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ULTRASONIC AND THERMODYNAMIC EFFECTS OF SELF-ASSOCIATION OF ALIPHATIC ALCOHOLS IN CYCLOHEXANE
III. SECONDARY AND TERTIARY BUTANOLS

K. BEBEK, E. GRZYWNA and S. ERNST

Silesian University, Institute of Chemistry,
(Szkolna 9, 40-006 Katowice, Poland)

The ultrasound velocities in and densities of mixtures of cyclohexane with 2-butanol

$$\{x_1 \sec -C_4H_9OH + (1-x_1)C_6H_{12}\}$$

and with 2-methyl-2-propanol

$$\{x_1 \text{ tert } - C_4H_9OH + (1-x_1)C_6H_{12}\}$$

have been measured at 293.15 K. The adiabatic compressibility coefficients, $\beta_s = -1/V(\partial V/\partial p)_s$, and compressibilities, $\kappa_s = -(\partial V/\partial p)_s$, as well as the excess molar volumes, V^E, and free intermolecular lengths, L, were determined in the whole concentration range for both the systems studied. Using the measurement results in connection with literature data, the isothermal compressibility coefficients, $\beta_T = -1/V(\partial V/\partial p)_T$, and isochoric molar heat capacities, C_v, for the pure components were calculated. The above values were used to estimate the excess adiabatic compressibilities, κ_s^E, of the mixtures under test accoring to the thermodynamically rigorous definitions recommended by Benson *et al.* The dependences of those excess functions on the mixture composition, reproduced by the Redlich–Kister equations, were compared and discussed in terms of the free intermolecular length and other factors affecting the self-association of alcohols (molecular geometry of the hydro-carbon chain and position of the OH group).

1. Introduction

Solutions of aliphatic alcohols in cyclohexane have been the subject of detailed studies in our laboratory. The thermodynamic and acoustic properties of binary mixtures of isomers of primary butanols and primary and tertiary pentanols with cyclohexane as a common component were reported in our previous papers of this series [1, 2]. From the results, in connection with the literature information, it could be concluded that the volume and compressibility effects of mixing of alcohols with cyclohexane are determined mainly by the intermolecular hydrogen bondings of the alcohol molecules (i.e. by their self-association potential) that result in molecular aggregates of different lenghts and/or branching of the alkyl chains, these factors determining predominantly the space-filling in the solution. In particular, it has been found that the length of the hydrocarbon chain and the position of the OH group are also the main factors determining the self-association capability of the aliphatic alcohols [1–5] and that the formation of alcohol oligomers through hydrogen-bondings may be inhibited by steric hindrances and/or by the physical dipole-dipole interactions between the monomers and multimers as well as by structural changes of the non-polar solvent accompanying the solvation process [6, 7].

In order to complete the previous results, we report in this paper the excess molar volumes, V^E, excess adiabatic compressibilities, κ_s^E, and free intermolecular lengths, L, for binary mixtures of cyclohexane with 2-butanol and 2-methyl-2-propanol at 293.15 K.

The molar volumes, V, and the adiabatic compressibilities, κ_s, as well as the free intermolecular lengths, L, for the pure components (except those of 2-methyl-2-propanol which at 293.15 K is a solid) and mixtures were obtained from density and ultrasonic velocity measurements. Studying both the mixtures of alcohols with the rather inert non-polar solvent (cyclohexane), we focused our attention on the possible multimerization of the alcohols by intermolecular hydrogen bondings and other factors determining their self-association as well as on the solvation of the alcohols.

2. Experimental

2-Butanol and cyclohexane (POCh Gliwice, Poland, analytical grade) were stored over molecular sieves (POCh Gliwice, type A3 and A4) and were partially purified by fractional distillation. The purified liquids were refluxed over calcium oxide to remove residual water and degassed under vacuum. The removal of water was checked by measurements of the densities and refractive indices (2-butanol: 806.8 $\mathrm{kg\,m^{-3}}$, 1.3961; cyclohexane – product No. 1: 778.3 $\mathrm{kg\,m^{-3}}$, 1.4265; cyclohexane – product No. 2: 778.8 $\mathrm{kg\,m^{-3}}$, 1.4265).

2-Methyl-2-propanol (UbiChem Eastleigh, England, analytical grade) was used without further purification (its freezing point was about 26° C, the water content was specified to be less than 0.05%).

The binary mixtures were prepared by mixing weighed portions of the pure components immediately before the measurements. The error in the mole fraction of the binaries was less than 3×10^{-5}.

The densities of the 2-butanol/cyclohexane system were determined by the Kohlrausch method described in [1]. The temperature fluctuations in the sample cell did not exceed ± 0.01 K and the accuracy of the density determination was estimated to be better than 0.1 $\mathrm{kg\,m^{-3}}$. The densities of 2-methyl-2-propanol/cyclohexane system were measured pycnometrically (bicapillary pycnometer, details can be found in [8]) and by using a vibrating tube densimeter (MG 2, Unilab). The temperature was (293.15 ± 0.01) K in both cases. The results obtained by these two methods were compared with each other (the differences did not exceed ± 0.03 $\mathrm{kg\,m^{-3}}$) and the accuracy was assumed to be better than 0.05 $\mathrm{kg\,m^{-3}}$.

All the weighings, i.e. those before mixing the components and during the density measurements, were made by an analytical balance WA-35 (ZMP Gdańsk), with the resolution of 10^{-5} g, and reduced to vacuum.

The ultrasound velocity measurements were carried out by the sing-around method using an equipment designed and constructed in our laboratory (the ultrasonic group velocity was measured at a frequency of about 4 MHz) [9, 10]. Purified water (electrolytic conductivity $1.8 \times 10^{-4}\,\Omega^{-1}\mathrm{m}^{-1}$ at 293.15 K) was used as standard for calibration and the ultrasound velocities in water were calculated from the polynomial of Del Grosso and Mader [11]. The precision of ultrasonic velocity measurements depended mainly on the difference between the measured velocity and that in water used as standard for calibration and varied from 0.05 to 0.30 $\mathrm{m\,s^{-1}}$. The sample cell was kept in a water bath and heated by a proportional-integrating temperature controller (Unipan 660) and cooled by water from another thermostat. The temperature deviations did not exceed ±0.005 K. The accuracy of the ultrasound velocity measurement was estimated to be better than ±0.5 $\mathrm{m\,s^{-1}}$ [9].

3. Measurement results

The ultrasound velocities in and the densities of both the binary liquid systems were measured at 293.15 K. The 2-butanol/cyclohexane system was investigated in the whole concentration range and the 2-methyl-2-propanol/cyclohexane one only up to 0.9113 because of the phase transition occurring at higher alcohol concentrations. Therefore the corresponding numerical values of the ultrasound velocity and the density for the pure 2-methyl-2-propanol were estimated by a best-fit extrapolation procedure.

The measured ultrasound velocities and densities together with those extrapolated for 2-methyl-2-propanol are given in Table 1.

Table 1. Ultrasound velocities and densities for the butanol (1) + cyclohexane (2) mixtures at 293.15 K.

x_1	c [$\mathrm{m\,s^{-1}}$]	ϱ [$\mathrm{kg\,m^{-3}}$]	x_1	c [$\mathrm{m\,s^{-1}}$]	ϱ [$\mathrm{kg\,m^{-3}}$]
$\{x_1\,\mathrm{sec}-\mathrm{C_4H_9OH} + (1-x_1)\mathrm{C_6H_{12}}\}$			$\{x_1\,\mathrm{tert}-\mathrm{C_4H_9OH} + (1-x_1)\mathrm{C_6H_{12}}\}$		
0.0	1281.0	778.8(8)	0.0	1281.6	778.3(3)
0.0032	1280.3	778.7(2)	0.0037	1280.2	778.3(3)
0.0062	1279.1	778.7(6)	0.0066	1278.8	778.1(9)
0.0092	1277.8	778.6(4)	0.0083	1277.9	778.0(9)
0.0114	1277.0	778.6(4)	0.0097	1277.3	778.0(3)
0.0374	1270.3	778.6(3)	0.0202	1273.6	777.9(7)
0.0585	1266.1	778.5(6)	0.0301	1270.5	777.6(5)
0.0877	1261.3	778.9(1)	0.0632	1262.2	777.3(3)
0.1273	1255.6	779.1(7)	0.0922	1256.1	777.3(3)
0.2814	1237.9	781.3(1)	0.1221	1249.5	777.0(1)
0.5047	1229.6	787.5(3)	0.2616	1222.2	776.5(2)
0.8252	1225.8	799.3(2)	0.5263	1177.3	776.9(8)
1.0	1231.9	806.8(4)	0.8149	1153.7	781.3(7)
			0.9113	1146.9	782.7(5)
			1.0	1144.5*	784.1(7)*

* extrapolated values

The molar volumes, V, and excess molar volumes, V^E, of the pure liquids and mixtures were calculated from the measured densities, ϱ, by the following equations:

$$V = (x_1 M_1 + x_2 M_2)/\varrho, \tag{1}$$

$$V^E = V - V^{\mathrm{id}}, \tag{2}$$

where x is the mole fraction and M the molar mass of the mixed components (the indices 1 and 2 refer to the aliphatic alcohol and to the cyclohexane, respectively) and V^{id} denotes the molar volume of the hypotetical thermodynamically ideal mixture:

$$V^{\mathrm{id}} = x_1 V_1 + x_2 V_2 . \tag{3}$$

The adiabatic compressibility coefficients, β_s, were calculated from the measured densities and ultrasound velocities, c, by the Laplace equation:

$$\beta_s = 1/(\varrho c^2) \tag{4}$$

and have been used to determine the isentropic compressibilities ($\kappa_s = -(\partial V/\partial p)_s$):

$$\kappa_s = V\beta_s . \tag{5}$$

The isothermic compressibility coefficients, β_T, and the molar heat capacities at the constant volume, C_v, for the pure components were calculated from the following equations:

$$\begin{aligned} \beta_T &= \beta_s + \alpha^2 VT/C_p , & (6)\\ C_v &= C_p\beta_s/\beta_T & (7) \end{aligned}$$

using the coefficients of thermal expansion ($\alpha = 1/V(\partial V/\partial T)_p$), estimated from the temperature dependence of density data (measured at 293.15 K and available in the literature for neighbouring temperatures [12]) and the isobaric heat capacities, C_p, taken as well from literature [13].

The values calculated for the pure components from Eqs. (6) and (7) together with the coefficients of thermal expansion and the isobaric heat capacities (taken from [13]) are collected in Table 2.

Table 2. Isothermic compressibility coefficients, isochoric and isobaric molar heat capacities and coefficients of thermal expansion for the pure components at 293.15 K.

	cyclohexane	sec $-C_4H_9OH$	tert $-C_4H_9OH$
β_T [Pa^{-1}] × 10^{12}	1091.1	963.7	1191.2
C_v [J mol^{-1}K^{-1}]	112.2	168.5	183.9
C_p [J mol^{-1}K^{-1}]	156.5	198.8	225.0
α [K^{-1}] × 10^3	1.38	1.01	1.33

The excess isentropic compressibilities, κ_s^E, were calculated using the following relation:

$$\kappa_s^E = \kappa_s - V^{\mathrm{id}}\beta_s^{\mathrm{id}}, \tag{8}$$

where the adiabatic compressibility coefficients related to the ideal mixtures, β_s^{id}, as well as the corresponding values of the isothermic compressibility coefficients, β_T^{id}, were obtained from the thermodynamically rigorous definitions recommended by DOUHERET *et al.* [14, 15] and BENSON *et al.* [16]:

$$\beta_s^{\mathrm{id}} = \beta_T^{\mathrm{id}} - (\alpha^{\mathrm{id}})^2 V^{\mathrm{id}} T / C_p^{\mathrm{id}}, \tag{9}$$

$$\beta_T^{\mathrm{id}} = (1/V^{\mathrm{id}})(x_1 V_1 \beta_{T,1} + x_2 V_2 \beta_{T,2}), \tag{10}$$

where α^{id} and C_p^{id} are given by:

$$\alpha^{\mathrm{id}} = (1/V^{\mathrm{id}})(x_1 V_1 \alpha_1 + x_2 V_2 \alpha_2), \tag{11}$$

$$C_p^{\mathrm{id}} = x_1 C_{p,1} + x_2 C_{p,2}\,. \tag{12}$$

Thus, the excess molar volumes as well as the excess adiabatic compressibilities have been estimated using the states of the pure components under the measurement conditions as standard states. In this way a common reference state has been chosen for all the quantities determined.

According to JACOBSON [17], the free intermolecular lengths, L, were obtained, based on the relation to the adiabatic compressibility coefficient, from the following relationship:

$$\beta_s = k_\beta L^{2.4}, \tag{13}$$

where k_β is an empirical constant slightly dependent on the temperature and given for associated and nonassociated liquids in [18].

Table 3. The A_j parameters and mean standard deviations s of the least squares fit by Eqs. (14) and (15) for the butanol (1) + cyclohexane (2) mixtures at 293.15 K.

F or F^E	A_1	A_2	A_3	A_4	A_5	s
	$\{x_1 \sec - C_4H_9OH + (1 - x_1)C_6H_{12}\}$					
V [m^{3}mol^{-1}] × 10^6	108.11	−13.84	−2.48	–	–	0.02
β_s [m^{2}N^{-1}] × 10^{12}	783.1	339.1	−746.6	−747.5	−306.3	0.22
κ_s [m^{3}Pa^{-1}mol^{-1}] × 10^{16}	847.5	202.5	−507.4	209.3	–	0.58
L [m] × 10^{12}	54.31	33.48	−50.73	20.93	–	0.07
V^E [m^{3}mol^{-1}] × 10^7	22.24	12.96	6.07	1.81	–	0.04
κ_s^E [m^{3}Pa^{-1}mol^{-1}] × 10^{15}	6.32	7.99	9.18	0.81	–	0.03
	$\{x_1 \mathrm{tert} - C_4H_9OH + (1 - x_1)C_6H_{12}\}$					
V [m^{3}mol^{-1}] × 10^6	108.15	−11.52	−2.17	–	–	0.01
β_s [m^{2}N^{-1}] × 10^{12}	784.1	351.2	−150.5	−11.6	–	0.45
κ_s [m^{3}Pa^{-1}mol^{-1}] × 10^{16}	848.2	279.5	−145.8	−147.1	85.4	0.51
L [m] × 10^{12}	54.25	43.59	−29.89	5.47	–	0.05
V^E [m^{3}mol^{-1}] × 10^7	21.93	−0.13	−3.78	19.78	–	0.09
κ_s^E [m^{3}Pa^{-1}mol^{-1}] × 10^{15}	10.97	−3.11	−23.89	4.55	35.89	0.02

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

$$F = \sum_{j=1}^{n} A_j \, x_1^{j-1}. \tag{14}$$

They were fitted to the experimental results by the method of unweighted least squares.

The composition dependence of the excess thermodynamic functions, V^E and κ_s^E, have been estimated smoothing the experimental values by the Redlich - Kister equation:

$$F^E = x_1(1 - x_1) \sum_{j=1}^{n} A_j (1 - 2x_1)^{j-1}. \tag{15}$$

The parameters A_j of the equations (14) and (15) and the corresponding mean standard deviations, s, are given in Table 3.

4. Discussion and conclusions

As shown in Fig. 1 the molar volumes of both systems studied decrease monotonically, although not linearly, with increasing concentration of alcohol, while the densities of the 2-methyl-2-propanol/cyclohexane mixture show a minimum at about $x_1 = 0.25$ (Table 1). Also the ultrasonic velocity in both the binaries decreases as the alcohol concentration increases, but for the mixtures of 2-butanol, a minimum appears in the alcohol-rich

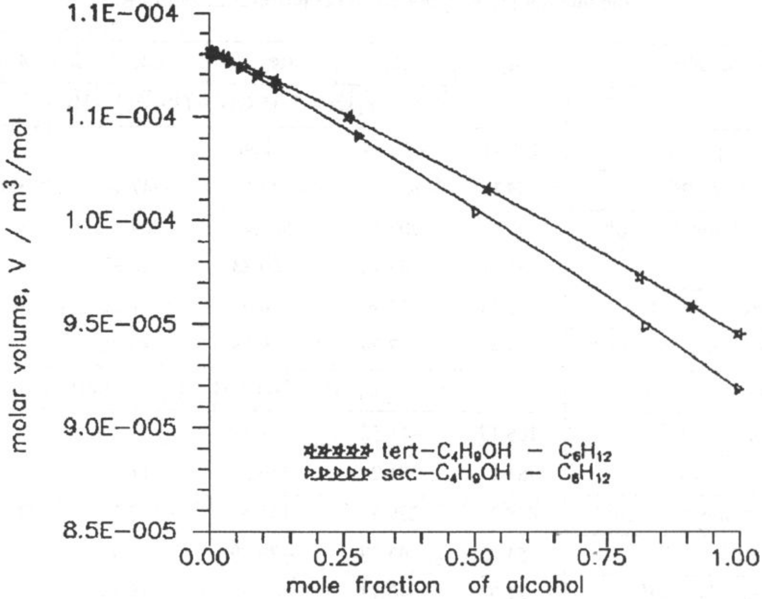

Fig. 1. Molar volumes of mixtures of secondary and tertiary butanols with cyclohexane at 293.15 K. Curves represent the best-fit values calculated from equation (14) with the coefficients given in Table 3.

region ($x_1 \approx 0.8$). The observed concentration dependences are doubtlessly related to the complex variations of the thermodynamic properties of the systems under test.

The self-association of pure alcohols, including that occurring in solutions in non-polar solvents, was discussed rather extensively in our earlier paper [1] in that the stronger self-association of n-butanol in comparison with that of iso-butanol was emphasized. Whatever the particular multimeric structures ("open" entities, with simple or branched multimeric hydrocarbon chains, or "closed" ones, the latters having possibly chains when a terminal OH group and an intermediate monomer are engaged in the "closing" reaction), the results of our measurements indicate clearly that the association potential decreases with increasing branching of the alcohol molecule.

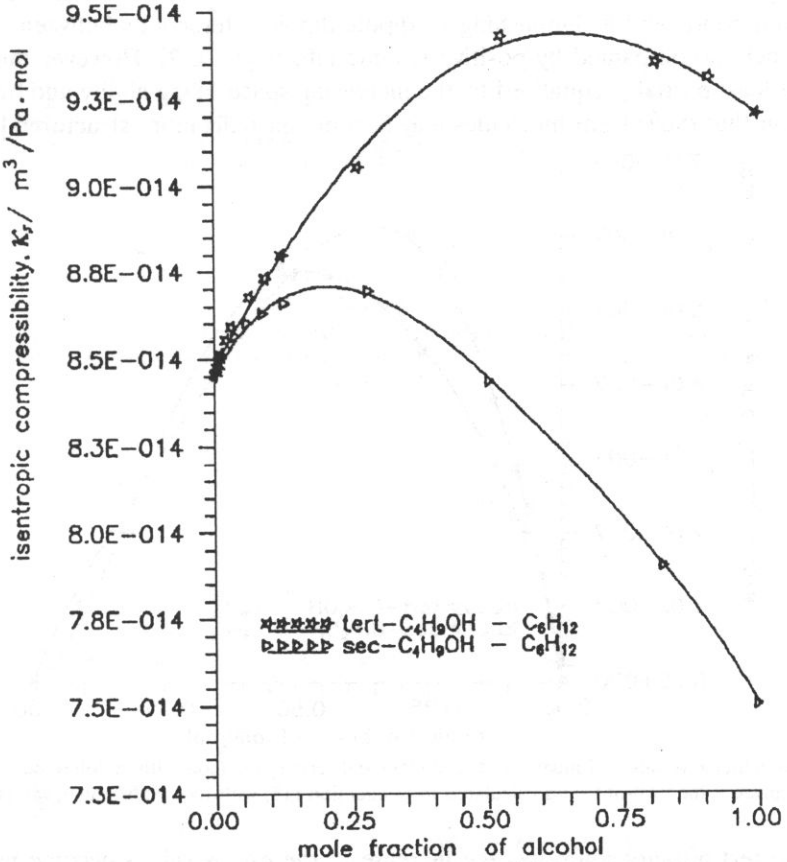

Fig. 2. Isentropic compressibilities of mixtures of secondary and tertiary butanols with cyclohexane at 293.15 K. Curves represent the best-fit values calculated from equation (14) with the coefficients given in Table 3.

For the pure butanol isomers, the molar volumes and the free intermolecular lengths, calculated from Eq. (13), increase in the sequence n – B < iso – B < sec – B < tert – B and in a very similar sequence (n – B < sec – B < iso – B < tert – B) increase the isentropic and isothermic compressibility coefficients (a similar relation of the properties of the n- and tert-pentanols was observed [2]). The isentropic compressibilities of the sec- and tert-butanols show the same sequence (Fig. 2). These sequences may result either from the decreasing space-filling ability when the alcohol molecules become more ball-shaped or from the decrease in the self-association due to steric obstacles. However, the evidently larger thermal expansion coefficients of the tert-butanol and tert-pentanol compared to those of the corresponding secondary alcohols indicate a rather important effect of the formation of hydrogen bonds (self-association) on the properties of the pure alcohols.

The positive excess molar volumes, excess compressibilities and excess compressibility coefficients are doubtlessly due to the self-association of the butanol isomers when dissolved in cyclohexane: the dilution of the alcohols with cyclohexane results in the rupture of hydrogen bonds and a diminishing of dipole-dipole interactions between monomers and oligomers accompanied by positive volume effects [1–3, 7]. However those effects may be, at least partially, equalized by the increasing space-filling ability and by solvation processes in that the solvent molecules may become partially more structured [6, 19, 20].

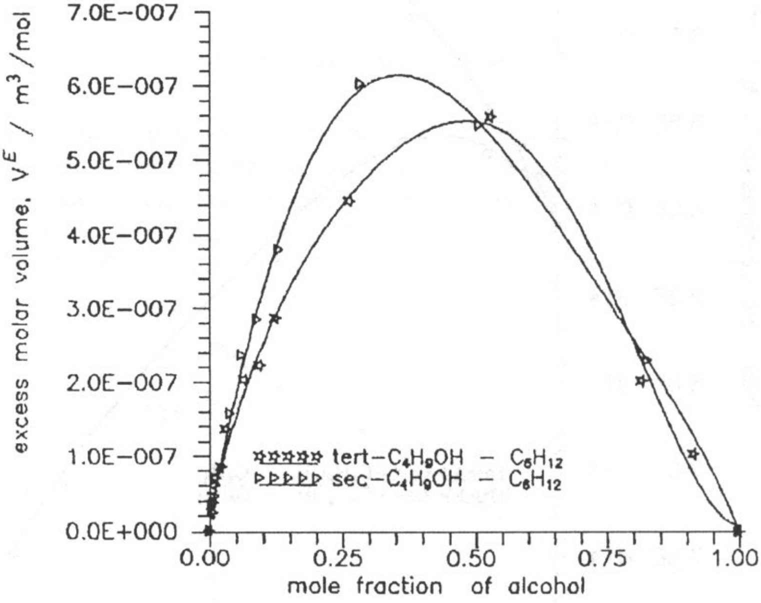

Fig. 3. Excess molar volumes of mixtures of secondary and tertiary butanols with cyclohexane at 293.15 K. Curves represent the best-fit values calculated from equation (15) with the coefficients given in Table 3.

For the tert-butanol solutions, the increase in the excess values become more rapid with increasing cyclohexane concentration and the maxima appear at higher alcohol concentrations suggesting a lower capability of self-association of the tert-butanol in comparison with that of the sec-butanol (Figs. 3 and 4) because of steric hindrances to the formation of intermolecular hydrogen bonds. Also the mean free intermolecular length increases slowly with increasing dilution of the sec-butanol (Fig. 5), most probably, because of the gradual breakage of the butanol oligomers. For the tert-butanol solutions, the mean free intermolecular length decreases monotonically with the increasing cyclohexane

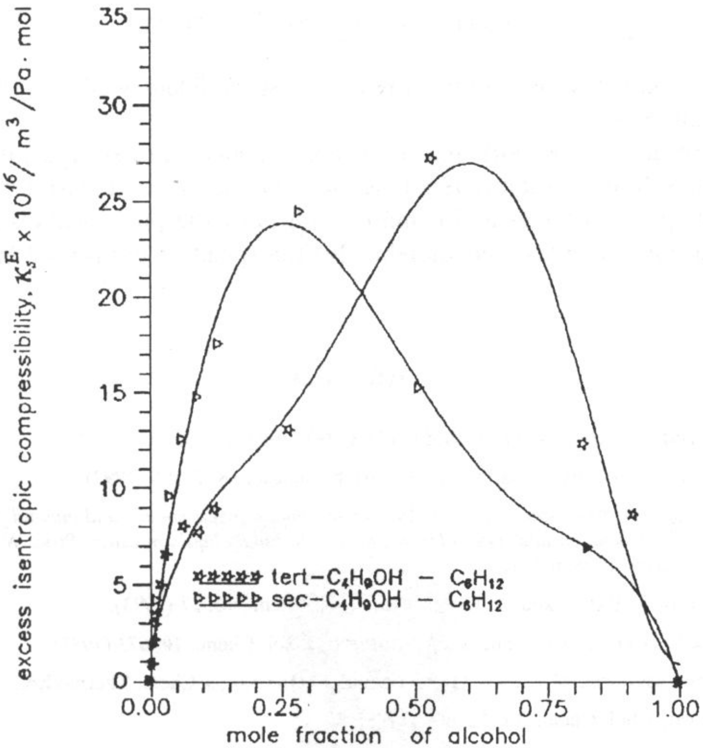

Fig. 4. Excess isentropic compressibilities of mixtures of secondary and tertiary butanols with cyclohexane at 293.15 K. Curves represent the best-fit values calculated from equation (15) with the coefficients given in Table 3.

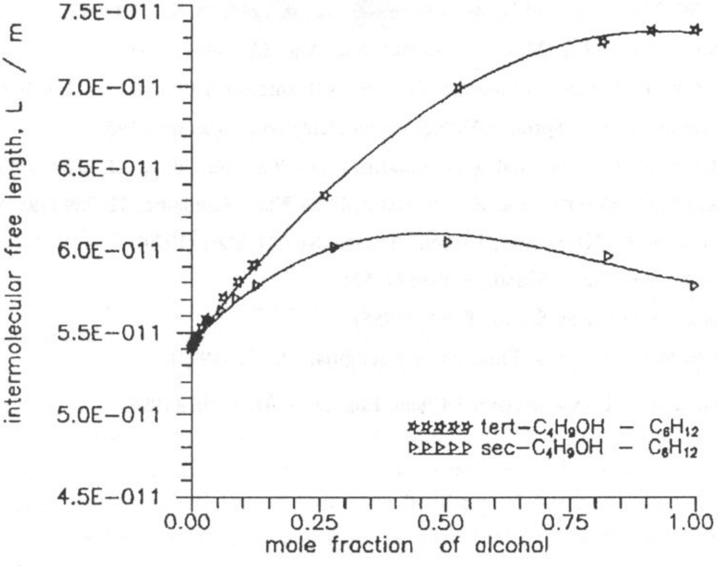

Fig. 5. The free intermolecular lengths for mixtures of secondary and tertiary butanols with cyclohexane at 293.15 K. Curves represent the best-fit values calculated from equation (14) with the coefficients given in Table 3.

concentration (Fig. 5) because of the more perfect space-filling, while the self-association plays a negligible role.

From the results of this work and from those obtained earlier [1, 2], it may be concluded that the self-association potential is the main factor, or at least a very important one, determining the volumes and compressibilities of the pure alcohols and their solutions in non-polar solvents, and thereby also the speed of ultrasound in those liquid systems.

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