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THERMOCHEMICAL PROPERTIES OF BINARY LIQUID SYSTEMS *N*-ALCOHOL/CYCLOHEXANE DETERMINED BY AN ACOUSTIC METHOD

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The results of ultrasonic and volumetric measurements were used to obtain the excess molar enthalpies for binary liquid mixtures containing cyclohexane, as the common component, and primary aliphatic alcohols (*n*-propanol, *n*-butanol and *n*-pentanol) at 293.15 K. The excess molar enthalpies of those systems are positive in the whole concentration range and show evidently different concentration dependences. The excess internal pressures of the liquid mixtures, determined in a few different ways, are negative for all the systems. The behaviour of those excesses are discussed in terms of intermolecular interactions in the binaries and the self-association potential of the alcohols.

1. Introduction

The molecules of aliphatic alcohols are highly associated by hydrogen bondings [1, 2]; the self-association in non-polar solvents results in the formation of multimeric ring or chain structures, i.e. the oligomers appearing in the solution are either "open" or "closed" entities [3-7]. Dielectric studies indicate that those various multimeric structures exist in the solution in different proportions depending on the alcohol concentration, its ability to hydrogen-bond formation and the van der Waals type molecular interactions of the non-polar solvent with the alcohol contained in oligomers that are constantly reorganizing [8-12].

The most reliable values of the enthalpies of hydrogen bond formation constants were found by calorimetric measurements in infinitely dilute solutions [13]. The enthalpy of the hydrogen bond formation in solutions of *n*-alcohols in *n*-heptane (23.5 ± 0.5 kJ/mol), determined calorimetrically, is almost independent of the lengths of the hydrocarbon chain of the aliphatic alcohol [14, 15].

Thermochemical data for aliphatic alcohol solutions (excess molar enthalpy and isobaric heat capacity) determined by calorimetric methods (that are sensitive to changes in the hydrogen bond energy) do not show even a qualitative agreement with those obtained by other thermodynamic methods [16]; the latter seem to reflect variations in the number of hydrogen bonds. Also, the temperature dependences of the thermochemical

quantities of pure aliphatic alcohols and their solutions are considerably more complex than for other organic liquids [17].

The thermochemical data differentiate evidently the homologous series of aliphatic alcohols since they depend on the branching of the alkyl chains [18]; the enthalpy of evaporation of primary alcohols, including those with non-branched hydrocarbon chains (*n*-alcohols), increase with increasing length of the alkyl chain, while for other alcohols the dependence on the chain length is opposite.

In this paper, we report the concentration dependences of the excess molar enthalpy, $H^E = H^E(x)$, at 293.15 K for binary solutions of *n*-propanol, *n*-butanol and *n*-pentanol in cyclohexane determined from internal pressure values, the latter being obtained in three different ways from ultrasonic and volumetric measurements [19] and the well-known thermodynamic relationships.

2. Experimental

The components, all of analytical grade, were obtained from POCh Gliwice (Poland) and purified by fractional distillation and dried as described previously [19, 20]. The binary mixtures were prepared by weighing immediately before the measurements (the accuracy of the mole fraction was better than 0.25×10^{-4} and the residual water content was less than 0.025%).

The ultrasonic group velocity was measured at a frequency of about 4 MHz by the ring-around method with an accuracy better than 0.5 m/s (the precision of the ultrasonic velocity measurements varied from 0.05 to 0.30 m/s); the measurement device (SA-V/Z) was designed and constructed in our laboratory [21–23].

The densities of the systems under test were determined by the Kohlrausch method with an accuracy better than 0.1 kg/m^3 . The methods of measurements and calibrations have been already published [19, 20, 24].

The thermal stability of the sample at $293.15 \pm 0.01 \text{ K}$ was ensured during the ultrasonic velocity and density measurements by a water bath that was heated by a proportional-integrating temperature controller (Unipan 660, Poland) and cooled by water from another thermostat.

3. Measurement results

The molar volumes, V , and excess molar volumes, V^E , of the binary liquid systems were calculated from the measured density, ρ , using the following equations:

$$V = (x_1 M_1 + x_2 M_2) / \rho, \quad (1)$$

$$V^E = V - (x_1 V_1 + x_2 V_2), \quad (2)$$

where x — mole fraction of the alcohol, M_i — molar mass of the components, the indices “1” and “2” refer to the alcohol (associating component) and to cyclohexane (non-polar component), respectively.

The internal pressure, \mathbb{P} , was calculated from the following relationship [25–27]:

$$\mathbb{P} = 2^{1/6} RT / (2^{1/6} V - 2rN^{1/3} V^{2/3}), \quad (3)$$

where R , T , N and r are the gas constant, temperature in K, Avogadro's number and mean molecular radius, respectively.

The mean molecular radii, r , were obtained, according to SCHAAFFS [28], from the density, ρ , and ultrasound velocity, c :

$$r = \left\{ 3M / (16\pi\rho N) [1 - \gamma RT / (Mc^2) ((1 + Mc^2 / (3\gamma RT))^{1/2} - 1)] \right\}^{1/3}, \quad (4)$$

where $\gamma = C_p / C_v$ is the ratio of the isobaric heat capacity to the isochoric one; this ratio can be determined from the isentropic and isothermal compressibility coefficients, β_s and β_T , using the well known thermodynamic relation $\beta_T / \beta_s = C_p / C_v$.

The isentropic and isothermal compressibility coefficients were calculated from the following equations:

$$\beta_s = 1 / (\rho c^2), \quad (5)$$

$$\beta_T = \beta_s + \alpha^2 VT / C_p, \quad (6)$$

using the isobaric thermal expansion coefficient, α , estimated from the temperature dependence of the densities (measured at 293.15 K in this work and available in the literature for neighbouring temperatures [30–32]) and the isobaric heat capacities, C_p , taken from the literature [30–33].

The molar volumes, molecular radii, coefficients of isothermal compressibility and the cubic thermal expansion coefficients together with the ratio of isobaric and isochoric heat capacities, γ , for the pure components at 293.15 K are collected in Table 1.

Table 1. Molar volumes, molecular radii, isothermal compressibility coefficients, cubic thermal expansion coefficients and the ratios of isobaric to isochoric heat capacities for the pure components at 293.15 K.

	V [m ³ mol ⁻¹] × 10 ⁵	r [m] × 10 ¹⁰	β_T [Pa ⁻¹] × 10 ¹²	α [kK ⁻¹]	$\gamma = C_p / C_v$
<i>n</i> -propanol	7.472	1.89 (8)	1087.5	0.99	1.18
<i>n</i> -butanol	9.145	2.03 (6)	891.3	0.94	1.14
<i>n</i> -pentanol	10.821	2.15 (7)	867.5	0.92	1.18
cyclohexane	10.815	2.15 (2)	1091.1	1.216	1.39

The internal pressures for the pure components and binaries were obtained from the estimated coefficients of thermal expansion and the isothermal compressibility by the following equation [27, 34]:

$$\mathbb{P} = T\alpha / \beta_T. \quad (7)$$

Because of the lack of α^E data of sufficient accuracy for the binary mixtures, the widely accepted assumption $\alpha^E = 0$ was made. Thus

$$\alpha \approx \alpha^{\text{id}} = (1/V^{\text{id}})(x_1 V_1 \alpha_1 + x_2 V_2 \alpha_2), \quad (8)$$

where $V^{\text{id}} = x_1 V_1 + x_2 V_2$.

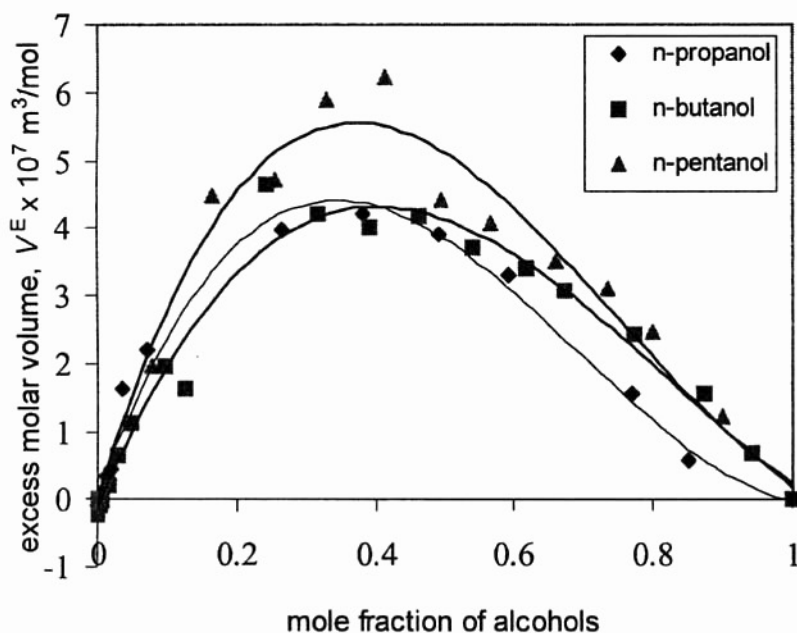


Fig. 1. Excess molar volume isotherms for the binary mixtures of alcohols with cyclohexane at 293.15 K. Points — experimental values.

However, for the binary mixtures under test, the volume effects of mixing are different from zero, $V^E \neq 0$, (the $V^E = V^E(x_1)$ isotherms are shown in Fig. 1) and the excess α^E is most often not small enough to be neglected. The reliable expansion coefficient,

$$\alpha = \alpha^{\text{id}} + \alpha^E, \quad (9)$$

can be calculated from the definition [33]:

$$\alpha^E = (1/V)[(\partial V^E/\partial T)_p - V^E \alpha^{\text{id}}] \quad (10)$$

using the $(\partial V^E/\partial T)_p$ values calculated as follows [33]:

$$(\partial V^E/\partial T)_p = -(\partial V/\partial T)_p^{\text{id}}(V^E/V^{\text{id}}) = -V^E \alpha^{\text{id}}. \quad (11)$$

Thus, the internal pressure can be obtained either from Eq. (3), or from Eqs. (7) and (8) (assuming $\alpha^E = 0$) or (7) and (9) (using Eqs. (10) and (11)).

The excess molar enthalpies of the solutions under test were determined using the internal pressures calculated in those three different ways and assuming that the mixing is not accompanied by a significant entropy effect [34]:

$$H^E = x_1 \bar{V}_1 + x_2 \bar{V}_2 - \bar{V}. \quad (12)$$

The isotherms of the excess molar enthalpy (calculated in the three ways described above) vs. mole fraction of alcohol ($H^E = H^E(x_1)$) are shown in Figs. 2–4, where the points represent values calculated from Eq. (12) using either Eq. (3) (Fig. 2) or Eqs. (7) and (8) (Fig. 3), or (7) and (9) (Fig. 4).

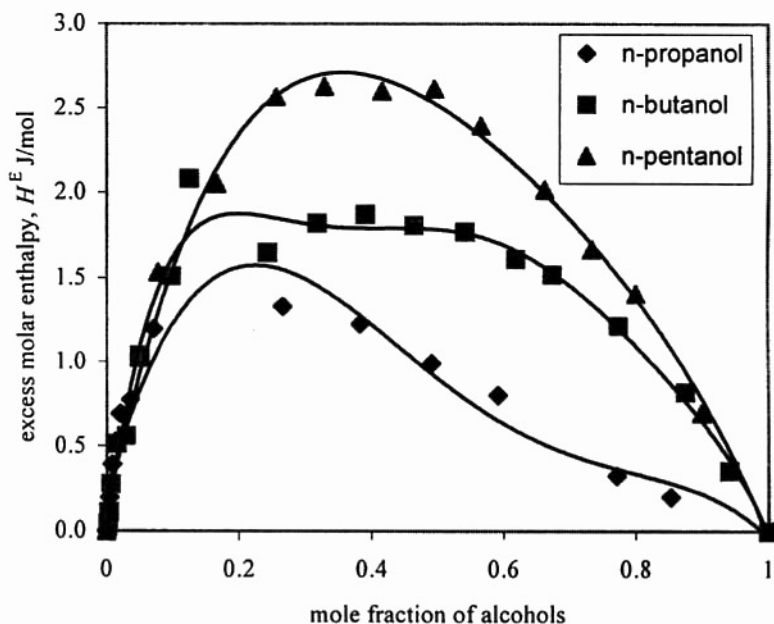


Fig. 2. Excess molar enthalpy isotherms for the binary mixtures of alcohols with cyclohexane at 293.15 K. Points — values calculated from Eq. (3).

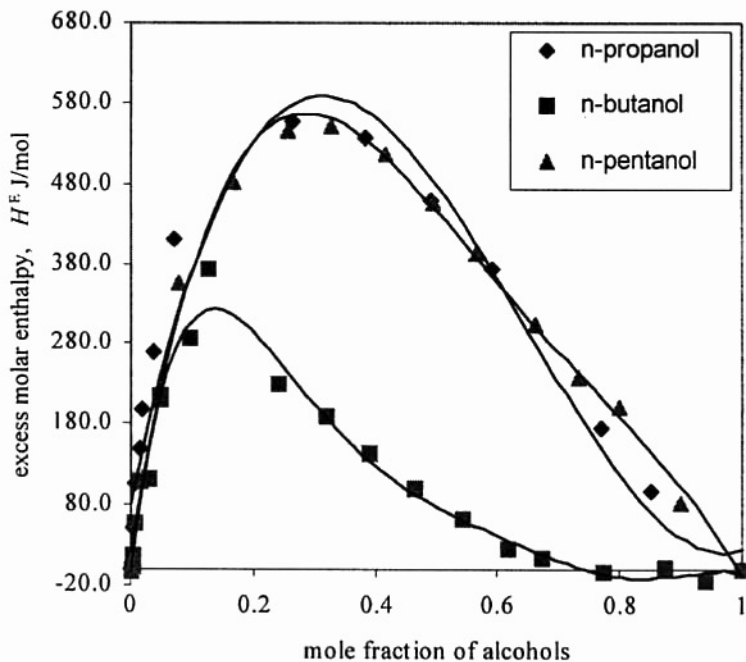


Fig. 3. Excess molar enthalpy isotherms for the binary mixtures of alcohols with cyclohexane at 293.15 K. Points — values calculated from Eq. (12) in connection with Eqs. (7) and (8).

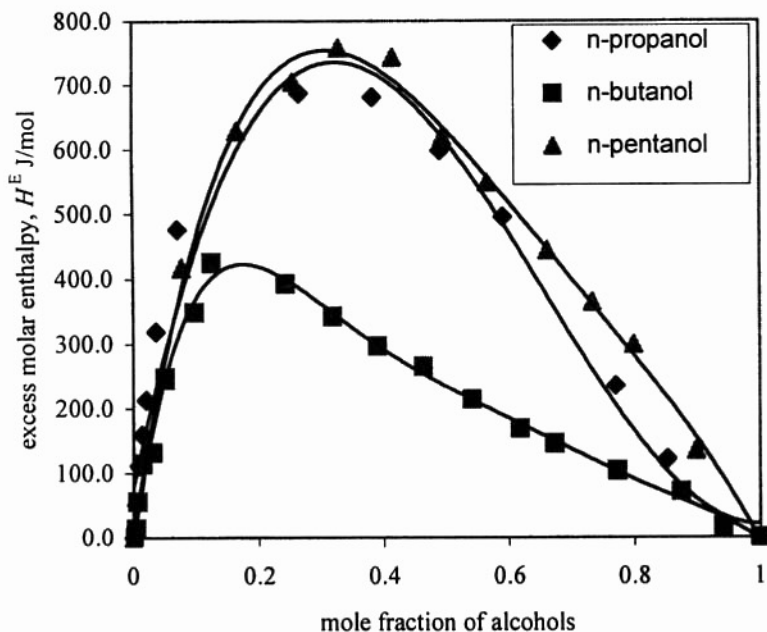


Fig. 4. Excess molar enthalpy isotherms for the binary mixtures of alcohols with cyclohexane at 293.15 K. Points — values calculated from Eq. (12) in connection with Eqs. (7) and (9).

4. Discussion and conclusions

The excess molar volumes for all the systems studied are positive over the whole concentration range and show a similar concentration dependence with a characteristic asymmetry; However, their maximum values are slightly different (Fig. 1). Dilution of the alcohols with cyclohexane results in a gradual decrease of the number of associated species. A more loosely packing of the molecules in solution than in the pure liquids seems to be likely; the solution should be therefore more compressible.

The excess molar enthalpies of the binary mixtures under test, irrespective of how they were determined, are also positive over the entire composition range and show concentration dependences that differ evidently in magnitude and asymmetry (Figs. 2–4).

The minima of the excess internal pressures correlate clearly with the magnitude of the internal pressures of the pure alcohols and their capability of association by hydrogen bonds [19, 20].

The isotherms of $H^E = H^E(x_1)$, calculated from the internal pressures obtained from Eq. (3), increase with increasing length of the hydrocarbon chain of the associating component (alcohol) of the mixture (Fig. 2).

The isotherms of $H^E = H^E(x_1)$ calculated from Eqs. (12) and (7) (Figs. 3 and 4) show a sequence inconsistent with the hydrocarbon chain length of the alcohols. For the *n*-butanol solutions, the excess enthalpies are lower and their maximum appears at

higher cyclohexane concentrations suggesting a higher capability of self-association of this alcohol in comparison with those of primary propanol and pentanol (Figs. 3 and 4).

From inspection of the isotherms $H^E = H^E(x_1)$ in Figs. 3 and 4, one learns that for all the systems investigated the values calculated by assuming $\alpha^E = 0$ (Fig. 3) are by about 15–20% lower than those calculated from Eq. (9), i.e. by taking into account the excess thermal expansion coefficients (Fig. 4).

Furthermore, it is worthy of notice that the excess molar enthalpies estimated from Eqs. (12) and (7), by either assuming $\alpha = \alpha^{\text{id}}$ or applying approximate $\alpha = \alpha^{\text{id}} + \alpha^E$ values, are in good accordance with data determined by other thermochemical methods [35].

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