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ULTRASONIC AND THERMODYNAMIC EFFECTS OF SELF-ASSOCIATION OF ALIPHATIC ALCOHOLS IN c–C_6H_{12}. II. PRIMARY AND TERTIARY PENTANOLS*

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The ultrasound velocities in and densities of mixtures of cyclohexane with n-pentanol $\{x_1\text{n}-C_5H_{11}OH+(1-x_1)C_6H_{12}\}$ and with 2-methylbutan-2-ol $\{x_1\text{tert}-C_5H_{11}OH+(1-x_1)C_6H_{12}\}$ have been measured at 293.15 K. Using the measurement results in connection with the literature data, the following quantities have been determined: isothermal and adiabatic compressibility coefficients, $\beta_T = -1/V(\partial V/\partial p)_T$ and $\beta_s = -1/V(\partial V/\partial p)_s$, respectively, the adiabatic compressibility, $\varkappa_s = -(\partial V/\partial p)_s$, the free intermolecular length, L, and the excess values of the molar volume, V^E, of the adiabatic compressibility coefficient, β_s^E, and of the adiabatic compressibility, $\varkappa_s^E$. The dependences of those excess functions on the mixture composition, expressed in mole fractions, were represented by Redlich-Kister equations.

1. Introduction

The subject of this paper were two binary liquid mixtures containing one rather inert component (cyclohexane) and another one capable of being highly associated by hydrogen bonds. Two monohydric pentanols, the primary n-pentanol and the tertiary 2–methylbutan–2–ol, were used as the associating components. We have focussed our attention especially on deviations of the properties of the mixtures under test from the thermodynamic ideality in relation to intermolecular interactions and the free intermolecular lengths.

Numerical values characterising the mixtures were determined from ultrasonic velocity and density measurements in connection with some auxiliary data available in literature.

The results have been discussed in the ligth of the intermolecular interactions and the capability of space-filling related to the molecular structure of the components and their capability for association by formation of hydrogen bonds. We have also tried to find some correlation between the excess thermodynamic functions and the intermolecular free length in the studied binary liquid mixtures.

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2. Experimental

For dehydration and purification, the components (cyclohexane, n-pentanol, POCh Gliwice, Poland, and 2-methylbutan–2–ol, BDH Chemicals, England, all of analytical grade) were shaked for a longer time with molecular sieves A3 and A4 of granulation 1/16″ (POCh Gliwice, Poland) and distilled under reduced pressure.

The mixtures were prepared by weighing immediately before the measurements.

The densities of the pure components and mixtures were determined by the Kohlrausch method, i.e. by using a quartz float that has been weighted at 293.15 + / − 0.01K in air and after immersing it in the liquid under test. The weights were reduced to vacuum. The accuracy was +/ − 0.1kg/m^3.

The ultrasound velocities were measured by the well-known sign-around method using an equipment designed and constructed at our laboratory (the frequency was measured with a frequency -meter KZ–2026A–2, ZOPAN Warsaw, Poland) [8]. The temperature deviations did not exceed +/ − 0.002K. The repeatability of the ultrasound velocity measurements was better than +/ − 0.05m/s.

3. Measurement results

The isentropic and isothermal compressibility coefficients, β_s and β_T, and the molar heat capacity under constant volume, C_v were calculated from the measured ultrasound velocity, c, and density, ϱ, using the following equations:

$$\begin{aligned} \beta_s &= 1/(\varrho c^2) \\ \beta_T &= \beta_s + \alpha^2 VT/C_p \\ C_V &= C_p \beta_s/\beta_T \end{aligned} \tag{1}$$

where T — temperature, V — molar volume, α — coefficient of thermal expansion, C_p — molar heat capacity under constant pressure.

The values calculated for the pure components from Eq. (1) together with the heat capacities under constant pressure and coefficients of thermal expansion taken from literature [1–3] are collected in Table 1.

Table 1. Properties for pure components at 293.15 K.

Property	n − $C_5H_{11}OH$	tert−$C_5H_{11}OH$	C_6H_{12}
c/(m/s)	1292.9	1192.3	1277.1
ϱ/(kg/m^3)	814.6	808.9	778.2
β_s/(1/TPa)	734.2	869.5	791.1
β_T/(1/TPa)	867.1	1100.8	1090.1
C_v/(J/molK)	170.71	193.01	113.01
C_p/(J/molK)	201.67[a]	244.35[a]	156.01[b]
α/(1/kK)	0.92[a]	1.33[a]	1.216[b]

[a] Reference [1]. [b] Reference [2].

The excess adiabatic compressibility coefficients were calculated according to BENSON et al. [4, 5] using the following relations:

$$\begin{aligned} \beta_s^E &= \beta_s - \beta_s^{\mathrm{id}}, \quad \beta_s^{\mathrm{id}} = \beta_T^{\mathrm{id}} - (\alpha^{\mathrm{id}})^2 V^{\mathrm{id}} T/C_p^{\mathrm{id}} \\ \beta_T^{\mathrm{id}} &= x_{V,1}\beta_{T,1}^0 + (1 - x_{V,1})\beta_{T,2}^0 \end{aligned} \tag{2}$$

$$x_{V,1} = x_1 V_1^0 / V^{id}$$
$$V^{id} = x_1 V_1^0 + (1 - x_1) V_2^0$$
$$\alpha^{id} = x_{V,1} \alpha_1^0 + (1 - x_{V,1}) \alpha_2^0 \qquad (2) \text{ [cont.]}$$
$$C_p^{id} = x_1 C_{p,1}^0 + (1 - x_1) C_{p,2}^0 ,$$

were the lower indices "1" and "2" refer to both the components and the upper ones "0" and "id" indicate quantities related to the pure components and to the thermodynamically ideal mixtures, respectively.

The excess volume and compressibility can be written as follows:

$$V^E = V - V^{id} \qquad (3)$$
$$\varkappa_s^E = \varkappa_s - V^{id} \beta_s^{id} \qquad (4)$$

where $\varkappa_s = (V^E + V^{id}) \beta_s$.

According to JAcobson [6], the free intermolecular length L is related to the adiabatic compressibility coefficient by the following equation:

$$\beta_s = k_\beta L^{2.4} \qquad (5)$$

where k_β is an empirical constant given in [3, 6].

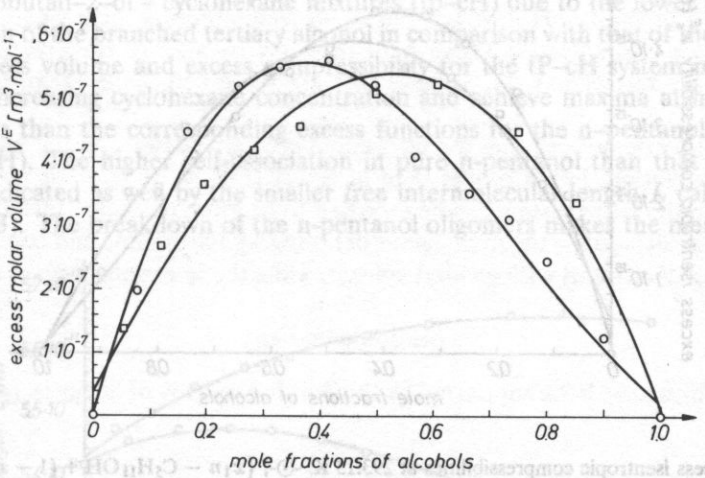

FIG. 1. Excess molar volumes at 293.15 K -⊙-, $\{x_1 n - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$; -□-, $\{x_1 \text{tert} - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$.
The lines represent the best-fit excess values calculated from Eq. (7).

It was found that the dependence of the ultrasound velocity, c, mean molar volume, V, as well as β_s, $\varkappa_s$ and L on the mole fraction of alcohol, x_1, can be satisfactorily represented by simple polynomials

$$F = \sum_{j=1}^{n} A_j x_1^{j-1} \qquad (6)$$

The A_j parameter values together with the mean standard deviations are given in Table 2.

Table 2. Parameters of equation (6) and standard deviations s.

	A_1	A_2	A_3	A_4	A_5	s
	$\{x_1 n - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$					
c/(m/s)	1275.41	−128.11	233.85	−89.04	–	0.18
V/(m³/mol) * 10^7	1081.0	41.11	−93.31	78.7	−25.7	0.21
β_s/(1/TPa)	789.7	185.3	−525.4	432.5	−147.9	0.60
$\varkappa_s$/(m³/Pa mol) * 10^{16}	854.951	607.954	−590.177	171.001	–	0.36
L/(m) * 10^{13}	542.240	137.303	−132.818	37.374	–	0.09
	$\{x_1$ tert $- C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$					
c/(m/s)	1273.66	−195.12	167.16	−54.13	–	0.15
V/(m³/mol) * 10^7	1082.46	23.104	−9.447	−6.172	–	0.17
β_s/(1/TPa)	791.10	282.52	−477.61	499.57	−226.19	0.40
$\varkappa_s$/(m³/Pa mol) * 10^{16}	858.085	479.159	−259.391	43.624	–	0.49
L/(m) * 10^{13}	542.798	121.079	−72.160	14.993	–	0.13

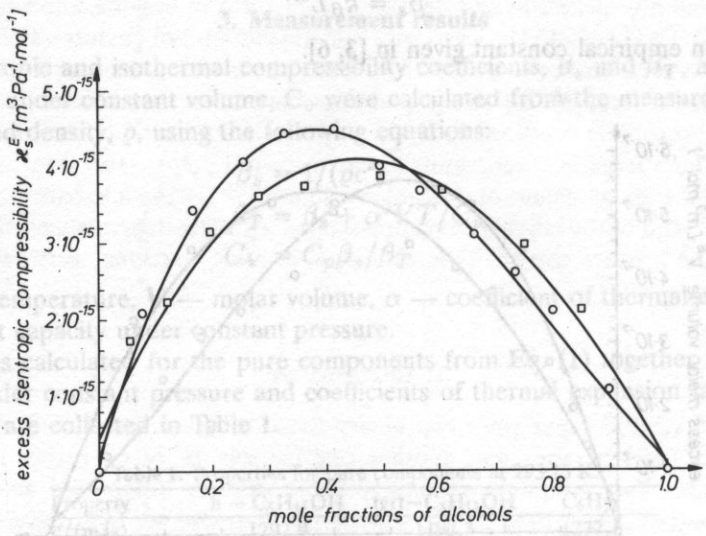

FIG. 2. Excess isentropic compressibilities at 293.15 K. -⊙-, $\{x_1 n - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$; -□-, $\{x_1$tert $- C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$.
The lines represent the best-fit excess values calculated from Eq. (7).

The dependence of the excess functions on the mole fraction of alcohol is described with good accuracy by the Redlich-Kister equation

$$F^E = x_1(1 - x_1)\sum_{j=1}^{n} A_j(1 - 2x_1)^{j-1} \tag{7}$$

The parameters A_j and the corresponding mean standard deviations are collected in Table 3.

Table 3. Parameters of Eq. (7) of the excess functions and standard deviations s.

	A_1	A_2	A_3	A_4	s
		$\{x_1 n - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$			
$V^E/(m^3/mol) * 10^8$	187.75	133.85	27.753	−12.147	0.06
$\beta_s^E/(1/TPa)$	77.773	60.696	37.112	−1.094	0.02
$\varkappa_s^E/(m^3/Pa\,mol) * 10^{16}$	99.090	77.158	42.203	−2.825	0.04
		$\{x_1$ tert $- C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$			
$V^E/(m^3/mol) * 10^8$	207.22	−20.058	50.394	49.519	0.10
$\beta_s^E/(1/TPa)$	93.738	18.503	60.743	9.335	0.15
$\varkappa_s^E/(m^3/Pa\,mol) * 10^{16}$	119.634	17.321	69.583	13.720	0.23

4. Discussion and conclusions

The excess molar volumes, V^E, and the excess adiabatic compressibilities, $\varkappa_s^E$, shown as functions of composition in Figs. 1 and 2 are positive in the whole concentration range for both the systems studied which suggests that the interaction between unlike molecules are weaker than those occurring in the pure components or at least in one of them [7]. This could be expected because of the high degree of self-association in the alcohols.

The dilution of the alcohols with cyclohexane results in a gradual breakage of the alcohol oligomers. As indicated by Figs. 1 and 2, this effect becomes more pronounced in the 2–metylbutan–2–ol – cyclohexane mixtures (tp–cH) due to the lower capability for self-association of the branched tertiary alcohol in comparison with that of the n–pentanol. Thus, the excess volume and excess compressibility for the tP–cH system increase more rapidly with increasing cyclohexane concentration and achieve maxima at higher alcohol concentrations than the corresponding excess functions for the n–pentanol–cyclohexane system (nP–cH). The higher self-association in pure n-pentanol than that in pure tert-pentanol is indicated as well by the smaller free intermolecular length L calculated from Eq. (5) (Fig. 3). The breakdown of the n-pentanol oligomers makes the mean free inter-

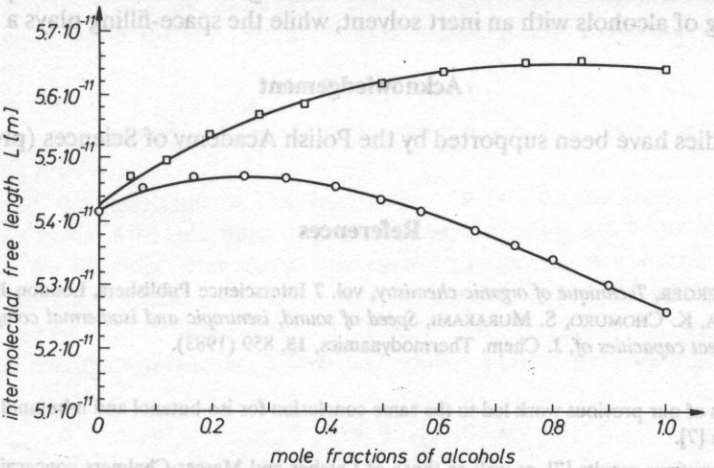

FIG. 3. The free intermolecular lengths at 293.15 K. -⊙-, $\{x_1 n - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$; -□-, $\{x_1$ tert $- C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$.
The lines represent the best-fit values calculated from Eq. (6).

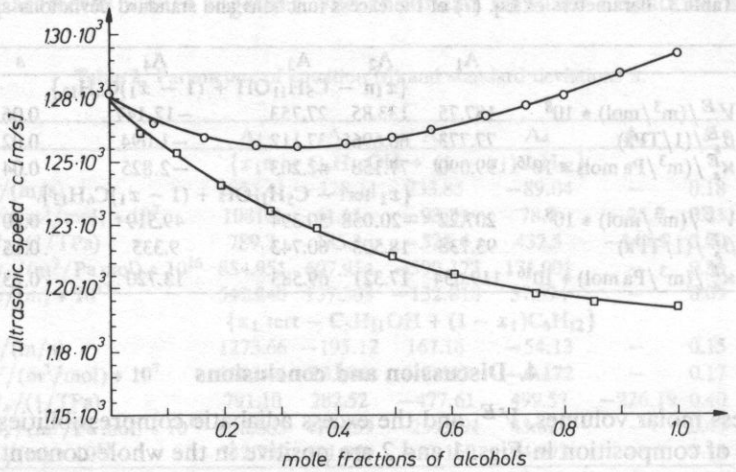

FIG. 4. Ultrasonic speed at 293.15 K. -⊙-, $\{x_1 n - C_5H_{11}OH + (1 - x_1)C_6H_{12}\}$; -□-, $\{x_1 \text{ tert} - c_5H_{11}OH + (1 - x_1)C_6H_{12}\}$.
The lines represent the best-fit values calculated from Eq. (6).

molecular length in the nP-cH mixtures increase with increasing dilution of the alcohols up to $x \approx 0.3$ in the tP-cH mixtures the mean free intermolecular length is decreasing within the same concentration range most probably because of the greater space-filling capability of the tert-pentanol molecules that are more ball-shaped than the n-pentanol molecules [1].

It should also be noticed that the ultrasound propagates faster in the system of higher molecular association, i.e. in nP-cH than in tP-cH (Fig. 4), in spite of the fact that the space-filling in the latter system can be expected to be more perfect. Thus, the results suggest that self-association is the main factor determining the volume and compressibility effects of mixing of alcohols with an inert solvent, while the space-filling plays a minor role [2].

Acknowledgement

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[1] The results of our previous work led to the same conclusion for iso-butanol and n-butanol binary mixtures with cyclohexane [7].

[2] Also our previous results [7], as well as those of Letcher and Mercer-Chalmers concerning cyclohexane-alcohol systems [9] indicate that association, decreasing with increasing length and branching of the carbon chain, is the main factor determining the volume and compressibility effects of dilution of the alcohols by the inert solvent.

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