

# Densities, Speeds of Sound, and Isentropic Compressibilities for Binary Mixtures of 2-Ethyl-1-hexanol with 1-Pentanol, 1-Heptanol, or 1-Nonanol at the Temperature 298.15 K

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Densities and speeds of sound for binary mixtures of 2-ethyl-1-hexanol with 1-pentanol, 1-heptanol, or 1-nonanol were measured over the entire composition range at the temperature 298.15 K by means of a vibrating tube densimeter and the pulse-echo-overlap method. Also, the densities for pure compounds in the temperature range from (288.15 to 318.15) K were measured. From experimental data, the excess molar volumes and excess molar isentropic compressibilities were calculated. The deviations of the speeds of sound were calculated as well. The Redlich–Kister polynomials were fitted to the results, and smooth representations of the results are presented. For the mixtures studied, the negative values of the excess molar isentropic compressibilities over the entire composition range are observed. The values of the excess molar volumes are negative over the entire composition range for mixtures of 2-ethyl-1-hexanol with 1-pentanol or 1-heptanol. For the mixtures of 2-ethyl-1-hexanol with 1-nonanol, the excess molar volume is slightly s-shaped; that is, the close zero or positive values in the 1-nonanol rich region are observed. The excesses are more negative as the carbon chain length of the 1-alkanol is shorter. The isobaric coefficients of thermal expansion for pure compounds were calculated by analytical differentiation of the density dependence on the temperature.

## Introduction

Binary systems of associated hydroxyl compounds with the prevailing role of the hydrogen bonds are an important and very interesting class of solutions because hydrogen bonds play a vital role in chemical, physical, and biological processes. At the same time, the treatment of this class of solutions is a hard test for any theoretical model, and the behavior of many of their properties is still not clear. The main difficulty is the overlapping of many effects taking place simultaneously during mixing. Recent papers from our laboratory have reported among others volume effects for binary mixtures of 1,2-ethanediol with 1-butanol, 1-hexanol, or 1-octanol<sup>1</sup> and volume effects, speeds of sound, and isentropic compressibilities for binary mixtures of 1,2-ethanediol with 1-pentanol<sup>2,3</sup> or 1-nonanol.<sup>4</sup> Binary mixtures containing monohydric alcohols were studied as well.<sup>5,6</sup>

The aim of this work is to study the composition dependence of volume and compressibility changes upon mixing for binary mixtures of 2-ethyl-1-hexanol with 1-pentanol, 1-heptanol, or 1-nonanol, that is, for systems with two self-associated hydroxyl compounds, and an extension of the available database for two alkanol mixtures. Contrary to most of our previous works, a branched alkanol is a common compound of the systems under testing. Generally, the type and extent of the association in alcohols is essentially determined by the two components of the alcohol molecule, that is, the hydrocarbon chain (length and/or degree of branching) and the hydroxyl groups (their number and positions). In the mixtures of alcohols, interplay of molecules of the same kind (self-association) and of different kinds (complexation) occurs.

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**Table 1.** Densities,  $\rho$ , and Speeds of Sound,  $u$ , of Pure Compounds Together with Absolute Average Deviations, % AAD, from Selected Literature Data at  $T = 298.15$  K

property	exptl.	lit.				% AAD <sup>a</sup>
1-Pentanol						
$\rho/\text{kg}\cdot\text{m}^{-3}$	810.750	810.80, <sup>5</sup> 810.84 <sup>11</sup>	810.82, <sup>7</sup>	810.70, <sup>8,9</sup>	810.86, <sup>10</sup>	0.009
$u/\text{m}\cdot\text{s}^{-1}$	1274.32	1274.64, <sup>2,10</sup>	1274.73, <sup>6</sup>	1275.24, <sup>11</sup>	1273.6 <sup>12</sup>	0.046
1-Heptanol						
$\rho/\text{kg}\cdot\text{m}^{-3}$	818.810	818.765, <sup>6</sup>	818.97, <sup>13</sup>	818.80 <sup>17</sup>		0.009
$u/\text{m}\cdot\text{s}^{-1}$	1327.56	1326.10, <sup>14</sup>	1327.01, <sup>6</sup>	1328.0, <sup>15</sup>	1327.27 <sup>17</sup>	0.052
1-Nonanol						
$\rho/\text{kg}\cdot\text{m}^{-3}$	824.238	824.48, <sup>4</sup>	824.271, <sup>6</sup>	824.23, <sup>16</sup>	824.24 <sup>17</sup>	0.009
$u/\text{m}\cdot\text{s}^{-1}$	1364.47	1364.41, <sup>4</sup>	1364.70, <sup>6</sup>	1364.64, <sup>17</sup>		0.011
2-Ethyl-1-hexanol						
$\rho/\text{kg}\cdot\text{m}^{-3}$	828.910	828.0, <sup>18</sup>	829.06, <sup>19</sup>			0.064
$u/\text{m}\cdot\text{s}^{-1}$	1318.07	1309.75, <sup>19</sup>	1321.8 <sup>15</sup>			0.46

<sup>a</sup> AAD =  $(100/n) \cdot \sum_{i=1}^n |y_{\text{exptl}} - y_{\text{lit}}/y_{\text{exptl}}|$ , where  $y$  is  $\rho$  or  $u$ .

## Experimental Section

**Materials.** 1-Pentanol (mass fraction 0.98 +, Lancaster), 1-heptanol (puriss, p.a. mass fraction > 0.99, Fluka), 1-nonanol (mass fraction 0.99, Alfa Aesar), and 2-ethyl-1-hexanol (mass fraction 0.996, Aldrich) were used without further purification. The mass fraction of water determined by the Karl Fischer method was  $0.65 \cdot 10^{-4}$  (1-pentanol),  $1.6 \cdot 10^{-4}$  (1-heptanol),  $3.2 \cdot 10^{-4}$  (1-nonanol), and  $1.6 \cdot 10^{-4}$  (2-ethyl-1-hexanol), respectively. The purities of the alcohols were checked also by comparing measured densities and speeds of sound with those reported in the literature (see Table 1). Most of the data are in satisfactory agreement. An exception makes the speed of sound for 2-ethyl-1-hexanol. In this case, however, there is considerable difference (ca. 0.9 %) between our own value and those of Awwad and Pethrick.<sup>19</sup>

**Methods.** Solutions were prepared by mass (precision  $\pm 6 \cdot 10^{-7}$  kg) using an OHAUS analytical standard balance (model AS 200) and stored in sealed flasks. The uncertainty of the determination for the mole fraction was estimated to be  $\pm 5 \cdot 10^{-5}$ .

The densities were measured with a vibrating tube densimeter DMA 5000 (Anton Paar, Austria). Before the measurements, the solutions and components were partially degassed (20 min) using ultrasound (ultrasonic cleaner Unitra-Unima, model UH-4,  $f = 25$  kHz). The densimeter was calibrated using the air and deionized and degassed (as above) water with an electrolytic conductivity of  $1.2 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$  as standard. The expected uncertainty and precision of the measured densities are ( $\pm 5 \cdot 10^{-2}$  and  $\pm 5 \cdot 10^{-3}$ )  $\text{kg} \cdot \text{m}^{-3}$ , respectively. More details concerning the density measurements can be found elsewhere.<sup>20,21</sup>

The speeds of sound were measured with an apparatus designed and constructed in our lab. The apparatus operates on the basis of the pulse-echo-overlap method. The basic advantages and disadvantages of this relative method have been reported recently.<sup>22</sup> Details of the apparatus and experimental procedure have already been published as well.<sup>23</sup> The temperature of the water bath in the ultrasonic experiment was measured by means of a calibrated (NIST certified) platinum resistance thermometer (ERTCO-HART, model 850, Pt100) with an uncertainty of better than  $\pm 0.05$  K and a precision of  $\pm 0.01$  K. Calibration of the cell was based on a value of  $1496.728 \text{ m} \cdot \text{s}^{-1}$  for the speed of sound in water at  $T = 298.15$  K.<sup>24</sup> The water used for the calibration was prepared as those for densimeter. Measurements of the speed of sound were reproducible better than  $\pm 0.1 \text{ m} \cdot \text{s}^{-1}$ , and their uncertainty is estimated to be better than  $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$ .

All temperatures are reported in terms of ITS-90 and the molar values in terms of the 1996 IUPAC relative atomic masses.<sup>25</sup>

## Results and Discussion

Densities,  $\rho$ , and speeds of sound,  $u$ , measured over the entire composition range at the temperature 298.15 K are summarized in Table 2. The values of the excess molar volumes  $V^E$  were determined from the equation:

$$V^E = V - \sum_{i=1}^2 x_i V_i \quad (1)$$

where  $V$  is the molar volume,  $x_i$  is the mole fraction of component  $i$  of the system, and  $V_i$  is the molar volume of component  $i$  of the system.

Each set of values of  $V^E$  was fitted to the Redlich–Kister type equation:

$$V^E/(\text{m}^3 \cdot \text{mol}^{-1}) = x(1-x) \sum_{i=1}^n a_i (1-2x)^{i-1} \quad (2)$$

where  $x$  is the mole fraction of the first component, that is, 2-ethyl-1-hexanol. Values of the coefficients  $a_i$ , determined by the unweighted least-squares method, are listed in the Table 3 where standard deviations  $\delta$  are also given; the optimum number of the coefficients was ascertained from an examination of the  $\delta$ . The results are shown in Figure 1. The corresponding values of  $V^E$  are reported in Table 1 of the Supporting Information.

The results shown in Figure 1 reveal that for (2-ethyl-1-hexanol + 1-pentanol) and (2-ethyl-1-hexanol + 1-heptanol)  $V^E < 0$  over the whole composition range. For the mixtures (2-ethyl-1-hexanol + 1-nonanol) the  $V^E(x)$  curve becomes slightly s-shaped, that is,  $V^E < 0$  with the exception of the mole fraction

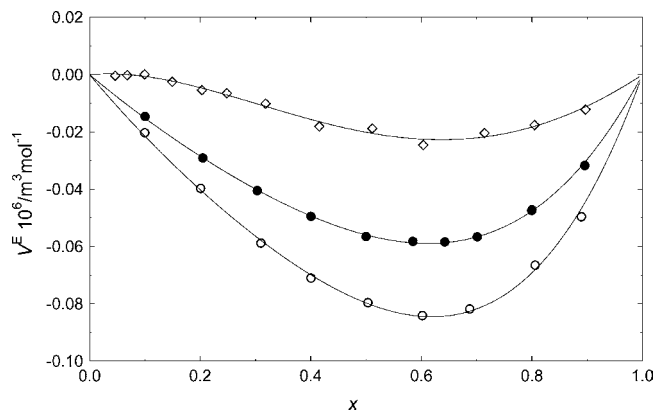
**Table 2. Densities,  $\rho$ , and Speeds of Sound,  $u$ , for the Investigated Systems at  $T = 298.15$  K**

$x$	$\rho$ $\text{kg} \cdot \text{m}^{-3}$	$x$	$u$ $\text{m} \cdot \text{s}^{-1}$
x 2-Ethyl-1-hexanol + (1 - x) 1-Heptanol			
0	818.810	0	1326.65
0.10028	820.003	0.10050	1326.41
0.20476	821.215	0.19820	1326.15
0.30333	822.322	0.30074	1325.84
0.40015	823.376	0.40088	1325.41
0.50001	824.428	0.50119	1324.97
0.58460	825.280	0.60095	1324.22
0.64242	825.849	0.70095	1323.30
0.70106	826.408	0.79908	1322.09
0.79961	827.300	0.90041	1320.34
0.80002	827.303	1	1318.07
0.89566	828.117		
1	828.910		
x 2-Ethyl-1-hexanol + (1 - x) 1-Pentanol			
0	810.750	0	1274.32
0.09956	813.397	0.09694	1280.91
0.20073	815.859	0.20110	1287.42
0.30979	818.283	0.30037	1293.47
0.40027	820.120	0.40311	1298.95
0.50330	822.032	0.49815	1303.61
0.60186	823.710	0.59886	1307.89
0.68752	825.040	0.70214	1311.71
0.80597	826.689	0.79940	1314.64
0.88949	827.743	0.89953	1316.82
x 2-Ethyl-1-hexanol + (1 - x) 1-Nonanol			
0	824.240	0	1364.47
0.04628	824.435	0.09945	1360.63
0.06793	824.526	0.19489	1356.91
0.09946	824.659	0.30306	1352.55
0.14937	824.886	0.40374	1348.42
0.20312	825.134	0.50160	1344.18
0.24811	825.337	0.59858	1339.75
0.31825	825.667	0.69621	1335.03
0.41523	826.146	0.80245	1329.65
0.51121	826.594	0.89819	1324.34
0.60358	827.060		
0.71428	827.574		
0.80465	828.006		
0.89704	828.444		

**Table 3. Values of the Coefficients,  $a_i$ , for the Redlich–Kister Type Equation 2 and Standard Deviations  $\delta$  for Various Properties of the Investigated Systems at  $T = 298.15$  K**

	$a_1$	$a_2$	$a_3$	$\delta$
x 2-Ethyl-1-hexanol + (1 - x) 1-Pentanol				
$V^E \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	-0.3188	0.1511	-0.0637	0.0016
$\kappa_{\text{S}}^E / \text{TPa}^{-1}$	21.732	6.3625		0.066
$K_{\text{S}}^E / \text{m}^3 \cdot \text{PPa}^{-1} \cdot \text{mol}^{-1}$	-3.1161	1.4656	-0.2670	0.008
$u^D / \text{m} \cdot \text{s}^{-1}$	18.042	-6.451	0.892	0.065
$\Delta u / \text{m} \cdot \text{s}^{-1}$	30.095	-4.884		0.064
x 2-Ethyl-1-hexanol + (1 - x) 1-Heptanol				
$V^E \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	-0.2238	0.09963	-0.03834	0.0005
$\kappa_{\text{S}}^E / \text{TPa}^{-1}$	-12.878	6.2479	-1.8638	0.025
$K_{\text{S}}^E / \text{m}^3 \cdot \text{PPa}^{-1} \cdot \text{mol}^{-1}$	-2.0824	1.1027	-0.3421	0.004
$u^D / \text{m} \cdot \text{s}^{-1}$	11.299	-5.540	1.686	0.024
$\Delta u / \text{m} \cdot \text{s}^{-1}$	10.307	-5.598	1.766	0.024
x 2-Ethyl-1-hexanol + (1 - x) 1-Nonanol				
$V^E \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	-0.08051	0.07158	0.0252	0.0012
$\kappa_{\text{S}}^E / \text{TPa}^{-1}$	-9.3420	5.3885	-1.5890	0.039
$K_{\text{S}}^E / \text{m}^3 \cdot \text{PPa}^{-1} \cdot \text{mol}^{-1}$	-1.6031	0.8537	-0.2138	0.006
$u^D / \text{m} \cdot \text{s}^{-1}$	9.059	-4.609	1.317	0.044
$\Delta u / \text{m} \cdot \text{s}^{-1}$	11.848	-4.701	1.309	0.038

up to  $x \approx 0.1$ . In this region, the  $V^E$  values are very close to zero or even positive. At equimolar composition the  $V^E$  values are equal to  $(-0.0797 \cdot 10^{-6}, -0.0560 \cdot 10^{-6}, \text{ and } -0.0201 \cdot 10^{-6}) \text{ m}^3 \cdot \text{mol}^{-1}$ , respectively. In other words, the deviations from ideality (generally small) fall in the above-mentioned order. Generally, the mixtures of 2-ethyl-1-hexanol with 1-alkanols



**Figure 1.** Excess molar volumes,  $V^E$ , plotted against mole fraction,  $x$ , for  $\{x \cdot 2\text{-ethyl-1-hexanol} + (1-x) \cdot 1\text{-alkanol}\}$  systems at the temperature 298.15 K:  $\circ$ , 1-pentanol;  $\bullet$ , 1-heptanol; and  $\diamond$ , 1-nonanol.

show a contraction of volume ( $V^E < 0$ ); that is, the packing of the molecules in mixtures is more compact than that in the pure components. On the other hand, the 2-ethyl-1-hexanol cannot readily be incorporated into the solution structure of 1-nonanol at the mole fraction up to  $x \approx 0.1$  ( $V^E \geq 0$ ).

It is interesting that as shown in Figure 1, in the mixtures of 2-ethyl-1-hexanol with 1-alkanols, as the length of the 1-alkanol is increased, the absolute value of  $V^E$  decreases. The above changes of  $V^E$  with the increasing chain length of 1-alkanol can be related to the differences in size and shape of the component molecules, as well as to the decrease in the difference in the intermolecular interaction energy between like molecules. The disruption of the hydrogen-bonded structures of pure alkanols gives rise to a positive contribution to  $V^E$ . Unlike specific interaction again making a negative contribution to  $V^E$ , however, this effect is sterically hindered (more and more as the differences in size and branching of the component molecules increase). Geometrical fitting makes a negative contribution to  $V^E$  as well. In general, the relative contributions of these effects depend on the relative molecular sizes and shapes of the alcohol molecules.

It is interesting that replacing 2-ethyl-1-hexanol by 1-octanol or 1-nonanol in mixtures with 1-pentanol results in positive  $V^E$  values (i.e., molecular packing is worse). In both cases, however, the magnitude of  $V^E$  is comparable (at equimolar composition  $V^E \approx 0.04 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ).<sup>26</sup> At the same time replacing 2-ethyl-1-hexanol by 1,2-ethanediol in mixtures with 1-pentanol results in  $V^E$  values very close to zero,<sup>2</sup> whereas for mixtures of 1,3-butanediol with 1-pentanol the  $V^E$  values are slightly s-shaped (negative or very close to zero values in the 1,3-butanediol rich region) and at equimolar composition  $V^E$  is equal to  $0.05 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ .<sup>10</sup> On the other hand, for (1,2-ethanediol + 1-nonanol) the  $V^E$  values are evidently positive (at equimolar composition  $V^E = 0.3372 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ )<sup>4</sup> contrary to the slightly s-shaped  $V^E$  values for (2-ethyl-1-hexanol + 1-nonanol) presented in this work.

The isentropic compressibility coefficients,  $\kappa_S$ , and molar isentropic compressibilities,  $K_S$ , as well as their excesses,  $\kappa_S^E$  and  $K_S^E$ , were obtained from experimental density and speed of sound. A cubic spline interpolation procedure was used to interpolate the values of molar volume at the mole fraction for which speeds of sound were determined.

The method used for calculating  $\kappa_S^E$  and  $K_S^E$  (the Benson–Kiyohara approach) has been outlined previously.<sup>2,27</sup> Needed for calculations, the values of the molar isobaric heat capacities  $C_p$  of the pure compounds at  $T = 298.15 \text{ K}$  (Table 4) were taken from

**Table 4.** Molar Isobaric Heat Capacities ( $C_p$ ), Isobaric Coefficients of Thermal Expansion ( $\alpha_p$ ), and Isothermal Compressibility Coefficients ( $\kappa_T$ ) of Pure Components at  $T = 298.15 \text{ K}$

$C_p$ $\text{J} \cdot \text{K} \cdot \text{mol}^{-1}$	$10^3 \cdot \alpha_p$ $\text{K}^{-1}$	$\kappa_T$ $\text{TPa}^{-1}$
208.27 <sup>a</sup>	1-Pentanol 0.9054 <sup>b</sup>	887.1
272.53 <sup>a</sup>	1-Heptanol 0.8579 <sup>b</sup>	808.2
337.98 <sup>a</sup>	1-Nonanol 0.8318 <sup>b</sup>	758.5
317.5 <sup>c</sup>	2-Ethyl-1-hexanol 0.8860 <sup>b</sup>	810.2

<sup>a</sup> Taken from ref 28. <sup>b</sup> Calculated on the basis of the temperature dependencies of density. <sup>c</sup> Taken from ref 29.

**Table 5.** Values of the Coefficients with Standard Deviations,  $a_i \pm \delta(a_i)$ , for the Polynomial (4) together with Standard Deviations  $\delta$  for Pure Components

$a_1$ $\text{kg} \cdot \text{m}^{-3}$	$a_2$ $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$	$a_3 \cdot 10^4$ $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-2}$	$a_4 \cdot 10^5$ $\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-3}$	$\delta$ $\text{kg} \cdot \text{m}^{-3}$
814.4179 $\pm 0.0057$	-0.73271 $\pm 0.00081$	1-Pentanol <sup>a</sup>	-1.79 $\pm 0.15$	0.011
822.3062 $\pm 0.0014$	-0.69717 $\pm 0.00027$	1-Heptanol <sup>b</sup>	-5.25 $\pm 0.11$	0.002
827.6518 $\pm 0.0015$	-0.68167 $\pm 0.00026$	1-Nonanol <sup>a</sup>	-3.95 $\pm 1.2$	0.003
832.5752 $\pm 0.0031$	-0.73351 $\pm 0.00041$	2-Ethyl-1-hexanol <sup>b</sup>	-1.149 $\pm 0.062$	0.004

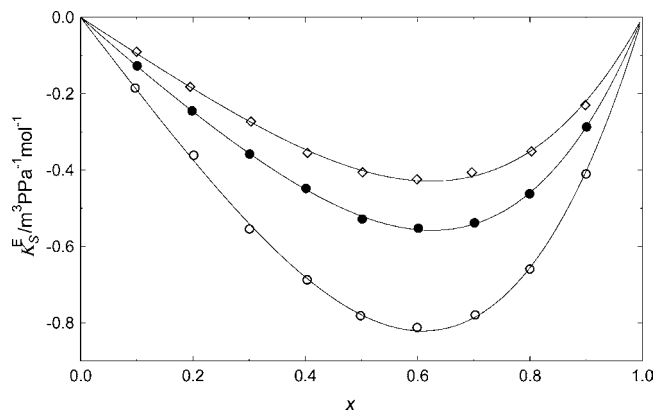
<sup>a</sup> Temperature range from (288.15 to 318.15) K. <sup>b</sup> Temperature range from (293.15 to 318.15) K.

the literature.<sup>28,29</sup> Needed values of the isobaric coefficients of thermal expansion  $\alpha_p$  were determined from experimental densities (the experimental values of density are reported in Table 2 of Supporting Information) measured as a function of temperature. Needed dependencies of the density on the temperature were approximated by equation:

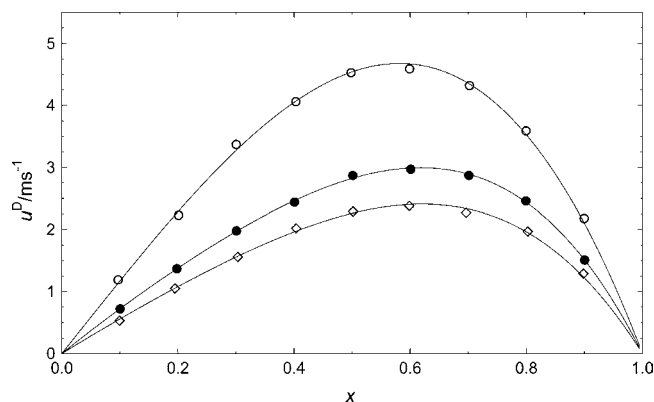
$$\rho / (\text{kg} \cdot \text{m}^{-3}) = \sum_{i=1}^4 a_i (T - 293.15)^{i-1} \quad (4)$$

where  $a_i$  are coefficients (listed in Table 5) calculated by the least-squares method and the F-test. Calculated in this way,  $\alpha_p$  values are summarized in Table 3 of Supporting Information. It appears that the  $\alpha_p$  values increase with the temperature, and the temperature dependence of  $\alpha_p$  is similar. The  $\alpha_p$  values for 1-alkanol reported in this work are compared with those reported by Dzida.<sup>11,17</sup> The agreement is satisfactory and very satisfactory because the absolute average deviations (AADs =  $(100/n) \cdot \sum_{i=1}^n |\alpha_{p,\text{exptl}} - \alpha_{p,\text{lit}} / \alpha_{p,\text{exptl}}|$ ) are (0.41, 0.073, and 0.043) % for 1-pentanol, 1-heptanol, and 1-nonanol, respectively. Moreover, for the readers' convenience, the isothermal compressibility coefficients  $\kappa_T$  (as mentioned above, the calculation method can be found elsewhere<sup>2,17,27</sup>) and  $\alpha_p$  at  $T = 298.15 \text{ K}$  are listed in Table 4.

The dependencies of  $\kappa_S^E$  and  $K_S^E$  upon composition are fitted by the conventional Redlich–Kister equation (see eq 2), and respective coefficients are given in Table 3. The results for  $K_S^E$  are plotted in Figure 2. The results for  $\kappa_S^E$  are not shown because the respective curves are similar in shape.



**Figure 2.** Excess molar isentropic compressibilities,  $K_S^E$ , plotted against mole fraction,  $x$ , for  $\{x$  2-ethyl-1-hexanol +  $(1-x)$  1-alkanol $\}$  systems at the temperature 298.15 K:  $\circ$ , 1-pentanol;  $\bullet$ , 1-heptanol; and  $\diamond$ , 1-nonanol.



**Figure 3.** Speed of sound deviations,  $u^D$ , plotted against mole fraction,  $x$ , for  $\{x$  2-ethyl-1-hexanol +  $(1-x)$  1-alkanol $\}$  systems at the temperature 298.15 K:  $\circ$ , 1-pentanol;  $\bullet$ , 1-heptanol; and  $\diamond$ , 1-nonanol.

For all studied systems, the  $K_S^E$  values are negative across the entire composition range. Thus, the shift from ideality in the direction of enhanced rigidity (the mixtures are less compressible as the pure compounds) is observed. The sequence of  $K_S^E$  is identical to that of the excess molar volumes. It appears that two systems studied show both the contraction of volume ( $V^E < 0$ ) and enhanced rigidity ( $K_S^E < 0$ ) over the entire composition range. The third system, that is, 2-ethyl-1-hexanol + 1-nonanol, shows  $V^E < 0$  and  $K_S^E < 0$  only for the mole fractions  $x > 0.1$ . It is interesting because in earlier works from our own lab mostly opposite signs of the  $V^E$  and  $K_S^E$  values for binary mixtures of alkanols, that is, positive excess volumes and negative excess compressibilities,<sup>5,6,26,30</sup> were reported. It has been suggested that there is an analogy to the effect of the phase transition, liquid water  $\rightarrow$  ice; that is, the volume increases, but simultaneously the whole system becomes more rigid.<sup>26</sup>

Interpretation of the  $K_S^E$  data is generally not simple because the  $K_S^E$  values are affected by both the molecular packing and the patterns of molecular aggregation induced by the molecular interactions. However, in the case of mixtures with two associated hydroxyl compounds, the interpretation is extremely difficult because of various possible molecular interactions and size effects. Comparing our results for binary mixtures of 2-ethyl-1-hexanol + 1-pentanol with those for 1-octanol + 1-pentanol,<sup>26</sup> it can be seen that the variation of compressibility upon mixing is considerably smaller in the case of 1-octanol (at equimolar compositions  $K_S^E$  are  $(-0.776$  and  $-0.11)$   $\text{m}^3 \cdot \text{PPa} \cdot \text{mol}^{-1}$ , respectively). On the other hand, replacing

2-ethyl-1-hexanol by 1,2-ethanediol or 1,3-butanediol in mixtures with 1-pentanol results in the considerable decrease (about three times and two times, respectively) of compressibility, that is, at equimolar composition  $K_S^E = -2.50 \text{ m}^3 \cdot \text{PPa} \cdot \text{mol}^{-1}$  (1,2-ethanediol + 1-pentanol<sup>2</sup>) and  $K_S^E = -1.60 \text{ m}^3 \cdot \text{PPa} \cdot \text{mol}^{-1}$  (1,3-butanediol + 1-pentanol<sup>10</sup>), respectively. This effect can here be explained by the dominant contribution of unlike specific interaction in mixtures (the whole system becomes more rigid).

Additionally, the deviations of the speed of sound from ideality have been calculated for all studied systems. In contrast to many other proposals (an overview can be found for example in papers of Douhéret et al.<sup>31,32</sup>), a thermodynamically correct rule (based on the Newton–Laplace equation) for expressing the speed of sound in ideal liquid,  $u^{\text{id}}$ , mixture has been used.

$$u^{\text{id}} = V^{\text{id}}(M^{\text{id}} \cdot K_S^{\text{id}})^{-1/2} \quad (5)$$

where  $V^{\text{id}}$ ,  $M^{\text{id}}$ , and  $K_S^{\text{id}}$  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 obtained by subtraction,  $u^D = u - u^{\text{id}}$ . More details about the method of calculation can be found elsewhere.<sup>27,31,32</sup> As shown in Figure 3, the  $u^D$  values are positive over the whole composition range for all studied systems. It is very interesting that for all studied systems, the  $K_S^E$  and  $u^D$  values are opposite in sign (minima and maxima are present, respectively). This finding is in agreement with previous reports about correlation between the  $K_S^E$  and the  $u^D$  extrema.<sup>2,4,33</sup> Simultaneously, the  $\Delta u$  values (not shown), that is, the deviations of the speed of sound from the mole fraction adduct of the speeds of sound for the pure compounds, are also positive over the whole composition range for all systems studied in this work. The respective coefficients of the Redlich–Kister equation for  $u^D(x)$  and  $\Delta u(x)$  curves are given in Table 3.

## Conclusions

All of the systems studied show nonideal behavior. This nonideality is manifested in all cases by enhanced rigidity (decrease of compressibility) observed in the whole concentration range. Simultaneously, with the exception of the range of low 2-ethyl-1-hexanol concentrations ( $x \leq 0.1$ ) for binary mixtures of 2-ethyl-1-hexanol with 1-nonanol, the contraction of volume is observed. The deviations from ideality are, however, relatively small. It is not surprising because such behavior is rather typical for binary mixtures of alkanols (with the exception of highly branched alkanols). When components are very similar also in size and shape, the deviations from ideality are extremely small.

## Supporting Information Available:

The values of excess molar volumes  $V^E$  and excess molar isentropic compressibilities  $K_S^E$  for the investigated systems at  $T = 298.15$  K. The values of density  $\rho$  and isobaric coefficient of thermal expansion  $\alpha_p$  for pure components in the temperature range from (288.15 or 293.15 to 318.15) K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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