

Ultrasonic Speed and Isentropic Compressibility of 2-propanol with Hydrocarbons at 298.15 and 308.15 K

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Abstract – Intermolecular interactions were studied for binary mixtures of 2-propanol + cyclohexane, n-hexane, benzene, toluene, o-, m- and p-xylenes by measuring ultrasonic speeds (u) over the entire range of composition at 298.15 K and 308.15 K. From these results the deviation in ultrasonic speed was calculated. These results were fitted to the Redlich-Kister equation to derive the binary coefficients along with standard deviations between the experimental and calculated data. Acoustic parameters such as excess isentropic compressibility (K_T^E), intermolecular free length (L_f) and available volume (V_a) were also derived from ultrasonic speed data and Jacobson's free length theory. The ultrasonic speed data were correlated by Nomoto's relation, Van Dael's mixing relation, impedance dependence relation, and Schaaff's collision factor theory. Van Dael's relation gives the best prediction of u in the binary mixtures containing aliphatic hydrocarbons. The ultrasonic speed data and isentropic compressibility were further analyzed in terms of Jacobson's free length theory.

Key words: Ultrasonic speed, Oxygenate, 2-Propanol, Hydrocarbon, Jacobson's free length theory, Graph theoretical approach

1. Introduction

Increasing global concern over greenhouse gas emissions has generated much interest in environmentally friendly alternative bio-fuels. Bio-fuels for internal combustion engines as oxygenated compounds are also becoming important due to depleting fossil fuel, occasional oil crises and increasing air pollution [1]. Oxygenates produced from renewable sources, including higher alcohol such as propanol, butanol and pentanol, may have acceptable properties as gasoline blend components and could be considered as potential second generation bio-fuel additives [2]. Propanol can be produced by microbial fermentation of cellulose [3]. This prompted us to study the thermo-physical properties of oxygenate additive with hydrocarbons that would be of great importance in process engineering design, in formulating motor fuels [4], and also in understanding the nature of intermolecular interactions in these binary mixtures [5-7].

In continuation of earlier work [8-11], ultrasonic speeds of 2-propanol + cyclohexane, n-hexane, benzene, toluene, o-, m- and p-xylenes over the entire range of composition at 298.15 K and at 308.15 K are reported in the present paper. The ultrasonic speeds data were correlated by various correlations like Nomoto's relation, Van Dael's mixing relation and impedance dependence relation, and Schaaff's collision factor theory. The acoustic data were further analyzed in terms of Jacobson's free length theory (FLT).

2. Experimental

2-1. Chemicals

Cyclohexane (Merck 99%) was washed several times with a mixture of concentrated nitric acid and concentrated sulfuric acid to nitrate any benzene that may have been present [12]. After repeated washing with NaHCO_3 solution and distilled water, it was fractionally distilled over and dried over 0.3 nm molecular sieves (Merck) in an amber colored bottle for several days before use.

n-Hexane (Merck AR grade 99.5%) was treated with concentrated sulfuric acid, then with a 0.1N solution of potassium permanganate in 10% sodium hydroxide [13]. The n-hexane was then washed with water, distilled and dried over type 0.3 nm molecular sieves (Merck). 2-Propanol, benzene, toluene and xylenes were purified as described earlier [14].

The purity of purified samples was checked by measuring densities and refractive indices of the pure compounds, and these agree well with their respective literature values as shown in Table 1 [5,15-23]. The purified samples were also analyzed by gas chromatography for their purity and found to have better than 99.6 wt% (Table 1).

2-2. Apparatus and procedure

The ultrasonic speed was measured by using a variable path single-crystal interferometer (Mittal Enterprises, Model M-81, India). A crystal-controlled high-frequency generator was used to excite the transducer at a frequency of 2 MHz. The interferometer cell was filled with the test liquid, and water was circulated around the measuring cell from a constant temperature bath maintained at (298.15 ± 0.01) K. Details of the ultrasonic speed measurements have been given ear-

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Table 1. Purities (wt%), measured densities (ρ) and refractive indices (n_D) of the pure components

Compound	GC results	T/K	$\rho / (\text{kg m}^{-3})$		n_D	
			This work	Literature	This work	Literature
2-propanol	99.8	298.15	781.16	781.28 ^a	1.3753	1.3751 ^b
		308.15	771.31	772.27 ^a	1.3714	1.3716 ^d
cyclohexane	99.6	298.15	774.2	773.5 ^f	1.4977	1.49792 ^f
		308.15	762.4	762.96 ^h	1.4913	1.4917 ⁱ
n-hexane	99.8	298.15	654.55	654.81 ^f	1.4977	1.49792 ^f
		308.15	644.7	645.8 ^h	1.4913	1.4917 ⁱ
benzene	99.7	298.15	871.54	873.60 ^f	1.4977	1.49792 ^f
		308.15	864.92	862.96 ^h	1.4913	1.4917 ⁱ
toluene	99.8	298.15	861.21	862.19 ^f	1.4944	1.49413 ^f
		308.15	853.84	852.85 ^h	1.4887	1.4887 ⁱ
o-xylene	99.7	298.15	874.92	875.94 ^f	1.5028	1.50295 ^f
		308.15	867.15	867.38 ^h	1.5027	1.50295 ^f
m-xylene	99.8	298.15	861.06	860.09 ^f	1.4949	1.49464 ^f
		308.15	850.53	851.57 ^h	1.468	1.488 ⁱ
p-xylene	99.9	298.15	856.65	856.61 ^f	1.4934	1.49325 ^f
		308.15	848.83	847.87 ^h	1.4886	1.4881 ^j

^a[5]; ^b[15]; ^c[16]; ^d[17]; ^e[18]; ^f[19]; ^g[20]; ^h[21]; ⁱ[23]; ^j[22]

lier [24] and the data are reproducible within $\pm 3\%$.

Refractive indices (± 0.001) and density ($\pm 5 \times 10^{-5} \text{ g cm}^{-3}$) of pure components were measured with a thermostatically controlled Abbe refractometer (OSAW, India) and dilatometric technique described elsewhere [25,26].

3. Results

The deviation in ultrasonic speed (Δu) was calculated using Eq. (1) and reported along with measured ultrasonic speed in Table 2. The variation of deviation in ultrasonic speed (Δu) with mole fraction of 2-propanol is represented graphically in Fig. 1.

$$\Delta u = u - (\rho^{id} K_s^{id})^{-1/2} \quad (1)$$

$$\rho^{id} = \phi_1 \rho_1 + \phi_2 \rho_2 \quad (2)$$

$$K_s^{id} = \phi_1 K_{s,1} + \phi_2 K_{s,2} + T \left[\frac{\phi_1 V_1 (\alpha_{p,1})^2}{C_{p,1}} + \frac{\phi_2 V_2 (\alpha_{p,2})^2}{C_{p,2}} - \frac{V^{id} (\alpha_p^{id})^2}{C_p^{id}} \right] \quad (3)$$

where

$$V^{id} = x_1 V_1 + x_2 V_2 \quad (4)$$

$$\alpha_p^{id} = \phi_1 \alpha_{p,1} + \phi_2 \alpha_{p,2} \quad (5)$$

$$C_p^{id} = x_1 C_{p,1} + x_2 C_{p,2} \quad (6)$$

where ϕ , V , α_p and C_p are the volume fraction, molar volume, isobaric expansivity and molar heat capacity, respectively. The values of α_p and C_p are taken from literature [19,27-29]. The values of excess compressibility calculated from Eq. (8) are tabulated in Table 2 and shown in Figs. 2 and 3.

$$K_s = (u^2 \rho)^{-1} \quad (7)$$

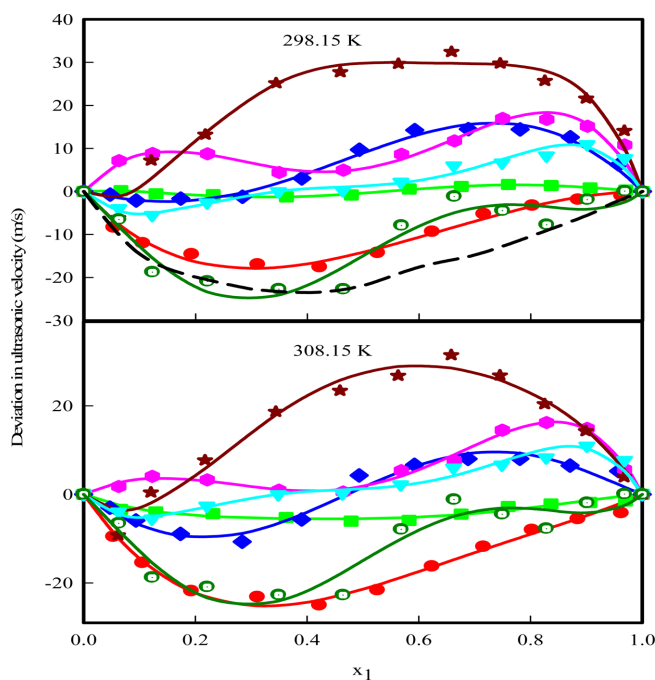


Fig. 1. Deviation in ultrasonic velocity of 2-propanol (1) + hydrocarbon (2) mixture as a function of mole fraction of 2-propanol at 298.15 and 308.15 K: ● cyclohexane, ■ n-hexane, ◆ benzene, ● toluene, ★ o-xylene, ▼ m-xylene, ○ p-xylene. The line represents the value calculated from Eq. (10) and dashed line represents literature value of cyclohexane (Savaroglu and Aral, 2004).

$$K_s^E = K_s - K_s^{id} \quad (8)$$

The densities, ρ_{ij} , of the binary mixtures were calculated from their excess molar volume data [14] using the Eq. (9)

$$V^E = \sum_{i=1}^2 x_i M_i (\rho_{ij})^{-1} - \sum_{i=1}^2 x_i M_i (\rho_i)^{-1} \quad (9)$$

Table 2. Experimental ultrasonic velocity (u), deviation in ultrasonic velocity (Δu) and excess isentropic compressibility (K_s^E) of binary mixtures at different temperatures

x_1	u (ms ⁻¹)	Δu (ms ⁻¹)	K_s^E ($\times 10^{-12}$ Nm s ⁻²)	u (ms ⁻¹)	Δu (ms ⁻¹)	K_s^E ($\times 10^{-12}$ Nm s ⁻²)
T = 298.15 K			T = 308.15 K			
2-propanol (1) + cyclohexane (2)						
0.0000	1267	0.0	0.000	1212	0.0	0.000
0.0535	1250	-9.6	13.603	1197	-8.4	14.786
0.1055	1237	-15.5	22.844	1187	-12.0	22.408
0.1931	1219	-21.8	33.922	1174	-14.6	29.248
0.3114	1202	-23.2	38.464	1158	-17.0	36.123
0.4221	1187	-25.0	43.106	1145	-17.6	39.513
0.5260	1178	-21.6	38.977	1137	-14.3	35.408
0.6238	1172	-16.3	31.060	1131.5	-9.4	27.622
0.7158	1166	-11.8	23.993	1126	-5.3	20.236
0.8027	1160	-8.0	17.423	1119	-3.3	15.644
0.8849	1154	-5.6	12.414	1112	-1.9	10.681
0.9627	1147	-4.2	8.501	1105	-1.1	4.890
1.0000	1146	0.0	0.000	1102	0.0	0.000
2-propanol (1) + n-hexane (2)						
0.0000	1085	0.0	0.000	1034	0.0	0.000
0.0679	1080	-3.4	10.693	1033	0.2	2.460
0.1319	1078	-4.0	13.818	1032	-0.6	6.759
0.2357	1077	-4.4	16.484	1031	-0.8	9.692
0.3681	1077	-5.2	19.292	1032	-1.3	12.541
0.4848	1079	-6.0	20.821	1036	-0.8	11.527
0.5884	1084	-5.9	19.484	1043	0.6	7.497
0.6811	1092	-4.5	15.176	1051	1.1	5.314
0.7644	1102	-2.7	10.227	1060	1.6	3.090
0.8398	1113	-2.2	7.627	1070	1.4	2.313
0.9083	1124	-1.8	5.468	1082	0.8	1.737
0.9708	1138	-1.5	3.271	1095	0.3	0.583
1.0000	1147	0.0	0.000	1102	0.0	0.000
2-propanol (1) + benzene (2)						
0.0000	1307	0.0	0.000	1260	0.0	0.000
0.0472	1293	-3.0	3.961	1249	-2.1	2.216
0.0937	1280	-5.9	7.824	1237	-1.7	5.030
0.1735	1260	-8.9	12.325	1221	-1.2	5.917
0.2839	1237	-10.7	15.612	1200	3.0	6.537
0.3904	1223	-5.7	9.826	1186	9.7	0.782
0.4932	1217	4.3	-3.434	1176	14.2	-9.685
0.5925	1204	6.7	-7.341	1166	14.5	-17.973
0.6884	1192	8.0	-10.166	1153	14.4	-20.075
0.7811	1180	8.0	-11.196	1142	12.6	-21.890
0.8708	1168	6.5	-9.760	1129	6.2	-20.715
0.9576	1157	5.2	-8.530	1113	4.4	-11.042
1.0000	1147	0.0	0.000	1102	0.0	0.000
2-propanol (1) + toluene (2)						
0.0000	1298	0.0	0.000	1262	0.0	0.000
0.0630	1290	1.8	-1.242	1259	7.2	-7.445
0.1230	1282	4.1	-3.402	1251	8.8	-9.026
0.2215	1271	3.3	-2.283	1235	8.7	-8.758
0.3496	1263	1.0	0.489	1210	4.4	-3.317
0.4648	1257	0.6	0.835	1192	4.9	-4.531
0.5689	1251	5.3	-6.008	1179	8.6	-10.750
0.6634	1248	7.6	-9.889	1167	11.8	-16.623
0.7497	1241	14.5	-20.800	1159	17.0	-26.368
0.8287	1234	16.2	-24.600	1146	16.8	-27.682
0.9014	1225	14.9	-23.731	1132.8	15.2	-26.534
0.9684	1214	5.7	-9.554	1118	10.8	-20.029
1.0000	1147	0.0	0.000	1102	0.0	0.000

Table 2. (continued)

x_1	u (ms ⁻¹)	Δu (ms ⁻¹)	K_s^E ($\times 10^{-12}$ Nm s ⁻²)	u (ms ⁻¹)	Δu (ms ⁻¹)	K_s^E ($\times 10^{-12}$ Nm s ⁻²)
T = 298.15 K				T = 308.15 K		
2-propanol (1) + toluene (2)						
0.0000	1298	0.0	0.000	1262	0.0	0.000
0.0630	1290	1.8	-1.242	1259	7.2	-7.445
0.1230	1282	4.1	-3.402	1251	8.8	-9.026
0.2215	1271	3.3	-2.283	1235	8.7	-8.758
0.3496	1263	1.0	0.489	1210	4.4	-3.317
0.4648	1257	0.6	0.835	1192	4.9	-4.531
0.5689	1251	5.3	-6.008	1179	8.6	-10.750
0.6634	1248	7.6	-9.889	1167	11.8	-16.623
0.7497	1241	14.5	-20.800	1159	17.0	-26.368
0.8287	1234	16.2	-24.600	1146	16.8	-27.682
0.9014	1225	14.9	-23.731	1132.8	15.2	-26.534
0.9684	1214	5.7	-9.554	1118	10.8	-20.029
1.0000	1147	0.0	0.000	1102	0.0	0.000
2-propanol (1) + o-xylene (2)						
0.0000	1355	0.0	0.000	1320	0.0	0.000
0.0616	1330	-9.2	9.670	1297	-6.1	7.614
0.1205	1325	0.5	0.841	1295	7.2	-5.852
0.2173	1309	7.7	-6.285	1277	13.2	-12.315
0.3443	1291	18.7	-19.008	1259	25.2	-27.811
0.4589	1271	23.4	-26.310	1235	27.7	-33.748
0.5631	1253	26.8	-32.701	1215	29.7	-39.518
0.6581	1239	31.5	-41.141	1198	32.5	-46.702
0.7452	1218	26.9	-37.481	1178	29.8	-45.889
0.8253	1197	20.4	-30.246	1159	25.7	-42.223
0.8993	1178	14.3	-22.489	1142	21.6	-37.617
0.9677	1156	3.9	-6.512	1122	14.1	-26.053
1.0000	1147	0.0	0.000	1102	0.0	0.000
2-propanol (1) + m-xylene (2)						
0.0000	1328	0.0	0.000	1285	0.0	0.000
0.0627	1314	-3.9	4.602	1275	-0.4	1.408
0.1224	1303	-5.5	6.918	1264	-2.5	4.568
0.2206	1290	-2.6	4.658	1252	2.0	0.001
0.3484	1271	0.0	2.362	1230	1.8	0.549
0.4635	1251	0.2	2.112	1210	2.1	0.059
0.5676	1234	2.2	-0.755	1192	3.5	-2.183
0.6622	1220	6.0	-6.519	1180	9.4	-11.775
0.7487	1204	6.7	-8.416	1164	9.8	-13.663
0.8280	1190	8.3	-11.792	1149	11.2	-17.331
0.9009	1178	11.0	-16.869	1137	14.5	-24.664
0.9682	1161	7.7	-12.617	1118	9.0	-16.564
1.0000	1147	0.0	0.000	1102	0.0	0.000
2-propanol (1) + p-xylene (2)						
0.0000	1317	0.0	0.000	1272	0.0	0.000
0.0629	1301	-6.5	7.521	1260	-3.2	4.806
0.1228	1280	-18.8	21.622	1242	-12.6	17.077
0.2213	1263	-20.9	25.434	1225	-14.9	21.391
0.3492	1241	-22.7	29.313	1207	-12.8	20.055
0.4644	1222	-22.7	30.834	1190	-10.9	18.275
0.5685	1219	-7.9	11.981	1187	4.0	-3.264
0.6631	1209	-1.2	2.854	1174	8.1	-10.170
0.7494	1190	-4.5	7.470	1155	4.5	-5.555
0.8285	1172	-7.7	12.523	1138	2.4	-2.785
0.9012	1164	-1.9	3.383	1126	4.3	-7.082
0.9684	1153	0.1	-0.026	1114	5.4	-10.036
1.0000	1147	0.0	0.000	1102	0.0	0.000

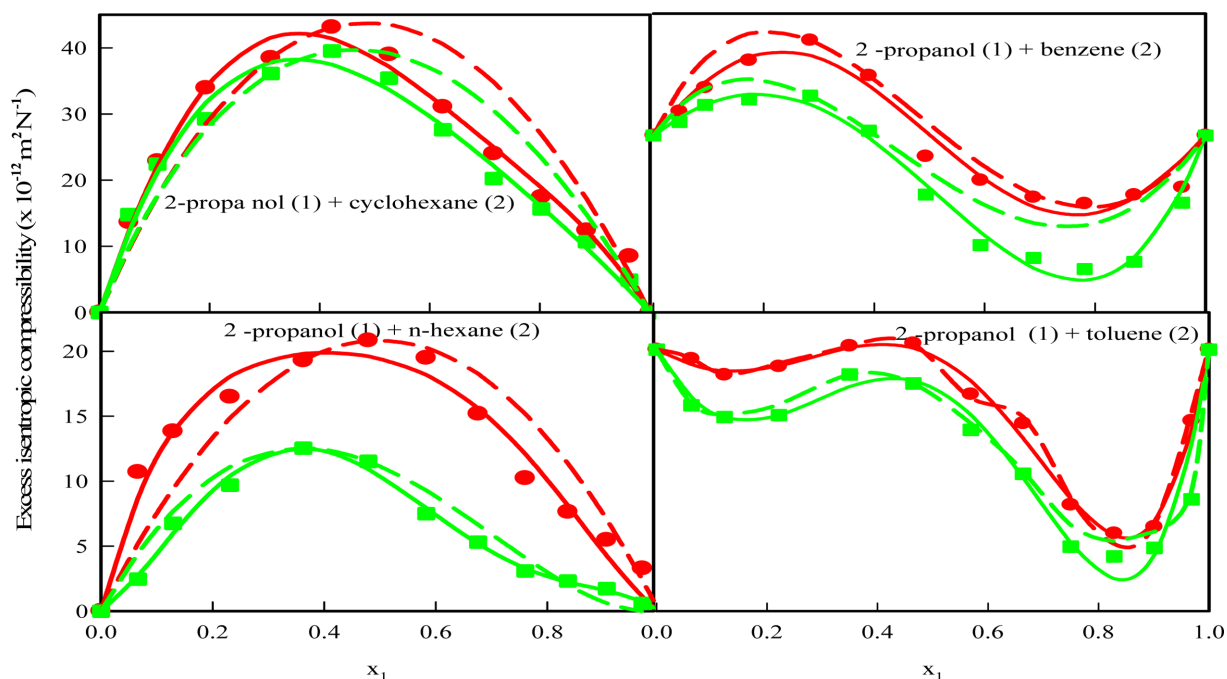


Fig. 2. Values of excess isentropic compressibility of 2-propanol (1) + hydrocarbon (2) mixture as a function of mole fraction of 2-propanol. Symbols represent experimental data; ● 298.15 K; ■ 308.15 K; Solid lines and dashed lines represent the values calculated from Eq. (10) and Graph theory, respectively.

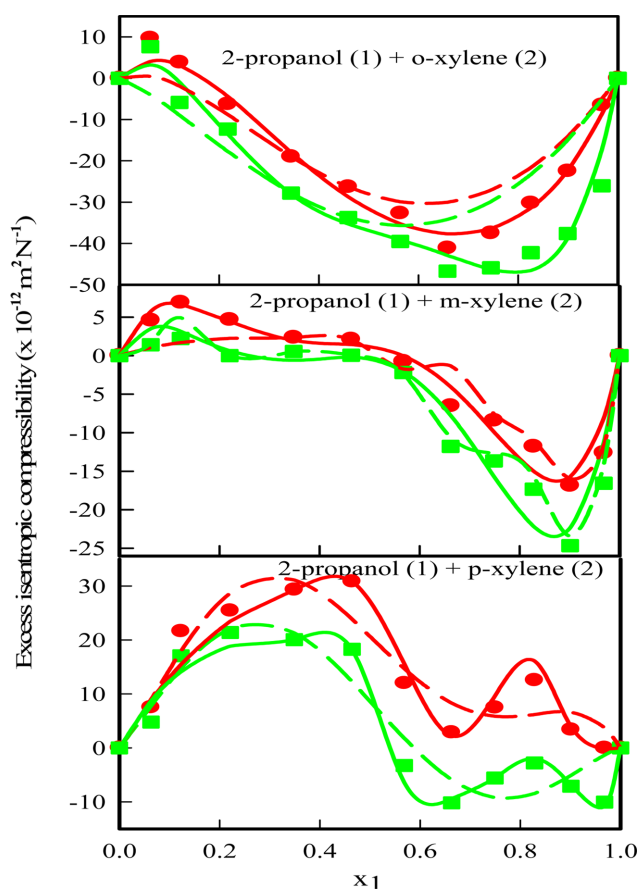


Fig. 3. Values of excess isentropic compressibility of 2-propanol (1) + hydrocarbon (2) mixture as a function of mole fraction of 2-propanol. Symbols represent experimental data; ● 298.15 K; ■ 308.15 K; Solid lines and dashed lines represent the values calculated from Eq. (10) and Graph theory, respectively.

where x_i , M_i and ρ_i are the mole fraction, molar mass and density of the pure components in 2-propanol (1) + hydrocarbon (2) mixtures.

The Δu data were also fitted to the following Redlich-Kister equation [30].

$$\Delta u = x_1(1-x_1) \left[\sum_{n=1}^4 A_n (1-2x_1)^{n-1} \right] \quad (10)$$

where A_n are the adjustable parameters that were evaluated by fitting measured Δu data to Eq. (10) by the least squares method and reported in Table 3 along with the standard deviations $\sigma(\Delta u)$ of Δu .

$$\sigma(\Delta u) = \{ [\sum (\Delta u_{\text{exptl.}} - \Delta u_{\text{calcd. (Eq. (10))}})^2 / (m-1)]^{1/2} \} \quad (11)$$

where m is the number of experimental values, and n is the number of adjustable parameters in Eq. (10). The choice of n to have 1-4 values was dictated by the consideration that the maximum deviation $\sigma_{\text{max}}(\Delta u)$ of Δu (as calculated from Eq. (10) from the corresponding experimental Δu values satisfied the relation $\sigma_{\text{max}}(\Delta u) \leq 2\sigma(\Delta u)$. Comparison of experimental Δu values for the studied systems together with smoothing curves from Eq. (10) is shown in Fig. 1.

The ultrasonic speed data for the present binary systems was also estimated theoretically by the following relations:

Nomoto's relation [31], which is based on assumption of additivity of ultrasonic speed and no volume change on mixing, is given as

$$u = \left(\frac{R_m}{V_{\text{mix}}} \right)^3 = \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \quad (12)$$

Table 3. Redlich-Kister equation parameters, A_n , and standard deviation, σ , (m s⁻¹) for deviation in ultrasonic speed, Δu , of 2-propanol (1) + hydrocarbon (2) system

T/K	A_1	A_2	A_3	A_4	σ
2-propanol (1) + cyclohexane (2)					
298.15	-85.82	72.49	-33.43	-8.94	1.42
308.15	-56.66	64.13	-15.74	7.52	1.29
2-propanol (1) + n-hexane (2)					
298.15	-21.99	3.35	-7.01	16.18	0.79
308.15	-1.56	18.52	10.17	-17.84	0.20
2-propanol (1) + benzene (2)					
298.15	6.32	112.84	-24.01	-44.47	1.98
308.15	35.75	95.05	13.88	-16.04	1.14
2-propanol (1) + toluene (2)					
298.15	7.33	47.77	144.84	47.62	1.98
308.15	21.11	43.19	176.57	12.34	1.14
2-propanol (1) + o-xylene (2)					
298.15	109.80	67.55	-69.95	83.89	3.08
308.15	119.51	13.78	19.15	210.11	3.30
2-propanol (1) + m-xylene (2)					
298.15	5.05	14.60	37.84	145.24	1.47
308.15	11.23	16.71	86.13	134.29	1.98
2-propanol (1) + p-xylene (2)					
298.15	-60.07	148.26	-53.71	-137.10	3.74
308.15	-17.23	147.02	-23.94	-102.27	3.57

$$\text{where } R_i = \left[\frac{(M_i u_i^{1/3})^3}{\rho_i^*} \right] \quad (13)$$

Van Dael's ideal mixing relation [32],

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{u_{id,mix}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \quad (14)$$

where $u_{id,mix}$ is the ultrasonic speed of the ideal mixture.

Impedance dependence relation [33],

$$u = \frac{\sum (x_i Z_i)}{\sum (x_i \rho_i^*)} \quad (15)$$

where $Z_i = \mu_i \rho_i^*$ is specific acoustic impedance of component i .

According to Schaaff's collision factor theory (CFT) [34-36],

$$u_{mix} = \frac{u_\infty (x_1 S_1 + x_2 S_2)(x_1 b_1 + x_2 b_2)}{V_{mix}} \quad (16)$$

where u_∞ is 1600 m/s and b and S are the geometric volume and collision factor, respectively. The actual volume of the molecules per mole of the liquid was computed using the relations.

$$b = \frac{4\pi r^3 N_A}{3} \quad (17)$$

where r is the molecular radius which has been computed using Schaaff's [36] relation

$$r = \left(\frac{M}{\rho N_A} \right)^{1/3} \left[\frac{3}{16\pi} \left[1 - \frac{\gamma R T}{M u^2} \left(\sqrt{1 + \frac{M u^2}{3 \gamma R T}} - 1 \right) \right] \right]^{1/3} \quad (18)$$

$$b' = \frac{M}{\rho} - \frac{\gamma R T}{M u^2} \left(\sqrt{1 + \frac{M u^2}{3 \gamma R T}} - 1 \right) \quad (19)$$

$$r = \left(\frac{3b'}{16\pi N_A} \right)^{1/3} \quad (20)$$

where b' is the van der Waals constant and is equal to four times the actual volume of the molecules per mole of the liquid, i.e., $b' = 4b$. The value of the collision factor S was calculated using the relation.

$$S = \frac{u V_T}{b u_\infty} \quad (21)$$

To make a numerical comparison of the estimation capability of the various relations, percentage standard deviations were calculated using above relation and given in Table 4.

$$\sigma(\%) = \left[\frac{\sum \{ 100(\Delta u_{exptl.} - \Delta u_{theo.}) / \Delta u_{exptl.} \}^2}{(n-1)} \right]^{1/2} \quad (22)$$

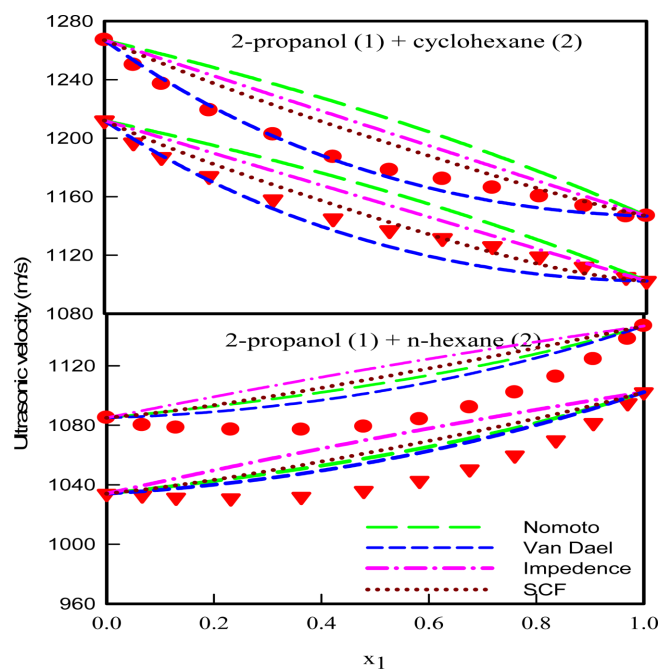
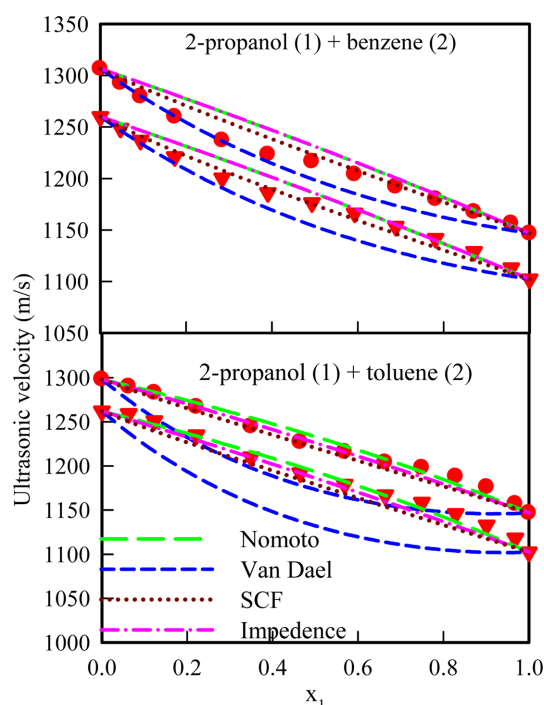
where n represents the number of experimental data points. A comparison of these correlated values with respective experimental ultrasonic speed values is shown in Figs. 4, 5 and 6.

4. Discussion

The Δu versus x_1 plots for these systems are shown in Fig. 1. The Δu values for the 2-propanol (1) + cyclohexane or p-xylene or n-hexane (2) systems are negative over the whole composition range, while these are positive for 2-propanol (1) + toluene or o-xylenes (2) and Δu versus x_1 plots are S-shape for benzene or m-xylene contain-

Table 4. Standard deviation of calculated values of ultrasonic speed using various correlations for the binary mixture at 298.15 K and 308.15 K

Binary mixture	T/K	Nomoto	Van Deal	Impedance	CFT
2-propanol (1) + cyclohexane (2)	298.15	2.691	0.559	2.001	1.470
	308.15	2.056	0.999	1.404	0.724
2-propanol (1) + n-hexane (2)	298.15	2.293	1.894	3.193	2.628
	308.15	1.851	1.602	2.899	2.142
2-propanol (1) + benzene (2)	298.15	1.539	1.213	1.552	1.001
	308.15	1.028	1.781	1.035	0.639
2-propanol (1) + toluene (2)	298.15	0.586	0.839	2.207	2.249
	308.15	0.699	4.649	0.943	1.333
2-propanol (1) + o-xylene (2)	298.15	0.815	7.118	0.949	1.295
	308.15	0.727	7.779	1.224	1.728
2-propanol (1) + m-xylene (2)	298.15	0.711	6.539	0.755	1.068
	308.15	0.613	6.987	1.031	1.452
2-propanol (1) + p-xylene (2)	298.15	2.040	5.047	1.181	0.861
	308.15	1.279	6.012	0.851	0.962

**Fig. 4. Ultrasonic velocity of 2-propanol (1) + hydrocarbon (2) predicted by various correlations. ● Exptl. 298.15 K, ▼ at 308.15 K.****Fig. 5. Ultrasonic velocity of 2-propanol (1) + benzene or toluene (2) predicted by various correlations. ● Exptl. 298.15 K, ▼ at 308.15 K.**

ing mixtures. The Δu values for equimolar mixtures follow the sequence: o-xylene > toluene > benzene > m-xylene > n-hexane > p-xylene > cyclohexane. The sign and magnitude of Δu play an important role in the understanding of molecular interactions occurring among the component molecules in the mixtures. Positive deviations indicate the increasing strength of interaction between component molecules of binary liquid mixtures. As excess ultrasonic speed is directly proportional to density, therefore, the denser the medium, the higher would be the ultrasonic speed. At the simplest qualitative level, Δu values may be attributed to the resultant of two opposing effects. The negative contribution to Δu values arises from the breaking of self-associated 2-propanol and dipole-dipole interactions between monomers and dimers of 2-propanol and from the disruption

in the favorable orientation order of the hydrocarbons. The positive contribution arises due to the presence of electron-donor-acceptor interactions between 2-propanol and hydrocarbons and change in free volume in real mixtures. The deviation in ultrasonic speed for the binary mixture of 2-propanol (1) + cyclohexane (2) has also been reported in literature and compared with our experimental values in Fig. 1 [37].

The K_s^E versus x_1 plots for these binary systems are shown in Figs. 2 and 3. It was found that K_s^E values for the 2-propanol (1) + cyclohexane (2) and 2-propanol (1) + n-hexane (2) systems are positive over the whole composition range and for 2-propanol (1) + benzene or toluene or xylenes (2), these are S-shape at both temperatures. The

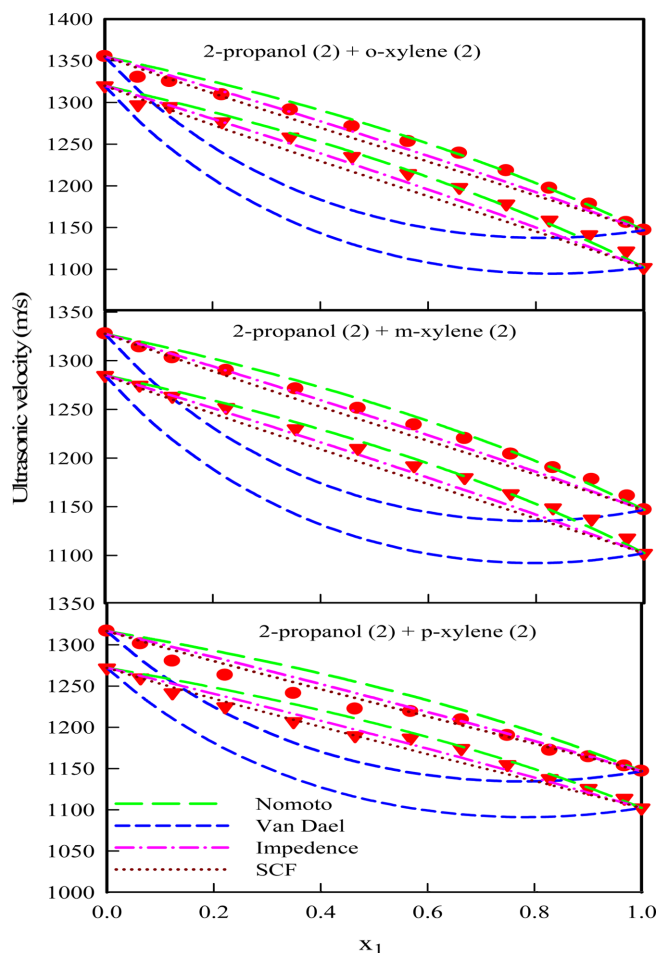


Fig. 6. Ultrasonic velocity of 2-propanol (1) + xylenes (2) predicted by various correlations. ● Exptl. 298.15 K, ▼ at 308.15 K.

positive contribution to K_s^E may be owing to expansion in volume resulting in increase in compressibility of the mixtures.

The observed negative values of K_s^E indicate the presence of specific interaction between 2-propanol and hydrocarbon molecules. In these mixtures the magnitude of K_s^E values at equimolar composition follows the sequence: cyclohexane > p-xylene > n-hexane > m-xylene > benzene > toluene > o-xylene. The above trend for isentropic compressibility should also be reflected by the available volume and intermolecular free length in these binary mixtures calculated from Jacobson's free length theory [37,38]

4-1. The Jacobson free length theory (FLT)

Jacobson derived the intermolecular free length from molar volume and surface area for a large number of liquids [39,40]. It was suggested that compressibility can be well understood in terms of the intermolecular free length, which is the distance between the surfaces of the molecule. The intermolecular free length is related to available volume and surface area per molecule. The intermolecular free length depends on the type of packing and extent of association in given liquid. L_f is the intermolecular free length of the binary mixture which is given by

$$L_f = \frac{2V_a}{Y} \quad (23)$$

Here, V_a represents the available volume per mole. Y is surface area per mole and these may be expressed as

$$V_a = V_T - V_o \quad (24)$$

$$Y = (36\pi N_A V_o^2)^{1/3} \quad (25)$$

where N_A is Avogadro's number and V_o and V_T are the molar volumes at 0 K and at temperature T respectively. V_o is calculated from Eq. (26) using critical temperature T_c . The value of critical temperature is taken from the literature [41].

$$V_o = V_T(1 - T/T_c)^{0.3} \quad (26)$$

The critical temperature of binary mixture is the mole fraction additive of the values of its pure components as given by the relation:

$$T_c = x_1 T_{c1} + x_2 T_{c2} \quad (27)$$

The intermolecular free lengths (L_f) were computed using Eq. (28):

$$L_f = \frac{2[V_T - \{x_1 V_o + x_2 V_{o2}\}]}{x_1 Y_1 + x_2 Y_2} \quad (28)$$

Intermolecular free length and available volume are shown in Figs. 7 and 8, respectively.

The values of ultrasonic speed (u) for these binary mixtures using

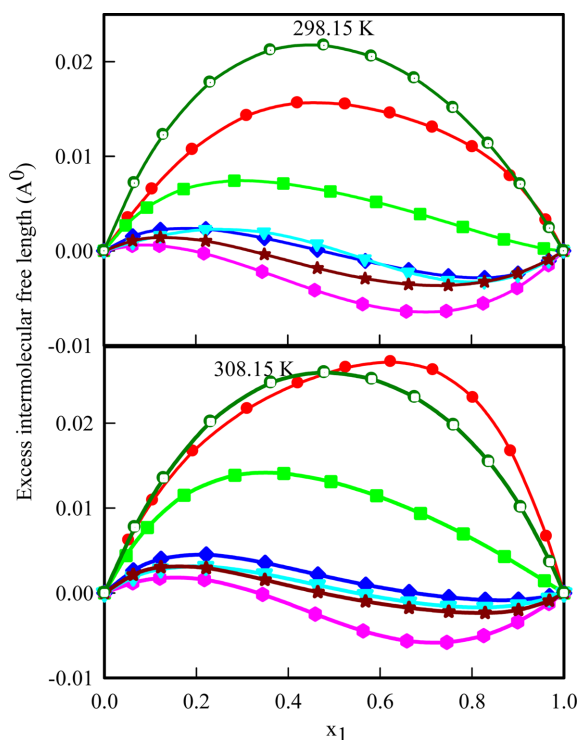


Fig. 7. Excess intermolecular free length of 2-propanol (1) + hydrocarbon (2) mixture as a function of mole fraction of 2-propanol at 298.15 and 308.15 K: ● cyclohexane, ■ n-hexane, ◆ benzene, ● toluene, ▼ o-xylene, ★ m-xylene, ○ p-xylene.

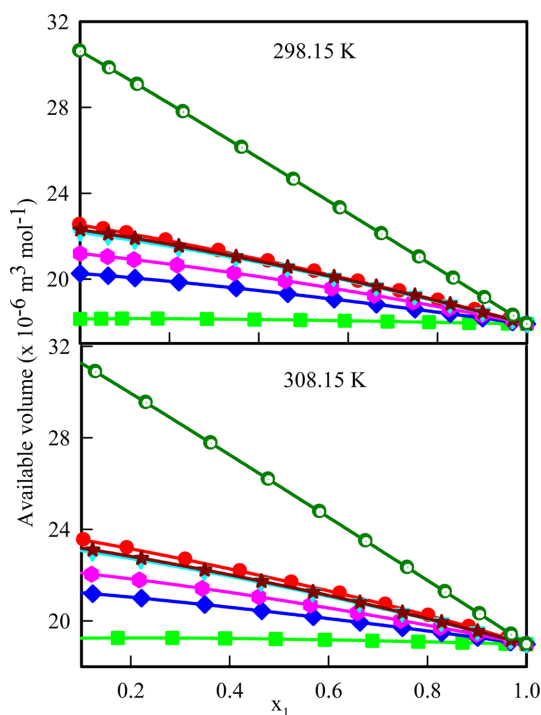


Fig. 8. Available volume of binary mixture of 2-propanol (1) + hydrocarbon (2) as a function of mole fraction of 2-propanol at 298.15 and 308.15 K: ● cyclohexane, ■ n-hexane, ◆ benzene, ⬡ toluene, ▼ o-xylene, ★ m-xylene, ○ p-xylene.

Table 5. Values of Graph theory interaction parameters χ_{12} and χ^* for excess isentropic compressibility

System	T/K	χ_{12}	χ^*
2-Propanol (1) + cyclohexane (2)	298.15	187.400	357.900
	308.15	197.700	267.400
2-Propanol (1) + n-hexane (2)	298.15	83.600	-31.900
	308.15	74.900	-77.400
2-Propanol (1) + benzene (2)	298.15	93.347	-262.057
	308.15	60.754	-240.706
2-Propanol (1) + toluene (2)	298.15	-1.425	14.553
	308.15	0.214	-54.134
2-Propanol (1) + o-xylene (2)	298.15	20.941	-515.759
	308.15	-24.751	-488.254
2-Propanol (1) + m-xylene (2)	298.15	10.094	-2.473
	308.15	6.787	-21.634
2-Propanol (1) + p-xylene (2)	298.15	77.922	214.020
	308.15	83.689	2.843

various correlations (Eqs. (12)–(16)) as well as experimental data are graphically represented in Figs. 4, 5 and 6. It has been observed that while Van Deaal's relation gives the best prediction of u in the binary mixtures containing n-hexane a

nd cyclohexane, the u values calculated by impedance dependent relation, Nomoto's relation and SCF theory also agree well with the experimental data. The difference in the experimental and calculated ultrasonic speed calculated using impedance dependence relation and Schaaff's collision factor theory may be due to non-ideal behavior of binary mixture.

Table 6. Comparison of excess isentropic compressibility (K_s^E) values calculated from Graph theory with their corresponding experimental values for binary mixtures

x ₁	K _s ^E (×10 ⁻¹² Nm s ⁻²)			
	Exptl.	Graph	Exptl.	Graph
	298.15 K		308.15 K	
2-propanol (1) + cyclohexane (2)				
0.0535	13.603	9.559	14.786	9.807
0.0535	13.603	9.559	14.786	9.807
0.1055	22.844	17.585	22.408	17.630
0.1931	33.922	28.510	29.248	27.683
0.3114	38.464	38.464	36.123	36.123
0.4221	43.106	43.106	39.513	39.513
0.5260	38.977	43.529	35.408	39.173
0.6238	31.060	40.560	27.622	35.978
0.7158	23.993	34.852	20.236	30.556
0.8027	17.423	26.925	15.644	23.381
0.8849	12.414	17.204	10.681	14.820
0.9627	8.501	6.036	4.890	5.164
2-propanol (1) + n-hexane (2)				
0.0679	10.693	5.179	2.460	4.433
0.1319	13.818	9.400	6.759	7.675
0.2357	16.484	14.855	9.692	11.105
0.3681	19.292	19.292	12.541	12.541
0.4848	20.821	20.821	11.527	11.527
0.5884	19.484	20.278	7.497	9.291
0.6811	15.176	18.260	5.314	6.644
0.7644	10.227	15.191	3.090	4.108
0.8398	7.627	11.385	2.313	2.026
0.9083	5.468	7.070	1.737	0.612
0.9708	3.271	2.415	0.583	-0.010
2-propanol (1) + benzene (2)				
0.0472	3.961	7.498	2.216	4.734
0.0937	7.824	12.544	5.030	7.626
0.1735	12.325	16.731	5.917	9.261
0.2839	15.612	15.612	6.537	6.537
0.3904	9.826	9.826	0.782	0.782
0.4932	-3.434	2.369	-9.685	-5.643
0.5925	-7.341	-4.630	-17.973	-11.077
0.6884	-10.166	-9.681	-20.075	-14.367
0.7811	-11.196	-11.754	-21.890	-14.734
0.8708	-9.760	-10.162	-20.715	-11.669
0.9576	-8.530	-4.468	-11.042	-4.862
2-propanol (1) + toluene (2)				
0.0630	-1.242	-1.194	-7.445	-7.215
0.1230	-3.402	-3.285	-9.026	-8.645
0.2215	-2.283	-1.801	-8.758	-7.321
0.3496	0.489	0.489	-3.317	-3.317
0.4648	0.835	0.835	-4.531	-4.531
0.5689	-6.008	-6.455	-10.750	-9.850
0.6634	-9.889	-8.993	-16.623	-16.231
0.7497	-20.800	-19.843	-26.368	-23.453
0.8287	-24.600	-26.032	-27.682	-25.647
0.9014	-23.731	-23.509	-26.534	-24.365
0.9684	-9.554	-8.550	-20.029	-19.024

Table 6. (continued)

x ₁	K _s ^E (×10 ⁻¹² Nm s ⁻²)			
	Exptl.	Graph	Exptl.	Graph
	298.15 K		308.15 K	
2-propanol (1) + o-xylene (2)				
0.0616	9.670	0.454	7.614	-4.011
0.1205	0.841	-1.940	-5.852	-8.973
0.2173	-6.285	-8.829	-12.315	-17.743
0.3443	-19.008	-19.008	-27.811	-27.811
0.4589	-26.310	-26.310	-33.748	-33.748
0.5631	-32.701	-29.924	-39.518	-35.691
0.6581	-41.141	-30.029	-46.702	-34.196
0.7452	-37.481	-27.095	-45.889	-29.882
0.8253	-30.246	-21.643	-42.223	-23.315
0.8993	-22.489	-14.155	-37.617	-14.976
0.9677	-6.512	-5.047	-26.053	-5.264
2-propanol (1) + m-xylene (2)				
0.0627	4.602	1.042	1.408	1.633
0.1224	6.918	1.694	4.568	4.917
0.2206	4.658	2.254	0.000	0.005
0.3484	2.362	2.362	0.549	0.549
0.4635	2.112	2.112	0.059	0.059
0.5676	-0.755	-1.736	-2.183	-2.340
0.6622	-6.519	-1.336	-11.775	-10.591
0.7487	-8.416	-7.542	-13.663	-12.685
0.8280	-11.792	-10.987	-17.331	-15.635
0.9009	-16.869	-15.987	-24.664	-23.458
0.9682	-12.617	-11.735	-16.564	-14.176
2-propanol (1) + p-xylene (2)				
0.0629	7.521	8.776	4.806	8.664
0.1228	21.622	15.456	17.077	14.103
0.2213	25.434	23.468	21.391	18.865
0.3492	29.313	29.313	20.055	20.055
0.4644	30.834	30.834	18.275	18.275
0.5685	11.981	15.587	-3.264	-6.435
0.6631	2.854	2.239	-10.170	-9.365
0.7494	7.470	9.638	-5.555	-5.635
0.8285	12.523	16.114	-2.785	-1.983
0.9012	3.383	3.961	-7.082	-6.837
0.9684	-0.026	-0.034	-10.036	-10.837

5. Conclusion

Ultrasonic speeds for binary mixtures of 2-propanol + cyclohexane, n-hexane, benzene, toluene, o-, m- and p-xylenes were reported as 298.15 K and 308.15 K over the whole composition range. The measured data were correlated by Nomoto's relation; Van Dael's mixing relation, impedance dependence relation and Schaaff's collision factor theory. The calculated deviations in ultrasonic speed were also fitted to the Redlich-Kister equation. Acoustic parameters such as excess isentropic compressibility (K_s^E), intermolecular free length (L_f) and available volume (V_a) were also derived from ultrasonic speed data and Jacobson's free length theory.

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