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Densities, Speeds of Sound, and Isentropic Compressibilities for Binary Mixtures of 1,2-Ethanediol with 2-Ethyl-1-hexanol, 1-Heptanol, or Ethanol at the Temperature 298.15 K and Densities for Mixtures of 1,2-Ethanediol with 1-Nonanol at the Temperatures (293.15 and 298.15) K

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Densities and speeds of sound for binary mixtures of 1,2-ethanediol with three alkanols (2-ethyl-1-hexanol, 1-heptanol, or ethanol) were measured over the entire composition range in the temperature 298.15 K by means of a vibrating-tube densimeter and pulse-echo-overlap method. Density measurements were also made for mixtures of 1,2-ethanediol with 1-nonanol at the temperatures (293.15 and 298.15) K. From these data, the excess molar volumes and excess molar isentropic compressibilities as well as the deviations of speed of sound were calculated and approximated by the Redlich−Kister polynomials. The negative values of the excess molar volumes and isentropic compressibilities over the entire composition range are observed only in the case of ethanol. In the cases of 2-ethyl-1-hexanol, 1-heptanol, and 1-nonanol, the positive values of the excess molar volumes over the entire composition range are observed. Simultaneously, the negative values of the excess molar isentropic compressibilities over the entire composition range are observed for 2-ethyl-1-hexanol and 1-heptanol.

Introduction

Although an interpretation of the mixing effects is very difficult, nonaqueous binary systems of highly associated hydroxyl compounds are an important and interesting subject of study from both a practical and a theoretical point of view. Particularly interesting are systems with bifunctional compound(s), e.g., (alkanol + alkanediol), all the more because the pure diols are interesting compounds due to the possibility of formation of both inter- and intramolecular hydrogen bonds. Obviously, the type and extent of the hydrogen bonding in diols (as a rule in alcohols) depend on the carbon chain (length and degree of branching) and the hydroxyl groups (their number and positions).

Our earlier papers have reported properties of 1,2-ethanediol with 1-butanol, 1-hexanol, or 1-octanol,[1] 1-pentanol,[2] and 1-nonanol.[3] The aim of this work is to study the composition dependence of volume and rigidity effects for 1,2-ethanediol with 2-ethyl-1-hexanol, 1-heptanol, or ethanol at the temperature 298.15 K. To the best of our knowledge, two data sets (covering the whole composition range) of the excess molar volumes for the system of 1,2-ethanediol with ethanol[4,5] are available in the literature. However, these data are inconsistent (excess molar volumes differ strongly, up to $0.313 \cdot 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$), and this situation has prompted us to reinvestigate the volume effects for this system.

Additionally, the volume effects for 1,2-ethanediol with 1-nonanol in the immediate vicinity of the miscibility gap, i.e., at (293.15 and 298.15) K, are studied because previously reported results[3] can raise some doubts. On one hand, the measured speed of sound shows no anomaly in the temperature range from (293.15 to 313.15) K. However, on the other hand, in the case of the volume effects studied at temperature 298.15 K (and higher), some irregularities in the vicinity of the critical composition have been obtained.[3] The system of {x 1,2-ethanediol + (1 − x) 1-nonanol} shows the upper critical temperature point (UCTP), and its coordinates, i.e., the critical temperature T_c and critical composition x_c, are $T_c = 293$ K and $x_c = 0.819$, respectively.[6]

Experimental Section

Materials. 1,2-Ethanediol (puriss, p.a., mass fraction > 0.995, Fluka), 1-heptanol (puriss, p.a. mass fraction > 0.99, Fluka), 1-nonanol (mass fraction 0.99, Alfa Aesar), ethanol (puriss, p.a. mass fraction > 0.998, POCh), and 2-ethyl-1-hexanol (mass fraction 0.996, Aldrich) were used without further purification. The water contents (mass fractions), determined by the Karl Fischer method, were found to be $1.6 \cdot 10^{-4}$ (1-heptanol), $3.2 \cdot 10^{-4}$ (1-nonanol), $6.2 \cdot 10^{-4}$ (ethanol), and $2.3 \cdot 10^{-4}$ (2-ethyl-1-hexanol). In the case of 1,2-ethanediol, two various samples were used: the water content was $1.4 \cdot 10^{-4}$ (sample I, mixtures with 2-ethyl-1-hexanol, or 1-heptanol) and $2.3 \cdot 10^{-4}$ (sample II, mixtures with ethanol, or 1-nonanol), respectively. Comparing measured densities and speeds of sound with the literature values (Table 1) also tested the purity of the alcohols. The agreement is satisfactory.

Methods. Solutions were prepared by mass using an analytical balance (Ohaus AS 200, repeatability $\pm\ 6 \cdot 10^{-4}$ g) and kept in sealed flasks. The uncertainty of the mole fraction was estimated to be of $\pm\ 1 \cdot 10^{-4}$ (mixtures with 2-ethyl-1-hexanol, or 1-heptanol) and $\pm\ 5 \cdot 10^{-5}$ (mixtures with ethanol, or 1-nonanol).

Just as in previous work,[12] the densities were measured with a vibrating-tube densimeter DMA 5000 (Anton Paar). Before the measurements, all samples were degassed using an ultrasound. The densimeter was calibrated using air and water (deionized and degassed by boiling) with an electrolytic conductivity of $1.2 \cdot 10^{-4}\ \mathrm{S \cdot m^{-1}}$ as standard. All measured

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Table 1. Densities, ρ, and Speeds of Sound, u, of Pure Compounds Together with the Selected Literature Data at $T = 298.15$ K

property	exptl	lit.
		1,2-Ethanediol
ρ/kg·m^{-3}	1109.84[a], 1109.88[b]	1109.88,[1,3] 1110.0,[8] 1109.97,[2] 1109.86,[7] 1109.91,[9,10] 1109.6[4]
u/m·s^{-1}	1655.2[a], 1654.4[b]	1654.66,[2] 1654.89,[3] 1654.35[11]
		2-Ethyl-1-hexanol
ρ/kg·m^{-3}	828.67	828.910,[12] 829.0[8]
u/m·s^{-1}	1318.4	1321.8,[13] 1318.07[12]
		1-Heptanol
ρ/kg·m^{-3}	818.79	818.765,[14] 818.810,[12] 818.851,[17] 818.894,[16] 818.80[15]
u/m·s^{-1}	1327.0	1327.01,[14] 1328.0,[13] 1326.65,[12] 1327.36,[17] 1327.27,[15] 1326.73,[16] 1326.10[18]
		Ethanol
ρ/kg·m^{-3}	785.14	784.93,[8] 785.2,[5,18] 785.1,[4] 785.13,[19] 785.36,[20,21]
u/m·s^{-1}	1142.0	1142.29,[19] 1142.95,[20] 1142.4,[22] 1142.15[18]
		1-Nonanol
ρ/kg·m^{-3}	824.24	824.48,[3] 824.271,[14] 824.24,[15] 824.238[12]

[a] Sample I. [b] Sample II.

Table 2. Densities, ρ, and Speeds of Sound, u, for the Investigated Systems as a Function of Mole Fraction x at $T = 298.15$ K

x	ρ/kg·m^{-3}	u/m·s^{-1}	x	ρ/kg·m^{-3}	u/m·s^{-1}
		x 1,2-Ethanediol + $(1 - x)$ 2-Ethyl-1-hexanol			
0	828.67	1318.4	0.5990	924.74	1394.9
0.1858	848.93	1334.2	0.6996	954.67	1423.5
0.2952	863.97	1345.5	0.7985	991.94	1468.2
0.4043	881.94	1358.8	0.8507	1015.69	1500.3
0.4512	890.81	1365.9	0.9000	1041.98	1539.4
0.4914	899.09	1372.4	1	1109.84	1655.2
		x 1,2-Ethanediol + $(1 - x)$ 1-Heptanol			
0	818.79	1327.0	0.5508	911.36	1384.3
0.0668	826.18	1330.3	0.6087	927.05	1398.5
0.1162	832.26		0.6766	948.15	1418.2
0.2007	843.63	1339.2	0.7988	994.195	1470.8
0.2946	858.17	1346.9	0.8940	1041.30	1537.9
0.4022	877.75	1359.6	1	1109.84	1655.2
0.4834	895.05	1371.6			
		x 1,2-Ethanediol + $(1 - x)$ Ethanol			
0	785.14	1142.0	0.49443	950.53	1374.9
0.10022	819.39	1187.5	0.64283	998.61	1454.5
0.19799	852.36	1231.7	0.74988	1032.40	1513.4
0.30140	886.92	1279.7	0.84978	1063.88	1569.5
0.34623	901.80		1	1109.88	1654.4
0.39979		1328.0			

Table 3. Densities, ρ, for {x 1,2-Ethanediol + $(1 - x)$ 1-Nonanol} as a Function of Mole Fraction x at Temperatures T

	ρ/kg·m^{-3}	
x	T/K = 298.15	T/K = 293.15
0	824.24	827.65
0.10470	833.67	837.12
0.20396	844.31	847.78
0.28781	855.06	858.55
0.39273	870.92	874.43
0.52030	895.13	898.67
0.59824	913.77	917.33
0.70298	944.57	948.15
0.78054	973.70	977.30
0.90045	1034.58	1038.17
1	1109.88	1113.37

densities include viscosity correction. The expected uncertainty and precision (expressed as the standard deviation obtained under repeatability conditions) of the measured densities are $(\pm\ 5\cdot10^{-2}$ and $\pm\ 5\cdot10^{-3})$ kg·m^{-3}, respectively.

The speeds of sound were measured using two measuring sets (OPE-4F type, homemade) operating on the principle of the pulse-echo-overlap method. In this work, the sets with various measuring cells were used. In the case of mixtures of 1,2-ethanediol with 2-ethyl-1-hexanol or 1-heptanol, the cell with a single transmitting−receiving transducer (operating at a frequency of 4 MHz) and an acoustic mirror has been used,[15] whereas in the case of mixtures of 1,2-ethanediol with ethanol the standard cell with two transducers (operating at a frequency of 2.1 MHz) has been used.[23] The temperatures were measured by means of platinum resistance thermometers (Ertco-Hart, models 850 and 850C, NIST certified) with uncertainty better than ± 0.05 K and repeatability ± 0.01 K. The measuring cells were calibrated using the water (prepared as those for the densimeter), and the standard values of the speed of sound are taken from ref 24. The repeatability of the measured speeds of sound was better than ± 0.02 % (the cell with acoustic mirror) and ± 0.1 m·s^{-1} (standard cell with two transducers). The uncertainty in the present study is estimated to be better than ± 1 m·s^{-1}. It should be noted here that acoustic impedance (ρu) varies strongly for the measured samples; i.e., a minimal acoustic impedance shows ethanol ($89.67\cdot10^4$ Pa·s·m^{-1}) and the maximal 1,2-ethanediol ($183.62\cdot10^4$ Pa·s·m^{-1}). More details (apparatus, procedure) can be found elsewhere.[23]

In this study, the temperatures are reported in terms of ITS-90 and the molar values in terms of the 1996 IUPAC relative atomic masses.[25]

Results and Discussion

Experimental densities, ρ, and speeds of sound, u, of binary mixtures of 1,2-ethanediol with 2-ethyl-1-hexanol, 1-heptanol, or ethanol measured over the entire composition range at $T = 298.15$ K are summarized in Table 2. Experimental densities of binary mixtures of 1,2-ethanediol with 1-nonanol at (298.15 and 293.15) K are presented in Table 3. Because in the present study two samples of 1,2-ethanediol were used, the average density and speed of sound have been calculated. The average values are equal to (1109.86 ± 0.018) kg·m^{-3} and (1654.8 ± 0.33) m·s^{-1} for density and speed of sound, respectively. Taking into account declared uncertainties, the consistency is very satisfactory and reasonable, respectively. The differences in the measured speed of sound values for 1,2-ethanediol are most probably connected with the various cell geometry and uncertainties of the thermometers (apart from those connected with samples).

The values of the excess molar volumes V^E were calculated in the same way (by standard relation) as in previous works.[1,3,12] The obtained values of V^E are reported in Tables 1 and 2 of the Supporting Information.

To each set of the values of V^E, the Redlich−Kister equation was fitted

$$f(x) = x(1 - x)\sum_{i=1}^{n} a_i(1 - 2x)^{i-1} \qquad (1)$$

where $f(x)$ is V^E in m^3·mol^{-1} and x is the mole fraction of the first component, i.e., 1,2-ethanediol. The coefficients a_i (estimated by the unweighted least-squares method) and the standard deviations δ from the regression lines are given in the Table 4. The optimum number of the coefficients was obtained from an examination of the mentioned standard deviation.

The results (Figure 1 and Supporting Information Table 1 and 2) reveal that for mixtures of 1,2-ethanediol with 2-ethyl-1-hexanol, 1-heptanol, or 1-nonanol $V^E > 0$ over the whole composition range. The equimolar V^E values at 298.15 K are

Table 4. Values of the Coefficients, a_i, for the Fitted Polynomials (Mostly Equation 2) and Standard Deviations δ for Various Properties of the Investigated Systems at T = 298.15 K

	a_1	a_2	a_3	a_4	δ
		x 1,2-Ethanediol + (1 − *x*) 2-Ethyl-1-hexanol			
$V^E \cdot 10^6/m^3 \cdot mol^{-1}$	0.7136	0.2449	0.1868		0.0056
$^a\kappa_S^E/TPa^{-1}$	−422.38	1105	−1144	420.5	0.25
$K_S^E/m^3 \cdot PPa^{-1} \cdot mol^{-1}$	−6.457	1.184	−2.941	3.301	0.03
$^a u^D/m \cdot s^{-1}$	1037	−3332	3901	−1585	0.40
$\Delta u/m \cdot s^{-1}$	−450.48	314.6	−219.5	127.9	0.41
		x 1,2-Ethanediol + (1 − *x*) 1-Heptanol			
$V^E \cdot 10^6/m^3 \cdot mol^{-1}$	0.9703	0.2919	0.3087		0.0079
$^a\kappa_S^E/TPa^{-1}$	−335.19	912.0	−929.5	347.1	0.24
$K_S^E/m^3 \cdot PPa^{-1} \cdot mol^{-1}$	−2.594	3.051	−2.185	2.32	0.03
$^a u^D/m \cdot s^{-1}$	812.5	−2605	2985	−1187	0.42
$\Delta u/m \cdot s^{-1}$	−465.25	298.1	−198.1	97.62	0.38
		x 1,2-Ethanediol + (1 − *x*) Ethanol			
$V^E \cdot 10^6/m^3 \cdot mol^{-1}$	−2.100	−0.2649	−0.1348		0.0049
κ_S^E/TPa^{-1}	−503.54	−90.12	−45.76	−37.45	0.17
$K_S^E/m^3 \cdot PPa^{-1} \cdot mol^{-1}$	−30.011	−6.610	−3.157	−2.39	0.01
$u^D/m \cdot s^{-1}$	514.85	−266.5	173.3	−59.27	0.39
$\Delta u/m \cdot s^{-1}$	−79.51	−7.938	28.89		0.34
		x 1,2-Ethanediol + (1 − *x*) 1-Nonanol			
$V^E \cdot 10^6/m^3 \cdot mol^{-1}$	1.2963	0.3262	0.4176		0.0074
$^bV^E \cdot 10^6/m^3 \cdot mol^{-1}$	1.2585	0.3202	0.3831		0.0073

[a] Equation 2. [b] T = 293.15 K.

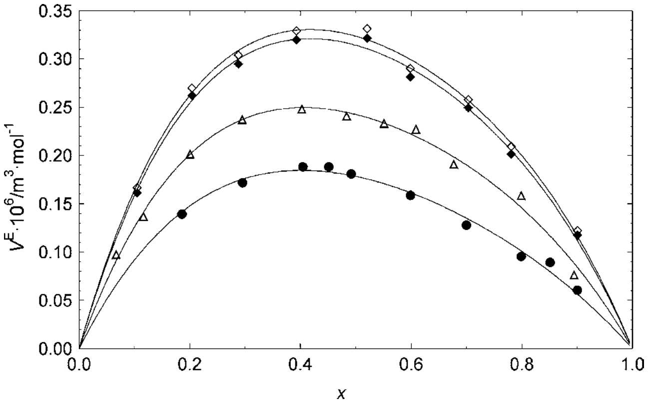

Figure 1. Excess molar volumes, V^E, plotted against mole fraction, x, for {x 1,2-ethanediol + (1 − x) an alkanol} at the temperature 298.15 K: ●, 2-ethyl-1-hexanol; Δ, 1-heptanol; ◇, 1-nonanol; and at the temperature 293.15 K: ◆, 1-nonanol. Lines, eq 1.

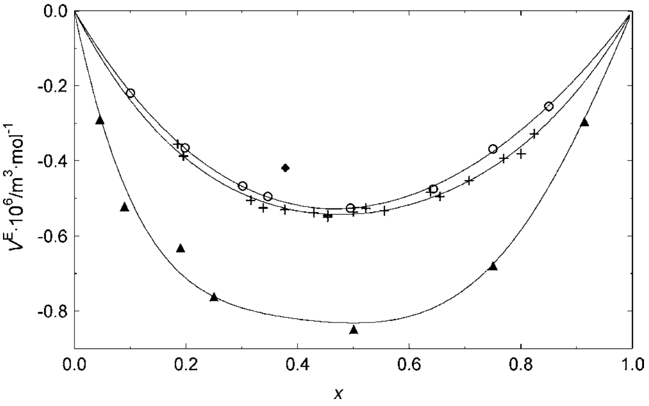

Figure 2. Excess molar volumes, V^E, plotted against mole fraction, x, for {x 1,2-ethanediol + (1 − x) ethanol} at the temperature 298.15 K: ○, this work; +, Jimenez and Paz Andrade;[4] ▲, Albuquerque et al.;[5] and ◆, Gurung and Roy.[26] Lines, eq 1.

equal to ($0.178 \cdot 10^{-6}$, $0.243 \cdot 10^{-6}$, and $0.324 \cdot 10^{-6}$) $m^3 \cdot mol^{-1}$, respectively. Consequently, the deviations from ideality increase in the above-mentioned order. Because the mixtures show expansion, the packing of the molecules in mixtures is more loose than that in pure components. It seems that the positive V^E values result here mainly from the disruption of the hydrogen bonded structures of pure alcohols upon mixing and creation of new structures between unlike molecules with worse geometrical packing. At 298.15 K, the V^E values obtained in this work for (1,2-ethanediol + 1-nonanol) show reasonable agreement with those reported recently[3] (at x = 0.5, the V^E values are equal to ($0.324 \cdot 10^{-6}$ and $0.3372 \cdot 10^{-6}$) $m^3 \cdot mol^{-1}$, respectively). With decreasing temperature, the V^E values decrease; i.e., a positive $(\partial V^E/\partial T)_p$ is observed. Simultaneously, no anomaly (as in the case of the speed of sound[3]) in the V^E values was detected even for the temperature in the immediate vicinity of the critical point, i.e., at 293.15 K. It is not completely surprising since V^E is a first-order derivative of the excess Gibbs energy. It seems that previously observed irregularities in the vicinity of the critical composition[3] (not confirmed in this study) are caused probably by the experimental error.

The relatively large positive V^E values (at x = 0.5 the V^E value is equal to $0.178 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$) obtained for mixtures of 1,2-ethanediol with 2-ethyl-1-hexanol are opposite in sign and magnitude to negative and small (absolute magnitude) values obtained previously for mixtures of 2-ethyl-1-hexanol with 1-pentanol, 1-heptanol, or 1-nonanol (the equimolar V^E values are equal to ($-0.0797 \cdot 10^{-6}$, $-0.0560 \cdot 10^{-6}$, and $-0.0201 \cdot 10^{-6}$) $m^3 \cdot mol^{-1}$, respectively).[12] In other words, the mixtures of 2-ethyl-1-hexanol with 1-alkanols generally show contraction of volume ($V^E < 0$); i.e., the packing of the molecules in mixtures is more compact than that in the pure components. Replacing 1-alkanol by 1,2-ethanediol leads to relative large expansion ($V^E > 0$, Figure 1); i.e., the packing of the molecules in mixtures is more loose than that in the pure components (i.e., the 2-ethyl-1-hexanol cannot readily be incorporated into the solution structure of 1,2-ethanediol and vice versa).

In the case of mixtures of 1,2-ethanediol with ethanol, the negative V^E values (at x = 0.5, the $V^E = -0.525 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$) over the whole composition range are observed. As shown in Figure 2, the agreement with the data reported by Albuquerque et al.[5] is very poor. Disagreement is also observed in the case of the single V^E value reported by Gurung and Roy.[26] At the same time, the agreement with the data reported by Jimenez and Paz Andrade[4] is satisfactory. It should be noted that the results of Jimenez and Paz Andrade[4] and those of Albuquerque et al.[5] differ at equimolar composition by $0.313 \cdot 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$, i.e., very strongly. In our opinion, the data reported by the last-mentioned authors are less reliable than those of Jimenez and Paz Andrade.[4] A similar conclusion (obtained however indirectly) was stated previously too.[1] It should also be noted here that the density value for 1,2-ethanediol reported by Albuquerque et al.[5] ($\rho = 1108.4\ \mathrm{kg \cdot m^{-3}}$) is distinctly smaller than those given in Table 1.

The magnitude and sign of the V^E values obtained in this work can be related to the increase difference in size and shape of the component molecules, as well as to the increase difference in the intermolecular interaction energy between like molecules. The negative V^E values are observed for mixtures with components with the same carbon chain (1,2-ethanediol with ethanol), whereas the positive V^E values are observed for mixtures with components with a clearly different carbon chain (1,2-ethanediol with 2-ethyl-1-hexanol, 1-heptanol, or 1-nonanol).

On the basis of the Newton−Laplace relation, the isentropic compressibility coefficients, κ_S, and molar isentropic compressibilities, K_S, were calculated. Their excesses, κ_S^E and K_S^E, were obtained in the next step by the use of a thermodynamically rigorous expression (Benson and Kiyohara approach) for the isentropic compressibility in an ideal mixture (the K_S^E values are reported in Table 1 of the Supporting Information). A more detailed description of the calculation procedure for κ_S^E and K_S^E has been outlined previously[2,3,14] (details can be found in the review paper of Douheret et al.[27]). The isobaric coefficients of thermal expansion α_p were taken directly (2-ethyl-1-hexanol and 1-heptanol) from the previous report,[12] were determined (ethanol) from the reported $\rho(T)$ dependence,[21] or were determined (1,2-ethanediol) from unpublished densities measured in our lab at various temperatures. Also the values of the molar isobaric heat capacities C_p of the compounds at 298.15 K were taken from the literature.[28−30] The α_p and C_p values are summarized in Table 3 of the Supporting Information. Moreover, the isentropic and isothermal compressibility coefficients, κ_S and κ_T (as mentioned, the calculation method can be found elsewhere[2,3,27]), are listed in the above table.

The composition dependencies of κ_S^E and K_S^E are generally approximated by the standard Redlich−Kister polynomial (eq 1), and respective coefficients are given in Table 3. Some highly skewed results (κ_S^E) are, however, represented by polynomial form in the square root of the mole fraction $(1 - x)$ of the second component (i.e., alkanol).

$$f(x) = x(1 - x)\sum_{i=1}^{n} a_i(1 - x)^{(i-1)/2} \qquad (2)$$

The results for K_S^E are plotted in Figure 3. The results for κ_S^E are not shown because the curves are similar in shape to those for K_S^E. Generally, the K_S^E values are negative for all systems studied. Thus, the mixtures are less compressible as the pure components, i.e., the greater resistance to compression (enhanced rigidity) is observed. However, in the case of mixtures with 1-heptanol, the K_S^E values are near zero for mixtures with the mole fraction $x < 0.07$ (s-shaped trend). This behavior is consistent with the recently reported results for 1-nonanol[3] where s-shaped $K_S^E(x)$ curves are observed. Two investigated systems (2-ethyl-1-hexanol and 1-heptanol) show both enhanced rigidity ($K_S^E < 0$) and expansion ($V^E > 0$) over the entire composition range (as stated previously,[12,14] such results have been reported for mixtures of alkanols). In other words, the volume increases, but simultaneously the whole system becomes more rigid. Thus, there is an analogy to the effect of the phase transition water → ice. The third system (ethanol) shows both enhanced rigidity ($K_S^E < 0$) and contraction ($V^E < 0$) over the entire composition range. In other words, the volume decreases (more compact packing of molecules), and simultaneously the whole system becomes more rigid (less compressible). It should be noted, however, that the compressibility is generally affected both by molecular packing and by the patterns of molecular aggregation induced by the molecular interactions.

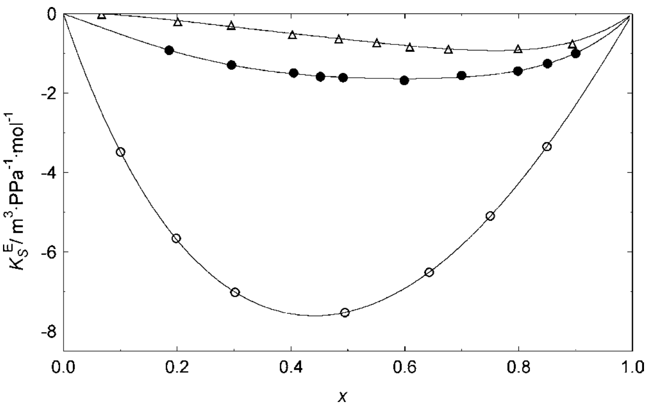

Figure 3. Excess molar isentropic compressibilities, K_S^E, plotted against mole fraction, x, for {x 1,2-ethanediol + (1 − x) an alkanol} at the temperature 298.15 K: ●, 2-ethyl-1-hexanol; Δ, 1-heptanol; and ○, ethanol. Lines, eq 1.

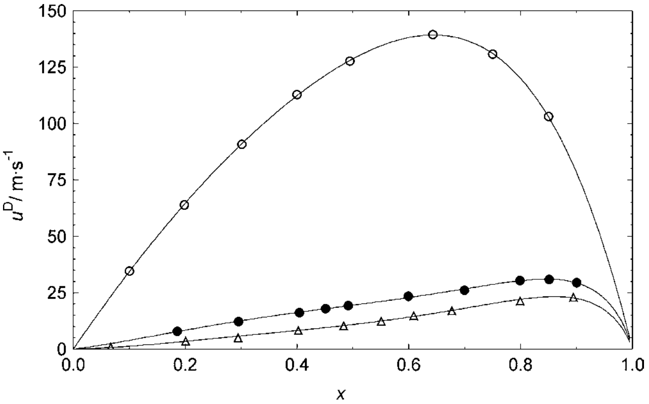

Figure 4. Speed of sound deviations, u^D, plotted against mole fraction, x, for {x 1,2-ethanediol + (1 − x) an alkanol} at the temperature 298.15 K: ●, 2-ethyl-1-hexanol; Δ, 1-heptanol; and ○, ethanol. Lines, eq 1 or 2.

Lastly, the deviations of the speed of sound based on two various approaches have been calculated to complete the study. On one hand, a thermodynamically correct rule (based on the Newton−Laplace equation) for expressing the speed of sound in an ideal liquid mixture, u^{id}, has been used.

$$u^{id} = V^{id}(M^{id}K_S^{id})^{-1/2} \qquad (3)$$

where V^{id}, M^{id}, and K_S^{id} are molar volume, molar mass, and molar isentropic compressibility of the ideal mixture. Deviations of the speed of sound from the ideal values, u^D, are thus accessible by subtraction, $u^D = u - u^{id}$. Details about the method of calculation can be found elsewhere.[3,27] Figure 4 shows that the u^D values are positive over the whole composition range for the systems under test. On the other hand, the Δu values (not shown), i.e., the deviations of the speed of sound from the mole fraction adduct of the speeds of sound for the pure compounds, have been calculated. In contrast to the u^D values, the Δu values are negative over the whole composition range for all systems studied in this work. The estimated coefficients of the Redlich−Kister equations (1 or 2) for $u^D(x)$ and $\Delta u(x)$ curves are given in Table 4.

It is noteworthy that the u^D and K_S^E values show opposite sign, i.e., are positive and negative, respectively. The present finding is consistent with previous reports about correlation between the $K_S^E(x)$ and $u^D(x)$ curves.[2,3,17]

Conclusions

In relation to V^E and K_S^E, the systems under test show nonideal behavior (the greatest 1,2-ethanediol with ethanol). This nonideality is manifested in all cases by enhanced rigidity ($K_S^E <$ 0). The volume effects are, however, opposite in sign, i.e., negative (contraction) for mixtures of 1,2-ethanediol with ethanol and positive (dilatation) for mixtures of 1,2-ethanediol with 2-ethyl-1-hexanol, 1-heptanol, or 1-nonanol. Thus, both 1,2-ethanediol and ethanol molecules can readily be incorporated into the solvent structure of the second compound. On the other hand, in the case of 2-ethyl-1-hexanol, 1-heptanol, and 1-nonanol, we have the opposite situation.

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Supporting Information Available:

The values of excess molar volumes V^E and excess molar isentropic compressibilities K_S^E for the investigated systems. The values of isobaric coefficients of thermal expansion α_p, isentropic and isothermal compressibility coefficients, κ_S and κ_T, and isobaric heat capacities C_p for pure components. This material is available free of charge via the Internet at http://pubs.acs.org.

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