation, Junjie's relation, and Collision Factor Theory (CFT) based relation for the theoretical prediction of ultrasonic velocity; six mixing rules [21,22], viz., Bingham's relation, Kendall–Munroe relation, Additive relation, Frankel's relation, Hind–Ubbelohde relation, and Sutherland–Wassiljewa relation for viscosity prediction and eight mixing rules [23,24], for the prediction of n, which are Gladstone–Dale (GD) relation, Arago–Biot (AB) relation, Heller's (H) relation, Wiener's (W) relation, Lorentz–Lorenz (LL) relation, Newton's (Nn) relation, Eykman's (Eyk) relation and Oster's (Os) relation. The results obtained have been used to assess the relative merits of these mixing rules.

2. Theory

2.1. *Mixing rules for ultrasonic velocity*

van Dael and Vangeel proposed the following ideal mixing relation for predicting speed of sound of a binary liquid mixture:

$$\left(\frac{1}{x_1M_1 + x_2M_2}\right)\frac{1}{u_m^2} = \left(\frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2}\right) \tag{1}$$

Nomoto, assuming the linearity of the molar sound velocity and the additivity of the molar volumes in liquid solutions, gave the following relation:

$$u_{\mathrm{m}} = \left(\frac{R_{\mathrm{m}}}{V_{\mathrm{m}}}\right)^3 = \left(\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2}\right)^3 \tag{2}$$

Zhang Junjie gave following relation for the ultrasonic velocity in a binary mixture:

$$u_{\mathrm{m}} = \frac{x_1 V_1 + x_2 V_2}{\sqrt{(x_1 M_1 + x_2 M_2)(x_1 V_1/\rho_1 u_1^2) + (x_2 V_2/\rho_2 u_2^2)}} \tag{3}$$

Nutsch-Kuhnkies [17] extended the relation given by Schaaffs [17] for predicting ultrasonic velocity in pure liquids on the basis of CFT, to the binary liquid mixtures. The relation is

$$u_{\mathrm{m}} = u_{\infty}(x_1 S_1 + x_2 S_2)\frac{(x_1 B_1 + x_2 B_2)}{V_{\mathrm{m}}} \tag{4}$$

2.2. *Mixing rules for viscosity*

Bingham proposed the following relation for ideal viscosity of a binary mixture:

$$\eta_{\mathrm{m}} = x_1 \eta_1 + x_2 \eta_2 \tag{5}$$

This relation assumes no changes in the volume of the mixture on mixing the components.

According to Kendall–Munroe, the viscosity of a binary mixture is

$$\ln \eta_{\mathrm{m}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 \tag{6}$$

and it assumes logarithmic additivity of viscosity

The Additive relation, based on Arrhenius' model [25] and Eyring's model [26] for the viscosity of pure liquids can be modified for binary mixtures as

$$\ln \eta_{\mathrm{m}} V_{\mathrm{m}} = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 \tag{7}$$

Frenkel, using the Eyring's model, developed the following logarithmic relation for non-ideal binary liquid mixtures:

$$\ln \eta_{\mathrm{m}} = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12} \tag{8}$$

which takes into account the molecular interaction.

Hind and Ubbelohde gave following relation for predicting viscosity of binary mixture, taking into consideration of the molecular interactions:

$$\eta_{\mathrm{m}} = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 \eta_{12} \tag{9}$$

The Sutherland–Wassiljewa equation for viscosity of liquid mixtures is:

$$\eta_{\mathrm{m}} = \sum_i \frac{x_i \eta_i}{\sum_j A_{ij} x_j} \tag{10}$$

2.3. *Mixing rules for refractive index*

Gladstone–Dale equation for predicting the refractive index of a binary mixture is as follows.

$$(n_{\mathrm{m}} - 1) = \varphi_1(n_1 - 1) + \varphi_2(n_2 - 1) \tag{11}$$

Arago–Biot, assuming volume additivity, proposed the following relation for refractive index of binary mixtures:

$$n_{\mathrm{m}} = \varphi_1 n_1 + \varphi_2 n_2 \tag{12}$$

Heller's relation is given by

$$\left(\frac{n_{\mathrm{m}} - n_1}{n_1}\right) = \frac{3}{2}\left(\frac{m^2 - 1}{m^2 + 2}\right)\varphi_2 \tag{13}$$

Wiener's relation may be represented as

$$\left(\frac{n_{\mathrm{m}}^2 - n_1^2}{n_{\mathrm{m}}^2 + 2n_1^2}\right) = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\varphi_2 \tag{14}$$

The L–L relation for refractive index is based on the change in the molecular polarizability with volume fraction.

$$\left(\frac{n_{\mathrm{m}}^2 - 1}{n_{\mathrm{m}}^2 + 2}\right)\frac{1}{\rho_{\mathrm{m}}} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\frac{w_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\frac{w_2}{\rho_2} \tag{15}$$

Newton gave the following equation:

$$(n_{\mathrm{m}}^2 - 1) = \varphi_1(n_1^2 - 1) + \varphi_2(n_2^2 - 1) \tag{16}$$

Eykman's relation may be represented as

$$\left(\frac{n_{\mathrm{m}}^2 - 1}{n_{\mathrm{m}} + 0.4}\right)V_{\mathrm{m}} = \left(\frac{n_1^2 - 1}{n_1 + 0.4}\right)\frac{M_1 x_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2 + 0.4}\right)\frac{M_2 x_2}{\rho_2} \tag{17}$$

Oster's relation can be given as

$$\left[\frac{(n_{\mathrm{m}}^2 - 1)(2n_{\mathrm{m}}^2 + 1)}{n_{\mathrm{m}}^2}\right]V_{\mathrm{m}} = \left[\frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2}\right]\frac{M_1 x_1}{\rho_1} + \left[\frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2}\right]\frac{M_2 x_2}{\rho_2} \tag{18}$$

Here u, ρ, V, η, n, R, M, x, w, and ϕ are ultrasonic velocity, mass density, molar volume, viscosity, refractive index, molar sound velocity, molecular weight, mole fraction, weight fraction, and volume fraction respectively. Symbols 1, 2, and m in suffix, represent pure THF, pure 1-p (or 2-p), and mixture respectively.

In equation (4), S and B respectively are collision factor and actual volume of the molecules per mole and are respectively given as:

$$S = \frac{uV}{u_\infty B} \qquad \text{and} \qquad B = \left(\frac{4}{3}\pi r^3\right)N_0$$

where, $u_\infty = 1600\,\mathrm{m\,s^{-1}}$, an empirical constant,
N_0 = Avogadro number

$$r = \sqrt[3]{\frac{3}{16\pi N} V\left[1 - \frac{RT}{Mu^2}\left\{\left(\sqrt{1 + \frac{Mu^2}{RT}}\right) - 1\right\}\right]},$$

the molecular radius of the given component [27].

η_{12} in equations (8) and (9) represents the viscosity of the mixture at equimolar composition, and signifies the molecular interactions.

In equation (10), A_{ij} is the Wassiljewa coefficient [22], which is independent of the composition of the mixture and is given as:

$$A_{ij} = \frac{1}{4}\left[1 + \left(\frac{\eta_i}{\eta_j}\right)^{1/2}\left(\frac{M_j}{M_i}\right)^{3/8}\right]^2$$

m in equation (13) is given as:

$$m = \frac{n_2}{n_1}$$

3. Results and discussion

The experimentally measured values of ultrasonic velocity (u), viscosity (η), and refractive index (n) along with their theoretically evaluated values at 293, 303, and 313 K temperatures for the two mixtures, viz. (THF + 1-p) and (THF + 2-p), are listed in the tables 1–3 respectively. Table 4 enumerates the average percentage deviation (APD) values corresponding to the various mixing rules employed here for these two mixtures.

3.1. *Ultrasonic velocity*

The values of the u, as predicted by the four mixing rules for two mixtures at three temperatures, show deviations from the respective measured values. The approximations and assumptions incorporated in the theories on which these mixing rules are based, may have a bearing on these deviations. The assumption that the liquid molecules in the mixtures are of spherical shape is not true every time. The van Dael and Vangeel mixing rule assumes mixture to be an ideal one with components having molar specific heat ratios equal to that of the mixture (i.e. $\gamma_1 = \gamma_2 = \gamma$). Also their molar volumes are assumed to be equal. Neither of these assumptions holds good for either of the two mixtures. Similarly, Nomoto based his mixing rule on the conditions of the linearity of the molar sound velocity and the additivity of the molar volumes in the liquid mixture. Thus, both the mixing rules take no account of the interactions between the component molecules.

Alternatively, it can be inferred that these deviations confirm the intermolecular interactions in the mixtures. Further, as is clear from table 4, and APD corresponding to the ideal mixing rule of van Dael and Vangeel is much larger, at each of the three temperatures, for (THF + 1-p) mixture than that for (THF + 2-p) mixture.

Table 1. Experimentally and theoretically estimated values of the ultrasonic velocity (u) in (THF + 1-p) and (THF + 2-p) mixtures at various temperatures.

Mole fraction	Experimental values of ultrasonic velocity (in m s^{-1})			Theoretically predicted values of ultrasonic velocity (in m s^{-1})											
				van Dael and Vangeel			Nomoto			Junjie			CFT		
of THF (x_1)	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
THF + 1-p															
0.0000	1224.0	1189.0	1155.0	1224.0	1189.0	1155.0	1224.0	1189.0	1155.0	1224.0	1189.0	1155.0	1224.0	1189.0	1155.0
0.0992	1232.0	1200.0	1164.0	1228.2	1192.3	1157.0	1232.2	1195.8	1160.0	1230.4	1194.4	1159.0	1232.6	1197.2	1164.4
0.1999	1242.0	1220.0	1175.0	1233.2	1196.3	1159.6	1240.4	1202.7	1165.0	1237.2	1200.1	1163.1	1241.5	1204.7	1172.5
0.2846	1250.4	1228.0	1188.0	1238.0	1200.2	1162.3	1247.3	1208.4	1169.1	1243.1	1205.1	1166.8	1247.8	1210.8	1177.5
0.3900	1256.9	1235.0	1194.0	1244.7	1205.7	1166.1	1255.7	1215.4	1174.2	1250.9	1211.5	1171.5	1256.8	1218.0	1183.5
0.5146	1265.1	1244.0	1196.0	1253.8	1213.4	1171.5	1265.5	1223.5	1180.1	1260.4	1219.5	1177.3	1266.6	1227.4	1189.7
0.5918	1271.0	1245.0	1197.0	1260.0	1218.4	1175.3	1271.5	1228.5	1183.7	1266.6	1224.6	1181.0	1273.9	1232.8	1194.1
0.7012	1278.8	1247.0	1198.0	1269.8	1226.6	1181.4	1279.9	1235.5	1188.7	1275.7	1232.1	1186.4	1282.6	1240.3	1198.8
0.8028	1286.8	1248.0	1199.0	1279.9	1235.0	1187.7	1287.7	1241.9	1193.3	1284.4	1239.3	1191.5	1288.5	1245.8	1200.7
0.8940	1294.0	1251.0	1200.0	1289.8	1243.4	1193.9	1294.5	1247.5	1197.4	1292.6	1246.0	1196.3	1294.9	1250.0	1200.1
0.9761	1300.3	1252.0	1201.0	1299.4	1251.5	1200.1	1300.6	1252.5	1201.0	1300.2	1252.2	1200.7	1300.3	1252.7	1201.5
1.0000	1302.4	1254.0	1202.0	1302.4	1254.0	1202.0	1302.4	1254.0	1202.0	1302.4	1254.0	1202.0	1302.4	1254.0	1202.0
THF + 2-p															
0.0000	1140.0	1114.0	1085.0	1140.0	1114.0	1085.0	1140.0	1114.0	1085.0	1140.0	1114.0	1085.0	1140.0	1114.0	1085.0
0.0983	1151.0	1123.0	1093.0	1149.6	1122.3	1091.9	1156.2	1127.8	1096.4	1151.8	1123.0	1091.4	1154.9	1124.5	1090.5
0.2085	1165.0	1136.0	1103.0	1161.6	1132.7	1100.5	1174.3	1143.2	1109.3	1165.9	1134.0	1099.3	1170.8	1135.1	1096.6
0.2911	1176.0	1145.0	1110.0	1171.6	1141.3	1107.8	1187.8	1154.7	1118.9	1177.1	1142.8	1105.8	1184.0	1144.4	1102.1
0.3728	1187.0	1155.0	1118.0	1182.3	1150.6	1115.6	1201.1	1166.2	1128.4	1188.9	1152.1	1112.6	1196.3	1152.9	1106.9
0.5014	1206.0	1170.0	1131.0	1201.1	1166.9	1129.2	1222.0	1184.2	1143.5	1208.6	1167.9	1124.3	1216.8	1168.1	1115.9
0.5976	1222.0	1183.0	1142.0	1216.9	1180.5	1140.7	1237.7	1197.7	1154.7	1224.4	1180.7	1133.9	1232.3	1180.2	1122.6
0.7483	1248.0	1207.0	1162.0	1244.9	1204.7	1160.9	1262.0	1218.8	1172.4	1251.2	1202.7	1150.4	1258.4	1199.9	1135.7
0.8001	1258.0	1216.0	1170.0	1255.5	1213.8	1168.6	1270.3	1226.0	1178.5	1261.1	1210.8	1156.6	1267.7	1207.2	1141.1
0.8939	1278.0	1232.0	1185.0	1276.3	1231.7	1183.5	1285.4	1239.2	1189.5	1279.8	1226.2	1168.3	1284.3	1221.3	1150.8
1.0000	1302.4	1254.0	1202.0	1302.4	1254.0	1202.0	1302.4	1254.0	1202.0	1302.4	1245.0	1182.6	1302.4	1254.0	1202.0

Table 2. Experimentally and theoretically estimated values of the viscosity (η) in (THF + 1-p) and (THF + 2-p) mixtures at various temperatures.

Mole fraction of THF (x_1)	Experimental values of viscosity ($\times10^{-3}\,\mathrm{N\,s\,m^{-2}}$)			Theoretically predicted values of viscosity ($\times10^{-3}\,\mathrm{N\,s\,m^{-2}}$)																	
				Bingham			Kendall–Munroe			Additive			Frankel			Hind–Ubbelohde			Sutherland–Wassiliewa		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
THF + 1-p																					
0.0000	2.19	1.61	1.34	2.19	1.61	1.34	2.19	1.61	1.34	2.19	1.61	1.34	2.19	1.61	1.34	2.19	1.61	1.34	2.19	1.61	1.34
0.0992	1.74	1.22	1.04	2.02	1.49	1.24	1.88	1.41	1.19	1.89	1.41	1.19	1.89	1.40	1.17	1.97	1.45	1.21	1.77	1.34	1.14
0.1999	1.49	1.08	0.90	1.85	1.37	1.15	1.62	1.23	1.05	1.62	1.23	1.05	1.63	1.22	1.03	1.75	1.30	1.09	1.47	1.14	0.98
0.2846	1.38	1.00	0.85	1.70	1.27	1.07	1.43	1.10	0.95	1.43	1.10	0.95	1.43	1.08	0.92	1.58	1.18	1.00	1.27	1.00	0.88
0.3900	1.21	0.91	0.77	1.52	1.14	0.97	1.22	0.95	0.83	1.22	0.95	0.84	1.22	0.94	0.81	1.39	1.04	0.88	1.07	0.86	0.76
0.5146	1.05	0.80	0.69	1.31	1.00	0.85	1.01	0.80	0.71	1.01	0.81	0.72	1.02	0.79	0.69	1.17	0.89	0.76	0.90	0.73	0.66
0.5918	0.95	0.73	0.65	1.18	0.90	0.78	0.90	0.72	0.65	0.90	0.73	0.66	0.90	0.71	0.63	1.04	0.80	0.69	0.81	0.66	0.60
0.7012	0.81	0.64	0.57	0.99	0.77	0.68	0.76	0.63	0.57	0.76	0.63	0.57	0.77	0.62	0.56	0.87	0.68	0.60	0.70	0.58	0.53
0.8028	0.70	0.57	0.51	0.82	0.65	0.58	0.65	0.55	0.50	0.65	0.55	0.51	0.66	0.54	0.49	0.73	0.58	0.52	0.61	0.52	0.48
0.8940	0.59	0.50	0.47	0.67	0.54	0.49	0.57	0.48	0.45	0.57	0.48	0.45	0.57	0.48	0.44	0.61	0.50	0.46	0.55	0.47	0.44
0.9761	0.50	0.44	0.42	0.53	0.45	0.42	0.50	0.43	0.41	0.50	0.43	0.41	0.50	0.43	0.41	0.51	0.44	0.41	0.50	0.43	0.40
1.0000	0.49	0.42	0.39	0.49	0.42	0.39	0.49	0.42	0.39	0.49	0.42	0.39	0.49	0.42	0.39	0.49	0.42	0.39	0.49	0.42	0.39
THF + 2-p																					
0.0000	2.10	1.49	1.13	2.10	1.49	1.13	2.10	1.49	1.13	2.10	1.49	1.13	2.10	1.49	1.13	2.10	1.49	1.13	2.10	1.49	1.13
0.0983	1.60	1.07	0.86	1.94	1.39	1.06	1.81	1.32	1.02	1.81	1.32	1.02	1.73	1.24	0.96	1.85	1.32	1.01	1.71	1.23	0.94
0.2085	1.28	0.86	0.70	1.76	1.27	0.98	1.54	1.15	0.91	1.53	1.14	0.90	1.41	1.02	0.82	1.59	1.14	0.89	1.39	1.02	0.80
0.2911	1.08	0.71	0.61	1.63	1.18	0.92	1.36	1.03	0.83	1.35	1.03	0.83	1.22	0.90	0.73	1.41	1.02	0.80	1.21	0.90	0.71
0.3728	0.91	0.58	0.54	1.49	1.09	0.86	1.20	0.93	0.76	1.19	0.92	0.76	1.07	0.79	0.66	1.25	0.91	0.73	1.06	0.80	0.65
0.5014	0.77	0.56	0.48	1.28	0.96	0.76	0.99	0.79	0.67	0.98	0.78	0.66	0.87	0.66	0.57	1.02	0.76	0.62	0.88	0.68	0.57
0.5976	0.70	0.54	0.46	1.12	0.85	0.69	0.85	0.70	0.60	0.85	0.69	0.60	0.76	0.59	0.52	0.88	0.66	0.56	0.77	0.61	0.52
0.7483	0.58	0.48	0.45	0.88	0.69	0.58	0.68	0.58	0.51	0.68	0.57	0.51	0.62	0.51	0.45	0.68	0.54	0.47	0.63	0.52	0.46
0.8001	0.55	0.47	0.43	0.79	0.63	0.54	0.63	0.54	0.49	0.63	0.54	0.48	0.58	0.48	0.44	0.63	0.51	0.45	0.59	0.50	0.45
0.8939	0.50	0.45	0.43	0.64	0.53	0.47	0.55	0.48	0.44	0.55	0.48	0.44	0.52	0.45	0.41	0.54	0.46	0.42	0.53	0.46	0.42
1.0000	0.47	0.42	0.39	0.47	0.42	0.39	0.47	0.42	0.39	0.47	0.42	0.39	0.47	0.42	0.39	0.47	0.42	0.39	0.47	0.42	0.39

Table 3. Experimentally and theoretically estimated values of the refractive index (n) of (THF + 1-p) and (THF + 2-p) mixtures at various temperatures.

Mole fraction of THF (x_1)	Experimental values of refractive index			Theoretically predicted values of refractive index																							
				Gladstone–Dale			Arago–Biot			Heller			Wiener			Lorentz–Lorenz			Newton			Eykman			Oster		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
THF + 1-p																								
0.0000	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378	1.385	1.382	1.378
0.0992	1.388	1.385	1.380	1.387	1.384	1.380	1.387	1.384	1.380	1.387	1.384	1.380	1.387	1.384	1.380	1.388	1.385	1.382	1.387	1.384	1.380	1.388	1.385	1.382	1.388	1.385	1.382
0.1999	1.391	1.387	1.383	1.390	1.386	1.382	1.390	1.386	1.382	1.390	1.386	1.382	1.390	1.386	1.382	1.391	1.387	1.385	1.390	1.386	1.382	1.390	1.387	1.385	1.390	1.387	1.385
0.2846	1.393	1.389	1.384	1.392	1.388	1.384	1.392	1.388	1.384	1.392	1.388	1.384	1.392	1.388	1.384	1.392	1.389	1.387	1.392	1.388	1.384	1.392	1.389	1.387	1.392	1.389	1.387
0.3900	1.395	1.391	1.386	1.394	1.390	1.386	1.394	1.390	1.386	1.394	1.390	1.386	1.394	1.390	1.386	1.395	1.391	1.390	1.394	1.390	1.386	1.395	1.391	1.389	1.395	1.391	1.389
0.5146	1.398	1.393	1.389	1.397	1.393	1.388	1.397	1.393	1.388	1.397	1.393	1.388	1.397	1.393	1.388	1.398	1.394	1.392	1.397	1.393	1.388	1.398	1.394	1.392	1.398	1.394	1.392
0.5918	1.400	1.395	1.391	1.399	1.394	1.390	1.399	1.394	1.390	1.399	1.394	1.390	1.399	1.394	1.390	1.400	1.396	1.394	1.399	1.394	1.390	1.400	1.396	1.393	1.400	1.396	1.393
0.7012	1.402	1.397	1.393	1.401	1.396	1.392	1.401	1.396	1.392	1.401	1.396	1.392	1.401	1.396	1.392	1.403	1.398	1.396	1.402	1.396	1.392	1.403	1.398	1.395	1.403	1.398	1.395
0.8028	1.403	1.399	1.394	1.404	1.398	1.393	1.404	1.398	1.393	1.404	1.398	1.393	1.404	1.398	1.393	1.404	1.400	1.396	1.404	1.398	1.394	1.404	1.400	1.396	1.404	1.400	1.396
0.8940	1.405	1.400	1.395	1.406	1.400	1.395	1.406	1.400	1.395	1.406	1.400	1.395	1.406	1.400	1.395	1.406	1.401	1.396	1.406	1.400	1.395	1.406	1.401	1.396	1.406	1.401	1.396
0.9761	1.407	1.401	1.396	1.407	1.402	1.397	1.407	1.402	1.397	1.407	1.402	1.397	1.407	1.402	1.397	1.407	1.402	1.397	1.407	1.402	1.397	1.407	1.401	1.396	1.407	1.402	1.397
1.0000	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397
THF + 2-p																								
0.0000	1.378	1.373	1.396	1.378	1.373	1.369	1.378	1.373	1.369	1.378	1.373	1.369	1.378	1.373	1.369	1.379	1.373	1.369	1.378	1.373	1.369	1.379	1.373	1.369	1.379	1.373	1.369
0.0983	1.381	1.376	1.372	1.381	1.376	1.372	1.381	1.376	1.372	1.381	1.376	1.372	1.381	1.376	1.372	1.381	1.375	1.371	1.381	1.376	1.372	1.381	1.375	1.371	1.381	1.376	1.371
0.2085	1.384	1.379	1.375	1.385	1.379	1.375	1.385	1.379	1.375	1.385	1.379	1.375	1.385	1.379	1.375	1.384	1.378	1.373	1.385	1.379	1.375	1.384	1.378	1.373	1.384	1.378	1.374
0.2911	1.387	1.382	1.378	1.387	1.382	1.378	1.387	1.382	1.378	1.387	1.382	1.378	1.387	1.382	1.378	1.386	1.380	1.375	1.387	1.382	1.378	1.386	1.380	1.375	1.386	1.380	1.376
0.3728	1.389	1.384	1.380	1.390	1.384	1.380	1.390	1.384	1.380	1.390	1.384	1.380	1.390	1.384	1.380	1.388	1.382	1.377	1.390	1.384	1.380	1.388	1.382	1.377	1.389	1.382	1.377
0.5014	1.393	1.388	1.384	1.394	1.388	1.384	1.394	1.388	1.384	1.393	1.388	1.384	1.394	1.388	1.384	1.392	1.385	1.380	1.394	1.388	1.384	1.392	1.385	1.380	1.392	1.386	1.381
0.5976	1.396	1.391	1.387	1.396	1.391	1.386	1.396	1.391	1.386	1.396	1.391	1.386	1.396	1.391	1.386	1.395	1.388	1.382	1.396	1.391	1.386	1.395	1.388	1.383	1.395	1.389	1.383
0.7483	1.401	1.395	1.390	1.401	1.395	1.390	1.401	1.395	1.390	1.401	1.395	1.390	1.401	1.395	1.390	1.400	1.393	1.387	1.401	1.395	1.390	1.400	1.393	1.387	1.400	1.393	1.388
0.8001	1.402	1.396	1.392	1.402	1.396	1.392	1.402	1.396	1.392	1.402	1.396	1.392	1.402	1.396	1.392	1.402	1.395	1.389	1.402	1.397	1.392	1.402	1.395	1.389	1.402	1.395	1.389
0.8939	1.405	1.399	1.394	1.405	1.399	1.394	1.405	1.399	1.394	1.405	1.399	1.394	1.405	1.399	1.394	1.405	1.398	1.392	1.405	1.399	1.394	1.405	1.398	1.393	1.405	1.398	1.393
1.0000	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397	1.408	1.402	1.397

Table 4. Average percentage deviation (APD) for the mixing rules for ultrasonic velocity (u), viscosity (η), and refractive index (n) for (THF + 1-p) and (THF + 2-p) mixtures at various temperatures.

		Temperature		
Thermodynamic parameter	Mixing rule	293 K	303 K	313 K
Ultrasonic velocity (u) (THF + 1-p)	van Deal and Vangeel	0.5315	1.2641	1.0989
	Nomoto	0.0648	0.8046	0.6965
	Junjie	0.2374	0.9809	0.8288
	CFT	0.0959	0.6189	0.2542
Ultrasonic Velocity (u) (THF + 2-p)	van Deal and Vangeel	0.2358	0.1759	0.1239
	Nomoto	0.7938	0.7009	0.6211
	Junjie	0.1321	0.2689	0.7103
	CFT	0.5577	0.2760	1.1973
Viscosity (η) (THF + 1-p)	Binbham	16.3669	16.3128	15.3745
	Kendall–Munroe	3.8313	4.5774	5.1738
	Additive	3.8098	4.5967	5.5414
	Frankel	3.7823	4.4985	4.8047
	Hind–Ubbelohde	8.1708	8.5329	8.4374
	Sutherland–Wassiljewa	7.1754	5.3412	4.4755
Viscosity (η) (THF + 2-p)	Binbham	38.4889	41.3011	31.2754
	Kendall–Munroe	16.5370	24.6592	20.4775
	Additive	16.2556	24.1630	19.8354
	Frankel	7.8933	12.1636	9.4980
	Hind–Ubbelohde	18.8107	21.1736	15.5686
	Sutherland–Wassiljewa	8.0902	13.3123	9.0304
Refractive index (n) (THF + 1-p)	Gladstone–Dale	0.0452	0.0390	0.0392
	Arago–Biot	0.0452	0.0390	0.0392
	Heller	0.0469	0.0405	0.0405
	Wiener	0.0456	0.0394	0.0395
	Lorentz–Lorenz	0.0311	0.0475	0.1421
	Newton	0.0439	0.0378	0.0380
	Eykman	0.0306	0.0379	0.1207
	Oster	0.0293	0.0387	0.1179
Refractive index (n) (THF + 1-p)	Gladstone–Dale	0.0199	0.0109	0.0178
	Arago–Biot	0.0199	0.0109	0.0178
	Heller	0.0181	0.0113	0.0197
	Wiener	0.0192	0.0105	0.0183
	Lorentz–Lorenz	0.0423	0.1100	0.1651
	Newton	0.0224	0.0124	0.0167
	Eykman	0.0371	0.1014	0.1544
	Oster	0.0302	0.0887	0.1385

This indicates that 1-p is much more associative than 2-p vis-a-vis THF, as has also been reported by us earlier [19,20]. From table 4, it is also seen that, while the Nomoto's relation gives encouraging results in the case of (THF + 1-p) mixture. It gives an overall maximum APD value in the case of (THF + 2-p) mixture, van Dael and Vangeel's relation gives minimum APD for (THF + 2-p) mixture at 313 K temperature besides giving the maximum APD value for (THF + 1-p) mixture at 303 K temperature. Junjie's relation, on the other hand, results in moderate APD values for either of the two mixtures. Lastly, the predictions made on the basis of the CFT show quite a good agreement with the respective experimentally observed values. The least value registered by APD corresponds to the one predicted by CFT at 293 K temperature for (THF + 1-p) mixture. Thus, in terms of relative merits of the mixing rules for ultrasonic velocity, it appears that the CFT is best suited for predicting the speed of sound, as it gives an overall smaller APD than that given by rest of the mixing rules.

3.2. *Viscosity*

The APD values corresponding to the six mixing rules employed for predicting the viscosity of two binary mixtures at three temperatures, as listed in table 4, are not very encouraging from the point of view of theoretical estimation of viscosity of liquid mixtures on the basis of known values of viscosities of pure components. The disagreement between the measured and predicted values of viscosity of the two mixtures can partly be attributed to the molecular interactions occurring within the mixtures and partly to the limitations in theories on which these mixing rules are based. A close perusal of APD values reveals that the results of the Frenkel's relation are the best among all the predicted values of viscosity. Not only this, the agreement between the experimental values and the predicted values of viscosity of (THF + 2-p) mixture is quite satisfactory in the case of Frenkel's relation when all other relations seem to be failing. This is perhaps because the Frenkel's relation incorporates all possible major interactions among the component molecules besides including the notion of logarithmic additivity of the viscosity. The Sutherland–Wassiljewa relations which though takes into account molecular interactions in the form of Wassiljewa coefficient A_{ij}, does not seem to be suitable enough to predict viscosity, particularly of (THF + 2-p) mixture. Further, in the case of (THF + 1-p) mixture, the Kendall–Munroe, Additive, and Frenkel's relations give almost equal APD at respective temperatures. A similar observation can be made for Kendall–Munroe, Additive and to a lesser extent for Hind's relation in the case of (THF + 2-p) mixture. The results of the Bingham's relation are not encouraging when seen in the light of exceptionally high values of APD, particularly in the case of (THF + 2-p) mixture. The main limitation of this relation seems to be the assumption of simple additivity of the viscosities of the component liquids. This particular assumption might even be responsible for high APD values in the case of Hind's relation, which though takes into account the possible major interactions among the component molecules.

3.3. *Refractive index*

Unlike the results of the mixing rules for viscosity, the results of all the eight mixing rules employed for predicting refractive indices of the two binary mixtures, show an extraordinary agreement with the respective experimental values of n. Considering the APD values corresponding to these eight mixing rules, it is observed that the Gladstone–Dale (GD) and Arago–Biot (AB) relations give completely identical results for both the mixtures at respective temperatures, while the results of Wiener's (W) and Heller's (H) relations are almost identical which must be the case because Heller's equation is simply a limiting form of Wiener's equation. Further, APD increases with temperature, for both the mixtures, in the case of LL, Eyk, and Os relations. At 293 K temperature, Heller's relation gives minimum APD for (THF + 2-p) mixture and maximum APD for (THF + 1-p) mixture when compared with all other mixing rules for refractive index. The LL relation gives maximum APD for all the three temperatures in the case of (THF + 2-p) mixture and at 303 and 313 K temperatures in the case of (THF + 1-p) mixture. The Newton's (Nn) relation gives minimum APD for (THF + 1-p) mixture at 303 and 313 K and for (THF + 2-p) mixture at only 313 K. On the whole, the predictions of GD, AB, H and W relations seem to be excellent, particularly in the case of (THF + 2-p) mixture. These very small deviations indicate that there is only a negligible change in the molecular polarizability on mixing of the component liquids. These deviations can further be reduced if the concept of excess molar volume (V_m^E) is taken into account in the formulation of these mixing rules, as has been suggested by Aminabhavi *et al.* [27,28].

4. Conclusions

The study indicates that almost all the mixing rules employed here, give reasonably good results with the exception of Bingham's relation for the prediction of viscosity. The mixing rules for refractive index give excellent results while those for ultrasonic velocity give quite good results when seen in the context of the experimental errors and limitations together with the consequence of molecular interactions on the physicochemical behaviour of the mixture.

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