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**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**

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Abstract

Excess molar enthalpies, H_m^E , have been measured using a Tian-Calvet microcalorimeter for the systems $\text{CH}_3(\text{CH}_2)_{u-1}\text{OH}$ ($u = 1, 2, 3, 4, 7, 10$) + cyclohexylamine at 298.15 K and 0.1 MPa. The H_m^E values are large and negative, indicating the existence of strong interactions between unlike molecules, which is consistent with the also large and negative excess molar volumes, V_m^E of these solutions, previously measured by us. The contribution from the equation of state term to H_m^E has been evaluated for the 1-alkanol + cyclohexylamine, or + 1-hexylamine, or + aniline mixtures, and the corresponding excess molar internal energies at constant volumes, $U_{m,V}^E$, determined. It is shown that such contribution is particularly important for the methanol + aniline system, in such way that the excess functions H_m^E and $U_{m,V}^E$ have different sign at $x_1 = 0.5$. The DISQUAC and ERAS models have been applied to the cyclohexylamine systems, and the interaction parameters reported. DISQUAC improves ERAS results on H_m^E . The latter model describes correctly the V_m^E curves. The variation of H_m^E of $\text{CH}_3(\text{CH}_2)_{u-1}\text{OH}$ + cyclohexylamine, or + 1-hexylamine, or + aniline mixtures with u along a homologous series with a given amine, or with the amine in mixtures with a given 1-alkanol is discussed in terms of the different interactional contributions to H_m^E .

Keywords: 1-alkanol; cyclohexylamine; H_m^E ; V_m^E ; DISQUAC; ERAS

1. Introduction

Alkanols and amines have many industrial applications. Alkanols are used in the manufacturing of fuels, perfumes, cosmetics, paints, drugs, explosives, fats, waxes, resins, plastics and more [1,2]. Cyclic amines are important in the production of pharmaceuticals and of chemicals which are included in insecticides, pesticides, dyes, or corrosion inhibitors [3]. The study of 1-alkanol + amine mixtures is required, *e.g.*, to a better understanding of solutions containing alkanolamines that are used in the chemical absorption of CO₂ emissions [4].

Over the last years, we have conducted a systematic research on mixtures containing amines, and, particularly on 1-alkanol + amine systems. This class of solutions is very interesting since they show rather different behaviours. For example, mixtures with linear or primary amines are characterized by strong negative deviations from the Raoult's law as it is demonstrated by their large and negative excess molar Gibbs energies (G_m^E) [5-10] and enthalpies, (H_m^E), [11-18]. Thus, for the methanol + 1-butylamine mixture at 348.15 K and equimolar composition, $G_m^E = -799 \text{ J}\cdot\text{mol}^{-1}$ [6] and for methanol + 1-hexylamine system at 298.15 K and $x_1 = 0.5$, $H_m^E = -3200 \text{ J}\cdot\text{mol}^{-1}$ [11]. These results reveal the existence of strong interactions between unlike molecules [11,12,18], which are even stronger than those between 1-alkanol molecules, and that lead to the formation of complexes as solid-liquid phase diagrams reveal [19,20]. In contrast, 1-alcohol + aniline mixtures show positive deviations from the Raoult's law as it can be seen from the following results for the ethanol system at 298.15 K and equimolar composition: $G_m^E = 515 \text{ J}\cdot\text{mol}^{-1}$ [21] and $H_m^E = 360 \text{ J}\cdot\text{mol}^{-1}$ [22]. Up to now, we have provided volumetric [23-30], calorimetric [31-33], phase equilibria [10,34], viscosimetric [27-29] and permittivity [27-30,35-37] data for binary mixtures formed by 1-alkanol and any of the following amines: linear primary or secondary amines, *N,N,N*-triethylamine, cyclohexylamine, aniline, benzylamine, quinoline or 1-*H*-pyrrole. We have also developed detailed theoretical investigations on this type of systems [35-44] by means of different models: DISQUAC [45], ERAS [46], Flory [47], Kirkwood-Buff integrals formalism [48,49], the concentration-concentration structure factor formalism [50,51], or the Kirkwood-Fröhlich theory [52]. As continuation of our works on 1-alkanol + cyclohexylamine systems [27-29], we report now H_m^E data, at 298.15 K and 0.1 MPa for systems involving methanol, ethanol, 1-propanol, 1-butanol, 1-heptanol or 1-decanol. In addition, these mixtures are studied in terms of the DISQUAC and ERAS models. Previously, we had provided ERAS parameters determined essentially from excess molar volume, V_m^E , data [29]. No interaction parameters for the present solutions are available in the framework of the UNIFAC (Dortmund) model [53,54].

2. Experimental

2.1 Materials

All the chemicals were supplied by Sigma-Aldrich. Their CAS number, purity, according to gas chromatographic analysis (GC) provided by the supplier, and densities are shown in Table 1. Densities of the pure liquids were determined from a vibrating-tube densimeter Anton Paar model DSA 602 with a temperature stability of 0.01 K. Calibration of the densimeter was conducted using the following pure liquids: heptane, 2,2,4-trimethylpentane, cyclohexane, benzene, toluene, 1-propanol and water. The estimated uncertainty for density is $\pm 8 \times 10^{-2} \text{ kg}\cdot\text{m}^{-3}$.

2.2 Apparatus and procedure

Compounds were weighed using an analytical balance A and D instrument model HR-202 (weighing uncertainty 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) [55]. H_m^E measurements were carried out at 298.15 K and 0.1 MPa by means of a standard Tian-Calvet microcalorimeter equipped with an aluminium mixing cell, designed by us, with a small (<2%) gas phase. The mixing process is the same as in previous applications [56]. Some improvements have been performed with regard to the thermal insulation and to the acquisition and processing of the data obtained from the apparatus. A new cable, a shielded twisted pair, has been used especially adapted for the type of thermocouples of the calorimeter. This allows reducing the appearance of parasitic voltages and noise in the output signal produced by external sources. The calibration of the calorimeter was conducted measuring H_m^E for the cyclohexane + benzene, and methanol + 1-butylamine systems at 298.15 K and 0.1 MPa. Results are collected in Table 2. A comparison with data from the literature [16,18,57-62] is shown in Figures 1a and 1b. At equimolar composition, our measurements deviate by $\sim 1\%$ with regard to the corresponding values from [16,18,57-60]. The values provided by Pradhan and Mathur ($-3866 \text{ J}\cdot\text{mol}^{-1}$ [61]) and by Dutta-Choudhury and Mathur ($-3850 \text{ J}\cdot\text{mol}^{-1}$ [62]) for the methanol + 1-butylamine mixture are lower than our result ($-3726 \text{ J}\cdot\text{mol}^{-1}$) by 3.7% and 3.3%, respectively. The estimated maximum relative uncertainty for H_m^E is 0.015. Since the systems selected for the calibration show very different H_m^E values (Table 2), this guarantees that the equipment is useful to perform H_m^E measurements over a wide range of values.

3. Experimental results

Our measurements on H_m^E for 1-alkanol + cyclohexylamine mixtures at 298.15 K and 0.1 MPa are listed in Table 3 (see Figures S1 and S2, supplementary material). Measurements of H_m^E for the methanol system have been reported by Mato and Berrueta [60]. At $x_1 = 0.5$, their value is ca. 600 J·mol⁻¹ higher than our experimental result (Figure 2). Partial excess molar enthalpies at infinite dilution of component i ($=1,2$), $H_{mi}^{E,\infty}$, are available in the literature for the methanol(1) + cyclohexylamine(2) mixture [63]. The results are: $H_{mi}^{E,\infty}$ /kJ·mol⁻¹ = -11.55 ($i = 1$); -14.90 ($i = 2$) [63]. Our values ($H_{mi}^{E,\infty}$ /kJ·mol⁻¹ = -11.1 ($i = 1$); -14.1 ($i = 2$)), determined from H_m^E measurements over the entire mole fraction range are in good agreement with the mentioned results. Excess molar internal energies of constant volume, $U_{m,V}^E$, can be determined from [64]:

$$U_{m,V}^E = H_m^E - T \frac{\alpha_p}{\kappa_T} V_m^E \quad (1)$$

where α_p and κ_T are, respectively, the isobaric thermal expansion coefficient and the coefficient of isothermal compressibility of the considered system. The $U_{m,V}^E$ values for 1-alkanol + cyclohexylamine mixtures were obtained (see Table S1, supplementary material) using the H_m^E values listed in Table 3 and V_m^E results at the same mole fractions determined from Redlich-Kister expansions previously obtained when volumetric properties for these solutions were measured [27-29]. The α_p and κ_T values were calculated assuming ideal behavior for the systems ($M^{\text{id}} = \phi_1 M_1 + \phi_2 M_2$; with $M_i = \alpha_{pi}$, or κ_{Ti} and $\phi_i = x_i V_{m,i} / (x_1 V_{m,1} + x_2 V_{m,2})$). For pure compounds, their α_{pi} , and κ_{Ti} values were taken from the literature [65-67]. The contribution of the equation of state (eos) term to H_m^E , defined as $T \frac{\alpha_p}{\kappa_T} V_m^E$, is ranged between 17% for the methanol mixture and 12% for the 1-decanol solution. However, the mentioned contribution may be much more important, as it will be seen below.

The data ($F_m^E = H_m^E$; $F_m^E = U_{m,V}^E$) were fitted by unweighted least-squares polynomial regression to the equation of the Redlich-Kister type [68]:

$$F_m^E = x_1 (1 - x_1) \sum_{i=0}^{k-1} A_i (2x_1 - 1)^i \quad (2)$$

The number, k , of needed coefficients for this regression was determined, for each system, by applying an F-test of additional term [69] at 99.5% confidence level. For cyclohexylamine mixtures, Table 4 lists the parameters A_i obtained in the regression, together with the standard deviations $\sigma(F_m^E)$ defined by:

$$\sigma(F_m^E) = \left[\frac{1}{N-k} \sum_{j=1}^N (F_{\text{mcal},j}^E - F_{\text{mexp},j}^E)^2 \right]^{1/2} \quad (3)$$

where N stands for the number of data points, and $F_{\text{mcal},j}^E$ is the value of the excess property calculated using equation (2). For the systems cyclohexane + benzene, and methanol + 1-butylamine, this information is given as a footnote in Table 2.

4. Models

4.1 DISpersive QUAsiChemical

DISQUAC is based on the rigid lattice theory developed by Guggenheim [70]. Some important features of the model are given. (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 [71], with the volume R_{CH_4} and surface Q_{CH_4} of methane taken arbitrarily as volume and surface units [72]. For the groups involved in this investigation, the geometrical parameters are available in the literature [72-74] (ii) The partition function is factorized into two terms. The excess functions G_m^E and H_m^E are the result of the sum of two contributions. The dispersive (DIS) term is linked to the contribution from dispersive forces; and the quasichemical (QUAC) term is due to the anisotropy of the field forces created by the solution molecules. In the case of G_m^E , a combinatorial term, $G_m^{\text{E,COMB}}$, calculated using the Flory-Huggins equation [72,75] must be included. Therefore,

$$G_m^E = G_m^{\text{E,DIS}} + G_m^{\text{E,QUAC}} + G_m^{\text{E,COMB}} \quad (4)$$

$$H_m^E = H_m^{\text{E,DIS}} + H_m^{\text{E,QUAC}} \quad (5)$$

(iii) The interaction parameters are dependent on the molecular structure of the mixture components; (iv) In the present status of the theory, it is not possible to characterize each polar

contact by its own coordination number (z). For this reason, $z = 4$ is used for all the polar contacts. This is a shortcoming of DISQUAC and is partially removed assuming that the interaction parameters are dependent on the molecular structure. (v) It is also assumed that $V_m^E = 0$.

The equations used to calculate the DIS and QUAC contributions to G_m^E and H_m^E can be found elsewhere [38,76]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [38,76], $C_{st,l}^{DIS}; C_{st,l}^{QUAC}$ where $s \neq t$ are two contact surfaces present in the mixture and $l = 1$ (Gibbs energy; $C_{st,1}^{DIS/QUAC} = g_{st}^{DIS/QUAC}(T_0) / RT_0$); $l = 2$ (enthalpy, $C_{st,2}^{DIS/QUAC} = h_{st}^{DIS/QUAC}(T_0) / RT_0$), $l = 3$ (heat capacity, $C_{st,3}^{DIS/QUAC} = c_{pst}^{DIS/QUAC}(T_0) / R$). $T_0 = 298.15$ K is the scaling temperature and R , the gas constant.

4.2 ERAS

The Extended Real Associated Solution (ERAS) model [46] combines the Real Association Solution Model [77,78] with Flory's equation of state [47]. We provide some relevant features of the model. (i) The excess molar functions ($F_m^E = H_m^E, V_m^E$) are calculated as the sum of two contributions. The chemical contribution, $F_{m,chem}^E$, arises from hydrogen bonding; the physical contribution, $F_{m,phys}^E$, is linked to nonpolar Van der Waals interactions and free volume effects. Expressions for H_m^E and V_m^E can be found elsewhere [38]. (ii) It is assumed that only consecutive linear association occurs. Accordingly, 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 this case, $i = A$ (1-alkanol) or $= B$ (cyclohexylamine)), according to the equations:



with m and n ranging from 1 to ∞ . The cross-association between two self-associated species A_m and B_n is represented by:



where cross-association constants, K_{AB} , are also considered to be independent of the chain length. Reactions described by equations (6)-(8) are characterized, respectively, by the molar enthalpies of intermolecular hydrogen-bonding Δh_A^* , Δh_B^* and Δh_{AB}^* , and by negative molar hydrogen-bonding volumes, Δv_A^* , Δv_B^* and Δv_{AB}^* , defined in order to take into account the decrease of the core volume of multimers in comparison to that of an isolated monomer. The three equilibrium constants depend on temperature according to the Δh_i^* values and the Van't Hoff equation. (iii) The $F_{m,phys}^E$ term is derived from the Flory's equation of state [47], which is assumed to be valid not only for pure compounds but also for the mixture [11,18]:

$$\frac{\bar{p}_i \bar{V}_i}{\bar{T}_i} = \frac{\bar{V}_i^{1/3}}{\bar{V}_i^{1/3} - 1} - \frac{1}{\bar{V}_i \bar{T}_i} \quad (9)$$

where $i = A, B$ or M (mixture). In equation (9), $\bar{V}_i = V_{m,i}/V_{m,i}^*$; $\bar{p}_i = p/p_i^*$; $\bar{T}_i = T/T_i^*$ are the reduced properties for volume, pressure and temperature, respectively. The pure component reduction parameters ($V_{m,i}^*$, p_i^* , T_i^*) are obtained from p - V - T data (density, α_{p_i} , and κ_{T_i}) and association parameters [11,18]. The reduction parameters for the mixture p_M^* and T_M^* are calculated from mixing rules [11,18]. 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 [71].

5. Adjustment of interaction parameters

5.1 DISQUAC

In terms of DISQUAC, 1-alkanol + cyclohexylamine mixtures are built by four types of surface: (i) type a, aliphatic (CH_3 , CH_2 , in 1-alkanols); (ii) type c, cyclic (c-CH_2 or c-CH in cyclohexylamine); (iii) type h, OH in 1-alkanols; (iv) type n, amine (NH_2 in cyclohexylamine). The four surfaces generate six contacts: (a,c), (a,h), (a,n), (c,h), (c,n) and (h,n). The (a,c) contact is represented by dispersive interaction parameters obtained from the study of cyclohexane + n -alkane mixtures [75]. The remainder contacts are described by both DIS and QUAC interaction parameters. The interchange coefficients $C_{an,l}^{\text{DIS}}$ and $C_{an,l}^{\text{QUAC}}$ are known from a general DISQUAC treatment of cyclic amine + alkane systems [79], and the $C_{sh,l}^{\text{DIS}}$ and $C_{sh,l}^{\text{QUAC}}$ coefficients from the corresponding investigation of 1-alkanol + n -alkane ($s = a$) [74], or + cyclohexane ($s = c$) [80] mixtures. Therefore, only the interaction parameters for the (h,n) contact must be determined.

The general procedure applied in the estimation of the interaction parameters has been explained in detail elsewhere [38,76]. Due to the VLE data for these systems is scarce [81,82],

the $C_{\text{hn},1}^{\text{QUAC}}$ coefficients ($l=1,2$) were adjusted together with the $C_{\text{hn},2}^{\text{DIS}}$ coefficients to get a good description of the symmetry of the H_m^E curves. The first DIS Gibbs energy parameters were then estimated using the few VLE available in the literature [81,82]. Final parameters are listed in Table 5.

5.2 ERAS

The values of the ERAS parameters for 1-alkanols, $K_A, \Delta h_A^*, \Delta v_A^*$ and for cyclohexylamine, $K_B, \Delta h_B^*, \Delta v_B^*$ are known from the study of the corresponding mixtures with alkanes [46,83]. The binary parameters to be fitted to the H_m^E and V_m^E data of the systems studied are then $K_{AB}, \Delta h_{AB}^*, \Delta v_{AB}^*$ and X_{AB} (Table 6).

6 Theoretical results

Comparison between experimental H_m^E data and theoretical results using DISQUAC and ERAS is shown Table 7 (see also Figures 2 and 3 and Figures S3 and S4 of supplementary material). We note that DISQUAC improves results from the ERAS model. Larger differences with the experimental values emerge for systems with 1-heptanol or 1-decanol (Table 7). ERAS correctly describes V_m^E (see Figure 3 and Figure S4 of supplementary material). On the other hand, DISQUAC provides, at equimolar composition and 407.1 K, $G_m^E/\text{J}\cdot\text{mol}^{-1} = -476$, (methanol); -460 (ethanol and -294 (1-propanol). The experimental results, in the same units, are respectively: -508 , -408 and -503 [82]. This experimental variation of G_m^E with the alkanol size should be taken with caution.

7. Discussion

Below, we are referring to values of the thermodynamic properties at equimolar composition and 298.15 K. On the other hand, n_{OH} stands for the number of C atoms of the 1-alkanol.

Figure 4 shows H_m^E and $U_{m,V}^E$ values for 1-alkanol + amine mixtures. The $U_{m,V}^E$ values for systems with 1-hexylamine or aniline were computed by means of the same method explained above, using values of α_{pi} , and κ_{T_i} from the literature [30, 65-67].

As already mentioned, the large and negative H_m^E values of 1-alkanol + 1-hexylamine mixtures (Figure 4) are due to the existence of strong interactions between unlike molecules [11,18,38]. On the other hand, H_m^E increases from $n_{\text{OH}} = 1$ up to $n_{\text{OH}} = 3$, and then increases smoothly (Figure 4). The corresponding V_m^E values are also negative (Figure 5), and it reveals that this excess function is determined mainly by interactional effects. The replacement of 1-

hexylamine by cyclohexylamine (cyclization effect) in systems with a given 1-alkanol leads to decreased values of H_m^E and V_m^E when $n_{OH} \leq 4$ (Figures 4 and 5). For mixtures including longer 1-alkanols, H_m^E and $U_{m,V}^E$ are more or less independent of the amine, while V_m^E becomes higher for systems with cyclohexylamine (Figures 4 and 5). The latter may be ascribed to the cyclic amine breaks a larger number of alkanol-alkanol interactions (see below), and, in some extent, to the existence of increased free volume effects in 1-hexylamine solutions, as the corresponding ($\alpha_p/10^{-3}$) values of pure compounds suggest (in K^{-1}): 8.52 (1-octanol) [65]; 8.18 (1-decanol) [65]; 10.5 (cyclohexylamine) [67]; 11.28 (1-hexylamine) [84]. It is to be noted that H_m^E and V_m^E change with n_{OH} in systems with cyclohexylamine more rapidly than in 1-hexylamine solutions (Figures 4 and 5). If 1-hexylamine is replaced by aniline (aromaticity effect), the values of H_m^E and V_m^E increase in line with n_{OH} . For the methanol mixture, H_m^E is negative ($-175 \text{ J}\cdot\text{mol}^{-1}$ [85]) while our $U_{m,V}^E$ result is positive ($143 \text{ J}\cdot\text{mol}^{-1}$). This huge variation underlines the importance of the eos contribution to H_m^E . In view of the positive $U_{m,V}^E$ values, one can conclude that interactions between like molecules are dominant in these mixtures. It is remarkable the opposite sign of the $U_{m,V}^E$ and V_m^E values (Figures 4 and 5), that indicates that the contribution to V_m^E arising from structural effects is here prevalent by far.

7.1 The enthalpy of the 1-alkanol-amine interactions

Next, we evaluate the enthalpy of the H-bonds between 1-alkanols and amines (termed as $\Delta H_{OH-NH_2}^{int}$). If structural effects are neglected [64,86], H_m^E can be considered the result of three contributions. Two of them, ΔH_{OH-OH} , $\Delta H_{NH_2-NH_2}$, are positive, and arise, respectively, from the breaking of alkanol-alkanol and amine-amine interactions upon mixing. In this process, new OH---NH₂ interactions are created, and it implies a negative contribution, ΔH_{OH-NH_2} , to H_m^E . Therefore [87-89]:

$$H_m^E = \Delta H_{OH-OH} + \Delta H_{NH_2-NH_2} + \Delta H_{OH-NH_2} \quad (10)$$

Values of $\Delta H_{OH-NH_2}^{int}$ can be obtained extending the equation (10) to $x_1 \rightarrow 0$ [89-91]. Then, ΔH_{OH-OH} and $\Delta H_{NH_2-NH_2}$ can be replaced by $H_{m1}^{E,\infty}$ of 1-alkanol(1) or amine(1) + alkane(2) systems. Thus,

$$\Delta H_{\text{OH-NH}_2}^{\text{int}} = H_{\text{m}1}^{\text{E},\infty} (1 - \text{alkanol} + \text{amine}) - H_{\text{m}1}^{\text{E},\infty} (1 - \text{alkanol} + \text{heptane}) - H_{\text{m}1}^{\text{E},\infty} (\text{amine} + \text{heptane, or} + \text{C}_6\text{H}_{12}) \quad (11)$$

Some shortcomings of this estimation of $\Delta H_{\text{OH-NH}_2}^{\text{int}}$ values are now given. (i) $H_{\text{m}1}^{\text{E},\infty}$ data used were determined from H_{m}^{E} measurements over the entire mole fraction range. (ii) For 1-alkanol + n -alkane systems, $H_{\text{m}1}^{\text{E},\infty}$ is assumed to be independent of the alcohol, a typical approach in the framework of association theories [46,92-94]. As in previous works [91,95], we have used here $H_{\text{m}1}^{\text{E},\infty} = 23.2 \text{ kJ}\cdot\text{mol}^{-1}$ [96-98]. Nevertheless, it should be remarked that the values of $\Delta H_{\text{OH-NH}_2}^{\text{int}}$ collected in Table 8 are still meaningful since they were obtained following the same procedure that in previous applications, which allows comparing enthalpies of interaction between 1-alkanols and different organic solvents. Inspection of Table 8 reveals that, for systems including 1-hexylamine or cyclohexylamine, $\Delta H_{\text{OH-NH}_2}^{\text{int}}$ values are quite similar, although, in the latter mixtures, interactions between unlike molecules become weaker in solutions including 1-heptanol or 1-decanol. The main feature of 1-alkanol-aniline interactions is their sharper dependence with n_{OH} . For the sake of comparison, we also provide the $\Delta H_{\text{OH-NH}_2}^{\text{int}}$ value for the methanol + piperidine mixture. It seems that interactions between unlike molecules in such solution are slightly weaker ($-36.9 \text{ kJ}\cdot\text{mol}^{-1}$) than those between methanol and cyclohexylamine ($-39.8 \text{ kJ}\cdot\text{mol}^{-1}$).

7.2. The $\Delta H_{\text{OH-OH}}$ term

This positive contribution depends on the considered solvent. For a given 1-alkanol, $H_{\text{m}}^{\text{E}}(\text{heptane}) < H_{\text{m}}^{\text{E}}(\text{cyclohexane})$ (cyclization effect) as it can be seen from the following experimental results. $H_{\text{m}}^{\text{E}}(\text{heptane})/\text{J}\cdot\text{mol}^{-1} = 591$ ($n_{\text{OH}} = 2$) [99]; 575 [100]; ($n_{\text{OH}} = 4$); 575 [101]; ($n_{\text{OH}} = 5$); 527 ($n_{\text{OH}} = 6$) [102]; 427 ($n_{\text{OH}} = 10$) [103] and $H_{\text{m}}^{\text{E}}(\text{cyclohexane})/\text{J}\cdot\text{mol}^{-1} = 624$ ($n_{\text{OH}} = 2$) [104]; 588 [105]; ($n_{\text{OH}} = 4$); 598 [106] ($n_{\text{OH}} = 5$); 604 [107] ($n_{\text{OH}} = 6$); 666 [106] ($n_{\text{OH}} = 10$). The differences $H_{\text{m}}^{\text{E}}(\text{cyclohexane}) - H_{\text{m}}^{\text{E}}(\text{heptane})$ become larger for systems formed by longer 1-alkanols. Similarly, we note that $H_{\text{m}}^{\text{E}}(\text{heptane}) < H_{\text{m}}^{\text{E}}(\text{toluene, isomeric molecule of aniline})$ (aromaticity effect) since $H_{\text{m}}^{\text{E}}(\text{toluene})/\text{J}\cdot\text{mol}^{-1} = 622$ ($n_{\text{OH}} = 1$); 881 ($n_{\text{OH}} = 3$); 942 ($n_{\text{OH}} = 4$); 912 ($n_{\text{OH}} = 5$). These values clearly indicate that an aromatic hydrocarbon such as toluene is a more efficient breaker of the alcohol network.

7.3 The $\Delta H_{\text{NH}_2\text{-NH}_2}$ term

This contribution is positive and increases in line with n_{OH} , which can be ascribed to the larger aliphatic surfaces of longer 1-alkanols break more easily the amine-amine interactions. Note that $H_{\text{m}}^{\text{E}}/\text{J}\cdot\text{mol}^{-1}$ of 1-hexylamine + n -alkane mixtures increases with the alkane size: 1064 (heptane); 1211 (decane); 1513 (hexadecane) [109]. The same occurs for the UCSTs of aniline systems: 342.6 (hexane) [110]; 343.1 (heptane) [111]; 356.8 (dodecane) [112] (all values in K). The existence of these miscibility gaps indicates that amine-amine interactions are much stronger in aniline systems. Accordingly, the $H_{\text{ml}}^{\text{E},\infty}$ value of the aniline + heptane (15 $\text{kJ}\cdot\text{mol}^{-1}$) [40,113] mixture is much higher than the results for mixtures 1-hexylamine + heptane ($H_{\text{ml}}^{\text{E},\infty}/\text{kJ}\cdot\text{mol}^{-1} = 5.7$ [114]), or cyclohexylamine + cyclohexane ($H_{\text{ml}}^{\text{E},\infty}/\text{kJ}\cdot\text{mol}^{-1} = 5.5$ [115]), characterized by rather similar $H_{\text{ml}}^{\text{E},\infty}$ results.

7.4 The $\Delta H_{\text{OH-NH}_2}$ term

This negative contribution can be roughly estimated from the product ($\Delta H_{\text{OH-NH}_2}^{\text{int}}$ x number of interactions between unlike molecules created during mixing) (see, *e.g.*, [116]). Values of $\Delta H_{\text{OH-NH}_2}^{\text{int}}$ have been already discussed (Table 8). One can expect that the second factor of the product decreases for larger n_{OH} values, since the OH group is then more sterically hindered and a lower number of alcohol-amine interactions are formed upon mixing. In summary, the present contribution becomes less negative when n_{OH} is increased.

7.5 Dependence of H_{m}^{E} with the 1-alkanol and with the amine

The observed variation of H_{m}^{E} with n_{OH} for mixtures including aniline or cyclohexylamine can be explained taking into account that the three contributions to H_{m}^{E} increase in line with n_{OH} , except for 1-hexylamine solutions, where the $\Delta H_{\text{OH-OH}}$ contribution decreases for longer 1-alkanols. In such a case, this effect is more or less counterbalanced with the increase of the $\Delta H_{\text{NH}_2\text{-NH}_2}$ and $\Delta H_{\text{OH-NH}_2}$ terms and then H_{m}^{E} slowly increases with n_{OH} .

For a given 1-alkanol, the much larger H_{m}^{E} values of solutions with aniline can be ascribed to the $\Delta H_{\text{OH-OH}}$ and $\Delta H_{\text{NH}_2\text{-NH}_2}$ terms contribute largely to H_{m}^{E} . On the other hand, interactions are of dipolar type since, for these systems, H_{m}^{E} is poorly described by the ERAS model [40].

Regarding mixtures with 1-hexylamine, or cyclohexylamine, both magnitudes, $\Delta H_{\text{NH}_2\text{-NH}_2}$ and $\Delta H_{\text{OH-NH}_2}^{\text{int}}$, are practically independent of the amine, while the $\Delta H_{\text{OH-OH}}$ contribution is larger for systems containing cyclohexylamine and longer 1-alkanols. Thus, the more negative H_{m}^{E} of systems including this amine and 1-alkanols with $n_{\text{OH}} \leq 4$ suggest that the

$\Delta H_{\text{OH-NH}_2}$ term must be more negative, probably due to the amine group is less sterically hindered and more interactions between unlike molecules are formed along the mixing process. In the case of systems with longer 1-alkanols, the difference $|\Delta H_{\text{OH-NH}_2}(\text{cyclohexylamine}) - \Delta H_{\text{OH-NH}_2}(\text{1-hexylamine})|$ is lower than the difference $|\Delta H_{\text{OH-OH}}(\text{cyclohexylamine}) - \Delta H_{\text{OH-OH}}(\text{1-hexylamine})|$, and the resulting H_m^E values are very similar, and eventually slightly higher for the 1-decanol + cyclohexylamine mixture (Figure 4). Similar considerations are still valid to explain the larger H_m^E result of the methanol + piperidine mixture ($-3160 \text{ J}\cdot\text{mol}^{-1}$ [117]).

For a binary mixture, the $S_{\text{CC}}(0)$ function is defined by [50, 51]:

$$S_{\text{CC}}(0) = \frac{RT}{(\partial^2 G_m^M / \partial x_1^2)_{P,T}} = \frac{x_1 x_2}{1 + \frac{x_1 x_2}{RT} \left(\frac{\partial^2 G_m^E}{\partial x_1^2} \right)_{P,T}} \quad (12)$$

For ideal mixtures, $G_m^{E,\text{id}} = 0$; and $S_{\text{CC}}^{\text{id}}(0) = x_1 x_2$. Stability conditions require that $S_{\text{CC}}(0) > 0$. Thus, if a system is close to phase separation, $S_{\text{CC}}(0)$ must be large and positive and the dominant trend is the separation between components (homocoordination), and $S_{\text{CC}}(0) > x_1 x_2$. If compound formation between components exists (heterocoordination), $S_{\text{CC}}(0)$ must be very low and $0 < S_{\text{CC}}(0) < x_1 x_2$. For more details, see reference [50]. Application of DISQUAC to calculate $S_{\text{CC}}(0)$ reveals that systems with 1-hexylamine or cyclohexylamine are characterized by heterocoordination, and that homocoordination is the dominant trend in aniline mixtures. For example, for 1-hexylamine mixtures, $S_{\text{CC}}(0) = 0.165$ (methanol), 0.198 (1-pentanol); for cyclohexylamine solutions, $S_{\text{CC}}(0) = 0.120$ (methanol), 0.128 (1-pentanol), and for aniline solutions, $S_{\text{CC}}(0) = 0.400$ (methanol), 0.504 (1-pentanol). Moreover, these data show that, in mixtures with a given 1-alkanol, $S_{\text{CC}}(0)$ changes in the sequence: aniline $>$ 1-hexylamine $>$ cyclohexylamine. This confirms that a larger number of interaction between unlike molecules exists in solutions involving the cyclic amine.

7.6 The interaction parameters

Firstly, it is to be noted that the $\Delta H_{\text{OH-NH}_2}^{\text{int}}$ (Table 8) and Δh_{AB}^* (Table 6) values are quite similar, and it supports our calculations. On the other hand, the variation of the ERAS parameters with n_{OH} for mixtures with cyclohexylamine is similar to those encountered when investigating other 1-alkanol + amine mixtures in terms of this model (Figures 6-8) [26,38,40].

The values of $|\Delta h_{AB}^*|$ and $|\Delta v_{AB}^*|$ are large since the present mixtures show large and negative H_m^E and V_m^E values (Figures 4 and 5) which arise from strong solvation effects. This means that the physical contributions to the excess functions, and therefore the physical parameter, are low as the following results for the methanol + cyclohexylamine system show. Thus, the chemical and physical contributions to H_m^E are, respectively: (-3815 and 37) $\text{J}\cdot\text{mol}^{-1}$. For the V_m^E function, the chemical and physical contributions are: (-1.696 and -0.089) $\text{cm}^3\cdot\text{mol}^{-1}$. Similar results are obtained for the ethanol solution (Figure S3, supplementary material). The main difference between members of a homologous series is linked to their different K_{AB} values (Figure 6). It is quite clear that the main solvation effects are encountered for the methanol system. We have determined the ERAS parameters for the methanol + piperidine mixture using data from reference [117] ($K_{AB} = 3500$; $\Delta h_{AB}^* = -39.6 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta v_{AB}^* = -9.8 \text{ cm}^3\cdot\text{mol}^{-1}$; $X_{AB} = 4 \text{ J}\cdot\text{cm}^{-3}$, and they fit well within the description provided above.

Regarding DISQUAC, we must underline some results. (i) The QUAC parameters are essentially the same for all the homologous series. A similar behaviour has been encountered for mixtures of the type 1-alkanol + *N,N*-dialkylamide [118], or + linear organic carbonate [119], or + cyclic ether [120]. (ii) In addition, they are very different to those of 1-alkanol + 1-hexylamine mixtures. Similarly, the $C_{\text{hn},l}^{\text{QUAC}}$ ($l=1,2,3$) coefficients are different for methanol + di-*n*-propylamine or + piperidine systems [38,76] and this remarks that cyclic molecules are difficult to be treated using group contribution models [121,122].

8. Conclusions

Excess molar enthalpies have been measured for the systems methanol, ethanol, 1-propanol, 1-butanol, 1-heptanol, or 1-decanol + cyclohexylamine at 298.15 K and 0.1 MPa. The large and negative H_m^E and V_m^E values of these solutions reveal that they are essentially characterized by strong interactions between unlike molecules. Values of $U_{m,V}^E$ have been computed for 1-alkanol + cyclohexylamine, or + 1-hexylamine, or + aniline systems. The eos contribution to H_m^E is particularly large for the methanol + aniline mixture, since H_m^E and $U_{m,V}^E$ show opposite signs at equimolar composition. DISQUAC improves ERAS results on H_m^E . ERAS describes correctly the V_m^E curves. The relative variation of H_m^E of 1-alkanol + cyclohexylamine, or + 1-hexylamine, or + aniline mixtures with n_{OH} in systems with a given amine, or with the amine in mixtures with a given 1-alkanol has been discussed taking into account the different interactional contributions to H_m^E .

CRedit authorship contribution statement

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

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TABLE 1

Properties of pure compounds

Compound	CAS	Purity ^a	ρ ^b /g·cm ⁻³	
			Exp.	Lit.
benzene	71-43-2	> 0.9995	0.873622	0.87360 [123]
cyclohexane	110-82-7	> 0.9999	0.773865	0.77366 [123]
1-butanamine	109-73-9	> 0.9996	0.732758	0.73225 [124] 0.73300 [125]
cyclohexanamine	108-91-8	> 0.999	0.862315	0.862207 [126]
methanol	67-56-1	> 0.9999	0.786716	0.78667 [127] 0.7869 [128]
ethanol	64-17-5	> 0.9999	0.785086	0.7854 [128] [0.78546 [129]
<i>n</i> -propan-1-ol	71-23-8	> 0.999	0.799770	0.79960 [130]
<i>n</i> -butan-1-ol	71-36-3	> 0.9986	0.805901	0.805762 [126] 0.80575 [130]
<i>n</i> -heptan-1-ol	111-70-6	> 0.999	0.818987	0.81875 [131]
<i>n</i> -decan-1-ol	112-30-1	> 0.987	0.826581	0.82644 [131]

^avalue in mole fraction provided by the manufacturer (gas chromatograph analysis);

^bdensity at 298.15 K and 0.1 MPa. The standard uncertainties are: $u(T) = \pm 0.01$ K; $u(p) = \pm 1$ kPa; $u(\rho) = \pm 8 \times 10^{-5}$ g·cm⁻³

TABLE 2

Experimental H_m^E results at 298.15 K and 0.1 MPa for the systems used in the calibration of the microcalorimeter Tian-Calvet.^a

x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
cyclohexane(1) + benzene (2) ^b		methanol(1) + 1-butylamine(2) ^c	
0.1054	349	0.0955	-1051
0.2063	545	0.1680	-1721
0.3056	686	0.2870	-2718
0.4078	761	0.3977	-3372.
0.5095	802	0.4440	-3583
0.5968	751	0.5181	-3738
0.7061	689	0.5795	-3771
0.7890	514	0.6597	-3511
0.8895	311	0.6975	-3338
		0.7945	-2548
		0.9032	-1306

^aThe standard uncertainties are: $u(T) = 0.01$ K, $u(p) = 1$ kPa, and $u(x_1) = 0.0005$. The relative combined expanded uncertainty (0.95 level of confidence) is $U_{rc}(H_m^E) = 0.03$;

^bcoefficients from the fitting of the H_m^E using equation (2): $A_0 = 3170$; $A_1 = 114$; $A_2 = 327$; $A_3 = -765$; $\sigma(H_m^E) = 14$ J·mol⁻¹ (equation 3); ^ccoefficients from the fitting of the H_m^E using equation (2): $A_0 = -14903$; $A_1 = -3492$; $A_2 = 2190$; $A_3 = 2696$; $\sigma(H_m^E) = 15$ J·mol⁻¹ (equation 3)

TABLE 3.

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

x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
methanol(1) + cyclohexylamine(2)		ethanol(1) + cyclohexylamine(2)	
0.1196	-1263	0.0746	-723
0.1574	-1624	0.1514	-1301
0.2181	-2182	0.1614	-1415
0.3253	-3030	0.2364	-1906
0.3906	-3422	0.2886	-2249
0.4494	-3704	0.3961	-2752
0.4993	-3849	0.4913	-3007
0.5491	-3845	0.6021	-2989
0.6003	-3832	0.7040	-2622
0.6974	-3438	0.7561	-2314
0.7965	-2578	0.7964	-2029
0.8452	-2083	0.8520	-1549
0.9005	-1392	0.9122	-990
1-propanol(1) + cyclohexylamine(2)		1-butanol(1) + cyclohexylamine(2)	
0.1009	-875	0.1003	-835
0.1524	-1296	0.1510	-1206
0.1982	-1612	0.2003	-1553
0.2573	-2016	0.2441	-1842
0.3038	-2290	0.3123	-2226
0.3996	-2726	0.4027	-2598
0.5003	-2948	0.5010	-2810
0.6089	-2855	0.6024	-2755
0.6967	-2573	0.6993	-2397
0.7909	-1975	0.7490	-2153

0.8500	-1467	0.8047	-1751
0.8845	-1183	0.8296	-1580
0.9474	-562	0.9062	-918
1-heptanol(1) + cyclohexylamine(2)		1-decanol(1) + cyclohexylamine(2)	
0.1012	-738	0.1050	-664
0.1496	-1083	0.1535	-959
TABLE 3 (continued)			
0.1946	-1373	0.2001	-1228
0.2572	-1740	0.2438	-1467
0.3013	-1974	0.3078	-1792
0.3923	-2338	0.4056	-2132
0.5159	-2581	0.5009	-2303
0.6057	-2510	0.6042	-2258
0.7004	-2213	0.7141	-1942
0.7578	-1919	0.7695	-1676
0.7979	-1666	0.8079	-1458
0.8613	-1216	0.8547	-1135
0.8928	-959	0.9058	-784

^aThe standard uncertainties are: $u(T) = 0.01$ K, $u(p) = 1$ kPa, and $u(x_1) = 0.0005$. The relative combined expanded uncertainty (0.95 level of confidence) is $U_{rc}(H_m^E) = 0.03$.

TABLE 4

Coefficients A_i and standard deviations, $\sigma(F_m^E)$ (equation (3)), for the representation of F_m^E data at 298.15 K and 0.1 MPa for 1-alkanol(1) + cyclohexylamine(2) mixtures by equation (1).

1-alkanol	F_m^E	A_0	A_1	A_2	A_3	$\sigma(F_m^E)/\text{J}\cdot\text{mol}^{-1}$
methanol	H_m^E	-15324	-3649	2686	2164	18
	$U_{V_m}^E$	-12748	-3430	2315	1773	18
ethanol	H_m^E	-12033	-2297	1426	1677	19
1-propanol	H_m^E	-11768	-1782	1959	1069	13
	$U_{V_m}^E$	-9745	-2303	1815	1093	13
1-butanol	H_m^E	-11209	-1639	1996	1005	11
	$U_{V_m}^E$	-9364	-1552	1697	916	11
1-heptanol	H_m^E	-10260	-1338	1904		13
	$U_{V_m}^E$	-8859	-1223	1624		13
1-decanol	H_m^E	-9207	-1414	1832		8
	$U_{V_m}^E$	-8108	-1152	1543		9

TABLE 5

Dispersive (DIS) and quasichemical (QUAC) interchange coefficients, $C_{hn,l}^{DIS}$ and $C_{hn,l}^{QUAC}$, for (h,n) contacts in 1-alkanol + cyclohexylamine mixtures ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity)

System	$C_{hn,1}^{DIS}$	$C_{hn,2}^{DIS}$	$C_{hn,3}^{DIS}$	$C_{hn,1}^{QUAC}$	$C_{hn,2}^{QUAC}$	$C_{hn,3}^{QUAC}$
methanol	0.55	-15.7	22 ^a	-3.85	-5	6 ^a
ethanol	2.5	-15.7	22 ^a	-3.85	-3	6 ^a
1-propanol	5	-15.7	22 ^a	-3.85	-3	6 ^a
1-butanol	5	-16.7	22 ^a	-3.85	-3	6 ^a
1-pentanol	5	-19.5	22 ^a	-3.85	-3	6 ^a
1-heptanol	5	-19.5	22 ^a	-3.85	-3	6 ^a
1-decanol	5	-19.5	22 ^a	-3.85	-3	6 ^a

^aguessed value

TABLE 6

ERAS parameters^a for 1-alkanol(A) + cyclohexylamine(B) mixtures at 298.15 k and 0.1 MPa

1-alkanol	K_{AB}	$\Delta h_{AB}^*/\text{J}\cdot\text{mol}^{-1}$	$\Delta v_{AB}^*/\text{cm}^3\cdot\text{mol}^{-1}$	$X_{AB}/\text{J}\cdot\text{mol}^{-3}$
methanol	3500	-42.8	-12.0	4
ethanol	2500	-38.4	-11.0	4
1-propanol	1500	-37.8	-10.7	4
1-butanol	1400	-37.3	-10.5	4
1-heptanol	650	-36.4	-10.2	5
1-decanol	300	-36.4	-10.0	7

^a K_{AB} , equilibrium constant; Δh_{AB}^* , molar enthalpies of intermolecular hydrogen-bonding; Δv_{AB}^* , molar hydrogen-bonding volumes; X_{AB} , physical parameter

TABLE 7

Molar excess enthalpies, H_m^E , at equimolar composition, 298.15 K and 0.1 MPa of 1-alkanol + cyclohexylamine mixtures. Comparison with ERAS and DISQUAC results obtained using parameters from Tables 5 and 6.

1-alkanol	$H_m^E / \text{J.mol}^{-1}$			$\sigma(H_m^E)^a / \text{J.mol}^{-1}$		
	Exp.	ERAS	DQ	Exp.	ERAS	DQ
methanol	-3831	-3778	-3857	18	102	47
ethanol	-3008	-3034	-3055	19	111	32
1-propanol	-2942	-2934	-2929	13	176	51
1-butanol	-2802	-2779	-2817	11	197	78
1-heptanol	-2565	-2511	-2577	13	275	140
1-decanol	-2302	-2190	-2308	8	325	160

^acalculated using equation 2 with $F_{\text{mcal},j}^E$ values determined from DISQUAC and ERAS models using interaction parameters from Tables 5 and 6, respectively.

TABLE 8

Partial molar excess enthalpies,^a $H_{ml}^{E,\infty}$, 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, $\Delta H_{OH-NH_2}^{int}$, for 1-alkanol- amine interactions.

System	$H_{ml}^{E,\infty} / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_{OH-NH_2}^{int} / \text{kJ}\cdot\text{mol}^{-1}$
1-hexylamine(1) + heptane(2)	5.7 [114]	
cyclohexylamine(1) + cyclohexane(2)	5.5 [115]	
piperidine(1) + cyclohexane(2)	4.7 [132]	
aniline(1) + heptane(2)	15.0 [40,113]	
methanol(1) + cyclohexylamine(2)	-11.1	-39.8
ethanol(1) + cyclohexylamine(2)	-10.0	-38.7
1-propanol(1) + cyclohexylamine(2)	-9.1	-37.8
1-butanol(1) + cyclohexylamine(2)	-8.6	-37.3
1-heptanol(1) + cyclohexylamine(2)	-7.0	-35.7
1-decanol(1) + cyclohexylamine(2)	-6.0	-34.7
methanol(1) + 1-hexylamine(2)	-9.7 [11]	-38.6
1-propanol (1) + 1-hexylamine(2)	-7.9 [11]	-36.8
1-pentanol(1) + 1-hexylamine(2)	-8.4 [11]	-37.3
1-octanol(1) + 1-hexylamine(2)	-8.1 [11]	-36.9
1-decanol(1) + 1-hexylamine(2)	-7.5 [11]	-36.4
methanol(1) + aniline(2)	-0.04 [85]	-38.2
ethanol (1) + aniline(2)	2.5 [85]	-35.7
1-propanol(1) + aniline(2)	3.9 [85]	-34.3

1-butanol(1) + aniline(2)	5.6 [133]	−32.6
1-pentanol(1) + aniline(2)	6.9 [85]	−31.3
methanol(1) + piperidine(2)	−9.0 [117]	−36.9

^avalues obtained from H_m^E data over the whole concentration range

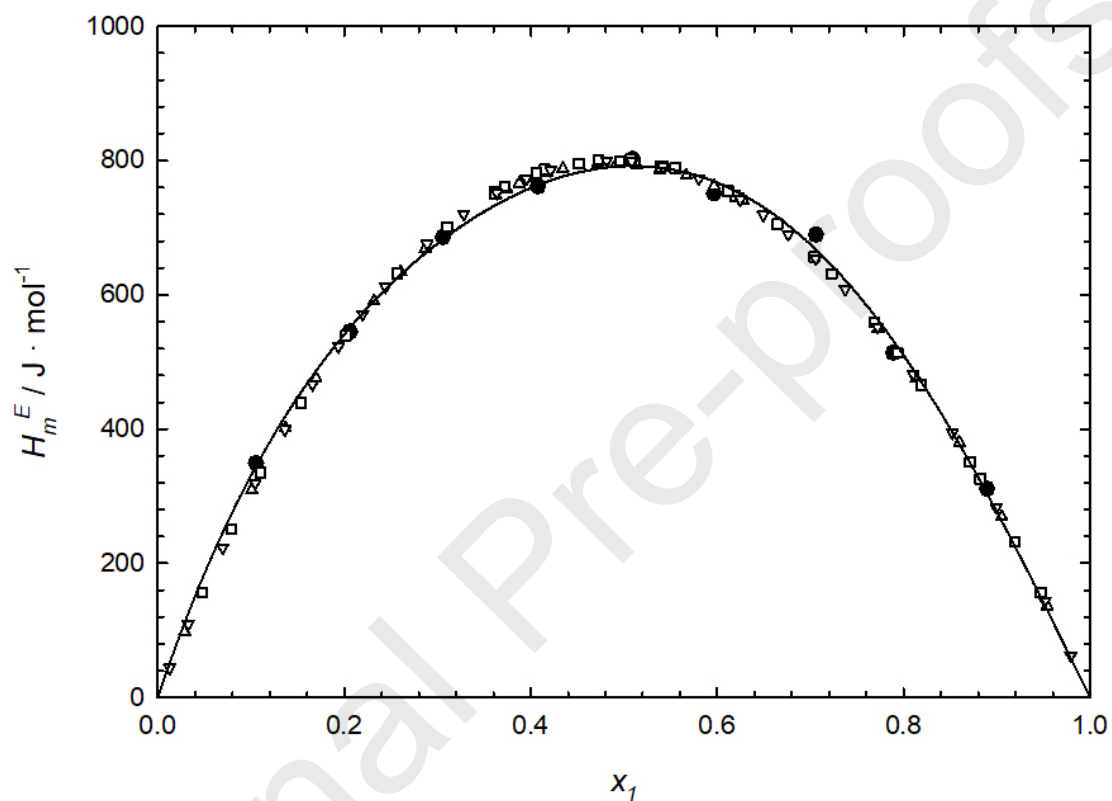


Figure 1a. H_m^E of the cyclohexane(1) + benzene(2) system at 298.15 K and 0.1 MPa. Symbols, experimental results: (●), this work, (▽), [57]; (□), [58]; (△), [59]. Solid line: calculations with equation 2 using coefficients from Table 4.

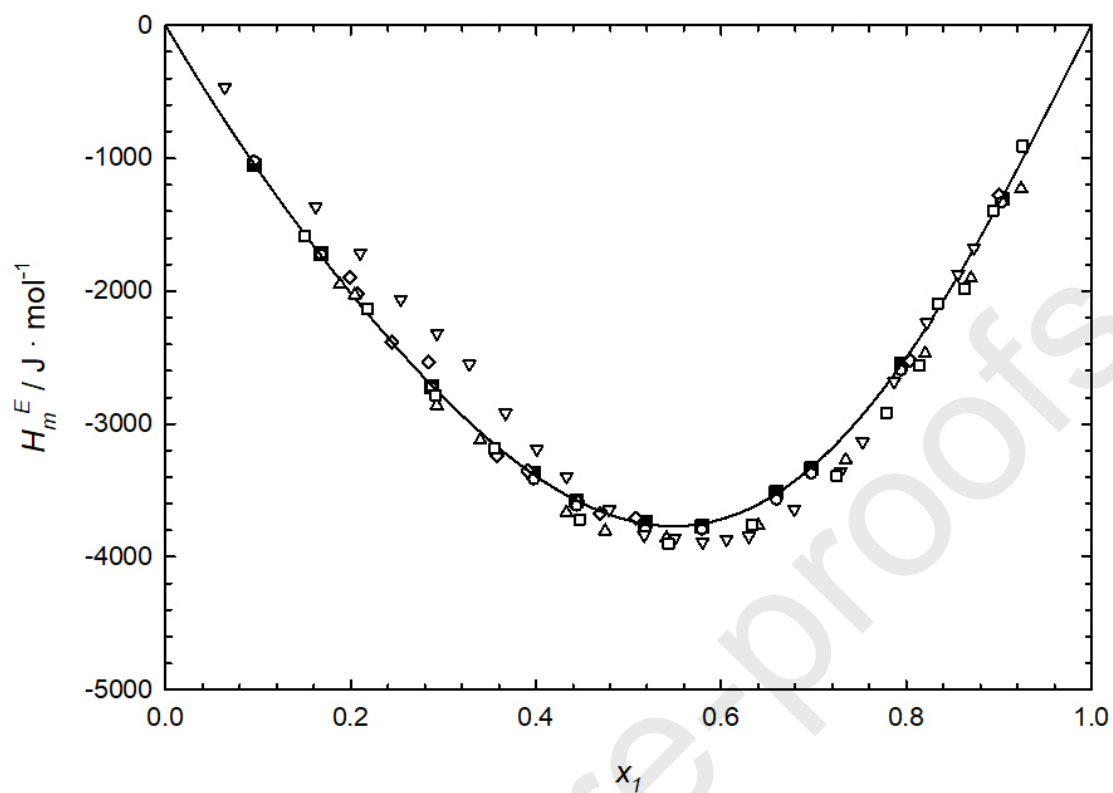


Figure 1b. H_m^E of the methanol(1) + 1-butylamine(2) system at 298.15 K and 0.1 MPa. Symbols, experimental results: (■), this work, (◇), [16]; (○), [18]; (▽), [60]; (□), [61]; (△), [62]. Solid line: calculations with equation 2 using coefficients from Table 4.

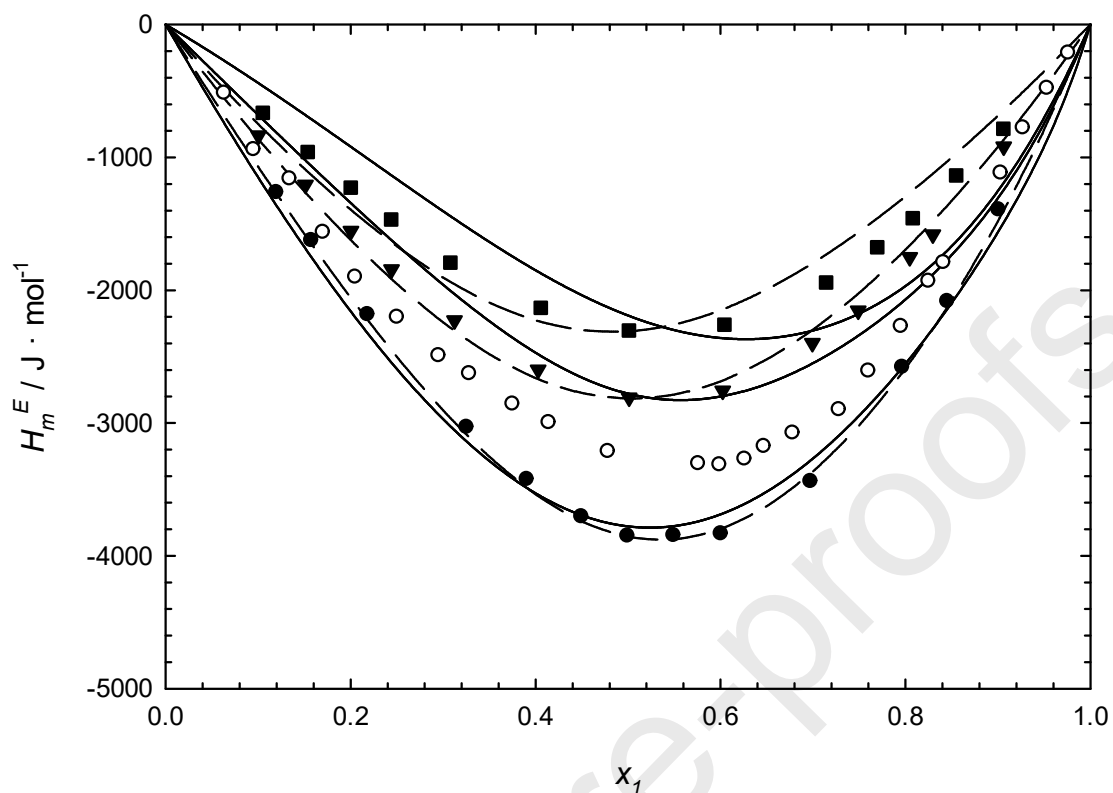


Figure 2. H_m^E of 1-alkanol (1) + cyclohexylamine (2) systems at 298.15 K and 0.1 MPa. Symbols, experimental results: (●) methanol; (▼) 1-butanol; (■) 1-decanol (this work); (○) methanol [60]; Solid lines, ERAS results using parameters listed in Table 6. Dashed lines, DISQUAC calculations using interaction parameters from Table 5.

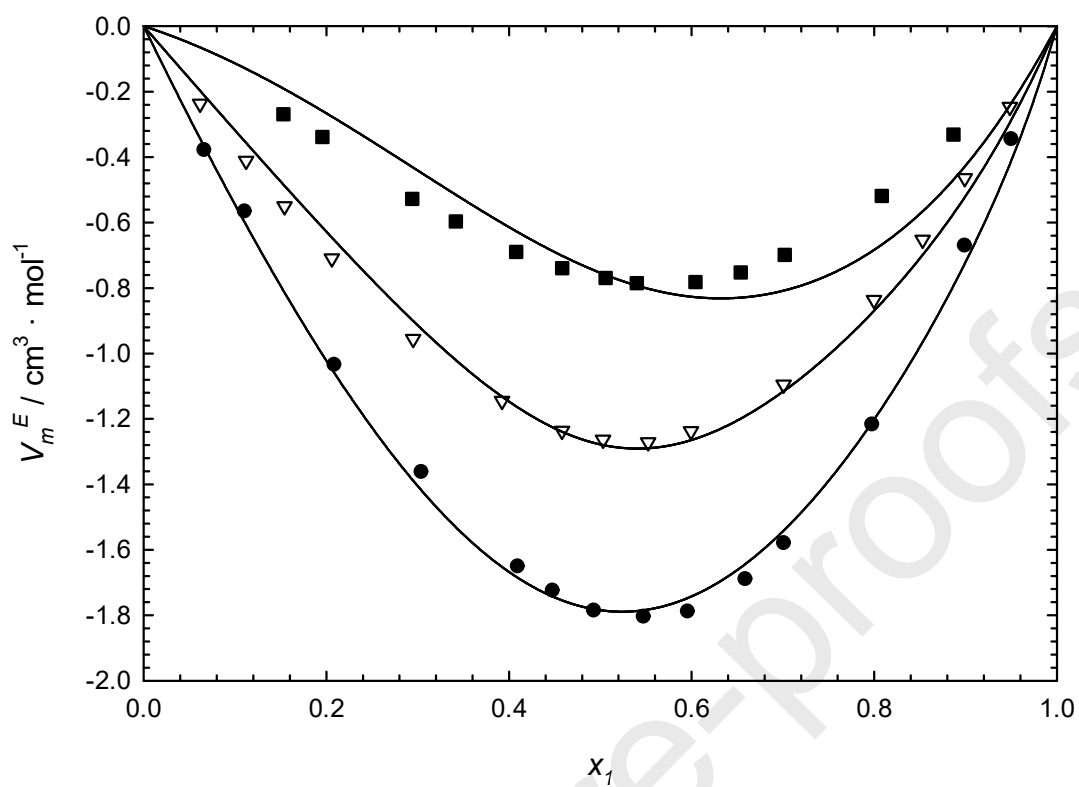


Figure 3. V_m^E of 1-alkanol (1) + cyclohexylamine(2) systems at 298.15 K and 0.1 MPa. Symbols, experimental results: (●), methanol [29]; (▽), 1-butanol [27]; (■), 1-decanol [28]. Solid lines, ERAS results obtained with parameters from Table 6.

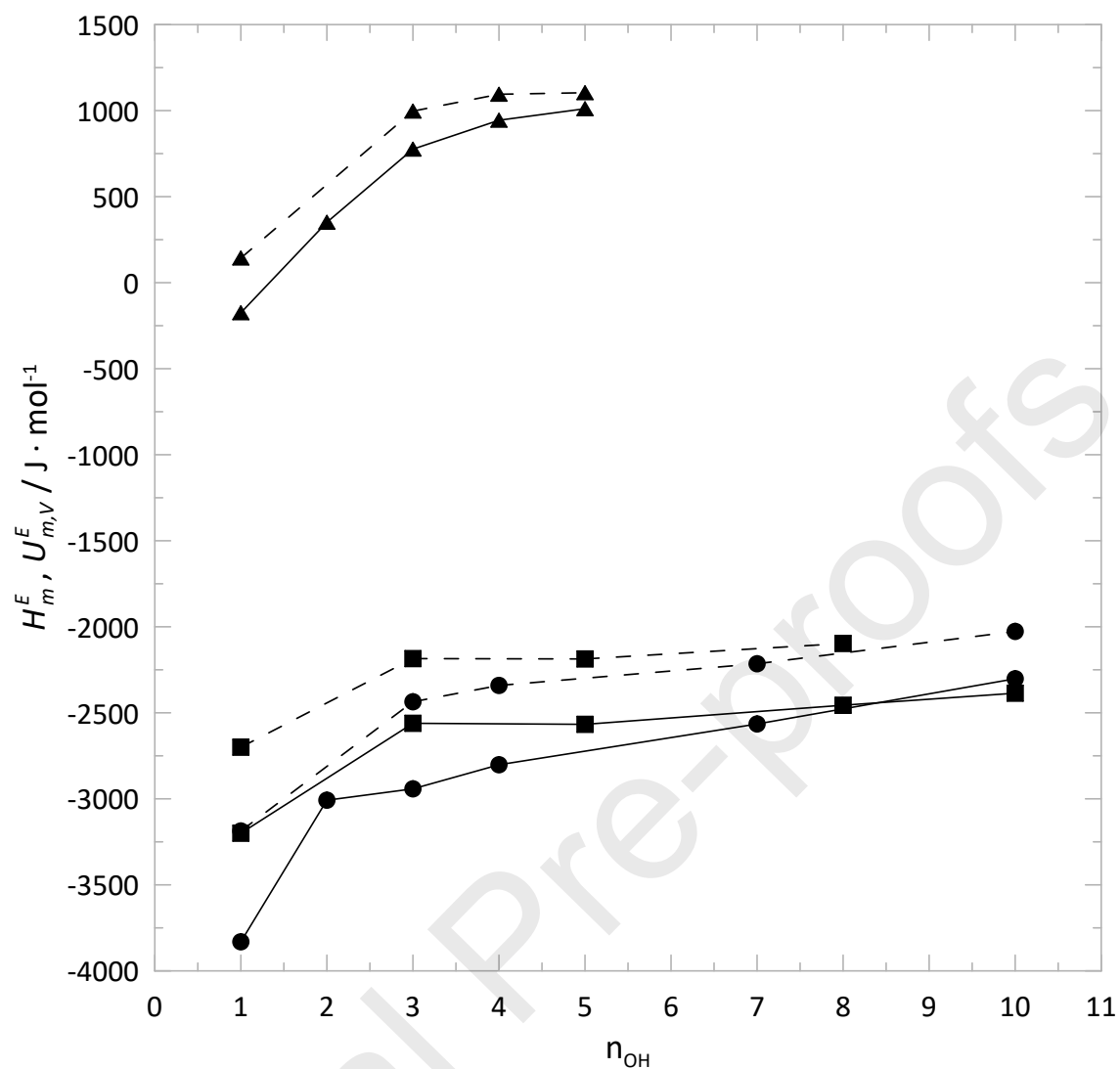


Figure 4. H_m^E (solid lines) and $U_{m,V}^E$ (dashed lines, this work) at equimolar composition, $T = 298.15$ K and 0.1 MPa for 1-alkanol + amine mixtures vs. n_{OH} , the number of C atoms in the 1-alkanol: (■) 1-hexylamine [11]; (●) cyclohexylamine (this work); (▲) aniline [85,133].

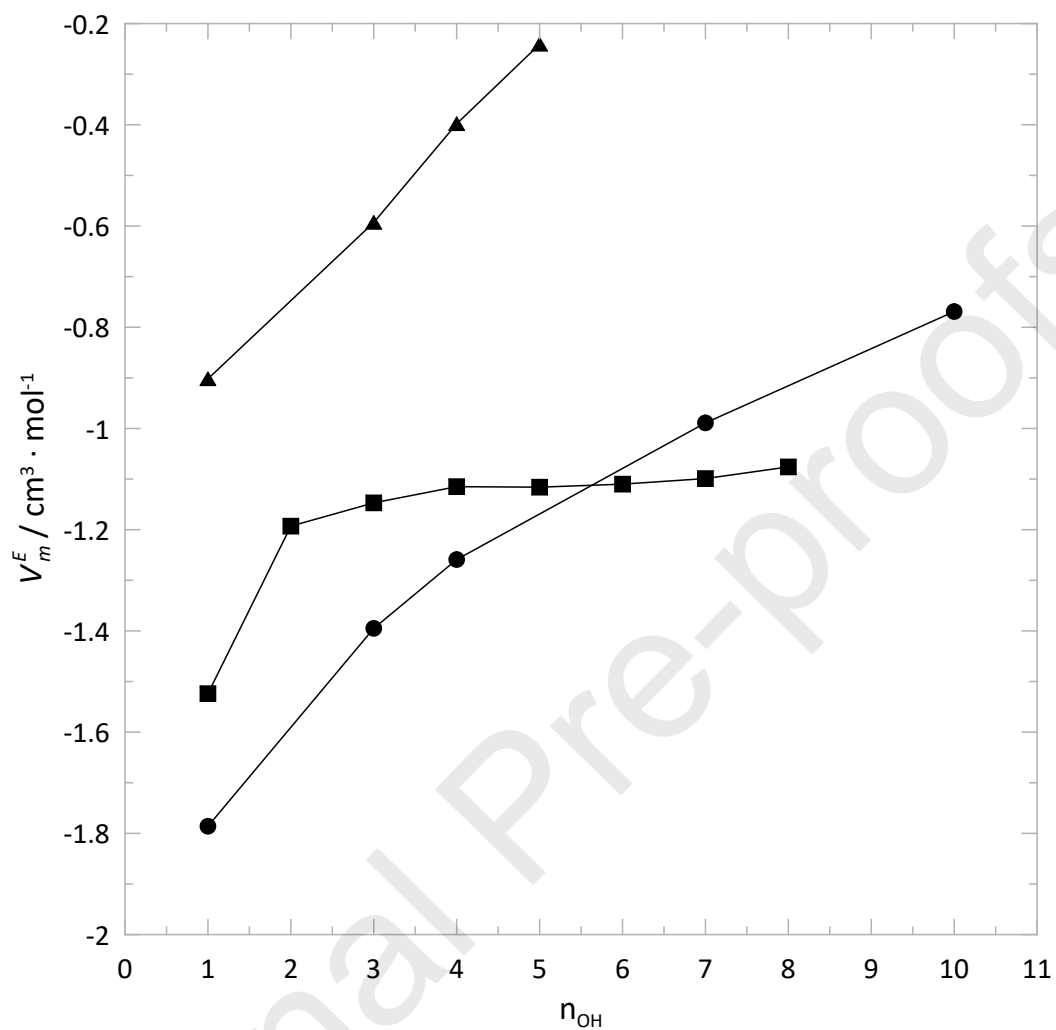


Figure 5. V_m^E at equimolar composition, $T = 298.15$ K and 0.1 MPa for 1-alkanol + amine mixtures vs. n_{OH} , the number of C atoms in the 1-alkanol: (■) 1-hexylamine [26]; (●) cyclohexylamine [27-29]; (▲) aniline [30,134]

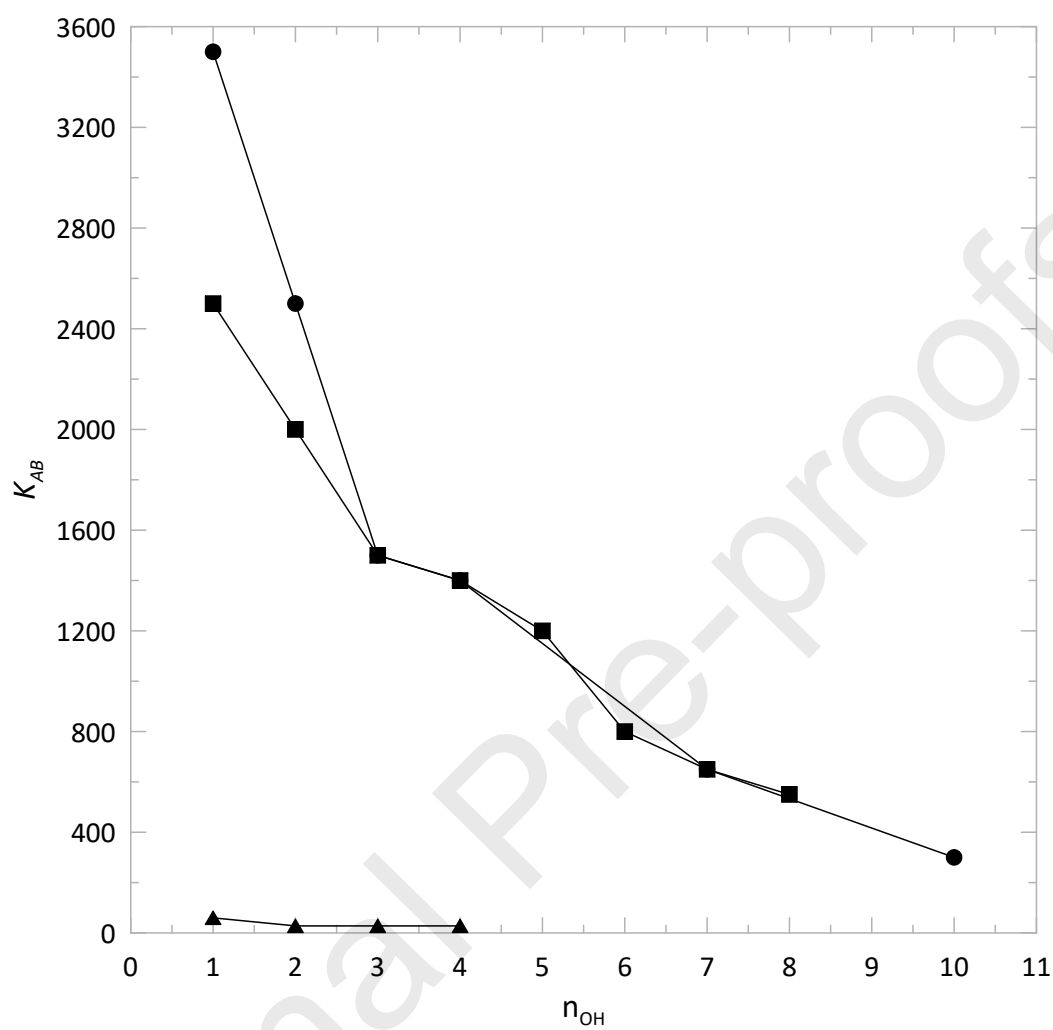


Figure 6: ERAS parameter K_{AB} for 1-alkanol + amine systems at 298.15 K vs. n_{OH} , the number of C atoms in the 1-alkanol: (■), 1-hexylamine [26]; (●), cyclohexylamine (this work); (▲) aniline [40].

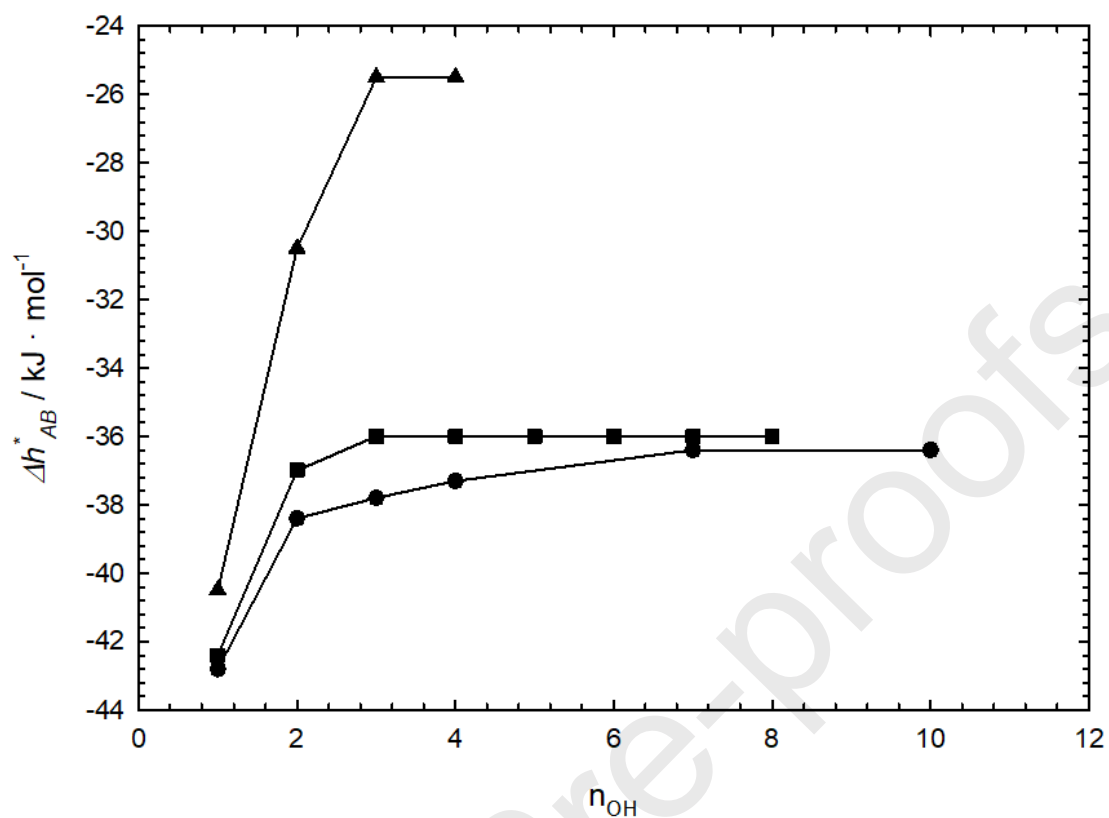


Figure 7. ERAS parameter Δh_{AB}^* for 1-alkanol + amine systems vs. n_{OH} , the number of C atoms in the 1-alkanol: (■), 1-hexylamine [26]; (●), cyclohexylamine (this work); (▲) aniline [40].

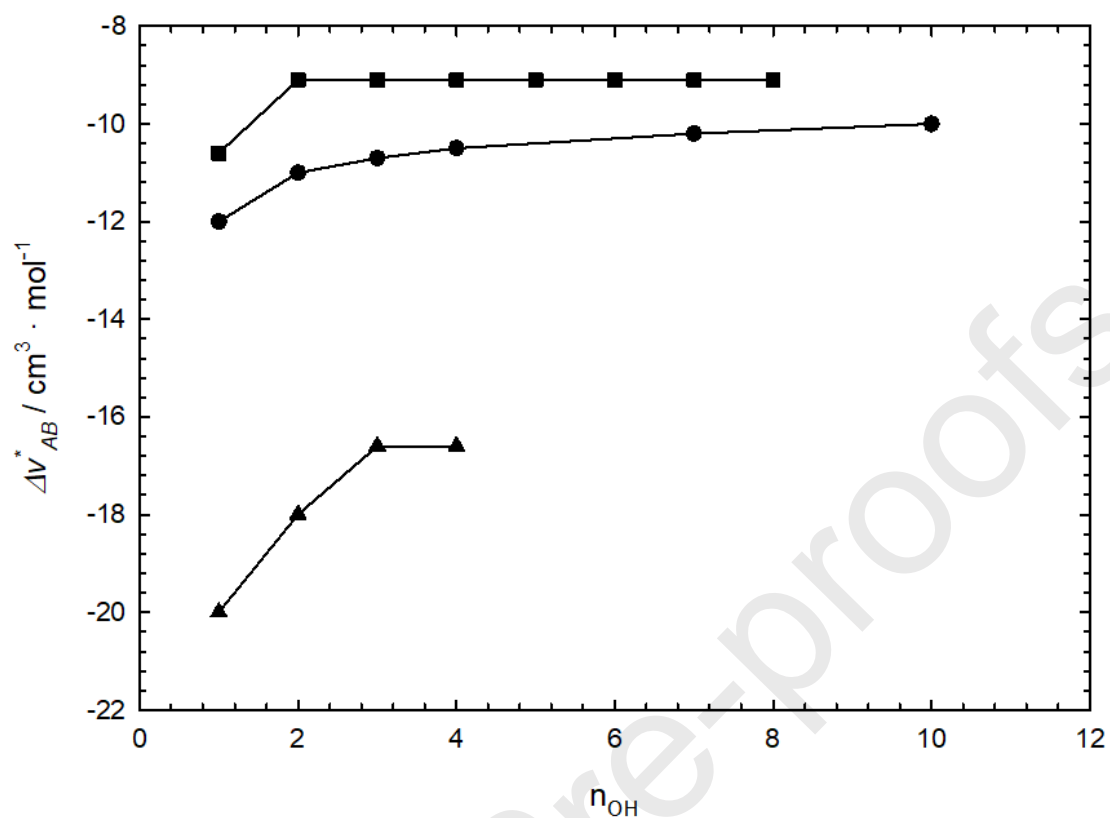


Figure 8. ERAS parameter Δv_{AB}^* for 1-alkanol + amine systems vs. n_{OH} , the number of C atoms in the 1-alkanol: (■), 1-hexylamine [26]; (●), cyclohexylamine (this work); (▲) aniline [40].

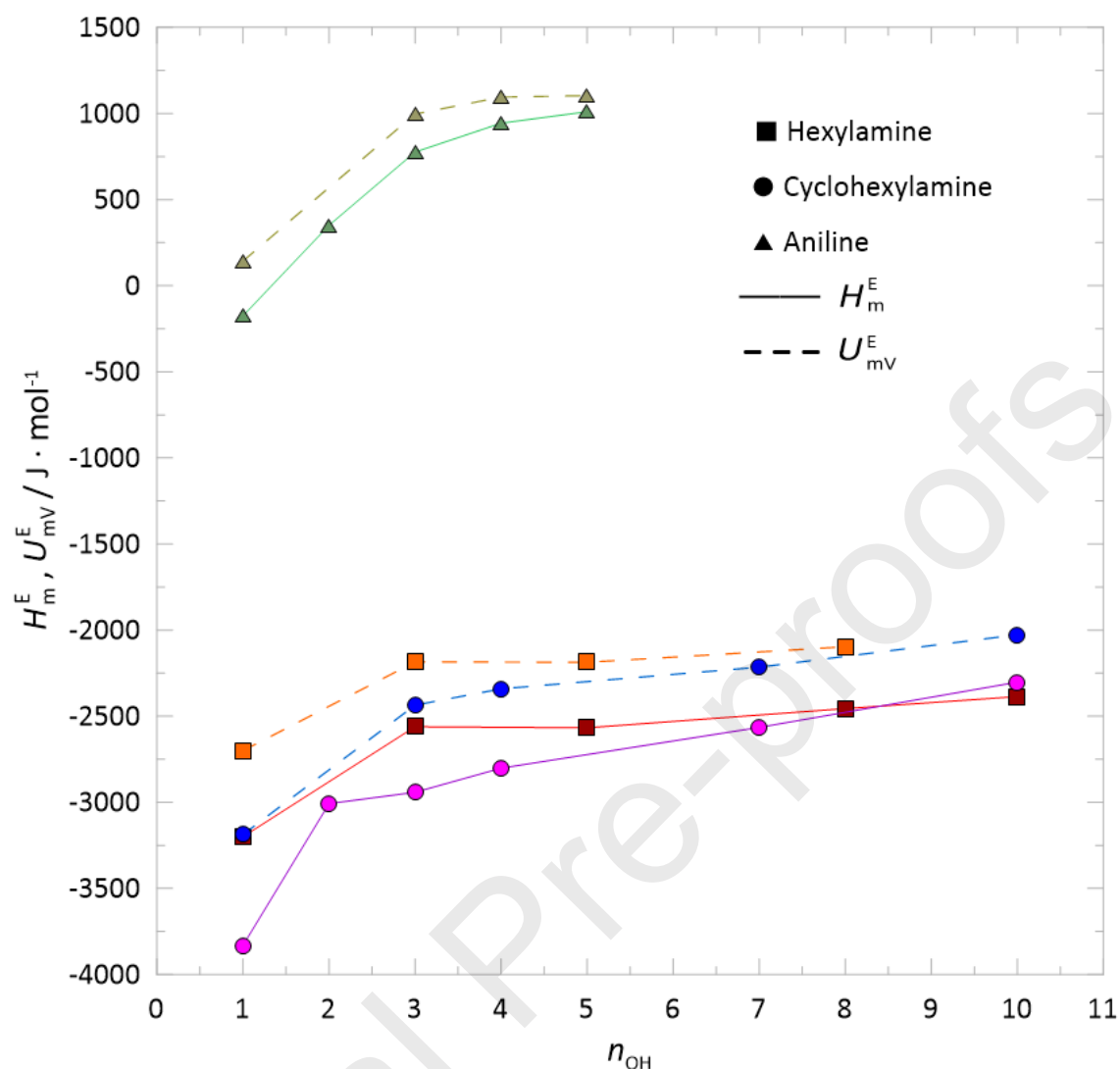
CRedit authorship contribution statement

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

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



- (●) H_m^E values have been measured at 298.15 K for 1-alkanol + cyclohexylamine systems
- (●) Large negative values are obtained due to strong interactions between unlike molecules
- (●) $U_{m,V}^E$ values have been determined for 1-alkanol + cyclohexylamine, or + 1-hexylamine, or + aniline systems
- (●) The enthalpy of the 1-alkanol-amine interactions have been evaluated
- (●) DISQUAC and ERAS have been applied