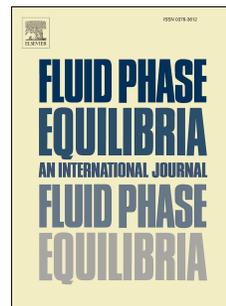# Journal Pre-proof

Thermodynamics of amide + amine mixtures. 5. excess molar enthalpies of *N,N*-dimethylformamide or *N,N*-dimethylacetamide + *N*-propylpropan-1-amine, + *N*-butylbutan-1-amine, + butan-1-amine, or + hexan-1-amine systems at 298.15 K. application of the ERAS model

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Legend

■	DMF+HxA
▲	DMF+DPA
●	DMA+HxA
◆	DMA+DPA
——	ERAS model

ERAS parameters

System	K_{AB}	Δh_{AB}^* / kJ·mol^{-1}	Δv_{AB}^* / cm³·mol^{-1}	X_{AB} / J·cm^{-3}
HxA + DMF	1	−9	−4.6	36.0
HxA + DMA	1	−9	−2.8	23.3
DPA + DMF	1	−2	−2.5	23.8
DPA + DMA	1	−2	−1.2	15.0

Thermodynamics of amide + amine mixtures. 5. Excess molar enthalpies of *N,N*-dimethylformamide or *N,N*-dimethylacetamide + *N*-propylpropan-1-amine, + *N*-butylbutan-1-amine, + butan-1-amine, or + hexan-1-amine systems at 298.15 K. Application of the ERAS model

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Abstract

Excess molar enthalpies, H_m^E, over the whole composition range have been determined for the liquid mixtures *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide (DMA) + butan-1-amine (BA), or + hexan-1-amine (HxA), or + *N*-propylpropan-1-amine (DPA), or *N*-butylbutan-1-amine (DBA) at 298.15 K and at 0.1 MPa using a BT2.15 calorimeter from Setaram adapted to work in dynamic mode at constant temperature and pressure. All the H_m^E values are positive, indicating that interactions between like molecules are predominant. The replacement of DMF by DMA in systems with a given amine leads to lower H_m^E results, which have been ascribed to stronger amide-amide interactions in DMF mixtures. The replacement of HxA by DPA in systems with a given amide leads to slightly higher H_m^E values, as interactions between unlike molecules are weaker for the latter. Structural effects in the investigated solutions are also present, since the corresponding excess molar volumes (V_m^E), previously determined, are negative or slightly positive. The systems have been characterized in terms of the ERAS model reporting the interaction parameters. The model correctly describes both H_m^E and V_m^E. The application of the model suggests that, in the systems under study, solvation effects are of minor importance and that physical interactions are dominant.

Keywords: Amides; amines; excess enthalpy; ERAS; physical interactions.

1. Introduction

It is well-known that a suitable approach for the investigation of the highly complex chemical environment of proteins is to study small organic molecules whose functional groups are similar to those present in the biomolecule [1]. The systematic physical and chemical characterization of such molecules and of their mixtures in terms of thermodynamic, transport and dielectric properties is necessary in this framework. The study of amide + amine systems is relevant, as it allows to gain insight into the behavior of the amide group when it is surrounded by different environments. In fact, the hydrogen-bonded structures where the amide group is involved can show very different biological activities depending on the mentioned environments [2]. On the other hand, the strong polarity of amides, which in the case of tertiary amide leads to the creation of a certain local order [3, 4], together with their high solvating capability and liquid state range –due to their ability to form hydrogen bonds– [5], makes them a very important kind of organic solvents. Similarly, amines are also an important class of substances since many biological relevant molecules contain the amine group [6-8]. In addition, the low vapor pressure of amines makes them useful in green chemistry. Thus, mixtures containing amines are being investigated to be used in CO_2 capture [9] and, interestingly, many of the ions of the technically important ionic liquids are related to amine groups [10].

In previous works, we have measured densities, speeds of sound and refractive indices of *N,N*-dimethylformamide (DMF) [11], or *N,N*-dimethylacetamide (DMA) [12] + *N*-propylpropan-1-amine (DPA) or + butan-1-amine (BA) at (293.15-303.15) K, and + *N*-butylbutan-1-amine (DBA) or + hexan-1-amine (HxA) at 298.15 K. In addition, we have reported low-frequency permittivity measurements of the mentioned systems and of the DMF + aniline mixture at (293.15-303.15) K [13, 14]. This database has been interpreted in terms of solute-solvent interactions and structural effects. We have also applied the ERAS [15] and the Kirkwood-Fröhlich models [16-19] to the study of amine + amide mixtures. The latter is useful for the calculation of the Balankina relative excess Kirkwood correlation factors [20], which provide information on the dipole correlations present in the considered systems. Calorimetric data are essential for the study of the type and strength of interactions present in liquid mixtures. As the data available in the literature on excess molar enthalpies, H_m^E, for amine + amide mixtures is scarce [21-23], we continue this series of works reporting H_m^E values for DMF or DMA + DPA, or + DBA, or + BA or + HxA systems at 298.15 K. Finally, the systems are characterized in terms of the ERAS model, revisiting the previously reported parameters which were determined using volumetric data only [14].

2. Experimental

2.1 Materials

Information about the purity and source of the pure compounds used along the experiments is collected in Table 1. They were used without further purification. It also shows their densities (ρ) at 0.1 MPa and at 298.15 K. These results agree well with literature data.

2.2 Apparatus and procedure

Molar quantities were calculated using the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [24].

Densities were obtained using a vibrating-tube densimeter DMA HPM from Anton Paar. The temperature regulation of the densimetric block is insured by use of a thermostatic bath from Julabo. The standard uncertainty in the temperature is 0.01 K. Experiments were performed at atmospheric pressure, in a static mode. The calibration was carried out using pure octane, dodecane and tridistilled water, and comparing with literature values.

The excess molar enthalpies were determined from heat of mixing measurements performed with a BT2.15 calorimeter from Setaram adapted to work in dynamic mode at constant temperature and pressure. The arrangement is depicted in Figure 1. The fluids flow in stainless steel tubes with an external diameter of 1.6 mm and an internal diameter of 1.0 mm and mix in a custom-made cell. They are injected into the system by means of two syringe pumps model Teledyne ISCO 260 D, which are controlled by a Teledyne ISCO D-Series Pump Controller. Mixtures of different concentrations are obtained varying the volumetric flow rates given by the pumps. This flow rates can be chosen from 1 $\mu L \cdot min^{-1}$ to 25 $mL \cdot min^{-1}$ with a relative standard uncertainty of 0.5%. The capacity of the pumps is 266.05 mL, and they can be regulated up to a pressure of 52 MPa with a 2% relative standard uncertainty. To ensure the stability of the molar flow rates, the fluids are kept inside the pumps at a constant temperature of 298.15 K by means of a thermostatic bath Fisher Scientific Polystat 36, with a stability of 0.03 K. The relative standard uncertainty in the mole fraction is estimated to be 0.004. The pressure in the system is maintained constant with the help of a pressure regulator located at the end of the flow line, and the pressure relative to the atmospheric pressure is determined by a Keller transducer with a relative standard uncertainty of 0.25% of full scale (40 MPa). For the measurements in this work, the pressure regulator was open to the atmospheric pressure. The temperature of the calorimetric block is regulated by heating a cold can by means of a Setaram G11 Universal Controller. The temperature of the can is maintained constant using a circulating fluid at 10 K below the expected temperature of the experiment, using an external ultra-cryostat Julabo FL1201. The temperature of the block is then regulated using the G11 Universal Controller with a stability of 0.01 K. The temperature of the injected fluids is adjusted to the working

temperature with the help of an external precooler and an internal preheater. The external precooler is situated on top of the calorimetric block and is connected in series to the cooler can of the calorimeter and to the ultra-cryostatic bath. The internal preheater is inside the calorimetric block; it supplies the necessary power to reach the exact temperature of the experiment using a heating cartridge, and its temperature is controlled by means of a platinum resistance connected to a Fluke Hart Scientific 2200 PID controller with a stability of 0.01 K. The heat flow is detected by a thermopile, generating an electromotive force (EMF) that is collected by a 6 ½ digit multimeter from Keysight model 34401A and sent to a computer through a GPIB connection. The thermopile EMF, S, is converted into the mixing enthalpy through the steady-state relation:

$$H_m^E = \frac{S - S_{BL}}{K(n_1 + n_2)}$$ (1)

where K is a temperature-dependent calibration constant, n_i is the molar flow rate of component i and S_{BL} is the baseline signal, recorded when only one of the fluids is flowing. The constant K is obtained by measuring the H_m^E of the system ethanol + water and comparing the results with reference values from Ott *et al*. [25, 26]. Taking into account uncertainties on fluid flow rates, thermopile calibration K, and calorimetric signal noises, the estimated maximum relative standard uncertainty on H_m^E for the set of experimental points in this work is 0.03.

3. Results

Data on H_m^E are listed in Table 2. They were fitted to a Redlich-Kister equation [27] by an unweighted linear least-squares regression. The Redlich-Kister equation for the excess property F^E is given by:

$$F^E = x_1 \left(1 - x_1\right) \sum_{i=0}^{k-1} A_i \left(2x_1 - 1\right)^i$$ (2)

The number, k, of necessary coefficients for this regression has been determined, for each system, by applying an F-test of additional term [28] at 99.5% confidence level. The standard deviations, $\sigma\left(F^E\right)$, are defined by:

$$\sigma\left(F^E\right) = \left[\frac{1}{N - k} \sum_{j=1}^{N} \left(F_{cal,j}^E - F_{exp,j}^E\right)^2\right]^{1/2}$$ (3)

where the index j takes one value for each of the N data points $F_{\text{exp},j}^{\text{E}}$, and $F_{\text{cal},j}^{\text{E}}$ is the corresponding value of the excess property calculated from equation (2).

Excess molar energies of constant volume, $U_{\text{m},V}^{\text{E}}$, are given by [29]:

$$U_{\text{m},V}^{\text{E}} = H_{\text{m}}^{\text{E}} - T\frac{\alpha_p}{\kappa_T}V_{\text{m}}^{\text{E}} \tag{4}$$

where α_p is the isobaric thermal expansion coefficient, κ_T is the coefficient of isothermal compressibility and V_{m}^{E} is the excess molar volume. The $U_{\text{m},V}^{\text{E}}$ curves of amide + amine systems were obtained at $\Delta x_1 = 0.05$ using smoothed values of H_{m}^{E} and of volumetric properties previously measured [11, 12]. Let us denote by $V_{\text{m},i}$, $\alpha_{p,i}$ and $C_{p,\text{m},i}$ the molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of component i respectively, and by $\phi_i = x_i V_{\text{m},i}/(x_1 V_{\text{m},1} + x_2 V_{\text{m},2})$ the volume fraction of component i. In the application of equation (4), α_p was assumed ideal ($\alpha_p^{\text{id}} = \phi_1\alpha_{p,1} + \phi_2\alpha_{p,2}$) for HxA and DBA mixtures; the error in using this assumption is negligible due to the smallness of V_{m}^{E} for these systems and, actually, the difference $U_{\text{m},V}^{\text{E}} - H_{\text{m}}^{\text{E}}$ is not relevant. κ_T was obtained from the equation:

$$\kappa_T = \kappa_S + \frac{TV_{\text{m}}\alpha_p^2}{C_{p,\text{m}}} \tag{5}$$

with the molar isobaric heat capacity of the mixture, $C_{p,\text{m}}$, taken as ideal ($C_{p,\text{m}}^{\text{id}} = x_1 C_{p,\text{m},1} + x_2 C_{p,\text{m},2}$). The $U_{\text{m},V}^{\text{E}}$ curves have also been adjusted to Redlich-Kister polynomials using the same procedure given above.

Table 3 includes the parameters A_i obtained for $F^{\text{E}}(=H_{\text{m}}^{\text{E}}, U_{\text{m},V}^{\text{E}})$, together with the standard deviations $\sigma(F^{\text{E}})$. Values of H_{m}^{E} at temperature 298.15 K are plotted in Figures 2 and 3, and their corresponding Redlich-Kister regressions in Figures S1 and S2. The corresponding $U_{\text{m},V}^{\text{E}}$ curves are depicted in Figures S3 and S4.

4. ERAS model

The Extended Real Associated Solution (ERAS) model [15, 30] combines the Real Association Solution Model [31-34] with Flory's thermal equation of state [35-39]. Some important features of this model are now given. (i) The excess molar functions of enthalpy and volume ($F_{\text{m}}^{\text{E}} = H_{\text{m}}^{\text{E}}$, V_{m}^{E}) are calculated as the sum of two contributions. The chemical

contribution, $F_{\mathrm{m,chem}}^{\mathrm{E}}$, arises from hydrogen bonding; the physical contribution, $F_{\mathrm{m,phys}}^{\mathrm{E}}$, is related to nonpolar Van der Waals interactions and free volume effects. Expressions for the molar excess functions $H_{\mathrm{m}}^{\mathrm{E}}$ and $V_{\mathrm{m}}^{\mathrm{E}}$ can be found elsewhere [40, 41]. (ii) It is assumed that only consecutive linear association occurs. Accordingly, self-association is described by a chemical equilibrium constant (K_{A}) independent of the chain length of the self-associated species A (in this case, amines), according to the equation:

$$\mathrm{A}_m + \mathrm{A} \xleftrightarrow{\quad K_{\mathrm{A}} \quad} \mathrm{A}_{m+1} \tag{6}$$

with m ranging from 1 to ∞. The cross-association between a self-associated species A_m and a non self-associated compound B (in this study, tertiary amides) is represented by

$$\mathrm{A}_m + \mathrm{B} \xleftrightarrow{\quad K_{\mathrm{AB}} \quad} \mathrm{A}_m\mathrm{B} \tag{7}$$

where cross-association constants, K_{AB}, are also considered to be independent of the chain length. The molar enthalpies of intermolecular hydrogen-bonding for these two kinds of reactions, $\Delta h_{\mathrm{A}}^{*}$ and $\Delta h_{\mathrm{AB}}^{*}$, are introduced, and the corresponding equilibrium constants depend on temperature according to them and the Van't Hoff equation. Moreover, negative molar hydrogen-bonding volumes, $\Delta v_{\mathrm{A}}^{*}$ and $\Delta v_{\mathrm{AB}}^{*}$, are defined in order to take into account the decrease of the core volume of the molecules upon multimer formation. (iii) The $F_{\mathrm{m,phys}}^{\mathrm{E}}$ term is derived from the Flory's equation of state [35-39], which is assumed to be valid not only for pure compounds but also for the mixture [42, 43]:

$$\frac{\overline{p}_i \overline{V}_i}{\overline{T}_i} = \frac{\overline{V}_i^{1/3}}{\overline{V}_i^{1/3} - 1} - \frac{1}{\overline{V}_i \overline{T}_i} \tag{8}$$

where i = A, B or M (mixture). In equation (8), $\overline{V}_i = V_{\mathrm{m},i} / V_{\mathrm{m},i}^{*}$; $\overline{p}_i = p / p_i^{*}$; $\overline{T}_i = T / T_i^{*}$ 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 (density, isobaric thermal expansion coefficient, and coefficient of isothermal compressibility) and association parameters [42, 43]. The reduction parameters for the mixture p_{M}^{*} and T_{M}^{*} are calculated from mixing rules [42, 43]. 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].

4.1. Adjustment of ERAS parameters

Values of $V_{\mathrm{m},i}$, $V_{\mathrm{m},i}^{*}$ and p_i^{*} of pure compounds [45-47] at T = 298.15 K, needed for calculations, are listed in Table S1 of supplementary material. K_{A}, $\Delta h_{\mathrm{A}}^{*}$, and $\Delta v_{\mathrm{A}}^{*}$ of the self-

associated amines are known from H_m^E and V_m^E data for the corresponding mixtures with alkanes [45-47], and are also collected in Table S1. The binary parameters to be fitted against H_m^E and V_m^E [11, 12] data of amine + amide systems are then K_{AB}, Δh_{AB}^*, Δv_{AB}^* and X_{AB}. They are collected in Table 4.

5. Discussion

We are referring throughout this section to values of the excess functions and of the thermophysical properties at 298.15 K and at $x_1 = 0.5$, except otherwise specified.

As previously mentioned, DMF and DMA are very polar substances since their dipole moment is 3.7 D [48, 49]. Consequently, their alkane mixtures show immiscibility gaps up to rather high temperatures. Thus, systems formed by DMF and heptane or hexadecane have upper critical solution temperatures (UCST) of 342.55 K [50] and 385.15 K [51] respectively, and the UCST of the DMA + heptane mixture is 309.40 K [52].

Primary and secondary amines are self-associated compounds [30, 45, 46, 53, 54] with lower dipole moments than tertiary amides: 1.3 D (BA) [55], 1.3 D (HxA) [48], 1.0 D (DPA) [55], and 1.1 D (DBA) [55]. For heptane solutions, H_m^E/J·mol⁻¹ = 1192 (BA) [56], 962 (HxA) [56], 424 (DPA) [57], and 317 (DBA) [57]. We note that H_m^E results are larger for systems with primary amines, and that they decrease with the chain length of the amine. Therefore, these values can be interpreted as arising from the rupture of interactions between like molecules in the mixing process.

Our H_m^E/J·mol⁻¹ values obtained for amide + amine systems are also positive. We have H_m^E(DMF)/J·mol⁻¹ = 386 (BA), 660 (HxA), 750 (DPA), 1103 (DBA); and H_m^E(DMA)/J·mol⁻¹ = 209 (BA), 425 (HxA), 510 (DPA), and 829 (DBA). They can be ascribed to the dominance of contributions from the breaking of amide-amide and amine-amine interactions over that related to the formation of interactions between unlike molecules. Note that H_m^E values of the DMA + cyclohexane mixture are much higher than those of DMA + linear amine systems (Figure S2). The same trend is observed, e.g., when H_m^E results are compared for BA + heptane and *N,N*-dialkylamide systems (Figures S1 and S2). For a fixed amide and along both series of primary or secondary linear amines, H_m^E becomes larger when the chain length of the amine is longer. This suggests that the lower contribution from the breaking of amine-amine interactions in longer amines is overcompensated by the higher contributions which arise from: i) the larger number of amide-amide interactions broken by longer amines; and ii) the lower number and

weaker amide-amine interactions created when longer amines are involved, since then the amine group is more sterically hindered.

For a fixed amine, the replacement of DMF by DMA leads to decreased H_m^E values. The difference in size between both amides suggests that the contribution from the disruption of amine-amine interactions should be higher for DMA mixtures. However, the amide group is less sterically hindered in DMF, and we recognize that, in pure state, DMF-DMF interactions are stronger than those between DMA molecules. In fact (see above), UCST(DMF + heptane) > UCST(DMA + heptane). This is also supported by calculations on entropy changes under the action of an electrostatic field and by the application of the Kirkwood-Fröhlich model [14]. Therefore, we can conclude that the breaking of DMF-DMF interactions contributes more positively to H_m^E than the disruption of DMA-DMA interactions, and that the formation of interactions between unlike molecules should contribute more negatively to H_m^E in the case of DMF systems. The mentioned trend suggests that the variation of the contribution of amide-amide interactions is predominant over the other two. The same phenomenon is encountered in 2-alkanone + amine mixtures when the chain length of the 2-alkanone is increased. For example, H_m^E(DPA)$/$J·mol^{-1} = 648 (propanone), 398 (butanone), 281 (2-pentanone) and 161 (2-heptanone) [58].

Interestingly, the replacement of HxA by DPA in systems involving a given amide leads to slightly higher H_m^E values. This can be explained taking into account that, since the amine group is less sterically hindered in HxA, a higher number of interactions between unlike molecules is formed in solutions with this amine and that such interactions are also stronger. It should be noted that the opposite trend is encountered for HxA or DPA + heptane mixtures, and that the difference H_m^E(HxA)$-H_m^E$(DPA) for these systems is remarkably higher than that for the corresponding amide solutions: 438 (*n*-heptane); –90 (DMF) and –85 (DMA) (all values in J·mol^{-1}). This underlines the relevance of amide-amine interactions in the studied solutions, which had already been mentioned [11, 12]. The previous statement could seem somewhat hasty, since the difference between H_m^E values for amide + HxA or + DPA solutions is rather low. In order to reinforce it, let us remove equation-of-state effects from H_m^E by the calculation of $U_{m,V}^E$ (equation (4)), retaining only interactional contributions. For our mixtures, $U_{m,V}^E$ /J·mol^{-1} = 489 (DMF + BA), 667 (DMF + HxA), 852 (DMF + DPA), and 1096 (DMF + DBA); 283 (DMA + BA), 423 (DMA + HxA), 590 (DMA + DPA), and 809 (DMA + DBA). The difference between $U_{m,V}^E$ values of amide + HxA or + DPA solutions is approximately twice the corresponding difference between their H_m^E results. This supports our previous discussion on

the importance of amide-amine interactions. Eventually, let us point out the large and negative value of the H_m^E of the system *N*-methylacetamide + HxA (–1000 J·mol^{-1}, T = 363.15 K) [23], for which the formation of amide-amine interactions is dominant by far.

The excess molar volumes, V_m^E /cm^3·mol^{-1}, of the considered mixtures are either negative or small and positive [11, 12]: –0.263 (DMF + BA), –0.021 (DMF + HxA), –0.289 (DMF + DPA), and 0.018 (DMF+DBA); –0.194 (DMA + BA), 0.006 (DMA + HxA), –0.228 (DMA + DPA), and 0.055 (DMA + DBA). It is to be noted that H_m^E and V_m^E change in line, which reveals that the interactional contribution to V_m^E is relevant. However, positive H_m^E values together with negative V_m^E results are indicative of the existence of structural effects [59]. Similar structural effects are also encountered in amine + *n*-alkane systems; for example, see the low value of V_m^E / cm^3·mol^{-1} in DBA + heptane, 0.0675 (DBA) [60], and the negative one of the DBA + hexane system, –0.1854 cm^3·mol^{-1} [61].

Mixtures of DMF or DMA with aniline contrast drastically with those of linear primary or secondary amines. The dipole moment of aniline (1.51 D [49]) is higher than that of linear primary and secondary amines, and proximity effects between the phenyl ring and the amine group lead to strong dipolar interactions between aniline molecules. As a consequence, aniline + *n*-alkane mixtures are characterized by relatively high UCST (343.11 K for the heptane solution [62]). When aniline molecules are mixed with DMF or DMA molecules, very strong interactions between unlike molecules are created, and we have H_m^E/J·mol^{-1} = − 2946 (DMF + aniline) [21]; − 352 (DMA + aniline) [22]. Similarly, large differences are also encountered between values of the excess relative permittivity for the DMF + linear primary or secondary amine or + aniline mixtures [13, 14]: –0.864 (DMF + BA), –1.262 (DMF + HxA), –1.372 (DMF + DPA), –1.733 (DMF + DBA), 1.806 (DMF + aniline). It must be observed that H_m^E values are very different for DMF and DMA + aniline systems, newly remarking that interactions between unlike molecules are much more relevant in DMF systems. The rather large and negative V_m^E / cm^3·mol^{-1} results for the mentioned aniline solutions (–0.6615 (DMF + aniline) [63] and – 0.6092 (DMA + aniline, T = 303.15 K) [64]) are in agreement with the H_m^E values and underline the importance of the interactional contribution to V_m^E .

5.1. ERAS results

Results from ERAS are collected in Tables 5 and 6 and are shown graphically in Figures 2-5. Both excess functions, H_m^E and V_m^E, are reasonably well represented by the model. Larger differences for V_m^E results are encountered for mixtures characterized by low V_m^E values, since

the overall result is obtained from the difference of two large magnitudes of different sign: the positive physical contribution and the negative chemical contribution (Table 6). ERAS calculations indicate that a better agreement with V_m^E data is obtained when the chemical contribution to V_m^E is higher (in absolute value). This occurs for the BA or DPA + DMF, systems (Figure 4). In terms of the model, such excess molar volumes are mainly determined by the interactions between unlike molecules. In contrast, structural effects seem to be relatively more important in the BA or DPA + DMA mixtures (Table 6). On the other hand, we note that ERAS results on H_m^E are, as an average, better for DMA systems (Table 5). This suggests that, in such a case, physical interactions are more properly described by ERAS, that is, dipolar interactions are more relevant in DMF mixtures, particularly in the BA solution.

The low K_{AB} and $\left| \Delta h_{AB}^* \right|$ values (Table 4) indicate that solvation effects are not relevant and that the enthalpy of the H bonds between unlike molecules is weak. The large X_{AB} values (Table 4) reveal that the physical contribution is important, particularly with regards to H_m^E. The present ERAS parameters largely differ from those determined for 1-alkanol + linear primary or secondary amine systems, which are characterized by strong solvation effects and, in consequence, by large K_{AB} and Δh_{AB}^* values and low X_{AB} values. For example, for the 1-hexanol + HxA mixture at 298.15 K: $K_{AB} = 800$; $\Delta h_{AB}^* = -36$ kJ·mol^{-1}; $X_{AB} = 5$ J·cm^{-3} [47]. As we have pointed out (see above), aniline-amide interactions are rather strong and, accordingly, the corresponding ERAS parameters are also very different. We have: $K_{AB} = 70$ (DMF); 2.2 (DMA); Δh_{AB}^* / kJ·mol^{-1} = –22 (DMF; DMA); Δv_{AB}^* /cm^3·mol^{-1} = –11.1 (DMF); –20 (DMA); X_{AB} / J·cm^{-3} = 4 (DMF); 3.2 (DMA) [14].

6. Conclusions

Excess molar enthalpies of amide (DMF or DMA) + linear primary or secondary amine (BA, HxA, DPA or DBA) have been reported at T = 298.15 K and p = 0.1 MPa. The positive H_m^E values arise from the dominant contribution from the rupture of amide-amide and amine-amine interactions along mixing. Dipolar interactions are stronger in DMF systems. DMA mixtures show lower H_m^E values for a fixed amine, suggesting that the variation of the rupture of amide-amide interactions is the predominant effect. Results on H_m^E and $U_{m,V}^E$ reveal that interactions between unlike molecules are stronger in mixtures containing HxA compared to those with DPA for a given amide. Negative or small positive V_m^E values point to the existence of important structural effects in the investigated solutions. The binary interaction parameters of the ERAS model have been adjusted to fit H_m^E and V_m^E curves simultaneously, and these

properties are represented with a rather good degree of approximation. The results from the model suggest that physical interactions are important when calculating the excess functions of the mixtures under study.

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References

[1]   E.S. Eberhardt, R.T. Raines, Amide-Amide and Amide-Water Hydrogen Bonds: Implications for Protein Folding and Stability, J. Am. Chem. Soc., 116 (1994) 2149-2150. https://doi.org/10.1021/ja00084a067.

[2]   T.W. Whitfield, G.J. Martyna, S. Allison, S.P. Bates, H. Vass, J. Crain, Structure and Hydrogen Bonding in Neat N-Methylacetamide: Classical Molecular Dynamics and Raman Spectroscopy Studies of a Liquid of Peptidic Fragments, J. Phys. Chem. B, 110 (2006) 3624-3637. https://doi.org/10.1021/jp053140+.

[3]   J.A. Gonzalez, J.C. Cobos, I. García de la Fuente, Thermodynamics of liquid mixtures containing a very strongly polar compound: Part 6. DISQUAC characterization of N,N-dialkylamides, Fluid Phase Equilib., 224 (2004) 169-183. https://doi.org/10.1016/j.fluid.2004.02.007.

[4]   J. Barthel, R. Buchner, B. Wurm, The dynamics of liquid formamide, N-methylformamide, N,N-dimethylformamide, and N,N-dimethylacetamide. A dielectric relaxation study, J. Mol. Liq., 98 (2002) 51-69. https://doi.org/10.1016/S0167-7322(01)00309-9.

[5]   W.L. Jorgensen, C.J. Swenson, Optimized intermolecular potential functions for amides and peptides. Structure and properties of liquid amides, J. Am. Chem. Soc., 107 (1985) 569-578. https://doi.org/10.1021/ja00289a008.

[6]   F.F. Liew, T. Hasegawa, M. Fukuda, E. Nakata, T. Morii, Construction of dopamine sensors by using fluorescent ribonucleopeptide complexes, Bioorg. Med. Chem., 19 (2011) 4473-4481. https://doi.org/10.1016/j.bmc.2011.06.031.

[7]   J.M. Sonner, R.S. Cantor, Molecular Mechanisms of Drug Action: An Emerging View, Annu. Rev. Biophys., 42 (2013) 143-167. https://doi.org/10.1146/annurev-biophys-083012-130341.

[8]   D.L. Nelson, M.M. Cox, Lehninger Principles of Biochemistry, 3rd ed., Worth Publishing, New York, 2000.

[9]   Y. Coulier, A. Lowe, P.R. Tremaine, J.Y. Coxam, K. Ballerat-Busserolles, Absorption of CO2 in aqueous solutions of 2-methylpiperidine: Heats of solution and modeling, Int. J. Greenh. Gas Control, 47 (2016) 322-329. https://doi.org/10.1016/j.ijggc.2016.02.009.

[10]   M. Götz, R. Reimert, S. Bajohr, H. Schnetzer, J. Wimberg, T.J.S. Schubert, Long-term thermal stability of selected ionic liquids in nitrogen and hydrogen atmosphere, Thermochim. Acta, 600 (2015) 82-88. https://doi.org/10.1016/j.tca.2014.11.005.

[11]   F. Hevia, A. Cobos, J.A. González, I. García de la Fuente, L.F. Sanz, Thermodynamics of Amide + Amine Mixtures. 1. Volumetric, Speed of Sound, and Refractive Index Data for N,N-Dimethylformamide + N-Propylpropan-1-amine, + N-Butylbutan-1-amine, + Butan-1-amine, or + Hexan-1-amine Systems at Several Temperatures, J. Chem. Eng. Data, 61 (2016) 1468-1478. https://doi.org/10.1021/acs.jced.5b00802.

[12]   F. Hevia, A. Cobos, J.A. González, I.G. de la Fuente, V. Alonso, Thermodynamics of Amide + Amine Mixtures. 2. Volumetric, Speed of Sound and Refractive Index Data for N,N-Dimethylacetamide + N-Propylpropan-1-Amine, + N-Butylbutan-1-Amine, + Butan-1-Amine, or + Hexan-1-Amine Systems at Several Temperatures, J. Solution Chem., 46 (2017) 150-174. https://doi.org/10.1007/s10953-016-0560-0.

[13]   F. Hevia, J.A. González, I. García de la Fuente, L.F. Sanz, J.C. Cobos, Thermodynamics of amide + amine mixtures. 3. Relative permittivities of N,N-dimethylformamide + N-propylpropan-1-amine, + N-butylbutan-1-amine, + butan-1-amine, or + hexan-1-amine systems at several temperatures, J. Mol. Liq., 238 (2017) 440-446. https://doi.org/10.1016/j.molliq.2017.05.025.

[14]   F. Hevia, J.A. González, A. Cobos, I. García de la Fuente, L.F. Sanz, Thermodynamics of amide + amine mixtures. 4. Relative permittivities of N,N-dimethylacetamide + N-propylpropan-1-amine, + N-butylbutan-1-amine, + butan-1-amine, or + hexan-1-amine systems and of N,N-dimethylformamide + aniline mixture at several temperatures. Characterization of amine + amide systems using ERAS, J. Chem. Thermodyn., 118 (2018) 175-187. https://doi.org/10.1016/j.jct.2017.11.011.

[15] A. Heintz, A New Theoretical Approach for Predicting Excess Properties of Alkanol/Alkane Mixtures, Ber. Bunsenges. Phys. Chem., 89 (1985) 172-181. https://doi.org/10.1002/bbpc.19850890217.

[16] H. Fröhlich, Theory of Dielectrics, Clarendon Press, Oxford, 1958.

[17] C. Moreau, G. Douhéret, Thermodynamic and physical behaviour of water + acetonitrile mixtures. Dielectric properties, J. Chem. Thermodyn., 8 (1976) 403-410. https://doi.org/10.1016/0021-9614(76)90060-4.

[18] P. Bordewijk, On the derivation of the Kirkwood-Fröhlich equation, Physica, 69 (1973) 422-432.

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

[20] J.C.R. Reis, T.P. Iglesias, Kirkwood correlation factors in liquid mixtures from an extended Onsager-Kirkwood-Frohlich equation, Phys. Chem. Chem. Phys., 13 (2011) 10670-10680. https://doi.org/10.1039/C1CP20142E.

[21] R.S. Ramadevi, P. Venkatesu, M.V. Prabhakara Rao, M.R. Krishna, Excess enthalpies of binary mixtures of N,N-dimethylformamide with substituted benzenes at 298.15 K, Fluid Phase Equilib., 114 (1996) 189-197. https://doi.org/10.1016/0378-3812(95)02816-1.

[22] G. Chandra Sekhar, M.V. Prabhakara Rao, D.H.L. Prasad, Y.V.L. Ravi Kumar, Excess molar enthalpies of N,N-dimethylacetamide with substituted benzenes at 298.15 K, Thermochim. Acta, 402 (2003) 99-103. https://doi.org/10.1016/S0040-6031(02)00542-7.

[23] A.B. de Haan, J. Gmehling, Excess Enthalpies for Various Binary Mixtures with N-Methylacetamide or Acetic Anhydride, J. Chem. Eng. Data, 41 (1996) 474-478. https://doi.org/10.1021/je950294h.

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

[25] J.B. Ott, C.E. Stouffer, G.V. Cornett, B.F. Woodfield, R.C. Wirthlin, J.J. Christensen, U.K. Deiters, Excess enthalpies for (ethanol + water) at 298.15 K and pressures of 0.4, 5, 10, and 15 MPa, J. Chem. Thermodyn., 18 (1986) 1-12. https://doi.org/10.1016/0021-9614(86)90036-4.

[26] J.B. Ott, G.V. Cornett, C.E. Stouffer, B.F. Woodfield, C. Guanquan, J.J. Christensen, Excess enthalpies of (ethanol+water) at 323.15, 333.15, 348.15, and 373.15 K and from

0.4 to 15 MPa, J. Chem. Thermodyn., 18 (1986) 867-875. https://doi.org/10.1016/0021-9614(86)90121-7.

[27]   O. Redlich, A.T. Kister, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, Ind. & Eng. Chem., 40 (1948) 345-348. https://doi.org/10.1021/ie50458a036.

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

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

[30]   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. https://doi.org/10.1351/pac198961081429.

[31]   C.B. Kretschmer, R. Wiebe, Thermodynamics of Alcohol☐Hydrocarbon Mixtures, J. Chem. Phys., 22 (1954) 1697-1701. https://doi.org/10.1063/1.1739878.

[32]   H. Renon, J.M. Prausnitz, On the thermodynamics of alcohol-hydrocarbon solutions, Chem. Eng. Sci., 22 (1967) 299-307. https://doi.org/10.1016/0009-2509(67)80116-7.

[33]   H.V. Kehiaian, Bull. Acad. Pol. Sci., 16 (1968) 165.

[34]   H.V. Kehiaian, A. Treszczanowicz, Bull. Acad. Pol. Sci., 16 (1968) 171.

[35]   P.J. Flory, R.A. Orwoll, A. Vrij, Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons, J. Am. Chem. Soc., 86 (1964) 3507-3514. https://doi.org/10.1021/ja01071a023.

[36]   P.J. Flory, R.A. Orwoll, A. Vrij, Statistical Thermodynamics of Chain Molecule Liquids. II. Liquid Mixtures of Normal Paraffin Hydrocarbons, J. Am. Chem. Soc., 86 (1964) 3515-3520. https://doi.org/10.1021/ja01071a024.

[37]   P.J. Flory, Statistical Thermodynamics of Liquid Mixtures, J. Am. Chem. Soc., 87 (1965) 1833-1838. https://doi.org/10.1021/ja01087a002.

[38]   A. Abe, P.J. Flory, The Thermodynamic Properties of Mixtures of Small, Nonpolar Molecules, J. Am. Chem. Soc., 87 (1965) 1838-1846. https://doi.org/10.1021/ja01087a003.

[39]   R.A. Orwoll, P.J. Flory, Thermodynamic properties of binary mixtures of n-alkanes, J. Am. Chem. Soc., 89 (1967) 6822-6829. https://doi.org/10.1021/ja01002a003.

[40] 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. https://doi.org/10.1139/v03-063.

[41] 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. https://doi.org/10.1016/S0378-3812(99)00326-X.

[42] 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. https://doi.org/10.1002/bbpc.19981020707.

[43] 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. https://doi.org/10.1016/S0040-6031(97)00224-4.

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

[45] 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-alkanol + isomeric amine (C6H15N) systems: Characterization in terms of the ERAS model, Fluid Phase Equilib., 216 (2004) 123-133. https://doi.org/10.1016/j.fluid.2003.10.008.

[46] S. Villa, J.A. González, I.G. De La Fuente, N. Riesco, J.C. Cobos, Thermodynamics of Organic Mixtures Containing Amines. II. Excess Molar Volumes at 25°C for Methylbutylamine + Alkane Systems and Eras Characterization of Linear Secondary Amine + Alkane Mixtures, J. Solution Chem., 31 (2002) 1019-1038. https://doi.org/10.1023/A:1021881627444.

[47] J.A. Gonzalez, U. Domanska, J. Lachwa, Thermodynamics of Binary Mixtures Containing a Very Strongly Polar Compound. 7. Isothermal VLE Measurements for NMP + 2-Propanol or + 2-Butanol Systems. DISQUAC and ERAS Characterization of NMP or N,N-Dialkylamide + 2-Alkanol Mixtures. Comparison with Results from Dortmund UNIFAC, Ind. Eng. Chem. Res., 44 (2005) 5795-5804. https://doi.org/10.1021/ie0580046.

[48] A.L. McClellan, Tables of Experimental Dipole Moments, Vols. 1,2,3, Rahara Enterprises, El Cerrito, US, 1974.

[49] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic solvents: physical properties and methods of purification, Wiley, New York, 1986.

[50] J. Lobos, I. Mozo, M. Fernández Regúlez, J.A. González, I. García de la Fuente, J.C. Cobos, Thermodynamics of Mixtures Containing a Strongly Polar Compound. 8. Liquid–Liquid Equilibria for N,N-Dialkylamide + Selected N-Alkanes, J. Chem. Eng. Data, 51 (2006) 623-627. https://doi.org/10.1021/je050428j.

[51] M. Rogalski, R. Stryjek, Mutual solubility of binary n-hexadecane and polar compound systems, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 28 (1980) 139-147.

[52] X. An, H. Zhao, F. Jiang, W. Shen, The (liquid + liquid) critical phenomena of (a polar liquid + an n-alkane) V. Coexistence curves of (N,N-dimethylacetamide + heptane), J. Chem. Thermodyn., 28 (1996) 1221-1232. https://doi.org/10.1006/jcht.1996.0109.

[53] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, Thermodynamics of organic mixtures containing amines. IV. Systems with aniline, Can. J. Chem., 83 (2005) 1812-1825. https://doi.org/10.1139/v05-190.

[54] J.A. González, L.F. Sanz, I. García De La Fuente, J.C. Cobos, Thermodynamics of mixtures containing amines: XIII. Application of the ERAS model to cyclic amine + alkane mixtures, Thermochim. Acta, 573 (2013) 229-236. https://doi.org/10.1016/j.tca.2013.09.033.

[55] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, McGraw-Hill, New York, US, 1987.

[56] E. Matteoli, L. Lepori, A. Spanedda, Thermodynamic study of heptane + amine mixtures: I. Excess and solvation enthalpies at 298.15 K, Fluid Phase Equilib., 212 (2003) 41-52. https://doi.org/10.1016/S0378-3812(03)00260-7.

[57] E. Matteoli, P. Gianni, L. Lepori, Thermodynamic study of heptane + secondary, tertiary and cyclic amines mixtures. Part IV. Excess and solvation enthalpies at 298.15 K, Fluid Phase Equilib., 306 (2011) 234-241. https://doi.org/10.1016/j.fluid.2011.04.013.

[58] J.A. González, I. Alonso, I. García De La Fuente, J.C. Cobos, Thermodynamics of ketone + amine mixtures. Part IX. Excess molar enthalpies at 298.15 K for dipropylamine, or dibutylamine + 2-alkanone systems and modeling of linear or aromatic amine + 2-alkanone mixtures in terms of DISQUAC and ERAS, Fluid Phase Equilib., 343 (2013) 1-12. https://doi.org/10.1016/j.fluid.2013.01.011.

[59]   L. Lepori, P. Gianni, E. Matteoli, The Effect of the Molecular Size and Shape on the Volume Behavior of Binary Liquid Mixtures. Branched and Cyclic Alkanes in Heptane at 298.15 K, J. Solution Chem., 42 (2013) 1263-1304. https://doi.org/10.1007/s10953-013-0023-9.

[60]   L. Lepori, P. Gianni, A. Spanedda, E. Matteoli, Thermodynamic study of (heptane + amine) mixtures. III: Excess and partial molar volumes in mixtures with secondary, tertiary, and cyclic amines at 298.15 K, J. Chem. Thermodyn., 43 (2011) 1453-1462. https://doi.org/10.1016/j.jct.2011.04.017.

[61]   T.M. Letcher, Thermodynamics of aliphatic amine mixtures I. The excess volumes of mixing for primary, secondary, and tertiary aliphatic amines with benzene and substituted benzene compounds, J. Chem. Thermodyn., 4 (1972) 159-173. https://doi.org/10.1016/S0021-9614(72)80021-1.

[62]   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. https://doi.org/10.1021/je020156+.

[63]   H.J. Noh, S.J. Park, S.J. In, Excess molar volumes and deviations of refractive indices at 298.15 K for binary and ternary mixtures with pyridine or aniline or quinoline, J. Ind. Eng. Chem., 16 (2010) 200-206. https://doi.org/10.1016/j.jiec.2010.01.038.

[64]   G. Chandrasekhar, P. Venkatesu, M.V. Prabhakara Rao, Excess Volumes and Ultrasonic Studies of n,n-Dimethyl Acetamide with Substituted Benzenes at 303.15 k, Phys. Chem. Liq., 40 (2002) 181-189. https://doi.org/10.1080/00319100208086661.

[65]   D. Keshapolla, V. Singh, R.L. Gardas, Volumetric, acoustic and transport properties of binary mixtures of benzyldimethylammonium based ionic liquids with N,N-dimethylformamide at temperature from 293.15 to 328.15 K, J. Mol. Liq., 199 (2014) 330-338. https://doi.org/10.1016/j.molliq.2014.09.030.

[66]   J. Krakowiak, H. Koziel, W. Grzybkowski, Apparent molar volumes of divalent transition metal perchlorates and chlorides in N,N-dimethylacetamide, J. Mol. Liq., 118 (2005) 57-65. https://doi.org/10.1016/j.molliq.2004.07.013.

[67]   F. Sarmiento, M.I. Paz Andrade, J. Fernandez, R. Bravo, M. Pintos, Excess enthalpies of 1-heptanol + n-alkane and di-n-propylamine + normal alcohol mixtures at 298.15 K, J. Chem. Eng. Data, 30 (1985) 321-323. https://doi.org/10.1021/je00041a025.

[68]   I. Alonso, I. Mozo, I.G. de la fuente, J.A. González, J.C. Cobos, Thermodynamics of ketone + amine mixtures Part IV. Volumetric and speed of sound data at (293.15; 298.15 and 303.15 K) for 2-butanone +dipropylamine, +dibutylamine or +triethylamine

systems, Thermochim. Acta, 512 (2011) 86-92. https://doi.org/10.1016/j.tca.2010.09.004.

[69]   S.S. Bittencourt, R.B. Torres, Volumetric properties of binary mixtures of (acetonitrile + amines) at several temperatures with application of the ERAS model, J. Chem. Thermodyn., 93 (2016) 222-241. https://doi.org/10.1016/j.jct.2015.09.002.

[70]   P. Góralski, M. Wasiak, A. Bald, Heat Capacities, Speeds of Sound, and Isothermal Compressibilities of Some n-Amines and Tri-n-amines at 298.15 K, J. Chem. Eng. Data, 47 (2002) 83-86. https://doi.org/10.1021/je010206v.

Table 1

Description, source and purity of the pure liquids and their density, ρ, at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa. [b]

Chemical name	CAS Number	Source	Purity[a]	ρ / g·cm^{-3}	
				Exp.	Lit.
N,N-dimethylformamide (DMF)	68-12-2	Sigma-Aldrich	0.9996	0.94378	0.944163 [65]
N,N-dimethylacetamide (DMA)	127-19-5	Honeywell	>0.999	0.93614	0.936233 [66]
N-propylpropan-1-amine (DPA)	142-84-7	Aldrich	0.999	0.73337	0.73321 [67]
N-butylbutan-1-amine (DBA)	111-92-2	Aldrich	0.997	0.75570	0.755457 [68]
butan-1-amine (BA)	109-73-9	Sigma-Aldrich	0.9978	0.73218	0.73233 [69]
hexan-1-amine (HxA)	111-26-2	Aldrich	0.999	0.76016	0.76013 [70]

[a] In mole fraction. By gas chromatography. Provided by the supplier.

[b] The standard uncertainties are: $u(T) = 0.01$ K, $u(p) = 1$ kPa. The relative standard uncertainty is: $u_{\mathrm{r}}(\rho) = 0.0012$.

Table 2

Excess molar enthalpies, H_m^E, of amide (1) + amine (2) liquid mixtures as functions of the mole

fraction of the amide, x_1, at temperature T = 298.15 K and pressure p = 0.1 MPa. [a]

x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}
			DMF (1) + DPA (2)				
0.0358	88	0.3016	595	0.5505	753	0.7983	542
0.1002	241	0.3483	657	0.6012	743	0.8485	441
0.1512	351	0.4005	695	0.6587	708	0.8991	318
0.1984	446	0.4495	737	0.6997	673	0.9504	170
0.2504	529	0.5005	748	0.7518	613		
			DMF (1) + DBA (2)				
0.0491	188	0.3006	877	0.5505	1118	0.7994	815
0.1014	386	0.3510	956	0.5990	1098	0.8503	669
0.1488	543	0.4021	1032	0.6500	1060	0.9000	488
0.2006	680	0.4497	1082	0.6997	1001	0.9501	270
0.2482	782	0.4982	1113	0.7506	921		
			DMF (1) + BA (2)				
0.0510	89	0.2498	320	0.5008	384	0.7559	245
0.1009	166	0.3007	352	0.5463	374	0.8005	208
0.1496	226	0.3496	373	0.6008	355	0.8495	158
0.1703	247	0.4008	391	0.6463	326	0.9003	106
0.2005	279	0.4508	393	0.7011	289	0.9519	55
			DMF (1) + HxA (2)				
0.0514	118	0.3006	533	0.5505	659	0.8005	441
0.1007	219	0.3519	586	0.5982	648	0.8506	354
0.1516	318	0.4007	619	0.6507	615	0.8995	246
0.2009	394	0.4518	648	0.7002	569	0.9502	129
0.2522	461	0.5003	661	0.7503	510		
			DMA (1) + DPA (2)				
0.0597	98	0.3009	399	0.5497	519	0.8009	385
0.0996	166	0.3462	435	0.5972	509	0.8504	318
0.1496	235	0.4062	477	0.6495	493	0.8989	239
0.2011	300	0.4491	495	0.6975	473	0.9368	156
0.2497	358	0.5035	514	0.7478	437	0.9507	126
			DMA (1) + DBA (2)				
0.0499	150	0.3002	673	0.5507	832	0.8004	618
0.0976	276	0.3526	732	0.6007	825	0.8512	508
0.1510	405	0.3983	774	0.6477	803	0.9019	371
0.1969	503	0.4472	807	0.6968	756	0.9507	203

0.2472	590	0.5007	833	0.7481	698		
			DMA (1) + BA (2)				
0.0498	48	0.3004	189	0.5509	201	0.9002	64
0.0992	89	0.3493	202	0.6005	195	0.9594	27
0.1518	123	0.4015	207	0.7008	160		
0.1985	152	0.4508	209	0.7995	120		
0.2512	165	0.5005	208	0.8502	94		
			DMA (1) + HxA (2)				
0.0509	71	0.3018	338	0.5493	424	0.7996	296
0.1005	141	0.3484	369	0.6002	416	0.8513	238
0.1507	196	0.3980	402	0.6492	401	0.9008	171
0.1994	244	0.4502	419	0.7001	375	0.9503	91
0.2488	295	0.5006	423	0.7491	341		

[a] The standard uncertainties are: $u(T)$ = 0.01 K, $u(p)$ = 1 kPa. The relative standard uncertainty is: $u_r(x_1)$ = 0.004. The relative combined expanded uncertainty (0.95 level of confidence) is $U_{rc}(H_m^E) = 0.06$.

Table 3

Coefficients A_i and standard deviations, $\sigma\left(F^E\right)$ (equation (3)), for the representation of F^E at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa for amide + amine liquid mixtures by equation (2).

Property F^E	System	A_0	A_1	A_2	A_3	$\sigma\left(F^E\right)$
H_m^E / J·mol^{-1}	DMF + DPA	2999	476	178		4
	DMF + DBA	4410	731	634		7
	DMF + BA	1545	–374	–75		1.9
	DMF + HxA	2639	238	–93		4
	DMA + DPA	2038	444	274		4
	DMA + DBA	3314	476	544	255	2
	DMA + BA	834	–158			3
	DMA + HxA	1699	234			3
$U_{m,V}^E$ / J·mol^{-1}	DMF + DPA	3408	657	338		0.7
	DMF + DBA	4385.4	841	758		0.5
	DMF + BA	1954.3	–193	45		0.4
	DMF + HxA	2669.7	376			0.7
	DMA + DPA	2359.7	457	368		0.4
	DMA + DBA	3237.3	436	532	250	0.3
	DMA + BA	1131	–59	93		0.3
	DMA + HxA	1690	269	31		0.6

Table 4

ERAS parameters for amine (A) + DMF (B) or + DMA (B) liquid mixtures at temperature 298.15 K and pressure 0.1 MPa. K_{AB}, association constant of component A with component B; Δh_{AB}^*, association enthalpy of component A with component B; Δv_{AB}^*, association volume of component A with component B; X_{AB}, physical parameter.

System	K_{AB}	$\Delta h_{AB}^* / \text{kJ·mol}^{-1}$	$\Delta v_{AB}^* / \text{cm}^3\text{·mol}^{-1}$	$X_{AB} / \text{J·cm}^{-3}$
BA + DMF	1.3	–9	–3.5	24.5
HxA + DMF	1	–9	–4.6	36.0
BA + DMA	1.3	–9	–2.5	13.4
HxA + DMA	1	–9	–2.8	23.3
DPA + DMF	1	–2	–2.5	23.8
DBA + DMF	1	–2	–3.8	47.8
DPA + DMA	1	–2	–1.2	15.0
DBA + DMA	1	–2	–2.2	35.1

Table 5

Excess molar enthalpies (H_m^E) at equimolar composition, temperature 298.15 K and pressure 0.1 MPa, of amine (A) + DMF (B) or DMA (B) liquid mixtures, and standard deviations, $\sigma\left(H_m^E\right)$.

System	N	H_m^E / J·mol⁻¹		$\sigma\left(H_m^E\right)$ / J·mol⁻¹	
		Exp.	ERAS	Exp.[a]	ERAS[b]
BA + DMF	20	386	380	1.9	50
HxA + DMF	19	660	651	4	51
BA + DMA	17	744	740	4	22
HxA + DMA	19	1102	1137	7	79
DPA + DMF	19	208	211	3	16
DBA + DMF	19	425	407	3	16
DPA + DMA	20	509	521	4	13
DBA + DMA	19	828	842	2	32

[a] Obtained from equation (3).

[b] Defined as: $\sigma\left(H_m^E\right) = \left[\dfrac{1}{N}\sum_{j=1}^{N}\left(F_{ERAS,j}^E - F_{exp,j}^E\right)^2\right]^{1/2}$, with notation similar to equation (3).

Table 6

Excess molar volumes (V_m^E) at equimolar composition, temperature 298.15 K and pressure 0.1 MPa, of amine (A) + DMF (B) or DMA (B) liquid mixtures[a]. The chemical, $V_{m,chem}^E$, and physical, $V_{m,phys}^E$, contributions to this excess function within ERAS model are also listed.

System	V_m^E / cm^3·mol^{-1}			
	Exp.	$V_{m,chem}^E$	$V_{m,phys}^E$	ERAS
BA + DMF	–0.263	–0.330	0.071	–0.259
HxA + DMF	–0.021	–0.501	0.478	0.023
DPA + DMF	–0.289	–0.223	–0.069	–0.292
DBA + DMF	0.018	–0.628	0.648	0.020
BA + DMA	–0.194	–0.122	–0.081	–0.203
HxA + DMA	0.006	0.230	–0.189	0.041
DPA + DMA	–0.228	0.022	–0.257	–0.235
DBA + DMA	0.055	–0.303	0.349	0.046

[a] Source of experimental data: [11] for DMF mixtures, [12] for DMA systems.

Figure 1

Schematic view of the experimental setup used to determine excess molar enthalpies.
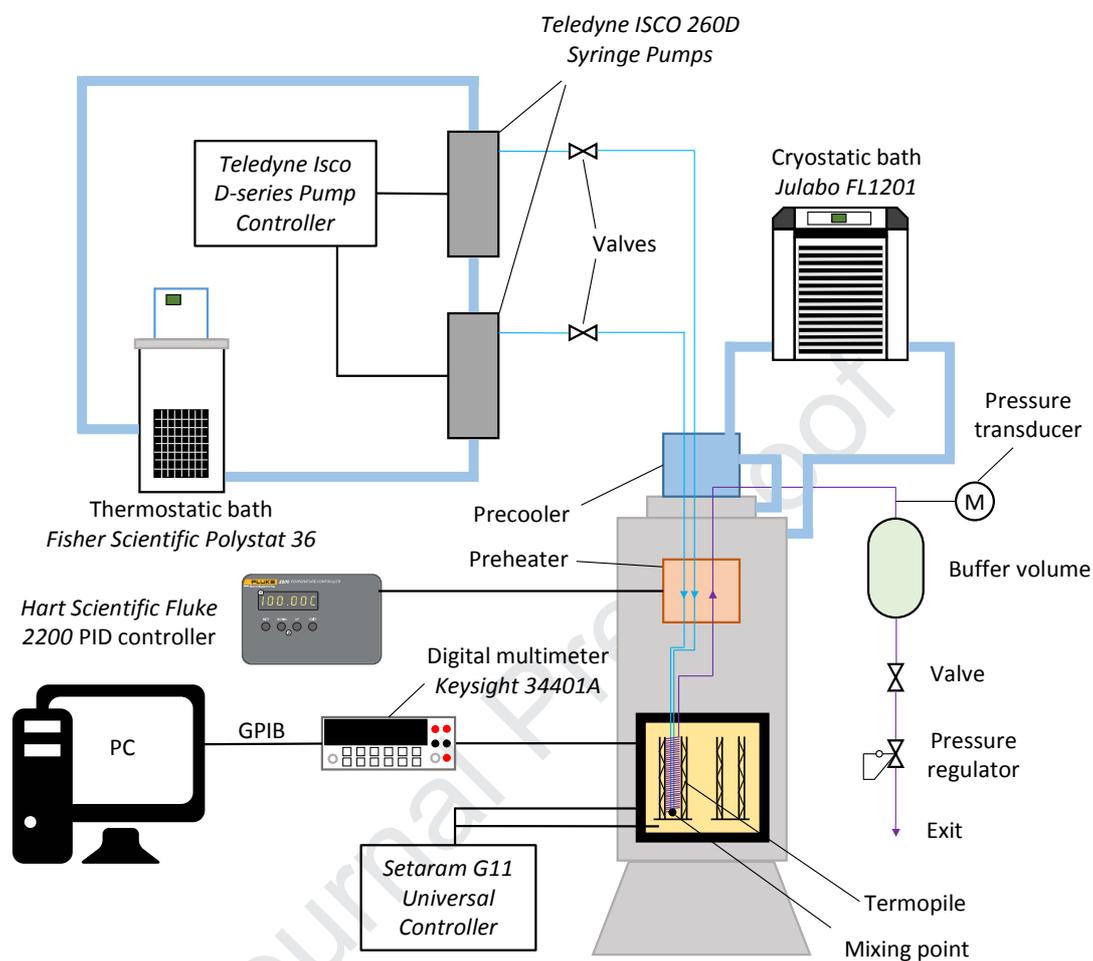
Figure 2

Excess molar enthalpies, H_m^E, of DMF (1) + amine (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, experimental values (this work): (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, ERAS results using interaction parameters listed in Table 4.
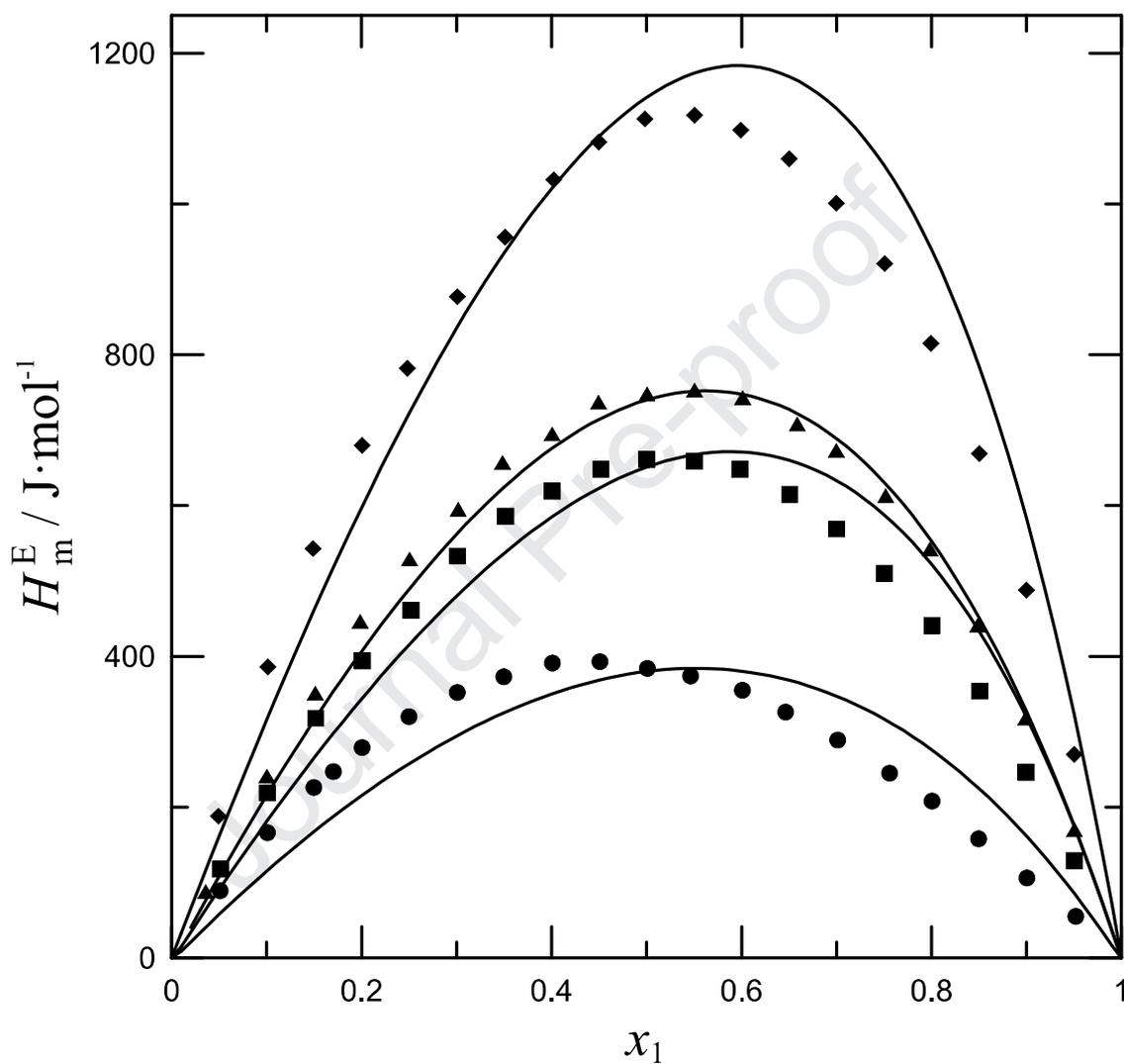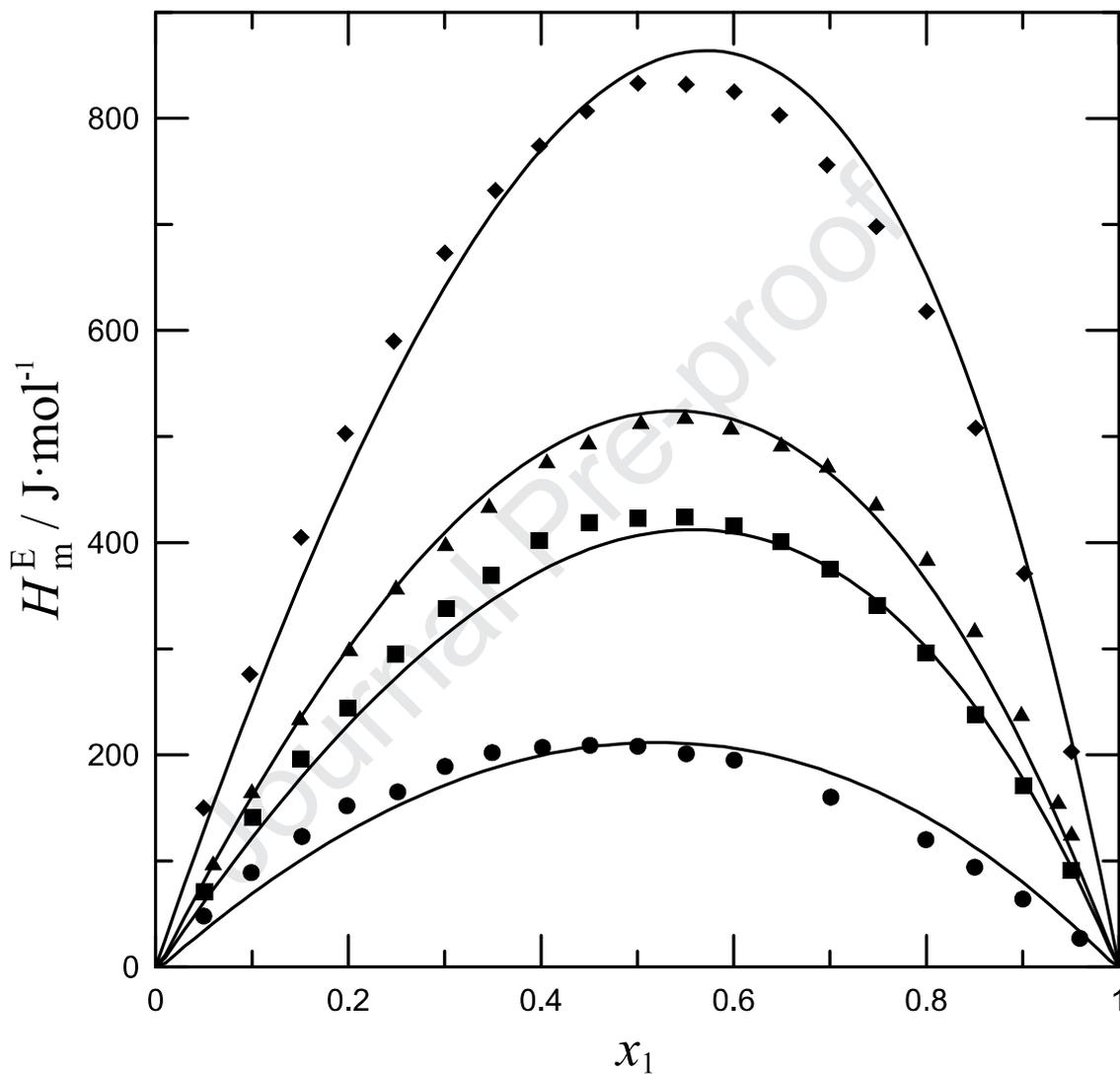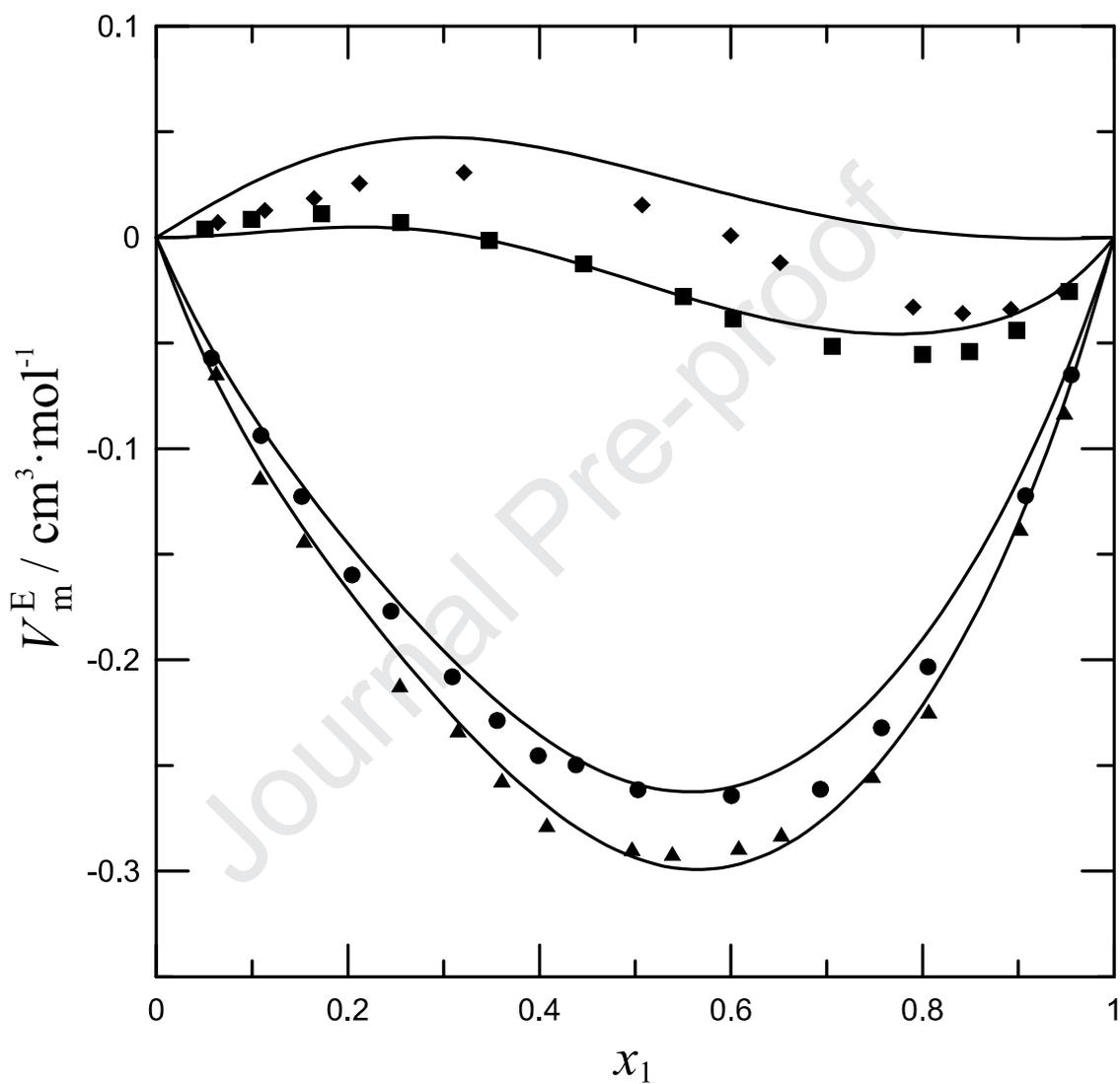
Figure 3

Excess molar enthalpies, H_m^E, of DMA (1) + amine (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, experimental values (this work): (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, ERAS results using interaction parameters listed in Table 4.

Figure 4

Excess molar volumes, V_m^E, of DMF (1) + amine (2) liquid mixtures at 0.1 MPa and 298.15 K.
Full symbols, experimental values [11]: (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines,
ERAS results using interaction parameters listed in Table 4.

Figure 5

Excess molar volumes, V_m^E, of DMA (1) + amine (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, experimental values [12]: (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, ERAS results using interaction parameters listed in Table 4.
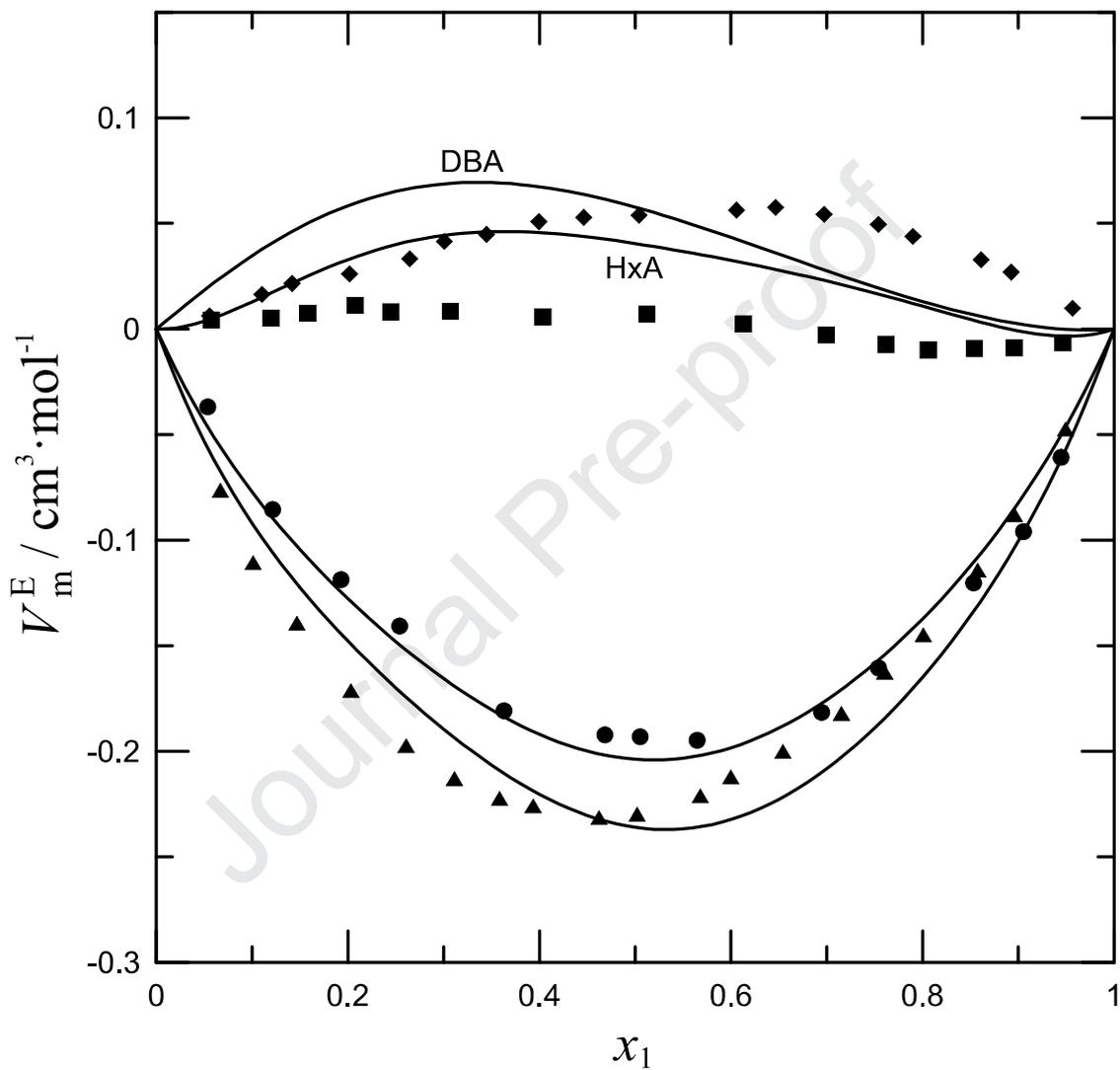
Highlights

- H_m^E of DMF or DMA + linear amine liquid mixtures are reported at 298.15 K

- Interactions between like molecules are dominant and stronger in DMF than DMA mixtures

- Amide-amine interactions are relevant, and stronger in HxA than in DPA mixtures

- Structural effects are important in the investigated solutions

- H_m^E and V_m^E are correctly described by ERAS; interaction parameters are provided

Thermodynamics of amide + amine mixtures. 5. Excess molar enthalpies of *N,N*-dimethylformamide or *N,N*-dimethylacetamide + *N*-propylpropan-1-amine, + *N*-butylbutan-1-amine, + butan-1-amine, or + hexan-1-amine systems at 298.15 K. Application of the ERAS model

Supplementary material

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Table S1

ERAS parameters[a] for pure liquids at temperature 298.15 K and pressure 0.1 MPa.

Compound	$V_{\mathrm{m},i}$ / cm^3·mol^{-1}	K_i	Δh_i^* / kJ·mol^{-1}	Δv_i^* / cm^3·mol^{-1}	$V_{\mathrm{m},i}^*$ / cm^3·mol^{-1}	p_i^* / J·cm^{-3}
BA[b]	99.89	0.96	–13.2	–2.8	77.59	565.7
HxA[b]	133.11	0.78	–13.2	–2.8	106.87	495.0
DPA[c]	138.07	0.55	–7.5	–2.8	106.50	526.0
DBA[c]	171.03	0.16	–4.5	–2.8	135.86	466.2
DMF[d]	77.44	0	0	0	62.07	714.1
DMA[d]	93.04	0	0	0	75.56	649.5

[a] $V_{\mathrm{m},i}$, molar volume; K_i, equilibrium constant; $V_{\mathrm{m},i}^*$ and p_i^*, reduction parameters for volume and pressure, respectively; Δh_i^*, hydrogen-bonding enthalpy; Δv_i^*, self-association volume; [b] Ref. [1]; [c] Ref. [2]; [d] [3].

Figure S1

Excess molar enthalpies, H_m^E, of DMF (1) + amine (2), or BA (1) + heptane (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, DMF (1) + amine (2) experimental values (this work): (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, calculations with equation (2) using the coefficients from Table 3. Dashed line, BA (1) + heptane (2) [4].
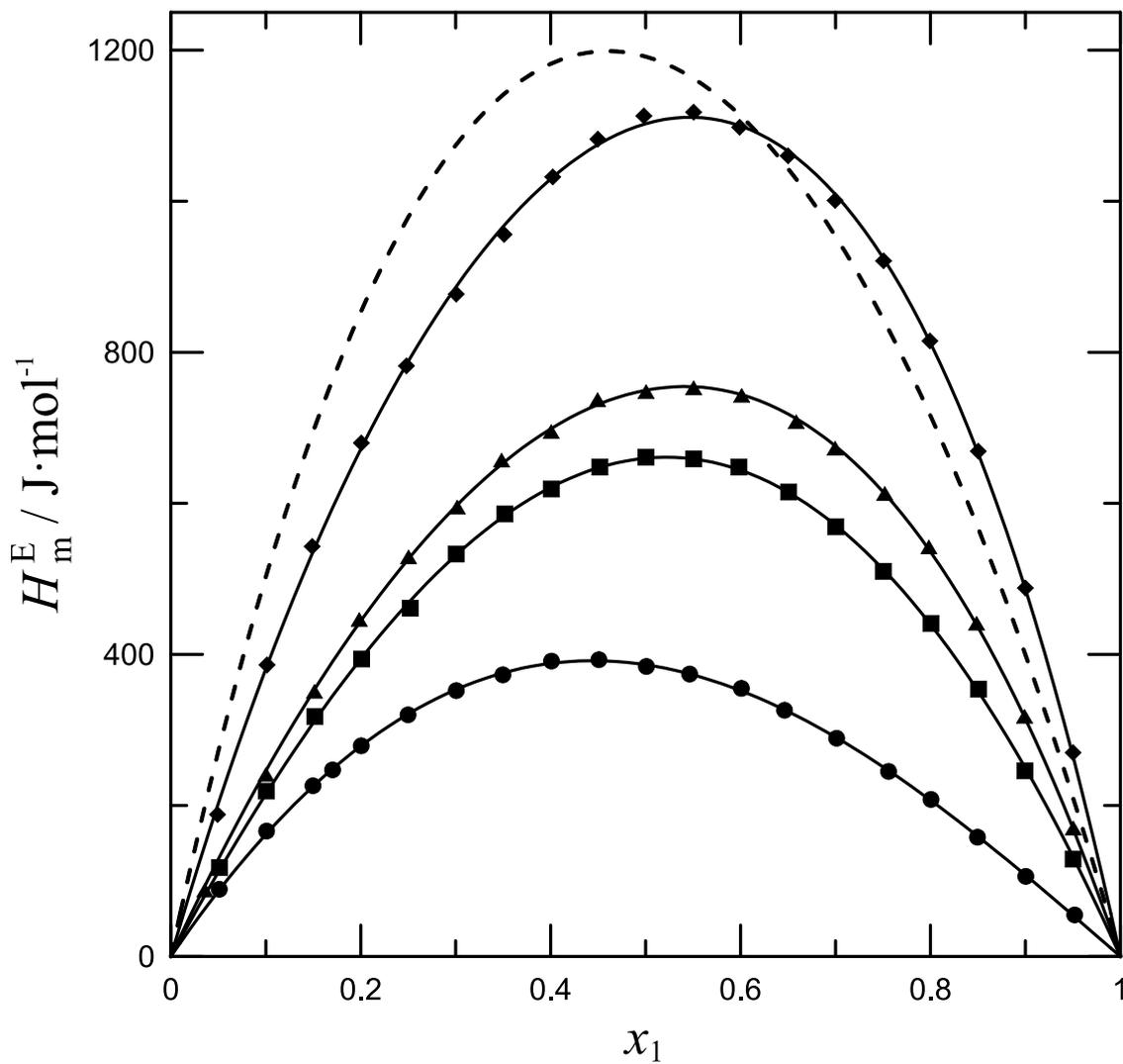
Figure S2

Excess molar enthalpies, H_m^E, of DMA (1) + amine (2), or + cyclohexane (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, DMA (1) + amine (2) experimental values (this work): (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, calculations with equation (2) using the coefficients from Table 3. Dashed line, DMA (1) + cyclohexane (2) [5].
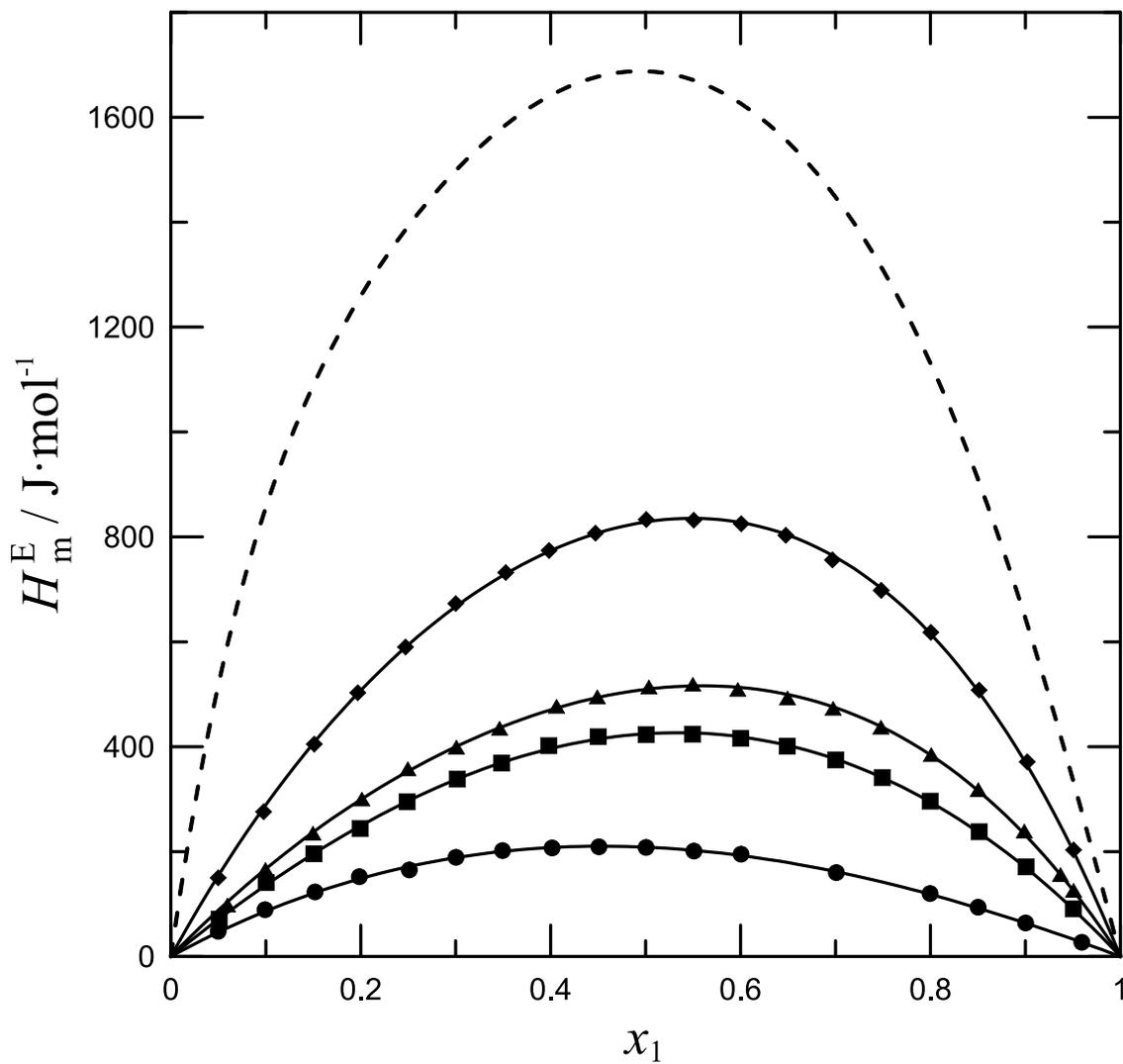
Figure S3

Excess molar energies at constant volume, $U_{m,V}^{E}$, of DMF (1) + amine (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, calculations at $\Delta x_1 = 0.05$ from smoothed experimental values: (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, calculations with equation (2) using the coefficients from Table 3.
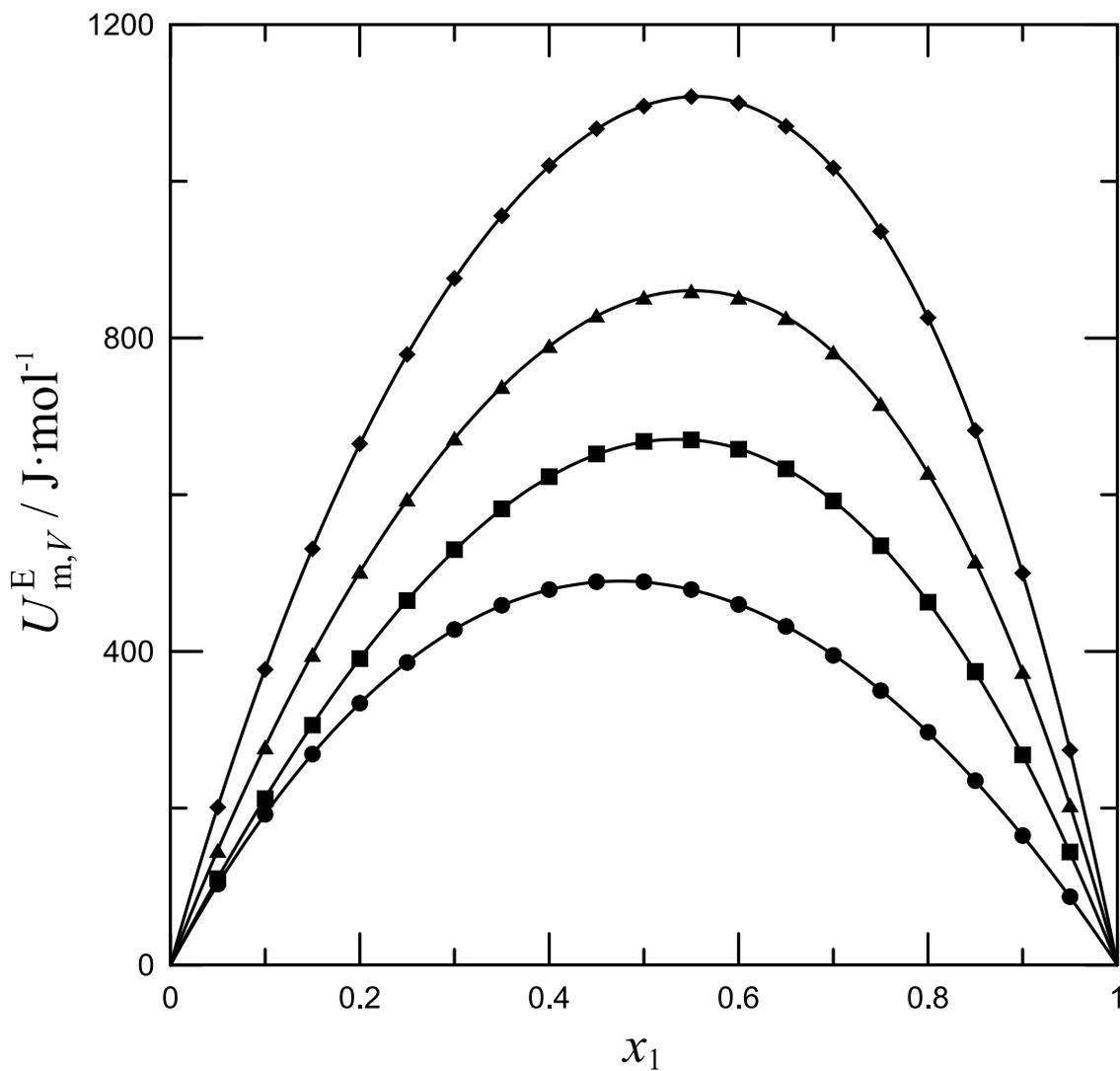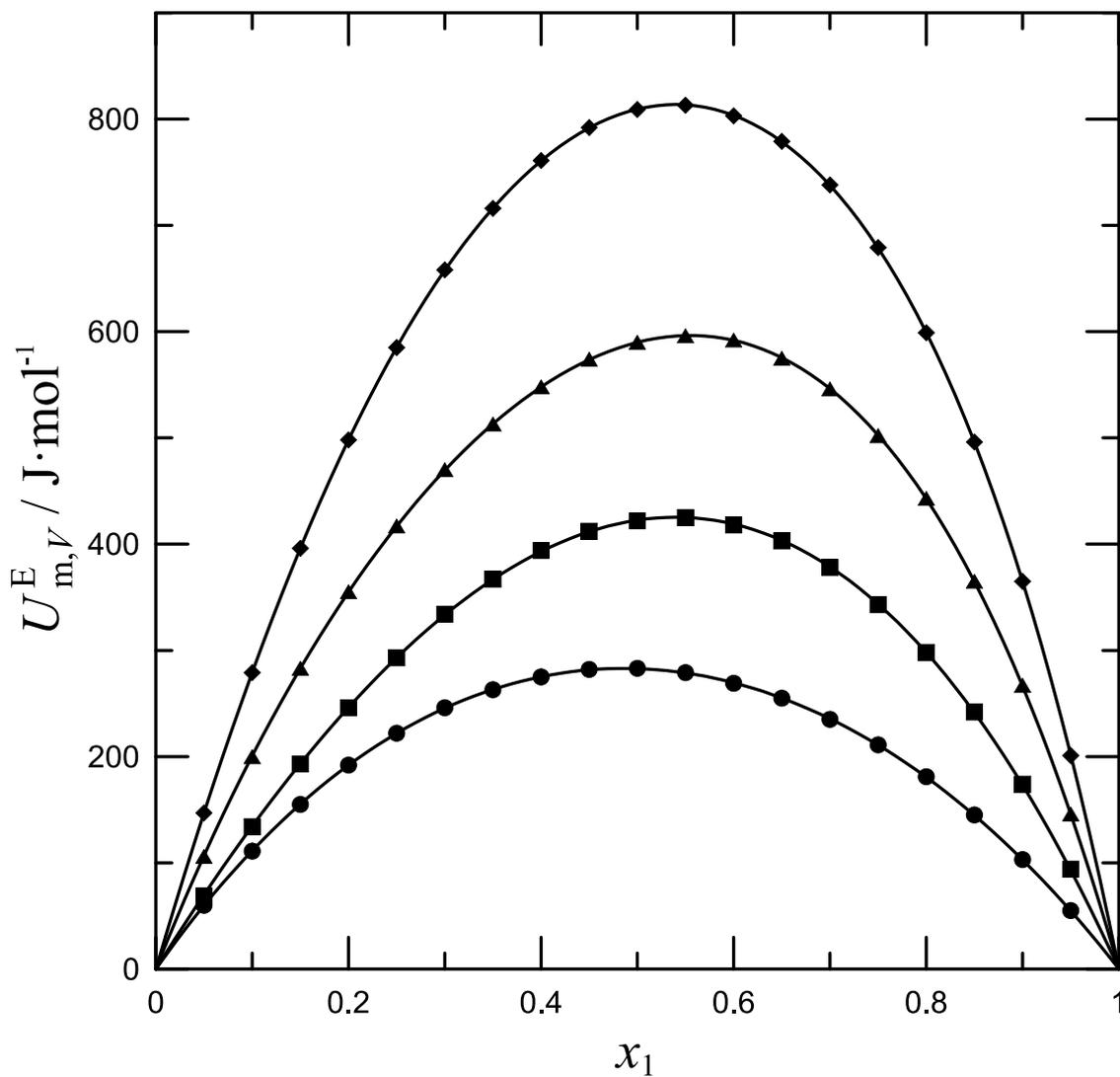
Figure S4

Excess molar energies at constant volume, $U_{m,V}^{E}$, of DMA (1) + amine (2) liquid mixtures at 0.1 MPa and 298.15 K. Full symbols, calculations at $\Delta x_1 = 0.05$ from smoothed experimental values: (●), BA; (■), HxA; (▲), DPA; (♦), DBA. Solid lines, calculations with equation (2) using the coefficients from Table 3.

References

[1]   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-alkanol + isomeric amine ($C_6H_{15}N$) systems: Characterization in terms of the ERAS model, Fluid Phase Equilib., 216 (2004) 123-133. https://doi.org/10.1016/j.fluid.2003.10.008.

[2]   S. Villa, J.A. González, I.G. De La Fuente, N. Riesco, J.C. Cobos, Thermodynamics of Organic Mixtures Containing Amines. II. Excess Molar Volumes at 25°C for Methylbutylamine + Alkane Systems and Eras Characterization of Linear Secondary Amine + Alkane Mixtures, J. Solution Chem., 31 (2002) 1019-1038. https://doi.org/10.1023/A:1021881627444.

[3]   J.A. Gonzalez, U. Domanska, J. Lachwa, Thermodynamics of Binary Mixtures Containing a Very Strongly Polar Compound. 7. Isothermal VLE Measurements for NMP + 2-Propanol or + 2-Butanol Systems. DISQUAC and ERAS Characterization of NMP or *N,N*-Dialkylamide + 2-Alkanol Mixtures. Comparison with Results from Dortmund UNIFAC, Ind. Eng. Chem. Res., 44 (2005) 5795-5804. https://doi.org/10.1021/ie0580046.

[4]   E. Matteoli, L. Lepori, A. Spanedda, Thermodynamic study of heptane + amine mixtures: I. Excess and solvation enthalpies at 298.15 K, Fluid Phase Equilib., 212 (2003) 41-52. https://doi.org/10.1016/S0378-3812(03)00260-7.

[5]   H. Ukibe, R. Tanaka, S. Murakami, R. Fujishiro, Excess enthalpies of *N,N*-dialkyl amides + cyclohexane, + benzene, and + toluene at 298.15 K, J. Chem. Thermodyn., 6 (1974) 201-206. https://doi.org/10.1016/0021-9614(74)90263-8.