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ULTRASONIC AND THERMODYNAMIC EFFECTS OF SELF-ASSOCIATION OF ALIPHATIC ALCOHOLS IN $\text{C-C}_6\text{H}_{12}$. I. PRIMARY BUTANOLS

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The ultrasound velocities in and densities of mixtures of n-butanol and iso-butanol with cyclohexane as a common component have been measured at 293.15 K. The adiabatic compressibility coefficients, $\beta_s = -1/V(\partial V/\partial p)_s$, compressibilities, $\kappa_s = \beta_s V$, and the free intermolecular lengths, L , of those mixtures were estimated and their dependence on the alcohol concentration reproduced by simple polynomials. The excess values of the above quantities, V^E , β_s^E and κ_s^E were calculated and discussed. The dependence of those excess functions on the mixture composition, expressed in mole fractions of alcohol, x_1 , can be successfully reproduced by the Redlich-Kister equation.

1. Introduction

Although the dependence of thermodynamic properties of binary liquid mixtures on their composition has been usually attributed to structural variations accompanying the mixing of the component, there is still lacking a theoretical foundation of that dependence in terms of microscopic characteristics determining the structure of the two-components liquid, i.e. on the size and shape of the molecules and intermolecular interactions affecting the liquid structure. However, significant progress in understanding the link between macroscopic properties and structure has been made by studying liquid mixtures in that relatively strong interactions by hydrogen bonding are expected to be the main structure determining factor, particularly by studying alcohols in dipolar and non-polar solvents.

The general problem which we address in this paper is the effect of variations in the self-association of n-butanol and iso-butanol caused by mixing with cyclohexane on the ultrasound velocity in and the volume and compressibility of those binary mixtures.

It is customary to analyze the effect of composition on a molar property Z in terms of deviations ΔZ from an arbitrary chosen ideal reference state $Z^{id} = \sum x_i Z_i^0$, where Z_i^0 are the corresponding molar properties of the pure components and x_i the molar fractions of the latter. We believe that, although the choice of the ideal reference state is merely a matter of convention, in order to achieve a compatibility of the deviations of different quantities, it is necessary to choose a common reference state for all those quantities. In this study we have therefore chosen the thermodynamically ideal two-component system defined by the equation

$G = \sum_{i=1}^2 x_i (\mu_i^0 + RT \ln x_i)$ (where G – molar free enthalpy, μ_i^0 – standard chemical potential of the i -th component) for determining both volume and compressibility deviations.

2. Experimental

For dehydration and purification, the pure components (n-butanol, iso-butanol and cyclohexane, POCh Gliwice, Poland, all of analytical grade) were shaken for a longer time with molecular sieves A3 and A4 of granulation 1/16" (POCh Gliwice) and distilled under reduced pressure. After purification the refractive indices and boiling points were controlled (n-butanol: 1.3992, 117.7 K; iso-butanol: 1.3959, 107.9 K; c-C₆H₁₂: 1.4464, 82.6 K).

The mixtures were prepared by weighing immediately before the measurements.

The densities of the pure components and mixtures were determined pycnometrically and by the Kohlrausch method, i.e. by using a quartz float that has been weighed at 293.15 \pm 0.01 K in air and after immersing it in the liquid under test. In both cases the weights were reduced to vacuum. The accuracy was \pm 0.1 kg/m³.

The ultrasound velocities were measured by a sing-around equipment designed and constructed in our laboratory (the frequency was measured with a frequency-meter KZ-2026A-2, ZOPAN Warsaw, Poland). The temperature deviations did not exceed \pm 0.002 K and \pm 0.005 K in n-butanol-cyclohexane and iso-butanol-cyclohexane, respectively. The repeatability of the ultrasound velocity measurements was better than \pm 0.05 m/s.

3. Measurement results

The measured sound velocities and densities are given in Table 1.

The molar volumes, V , isentropic compressibility coefficients, β_s , and isentropic compressibilities, κ_s , were calculated from the following equations

$$\begin{aligned} V &= (x_1 M_1 + x_2 M_2) / \rho \\ \beta_s &= 1 / \rho c^2 \\ \kappa_s &= \beta_s V \end{aligned} \quad (1)$$

Table 1. Speeds of sound and densities at 293.15 K

x_1	$c/(m/s)$	$\rho/(kg/m^3)$	x_1	$c/(m/s)$	$\rho/(kg/m^3)$
{ $x_1 n - C_4H_9OH + (1 - x_1)C_6H_{12}$ }			{ $x_1 iso - C_4H_9OH + (1 - x_1)C_6H_{12}$ }		
0	1277.4	778.4	0	1276.7	778.1
0.0499	1266.5	779.0	0.1356	1250.1	779.3
0.0972	1259.9	779.7	0.2212	1239.7	780.4
0.1246	1255.3	780.7	0.3394	1229.5	783.1
0.2426	1249.8	781.8	0.4442	1222.8	785.6
0.3179	1246.5	784.3	0.5358	1218.0	787.9
0.3901	1244.4	786.6	0.6649	1212.3	791.3
0.4636	1243.2	788.7	0.7845	1208.0	794.7
0.5409	1242.7	791.5	0.8612	1205.6	797.2
0.6178	1243.2	794.2	1	1204.1	801.9
0.6730	1243.8	796.3			
0.7728	1246.1	800.2			
0.8741	1249.6	804.5			
0.9415	1253.4	807.7			
1	1256.6	810.5			

where M_1 and M_2 are the molar masses of the mixed components, c is the ultrasound velocity and ρ is the density of the mixture.

Using the isobaric coefficients of thermal expansion, α_i^0 , calculated from the measured densities and density data available in literature [1] and the isobaric molar heat capacities, $C_{p,i}^0$, taken as well from literature [1–3], the corresponding isothermic quantities for the pure components, $\beta_{T,i}^0$ and $\kappa_{T,i}^0$, as well as their isochoric molar heat capacities, $C_{V,i}^0$, were calculated from the following equations

$$\begin{aligned}\beta_{T,i}^0 &= \beta_{s,i}^0 + (\alpha_i^0)^2 VT/C_{p,i}^0 \\ \kappa_{T,i}^0 &= \beta_{T,i}^0 V_i^0 \\ C_{V,i}^0 &= C_{p,i}^0 \beta_{s,i}^0 / \beta_{T,i}^0\end{aligned}\quad (2)$$

(where V_i^0 are the molar volumes of the pure components and T is temperature) and collected in Table 2.

Table 2. Isothermic compressibility coefficients, isothermic compressibilities and isochoric molar heat capacities for pure components at 293.15 K

Property	n-butanol	iso-butanol	cyclohexane
$\beta_T^0/(1/TPa)$	889.93	995.18	1088.53
$\kappa_T^0/(m^3/Pa \cdot mol) \cdot 10^{14}$	8.1354	9.1990	11.7725
$C_V^0/(J/mol K)$	188.91	158.58	112.97

The excess quantities V^E , β_s^E and κ_s^E were obtained from the equations

$$\begin{aligned} V^E &= V - V^{id} \\ \beta_s^E &= \beta_s - \beta_s^{id} \\ \kappa_s^E &= \kappa_s - \beta_s^{id} V^{id} \end{aligned} \quad (3)$$

where $V^{id} = x_1 V_1^0 + (1 - x_1) V_2^0$ (x_1 is the mole fraction of alcohol, V_1^0 and V_2^0 are the molar volumes of alcohol and cyclohexane, respectively) β_s^{id} is the isentropic compressibility coefficient of the corresponding ideal mixture calculated as suggested by BENSON et al. [4, 5]:

$$\begin{aligned} \beta_s^{id} &= \beta_T^{id} - (\alpha^{id})^2 V^{id} T / C_p^{id} \\ \beta_T^{id} &= x_{v,1} \beta_{T,1}^0 + (1 - x_{v,1}) \beta_{T,2}^0 \\ x_{v,1} &= x_1 V_1^0 / V^{id} \\ \alpha^{id} &= x_{v,1} \alpha_1^0 + (1 - x_{v,1}) \alpha_2^0 \\ C_p^{id} &= x_1 C_{p,1}^0 + (1 - x_1) C_{p,2}^0 \end{aligned} \quad (4)$$

where the lower indices "1" and "2" refer to alcohol and cyclohexane, respectively, and the upper one "id" indicates quantities related to ideal mixtures. Thus, the excess functions have been calculated using the states of the pure components under the measurement conditions as their standard states: $\mu_i^\theta = \mu_i^0$ (where μ_i^θ and μ_i^0 are the standard chemical potential and the chemical potential of the pure components, respectively).

The free intermolecular lengths, L , were obtained, according to JACOBSON [6], from the following relationship

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

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

It was found that the dependences of V , β_s , κ_s and L on the mole fraction of alcohol, x_1 , can be satisfactorily represented by simple polynomials

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

and those of V^E , β_s^E and κ_s^E by the Redlich-Kister equations:

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

The A_j parameter values together with the mean standard deviations, s , are given in Table 3.

Table 3. Parameters of equations (6) and (7) and standard deviations *s*.

<i>F</i> or <i>F^E</i>	<i>A</i> ₁	<i>A</i> ₂	<i>A</i> ₃	<i>A</i> ₄	<i>A</i> ₅	<i>s</i>
{ <i>x</i> ₁ <i>n</i> - C ₄ H ₉ OH + (1 - <i>x</i> ₁)C ₆ H ₁₂ }						
<i>V</i> /(m ³ /mol) × 10 ⁷	1081.4	-149.23	-18.73	1.22	-	0.91
<i>β</i> ₁ /(1/TPa)	788.21	256.68	-665.34	698.08	-297.57	0.99
<i>x</i> ₂ /(m ³ /Pa · mol) × 10 ¹⁶	852.05	167.37	-795.55	848.25	-359.11	0.09
<i>L</i> /(m) × 10 ¹⁴	5415.1	728.53	-1898.0	2005.4	-859.46	0.07
<i>V^E</i> /(m ³ /mol) × 10 ⁹	160.77	9.6228	97.499	-	-	0.78
<i>β</i> ₂ ^{<i>E</i>} /(1/TPa)	30.194	38.016	63.437	-	-	0.27
<i>x</i> ₂ ^{<i>E</i>} /(m ³ /Pa · mol) × 10 ¹⁶	43.326	43.334	43.926	-	-	0.27
{ <i>x</i> ₁ iso - C ₄ H ₉ OH + (1 - <i>x</i> ₁)C ₆ H ₁₂ }						
<i>V</i> /(m ³ /mol) × 10 ⁷	1081.7	-139.99	-29.879	12.716	-	0.27
<i>β</i> ₁ /(1/TPa)	789.72	297.47	-559.51	554.34	-221.81	0.18
<i>x</i> ₂ /(m ³ /Pa · mol) × 10 ¹⁶	854.10	214.77	-679.97	670.27	-264.07	0.05
<i>L</i> /(m) × 10 ¹⁴	5419.3	842.81	-1606.5	1597.4	-637.15	0.10
<i>V^E</i> /(m ³ /mol) × 10 ⁹	1063.8	647.11	762.33	-	-	0.03
<i>β</i> ₂ ^{<i>E</i>} /(1/Pa) × 10 ¹⁴	6299.5	5450.7	5534.6	-	-	0.43
<i>x</i> ₂ ^{<i>E</i>} /(m ³ /Pa · mol) × 10 ¹⁶	72.253	66.184	65.860	-	-	0.06

4. Discussion of measurement results

The ultrasonic velocity does not vary linearly with the concentration of alcohols which is obviously related to the complex variations of the thermodynamic parameters. The excessive values of those parameters are positive in the whole concentration range (Figs. 1-3, Table 3) and, except that of the excess volume, are

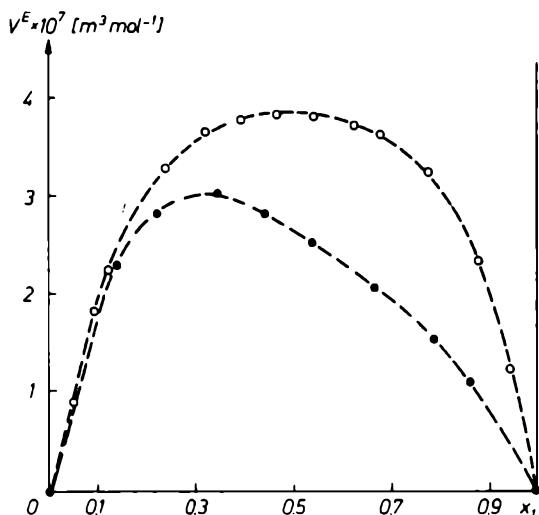


FIG. 1. Excess molar volumes at 293.15 K. - - o - -, {*x*₁*n* - C₄H₉OH + (1 - *x*₁)C₆H₁₂}; - ● -, {*x*₁iso - C₄H₉OH + (1 - *x*₁)C₆H₁₂}. Broken lines were calculated from eq. (7) by the best-fit procedure

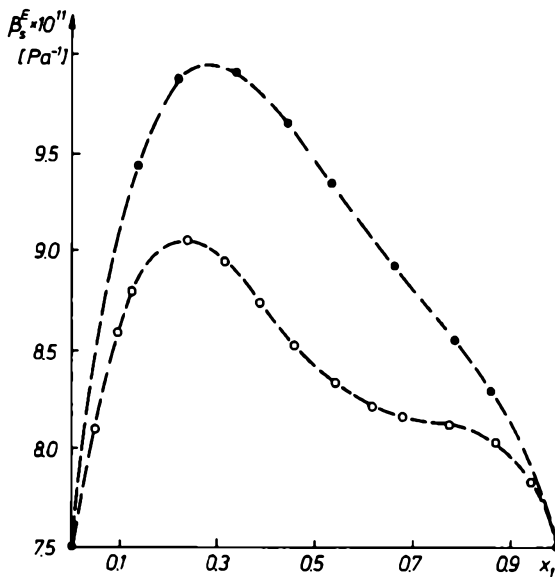


FIG. 2. Excess isentropic compressibility coefficients at 293.15 K --o-- , $\{x_1 n\text{-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$; --●--, $\{x_1 \text{iso-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$. Broken lines were calculated from eq. (7) by the best-fit procedure

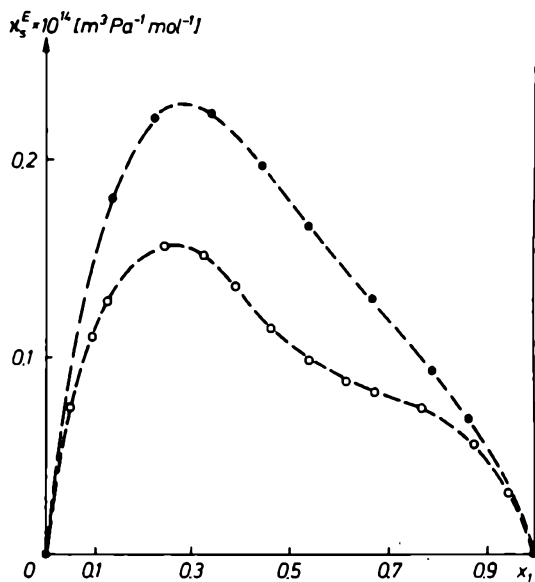


FIG. 3. Excess isentropic compressibilities at 293.15 K --o-- , $\{x_1 n\text{-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$; --●--, $\{x_1 \text{iso-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$. Broken lines were calculated from eq. (7) by the best-fit procedure

larger for the iso-butanol solutions than for the n-butanol ones of corresponding composition. Furthermore, the concentration dependences of the excess parameters show a clear-cut dissymmetry, except that of the excess volume of n-butanol which is almost symmetrical. From inspection of the figures in Table 2 one learns also that the values of all the parameters of pure iso-butanol collected in this table (molar volumes, isothermic and isentropic compressibilities and compressibility coefficients, expansion coefficients and free path lengths) are larger than the corresponding values of pure n-butanol and the difference in the molar volumes of the pure alcohols is almost negligible if compared to those in the compressibility and free path length.

Basing on the Jacobson's model [3], according to which molecular association should result in an increase of the free path length, i.e. in an increase in the intermolecular distance and thereby in a corresponding increase in compressibility, positive deviations of the compressibility of binary mixtures from additivity have been sometimes interpreted as a result of the formation of complexes between the components (for instance [7] and [8]). However it can be easily shown that the reasoning based on this model would be completely justifiable if the volume effect of mixing were zero [9]. As indicated by the above and other data [10–12], mixing of polar liquids with non-polar solvents (e.g. ketones with alicyclic and aliphatic hydrocarbons [14]) is accompanied, as a rule, by positive volume effects (positive excess volumes), i.e. the increase in self-association of the polar component with the increase of its concentrations does not proceed isochorically but results in an decrease of the mean molar volume, while the break-up of multimers of the associating component when, diluted by the non-polar solvent, leads to an increase in volume. There is also convincing evidence that, in spite of the expectations arising from Jacobson's model, if interactions between the components are likely to occur (e.g. interactions of dipole – dipole induced type in mixtures of ketones with aromatic hydrocarbons [15] or specific hydrogen-bondings [16]), the excess volumes and excess compressibilities are negative, while for solutions of alcohols and ketones in aliphatic non-polar solvents, where only London type interactions between solute and solvent are likely to occur, both the excess volumes and excess compressibilities are positive [10, 11, 14, 15, 17].

The difficulties in the physico-chemical analysis based on the isentropic compressibility coefficient, and thereby the diversity of the interpretations of the concentration dependence of this thermodynamic coefficient in terms of intermolecular interactions, is in our opinion due mainly to the fact that β_s is not an extensive quantity and it is therefore impossible to define a corresponding partial molar quantity. Nevertheless, the excess compressibility coefficient, β_s^E , characterizing the deviations of a real mixture from the thermodynamically ideal one must be related to intermolecular interactions. Despite the difficulty cited, it is believed [32] that

- i. if there is no difference, or only a negligible one, between the intermolecular interactions in the pure components and that between heterogeneous molecules in the mixtures, $\beta_s^E = 0$,
- ii. if the interactions between the heterogeneous molecules are weaker than those

between the molecules in the pure components or, at least, between the molecules in one of them (for instance, because of molecular self-association). $\beta_s^E > 0$,

iii. if, on the contrary, there are only weak intermolecular interactions in the pure components but the components are able to interact effectively with one another (for instance by forming complexes), $\beta_s^E < 0$,

iv. if the effects of self-association and complexation are overlapping, the concentration dependence of β_s^E may be very complex, sometimes β_s^E even changes sign at particular concentrations.

Pure butanols, like other alcohols, are remarkably associated [18, 19], being composed most probably of "open" entities with free OH groups (simple or branched multimeric chains), as well as of "closed" ones. Also in solutions in non-polar solvents, butanols are self-associated [20–27] and form various structures (oligomers): rings or chains with oxygen atoms engaged in one or two hydrogen bonds [19, 20] or, as indicated by the relatively large dipole moments, rings with chains when the "closing" occurs between a terminal OH group and the residual lone-pair of electrons of the oxygen atom of an intermediate mer of the chain [21]. Dielectric studies indicate that the different entities resulting from self-association exist in the solution in different proportions depending on the alcohol concentration.

Some authors suggested that rings are typical rather of multimers of lower order existing in dilute solutions [28], while others believe that those structures exist only in concentrated solutions and are rather typical of higher order multimers [21, 25, 29].

Whatever the particular multimeric structures, it seems to be beyond all question that the observed excessive volumes and compressibilities observed for solutions of alcohols in inert non-polar solvents should be attributed to the weakened hydrogen bonds between the alcohol molecules resulting in an increase in volume and compressibility. This conclusion is corroborated by the positive zeotropy observed for those solutions. Though measurements of dielectric saturation in solutions of n-butanol, iso-butanol and some other alcohols in benzene [22] indicate relatively strong interactions between the molecules of the alcohol and those of benzene leading to the formation of alcohol-solvent assemblies that may compete successfully with the self-association of the alcohols, this effect seems to be due mainly to the easiness of the deformation of the delocalized π -electron orbitals of benzene and distinguish the benzenic solutions from those in cyclohexane. Also, the values of the partition coefficient of n-butanol between water and various organic solvents [21], as well as the data of STEURER and WOLF [30], referring to the self-association of ethanol in cyclohexane, benzene and dioxane, showed the interactions of alcohols with cyclohexane to be markedly weaker than those with other solvents. Thus, it can be assumed that the interactions of the alcohol molecules with most non-polar solvents, and particularly with the low-polarizable cyclohexane, are only weak interactions of Van der Waals type.

Assuming, according to [32] that the maximum compressibility coefficient appears at the concentration at which the main contribution to the total compressibility coefficient arises from intermolecular interactions between heterogeneous

molecules, i.e. from alcohol – cyclohexane Van der Waals interactions, the more pronounced asymmetry of the excess compressibility of n-butanol solutions indicate that the self-association of n-butanol is stronger than that of iso-butanol, while the shape of this concentration dependence, showing, except the maximum, two distinct inflexion points (Table 4), suggests that, at least two kinds of multimers differing in composition and/or structure predominate depending on the composition of the mixtures, while in the iso-butanol solutions the shift of the equilibrium between the different possible multimers is rather a “smooth” one.

Table 4. Maxima and inflexion points of the values determined from measurements

	$\{x_1 n - C_4H_9OH + (1-x_1)C_6H_{12}\}$		$\{x_1 \text{ iso} - C_4H_9OH + (1-x_1)C_6H_{12}\}$	
$\beta_{s, \max}/(1/TPa)$	822.03	for $x = 0.339$	862.98	for $x = 0.864$
$\kappa_{s, \max}/(m^3/Pa \cdot mol) \times 10^{16}$	862.12	$x = 0.130$	874.96	$x = 0.223$
$L_{\max}/(m) \times 10^{13}$	551.07	$x = 0.340$	562.35	$x = 0.865$
$V_{\max}^E/(m^3/mol) \times 10^9$	402.82	$x = 0.463$	303.72	$x = 0.314$
$\beta_{s, \max}^E/(1/Pa) \times 10^{13}$	122.59	$x = 0.229$	196.98	$x = 0.285$
$\beta_{s, \text{infl}}^E/(1/Pa) \times 10^{13}$	94.743	$x = 0.409$	150.31	$x = 0.526$
	51.083	$x = 0.741$	100.25	$x = 0.720$
$\kappa_{s, \max}^E/(m^3/Pa \cdot mol) \times 10^{17}$	156.60	$x = 0.243$	230.08	$x = 0.280$
$\kappa_{s, \text{infl}}^E/(m^3/Pa \cdot mol) \times 10^{17}$	126.34	$x = 0.423$	174.90	$x = 0.517$
	77.456	$x = 0.724$	108.79	$x = 0.734$

This corresponds well with IR spectra of alcohol- CCl_4 solutions from which it is evident that most solutions of monohydroxy alcohols, except certain sterically hindered ones, contain at moderate concentrations at least two associated species having different numbers of monomer units [31].

The difference in the association potential of both the isomeric alcohols studied arises most probably from the presence of the methyl group at the second carbon atom of the iso-butanol molecule which prevents to a certain degree the self-association since it may act as a small steric obstacle [25] and may also decrease the polarization of the OH group exerting an inductive effect on the latter. Also other physico-chemical constants collected in Table 5 furnish evidence of the difference in the self-association potential of n- and iso-butanol.

Table 5. Physico-chemical properties for the pure alcohols at 293.15 K

	Boiling point [K]	Freezing point [K]	Saturated vapour pressure [kPa]	Density [kg/m ³]	Viscosity [Pa · s] × 10 ³	Refractive index (n_D)
n-butanol	390.88	183.55	0.60	809.8	2.948	1.3922
iso-butanol	381.04	165.15	1.17	801.9	3.9068	1.3959

Because of the branched carbon chain, the size of the iso-butanol is smaller than that of n-butanol [7]. Thus, in spite of what is observed (Figs. 4, 5 and 6), the molar volume, compressibility and the free path length of pure iso-butanol are expected to be smaller than the corresponding parameters of n-butanol. This discrepancy may be

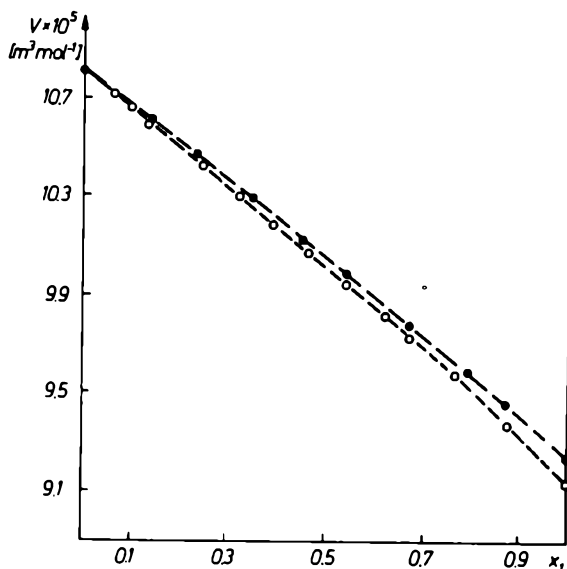


FIG. 4. Molar volumes at 293.15 K. $-\circ-$, $\{x_1 n\text{-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$; $-\bullet-$, $\{x_1 \text{iso-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$. Broken lines were calculated from eq. (6) by the best-fit procedure

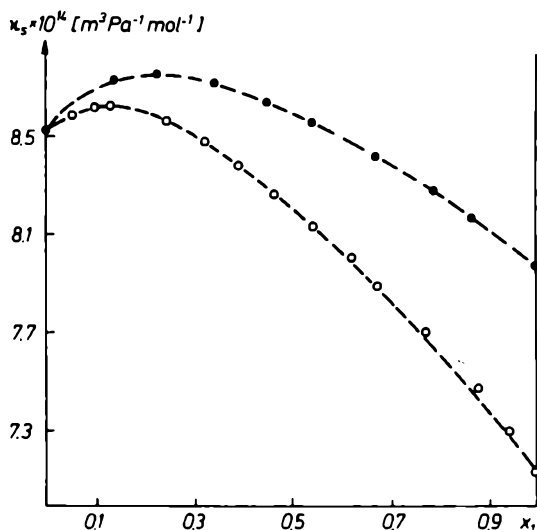


FIG. 5. Isentropic compressibilities at 293.15 K. $-\circ-$, $\{x_1 n\text{-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$; $-\bullet-$, $\{x_1 \text{iso-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$. Broken lines were calculated from eq. (6) by the best-fit procedure

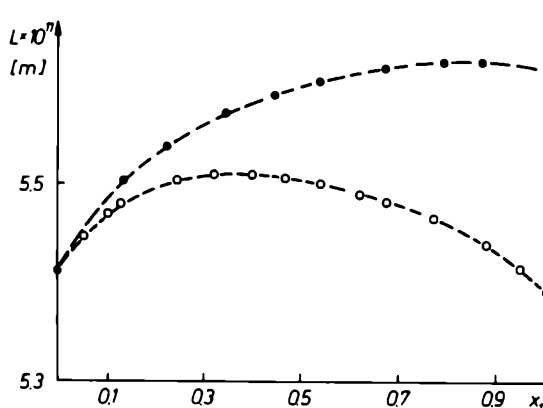


FIG. 6. The free intermolecular lengths at 293.15 K. —○—, $\{x_1 n\text{-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$; —●—, $\{x_1 \text{iso-C}_4\text{H}_9\text{OH} + (1-x_1)\text{C}_6\text{H}_{12}\}$. Broken lines were calculated from eq. (6) by the best-fit procedure

easily explained if, in accordance with the above discussion, a smaller degree of self-association in iso-butanol is assumed. That difference in the self-association potential also makes of the iso-butanol solution the excessive volume increase more slowly when the associates gradually break-down with increasing dilution (Fig. 1).

The results of our measurements, in connection with the literature information, lead to the conclusion that the acoustic and thermodynamic properties of the liquid systems studied are determined mainly by the extent of hydrogen bondings occurring between the molecules of the associating component, i.e. by the "chemical nature" of the alcohols, while the "physical" properties, i.e. the Van der Waals interactions and the space-filling ability, seem to be of lower significance. The results also constitute strong evidence that, despite the anticipation arising from the Jacobson's model, the increase in self-association does not increase the compressibility, but, on the contrary, makes it become smaller than in a corresponding hypothetical non-associated liquid in accordance with the considerations given in [17].

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