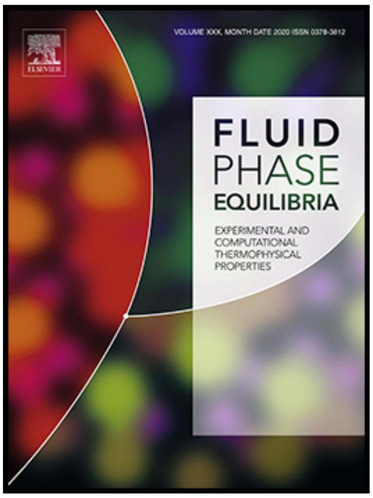

THERMODYNAMICS OF MIXTURES CONTAINING AMINES. XVII. H_m^E and V_m^EMEASUREMENTS FOR BENZYLAMINE+HEPTANE OR+1-ALKANOL MIXTURES AT 298.15 K. APPLICATION OF THE DISQUAC AND ERAS MODELS

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HIGHLIGHTS

- H_m^E data at 298.15 K and 0.1 MPa are reported for the systems benzylamine + heptane, or + $CH_3(CH_2)_{n-1}OH$ (n =1, 3,5,7,10)
- V_m^E data at the same conditions are also given for the benzylamine + heptane mixture.
- Mixtures with *n*-alkanes are characterized by positive deviations from the Raoult's law
- Systems with 1-alkanols show negative negative deviations from the Raoult's law.
- The mixtures have been studied using DISQUAC and ERAS models.

THERMODYNAMICS OF MIXTURES CONTAINING AMINES. XVII. H_m^E and V_m^E MEASUREMENTS FOR BENZYLAMINE + HEPTANE OR + 1-ALKANOL MIXTURES AT 298.15 K. APPLICATION OF THE DISQUAC AND ERAS MODELS

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ABSTRACT

Excess molar enthalpies, $H_{\mathrm{m}}^{\mathrm{E}}$, at 298.15 K and 0.1 MPa have been measured by means of a Tian-Calvet microcalorimeter for the systems benzylamine (phenylmethanamine) + heptane, or + methanol, or + 1-propanol, or + 1-pentanol, or + 1-heptanol, or + 1-decanol. In addition, excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, at the same conditions have been also determined using a densimeter Anton Paar model DSA 5000 for the benzylamine + heptane mixture. The $H_{\mathrm{m}}^{\mathrm{E}}$ of this solution is large and positive since at 298.15 K the system temperature is close to its upper critical solution temperature. Thus, systems with *n*-alkanes show positive deviations from the Raoult's law. The measured $\left|V_{\mathrm{m}}^{\mathrm{E}}\right|$ values are low, indicating the existence of large structural effects. $H_{\mathrm{m}}^{\mathrm{E}}$ values of mixtures involving 1-alkanols are large and negative. That is, interactions between unlike molecules are dominant and the systems are characterized by negative deviations from Raoult's law. It is shown that the enthalpy of the hydrogen bonding between molecules of 1-alkanol and benzyalmine are more negative than those between 1-alkanol molecules. The $V_{\mathrm{m}}^{\mathrm{E}}$ values of the systems with 1-alkanols are also large and negative, and are determined mainly by interactional effects since they increase in line with $H_{\mathrm{m}}^{\mathrm{E}}$ and with the alcohol size. The different contributions to $H_{\mathrm{m}}^{\mathrm{E}}$ have been evaluated. The systems have been studied using the DISQUAC and ERAS models. ERAS describes correctly the $V_{\mathrm{m}}^{\mathrm{E}}$ function. DISQUAC largely improves ERAS results on $H_{\mathrm{m}}^{\mathrm{E}}$ or on excess molar heat capacities at constant pressure for the mixtures with 1-alkanols, which underlines that physical interactions are very relevant in such solutions.

KEYWORDS: benzylamine; *n*-alkanes; 1-alkanols; excess molar functions; DISQUAC; ERAS; interactions

l. Introduction

Along the last years, we have developed a systematic research on 1-alkanol + amine mixtures. In fact, this type of solutions is very interesting since their behaviour is very different depending on the considered amine. Thus, 1-alkanol + linear primary or secondary amine, or + cyclohexylamine systems show large negative deviations from the Raoult's law [1-4], while the corresponding solutions with aniline [1,5] are characterized by positive deviations from the Raoult's law. In addition, structural effects may be highly relevant as, e.g., in 1-alkanol + *N*,*N*,*N*-triethylamine mixtures [4], or in the methanol + aniline solution [1]. Up to now, we have provided volumetric [4,6-12], calorimetric [1,13], phase equilibria [3], viscosimetric [9-11] or dielectric [11,12,14-17] data for this type of solutions, including those with benzylamine [18-20]. Simultaneously, theoretical studies have been conducted [l, 2,4-12,14-17,21-23] by means of several models such as: DISQUAC [24], ERAS [25], UNIFAC [26], Flory [27], the concentration-concentration structure factor [28], the formalism of the Kirkwood-Buff integrals [29,30], or the Kirkwood-Fröhlich's theory [31]. As continuation of this effort, we provide now excess molar enthalpies, H_m^E, for methanol or 1-propanol or 1-pentanol, or 1-heptanol or 1-decanol + benzylamine systems at 298.15 K and 0.1 MPa, which are also investigated using the DISQUAC and ERAS models. In order to attain a complete characterization of benzylamine in terms of ERAS, we also report H_m^E and V_m^E (excess molar volume) data for the benzylamine + heptane mixture also at 298.15 K and 0. l MPa.

Benzylamine and its derived chemicals are important since their use has benefits on human health and safety and for the environment in comparison with benzene which has carcinogenic effects. lt is to be noted that benzylamine is not included as a human carcinogen by the International Agency for Research on Cancer. In addition, benzylamine is biodegradable [32]. All this facilitates its use in technical applications, such as pharmaceuticals, cosmetics, surface active reagents, corrosion inhíbitors, antiseptics or in antimicrobial agents [33-35]. Solutions including benzylamine are also used for CO_2 capture [36,37].

2. Experimental

2.1 Materials

All the chemicals were used as received, without any further purification. Table 1 lists the CAS number of the pure compounds, their source, purity, according to gas chromatographic analysis (GC) provided by the supplier and water contents. In addition, Table 1 also contains a comparison between densities, ρ, of the pure compounds and values available in the literature.

2.2 Apparatus and procedure

Compounds were weighted using an analytical balance A and D instrument model HR-202 (weighing accuracy 0.1 mg), taking into account the corresponding corrections on buoyancy effects. The standard uncertainty in the final mole fraction is 0.0005. Molar quantities were calculated using the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [38]. All the measurements were carried out at 298.15 K and 0.1 MPa. Calorimetric data were obtained by means of a standard Tian-Calvet microcalorimeter with a temperature stability of 0.01 K. The mixing cell, designed by us, is of aluminium and has a small (< 2%) gas phase. Details on the mixing process and on the calibration of the apparatus have been given previously [1,39]. The estimated maximum standard relative uncertainty for $H_{\mathrm{m}}^{\mathrm{E}}$ is 0.015.

Pt-100 resistances, calibrated using the triple point of water and the melting point of Ga, were used to measure the temperature of the samples, with a standard uncertainty of 0.01 K for ρ measurements. Densities of the pure compounds and of the benzylamine + heptane mixtures were determined using a densimeter and sound analyser Anton Paar, model DSA 5000 with a temperature stability of 0.001 K. More details about the technique, calibration and test of the apparatus can be found elsewhere [12,40]. The standard relative uncertainties of ρ and $V_{\mathrm{m}}^{\mathrm{E}}$ data are estimated to be, respectively, 0.0008 and 0.010.

3. Experimental results

Our measurements on $H_{\mathrm{m}}^{\mathrm{E}}$ and $V_{\mathrm{m}}^{\mathrm{E}}$ for the benzylamine + heptane system at 298.15 K and 0.1 MPa are listed in Table 2. Similarly, Table 3 contains $H_{\mathrm{m}}^{\mathrm{E}}$ results for 1-alkanol + benzylamine mixtures at the same conditions. No data have been found in the literature for comparison.

The data ($F_{\mathrm{m}}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}}; V_{\mathrm{m}}^{\mathrm{E}}$) were fitted by unweighted least-squares polynomial regression to the equation of the Redlich-Kister type [41]:

$$F_{\mathrm{m}}^{\mathrm{E}} = x_1(1-x_1)\sum_{i=0}^{k-1} A_i (2x_1 - 1)^i \qquad (1)$$

The number, k, of needed coefficients for this regression was determined, for each system, by applying an F-test of additional term [42] at 99.5% confidence level. Tables 4 and 5 list the parameters A_{i} obtained in the regression, together with the standard deviations $\sigma\left(F_{\mathrm{m}}^{\mathrm{E}}\right)$ defined by:

$$\sigma\left(F_{\mathrm{m}}^{\mathrm{E}}\right) = \left[\frac{1}{N-k}\sum_{j=1}^{N}\left(F_{\mathrm{mcal},j}^{\mathrm{E}} - F_{\mathrm{mexp},j}^{\mathrm{E}}\right)^2\right]^{1/2} \qquad (2)$$

where N stands for the number of data points, and $F_{\mathrm{mcal},j}^{\mathrm{E}}$ is the value of the excess property calculated using equation (1). Figures S1-S3 (supplementary material) show our experimental values of the excess molar functions together with the results from the corresponding fittings by means of equation (1).

4. Models

4.1 DISQUAC

DISQUAC is based on the rigid lattice theory developed by Guggenheim [43]. Some important features of the model are summarized. (i) The geometrical parameters: total molecular volumes, r_{i}, surfaces, q_{i}, and the molecular surface fractions, α_{si}, of the mixture components are calculated additively using the group volumes R_{G} and surfaces Q_{G} recommended by Bondi [44], with the volume R_{CH4} and surface Q_{CH4} of methane taken arbitrarily as volume and surface units [45]. For the groups involved in this investigation, the geometrical parameters are available in the literature [45-47]. (ii) The partition function is factorized into two terms. The excess functions $G_{\mathrm{m}}^{\mathrm{E}}$ and $H_{\mathrm{m}}^{\mathrm{E}}$ are the result of two contributions. The dispersive (DIS) term arises from the contribution of dispersive forces; while the quasichemical (QUAC) term is due to the anisotropy of the field forces created by the solution molecules. The Flory-Huggins equation is used to represent the combinatorial contribution, $G_{\mathrm{m}}^{\mathrm{E,COMB}}$, to $G_{\mathrm{m}}^{\mathrm{E}}$ [45,48]. Therefore,

$$G_{\mathrm{m}}^{\mathrm{E}} = G_{\mathrm{m}}^{\mathrm{E,DIS}} + G_{\mathrm{m}}^{\mathrm{E,QUAC}} + G_{\mathrm{m}}^{\mathrm{E,COMB}} \qquad (3)$$

$$H_{\mathrm{m}}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E,DIS}} + H_{\mathrm{m}}^{\mathrm{E,QUAC}} \qquad (4)$$

(iii) The interaction parameters are assumed to depend on the molecular structure of the mixture components; (iv) The same value of the coordination number (z = 4) is used for all the polar contacts. This is an important shortcoming of the model, partially removed assuming that the interaction parameters are dependent on the molecular structure. (v) It is also assumed that no change in volume is produced upon mixing (i.e., $V_{\mathrm{m}}^{\mathrm{E}}$ = 0).

The equations used to calculate the DIS and QUAC contributions to $G_{\mathrm{m}}^{\mathrm{E}}$ and $H_{\mathrm{m}}^{\mathrm{E}}$ can be found elsewhere [2,49]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [2,49], $C_{\mathrm{st,l}}^{\mathrm{DIS}};C_{\mathrm{st,l}}^{\mathrm{QUAC}}$ where s ≠ t are two contact surfaces present in the mixture and l = 1 (Gibbs energy; $C_{\mathrm{st,1}}^{\mathrm{DIS/QUAC}} = g_{\mathrm{st}}^{\mathrm{DIS/QUAC}}(T_{\mathrm{o}})/RT_{\mathrm{o}}$); l = 2 (enthalpy, $C_{\mathrm{st,2}}^{\mathrm{DIS/QUAC}} = h_{\mathrm{st}}^{\mathrm{DIS/QUAC}}(T_{\mathrm{o}})/RT_{\mathrm{o}}$)), l = 3 (heat capacity, $C_{\mathrm{st,3}}^{\mathrm{DIS/QUAC}} = c_{\mathrm{pst}}^{\mathrm{DIS/QUAC}}(T_{\mathrm{o}})/R$)). T_{o} = 298.15 K is the scaling temperature and R, the gas constant.

4.2 ERAS

The Extended Real Associated Solution (ERAS) model [25] combines the Real Association Solution Model [50,51] with Flory's equation of state [27]. Some relevant features of the model are the following. (i) The excess molar functions ($F_{\mathrm{m}}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}}, V_{\mathrm{m}}^{\mathrm{E}}$) are the result of two contributions. The chemical contribution, $F_{\mathrm{m,chem}}^{\mathrm{E}}$, is linked to hydrogen bonding; the physical contribution, $F_{\mathrm{m,phys}}^{\mathrm{E}}$, arises from nonpolar Van der Waals interactions and free volume effects. Expressions for $H_{\mathrm{m}}^{\mathrm{E}}$ and $V_{\mathrm{m}}^{\mathrm{E}}$ can be found in previous works [2]. (ii) It is assumed that only consecutive linear association occurs. Thus, self-association is described by a chemical equilibrium constant (K_{i}) independent of the chain length of the self-associated species A or B. In the case of 1-alkanol + benzylamine systems, i = A (1-alkanol) or = B (benzylamine), and the self-association of the compounds is represented by the equations:

$$\mathrm{A_m} + \mathrm{A} \xleftrightarrow{K_{\mathrm{A}}} \mathrm{A_{m+1}} \qquad (5)$$

$$\mathrm{B_n} + \mathrm{B} \xleftrightarrow{K_{\mathrm{B}}} \mathrm{B_{n+1}} \qquad (6)$$

with m and n ranging from 1 to ∞. The cross-association between two self-associated species $\mathrm{A_m}$ and $\mathrm{B_n}$ is described by:

$$\mathrm{A_m} + \mathrm{B_n} \xleftrightarrow{K_{\mathrm{AB}}} \mathrm{A_mB_n} \qquad (7)$$

The cross-association constants, K_{AB}, are also assumed that are independent of the chain length. Reactions described by equations (5)-(7) are characterized, respectively, by the molar enthalpies of intermolecular hydrogen-bonding $\Delta h_{\mathrm{A}}^{*}$, $\Delta h_{\mathrm{B}}^{*}$ and $\Delta h_{\mathrm{AB}}^{*}$, and by negative molar hydrogen-bonding volumes, $\Delta v_{\mathrm{A}}^{*}$, $\Delta v_{\mathrm{B}}^{*}$ and $\Delta v_{\mathrm{AB}}^{*}$, which are needed to take into account the decrease of the core volume of the molecules upon multimer formation. The three equilibrium constants depend on temperature according to the $\Delta h_{\mathrm{i}}^{*}$ values and the Van't Hoff equation. (iii) The $F_{\mathrm{m,phys}}^{\mathrm{E}}$ term is obtained from the Flory's equation of state [27], which is assumed to be valid for pure compounds and for mixtures [52,53]:

$$\frac{\bar{p}_i\bar{V}_i}{\bar{T}_i} = \frac{\bar{V}_i^{1/3}}{\bar{V}_i^{1/3}-1} - \frac{1}{\bar{V}_i\bar{T}_i} \qquad (8)$$

where i = A, B or M (mixture). In equation (8), $\bar{V}_i = V_{\mathrm{m},i}/V_{\mathrm{m},i}^{*}$; $\bar{p}_i = p/p_i^{*}$; $\bar{T}_i = T/T_i^{*}$ are the reduced properties for volume, pressure and temperature, respectively. The pure component reduction parameters ($V_{\mathrm{m},i}^{*}$, p_i^{*}, T_i^{*}) are obtained from p-V-T data (ρ, $\alpha_{p\mathrm{i}}$, (isobaric thermal expansión coefficient) and $\kappa_{T_{\mathrm{i}}}$ (isothermal compressibility) and association parameters [52,53]. The reduction parameters for the mixture p_{M}^{*} and T_{M}^{*} are calculated from mixing rules [52,53]. The total relative molecular volumes and surfaces of the compounds were calculated additively on the basis of the group volumes and surfaces recommended by Bondi [44].

5. Adjustment of interaction parameters

5.1 DISQUAC

In terms of DISQUAC, the following surfaces may be present in the investigated systems: (i) type a, aliphatic (CH_3, CH_2, in 1-alkanols, benzylamine, or *n*-alkanes); (ii) type b, aromatic (C_6H_5- in benzylamine or C_6H_6 in benzene); (iii) type h, OH in 1-alkanols; (iv) type n, amine (NH_2 in benzylamine).

5.1.1 Benzylamine + n-alkane or + benzene

These mixtures are built by three surfaces, a, b and n, which generate three contacts: (a,b), (a,n) and (b,n), The (a,b) contact is represented by dispersive interaction parameters obtained from the study of alkylbenzene (in this case ethylbenzene) + *n*-alkane mixtures [47]. The (a,n) and (b,n) contacts are described by both DIS and

QUAC interaction parameters, which must be fitted simultaneously using $H_{\mathrm{m}}^{\mathrm{E}}$ data for the benzylamine + benzene [54] system and liquid-liquid equilibria (LLE) [55] and calorimetric data for the *n*-alkane solutions (this work, [19]). Due to the lack of experimental data, and for the sake of simplicity, we have assumed that the interchange coefficients for *l* = 1 (Gibbs energy) of the (b,n) contacts are the same that for aniline mixtures [5]. Final values of the $C_{\mathrm{sn},1}^{\mathrm{DIS}}$ and $C_{\mathrm{sn},1}^{\mathrm{QUAC}}$ $(\mathrm{s} = \mathrm{a},\mathrm{b};\ \mathrm{l} = 1,2,3)$ coefficients are listed in Table 6.

5.1.2 1-alkanol + benzylamine

These systems are built by four surfaces, a,b,h,n, which generate six contacts: (a,b), (a,h), (a,n), (b,h), (b,n) and (h,n). The interaction parameters for the contacts (a,n) and (b,n) have been determined above. The interaction parameters for the contacts (a,h) and (b,h) are known from our DISQUAC studies on 1-alkanol + *n*-alkane [46] or + alkylbenzene [56] systems, respectively. For the (a,b) contacts, the interaction parameters are equal to those used in the preceding subsection. Therefore, only the interaction parameters for the (h,n) contacts must be determined. The general procedure applied in the estimation of the interaction parameters has been explained in detail elsewhere [2,49]. However, the task is now somewhat difficult since no data on vapour-liquid equilibria (VLE) are available for these mixtures. The $C_{\mathrm{nh},1}^{\mathrm{QUAC}}$ $(\mathrm{l} = 1,2)$ were adjusted together with the $C_{\mathrm{hn},2}^{\mathrm{DIS}}$coefficients to get a good description of the symmetry of the $H_{\mathrm{m}}^{\mathrm{E}}$ curves [49]. The first DIS Gibbs energy parameters were then estimated taking into account VLE data for other 1-alkanol + amine systems. Final parameters are listed in Table 6.

5.2 ERAS

The values of the ERAS parameters K_{A}, $\Delta h_{\mathrm{A}}^{*}$, $\Delta v_{\mathrm{A}}^{*}$ for 1-alkanols, and of their reduction parameters are known from the study of 1-alkanol + *n*-alkane mixtures [25,53,57]. The values of K_{A}, $\Delta h_{\mathrm{A}}^{*}$, and $\Delta v_{\mathrm{A}}^{*}$ of benzylamine (Table 7) have been determined using the data reported in this work for the system with heptane. The reduction parameters of benzyalmine (Table 7) were calculated using values of $\alpha_{p\mathrm{i}}$, and $\kappa_{T_{\mathrm{i}}}$ from reference [18]. The reduction parameters of heptane are available elsewhere [58]. 1-Alkanol + benzylamine systems are characterized by the binary parameters K_{AB}, $\Delta h_{\mathrm{AB}}^{*}$, $\Delta v_{\mathrm{AB}}^{*}$ and X_{AB} (Table 8), which are fitted to the $H_{\mathrm{m}}^{\mathrm{E}}$ and $V_{\mathrm{m}}^{\mathrm{E}}$ data [18]. For the mixtures benzylamine, + heptane, or + benzene, $K_{\mathrm{AB}} = \Delta h_{\mathrm{AB}}^{*} = \Delta v_{\mathrm{AB}}^{*} = 0$ and only the

X_{AB} values must be fitted (Table 8). It is known that the enthalpy of vaporization of a pure compound, in the framework of the ERAS model, can be determined from the K_A, Δh_A^*, Δv_A^* values [59]. Thus, at 298.15 K, ERAS yields 60.7 kJ mol^{-1} for the enthalpy of vaporization of benzylamine, in excellent agreement with the experimental result (60.16 kJ mol^{-1} [60]).

6. Theoretical results

DISQUAC results on LLE of benzyalmine + *n*-alkane systems are shown in Table 9 and Figure S4. The model describes correctly the coordinates of the critical points, compositions and upper critical solution temperatures (UCSTs) (Table 9). The coexistence curves are much rounded than the experimental ones (Figure S4) due to DISQUAC is a mean field theory and provides LLE curves which are too high at the UCST and too low at the LCST (lower critical solution temperature) [61-63].

Table 10 contains comparisons between experimental H_m^E data and theoretical results using DISQUAC and ERAS models (see also Figures 1-3). DISQUAC improves results from ERAS for mixtures involving 1-alkanols. Larger differences between ERAS calculations and experimental values emerge for systems with 1-heptanol or 1-decanol (Table 10, Figures 2,3). It is remarkable that ERAS correctly describes the V_m^E curves (see Figure 4). Finally, Table 11 compares DISQUAC results on C_{pm}^E with experimental results for the investigated systems. Figures 5 and 6 show such comparison including ERAS results for the mixtures with heptane or methanol. DISQUAC also improves ERAS calculations for the latter system.

7. Discussion

Below, we are referring to values of the thermodynamic properties at equimolar composition and 298.15 K. The number of C atoms of the 1-alkanol is represented by $n_{OH.}$

7.1 Benzylamine + n-alkane, or + benzene

Systems with *n*-alkanes are characterized by the antipathy between unlike molecules, i.e., by positive deviations from the Raoult's law. This is supported by the large and positive H_m^E result of the heptane mixture (1778 J mol^{-1}, this work) and by the existence of LLE curves with upper critical solution temperatures close to 298.15 K (e.g, 280. l K for the mixture with decane [55], Table 9), which, in addition, suggests that interactions between benzylamine molecules are mainly of dipolar type. We note that the $H_{\mathrm{m}}^{\mathrm{E}}$ curve is flattened at the top (Figure 1) and that the concentration dependence of $C_{p\mathrm{m}}^{\mathrm{E}}$ is W shaped (Figure 5, [19]). Similar features have been also encountered for systems at temperatures close to the UCST [64-66]. The flattening of the $H_{\mathrm{m}}^{\mathrm{E}}$ curves is encountered, e.g., in the mixtures 2,5,8,11-tetraoxadodecane + dodecane [66] (UCST = 280.81 K, [67]) or dimethyl carbonate + heptane [68] (UCST = 272.7 K, value estimated from experimental data provided in [69]), or butyric anhydride + heptane [70] (UCST = 237.5 K, DISQUAC result), or propanone + heptane (245.2 K, [71]). The experimental data show that the $C_{p\mathrm{m}}^{\mathrm{E}}$ curves are W-shaped for the mixtures 2,5,8,11-tetraoxadodecane + dodecane [72,73] or dimethyl carbonate + *n*-alkane [74,75], or acetone + alkane [64] . On the other hand, the $V_{\mathrm{m}}^{\mathrm{E}}$ curve of the benzylamine + heptane system, is S-shaped and the absolute value of this excess function at equimolar composition is low (Figure S2), which contrasts with the large and positive $H_{\mathrm{m}}^{\mathrm{E}}$ result. This reveals the existence of structural effects. Taking into account the large difference between $\alpha_{p\mathrm{i}}$, values of the mixture components (0.887 10^{-3} K^{-1} for benzylamine [18] and 1.256 10^{-3} K^{-1} for heptane [76]), the mentioned effects can be of free volume type.

It is interesting to compare thermodynamic properties of systems containing aniline, benzylamine or *N*-methylaniline (NMA). Thus, UCST (aniline + heptane) = 343. I K [77] and UCST (tetradecane)/K = 291.96 (benzylamine) [55], 286.85 (NMA) [78]. That is, interactions between amine molecules become weaker in the sequence: aniline > benzylamine > NMA. The excess molar enthalpies at infinite dilution of the amine, $H_{\mathrm{m1}}^{\mathrm{E},\infty}$, in amine + heptane solutions are (in kJ mol^{-1}): 15 (aniline) [79] and 10 (for both benzylamine (this work, see below) or NMA [78]).

The concentration-concentration structure factor, $S_{\mathrm{CC}}(0)$, [28,80] is a magnitude that allows to investigate the degree of non-randomness in a given system. The ideal mixture is characterized by $S_{\mathrm{CC}}(0)$ = 0.25. Interactions between like molecules (homocoordination) are dominant when $S_{\mathrm{CC}}(0)$ > 0.25. Interactions between unlike molecules are prevalent when $S_{\mathrm{CC}}(0)$ < 0.25. We have evaluated $S_{\mathrm{CC}}(0)$ for the benzylamine or NMA + heptane mixtures and the results are, respectively, 1.436 and 0.777 (Figure S5). Thus, homocoordination is much higher in the former system, since this solution at 298.15 K is closer to its UCST. In fact, W-shaped $C_{p\mathrm{m}}^{\mathrm{E}}$ curves together with large values of $S_{\mathrm{CC}}(0)$ have been considered as a manifestation of non-randomness effects [73,80,81] which can be detected even above 100 K from the UCST

[81].

For systems containing benzene, $H_{\mathrm{m}}^{\mathrm{E}}$/J mol^{-1} changes in the order: 751 (aniline) [82] > 490 (benzylamine, T= 303.15 K) [54] > 457 (NMA) [83], which may be ascribed to aniline-aniline interactions are stronger.

7.2. 1-alkanol + benzylamine

These systems show large and negative $H_{\mathrm{m}}^{\mathrm{E}}$ values, particulary when the shorter 1-alkanols are involved (Table 10, Figure 7a) and, therefore, are characterized by interactions between unlike molecules (negative deviations from Raoult’s law). The $V_{\mathrm{m}}^{\mathrm{E}}$ values are also large and negative: -1.542 (n_{OH} = 1); -1.034 (n_{OH} = 3); -0.765 (n_{OH} = 5) [18]. We note that $V_{\mathrm{m}}^{\mathrm{E}}$ and $H_{\mathrm{m}}^{\mathrm{E}}$ results change in line and increase when n_{OH} is increased. Consequently, the main contribution to $V_{\mathrm{m}}^{\mathrm{E}}$ arises from interactional effects. Systems formed by 1-alkanol and 1-hexylamine [4,52], or cyclohexylamine [1], or di-*n*-propylamine [6] show similar trends. The $C_{p\mathrm{m}}^{\mathrm{E}}$ values of the studied mixtures are large and positive, a typical feature of solutions where association/solvation effects are determinant when describing their thermodynamic properties. Thus, $C_{p\mathrm{m}}^{\mathrm{E}}$ (heptane)/J mol^{-1} K^{-1} = 11.7 (ethanol); 11.1 (1-butanol) [84] and $C_{p\mathrm{m}}^{\mathrm{E}}$/J mol^{-1} K^{-1} = 13.4 (1-octanol + di-*n*-ethylamine) [85] or $C_{p\mathrm{m}}^{\mathrm{E}}$(benzylamine)/J mol^{-1} K^{-1} = 12.9 (methanol) [19]; 12 (1-butanol) [20]. These values suggest that solvation effects contribute more largely to $C_{p\mathrm{m}}^{\mathrm{E}}$ than those related to alcohol self-association. On the other hand, both the $H_{\mathrm{m}}^{\mathrm{E}}$ and $C_{p\mathrm{m}}^{\mathrm{E}}$ curves are slightly shifted to higher 1-alkanol concentrations (Figures 2,3 and 6) which may be ascribed to solvation effects become more relevant at the mentioned concentrations.

Now, the enthalpy of the 1-alkanol-benzylamine interactions (termed $\Delta H_{\mathrm{OH\text{-}NH2}}^{\mathrm{int}}$) is evaluated. Neglecting structural effects [61,86], it is possible to assume that $H_{\mathrm{m}}^{\mathrm{E}}$ is the result of three contributions. The positive contributions $\Delta H_{\mathrm{OH\text{-}OH}}, \Delta H_{\mathrm{NH2\text{-}NH2}}$ are related, respectively, to the breaking of the alkanol and amine networks along the mixing process. When the mixture takes place, new OH---NH2 interactions are created, and it implies a negative contribution, $\Delta H_{\mathrm{OH\text{-}NH2}}$, to $H_{\mathrm{m}}^{\mathrm{E}}$. Thus [87-89]:

$$H_{\mathrm{m}}^{\mathrm{E}} = \Delta H_{\mathrm{OH\text{-}OH}} + \Delta H_{\mathrm{NH2\text{-}NH2}} + \Delta H_{\mathrm{OH\text{-}NH2}} \tag{9}$$

The values of $\Delta H_{\mathrm{OH\text{-}NH2}}^{\mathrm{int}}$ can be obtained extending the equation (9) to $x_1 \to 0$ [89-91]. Then,

$\Delta H_{\text{OH-OH}}$ and $\Delta H_{\text{NH2-NH2}}$ can be replaced by $H_{\text{m1}}^{\text{E},\infty}$ (partial excess molar enthalpy at infinite dilution of the first component) of 1-alkanol or benzylamine + *n*-alkane systems. In such a case,

$$\Delta H_{\text{OH-NH2}}^{\text{int}} = H_{\text{m1}}^{\text{E},\infty}(1-\text{alkanol} + \text{benzylamine})$$
$$-H_{\text{m1}}^{\text{E},\infty}(1-\text{alkanol} + \text{heptane}) - H_{\text{m1}}^{\text{E},\infty}(\text{benzylamine} + \text{heptane}) \qquad (10)$$

For 1-alkanol + *n*-alkane systems, we have taken $H_{\text{m1}}^{\text{E},\infty}$ = 23.2 kJ·mol^{-1} [92-94], the same value for all the 1-alkanols, which is a common approach within association theories [25,95-97]. For the systems 1-alkanol + benzylamine or benzylamine + heptane, $H_{\text{m1}}^{\text{E},\infty}$ data were determined from H_{m}^{E} measurements over the entire mole fraction range. A similar procedure was applied when we determined the enthalpy of interactions between 1-alkanol and different organic solvents, such linear monoether [89] or polyether [98], or linear alkanone [99], or nitrile [100], or nitroalkane [101] or linear organic carbonate [l02]. This makes that $\Delta H_{\text{OH-NH2}}^{\text{int}}$ values collected in Table 12 (Figure 7b) are meaningful. Inspection of the mentioned Table shows that interactions between unlike molecules are stronger in the methanol system, and weaker in the mixture with 1-decanol. For the remainder solutions, $\Delta H_{\text{OH-NH2}}^{\text{int}}$ decreases smoothly. lt is remarkable that $\Delta H_{\text{OH-NH2}}^{\text{int}}$ values are lower than those corresponding to the alkanol-alkanol interactions (-23.2 kJ mol^{-1}). That is, alkanol-amine interactions are stronger than those between alkanol molecules. This result has been also encountered for other 1-alkanol + amine systems [52,53,57]. We investigate now the variation with n_{OH} of the different contributions to H_{m}^{E}

7.2.1 The $\Delta H_{\text{OH-OH}}$ term

For mixtures involving ethylbenzene (isomeric molecule of benzylamine), H_{m}^{E}/J mol^{-1} = 684 (n_{OH} = 1); 908; (n_{OH} = 3); 932 (n_{OH} = 5); 895 (n_{OH} = 8) [103]. Such values suggest that the positive $\Delta H_{\text{OH-OH}}$ contribution remains nearly constant for larger 1-alkanols.

7.2.2 The $\Delta H_{\text{NH2-NH2}}$ term

This is positive contribution to H_{m}^{E} increases in line with n_{OH} since the larger aliphatic surfaces of longer 1-alkanols break more easily the interactions between benzyalmine molecules. Note that the UCSTs of the benzylamine + *n*-alkane systems increase with the number of C atoms in the alkane (Table 9).

7.2.3 The $\Delta H_{\text{OH-NH2}}$ term

This term contributes negatively to $H_{\mathrm{m}}^{\mathrm{E}}$ and increases with n_{OH} due to: (i) interactions between unlike molecules become weaker at the mentioned condition (Table 12); and (ii) the creation of interactions between unlike molecules is less probable since the OH group is more sterically hindered in longer 1-alkanols.

The increase of the $H_{\mathrm{m}}^{\mathrm{E}}$ (Figure 7a) values with n_{OH} may be now explained taking into account that the contributions $\Delta H_{\mathrm{NH2\text{-}NH2}}$ and $\Delta H_{\mathrm{OH\text{-}NH2}}$ increase in line with n_{OH} while the term $\Delta H_{\mathrm{OH\text{-}OH}}$ is more or less constant for larger n_{OH} values. In the temperature range (298.15-308.15) K, $C_{\mathrm{pm}}^{\mathrm{E}}$ slightly increases for the system with methanol, and slightly decreases for the remainder solutions (Table 11), which is probably due to solvation effects are more relevant in the former mixture. At higher temperatures, e.g., 333.15 K, the $C_{\mathrm{pm}}^{\mathrm{E}}$ / J mol^{-1} K^{-1} values become lower and change in the order: 9.9 (1-butanol) > 7.0 (1-octanol) > 6.2 (1-decanol) [20]. Such variation may be explained in terms of large alcohol dissociation produced at high temperatures [104], and to a weakening of alkanol-amine interactions (lower solvation effects) (Table 12). A similar temperature dependence of C_{pm}^{E} has been also observed in the systems 1-butanol + toluene [104], or 1-alkanol + acetophenone [105,106], or + dimethylsulfoxide [107].

Finally, we show in Figure 7b a comparison between $\Delta H_{\mathrm{OH\text{-}NH2}}^{\mathrm{int}}$ values for 1-alkanol + benzylamine, or + aniline, or + NMA mixtures. Similarly, the corresponding $H_{\mathrm{m}}^{\mathrm{E}}$ results are compared in Figure 7a. We note that, for a given 1-alkanol, interactions between unlike molecules become stronger in the sequence: NMA < aniline < benzylamine. This, together with the fact that the amine group is more sterically hindered in NMA, explains that $H_{\mathrm{m}}^{\mathrm{E}}$ changes in the order: NMA > aniline > benzylamine and that the $H_{\mathrm{m}}^{\mathrm{E}}$ variation is sharper in mixtures containing NMA.

7.3 Excess molar internal energies at constant volume

This magnitude, represented by $U_{\mathrm{m},V}^{\mathrm{E}}$, can be determined from [61]:

$$U_{\mathrm{m},V}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}} - T\frac{\alpha_p}{\kappa_T}V_{\mathrm{m}}^{\mathrm{E}} \qquad (11)$$

where α_p and κ_T are, respectively, the isobaric thermal expansion coefficient and the coefficient of isothermal compressibility of the considered system. The $T\frac{\alpha_p}{\kappa_T}V_{\mathrm{m}}^{\mathrm{E}}$ is the equation of state (eos) contribution to $H_{\mathrm{m}}^{\mathrm{E}}$. Here, the α_p and κ_T values were calculated assuming ideal behavior for the systems ($M^{\mathrm{id}} = \phi_1 M_1 + \phi_2 M_2$; with $M_{\mathrm{i}} = \alpha_{p\mathrm{i}}$, or κ_{T_i} and $\phi_i = x_i V_{\mathrm{m},i} / (x_1 V_{\mathrm{m},1} + x_2 V_{\mathrm{m},2})$). For pure compounds, their $\alpha_{p\mathrm{i}}$, and κ_{T_i} values were taken from the literature [89,108]. For heptane mixtures, $U^{\mathrm{E}}_{\mathrm{m},V}$ /J mol^{-1} = 1743 (NMA) and 1784 (benzylamine). These similar results reveal that more interactions between NMA molecules are broken upon mixing which is in agreement with the fact that NMA-NMA interactions are weaker. In the case of systems with 1-alkanols, the contributions to $H^{\mathrm{E}}_{\mathrm{m}}$ from the eos term are large an negative. They are 22.7%, 26.4% and 25% for the systems with methanol, 1-propanol or 1-pentanol, respectively. The values of ($U^{\mathrm{E}}_{\mathrm{m},V}$ /J mol^{-1}) in the same order as above, are: -2071, -1098 and -861. The $U^{\mathrm{E}}_{\mathrm{m},V}$ variation is smoother than the $H^{\mathrm{E}}_{\mathrm{m}}$ variation, which may be ascribed, at least in part, to the large contribution to $H^{\mathrm{E}}_{\mathrm{m}}$ from the eos term. No $V^{\mathrm{E}}_{\mathrm{m}}$ data have been encountered in the literature to calculate $U^{\mathrm{E}}_{\mathrm{m},V}$ of 1-alkanol + NMA mixtures. However, in a previous work [12], we determined this property for solutions containing aniline and the results were (in J mol^{-1}): 143 (methanol); 997 (1-propanol) and 1104 (1-pentanol). The corresponding ($H^{\mathrm{E}}_{\mathrm{m}}$/J mol^{-1}) values, in the same sequence, are: -175, 776, 1011 [109]. We note that $U^{\mathrm{E}}_{\mathrm{m},V}$ changes more smoothly with the alkanol size and particularly the large contribution from the eos term to $H^{\mathrm{E}}_{\mathrm{m}}$ in the case of the mixture with methanol.

7.4 The interaction parameters

7.4.1 ERAS parameters

Firstly, we underline that our values of the K_{A} , Δh^*_{A} , Δv^*_{A} parameters for benzyalmine are reliable since they conduct to a value of the enthalpy of vaporization in good agreement with the experimental value (see above). Othe other hand, these parameters for aniline [5], benzylamine (this work) and *N*-methylaniline [108] are rather consistent between them. Thus, self-association is higher in aniline or benzylamine (K_{A} = 14.8) than in NMA (K_{A} = 6). Amine-amine interactions are stronger between aniline molecules ($\Delta h^*_{\mathrm{A}} = -15$ kJ mol^{-1}) since $\Delta h^*_{\mathrm{A}} = -12.5$ kJ mol^{-1} for benzylamine and NMA. The latter result is supported by the similar values of the UCST of systems with tetradecane and benzylamine (290 K [78]) or NMA (286.8 K [55]). In any case, mixtures with alkanes are characterized by large X_{AB} values ([5,78] and Table 8), and this means that physical interactions are determinant in such solutions. Thus, for the benzylamine + heptane mixture we have: $H^{\mathrm{E}}_{\mathrm{m,phys}}$ = 1317 J mol^{-1} and $H^{\mathrm{E}}_{\mathrm{m,chem}}$ = 485 J mol^{-1}. For 1-alkanol + benzylamine mixtures, we note that the Δh^*_{AB} values are close to those of $\Delta H^{\mathrm{int}}_{\mathrm{OH\text{-}NH2}}$ (Tables 8 and 12, Figure 7b), which supports our calculations. The physical parameters are low, and thermodynamic properties are mainly determined by association/solvation effects. For example, in the case of the methanol mixture, $H^{\mathrm{E}}_{\mathrm{m,phys}}$ = 11 J mol^{-1} and $H^{\mathrm{E}}_{\mathrm{m,chem}} = -2690$ J mol^{-1}, and for the 1-pentanol system: $H^{\mathrm{E}}_{\mathrm{m,phys}}$ = 127 J mol^{-1} and $H^{\mathrm{E}}_{\mathrm{m,chem}} = -1218$ J mol^{-1}. The poor $H^{\mathrm{E}}_{\mathrm{m}}$ results obtained for 1-alkanols ($\neq$ methanol) remark the importance of dipolar interactions, particularly for systems with the longer 1-alkanols. We also show some results on $C^{\mathrm{E}}_{\mathrm{pm}}$ (Figures 5 and 6). Calculations require an additional parameter [110], $\frac{dX_{\mathrm{AB}}}{dT}$/J cm^{-3} K^{-1} = 0.13 (benzylamine + heptane, T = 293.15 K); 1.0 (methanol + benzylamine). Of course, the W-shaped $C^{\mathrm{E}}_{\mathrm{pm}}$ curve of the heptane system is not described by the model (DISQUAC also does not represent this complex dependence with the concentration of $C^{\mathrm{E}}_{\mathrm{pm}}$ (Figure 5)) . For the mixture with methanol, $C^{\mathrm{E}}_{\mathrm{pm}}$ is shifted towards low mole fractions of the alcohol, which seems to indicate that self-association effects are overestimated.

7.4.2 DISQUAC interaction parameters.

The $C^{\mathrm{DIS}}_{\mathrm{an,1}}$ coefficients slightly change with the *n*-alkane size (Table 6). As already mentioned, DISQUAC provides LLE curves which are too high at the UCST and too low at the LCST, which explains the mentioned variation of the $C^{\mathrm{DIS}}_{\mathrm{an,1}}$ coefficients in order to provide not very high calculated UCSTs [62,63]. In mixtures including 1-alkanols, the QUAC parameters are independent of the alcohol, a behavior often observed when mixtures with alcohols are investigated in terms of DISQUAC. Here, we remark, that these parameters largely differ from those of systems with aniline [5] or NMA [78], which may be related to the thermodynamic properties of 1-alkanol + aniline or + NMA systems are quite similar between them and that differ from those of the benzyalmine mixtures. Figure 7a illustrates this fact since we can see that the $H^{\mathrm{E}}_{\mathrm{m}}$ values of systems with aniline or NMA are very different to those of benzylamine. Finally, we remark that DISQUAC describes correctly $C^{\mathrm{E}}_{\mathrm{pm}}$ and the temperature dependence of this excess function in the case of systems with 1-alkanols (Table 11, Figure 6)). In view of the results, one can conclude that DISQUAC is a useful tool to describe consistently a set of thermodynamic properties of systems, independently of their deviations from the Raoult’s law (positive or negative). At this regards, it is remarkable that, e.g., model calculations show that heterocoordination (interactions between unlike molecules) is the dominant trend in the mixture with methanol (Figure S5).

8. Conclusions

Measurements on $H^{\mathrm{E}}_{\mathrm{m}}$ at 298.15 K and 0.1 MPa have been are reported for the benzylamine + heptane, or + methanol, or + 1-propanol, or + 1-pentanol, or + 1-heptanol, or + 1-

decanol systems. $V_{\mathrm{m}}^{\mathrm{E}}$ data at the same conditions are also given for the benzylamine + heptane mixture. Mixtures with *n*-alkanes are characterized by positive deviations from the Raoult's law. Structural effects exist in the solution with heptane. Systems with 1-alkanols show negative $H_{\mathrm{m}}^{\mathrm{E}}$ values which increase with the alcohol size, and therefore, are characterized by interactions between unlike molecules (negative deviations from the Raoult's law). The $V_{\mathrm{m}}^{\mathrm{E}}$ values of these systems are essentially determined by interactional effects. 1-Alkanol-benzylamine interactions become weaker when the chaing length of the 1-alcohol increases, and are stronger than those between 1-alkanol molecules. It has been shown that the $\Delta H_{\mathrm{NH2\text{-}NH2}}$ and $\Delta H_{\mathrm{OH\text{-}NH2}}$ contributions increase in line with n_{OH} while the term $\Delta H_{\mathrm{OH\text{-}OH}}$ is nearly constant. The mixtures have been studied using DISQUAC and ERAS. The latter model describes correctly the $V_{\mathrm{m}}^{\mathrm{E}}$ curves. DISQUAC largely improves ERAS results on $H_{\mathrm{m}}^{\mathrm{E}}$ or on $C_{\mathrm{pm}}^{\mathrm{E}}$ for systems including 1-alkanols, which reamrks the importance of physical interactions in the investigated solutions.

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CRediT authorship contribution statement

L.F. Sanz, Conceptualization, Data Curation, Software, Validation, Original Draft. J.A. González, Conceptualization, Formal Analysis, Methology, Review and Editing. F. Hevia, Data Curation, Formal Analysis, Investigation, Writing. I. García de la Fuente, Investigation, Supervision, Original Draft, Writing. J.C. Cobos, Methodology, Investigation, Supervision, Validation.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

9. List of symbols

C	interchange coefficient in DISQUAC
C_p	heat capacity at constant pressure
ΔH	enthalpy of interaction
G	Gibbs energy
H	enthalpy
$\Delta h_{\mathrm{i}}^{*}$	self-association enthalpy of component i (ERAS model)
$\Delta h_{\mathrm{AB}}^{*}$	association enthalpy of component A with component B (ERAS model)

K_i	self-association constant of component I (ERAS model)
K_{AB}	association constant of component A with component B (ERAS model)
n_{OH}	number of C atoms in 1-alkanol
P	pressure
P_i^*	reduction parameter for pressure of the component i
$\bar{P}_i$	reduced pressure of component i
$S_{CC}(0)$	concentration-concentration structure factor (eq. 7)
T	temperature
U_V	internal energy at constant volume
V	volume
V_{mi}^*	reduction parameter for molar volume of the component i
$\bar{V}_i$	reduced volume of component i
Δv_i^*	self-association volume of component I (ERAS model) (ERAS model)
Δv_{AB}^*	association volume of component A with component B
x	mole fraction in liquid phase

Greek letters

α_P	isobaric themal expansion coefficient
κ_T	isothermal compressibility
X_{12}	physical parameter (ERAS model)

Superscripts

E	excess property
∞	infinite dilution

Subscripts

i,j	compound in the mixture, (i, j =1,2)
m	molar property
s,t	type of contact surface in DISQUAC ($s \neq t$ = a (CH_3; CH_2); b (C_6H_o or C_6H_5); h, (OH); n (NH2)

10. References

[1] L.F. Sanz, J.A. González, I. García de la Fuente, J.C. Cobos, F. Hevia. Thermodynamics of mixtures with strong negative deviations from Raoult's law. XVIII. Excess molar enthalpies for the (1-alkanol + cyclohexylamine) systems at 298.15 K and modelling. J. Chem. Thermodyn. 157 (2021) 106395.

[2] J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 4. Application of the DISQUAC model to mixtures of 1-alkanols with primary or secondary linear amines. Comparison with Dortmund UNIFAC and ERAS results. Fluid Phase Equilib. 168 (2000) 31- 58.

[3] S. Villa, R. Garriga, P. Pérez, M. Gracia, J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 9. Vapor-liquid equilibria for the system 1-propanol plus di-*n*-propylamine at six temperatures between 293.15 and 318.15 K. Fluid Phase Equilib. 231 (2005) 211-220.

[4] S. Villa, N. Riesco, I. García de la Fuente, J.A. González, J. C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 8. Excess molar volumes at 298.15 K for 1-alkanols + isomeric amine ($C_6H_{15}N$). Characterization in terms of the ERAS model. Fluid Phase Equilib. 216 (2004) 123-133.

[5] J.A. González, I. Mozo, l. García de la Fuente, J.C. Cobos. Thermodynamics of binary mixtures containing amines. IV. Systems with aniline. Can. J. Chem. 83 (2005) 1812-1825.

[6] S. Villa, N. Riesco, I. García de la Fuente, J.A. González, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 5. Excess molar volumes at 298.15 K for 1-alkanols + dipropylamine systems. Characterization in terms of the ERAS model. Fluid Phase Equilib. 190 (2001) 113-125.

[7] S. Villa, N. Riesco, I. García de la Fuente, J.A. González, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 6. Excess molar volumes at 298.15 K for 1-alkanols + dibutylamine systems. Characterization in terms of the ERAS model. Fluid Phase Equilib. 198 (2002) 313-329.

[8] S. Villa, N. Riesco, l. García de la Fuente, J.A. González, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. VII. Excess molar volumes at 25 ^{o}C for 1-alkanol + *n*-methylbutylamine systems. Characterization in terms of the ERAS model. J. Solution Chem. 32 (2003) 179-194.

[9] L.F. Sanz, J.A. González, l. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XI. Densities, viscosities and refractives indices at (293.15–303.15) K for cyclohexylamine +1-propanol, or +1-butanol systems. J. Mol. Liq. 172 (2012) 26-33.

[10] L.F. Sanz, J.A. González, l. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XII. Densities, viscosities

and refractive indices at T = (293.15 to 303.15) K for (1-heptanol, or 1-decanol + cyclohexylamine) systems. Application of the ERAS model to (1-alkanol + cyclohexylamine) mixtures. J. Chem. Thermodyn. 80 (2015) 161-171.

[11] L.F. Sanz, J.A. González, l. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strong negative deviations from Raoult's law. XIV. Density, permittivity, refractive index and viscosity data for the methanol + cyclohexylamine mixture at (293.15-303.15) K. Thermochim. Acta 631 (2016) 18- 27.

[12] F. Hevia, V. Alonso, J.A. González, L.F. Sanz, l. García de la Fuente, J.C. Cobos. Density, speed of sound, refractive index and relative permittivity of methanol, propan-1-ol or pentan-1-ol + aniline liquid mixtures. Application of the Kirkwood-Fröhlich model. J. Mol. Liq. 322 (2021) 114988.

[13] U. Domanska, M. Zawadzki, M. Królikowski, J.A González. Phase equilibria and excess molar enthalpies study of the binary systems (pyrrole + hydrocarbon, or an alcohol) and modelling. Fluid Phase Equilib. 361 (2014) 116-129.

[14] J.A. González, L.F. Sanz, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strong negative deviations from Raoult's law. XIII. Relative permittivities for (1-alkanol + cyclohxylamine) systems, and dielectric study of (1-alkanol + polar compound (amine, amide or ether)) mixtures. J. Chem. Thermodyn. 91 (2015) 267-278.

[15] F. Hevia, J.A. González, A. Cobos, J. García de la Fuente, C. Alonso-Tristán. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XV. Permittivities and refractive indices for 1-alkanol + *n*-hexylamine systems at (293.15-303.15) K. Application of the Kirkwood-Fröhlich model. Fluid Phase Equilib. 468 (2018) 18-28.

[16] F. Hevia, J.A. González, A. Cobos, I. García de la Fuente, L.F. Sanz. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVI. Permittivities and refractive indices for 1-alkanol + di-*n*-proylamine systems at (293.15-303.15) K. Application of the Kirkwood-Fröhlich model. J. Mol. Liq. 271 (2018) 704-714.

[17] F. Hevia, J.A. González, A. Cobos, I. García de la Fuente, L.F. Sanz. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVII. Permittivities and refractive indices for alkan-1-ol + *N,N*-diethylethanamine systems (293.15-303.15) K. Application of the Kirkwood-Fröhlich model. J. Chem. Thermodyn. 141 (2020) 105397.

[18] F. Hevia, V. Alonso, A. Cobos, J.A. González, L.F. Sanz, I. García de la Fuente. Density, speed of sound, refractive index and relative permittivity of methanol, propan-1-ol or pentan-1-ol + benzylamine liquid mixtures. Application of the Kirkwood-Fröhlich

model. J. Chem. Thermodyn. (submitted).

[19] R. Páramo, V. Alonso, J.A. González, J. García de la Fuente, C. Casanova, J.C. Cobos. Thermodynamics of mixtures containing amines. XIV. $C_{\mathrm{pm}}^{\mathrm{E}}$ of benzylamine with heptane at 293.15 K, or with methanol, 1-propanol, or 1-pentanol at (293.15-308.15) K. Thermochim. Acta, 586 (2014) 75-79.

[20] R. Páramo, J.A. González, I. García de la Fuente, C. Casanova, J.C. Cobos. Thermodynamics of mixtures containing amines. XVI. $C_{\mathrm{pm}}^{\mathrm{E}}$ of 1-butanol, 1-octanol or 1-decanol + benzylamine systems at (298.15, 308.15, 318.15 and 3331.5) K. Thermochim. Acta, 600 (2015) 110-115.

[21] J.A. González, I. García de la Fuente, I. Mozo, J.C. Cobos, N. Riesco. Thermodynamics of organic mixtures containing amines. Part VII. Study of systems containing pyridines in terms of the Kirkwood-Buff formalism. Ind. Eng. Chem.Res. 47 (2008) 1729-1737.

[22] J.A. González, J. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 3. Application of the DISQUAC model to mixtures of triethylamine with alkanols. Comparison with Dortmund UNIFAC and ERAS results. Can. J. Chem. 78 (2000) 1272-1284.

[23] J.A. González, J.C. Cobos, I. García de la Fuente, l. Mozo. Thermodynamics of mixtures containing amines. IX. Application of the concentration-concentration structure factor to the study of binary mixtures containing pyridines Thermochim. Acta 494 (2009) 54-64.

[24] H.V. Kehiaian. Group contribution methods for liquid mixtures: a critical review. Fluid Phase Equilib. 13 (1983) 243-252.

[25] A. Heintz. A new theoretical approach for predicting excess properties of alkanol/alkane mixtures. Ber. Bunsenges. Phys. Chem. 89 (1985) 172-181.

[26] J. Gmehling, J. Li, M. Schiller. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. Ind. Eng. Chem. Res. 32 (1993) 178-193.

[27] P.J. Flory. Statistical thermodynamics of liquid mixtures. J. Am. Chem. Soc. 87 (1965) 833-1838.

[28] J.C. Cobos. An exact quasi-chemical equation for excess heat capacity with W-shaped concentration dependence. Fluid Phase Equilib. 133 (1997) 105-127.

[29] J.G. Kirkwood, F.P. Buff. The statistical mechanical theory of solutions. J. Chem. Phys. 19 (1954) 774-777.

[30] A. Ben-Naim. Inversion of the Kirkwood–Buff theory of solutions: Application to the water– ethanol system. J. Chem. Phys. 67 (1977) 4884-4889.

[31] A. Chelkowski, Dielectric Physics, Elsevier, Amsterdam, 1980.

[32] R. Pirisino, G.B. Ciottoli, F. Buffoni, B. Anselmi, C. Curradi. *N*-methyl-benzylamine, a metabolite of pargyline in man. Br. J. Clin. Pharmac 7 (1979) 595-598.

[33] D. Choi, J.P. Stables, H. Kohn. Synthesis and anticonvulsant activities of *N*-benzyl-2-acetamidopropionamide derivatives. J. Med. Chem. 39 (1996) 1907-1916.

[34] A.K. Gupta, R.L. Gardas. The constitutive behavior of ammonium ionic liquids: a physiochemical approach. RSC Adv. 5 (2015) 46881-46889.

[35] L. Heuer, Benzylamine, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley VCH Verlag GmbH & Co. KGaA, Weinheim, 2000.

[36] G. Richner. Promoting CO_2 absorption in aqueous amines with benzylamine. Energy Procedía 37 (2013) 423-430.

[37] S. Mukherjee, A.N. Samanta. Heat of absorption of CO_2 and heat capacity measurements in aqueous solutions of benzylamine, *N*-(2-aminoethyl)-ethanolamine, and their blends using a reaction calorimeter. J. Chem. Eng. Data 64 (2019) 3392-3406.

[38] CIAAW, Atomic weights of the elements 2015, ciaaw.org/atomic-weights.htm (accessed 2020).

[39] I. Alonso, I. Mozo, I. García de la Fuente, J. A. González, J. C. Cobos. Thermodynamics of ketone + amine mixtures. Part VIII. Molar excess enthalpies at 298.15 K for *n*-alkanone + aniline or + *N*-methylaniline systems. J. Chem. Eng Eng. Data 56 (2011) 3236-3241.

[40] J. A. González, I. Alonso, I. Mozo, I. García de la Fuente, J.C. Cobos. Thermodynamics of ketone + amine mixtures. Part VI. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for (2-heptanone + dipropylamine, + dibutylamine or + triethylamine) systems. J. Chem. Thermodyn. 43 (2011) 1506-1514.

[41] O. Redlich, A.T. Kister. Algebraic representation of thermodynamic properties and the classification of solutions. Ind. & Eng. Chem. 40 (1948) 345-348.

[42] P.R. Bevington, D.K. Robinson, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 2000

[43] E.A. Guggenheim, Mixtures, Oxford University Press, Oxford, 1952.

[44] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.

[45] H.V. Kehiaian, J.-P.E. Grolier, G.C. Benson. Thermodynamics of organic mixtures. A generalized quasichemical theory in terms of group surface interactions. J. Chim. Phys.

75 (1978) 1031-1048.

[46] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova. A characterization of the aliphatic/hydroxyl interactions using a group contribution model (DISQUAC). Ber. Bunsenges. Phys. Chem. 95 (1991) 1658-1668.

[47] A. Cannas, B. Marongiu, S. Porcedda. Thermodynamic properties of *n*-alkylbenzene + *n*-alkane or cyclohexane mixtures. Comparison with DISQUAC predictions. Thermochim. Acta 311 (1998) 1-19.

[48] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, A. Ait-Kaci. Application of the zeroth approximation of the DISQUAC model to cyclohexane (1) + *n*-alkane (2) mixtures. Comparison of results obtained for these systems using differents combinatorial entropy terms. Fluid Phase Equilib. 112 (1995) 63-87.

[49] J.A. González, I. García de la Fuente, J.C. Cobos. Correlation and prediction of excess molar enthalpies using DISQUAC in: E. Wilhelm, T.M. Letcher (Eds.), Enthalpy and Internal Energy: Liquids, Solutions and Vapours, Royal Society of Chemistry, Croydon 2017

[50] C.B. Kretschmer, R. Wiebe. Thermodynamics of alcohol· hydrocarbon mixtures. J. Chem. Phys. 22 (1954) 1697-1701.

[51] H.V. Kehiaian, A. Treszczanowicz. Excess enthalpy and excess entropy of athermal associated mixtures of the type $A + A_i + B$. Bull. Acad. Pol. Sci. 16 (1968) 171-175.

[52] A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestorf. Thermodynamics of alkanol + amine mixtures. Experimental results and ERAS model calculations of the heat of mixing. Ber. Bunsenges. Phys. Chem. 102 (1998) 953-959.

[53] A. Heintz, D. Papaioannou**.** Excess enthalpies of alcohol + amine mixtures. Experimental results and theoretical description using the ERAS-model, Thermochim. Acta 310 (1998) 69-76**.**

[54] I. Velasco, S. Otín, C. Gutiérrez Losa, Int Data Ser. Selec. DATA Mixtures, Ser. A. (1979) 8-11.

[55] C. Alonso-Tristán, J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing amines. XV. Liquid-liquid equilibria for benzylamine + $CH_3(CH_2)_nCH_3$ (n = 8,9,10,12,14). J. Chem. Eng.Data 59 (2014) 2101-2105.

[56] J.A. González, 1. Mozo, M. Fernández, I. García de la Fuente, J.C. Cobos. Thermodynamics of 1-alkanol + aromatic compound mixtures. Systems with dimethylbenzene, ethylbenzene or trimethylbenzene. J. Mol. Liq.133 (2007) 77-88.

[57] H. Funke, M. Wetzel, A. Heintz. New applications of the ERAS model. Thermodynamics of amine + alkane and alcohol + amine mixtures. Pure Appl. Chem. 61 (1989) 1429-1439.

[58] F. Hevia, J.A. González, C. Alonso-Tristán, I. García de la Fuente, L.F. Sanz. Orientational effects in alkanone, alkanal or dialkyl carbonate + alkane mixtures, or in alkanone + alkanone, or + dialkyl carbonate systems. J. Mol. Liq. 233 (2017) 517-527.

[59] M. Bender, A. Heintz. Thermodynamics of 1-alkanol + *n*-alkane mixtures based on predictions of the ERAS model. Fluid Phase Equilib. 89 (1993) 197-215.

[60] V. Majer, V. Svoboda. Enthalpies of Vaporization of Organic Compounds. Blackwell, Oxford, 1985**.**

[61] J.S. Rowlinson, F.L. Swinton, Liquids and Liquid Mixtures, 3rd Edition, Butterworths, G. B., 1982.

[62] J.A. González, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Liquid-liquid equilibria for acetophenone + *n*-alkane mixtures and characterization of acetophenone system using DISQUAC. Fluid Phase Equilib. 391 (2015) 39-48.

[63] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos**.** Thermodynamics of binary mixtures containing amines. V. Systems with pyridines. Thermochim. Acta. 441 (2006) 53-68.

[64] M.-E. Saint-Víctor, D. Patterson. The w-shape concentration dependence of $C_{\mathrm{pm}}^{\mathrm{E}}$ and solution non-randomness: ketones + normal and branched alkanes. Fluid Phase Equilib. 35 (1987) 237-252.

[65] E. Wilhelm. The fascinating world of pure and mixed nonelectrolytes, Pure Applied Chem. 77 (2005) 1317-1330.

[66] H.V. Kehiaian, M.R. Tiné, L. Lepori, E. Matteoli, B. Marongiu. Thermodynamics of binary mixtures containing oxaalkanes. Part 3. Monoethers, polyethers, acetals, orthoesters and cyclic monoethers + n-alkanes or cyclohexane. Fluid Phase Equilib. 46 (1989) 131-177.

[67] T. Treszczanowicz, D. Cieslak. (Liquid + liquid) equilibria in (a dimethyl ether of a polyethene glycol + an *n*-alkane). J. Chem. Thermodyn. 25 (1993) 661-665.

[68] H.V. Kehiaian, J.A. González, l. García, J.C. Cobos, C. Casanova, M.J. Cocero. Prediction of vapour-liquid and liquid-liquid equilibria and of enthalpies of mixing in linear carbonates + *n*-alkane or + cyclohexane mixtures using DISQUAC. Fluid Phase Equilib. 64 (1991) 1-11.

[69] J.A. González, l. García, J.C. Cobos, C. Casanova. Thermodynamics of binary mixtures containing organic carbonates. 4. Liquid-liquid equilibria of dimethyl carbonate + selected *n*-alkanes. J. Chem. Eng. Data 36 (1991) 162-164.

[70] H. Kehiaian, J.A. González, l. García, R. Escarda, J.C. Cobos, C. Casanova. Prediction of liquid-liquid equilibria and of enthalpies of mixing in alkanoic acid anhydride + *n*-alkane mixtures using DISQUAC. Fluid Phase Equilib. 69 (1991) 91-

98.

[71] G. Spinolo, R. Riccardi, Int. DATA Ser., Ser. A., Sel. Data Mixtures (1977) 91-94.

[72] G.C. Benson, M.K. Kumaran, P.J. D'Arcy, C.J. Halpin. Thermodynamic properties for 2,5,8,11-tetraoxadodecane + *n*-dodecane mixtures at 298.15 K. Thermochim. Acta 95 (1985) 59-66.

[73] L.M. Trejo, M. Costas, D. Patterson. Effect of molecular size on the W-shaped excess heat capacities: oxaalkane-alkane systems. J. Chem. Soc. Faraday Trans 87 (1991) 3001-3008.

[74] J.M. Pardo, C.A. Tovar, C.A. Cerdeiriña, E. Carballo, L. Romaní. Excess molar volumes and excess molar heat capacities of (dimethyl carbonate, or diethyl carbonate plus *n*-heptane) at several temperaturas. J. Chem. Thermodyn. 31 (1999) 787-796.

[75] J.M. Pardo, C.A. Tovar, J. Troncoso, E. Carballo, L. Romaní. Thermodynamic behaviour of the binary systems dimethyl carbonate + *n*-octane or *n*-nonane Thermochim. Acta 433 (2005) 128-133.

[76] J.A. Riddick, W.B. Bunger, T.K. Sakano. Organic solvents. Physical Properties and Methods of Purification. (Fourth edition). John Wiley & Sons, 1986.

[77] H. Matsuda, K. Ochi, K. Kojima. Determination and correlation of LLE and SLE data for the methanol + cyclohexane, aniline + heptane, and phenol + hexane system. J. Chem. Eng. Data 48 (2003) 184-189.

[78] J.A. González, l. Alonso, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing amines. XI. Liquid + liquid equilibria and molar excess enthalpies at 298.15 K for *N*-methylaniline + hydrocarbon systems. Characterization in terms of DISQUAC and ERAS models. J. Chem. Thermodyn. 56 (2013) 89-98

[79] K. Stephenson, R. Fuchs. Enthalpies of interaction of nitrogen base solutes with organic solvents. Can. J. Chem. 63 (1985) 2540-2544.

[80] L. Andreolli-Ball, S.J. Sun, L.M. Trejo, M. Costas, D. Patterson. Thermodynamics and structure in nonelectrolyte solutions. Pure Appl. Chem. 62 (1990) 2097-2106.

[81] L. Andreolli-Ball, M. Costas, D. Patterson, R.G. Rubio, R.M. Masegosa, M. Cáceres. Solution non-randomness and the W-shape concentration dependence of C_p^{E} for hexafluorobenzene and chloronaphthalene in hydrocarbons. Ber Bunsenges. Phys. Chem. 93 (l989) 882-887.

[82] I. Nagata, K. Tamura. Excess enthalpies of (aniline + acetonitrile or benzene) and of (aniline + acetonitrile + benzene) at the temperature 298.15 K. J. Chem.

Thermodyn. 24 (1992) 613-617.

[83] G. Pannetier, L. Abello. H bond study: H-N-H. Bull. Soc. Chim. Fr. (1965) 2048-2058.

[84] R. Tanaka, S. Toyama, S. Murakami. Heat capacities of $\{xC_nH_{2n+1}OH + (1-x)C_7H_{16}\}$ for $n = 1$ to 6 at 298.15 K. J. Chem. Thermodyn. 18 (1986) 63-73.

[85] R.F. Checoni, A.Z Francesconi. Measurements of excess molar enthalpy and excess molar heat capacity of (1-heptanol or 1-octanol) + (diethylamine or *s*-butylamine) mixtures at 298.15 K and 0.1 MPa. J. Therm. Anal. Calorim. 97 (2009) 747-753.

[86] H. Kalali, F. Kohler, P. Svejda. Excess properties of binary mixtures of 2,2,4-trimethylpentane with one polar component. Fluid Phase Equilib. 20 (1985) 75-80.

[87] T.M. Letcher, U.P. Govender. Excess molar enthalpies of an alkanol + a cyclic ether at 298.15 K, J. Chem. Eng. Data 40 (1995) 1097-1100.

[88] E. Calvo, P. Brocos, A. Piñeiro, M. Pintos, A. Amigo, R. Bravo, A.H. Roux, G. Roux-Desgranges. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 4. Binary systems 1,4-dioxane + 1-alkanols. J. Chem. Eng. Data 44 (1999) 948-954.

[89] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, N. Riesco. Thermodynamics of (1-alkanol + linear monoether) systems. J. Chem. Thermodyn. 40 (2008) 1495-1508.

[90] M. Letcher, B.C. Bricknell. Calorimetric investigation of the interactions of some hydrogen-bonded systems at 298.15 K. J. Chem. Eng. Data 41 (1996) 166-169.

[91] J.A. González, l. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing oxaalkanes. 5. Ether + benzene, or + toluene systems. Fluid Phase Equilib. 301 (2011) 145-155.

[92] R.H. Stokes, C. Burfitt. Enthalpies of dilution and transfer of ethanol in non-polar solvents. J. Chem. Thermodyn. 5 (1973) 623-631.

[93] S.J. O'Shea, R.H. Stokes. Activity coefficients and excess partial molar enthalpies for (ethanol+ hexane) from 283 to 318 K. J. Chem. Thermodyn. 18 (1986) 691-696.

[94] H.C. Van Ness, J. Van Winkle, H.H. Richtol, H.B. Hollinger. Infrared spectra and the thermodynamics of alcohol-hydrocarbon systems. J. Phys. Chem. 71 (1967) 1483-1494.

[95] V. Brandani, J.M. Prausnitz. A free-volume, non-random-mixing theory for liquid mixtures. Fluid Phase Equilib. 7 (1981) 233-257.

[96] A. Liu, F. Kohler, L. Karrer, J. Gaube, P.A. Spelluci. A model for the excess properties of 1-alkanol + alkane mixtures containing chemical and physical term. Pure & Appl. Chem. 61 (1989) 1441-1452.

[97] H. Renon, J.M. Prausnitz. On the Thermodynamics of alcohol-hydrocarbon solutions. Chem. Eng. Sci. 22 (1967) 299-307.

[98] J.A. González, A. Mediavilla, I. García de la Fuente, J.C. Cobos. Thermodynamics of (1-alkanol + linear polyether) mixtures. J. Chem. Thermodyn. 59 (2013) 195-208.

[99] J.A. González, A. Mediavilla, I. García de la Fuente, J.C. Cobos, C. Alonso-Tristán, N. Riesco. Orientational effects in 1-alkanol + alkanone mixtures. Ind. Eng. Chem. Res. 52 (2013) 10317-10328.

[100] J.A. González, I. García de la Fuente, J.C. Cobos, C. Alonso-Tristán, L.F. Sanz. Orientational effects and random mixing in 1-alkanol + nitrile mixtures. Ind. Eng. Chem. Res. 54 (2015) 550-559.

[101] J.A. González, F. Hevia, L.F. Sanz, I. García de la Fuente, C. Alonso-Tristán. Thermodynamics of mixtures containing a very strongly polar compound. 12. Systems with nitrobenzene, or 1-nitroalkane and hydrocarbons or 1-alkanols. Fluid Phase Equilib. 471 (2018) 24-39.

[102] J.A. González, F. Hevia, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Orientational effects in mixtures of organic carbonates with alkanes or 1-alkanols. Fluid Phase Equilib. 449 (2017) 91-103.

[103] R.V. Mrazek, H.C. Van Ness. Heats of mixing: alcohol-aromatic binary systems at 25°, 35° and 45° C. AIChE J. 7 (1961) 190-195.

[104] J.C. Cobos, I. García, C. Casanova, A.H. Roux, C. Roux-Desgranges, J.-P.E. Grolier. Excess heat capacities of 1-butanol + toluene from 298 to 368 K. Fluid Phase Equilib. 69 (1991) 223-233.

[105] S. Li, H. Gao, W. Yan. Determination and correlation of excess molar enthalpies of eight binary systems containing acetophenone at different temperatures. J. Chem. Eng. Data 53 (2008) 1630-1634.

[106] S. Li, W. Yan, Excess molar enthalpies of acetophenone + (methanol, + ethanol, 1-propanol, and + 2-propanol) at different temperatures and pressures. J. Chem. Eng. Data 53 (2008) 551-555.

[107] F. Comelli, R. Francesconi, A. Bigi, K. Rubini. Excess molar enthalpies, molar heat capacities, densities, viscosities, and refractive indices of dimethyl dulfoxide + 1-propanol at (288.15, 298.15, and 308.15) K and at normal pressure. J. Chem. Eng. Data 51 (2006) 1711-1716.

[108] I. Alonso, I. García de la Fuente, J.A. González, J.C. Cobos. Thermodynamics of mixtures containing amines. XII. Volumetric and Speed of sound data at (293.15, 298.15 and 303.15) K for *N*-methylaniline + hydrocarbon systems. J. Chem. Eng. Data, 58 (2013) 1697-1705.

[109] Y.X. Wang, J.P. Chao, M. Dai, Studies on the thermodynamic properties of binary

mixtures containing an alcohol: XIII. Excess molar enthalpies of some mixtures of *n*-alcohols with aniline or chlorobenzene at 298.15 K. Thermochim. Acta 169 (1990) 161-169.

[110] J.A. González, S. Villa, N. Riesco, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing alkoxyethanols: Part XVII. ERAS characterization of alkoxyethanol + alkane systems. Can. J. Chem. 81 (2003) 319-329.

[111] S. Toscani, P. Figuiere, H. Szwarc. A magnetic-suspension apparatus to measure densities of liquids as function of temperature at pressures up to 100 MPa. Application to *n*-heptane. J. Chem. Thermodyn. 21 (1989) 1263-1277.

[112] D. Luning Prak, J. Cowart, P. Trulove, Density, viscosity, speed of Sound, bulk modulus, and surface tension of binary mixtures of *n*-heptane + 2,2,4-trimethylpentane at (293.15 to 338.15) K and 0.1 MPa. J. Chem. Eng. Data. 59 (2014) 3842-3851.

[113] K. N. Marsh, TRC Data Bases for Chemistry and Engineerings, TRC Thermodynamic Tables; TexasA&M University System: College Station, TX, 1994.

[114] A. Blanco, A. Gayol, D. Gómez-Díaz, J.M. Navaza. Density, speed of sound, refractive index and derivatives properties of the binary mixture *n*-hexane + *n*-heptane (or *n*-octane or *n*-nonane), T = (288.15-313.15) K. Phys. Chem. Liq. 51 (2013) 404-413.

[115] E. Alonso, H. Guerrero, D. Montaño, C. Lafuente, H. Artigas. Thermophysical study of the *n*-hexane or *n*-heptane with 1-chloropropane systems. Thermochim. Acta 525 (2011) 71-77.

[116] T.M. Aminabhavi, V.B. Patil. Density, refractive index, viscosity, and speed of sound in binary mixtures of ethenylbenzene with hexane, heptane, octane, nonane, decane, and dodecane. J. Chem. Eng. Data 42 (1997) 641-646.

[117] A.S. Carson, P.G. Laye, M. Yürekli. The enthalpy of formation of benzylamine. J. Chem. Thermodyn. 9 (1977) 827-829.

[118] S. Panda, D. Singh, G. Sharma, A. Basaiahgari, R.L. Gardas. Measurement and correlation for acoustic, transport, refractive, and high-temperature volumetric data of substituted benzylamines. J. Chem. Eng. Data 62 (2017) 1189-1197.

[119] M.I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi. Density, viscosity, refractive index, and speed of sound in binary mixtures of acrylonitrile with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, and butan-2-ol. J. Chem. Eng. Data 44 (1999) 216-221.

[120] R. Anwar Naushad, S. Yasmeen. Volumetric, compressibility and viscosity studies of binary mixtures of [EMIM][NTf2] with ethylacetate/methanol at (298.15-323.15) K. J. Mol. Liq. 224 (2016) 189-200.

[121] J.L. Hales, J.H. Ellender, Liquid densities from 293 to 490 K of nine aliphatic alcohols. J. Chem. Thermodyn. 8 (1976) 1177-1184.

[122] G.A. Iglesias-Silva, A. Guzmán-López, G. Pérez-Durán, M. Ramos-Estrada, Densities and viscosities for binary liquid mixtures of *n*-undecane + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol from 283.15 to 363.15 K at 0.1 MPa. J. Chem. Eng. Data 61 (2016) 2682-2699.

[123] A. Piñeiro, P. Brocos, A. Amigo, M. Pintos, R. Blanco. Refractive indexes of binary mixtures of tetrahydrofuran with 1-alkanols at 25° C and temperature dependence of n and ρ for the pure liquids. J. Solution Chem. 31 (2002) 369-380.

TABLE 1 Properties of pure compounds: CAS number, source, purity, water content and density, ρ, at 298.15 K and 0.1 MPa.

Compound	CAS	Source	Purity^a	Water content^a	ρ ^{b}/g cm^{-3}	
					Experimental	Literature
Heptane	142-82-5	Sigma-Aldrich	0.998	4 10^{-5}	0.679606	0.6796 [111,112] 0.6794 [113,114] 0.67978 [115] 0.6794 [116]
benzylamine	100-46-9	Fluka	0.998	6.8 10^{-4}	0.97809	0.981 [117] 0.978337 [19] 0.97935 [118]
Methanol	67-56-1	Sigma-Aldrich	0.999	2 10^{-5}	0.78720	0.7869 [119] 0.786884 [120]
1-propanol	71-23-8	Fluka	0.999	1 10^{-3}	0.79951	0.79960 [76,121] 0.79959 [122]
1-pentanol	71-41-0	Sigma-Aldrich	0.999	3 10^{-4}	0.81087	0.81080 [121] 0.81103 [122]
1-heptanol	111-70-6	Sigma-Aldrich	0.998	3 10^{-3}	0.818987	0.81875 [123]
1-decanol	112-30-1	Sigma-Aldrich	0.987	3 10^{-3}	0.826581	0.82644 [123]

^{a}in mole fraction, by gas chromatography. Initial purity provided by the supplier.^{b}in mass fraction (Karl-Fischer titration); ^{c}standard uncertainties (u): $u(T)$ = 0.01 K; $u(p)$ = 10 kPa; relative standard uncertainty, $u_r(\rho)$ = 0.0008

TABLE 2 Excess molar volumes, V_m^E, and excess molar enthalpies, H_m^E, at 298.15 K and 0.1 MPa for the benzylamine(1) + heptane(2) mixture.[a]

x_1	V_m^E /cm^3 mol^{-1}	x_1	H_m^E/J mol^{-1}
0.0500	0.0667	0.0547	505
0.1003	0.1179	0.1003	823
0.1468	0.1240	0.1475	1091
0.1973	0.1196	0.1991	1325
0.2398	0.1008	0.3003	1625
0.2996	0.0628	0.4077	1754
0.3989	0.0123	0.4972	1809
0.4991	− 0.0218	0.5969	1678
0.6010	− 0.0586	0.6926	1532
0.7000	− 0.0804	0.7935	1230
0.7984	− 0.1027	0.8551	961
0.8491	− 0.1113	0.9049	687
0.9005	− 0.1127	0.9541	359
0.9486	− 0.0789		

[a] Standard uncertainties (u): $u(T)$ = 0.01 K; $u(p)$ = 10 kPa ; $u(x_1)$ = 0.0005; $u(V_\mathrm{m}^\mathrm{E})$ = 0.010·$|V_\mathrm{m}^\mathrm{E}|_\mathrm{max}$ + 0.005 cm^3·mol^{-1}. For H_m^E, the relative combined expanded uncertainty (0.95 level of confidence) is $U_\mathrm{rc}\left(H_\mathrm{m}^\mathrm{E}\right) = 0.03$.

TABLE 3 Excess molar enthalpies, H_m^E, at 298.15 K and 0.1 MPa for 1-alkanol(1) + benzylamine(2) mixtures.[a]

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
	methanol(1) + benzylamine(2)		
0.0665	− 524	0.6009	− 2668
0.1204	− 926	0.7039	− 2293
0.1785	− 1335	0.7665	− 2079
0.2020	− 1488	0.7943	− 1878
0.2661	− 1874	0.8460	− 1486
0.3112	− 2103	0.8929	− 1080
0.4067	− 2477	0.9494	− 547
0.4921	− 2692		
	1-propanol(1) + benzylamine(2)		
0.0601	− 289	0.5971	− 1464
0.1036	− 484	0.6945	− 1265
0.1555	− 700	0.7447	− 1117
0.1987	− 866	0.7998	− 926
0.2464	− 1029	0.8508	− 720
0.3003	− 1186	0.8993	− 499
0.4068	− 1405	0.9488	− 259
0.5076	− 1491		
	1-pentanol(1) + benzylamine(2)		
0.0542	− 188	0.6010	− 1119
0.0979	− 337	0.7053	− 962
0.1462	− 493	0.7514	− 866
0.2001	− 617	0.8058	− 695

0.2452	−766	0.8487	−562
0.2928	−874	0.9009	−366
0.4023	−1072	0.9442	−215
0.4997	−1159	0.9466	−202
	1-heptanol(1) + benzylamine(2)		
0.0535	−127	0.6007	−963
0.1010	−232	0.7036	−855
0.1486	−346	0.7488	−755
0.1971	−466	0.7974	−648

Table 3 (continued)

0.2629	−623	0.8531	−470
0.2967	−691	0.8972	−344
0.3984	−869	0.9392	−211
0.5044	−988		
	1-decanol(1) + benzylamine(2)		
0.0568	−19	0.6032	−729
0.1020	−61	0.6994	−658
0.1329	−100	0.7400	−593
0.1986	−211	0.7867	−509
0.2486	−295	0.8444	−403
0.3038	−415	0.8857	−306
0.3964	−574	0.9388	−165
0.4971	−687		

[a] The standard uncertainties are: $u(T)$ = 0.01 K, $u(p)$ = 10 kPa, and $u(x_1)$ = 0.0005. The relative combined expanded uncertainty of $H_{\mathrm{m}}^{\mathrm{E}}$ (0.95 level of confidence) is $U_{\mathrm{rc}}\left(H_{\mathrm{m}}^{\mathrm{E}}\right) = 0.03$

TABLE 4 Coefficients A_i and standard deviations, $\sigma(F_m^E)$ (equation (2)), for the representation of F_m^E (= H_m^E; V_m^E) data at 298.15 K and 0.1 MPa of the benzylamine(1) + heptane(2) mixture by equation (1).

F_m^E	A_0	A_1	A_2	A_3	A_4	$\sigma(F_m^E)$ [a]
H_m^E / J mol^{-1}	7113	–689	2234			14
V_m^E /cm^3 mol^{-1}	–0.1143	–0.6480	–1.3988	–0.7406	–0.7406	0.005

[a] in the same units that F_m^E

TABLE 5 Coefficients A_i and standard deviations, $\sigma(H_m^E)$ (equation (2)), for the representation of H_m^E data at 298.15 K and 0.1 MPa of 1-alkanol(1) + benzylamine(2) mixtures by equation (1).

1-alkanol	A_0	A_1	A_2	A_3	$\sigma(H_m^E)$ / J mol^{-1}
Methanol	–10713	–1977	1106	375	25
1-propanol	–5968	–487	977	498	5.9
1-pentanol	–4605	–594	986	487	11
1-heptanol	–3898	–1007	1202	470	7.4
1-decanol	–2769	–1466	1549		6.5

TABLE 6 Dispersive (DIS) and quasichemical (QUAC) interchange coefficients, $C_{\mathrm{sn},l}^{\mathrm{DIS}}$ and $C_{\mathrm{sn},l}^{\mathrm{QUAC}}$, for (s,n) contacts (s = a, aliphatic; b, aromatic; h, OH) in benzylamine + organic solvent mixtures mixtures (*l* = 1, Gibbs energy; *l* = 2, enthalpy; *l* = 3, heat capacity)

Solvent	contact	$C_{\mathrm{sn},1}^{\mathrm{DIS}}$	$C_{\mathrm{sn},2}^{\mathrm{DIS}}$	$C_{\mathrm{sn},3}^{\mathrm{DIS}}$	$C_{\mathrm{sn},1}^{\mathrm{QUAC}}$	$C_{\mathrm{sn},2}^{\mathrm{QUAC}}$	$C_{\mathrm{sn},3}^{\mathrm{QUAC}}$
Benzene	(b,n)	3.7	−5.05	−4	1.25	10	4
n-alkane	(a,n)	1.65	−1.25	3.2	5	10	1.5
Methanol	(h,n)	1.4[b]	−11	21	−3	−2	7.5
1-propanol	(h,n)	1.8[b]	−2.9	−10	−3	−2	7.5
1-butanol	(h,n)	1.8[b]	−1.7	−15	−3	−2	7.5
1-pentanol	(h,n)	1.8[b]	−0.5	−30	−3	−2	7.5
1-heptanol	(h,n)	1.8[b]	1.5	−70	−3	−2	7.5
1-decanol	(h,n)	1.8[b]	5.5	−90	−3	−2	7.5

[a] $C_{\mathrm{sn},1}^{\mathrm{DIS}}$ = 1.6 (dodecane); 1.55 (≥ tetradecane); [b]guessed value

TABLE 7 Physical properties and ERAS parameters for benzylamine at 298.15 K and 0.1 MPa: V_m, molar volume; α_p isobaric thermal expansion coefficient; κ_T, isothermal compressibility; K_A, equilibrium constant of self-association; Δh_A^*, molar enthalpy of intermolecular hydrogen-bonding between benzylamine molecules; Δv_A^*, molar hydrogen-bonding volume between benzylamine molecules, V_m^*, reduction parameter for volume; p*, reduction parameter for pressure

Property/parameter	
V_m/cm^3 mol^{-1}	109.55
α_p /10^{-3} K^{-1}	0.887 [18]
κ_T /10^{-12} Pa	544.5 [18]
K_A	14.8
Δh_A^* /kJ mol^{-1}	−12.5
Δv_A^* / cm^3 mol^{-1}	−5
V_m^* /cm^3 mol^{-1}	90.88
p*/ J cm^{-3}	643.9

TABLE 8 ERAS parameters[a] for benzylamine(A) + benzene(B) or + heptane(B) and for 1-alkanol(A) + benzylamine(B) mixtures at 298.15 K and 0.1 MPa

System	K_AB	Δh_AB^* / kJ mol^{-1}	Δv_AB^* / cm^3 mol^{-1}	X_AB / J mol^{-3}
benzylamine + benzene[b]	0	0	0	11.50
benzylamine + heptane	0	0	0	50
methanol + benzylamine	3500	−46.2	−13.2	2
1-propanol + benzylamine	1500	−38.2	−11.2	4
1-pentanol + benzylamine	1000	−36.7	−10.9	6

1-heptanol + benzylamine	600	−35.5	−10.7	8
1-decanol + benzylamine	120	−35.2	−10.4	9

[a] K_{AB}, equilibrium constant; $\Delta h^{*}_{\mathrm{AB}}$, molar enthalpies of intermolecular hydrogen-bonding; $\Delta v^{*}_{\mathrm{AB}}$, molar hydrogen-bonding volumes; X_{AB}, physical parameter; [b]system at 303.15 K

TABLE 9 Critical points, temperatures, T_c, and compositions, x_{1c}, for benzylamine(1) + *n*-alkane(2) mixtures. Comparison of experimental results (Exp.) [55] with DISQUAC (DQ) values obtained using interaction parameters from Table 6.

n-alkane	T_c /K		x_{1c}	
	Exp.	DQ.	Exp.	DQ.
n-C_{10}	280.1	283.7	0.569	0.572
n-C_{12}	286.8	290.5	0.632	0.630
n-C_{14}	291.9	295	0.707	0.680
n-C_{16}	298.3	301.3	0.745	0.722

TABLE 10 Molar excess enthalpies, $H^{\mathrm{E}}_{\mathrm{m}}$, at equimolar composition, 298.15 K and 0.1 MPa of binary mixtures involving benzylamine. Comparison with ERAS[a] and DISQUAC results obtained using parameters from Tables 6-8.

Solvent	*N*	$H^{\mathrm{E}}_{\mathrm{m}}$ / J mol^{-1}			$dev(H^{\mathrm{E}}_{\mathrm{m}})$ [b]		
		Exp.	ERAS	DQ	Exp.	ERAS	DQ
Benzene[c]	13	498	507	510	0.013	0.141	0.022
Heptane	13	1778	1803	1818	0.008	0.021	0.026
Methanol	15	–2678	–2680	–2670	0.009	0.163	0.019
1-propanol	15	–1492	–1390	–1525	0.039	0.152	0.033
1-pentanol	16	–1151	–1091	–1180	0.011	0.215	0.038
1-heptanol	15	–974	–807	–934	0.008	0.222	0.054
1-decanol	15	–692	–474	–690	0.009	0.267	0.068

[a]In ERAS calculations, benzylamine is the first component in systems with heptane or benzene, and the second component in mixtures including 1-alkanols;

[b] $dev(H^{\mathrm{E}}_{\mathrm{m}}) = \left[\frac{1}{N}\sum\left(\frac{H^{\mathrm{E}}_{\mathrm{m,calc}} - H^{\mathrm{E}}_{\mathrm{m,exp}}}{H^{\mathrm{E}}_{\mathrm{m,exp}}(x_1 = 0.5)}\right)^2\right]^{1/2}$ (*N*, number of data points); [c]system at 303.15 K

TABLE 11 Molar heat capacities at constant pressure, $C_{\mathrm{pm}}^{\mathrm{E}}$ at equimolar composition, 298.15 K and 0.1 MPa of benzylamine + organic solvent mixtures. Comparison of experimental values (Exp.) with DISQUAC (DQ) results obtained using parameters from Table 6.

System	*T*/K	$C_{\mathrm{pm}}^{\mathrm{E}}$ / J mol^{-1} K^{-1}		Ref.
		Exp.	DQ	
Benzylamine + heptane	293.15	6.3	6.3	19
Methanol + benzylamine	298.15	12.9	13	19
	308.15	13.3	14.6	19
1-propanol + benzylamine	298.15	12.7	13	19
	308.15	12.4	13.2	19
1-butanol + benzylamine	298.15	12	12	20
	308.15	11.6	11.8	20
	333.15	9.9	8.4	20
1-pentanol + benzylamine	298.15	13.0	13.1	19
	308.15	11.9	12.7	19
1-decanol + benzylamine	298.15	11.4	11.7	20
	308.15	9.9	11.1	20
	333.15	6.2	7.2	20

TABLE 12 Partial molar excess enthalpies at infinite dilution of the first component,[a] $H_{\mathrm{m1}}^{\mathrm{E},\infty}$, at 298.15 K at 0.1 MPa for amine(1) + alkane(2) and for 1-alkanol(1) + amine(2) mixtures and hydrogen bond enthalpies, $\Delta H_{\mathrm{OH\text{-}NH2}}^{\mathrm{int}}$, for 1-alkanol-amine interactions.

System	$H_{\mathrm{m1}}^{\mathrm{E},\infty}$ /kJ mol^{-1}	$\Delta H_{\mathrm{OH\text{-}NH2}}^{\mathrm{int}}$ /kJ mol^{-1}
benzylamine(1) + heptane(2)	10	
methanol(1) + benzylamine(2)	−7.8	−41
1-propanol(1) + benzylamine(2)	−4.5	−37.7
1-pentanol(1) + benzylamine (2)	−3.5	−36.7
1-heptanol(1) + benzylamine (2)	−2.2	−35.4
1-decanol(1) + benzylamine e(2)	0.2	−33

[a] values obtained from $H_{\mathrm{m}}^{\mathrm{E}}$ data over the whole concentration range

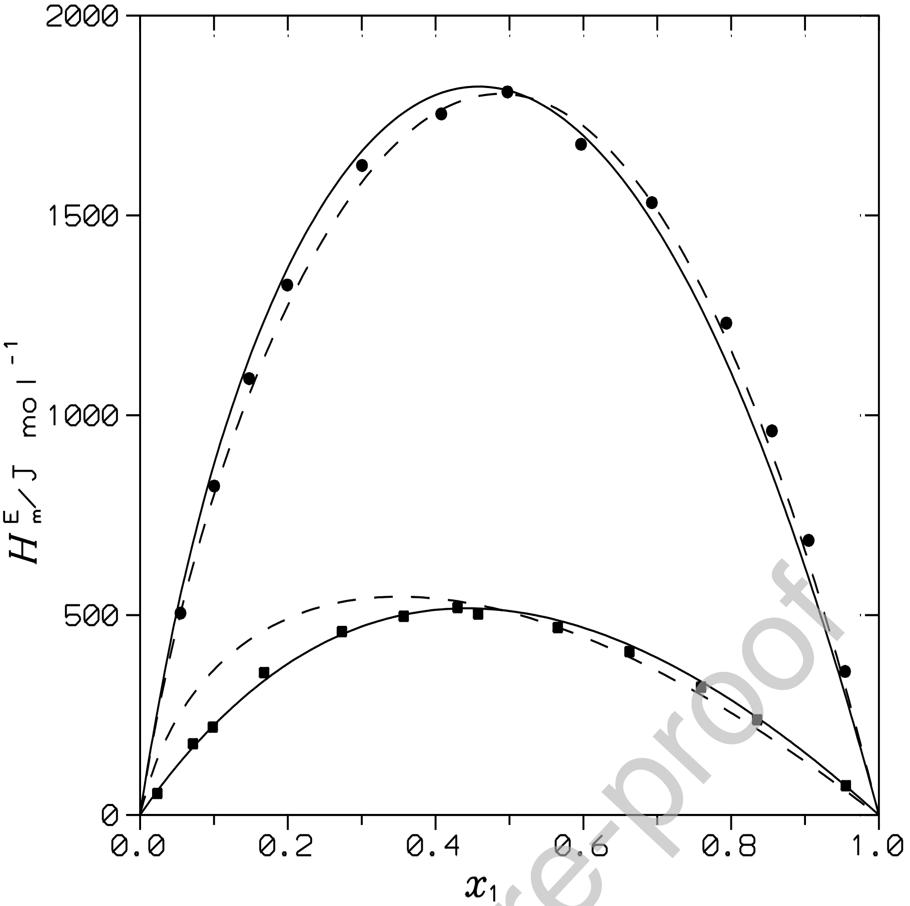

Figure 1. $H^{\mathrm{E}}_{\mathrm{m}}$ of benzylamine(1) + hydrocarbon(2) mixtures at temperature *T* and 0.1 MPa. Points, experimental results: (●), heptane (*T* = 298.15 K, this work); (■), benzene (*T* = 303.15 K, [54]). Solid lines, DISQUAC calculations with interaction parameters listed in Table 6. Dashed lines, ERAS results using parameters from Tables 7 and 8.

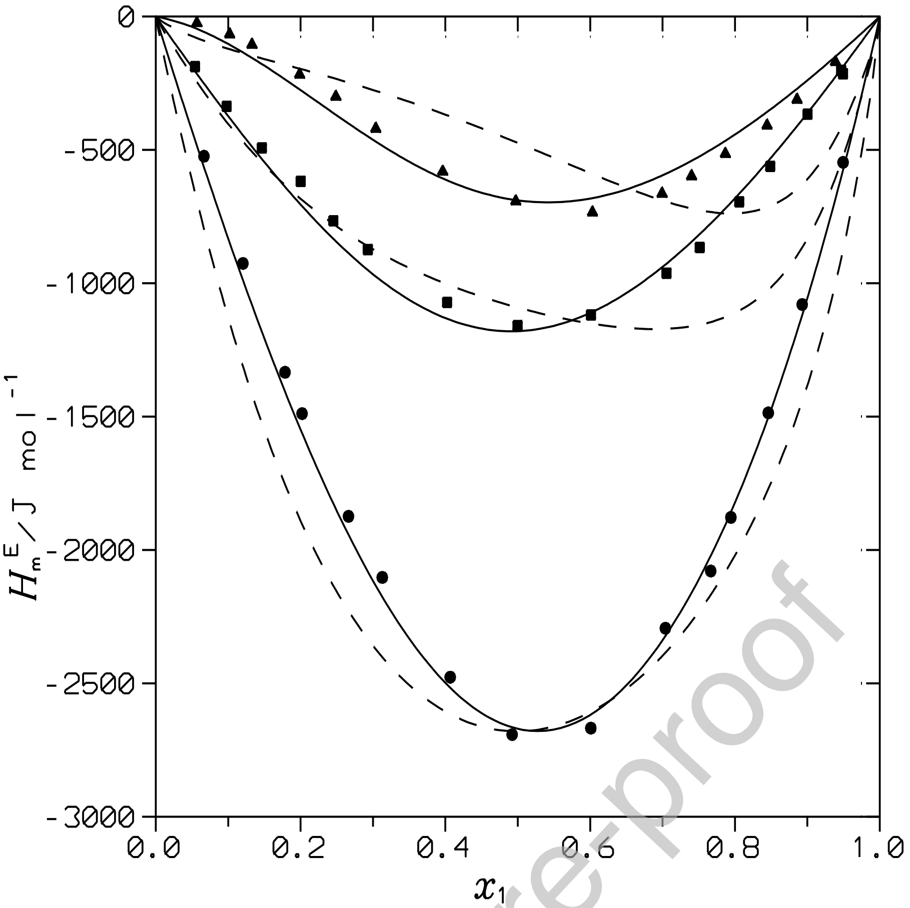

Figure 2. H_m^E of 1-alkanol(1) + benzylamine(2) mixtures at 298.15 K and 0.1 MPa. Points, experimental results (this work): (●), methanol; (■), 1-pentanol; (▲), 1-decanol. Solid lines, DISQUAC calculations with interaction parameters listed in Table 6. Dashed lines, ERAS results using parameters from Tables 7 and 8.

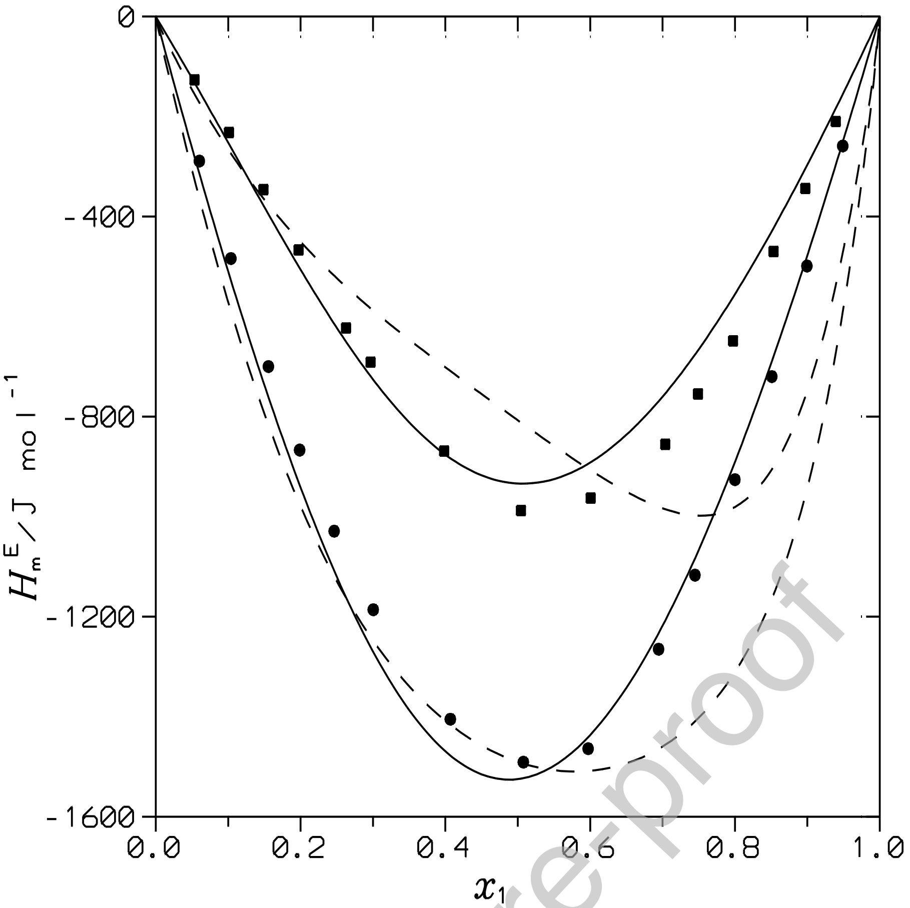

Figure 3. H_m^E of 1-alkanol(1) + benzylamine(2) mixtures at 298.15 K and 0.1 MPa. Points, experimental results (this work): (●), 1-propanol; (■), 1-heptanol. Solid lines, DISQUAC calculations with interaction parameters listed in Table 6. Dashed lines, ERAS results using parameters from Tables 7 and 8.

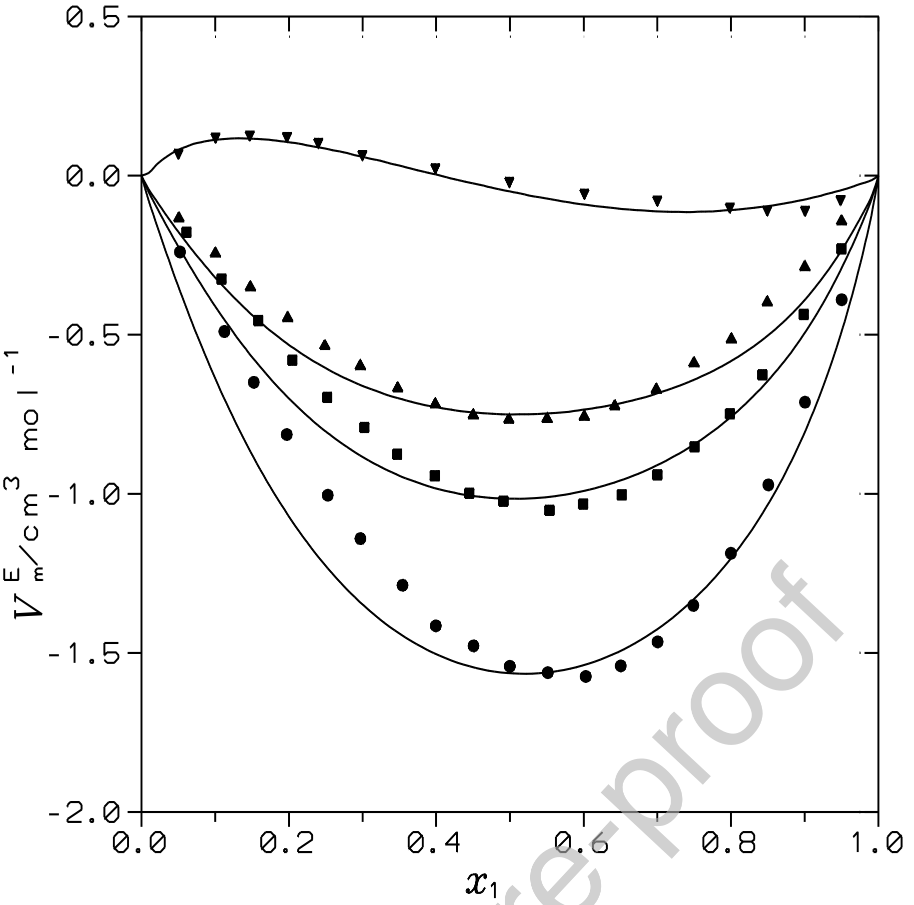

Figure 4. V_m^E of mixtures containing benzylamine at 298.15 K and 0.1 MPa. Points experimental results: (▼), benzylamine(1) + heptane(2) (this work); (□), methanol(1) + benzylamine(2); (■), 1-propanol(1) + benzylamine(2); (▲), 1-pentanol(1) + benzylamine(2) [18]. Solid lines, ERAS calculations using parameters listed in Tables 7 and 8.

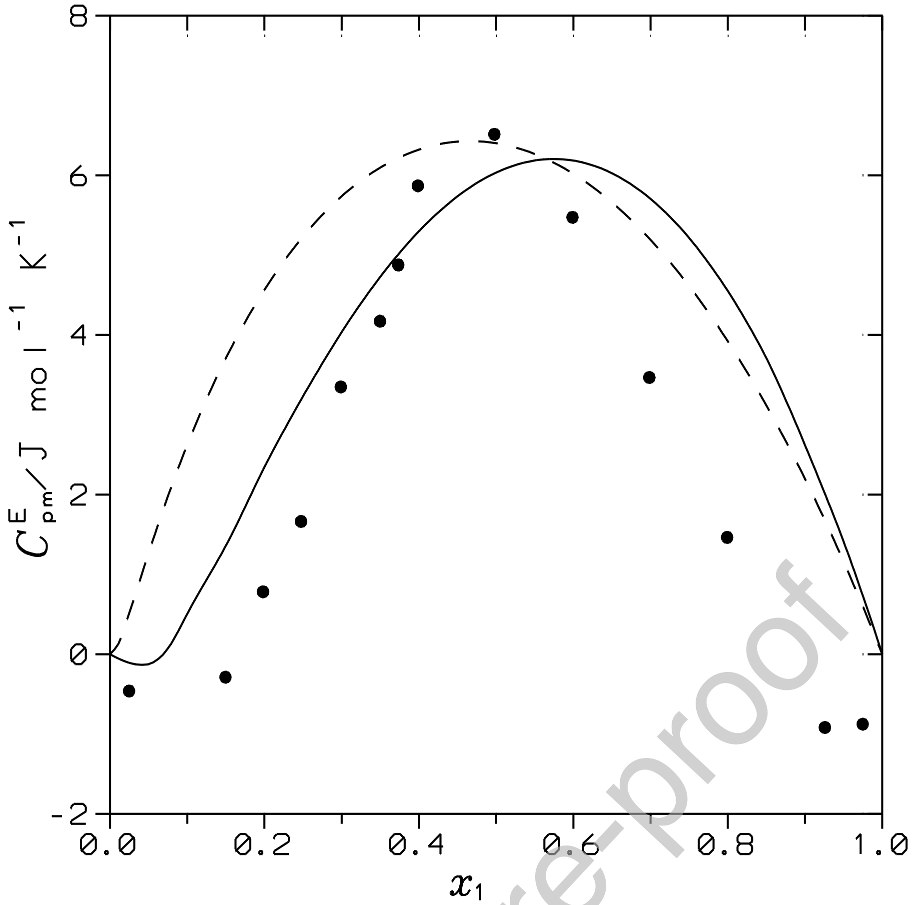

Figure 5. $C^{\rm E}_{\rm pm}$ of the benzylamine(1) + heptane(2) mixture at 293.15 K and and 0.1 MPa. Points, experimental results [19]. Solid line, DISQUAC calculations with interaction parameters listed in Table 6. Dashed line, ERAS results using parameters from Tables 7 and 8 and $\frac{dX_{\rm AB}}{dT}$ = 0.13 J cm^{-3} K^{-1}.

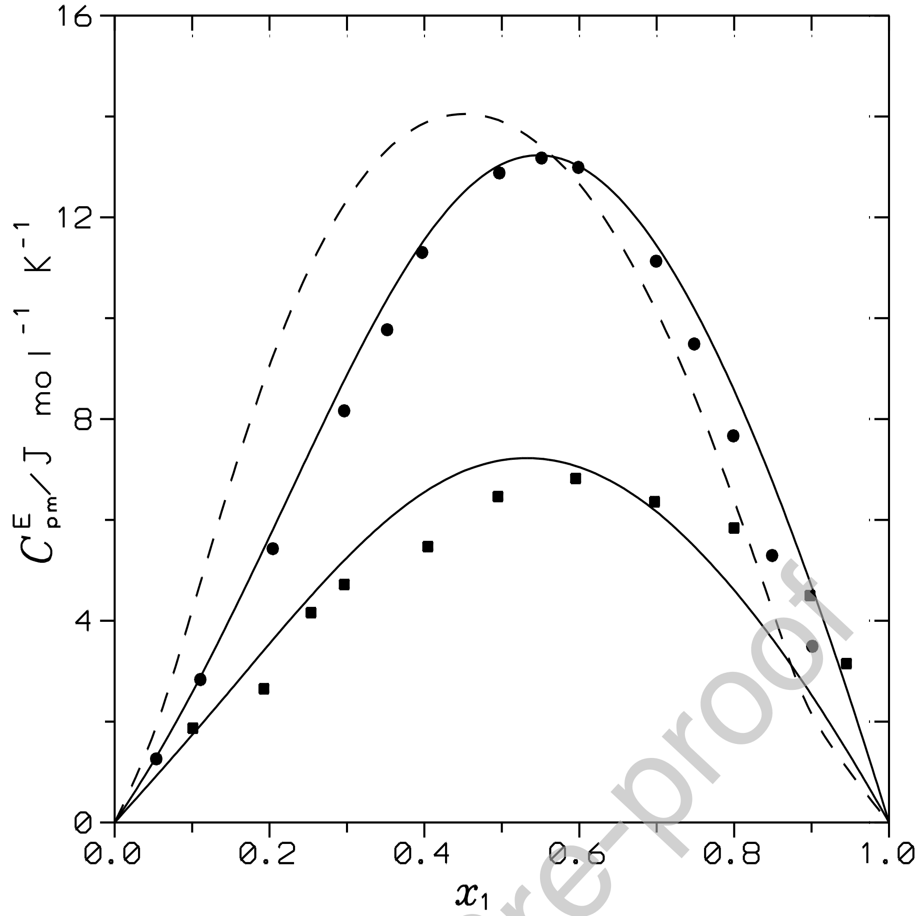

Figure 6. C^{E}_{pm} of 1-alkanol(1) + benzylamine(2) mixtures at temperature T and and 0.1 MPa. Points, experimental results [19]: (●), methanol (T = 298.15 K); (■), 1-pentanol (T = 333.15 K). Solid lines, DISQUAC calculations with interaction parameters listed in Table 6. Dashed line, ERAS results for the methanol system using parameters from Tables 7 and 8 and $\frac{dX_{AB}}{dT}$ = 1 J cm^{-3} K^{-1}.

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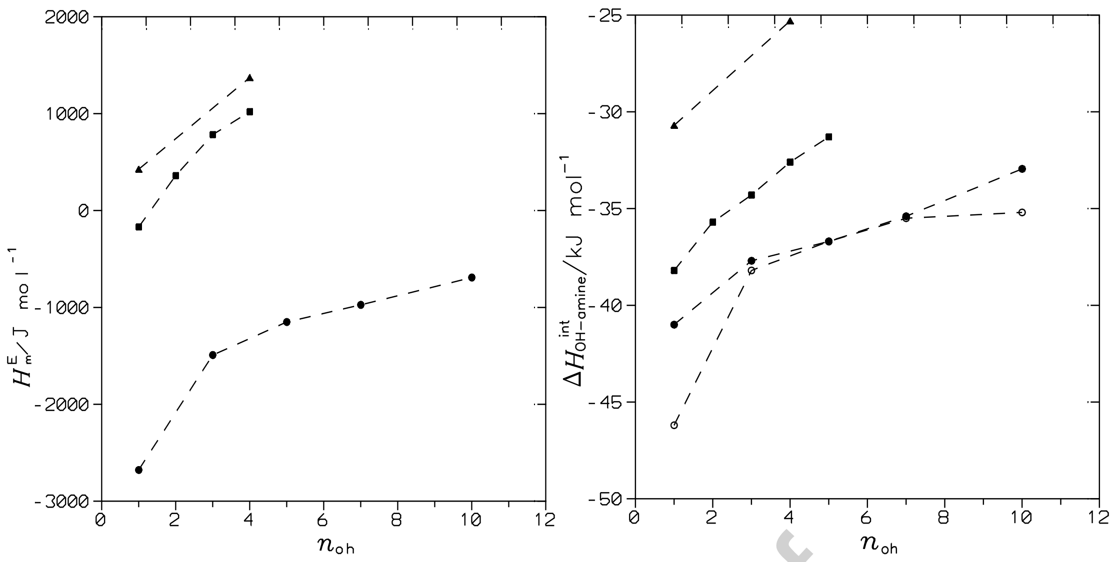
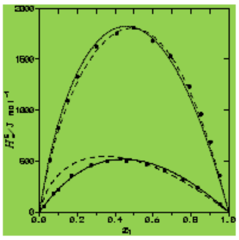


Figure 7a **Figure 7b**

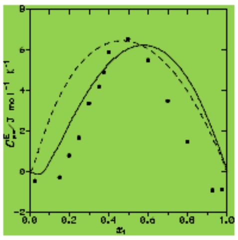
Figure 7 H_m^E values at equimolar composition, 298.15 K and 0.1 MPa (Figure 7a) and $\Delta H^{int}_{OH\text{-}NH2}$ results at 298.15 K and 0.1 MPa (Figure 7b) for 1-alkanol(1) + aromatic amine mixtures(2): (□), benzylamine systems (this work); (■), aniline mixtures [1]; (▲), solutions involving *N*-methylaniline [78]. Open symbols, Δh^*_{AB} values from the ERAS model for benzylamine mixtures (this work). Lines, are for the aid of the eye.

SYSTEMS WITH BENZYLAMINE:
DEVIATIONS FROM RAOULT'LAW

mixtures with alkanes: positive deviations

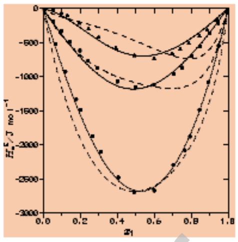


(●), heptane; (■), benzene

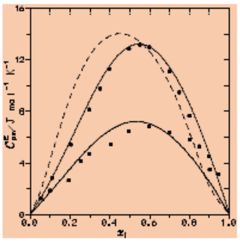


(●), heptane

mixtures with 1-alkanols: negative deviations



(●), methanol; (■), 1-pentanol;
(▲), 1-decanol



(●), methanol (T = 298.15 K)
(■), 1-pentanol (T = 333.15 K

GRAPHICAL ABSTRACT