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Speeds of Sound and Isentropic Compressibilities in Binary Mixtures of 2-Propanol with Several 1-Alkanols at 298.15 K

G. Savaroglu[1,2] and E. Aral[1]

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Speeds of sound and densities of 2-propanol + 1-propanol, 2-propanol + 1-butanol, 2-propanol + 1-octanol, and 2-propanol + 1-hexanol have been measured over the entire composition range at 298.15 K. Speeds of sound of the binary mixtures have also been estimated from free length theory (FLT), collision factor theory (CFT), and Nomoto's relation (NR) and have been compared with experimental speeds of sound. The isentropic compressibilities, molar isentropic compressibilities, excess molar isentropic compressibilities, and excess speeds of sound have been calculated from experimental densities and speeds of sound. Excess molar isentropic compressibilities and excess speeds of sound of the binary mixtures were fitted to the Redlich–Kister equation.

KEY WORDS: binary mixture; 1-butanol; densities; 1-hexanol; isentropic compressibilities; 1-octanol; 2-propanol; 1-propanol; speed of sound.

1. INTRODUCTION

Thermophysical properties of binary liquid mixtures containing a 1-alkanols and a second inert or polar component have been extensively studied. Yet there is no systematic study on the behavior of 2-propanol with 1-alkanols.

In this study, the measurements of densities and speeds of sound for 2-propanol + 1-propanol, 2-propanol + 1-butanol, 2-propanol + 1-octanol, and 2-propanol + 1-hexanol have been made at 298.15 K and atmospheric

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[1] Department of Physics, Osmangazi University, 26480 Eskisehir, Turkey.
[2] To whom correspondence should be addressed. E-mail: gsavarog@ogu.edu.tr

pressure. The experimental data were used to calculate the isentropic compressibility, κ_s, molar isentropic compressibility, K_S, excess molar isentropic compressibility, K_S^E, and excess speed of sound, u^E. The excess molar isentropic compressibility, K_S^E, and excess speed of sound, u^E, are used in explaining the molecular interactions in the liquid mixtures.

The data for the binary systems were fitted to the Redlich–Kister equation [1]. Theoretical values of the speeds of sound has been calculated using the free length theory (FLT) [2, 3], collision factor theory (CFT) [4], and Nomoto's relation (NR) [5], and the results compared with experimental values at 298.15 K.

2. EXPERIMENTAL

2-propanol (> 99 mass%), 1-propanol (> 99 mass%), 1-butanol (> 99 mass%), 1-octanol (>97 mass%), and 1-hexanol (>98 mass%) were obtained from Merck. The purities of these compounds were checked by comparing measured densities and speeds of sound with those reported in the literature. These compounds were used as received without further purification. The pure compound densities, speeds of sound, and molar isentropic compressibilities at 298.15 are shown in Table I together with literature data required for the calculation of K_S^E and u^E [6–23].

The mixtures in this study were prepared gravimetrically using an electronic balance (Scaltec, SBC22) accurate to 0.01 mg. The precision of the mole fraction is estimated to be better than $\pm 1 \times 10^{-4}$. The densities and speeds of sound of both pure liquids and liquid mixtures were measured using a vibrating tube densimeter and sound analyzer, Anton Paar DSA-5000, automatically thermostated at ±0.01 K. The calibration of the apparatus was carried out with air and deionized double-distilled water. The uncertainty of the measurements was estimated to be $\pm 5 \times 10^{-6}\,\mathrm{g \cdot cm^{-3}}$ for density and $\pm 0.5\,\mathrm{m \cdot s^{-1}}$ for speeds of sound; the respective reproducibility was $\pm 1 \times 10^{-6}\,\mathrm{g \cdot cm^{-3}}$ and $\pm 0.1\,\mathrm{m \cdot s^{-1}}$. The precision of the temperature measurements was ±0.001 K.

3. RESULTS AND DISCUSSION

The values of the density, ρ, speeds of sound, u, isentropic compressibilities, κ_S, molar isentropic compressibilities K_S, excess molar isentropic compressibilities, K_S^E, and excess speeds of sound, u^E, for 2-propanol + 1-propanol, 2-propanol + 1-butanol, 2-propanol + 1-octanol, and 2-propanol + 1-hexanol at 298.15 K and atmospheric pressure are given in Table II.

Table I. Physical Properties of the Pure Components at 298.15 K

Property	ρ^* $(\mathrm{kg \cdot m^{-3}})$	u^* $(\mathrm{m \cdot s^{-1}})$	$A^*_{p,\mathrm{m}}$ $(\mathrm{mm^3 \cdot K^{-1} \cdot mol^{-1}})$	$C^*_{p,\mathrm{m}}$ $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$K^*_{S,\mathrm{m}}$ $(\mathrm{m^3 \cdot PPa^{-1} \cdot mol^{-1}})$
2-propanol	exp. 781.91 lit. 781.2 [6] 781.26 [7] 780.89 [8]	exp. 1141.3 lit. 1139 [14] 1141 [15] 1140.1 [6]	81.24[a]	155.78 [9]	75.472
1-propanol	exp. 800.62 lit. 799.982 [9] 799.60 [7]	exp. 1208.1 lit. 1207.1 [16] 1205.42 [17]	76.57[b]	143.85 [22]	64.245
1-butanol	exp. 806.14 lit. 805.76 [10]	exp. 1240.8 lit. 1240.2 [10]	84.96[b]	176.48 [23]	74.079
1-octanol	exp. 821.72 lit. 821.62 [11]	exp.1347.9 lit.1348 [18]	133.10[c]	305.25 [23]	106.153
1-hexanol	exp. 815.15 lit. 815.1 [12] 815.12 [13]	exp. 1303.6 lit. 1303.6 [12]	110.06[d]	241.32 [7]	90.490

[a] Derived from our measured densities and the isobaric expansivity $\alpha^*_{p,i}$ in Ref. 19.

[b] Derived from our measured densities and the isobaric expansivity $\alpha^*_{p,i}$ in Ref. 20.

[c] Derived from our measured densities and the isobaric expansivity $\alpha^*_{p,i}$ in Ref. 21.

[d] Derived from our measured densities and the isobaric expansivity $\alpha^*_{p,i}$ in Ref. 7.

κ_S and K_s have been calculated from the equations:

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

$$K_\mathrm{s} = -(\partial V/\partial p)_\mathrm{S} = V\kappa_s = \sum_{i=1}^{2} x_i M_i/(\rho u^2) \tag{2}$$

where ρ is the density, V is the molar volume, and x_i and M_i are the mole fraction and molar mass of component i in the mixture, respectively.

The excess molar isentropic compressibilities, K_s^E, were estimated by means of the equation:

$$K_\mathrm{s}^\mathrm{E} = K_\mathrm{s} - K_\mathrm{s}^\mathrm{id} \tag{3}$$

where the molar isentropic compressibilities for the ideal mixture, K_S^id, were calculated by the following relation [24–25]:

$$K_\mathrm{S}^\mathrm{id} = \sum_\mathrm{i} x_\mathrm{i} \left[K_{\mathrm{S},i}^* - T A_{p,i}^* \left\{ \left(\sum_i x_i A_{p,i}^* \Big/ \sum_i x_i C_{p,i}^* \right) - \left(A_{p,i}^*/C_{p,i}^* \right) \right\} \right] \tag{4}$$

$A_{p,i}^*$, $C_{p,i}^*$, and $K_{\mathrm{S},i}^*$ are the product of the molar volume V_i and the isobaric expansivity $\alpha_{p,i}^*$, the isobaric molar heat capacity of pure component i, and the product of the molar volume V_i and the isentropic compressibility $\kappa_{S,i}^*$ (for pure liquid component i), respectively. The excess speed of sound, u^E, of each sample with respect to ideal behavior is defined by the equation:

$$u^\mathrm{E} = u - u^\mathrm{id} = u - (\rho^\mathrm{id}\kappa_\mathrm{S}^\mathrm{id})^{-1/2} \tag{5}$$

where u is the speed of sound of the mixture, $\rho^\mathrm{id} = \sum_{i=1} \phi_i \rho_i$ is the density of the corresponding ideal mixture [26], and ρ_i is the density of pure component i. ϕ_i is defined by the relation:

$$\phi_i = \frac{x_i V_i}{\left(\sum_i x_i V_i\right)} \tag{6}$$

The excess molar isentropic compressibilities, K_S^E, and excess speeds of sound, u^E, of the binary mixtures were fitted with a Redlich–Kister equation [1]:

$$\Delta Q = x(1-x)\sum_{k=0}^{m} A_k (2x-1)^k \tag{7}$$

Table II. Experimental Densities, ρ, and Speeds of Sound, u, and Calculated K_s, K_s^E, and u^E for 2-Propanol + 1-Propanol, + 1-Butanol, + 1-Octanol, and + 1-Hexanol Binary Mixtures at 298.15 K

x_1	ρ $(\mathrm{kg \cdot m^{-3}})$	u $(\mathrm{m \cdot s^{-1}})$	K_s $(\mathrm{m^3 \cdot PPa^{-1} \cdot mol^{-1}})$	u^E $(\mathrm{m \cdot s^{-1}})$	K_s^E $(\mathrm{m^3 \cdot PPa^{-1} \cdot mol^{-1}})$
2-propanol + 1-propanol					
0.1051	798.37	1201.0	65.364	0.9	−0.061
0.195	796.76	1195.4	66.258	1.8	−0.177
0.3049	794.67	1187.9	67.446	2.2	−0.223
0.4062	792.80	1181.3	68.530	2.6	−0.277
0.4941	791.17	1175.4	69.491	2.7	−0.302
0.6029	789.12	1168.0	70.738	2.4	−0.277
0.7067	787.16	1161.0	71.960	1.9	−0.220
0.8063	785.31	1154.2	73.148	1.4	−0.150
0.91	783.37	1147.5	74.380	0.9	−0.082
0.9515	782.54	1144.5	74.927	0.4	0.000
2-propanol + 1-butanol					
0.0596	804.62	1235.6	74.148	0.7	−0.019
0.1039	803.68	1231.8	74.139	1.3	−0.092
0.2093	801.62	1223.2	74.043	3.0	−0.340
0.3024	799.57	1214.8	74.069	3.9	−0.447
0.3977	797.49	1206.1	74.089	4.6	−0.563
0.5033	794.92	1195.9	74.208	4.9	−0.592
0.599	792.68	1186.5	74.297	5.1	−0.636
0.6946	790.21	1176.4	74.500	4.5	−0.564
0.8062	787.19	1164.1	74.812	3.3	−0.403
0.8938	784.58	1153.6	75.179	1.7	−0.153
2-propanol + 1-octanol					
0.0862	819.96	1338.7	103.063	3.1	−0.473
0.2078	817.18	1324.2	98.775	7.2	−1.065
0.2977	814.58	1311.6	95.796	9.4	−1.306
0.4059	811.74	1296.0	91.956	12.9	−1.846
0.5012	808.60	1279.4	88.837	14.6	−2.051
0.5991	804.77	1259.8	85.829	15.2	−2.059
0.6994	800.52	1237.7	82.690	15.6	−2.113
0.7985	795.28	1211.1	80.020	13.2	−1.724
0.8993	789.09	1179.3	77.555	8.4	−1.061
0.9453	785.80	1162.8	76.580	5.1	−0.603

Table II. *(Continued)*

x_1	ρ (kg·m^{-3})	u (m·s^{-1})	K_s (m^3·PPa^{-1}·mol^{-1})	u^E (m·s^{-1})	K_s^E (m^3·PPa^{-1}·mol^{-1})
2-propanol + 1-hexanol					
0.039	814.40	1299.6	89.762	1.0	−0.150
0.1037	813.00	1292.9	88.528	3.0	−0.424
0.2075	810.57	1281.1	86.662	5.5	−0.748
0.3051	808.20	1269.2	84.909	7.6	−1.047
0.4032	805.42	1255.9	83.275	9.0	−1.215
0.5067	802.47	1241.4	81.476	10.8	−1.465
0.6044	799.08	1225.0	80.091	10.4	−1.382
0.7047	795.43	1207.3	78.651	9.9	−1.311
0.8059	791.12	1186.8	77.439	7.8	−0.992
0.9081	786.44	1164.3	76.303	4.6	−0.574

where ΔQ is K_s^E and u^E, x_i is the mole faction of component i, A_k is the polynomial coefficient, k is the number of the polynomial coefficients, and m is the number of parameters. The coefficients A_k of Eq. (7) are presented in Table III.

The root-mean-square deviations were calculated using the expression,

$$\sigma = \left[\frac{\sum_i^N \left(Z_{\text{exp}} - Z_{\text{pred}}\right)^2}{N} \right]^{1/2} \tag{8}$$

Table III. Values of the Parameters A_i of the Redlich–Kister Equation and Corresponding Root-Mean-Square Deviations, at 298.15 K

	A_0	A_1	A_2	A_3	σ
2-propanol+1-propanol					
u^E (m·s^{-1})	10.4	−2.5	−1.1	3.5	0.1
K_s^E (m^3·PPa^{-1}·mol^{-1})	−1.187	0.020	0.608		0.015
2-propanol+1-butanol					
u^E (m·s^{-1})	20.3	3.6	−4.7	−1.5	0.1
K_s^E(m^3·PPa^{-1}·mol^{-1})	−2.548	−0.569	1.402		0.032
2-propanol+1-octanol					
u^E (m·s^{-1})	57.9	32.7	13.1	1.4	0.2
K_s^E(m^3·PPa^{-1}·mol^{-1})	−8.082	−4.092	−1.131	0.898	0.050
2-propanol+1-hexanol					
u^E (m·s^{-1})	41.3	14.5	1.5	−0.7	0.2
K_s^E(m^3·PPa^{-1}·mol^{-1})	−5.572	−1.773	0.122	0.564	0.030

where Z is the value of the property and N is the number of experimental data.

The values of the excess molar isentropic compressibilities, K_s^E and excess speeds of sound, u^E, plotted against the mole fraction of 2-propanol of the binary liquid mixtures are shown in Figs. 1 and 2, respectively.

The excess molar isentropic compressibilities, K_s^E, are negative over the entire composition for all studied binary mixtures. The excess speed of sound, u^E are positive over the whole composition range for all the binary mixtures. For all binary liquid mixtures, u^E curves show similar behaviors, while K_s^E shows an opposite trend (Figs. 1 and 2).

In these binary liquid systems with 2-propanol as one component, negative values of K_s^E and positive values of the excess speed of sound, u^E are in the order:

1-octanol > 1-hexanol > 1-butanol > 1-propanol.

This order may be explained by the differences in length of the chains and the number of C atoms in 1-alkanols. K_s^E becomes more negative for 2-propanol + 1-octanol than for the other mixtures, while u^E becomes

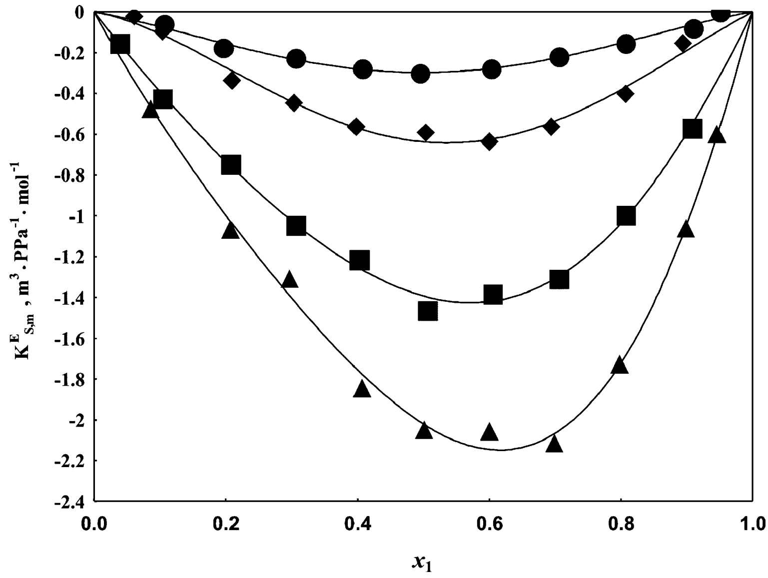

Fig. 1. Excess isentropic compressibilities, $K^E_{s,m}$, for the binary mixtures at 298.15 K: 2-propanol (1) + 1-propanol (2) (●), 2-propanol (1) + 1-butanol (2) (♦), 2-propanol (1) + 1-octanol (2) (▲), 2-propanol (1) + 1-hexanol (2) (■), and Redlich–Kister correlations (–).

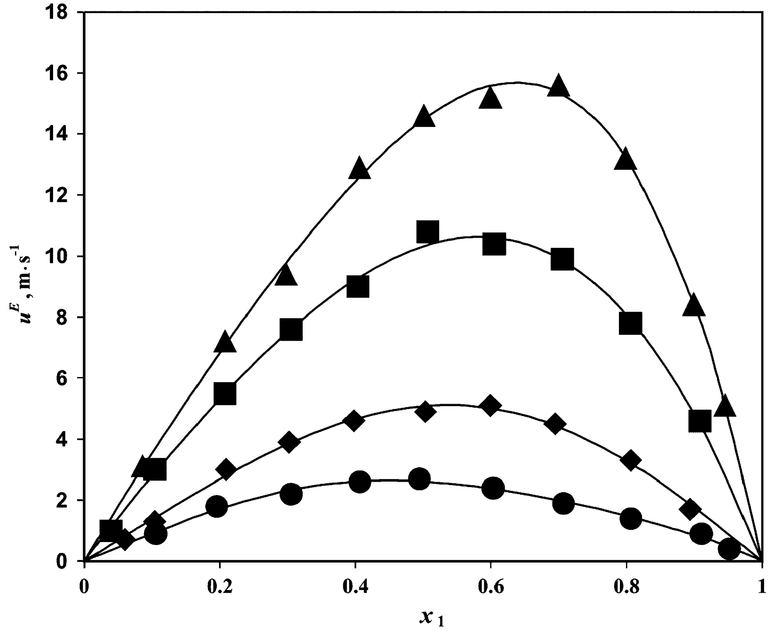

Fig. 2. Excess speeds of sound, u^E, for the binary mixtures at 298.15 K: 2-propanol (1) + 1-propanol (2) (●), 2-propanol (1) +1-butanol (2) (◆), 2-propanol (1) + 1-octanol (2) (▲), 2-propanol (1) + 1-hexanol (2) (■), and Redlich-Kister correlations (–).

more positive. This may be due to the fact that intermolecular hydrogen bonding in 2-propanol + 1-octanol seems to be more stable than self-association in 2-propanol or 1-octanol.

4. THEORETICAL

The empirical and semi-empirical theories of Jacobson, Schaaff, and Nomoto were used to obtain speeds of sound in binary liquid mixtures.

4.1. Jacobson's Free Length Theory (FLT) [2, 3]

$$u_{\mathrm{m}} = \frac{K}{L\rho_{\mathrm{m}}^{1/2}} \tag{9}$$

where K is a temperature-dependent constant whose value at 298.15 K is 625, ρ_{m} is the density of the mixture, and L is the free length of the mixture. Here

$$L = \frac{2\left(\frac{1}{\rho} - \sum_{i=1}^{2} \frac{w_i V_{oi}}{M_i}\right)}{\sum_{i=1}^{2} \frac{w_i Y_i}{M_i}} \tag{9a}$$

where M_i is the molar mass of component i, w_i is mass fraction of component i, and Y_i and V_{oi} are the surface area per mole and the molar volume at absolute zero of component i, respectively. Y and V_{oi} are given by

$$Y = (36\pi N_A V_{oi}^2)^{1/3} \tag{9b}$$

$$V_{oi} = V_T(1 - T/T_c)^{0.3} \tag{9c}$$

where V_T and T_c are, respectively, the molar volume of a pure component at temperature T and the critical temperature.

4.2. Schaaff's Collision Factor Theory [4]

$$u_m = u_\infty \frac{\left(\sum_{i=1}^{2} x_i s_i\right)\left(\sum_{i=1}^{2} x_i B_i\right)}{V_m} \tag{10}$$

where $u_\infty = 1600\ \mathrm{m \cdot s^{-1}}$ and s_i is the space filling factor of component i in the mixture. V_m is the molar volume of the mixture and can be evaluated as

$$V_m = \frac{\sum_{i=1}^{2} x_i M_i}{\rho_m} \tag{10a}$$

where x_i is the mole fraction. B_i is the actual volume of the molecule per mole of component i and can be evaluated as

$$B = 4/3\, \pi r^3 N_A \tag{10b}$$

where N_A is Avogadro's number and r is the molecular radius of the pure component. The molecular radius is calculated as

$$r = \left[\frac{3b}{16\pi N}\right]^{1/3} \tag{10c}$$

where b is the Van der Waals constant.

Table IV. Root-Mean-Square Deviations Relative to the Predicted Speeds of Sound by Means of FLT, CFT, and NR Theories

	$\mathrm{RMSD_r}$ (%)		
	u_{FLT}	u_{CFT}	u_{NR}
2-propanol (1) + 1-propanol (2)	0.2	0.1	0.2
2-propanol (1) + 1-butanol (2)	0.4	0.3	0.2
2-propanol (1) + 1-octanol (2)	1.1	1.3	0.2
2-propanol (1) + 1-hexanol (2)	0.6	1.0	0.2

4.3. Nomoto's Relation [5]

$$u_{\mathrm{m}} = \left[\frac{\sum_{i=1}^{2} x_i R_i}{\sum_{i=1}^{2} x_i V_i}\right]^3 \tag{11}$$

where R_i and V_i stand for the molar sound speed and molar volume of component i in the mixture, respectively.

The root-mean-square deviation relative ($\mathrm{RMSD_r}$) between the experimental and calculated speeds of sound and the isentropic compressibilities for FLT, CFT, and NR is defined by the equation:

$$\mathrm{RMSD_r} = \left[\frac{1}{m}\sum\left(\frac{Z^{\mathrm{calc}} - Z^{\mathrm{exp}}}{Z^{\mathrm{exp}}}\right)^2\right]^{1/2} \tag{12}$$

where m is the number of experimental points and Z is the value of the property.

Table IV gives the root-mean-square deviations relative to the speeds of sound calculated by Jacobson's free length theory (FLT), Schaaffs collision factor theory (CFT), and Nomoto's relation (NR). NR gives the best results for all studied liquid mixtures except for 2-propanol + 1-propanol. CFT gives the best results for 2-propanol + 1-propanol. FLT gives the worst results for all studied liquid mixtures.

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