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Acoustic and Thermophysical Properties of Binary Liquid Mixtures of Primary Butanols with Hexane and Cyclohexane at 293.15 K

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Abstract The experimental density and speed of ultrasound measurements, along with literature data, were used to calculate adiabatic and isothermal compressibility coefficients, the specific heat ratio, and isobaric thermal expansion coefficients for the binaries of 1-butanol with hexane and cyclohexane. They were also used to determine Beyer's parameter of nonlinearity, B/A, and free intermolecular lengths, L. The free intermolecular lengths, L, calculated according to the Jacobson equation, were compared with values estimated from thermoacoustical parameters.

Keywords Available volume · Beyer's parameter of nonlinearity · Binary liquid mixtures · 1-Butanol · Cyclohexane · Hexane · Isobaric thermal expansion coefficient · Speed of ultrasound

1 Introduction

Dilution of aliphatic alcohols in non-polar solvents results not only in gradual breakage of the alcohol self-associated multimers, but also in structural changes of the non-polar solvent due to volume and space-filling effects connected with solvation processes. Self-association between alcohol molecules decreases with increasing concentration of the non-polar solvent while displacement of solvate equilibrium is

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Paper dedicated to Professor Dr. Stefan Ernst on the occasion of His 75th Birthday.

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generally determined by physical properties of a hydrocarbon solvent and the self-association potential of aliphatic alcohols [1,2]. The speed of ultrasound, like any other physicochemical property in binary liquid mixtures, could be related either to size and shape of the molecules [3,4] or to the entropy effect connected with mixing processes (because of the volume and space-filling effects) [5]. Also the free intermolecular length, calculated according to the Jacobson equation, and the ratios of free volume and available volume to the molar volume in binary liquid mixtures of aliphatic alcohols with hexane and cyclohexane could be related to the space-filling ability [5]. From the experimental results and from Schaaffs theory, it can be derived that in organic liquids the speed of ultrasound decreases with increasing temperature and increases with increasing pressure. It also could be shown that, in general, acoustic parameters depend on the ratio of the molar volume of the liquid to the real volume of the molecules in a mole of liquid (molecules treated as rigid balls with a uniform radius r) [6,7].

The differences in acoustic and thermodynamic properties caused by different intermolecular interactions and structural rearrangement of hexane and cyclohexane molecules in binary liquid mixtures with primary butanols (1-butanol and 2-methyl-1-propanol) are discussed in this paper. We report the results of ultrasonic and volumetric investigations of self-association of 1-butanol in binary mixtures with hexane and cyclohexane in the whole concentration range at 293.15 K, together with similar results of 2-methyl-1-propanol binaries with hexane and cyclohexane partially presented in [1]. In the four binary liquid mixtures, the relationships among the speed of ultrasound, free intermolecular lengths, available volume, and Beyer's nonlinearity parameter B/A were compared and discussed in terms of the space-filling ability and other factors that affect structural changes in non-polar solvents and self-association in primary butanols.

2 Experimental

The binary solutions of 1-butanol (Aldrich, 99.8 %, HPLC grade, $H_2O \leq 0.03$ %) with hexane (Riedel de Haën, 99 %, GC grade, $H_2O \leq 0.01$ %) and cyclohexane (Aldrich, 99.9 %, HPLC grade, $H_2O \leq 0.01$ %) were prepared by mixing weighed portions of the pure liquids without preliminary purification. Each weighing was made using the analytical balance Ohaus AS-200, with a resolution of 10^{-5} g. The uncertainty of the mole fraction values in both binaries prepared by the weighing method was about 3×10^{-5}.

Speeds of ultrasound were measured with a sing-around type ultrasound velocimeter and by a pulse-echo-overlap method at 2.1 MHz, with an uncertainty better than $0.5\ \mathrm{m \cdot s^{-1}}$ (details of the measuring set, designed and constructed in our laboratory, can be found in [8,9]). Densities of both studied systems were determined with Anton Paar DMA 5000 and Unilab MG-2 vibrating tube densimeters with an uncertainty better than $0.05\ \mathrm{kg \cdot m^{-3}}$ [10].

Sample cell thermal stabilization during ultrasonic velocity measurements and density measurements at (293.15 ± 0.01) K was maintained by a water bath heated by a proportional-plus-integral temperature controller (Unipan 660, Poland) and cooled by water from an external thermostat. The temperature was determined with an Ertco Hart 850C thermometer provided with a Pt100 probe. The precision of the temperature measurements was about 0.01 K, and the uncertainty was better than 0.05 K.

3 Measurements Results

Adiabatic compressibility coefficients, $\kappa_s = -V^{-1}(\partial V/\partial p)_s$, and isothermal compressibility coefficients, κ_T, were calculated from the density, ρ, measurements and speed of ultrasound, c, measurements according to the relations:

$$\kappa_s = 1/(\rho/c^2), \tag{1}$$

$$\kappa_T = \kappa_s + \alpha^2 VT/C_p, \tag{2}$$

using the isobaric thermal expansion coefficient, α, estimated from the temperature relation between densities (measured in this work at 293.15 K and available in the literature for neighboring temperatures [11,12]) and isobaric heat capacities, C_p (taken from literature data [13–15]).

The mean molecular radii, r, and available volume, V_a, were obtained from the following relations according to Schaaffs [6,7]:

$$r = \left\{3M/(16\pi\rho N)\left[1-\gamma RT/\left(Mc^2\right)\left((1+Mc^2/(3\gamma RT))^{1/2}-1\right)\right]\right\}^{1/3}, \tag{3}$$

$$V_\mathrm{a} = V\left(1 - c/c_\infty\right), \tag{4}$$

where M is the molar mass, ρ is the density, c is the speed of ultrasound, N is Avogadro's number, $\gamma = C_p/C_v = \kappa_T/\kappa_s$ is the specific heat ratio, and c_∞ is $1600\,\mathrm{m\cdot s^{-1}}$.

Available volumes, V_a, were also calculated basing on thermoacoustical parameters from the following equations [16]:

$$V_\mathrm{a} = V/\{5/2 + [S^*(1+aT)+X]/2\alpha T\}, \tag{5}$$

$$S^* = 1 + 4\alpha T/3, \tag{6}$$

$$X = -2(1+2\alpha T)/V_\mathrm{r}^{C*}, \tag{7}$$

where the reduced molar volume, V_r, and the Moelwyn-Hughes parameter, C^*, were calculated from the following relations [16,17]:

$$V_\mathrm{r} = [1 + (\alpha T/3)/(1+\alpha T)]^3, \tag{8}$$

$$C^* = 13/3 + 1/\alpha T + 4\alpha T/3. \tag{9}$$

The available volumes calculated from Eqs. 4 and 5 were used to estimate free intermolecular lengths, L, given by the relation,

$$L = 2V_\mathrm{a}/Y, \tag{10}$$

Table 1 Speeds of ultrasound, nonlinearity parameters B/A, volume of molecules in a mole of liquid to molar volume ratios, thermal expansion coefficients, and literature values of critical or apparent critical temperatures [19] for the pure components at 293.15 K

	$c(\mathrm{m \cdot s^{-1}})$	*B/A*	*b/V*	$\alpha(\mathrm{kK^{-1}})$	T_c or $T_\mathrm{c,app}(\mathrm{K})$
2-Methyl-1-propanol	1204.1	10.71	0.2323	0.949	636
1-Butanol	1256.3	10.99	0.2328	0.947	639
Hexane	1098.9	10.47	0.2313	1.364	508
Cyclohexane	1279.0	11.42	0.2329	1.226	553.4

where, according to Jacobson [18,19], $Y = (36\pi N V_\mathrm{o}^2)^{1/3}$ is the total surface of all molecules in one mole of liquid and $V_\mathrm{o} = V(1 - T/T_\mathrm{c})^{0.3}$ was calculated using critical temperatures, T_c, for non-polar pure components and apparent critical temperatures, $T_\mathrm{c,app}$, for pure butanols (for binaries the mole fraction additivity of the values of its pure components was assumed).

Free intermolecular lengths, L, estimated from Eq. 10 were compared with the values obtained by the Jacobson equation based on the relation to the adiabatic compressibility coefficient [18,19];

$$L = (\kappa_s/k)^{1/2.4}, \tag{11}$$

where k is an empirical constant provided for associated and non-associated liquids in [19].

Beyer's parameters of nonlinearity defined as $B/A = 2\rho c(\partial c/\partial p)_s$, describing nonlinear properties of fluid [20], were calculated from the relation [6],

$$B/A = (\gamma - 1)/T\alpha + 2\,(3 - 2z)^2\,/3\,(z - 1)\,(6 - 5z)\,, \tag{12}$$

using $z = V/4b = 3V/16\pi r^3 N$ where b is the volume of molecules treated as rigid balls with a uniform radius r, in a mole of liquid (volume of a mole of molecules).

The values of the thermodynamic and acoustic quantities mentioned above, calculated for the pure components, are reported in Table 1.

Experimental densities and speeds of ultrasound, together with calculated thermal expansion coefficients for binary liquid mixtures of 1-butanol with hexane and cyclohexane at 293.15 K, are reported in Table 2.

4 Discussion and Conclusions

For the investigated systems it was found that self-association between alcohol molecules decreases with increasing concentration of the non-polar solvent (gradual breakage of alcohol multimers and structural rearrangement of non-polar solvent connected with solvation processes) [1,2]. Furthermore, non-polar components of the binaries under test (cyclohexane and hexane) undisputably show different compressibilities and space filling abilities in the pure liquid state [1,5]. Therefore, mixing primary

Table 2 Densities, speeds of ultrasound, and thermal expansion coefficients for binary liquid mixtures of 1-butanol with cyclohexane and hexane at 293.15 K

x_1	$C_4H_9OH(1) + C_6H_{12}(2)$			x_1	$C_4H_9OH(1) + C_6H_{14}(2)$		
	$\rho(\mathrm{kg \cdot m^{-3}})$	$c(\mathrm{m \cdot s^{-1}})$	$\alpha(\mathrm{kK^{-1}})$		$\rho(\mathrm{kg \cdot m^{-3}})$	$c(\mathrm{m \cdot s^{-1}})$	$\alpha(\mathrm{kK^{-1}})$
0.00115	778.6	1278.7	1.226	0.00305	659.9	1099.0	1.364
0.00245	778.5	1277.7	1.226	0.04764	664.4	1099.2	1.358
0.01240	778.5	1274.6	1.225	0.10262	670.3	1099.8	1.349
0.02620	778.7	1271.5	1.225	0.12246	672.4	1100.5	1.346
0.04084	778.8	1269.3	1.224	0.15089	675.6	1101.6	1.340
0.07249	779.3	1265.3	1.222	0.22610	684.4	1105.9	1.325
0.13953	780.4	1258.6	1.214	0.29788	693.4	1112.1	1.307
0.18966	781.4	1254.6	1.205	0.49651	720.9	1140.0	1.241
0.30171	784.0	1248.8	1.178	0.61276	738.8	1160.2	1.188
0.51749	790.4	1244.4	1.107	0.68166	750.1	1174.0	1.152
0.61622	793.7	1244.8	1.071	0.76577	764.5	1192.1	1.101
0.79829	800.8	1248.2	1.008	0.89374	788.1	1224.5	1.010

butanols with cyclic and linear hydrocarbons does not proceed isochorically and is accompanied by different volume effects. The isotherms of excess molar volumes are positive over the whole concentration range for systems with cyclohexane, contrary to the s-shaped isotherms in binary solution of 1-butanol or 2-methyl-1-propanol with linear molecules of hexane [1,5].

In our previous work it was found that the free intermolecular length, calculated according to Jacobson, and the ratio of the free volume to the molar volume in binary liquid mixtures of aliphatic alcohols with hexane and cyclohexane could be related to the space-filling ability and, in general, show good accordance with the results obtained from the well-known formalism of thermodynamic excess functions [2,5,21,22].

Free intermolecular lengths, L, calculated according to Jacobson, were compared with the values estimated from Eq. 10 based on the V_a values given by the Schaaffs relation in Eq. 4 and the thermoacoustical approach from Eq. 5. For the investigated systems it has been shown, that L estimated from V_a values obtained by a thermoacoustical approach gives very good agreement with L calculated from the Jacobson semi-empirical Eq. 11 for systems with hexane (Figs. 1, 2). However, for the systems with cyclohexane the L values obtained using Eqs. 4 and 5 are slightly less consistent and show comparable deviations in opposite mole fraction ranges (Figs. 3, 4). Moreover, the L values estimated from Eq. 10 using V_a values obtained from Eq. 4 demonstrate significant incompatibility for the systems with hexane (Figs. 1, 2).

We can also note that Beyer's nonlinearity parameter value B/A is determined mainly by the variable z, which represents the ratio of the liquid molar volume to the real volume of a mole of molecules ($z = V/4b$). It was found that in binary liquid mixtures of 1-butanol and 2-methyl-1-propanol with cyclohexane and hexane, the differences between isotherms of the nonlinearity parameter B/A (Fig. 5) demonstrate

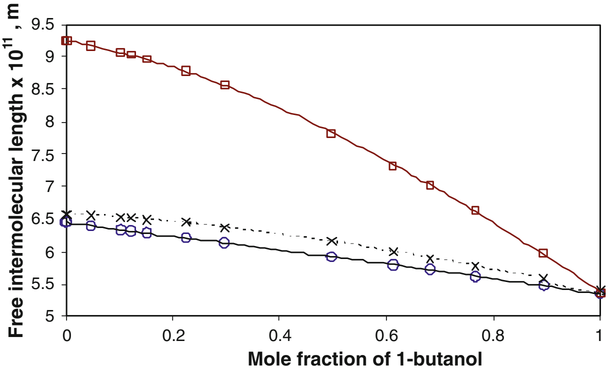

Fig. 1 Free intermolecular length for binary mixtures of 1-butanol with hexane at 293.15 K (×) calculated from semi-empirical Eq. 11 and estimated from Eq. 10 using V_a values (☐) obtained from Eq. 4 and (○) from Eq. 5

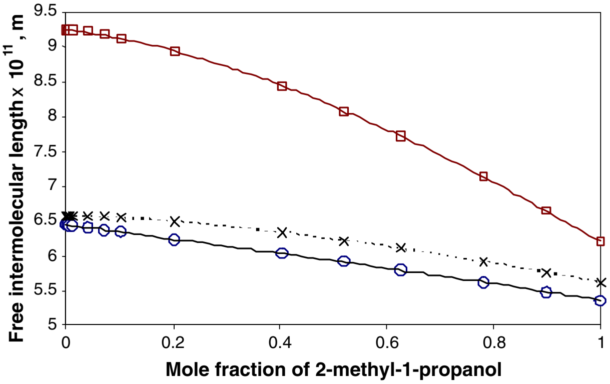

Fig. 2 Free intermolecular length for binary mixtures of 2-methyl-1-propanol with hexane at 293.15 K (×) calculated from semi-empirical Eq. 11 and estimated from Eq. 10 using V_a values (☐) obtained from Eq. 4 and (○) from Eq. 5

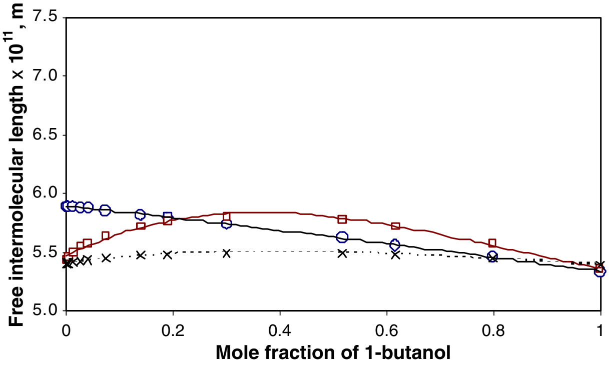

Fig. 3 Free intermolecular length for binary mixtures of 1-butanol with cyclohexane at 293.15 K (×) calculated from semi-empirical Eq. 11 and estimated from Eq. 10 using V_a values (☐) obtained from Eq. 4 and (○) from Eq. 5

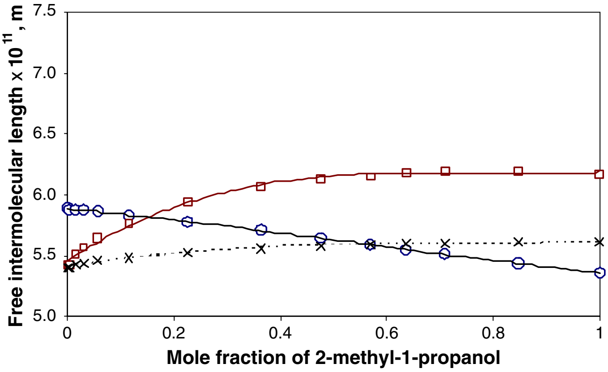

Fig. 4 Free intermolecular length for binary mixtures of 2-methyl-1-propanol with cyclohexane at 293.15 K (×) calculated from semi-empirical Eq. 11 and estimated from Eq. 10 using V_a values (□) obtained from Eq. 4 and (○) from Eq. 5

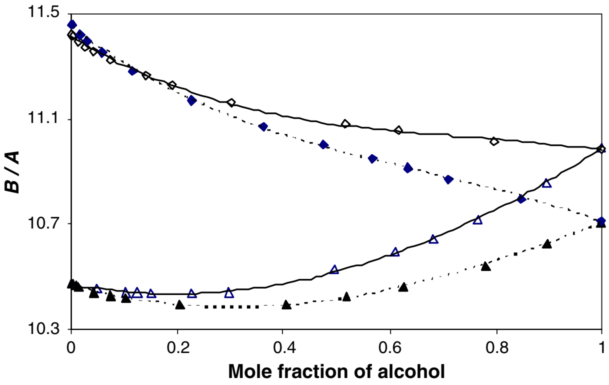

Fig. 5 Nonlinearity parameter B/A in binary mixtures of 1-butanol with (△) hexane and (◇) cyclohexane and 2-methyl-1-propanol with (▲) hexane and (◆) cyclohexane at 293.15 K

similar relations to the b/V ratio, for which the mole fraction dependence is similar to the speed of ultrasound isotherms in the binaries under test [1,5]. Mentioned parameters show, in general, greater values at high cyclohexane mole fraction than in the corresponding hexane solutions (Fig. 5). Therefore, the speed of ultrasound, the b/V ratio, and the nonlinearity parameter B/A could be related to the space-filling ability for binaries and pure liquids [5,22–24].

For the investigated systems it has been shown that the molecules of two typical non-polar aliphatic solvents interact with two primary butanol molecules indicating different volume effects, mainly connected to size and shape of the molecules (for the pure components the values of V, b, and r show the same relation: hexane > cyclohexane > 2-methyl-1-propanol > 1-butanol). Thus, most of the thermodynamic and acoustic quantities together with the speed of ultrasound and nonlinearity parameter B/A could be related to the space-filling ability and depend mainly on the b/V ratio (Table 1).

The relation between the b/V ratio and nonlinearity parameter B/A for the pure components (cyklohexane > 1-butanol > 2-methyl-1-propanol > hexane) could be simply related to the free intermolecular length L estimated from Eqs. 10 and 4. It is worthwhile to note that L values calculated using V_a obtained from Eq. 4, under the fundamental Schaaffs assumption that molecules could be treated as rigid balls, give better consistency with L calculated from the Jacobson semi-empirical Eq. 11 for systems that contain more ball-shaped molecules with higher values of the b/V ratio and nonlinearity parameter B/A (Figs. 1–4). The estimation mentioned above for systems with "linear" molecules of hexane (the lowest values of b/V and B/A parameters) shows a significant inconsistency at high hexane mole fractions and is in good accordance at high alcohol mole fractions (Figs. 1, 2).

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