

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

Fernando Hevia, Ana Cobos, Juan Antonio González*, Isáías García de la Fuente, Luis Felipe Sanz

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain.

*e-mail: jagl@termo.uva.es; Fax: +34-983-423136; Tel: +34-983-423757

Abstract

Values of density (ρ), speed of sound (c) and refractive index (n_D) for *N,N*-dimethylformamide (DMF) + *N*-propylpropan-1-amine (DPA) or + butan-1-amine (BA) mixtures at (293.15-303.15) K, and for DMF + *N*-butylbutan-1-amine (DBA) or hexan-1-amine (HxA) mixtures at 298.15 K are reported. Density and speed of sound measurements were conducted using a vibrating-tube densimeter and sound analyzer, Anton Paar model DSA5000; refractive index, n_D , values were obtained by means of a RFM970 refractometer from Bellingham+Stanley. The experimental ρ , c and n_D values have been used to determine excess molar volumes, V_m^E , excess adiabatic compressibilities, κ_S^E , excess speeds of sound, c^E , excess thermal expansion coefficients, α_p^E , and excess refractive indices, n_D^E . This set of data show the existence of interactions between unlike molecules and of structural effects in the mixtures under study. V_m^E values of solutions including linear secondary amines are lower than those of mixtures with linear primary amines. In fact, the contribution to V_m^E from the breaking of amine-amine interactions is larger for the latter systems. Calculations on Rao's constant point out that there is no complex formation between the mixture components. Dispersive interactions have been analyzed by means of the molar refraction. It is shown that solutions with DPA or HxA are characterized by similar dispersive interactions and that they mainly differ in dipolar interactions.

Keywords: DMF; amine; volumetric; speed of sound; refractive index; interactions; structural effects.

1. Introduction

N,N-dimethylformamide (DMF) is a very polar liquid (3.7 D [1]) which is able to dissolve many organic substances, as it is an aprotic protophilic compound with excellent donor-acceptor properties. Consequently, this amide has many technical applications. For example, it is used for the production of acrylic fibers, plastics, pesticides or surface coatings [2]. In the oil industry, due to its good properties as selective extractant, it is used for the extraction of aromatic and saturated hydrocarbons and of compounds containing nitrogen [3, 4]. In addition, it results very effective in nanotechnology [5-7]. Interestingly, the detailed knowledge of liquid mixtures containing the amide functional group is essential for the understanding of complex molecules of biological interest [8]. In this context, DMF is useful as a model compound for peptides. The aqueous solution of DMF is a simple biochemical model of biological aqueous solutions [9, 10]. On the other hand, the significant local order characteristic of pure DMF and of other *N,N*-dialkylamides, related to the existence of strong dipole-dipole interactions [11], makes their theoretical study of high interest [12].

Primary and secondary amines are polar molecules (see below) which can also form hydrogen bonds giving self-associated complexes or, with the appropriate group, heterocomplexes [13-15]. Amines are also very common in Biology. In fact, the breaking of amino acids releases amines; neurotransmitters as dopamine or histamine are amines [16, 17], and the polymer DNA is usually bound to proteins which contain several amine groups [18]. In addition, many of the cations and anions of the technically important ionic liquids are related to amine groups [19].

We start this series of articles reporting density, ρ , data, speeds of sound, c , and refractive indices, n_D , at (293.15 K-303.15) K for DMF mixtures with *N*-propylpropan-1-amine (DPA) or butan-1-amine (BA), and at 298.15 K for DMF systems with *N*-butylbutan-1-amine (DBA) or hexan-1-amine (HxA). A literature survey shows that there are no such data for the systems under study. In contrast, volumetric [4, 20], n_D [4], vapor-liquid equilibrium [21] or excess molar enthalpy [22] (H_m^E) measurements are available for the DMF + aniline mixture. Data on H_m^E are also available for the *N*-methylethanamide + HxA system at 363.15 K [23]. The large and negative H_m^E value at equimolar composition for this mixture ($-1005 \text{ J}\cdot\text{mol}^{-1}$) [23], and for the DMF + aniline system at 298.15 K ($-2946 \text{ J}\cdot\text{mol}^{-1}$) [22] reveal the existence of strong interactions between unlike molecules in amide + amine mixtures.

2. Experimental

Materials. All the compounds were used without further purification. Table 1 contains information regarding their source and purity, and Table 2 shows their physical properties, ρ , c , n_D , thermal expansion coefficient, α_p , adiabatic compressibility, κ_S , and isothermal compressibility, κ_T . The values listed in Table 2 are in good agreement with the data available in the literature.

Apparatus and procedure. Binary mixtures were prepared by mass in small vessels of about 10 cm³, using an analytical balance HR-202 (weighing accuracy 0.01 mg), with all weighings corrected for buoyancy effects. The standard uncertainty in the final mole fraction is estimated to be 0.0008. Molar quantities were calculated on the basis of the relative atomic mass table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [24].

Temperatures were measured using Pt-100 resistances, calibrated according to the ITS-90 scale of temperature, against the triple point of water and the melting point of Ga. The repeatability of the equilibrium temperature measurements is 0.01 K. The standard uncertainties for this quantity are 0.02 K and 0.03 K for ρ and n_D measurements, respectively (see below).

Densities and speeds of sound of both pure liquids and of the mixtures were measured by means of a vibrating-tube densimeter and sound analyzer, Anton Paar model DSA 5000, automatically thermostated within 0.01 K. A detailed description of the calibration of the apparatus has been given in an earlier work [25]. The repeatability of the ρ measurements is $5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$, while the relative standard uncertainty of the measurements is estimated to be 0.12%. The determination of the speed of sound is based on the measurement of the propagation time of short acoustic pulses (3 MHz center frequency [26]), which are repeatedly transmitted to the sample. The repeatability and standard uncertainty of the c measurements are, respectively, 0.1 and $0.4 \text{ m} \cdot \text{s}^{-1}$. The experimental technique was checked through the determination of V_m^E and c^E of the (cyclohexane + benzene) mixture at (293.15-303.15) K. Our results and published values [27-29] are in good agreement. The standard uncertainty in V_m^E is $(0.012 |V_{m,\max}^E| + 0.005 \text{ cm}^3 \cdot \text{mol}^{-1})$, where $|V_{m,\max}^E|$ stands for the maximum experimental value of V_m^E with respect to the mole fraction. The standard uncertainty of c^E is estimated to be $0.8 \text{ m} \cdot \text{s}^{-1}$.

Refractive indices were measured using a refractometer model RFM970 from Bellingham+Stanley, with the temperature controlled by means of Peltier modules. The measurement technique is based on the optical detection of the critical angle at the wavelength of the sodium D line (589.6 nm). Calibration of the apparatus was undertaken using 2,2,4-

trimethylpentane and toluene at (293.15-303.15) K, the working temperatures, as indicated by Marsh [30]. The temperature stability is 0.02 K, the repeatability of the n_D measurements is 0.00004 and the relative standard uncertainty is 0.0015.

3. Equations

The densimeter and sound analyzer Anton Paar DSA 5000 allows to obtain in straight form ρ , the molar volume, V_m , the coefficient of thermal expansion, $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$ and the isentropic compressibility, κ_S . As in other previous applications, α_p values were determined assuming that ρ changes linearly with T . In addition, κ_S can be determined from the Newton-Laplace equation assuming that the absorption of the acoustic wave is negligible:

$$\kappa_S = \frac{1}{\rho c^2} \quad (1)$$

The values F^{id} of a given thermodynamic property, F , for an ideal mixture at the same temperature and pressure as the investigated solution, are calculated by means of the well-established equations [31-33]:

$$F^{\text{id}} = x_1 F_1^* + x_2 F_2^* \quad (F = V_m, C_{pm}) \quad (2)$$

$$F^{\text{id}} = \phi_1 F_1^* + \phi_2 F_2^* \quad (F = \alpha_p, \kappa_T) \quad (3)$$

where F_i^* is the value of the property F of pure component i , and C_{pm} is the molar isobaric heat capacity. In equation (3), $\phi_i = x_i V_{mi}^*/V_m^{\text{id}}$ represents the volume fraction of component i , where V_{mi}^* is the molar volume of that component. Ideal values of κ_S and c are calculated from the expressions [31]:

$$\kappa_S^{\text{id}} = \kappa_T^{\text{id}} - \frac{TV_m^{\text{id}}(\alpha_p^{\text{id}})^2}{C_{pm}^{\text{id}}} \quad (4)$$

$$c^{\text{id}} = \left(\frac{1}{\rho^{\text{id}} \kappa_S^{\text{id}}} \right)^{1/2} \quad (5)$$

being $\rho^{\text{id}} = (x_1 M_1 + x_2 M_2)/V_m^{\text{id}}$ (M_i , molar mass of the i component). Finally, the ideal values of n_D are determined using the equation proposed by Reis *et al.* [34]:

$$n_D^{\text{id}} = \left[\phi_1 (n_{D1}^*)^2 + \phi_2 (n_{D2}^*)^2 \right]^{1/2} \quad (6)$$

The excess functions are then determined from the equation:

$$F^E = F - F^{\text{id}} \quad (F = V_m, \kappa_S, c, \alpha_p, n_D) \quad (7)$$

4. Results

Values, at the considered temperatures, ρ and c vs. x_1 , the mole fraction of DMF, are collected in Table 3, while n_D results are shown in Table 4. Derived properties, as excess functions, are given in the supporting information: V_m^E (Table S1); α_p and α_p^E at 298.15 K (Table S2); κ_S^E and c^E at 298.15 K (Table S3) and n_D^E (Table S4). These results are shown graphically in Figures 1-7. We have not found data available in the literature for comparison. The current data were fitted by unweighted least-squares polynomial regressions to the Redlich-Kister equation:

$$F^E = x_1(1-x_1) \sum_{i=0}^{k-1} A_i (2x_1 - 1)^i \quad (8)$$

where $F = V_m, \kappa_S, c, \alpha_p, n_D$. For each mixture, the number of the needed coefficients, k , in equation (8) was determined by applying an F-test of additional term [35] at the 99.5 % confidence level. Table 5 lists the parameters A_i obtained along the adjustments, and the corresponding standard deviations $\sigma(F^E)$, calculated from the expression:

$$\sigma(F^E) = \left[\frac{1}{N-k} \sum (F_{\text{cal}}^E - F_{\text{exp}}^E)^2 \right]^{1/2} \quad (9)$$

where N is the number of direct experimental values.

5. Discussion

Along this section, we are referring to values of the excess functions and of the thermophysical properties at 298.15 K and at $x_1 = 0.5$, except in specific cases duly indicated.

As we have previously mentioned, DMF is a very polar substance. As a consequence, its alkane mixtures show immiscibility regions up to rather high temperatures. For example, the upper critical solution temperatures of systems involving heptane or hexadecane are, respectively, 342.55 K [36] and 385.15 K [37].

Linear primary or secondary amines are weakly self-associated compounds with rather low dipole moments. For the amines considered, the values of this quantity are (in D): 1.3 (BA) [38], 1.3 (HxA) [1], 1.0 (DPA) [38], or 1.1 (DBA) [38]. $H_m^E/\text{J}\cdot\text{mol}^{-1}$ values of mixtures including a given alkane, say heptane, are: 1192 (BA) [39], 962 (HxA) [39], 424 (DPA) [40], and 317 (DBA) [40]. These positive H_m^E values can be explained in terms of the disruption of amine-amine interactions along the mixing process. We note that H_m^E decreases when the self-association of the amine becomes weaker, as the amine group is more sterically hindered in longer amines, and in secondary amines than in primary amines. On the other hand, it is well stated that positive V_m^E values are related to the breaking of interactions between like molecules, while negative values come from the creation of solute-solvent interactions and/or structural effects (geometrical factors including differences in size and shape between the mixture compounds [41-43] or interstitial accommodation [44]). The $V_m^E(\text{heptane})/\text{cm}^3\cdot\text{mol}^{-1}$ values are: 0.7171 (BA) [45], 0.3450 (HxA) [45], 0.2752 (DPA) [46], and 0.0675 (DBA) [46]. Interestingly, the H_m^E and V_m^E values are positive and change in line, which reveals that the most important contribution to V_m^E comes from the disruption of amine-amine interactions upon mixing. However, structural effects may also be present. The low V_m^E value of DBA + heptane system, and the negative value of the DBA + hexane mixture ($-0.185 \text{ cm}^3\cdot\text{mol}^{-1}$) [47] support this statement, as positive H_m^E values and those negative of V_m^E for a given solution suggest that the most relevant contribution to the latter excess function arises from structural effects [43].

In view of the mentioned features, the negative $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ values of DMF + amine mixtures for systems containing DPA (-0.289), BA (-0.263) or HxA (-0.021) and the low V_m^E positive value for the DBA solution ($0.018 \text{ cm}^3\cdot\text{mol}^{-1}$) can be ascribed to the existence of DMF-amine interactions as well as to structural effects. It must be noted that the increase of the amine size along a homologous series leads to increased V_m^E values. This means that the contributions that increase V_m^E (larger number of DMF-DMF interactions broken by the longer amines and the weakening of the amide-amine interactions related to the fact that the amine group is more sterically hindered in such amines) are predominant over those decreasing V_m^E (difference in size between components, lower positive contribution from the disruption of the amine-amine interactions).

The replacement of a primary linear amine (HxA) by a linear secondary amine (DPA) leads to decreased V_m^E values. It is remarkable that the same behavior is encountered for HxA or DPA + heptane mixtures (see above). Therefore, the observed variation in DMF solutions can be ascribed to a lower positive contribution to V_m^E from the breaking of the amine-amine interactions. A similar trend is encountered in 1-alkanol + HxA, or + DPA systems [48, 49]. The more negative V_m^E value of the DMF + aniline mixture ($-0.6931 \text{ cm}^3 \cdot \text{mol}^{-1}$) [20] compared to those of the systems with HxA or DPA suggests that the presence of an aromatic ring leads to stronger interactions between unlike molecules, which is in agreement with the largely negative H_m^E value of this system (see Introduction). Solutions including DPA or BA show negative values of $A_p = \left(\Delta V_m^E / \Delta T\right)_p$ and α_p^E (Table S2). Thus, the use of $V_m^E(x_1 = 0.5)$ values obtained at different temperatures gives $A_p / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -1.8 \cdot 10^{-3}$ (DPA); $-2 \cdot 10^{-4}$ (BA). This means that the structure of the mixture is more difficult to be broken than that of the pure liquids, which may be considered as an evidence of the existence of interactions between unlike molecules. In fact, values of A_p and α_p^E are positive at any composition for solutions where strong interactions between like molecules are present. This is the case, e.g. of the 2-ethoxyethanol + octane [50] or the pentan-1-ol + cyclohexane [51] systems ($A_p / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 7.6 \cdot 10^{-3}$; $2.3 \cdot 10^{-3}$, respectively). However, A_p values are also negative for solutions characterized by relevant structural effects ($-1.3 \cdot 10^{-2} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the hexane + hexadecane mixture [52]). Taking into account the different molar volumes of DPA ($137.93 \text{ cm}^3 \cdot \text{mol}^{-1}$) and BA ($99.88 \text{ cm}^3 \cdot \text{mol}^{-1}$), the more negative A_p value of the DPA system may be related, at least partially, to structural effects. On the other hand, A_p (DMF + aniline) [20] = $-2.9 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, which is a more negative value than that of the DPA solution. This supports our previous statement, that DMF-amine interactions are stronger in the aniline system. The κ_S^E values can be also interpreted in terms of structural and interactional effects [53]. Structural effects and interactions between unlike molecules lead to negative values of this magnitude ($\kappa_S^E / \text{TPa}^{-1} = -142$ (aniline + propanone) [54]). Positive values are encountered in solutions where interactions between like molecules are predominant ($\kappa_S^E / \text{TPa}^{-1} = 15.3$ (2-ethoxyethanol + *n*-octane) [55]). For the systems under study, $\kappa_S^E / \text{TPa}^{-1} = -47.8$ (DPA); -17.7 (DBA); -41.9 (BA); -13.3 (HxA), which is consistent with the trends mentioned above. In addition, the consistency between the signs of the V_m^E , κ_S^E and c^E functions must be remarked, as V_m^E , κ_S^E are negative and c^E is positive (Tables S1 and S3; Figures 1-6). The

DBA mixture slightly separates from this trend and V_m^E is small and positive. However, we underline the strong asymmetry of the κ_S^E curve, with a minimum in the region where V_m^E shows negative values (Figures 1 and 3).

We have also determined the internal pressures, P_{int} [56-59]:

$$P_{\text{int}} = \frac{\alpha_p T}{\kappa_T} - p \quad (10)$$

and the excess internal pressures, $P_{\text{int}}^E = P_{\text{int}} - P_{\text{int}}^{\text{id}}$, with $P_{\text{int}}^{\text{id}} = \alpha_p^{\text{id}} T / \kappa_T^{\text{id}} - p$ [60]. The κ_T values of the mixtures were obtained from

$$\kappa_T = \kappa_S + \frac{TV_m \alpha_p^2}{C_{p,m}} \quad (11)$$

assuming that $C_{pm}^E = 0$, and that $\alpha_p = \alpha_p^{\text{id}}$ (equation 3) when experimental data are not available. For pure compounds, we have $P_{\text{int}}/\text{MPa} = 455.7$ (DMF); 303.9 (DPA); 306.7 (DBA); 339.2 (BA); 345 (HxA), and for the DMF mixtures, $P_{\text{int}}/\text{MPa} = 353.9$ (DPA); 345.9 (DBA); 389.4 (BA); 382.2 (HxA). Because the main contributions to P_{int} are related to dispersion forces and weak dipole-dipole interactions [58], these values suggest that dipolar interactions between unlike molecules are more relevant in systems including linear primary amines. On the other hand, $P_{\text{int}}^E/\text{MPa} = 14.6$ (DPA); 6.5 (DBA); 14.4 (BA); 5.9 (HxA). Large positive P_{int}^E values are encountered in systems characterized by strong interactions between unlike molecules. For example, P_{int}^E (aniline + propanone) = 61.4 MPa [54]. It is rather clear that the higher P_{int}^E value of the DPA system compared to that of the HxA mixture cannot be ascribed to stronger interactions between unlike molecules but to structural effects.

On the other hand, P_{int} values can be calculated using the equation [57]:

$$P_{\text{int}} = \frac{RT}{x_1 v_{f1} + x_2 v_{f2} + V_m^E} - p \quad (12)$$

In this expression, v_{fi} denotes the molar free volume of component i , obtained from $v_{fi} = RT / (p + P_{\text{int},i})$ [57]. Results on $P_{\text{int}}/\text{MPa}$ from equation (12) are: 380.7 (DPA), 365.7 (DBA), 389.4 (BA) and 394.1 (HxA). The differences with the experimental values (equation. 10) are: 7.6%, 5.7%, 4.2% and 3.1%, respectively. This demonstrates that the van der Waals

equation holds to a rather large extent for the investigated solutions, as equation (12) is derived from this equation of state [57].

The Rao's constant [61], R_c , (also termed molar sound velocity, $R_c = V_m c^{1/3}$) is a quantity commonly used to investigate molecular interactions in liquid mixtures from ultrasonic measurements. In fact, if there is no association, or if the degree of association does not depend on concentration, R_c changes linearly on the mole fractions of the components and one can write [62-64]: $R_c = x_1 R_{c1} + x_2 R_{c2}$. Systems where complex formation is present show deviations from this behavior [64]. For the actual mixtures under study, R_c varies linearly with x_1 (Figure 8), and this indicates that there is no complex formation [62, 63].

Finally, the n_D values can be used for the determination of the molar refraction R_m , a quantity closely related to the dispersion forces of the considered system, as n_D at optical wavelengths is related to the mean electronic polarizability [65]. R_m can be calculated using the Lorentz-Lorenz equation [65, 66]:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \quad (13)$$

We have R_m (DMF)/cm³·mol⁻¹ = 26.7 (DPA); 31.4 (DBA); 22.0 (BA); 26.7 (HxA). These results allow to state that: (i) as expected, dispersive interactions become more relevant when the amine size increases along a homologous series; (ii) dispersive interactions are more or less similar in DPA and HxA mixtures, which means that such solutions mainly differ in dipolar interactions.

6. Conclusions

Data on ρ , c and n_D for DMF + DPA, + DBA, + BA or + HxA mixtures at different temperatures have been reported, and the excess functions V_m^E , κ_S^E , c^E , α_p^E and n_D^E have been calculated. The data show the existence of interactions between unlike molecules and of structural effects in the investigated systems. V_m^E values of mixtures including linear secondary amines are lower than those of systems with linear primary amines, as for the latter solutions the contribution to V_m^E from the breaking of amine-amine interactions is larger. Mixtures with DPA or HxA differ essentially in dipolar interactions.

Acknowledgements

F. Hevia acknowledges the grant received from the program ‘Ayudas para la Formación de Profesorado Universitario (convocatoria 2014), de los subprogramas de Formación y de Movilidad incluidos en el Programa Estatal de Promoción del Talento y su Empleabilidad, en el marco del Plan Estatal de Investigación Científica y Técnica y de Innovación 2013-2016, de la Secretaría de Estado de Educación, Formación Profesional y Universidades, Ministerio de Educación, Cultura y Deporte, Gobierno de España’.

Supporting information

This material contains values of V_m^E and n_D^E at the working temperatures and values of α_p , α_p^E , κ_S^E , c^E at 298.15 K.

References

- [1] A.L. McClellan, *Tables of Experimental Dipole Moments*. Vols. 1,2,3, Rahara Enterprises, El Cerrito, US, 1974.
- [2] P. Venkatesu, *Thermophysical contribution of N,N-dimethylformamide in the molecular interactions with other solvents*. *Fluid Phase Equilib.* **298** (2010) 173-191. <https://doi.org/10.1016/j.fluid.2010.07.010>
- [3] B. Blanco, M.T. Sanz, S. Beltrán, J.L. Cabezas, J. Coca, *Vapor-liquid equilibria for the ternary system benzene+n-heptane+N,N-dimethylformamide at 101.33 kPa*. *Fluid Phase Equilib.* **175** (2000) 117-124. [https://doi.org/10.1016/S0378-3812\(00\)00438-6](https://doi.org/10.1016/S0378-3812(00)00438-6)
- [4] 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>
- [5] F. Inam, H. Yan, M.J. Reece, T. Peijs, *Dimethylformamide: an effective dispersant for making ceramic-carbon nanotube composites*. *Nanotech.* **19** (2008) 195710. <https://doi.org/10.1088/0957-4484/19/19/195710>
- [6] T.T. Nguyen, S.U. Nguyen, D.T. Phuong, D.C. Nguyen, A.T. Mai, *Dispersion of denatured carbon nanotubes by using a dimethylformamide solution*. *Adv. Nat. Sci.: Nanosci. Nanotech.* **2** (2011) 035015. <https://doi.org/10.1088/2043-6262/2/3/035015>
- [7] Y. Chen, B. Zhang, Z. Gao, C. Chen, S. Zhao, Y. Qin, *Functionalization of multiwalled carbon nanotubes with uniform polyurea coatings by molecular layer deposition*. *Carbon* **82** (2015) 470-478. <https://doi.org/10.1016/j.carbon.2014.10.090>
- [8] 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>
- [9] G.-Z. Jia, K.-M. Huang, L.-J. Yang, X.-Q. Yang, *Composition-Dependent Dielectric Properties of DMF-Water Mixtures by Molecular Dynamics Simulations*. *Int. J. Mol. Sci.* **10** (2009) 1590-1600. <https://doi.org/10.3390/ijms10041590>
- [10] G.R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press, Oxford, UK, 1999.

- [11] 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>
- [12] 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>
- [13] J.S. Rowlinson, F.L. Swinton, *Liquids and Liquid Mixtures*. 3rd Edition, Butterworths, G. B., 1982.
- [14] 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](https://doi.org/10.1016/S0378-3812(99)00326-X)
- [15] U. Domańska, M. Marciniak, *Volumetric and Solid + Liquid Equilibrium Data for Linear 1-Alkanol + Decylamine Mixtures. Analysis in Terms of ERAS, DISQUAC, and Modified UNIFAC†*. Ind. Eng. Chem. Res. **43** (2004) 7647-7656. <https://doi.org/10.1021/ie0401206>
- [16] 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>
- [17] 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>
- [18] D.L. Nelson, M.M. Cox, *Lehninger Principles of Biochemistry*. 3rd ed., Worth Publishing, New York, 2000.
- [19] 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>
- [20] P.S. Nikam, S.J. Kharat, *Excess Molar Volumes and Deviations in Viscosity of Binary Mixtures of N,N-Dimethylformamide with Aniline and Benzonitrile at (298.15, 303.15, 308.15, and 313.15) K*. J. Chem. Eng. Data **48** (2003) 972-976. <https://doi.org/10.1021/je030101n>
- [21] T.E. Vittal Prasad, A. Adi Sankara Reddy, S. Kailash, D.H.L. Prasad, *Activity coefficients and excess Gibbs energy of binary mixtures of N,N-dimethyl formamide with selected compounds at 95.5 kPa*. Fluid Phase Equilib. **273** (2008) 52-58. <https://doi.org/10.1016/j.fluid.2008.07.018>
- [22] 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](https://doi.org/10.1016/0378-3812(95)02816-1)
- [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] M. Wieser, N. Holden, T.B. Coplen, J.K. Böhlke, M. Berglund, W.A. Brand, P. De Bièvre, G. M., R.D. Loss, J. Meija, T. Hirata, T. Prohaska, R. Schoenberg, G. O'Connor, T. Walczyk, S. Yoneda, Z. X-K, *Atomic weights of the elements 2011 (IUPAC Technical Report)*. Pure Appl. Chem. **85** (2013) 1047-1078. <https://doi.org/10.1351/PAC-REP-13-03-02>
- [25] J.A. González, I. Alonso, I. Mozo, I. García de la Fuente, J.C. Cobos, *Thermodynamics of (ketone + amine) mixtures. Part VI. Volumetric and speed of sound data at (293.15, 298.15, and 303.15) K for (2-heptanone + dipropylamine, +dibutylamine, or +triethylamine) systems*. J. Chem. Thermodyn. **43** (2011) 1506-1514. <https://doi.org/10.1016/j.jct.2011.05.003>

- [26] D. Schneditz, T. Kenner, H. Heimel, H. Stabinger, *A sound-speed sensor for the measurement of total protein concentration in disposable, blood-perfused tubes*. J. Acoust. Soc. Am. **86** (1989) 2073-2080. <https://doi.org/10.1121/1.398466>
- [27] E. Junquera, G. Tardajos, E. Aicart, *Speeds of sound and isentropic compressibilities of (cyclohexane + benzene and (1-chlorobutane + n-hexane or n-heptane or n-octane or n-decane) at 298.15 K*. J. Chem. Thermodyn. **20** (1988) 1461-1467. [https://doi.org/10.1016/0021-9614\(88\)90041-9](https://doi.org/10.1016/0021-9614(88)90041-9)
- [28] K. Tamura, K. Ohomuro, S. Murakami, *Speeds of sound, isentropic and isothermal compressibilities, and isochoric heat capacities of $\{x\text{-C}_6\text{H}_{12}+(1-x)\text{C}_6\text{H}_6\}$, $x\{\text{C}_2\text{Cl}_4+(1-x)\text{C}_6\text{H}_6\}$, and $x\{\text{C}_7\text{H}_{16}+(1-x)\text{C}_6\text{H}_6\}$ at 298.15 K*. J. Chem. Thermodyn. **15** (1983) 859-868. [https://doi.org/10.1016/0021-9614\(83\)90092-7](https://doi.org/10.1016/0021-9614(83)90092-7)
- [29] K. Tamura, S. Murakami, *Speeds of sound, isentropic and isothermal compressibilities, and isochoric heat capacities of $\{x\text{-C}_6\text{H}_{12} + (1 - x)\text{C}_6\text{H}_6\}$ from 293.15 to 303.15 K*. J. Chem. Thermodyn. **16** (1984) 33-38. [https://doi.org/10.1016/0021-9614\(84\)90072-7](https://doi.org/10.1016/0021-9614(84)90072-7)
- [30] K.N. Marsh, *Recommended reference materials for the realization of physicochemical properties*. Blackwell Scientific Publications, Oxford, UK, 1987.
- [31] G.C. Benson, C.J. Halpin, A.J. Treszczanowicz, *Excess volumes and isentropic compressibilities for (2-ethoxyethanol + n-heptane) at 298.15 K*. J. Chem. Thermodyn. **13** (1981) 1175-1183. [https://doi.org/10.1016/0021-9614\(81\)90017-3](https://doi.org/10.1016/0021-9614(81)90017-3)
- [32] G. Douhéret, M.I. Davis, J.C.R. Reis, M.J. Blandamer, *Isentropic Compressibilities—Experimental Origin and the Quest for their Rigorous Estimation in Thermodynamically Ideal Liquid Mixtures*. ChemPhysChem **2** (2001) 148-161. [https://doi.org/10.1002/1439-7641\(20010316\)2:3<148::AID-CPHC148>3.0.CO;2-J](https://doi.org/10.1002/1439-7641(20010316)2:3<148::AID-CPHC148>3.0.CO;2-J)
- [33] G. Douhéret, C. Moreau, A. Viillard, *Excess thermodynamic quantities in binary systems of non electrolytes.: Different ways of calculating excess compressibilities*. Fluid Phase Equilib. **22** (1985) 277-287. [https://doi.org/10.1016/0378-3812\(85\)87027-8](https://doi.org/10.1016/0378-3812(85)87027-8)
- [34] J.C.R. Reis, I.M.S. Lampreia, Â.F.S. Santos, M.L.C.J. Moita, G. Douhéret, *Refractive Index of Liquid Mixtures: Theory and Experiment*. ChemPhysChem **11** (2010) 3722-3733. <https://doi.org/10.1002/cphc.201000566>
- [35] P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill, New York, 1969.
- [36] 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>
- [37] 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.
- [38] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*. McGraw-Hill, New York, US, 1987.
- [39] 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](https://doi.org/10.1016/S0378-3812(03)00260-7)
- [40] 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>
- [41] D. Patterson, *Free Volume and Polymer Solubility. A Qualitative View*. Macromolecules **2** (1969) 672-677. <https://doi.org/10.1021/ma60012a021>
- [42] S.N. Bhattacharyya, M. Costas, D. Patterson, H.V. Tra, *Thermodynamics of mixtures containing alkanes*. Fluid Phase Equilib. **20** (1985) 27-45. [https://doi.org/10.1016/0378-3812\(85\)90019-6](https://doi.org/10.1016/0378-3812(85)90019-6)
- [43] 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>

- [44] A.J. Treszczanowicz, G.C. Benson, *Excess volumes for n-alkanols + n-alkanes II. Binary mixtures of n-pentanol, n-hexanol, n-octanol, and n-decanol + n-heptane*. J. Chem. Thermodyn. **10** (1978) 967-974. [https://doi.org/10.1016/0021-9614\(78\)90058-7](https://doi.org/10.1016/0021-9614(78)90058-7)
- [45] L. Lepori, P. Gianni, A. Spanedda, E. Matteoli, *Thermodynamic study of (heptane + amine) mixtures. II. Excess and partial molar volumes at 298.15 K*. J. Chem. Thermodyn. **43** (2011) 805-813. <https://doi.org/10.1016/j.jct.2010.12.025>
- [46] 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>
- [47] 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](https://doi.org/10.1016/S0021-9614(72)80021-1)
- [48] S. Villa, N. Riesco, I. García de la Fuente, J.A. González, J.C. Cobos, *Thermodynamics of mixtures with strongly negative deviations from Raoult's law: Part 5. Excess molar volumes at 298.15 K for 1-alkanols+dipropylamine systems: characterization in terms of the ERAS model*. Fluid Phase Equilib. **190** (2001) 113-125. [https://doi.org/10.1016/S0378-3812\(01\)00595-7](https://doi.org/10.1016/S0378-3812(01)00595-7)
- [49] 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>
- [50] H. Ohji, H. Ogawa, S. Murakami, K. Tamura, J.-P.E. Grolier, *Excess volumes and excess thermal expansivities for binary mixtures of 2-ethoxyethanol with non-polar solvents at temperatures between 283.15 K and 328.15 K*. Fluid Phase Equilib. **156** (1999) 101-114. [https://doi.org/10.1016/S0378-3812\(99\)00035-7](https://doi.org/10.1016/S0378-3812(99)00035-7)
- [51] O. Hiroyuki, *Excess volumes of (1-pentanol + cyclohexane or benzene) at temperatures between 283.15 K and 328.15 K*. J. Chem. Thermodyn. **34** (2002) 849-859. <https://doi.org/10.1006/jcht.2001.0940>
- [52] M.F. Bolotnikov, Y.A. Neruchev, Y.F. Melikhov, V.N. Vervevko, M.V. Vervevko, *Temperature Dependence of the Speed of Sound, Densities, and Isentropic Compressibilities of Hexane + Hexadecane in the Range of (293.15 to 373.15) K*. J. Chem. Eng. Data **50** (2005) 1095-1098. <https://doi.org/10.1021/je050060q>
- [53] L. Venkatramana, R.L. Gardas, K. Sivakumar, K. Dayananda Reddy, *Thermodynamics of binary mixtures: The effect of substituents in aromatics on their excess properties with benzylalcohol*. Fluid Phase Equilib. **367** (2014) 7-21. <https://doi.org/10.1016/j.fluid.2014.01.019>
- [54] I. Alonso, V. Alonso, I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos, *Thermodynamics of Ketone + Amine Mixtures. I. Volumetric and Speed of Sound Data at (293.15, 298.15, and 303.15) K for 2-Propanone + Aniline, + N-Methylaniline, or + Pyridine Systems*. J. Chem. Eng. Data **55** (2010) 2505-2511. <https://doi.org/10.1021/je900874z>
- [55] K. Tamura, A. Osaki, S. Murakami, B. Laurent, J.-P.E. Grolier, *Thermodynamic properties of binary mixtures {x(2-alkoxyethanol)+(1-x)n-octane}: densities at 298.15 and 303.15 K and speeds of sound at 298.15 K*. Fluid Phase Equilib. **173** (2000) 285-296. [https://doi.org/10.1016/S0378-3812\(00\)00434-9](https://doi.org/10.1016/S0378-3812(00)00434-9)
- [56] E.B. Bagley, T.P. Nelson, J.W. Barlow, S.A. Chen, *Internal Pressure Measurements and Liquid-State Energies*. Ind. Eng. Chem. Fundamen. **9** (1970) 93-97. <https://doi.org/10.1021/i160033a015>
- [57] E.B. Bagley, T.P. Nelson, J.M. Scigliano, *Internal pressures of liquids and their relation to the enthalpies and entropies of mixing in nonelectrolyte solutions*. J. Phys. Chem. **77** (1973) 2794-2798. <https://doi.org/10.1021/j100641a016>

- [58] M.R.J. Dack, *Solvent structure. The use of internal pressure and cohesive energy density to examine contributions to solvent-solvent interactions*. Aust. J. Chem. **28** (1975) 1643-1648. <https://doi.org/10.1071/CH9751643>
- [59] E. Zorebski, *Internal pressure studies of alcohols on the basis of ultrasonic measurements*. Mol. Quantum Acoust. **26** (2005) 317-326.
- [60] R. Dey, A.K. Singh, J.D. Pandey, *A new theoretical approach for estimating excess internal pressure*. J. Mol. Liq. **124** (2006) 121-123. <https://doi.org/10.1016/j.molliq.2005.09.005>
- [61] O. Nomoto, *Molecular Sound Velocity and Molecular Compressibility of Liquid Mixtures*. J. Chem. Phys. **21** (1953) 950-951. <https://doi.org/10.1063/1.1699084>
- [62] O. Nomoto, *Deviation from Linearity of the Concentration Dependence of the Molecular Sound Velocity in Liquid Mixtures*. J. Phys. Soc. Jpn. **13** (1958) 1524-1528. <https://doi.org/10.1143/JPSJ.13.1524>
- [63] R. Abraham, M. Abdulkhadar, C.V. Asokan, *Ultrasonic investigation of molecular interaction in binary mixtures of nitriles with methanol/toluene*. J. Chem. Thermodyn. **32** (2000) 1-16. <https://doi.org/10.1006/jcht.1999.0608>
- [64] S.L. Oswal, P. Oswal, J.P. Dave, *Speed of sound and isentropic compressibility of binary mixtures containing alkyl acetate or ethyl alkanoate, or ethyl bromo-alkanoate with hexane*. J. Mol. Liq. **94** (2001) 203-219. [https://doi.org/10.1016/S0167-7322\(01\)00269-0](https://doi.org/10.1016/S0167-7322(01)00269-0)
- [65] A. Chelkowski, *Dielectric Physics*. Elsevier, Amsterdam, 1980.
- [66] P. Brocos, A. Piñeiro, R. Bravo, A. Amigo, *Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations*. Phys. Chem. Chem. Phys. **5** (2003) 550-557. <https://doi.org/10.1039/B208765K>
- [67] 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>
- [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] M. Domínguez, H. Artigas, P. Cea, M.C. López, J.S. Urieta, *Speed of sound and isentropic compressibility of the ternary mixture (2-Butanol + n-Hexane + 1-Butylamine) and the constituent binary mixtures at 298.15 K and 313.15 K*. J. Mol. Liq. **88** (2000) 243-258. [https://doi.org/10.1016/S0167-7322\(00\)00143-4](https://doi.org/10.1016/S0167-7322(00)00143-4)
- [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>
- [71] S.L. Oswal, P. Oswal, R.L. Gardas, S.G. Patel, R.G. Shinde, *Acoustic, volumetric, compressibility and refractivity properties and reduction parameters for the ERAS and Flory models of some homologous series of amines from 298.15 to 328.15 K*. Fluid Phase Equilib. **216** (2004) 33-45. <https://doi.org/10.1016/j.fluid.2003.09.007>
- [72] Neeti, S.K. Jangra, J.S. Yadav, Dimple, V.K. Sharma, *Thermodynamic investigations of ternary o-toluidine + tetrahydropyran + N,N-dimethylformamide mixture and its binaries at 298.15, 303.15 and 308.15 K*. J. Mol. Liq. **163** (2011) 36-45. <https://doi.org/10.1016/j.molliq.2011.07.008>
- [73] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic solvents: physical properties and methods of purification*. Wiley, New York, 1986.
- [74] S. Miyanaga, K. Tamura, S. Murakami, *Excess molar volumes, isentropic and isothermal compressibilities, and isochoric heat capacities of (acetonitrile + benzene), (benzene + dimethylformamide), and (acetonitrile + dimethylformamide) at the temperature 298.15 K*. J. Chem. Thermodyn. **24** (1992) 1077-1086. [https://doi.org/10.1016/S0021-9614\(05\)80018-7](https://doi.org/10.1016/S0021-9614(05)80018-7)

- [75] M.S. AlTuwaim, K.H.A.E. Alkhaldi, A.S. Al-Jimaz, A.A. Mohammad, *Comparative study of physico-chemical properties of binary mixtures of N,N-dimethylformamide with 1-alkanols at different temperatures*. J. Chem. Thermodyn. **48** (2012) 39-47. <https://doi.org/10.1016/j.jct.2011.12.002>
- [76] J.P.E. Grolier, G. Roux-Desgranges, M. Berkane, E. Jiménez, E. Wilhelm, *Heat capacities and densities of mixtures of very polar substances 2. Mixtures containing N, N-dimethylformamide*. J. Chem. Thermodyn. **25** (1993) 41-50. <https://doi.org/10.1006/jcht.1993.1005>
- [77] J. Konicek, I. Wadso, *Thermochemical Properties of Some Carboxylic Acids, Amines and N-Substituted Amides in Aqueous Solution*. Acta Chem. Scand. **25** (1971) 1541-1551. <https://doi.org/10.3891/acta.chem.scand.25-1541>
- [78] H. Iloukhani, Z. Rostami, *Measurement of Some Thermodynamic and Acoustic Properties of Binary Solutions of N,N-Dimethylformamide with 1-Alkanols at 30°C and Comparison with Theories*. J. Solution Chem. **32** (2003) 451-462. <https://doi.org/10.1023/A:1024524928767>
- [79] C.M. Kinart, W.J. Kinart, D. Chęcińska-Majak, *Relative Permittivity, Viscosity, and Speed of Sound for 2-Methoxyethanol + Butylamine Mixtures*. J. Chem. Eng. Data **48** (2003) 1037-1039. <https://doi.org/10.1021/je030127e>
- [80] T.M. Aminabhavi, V.B. Patil, *Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Ethenylbenzene with N,N-Dimethylacetamide, Tetrahydrofuran, N,N-Dimethylformamide, 1,4-Dioxane, Dimethyl Sulfoxide, Chloroform, Bromoform, and 1-Chloronaphthalene in the Temperature Interval (298.15–308.15) K*. J. Chem. Eng. Data **43** (1998) 497-503. <https://doi.org/10.1021/je980031y>

Table 1
Sample description.

Chemical name	CAS number	Source	Purification method	Mole fraction purity	Analysis method
<i>N,N</i> -dimethylformamide (DMF)	68-12-2	Fluka	none	≥ 0.995	GC ^a
<i>N</i> -propylpropan-1-amine (DPA)	142-84-7	Fluka	none	≥ 0.99	GC ^a
<i>N</i> -butylbutan-1-amine (DBA)	111-92-2	Aldrich	none	≥ 0.995	GC ^a
butan-1-amine (BA)	109-73-9	Sigma-Aldrich	none	≥ 0.99	GC ^a
hexan-1-amine (HxA)	111-26-2	Aldrich	none	≥ 0.995	GC ^a

^aGas-liquid chromatography.

Table 2

Physical properties of pure compounds at temperature T and pressure $p = 0.1$ MPa. ^a

Property	T/K	DMF	DPA	DBA	BA	HxA	
$\rho^*/\text{g}\cdot\text{cm}^{-3}$	293.15	0.948881	0.738194	0.759695	0.737048	0.764423	
		0.948922 ^b	0.738188 ^c	0.759571 ^c			
	298.15	0.944081	0.733618	0.755525	0.732231	0.760073	
		0.944163 ^b	0.733683 ^c	0.755457 ^c	0.7327 ^d	0.76013 ^e	
	303.15	0.939361	0.729098	0.751458	0.727452	0.755848	
		0.939390 ^b	0.729087 ^c	0.751329 ^c			
$c^*/\text{m}\cdot\text{s}^{-1}$	293.15	1476.8	1209.4	1261.1	1268.3	1324.0	
		1477.8 ^b	1209 ^c	1261.2 ^c			
	298.15	1457.2	1187.7	1241.5	1246.0	1303.6	
		1458.5 ^b	1198 ^f	1248 ^f	1247.8 ^d	1304.7 ^e	
	303.15	1458.6 ^g					
		1438.2	1167.2	1222.5	1224.6	1283.6	
$\alpha_p^*/10^{-3}\text{K}^{-1}$	298.15	1439 ^b	1174 ^f	1227 ^f	1227 ^f	1285 ^f	
		1440.3 ^g					
	298.15	1.008	1.240	1.090	1.311	1.128	
		1.010 ^g	1.29 ^h	1.12 ^h	1.314 ^f	1.13 ^e	
	$\kappa_S^*/\text{TPa}^{-1}$	293.15	483.2	926.2	827.7	843.4	746.3
			485 ^b	926.5 ^f			
298.15		498.8	966.3	858.7	879.7	774.2	
		498.7 ⁱ	947 ^f	849 ^f	876.6 ^d	773 ^e	
303.15		497.9 ^b					
		514.7	1006.7	890.4	916.7	802.9	
$\kappa_T^*/\text{TPa}^{-1}$	298.15	514 ^b	992 ^f	883 ^f	912 ^f	800 ^f	
		512.9 ^g					
	298.15	659.4	1216.4	1059.4	1151.9	974.6	
		650 ^h	1183 ^f	1039 ^f	1145 ^f	975 ^e	
	303.15	662 ^j					
		146.05 ^k	252.84 ^h	302 ^f	188 ^l	252 ^l	
$C_{pm}^*/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	293.15	1.43055	1.40432	1.41724	1.40060		
		1.43047 ^h	1.4043 ^h	1.4177 ^h	1.40106 ⁿ		
	298.15	1.4281 ^m					
		1.42828	1.40139	1.41488	1.39786	1.41577	
	303.15	1.42817 ^h	1.4053 ^f	1.4152 ^h	1.3987 ^h	1.4160 ^f	
		1.4280 ^j					
n_D^*	298.15	1.42603	1.39883	1.41253	1.39500		
		1.4267 ^o	1.4022 ^f	1.4143 ^f	1.3978 ^f		
	303.15	1.4271 ^j			1.39744 ⁿ		

^a ρ^* , density; c^* , speed of sound; α_p^* , isobaric thermal expansion coefficient; κ_s^* , adiabatic compressibility; κ_T^* , isothermal compressibility; C_{pm}^* , isobaric molar heat capacity; and n_D^* , refractive index. Standard uncertainties, u , are: $u(T)=0.02$ K (for n_D^* values, $u(T)=0.03$ K); $u(p)=1$ kPa; $u(c^*)=0.4$ m·s⁻¹. Relative standard uncertainties, u_r , are: $u_r(\rho^*)=0.0012$; $u_r(\alpha_p^*)=0.028$; $u_r(\kappa_s^*)=0.002$; $u_r(\kappa_T^*)=0.015$; $u_r(n_D^*)=0.0015$. ^bRef. [67]; ^cRef. [68]; ^dRef. [69]; ^eRef. [70]; ^fRef. [71]; ^gRef. [72]; ^hRef. [73]; ⁱRef. [74]; ^jRef. [75]; ^kRef. [76]; ^lRef. [77]; ^mRef. [78]; ⁿRef. [79]; ^oRef. [80].

Table 3

Densities, ρ , and speeds of sound, c , for *N,N*-dimethylformamide (1) + amine (2) mixtures at temperature T and pressure $p = 0.1$ MPa. ^a

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$c/\text{m}\cdot\text{s}^{-1}$	x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$c/\text{m}\cdot\text{s}^{-1}$
DMF (1) + DPA (2) ; $T/\text{K} = 293.15$ K					
0.0600	0.745894	1218.2	0.4974	0.815656	1299.2
0.1071	0.752141	1225.0	0.5487	0.825989	1312.0
0.1560	0.758933	1232.9	0.6562	0.849651	1342.1
0.1975	0.764870	1239.3	0.7514	0.873097	1373.4
0.2490	0.772540	1248.1	0.8216	0.892212	1399.8
0.3099	0.782194	1259.4	0.8501	0.900523	1411.2
0.3463	0.788151	1266.2	0.9025	0.916508	1433.3
0.3985	0.797199	1276.9	0.9486	0.931283	1453.4
0.4480	0.806192	1287.6			
DMF (1) + DPA (2) ; $T/\text{K} = 298.15$ K					
0.0626	0.741577	1196.9	0.5386	0.819199	1288.9
0.1083	0.747697	1204.0	0.6082	0.833997	1307.9
0.1544	0.754025	1211.2	0.6527	0.844084	1321.1
0.2541	0.768732	1228.1	0.7477	0.867448	1352.4
0.3148	0.778293	1239.3	0.8063	0.883226	1374.0
0.3609	0.786012	1248.3	0.9020	0.911457	1413.1
0.4077	0.794223	1258.2	0.9482	0.926367	1433.5
0.4966	0.810800	1278.5			
DMF (1) + DPA (2) ; $T/\text{K} = 303.15$ K					
0.0453	0.734885	1174.0	0.5415	0.815193	1270.3
0.1034	0.742550	1183.0	0.6016	0.827909	1286.6
0.1963	0.755529	1198.0	0.6517	0.839209	1301.4
0.2582	0.764775	1208.8	0.7502	0.863388	1334.0
0.3559	0.780614	1227.6	0.8498	0.890941	1372.0
0.4099	0.790030	1239.0	0.9000	0.906165	1393.2
0.4565	0.798539	1249.4	0.9498	0.922203	1415.2
DMF (1) + DBA (2) ; $T/\text{K} = 298.15$ K					
0.0642	0.761171	1246.4	0.5574	0.823977	1307.9
0.1134	0.765782	1250.5	0.5996	0.831688	1316.3
0.1647	0.770882	1255.0	0.6514	0.842013	1328.1
0.2121	0.775872	1259.5	0.6869	0.849571	1336.8
0.2734	0.782835	1266.1	0.7361	0.860924	1350.4
0.3213	0.788624	1271.6	0.7904	0.874714	1367.5
0.4114	0.800702	1283.5	0.8418	0.889103	1385.9

0.4526	0.806766	1289.7	0.8921	0.904666	1406.1
0.5072	0.815344	1298.6	0.9471	0.923650	1431.0
DMF (1) + BA (2) ; $T/K = 293.15$ K					
0.0599	0.747390	1277.7	0.5483	0.842154	1368.9
0.1056	0.755445	1285.0	0.6569	0.866102	1393.7
0.1591	0.765035	1293.8	0.6999	0.875844	1404.0
0.2505	0.782005	1309.6	0.7537	0.888314	1416.7
0.3017	0.791811	1318.9	0.8036	0.900101	1429.0
0.3583	0.802880	1329.6	0.8579	0.913315	1442.3
0.3992	0.811114	1337.8	0.9048	0.924751	1453.7
0.5059	0.833130	1359.6	0.9546	0.937212	1465.6
DMF (1) + BA (2) ; $T/K = 298.15$ K					
0.0575	0.742224	1255.4	0.4381	0.814268	1324.9
0.1092	0.751333	1263.9	0.5028	0.827736	1338.6
0.1519	0.759015	1271.1	0.6005	0.848795	1360.6
0.2043	0.768674	1280.1	0.6934	0.869781	1382.5
0.2448	0.776215	1287.4	0.7572	0.884516	1398.0
0.3090	0.788510	1299.3	0.8056	0.895958	1410.0
0.3558	0.797705	1308.4	0.9076	0.920837	1435.1
0.3986	0.806285	1317.0	0.9553	0.932723	1446.6
DMF (1) + BA (2) ; $T/K = 303.15$ K					
0.0505	0.736213	1233.0	0.5281	0.828281	1324.0
0.1477	0.753539	1249.4	0.6056	0.845104	1341.6
0.2019	0.763466	1259.0	0.6960	0.865473	1363.2
0.2410	0.770708	1266.0	0.7558	0.879286	1377.7
0.3024	0.782423	1277.5	0.8006	0.889962	1389.0
0.3558	0.792882	1287.8	0.8544	0.902880	1402.3
0.4358	0.808960	1304.1	0.8998	0.914033	1413.7
0.5114	0.824673	1320.3	0.9466	0.925732	1425.2
DMF (1) + HxA (2) ; $T/K = 298.15$ K					
0.0506	0.765582	1307.1	0.6022	0.846551	1368.3
0.0992	0.771096	1310.8	0.7056	0.867688	1387.1
0.1725	0.779897	1316.7	0.7996	0.889217	1406.8
0.2548	0.790546	1324.2	0.8492	0.901602	1418.4
0.3476	0.803611	1333.7	0.8982	0.914549	1430.4
0.4461	0.818861	1345.5	0.9530	0.929990	1444.7
0.5500	0.836751	1360.1			

^a The standard uncertainties, u , are: $u(x_1) = 0.0008$; $u(p) = 1 \text{ kPa}$; $u(T) = 0.02 \text{ K}$. The combined expanded standard uncertainties (0.95 level of confidence) are: $U_{\text{rc}}(\rho) = 0.0024$ (relative value); $U_c(c) = 0.8 \text{ m}\cdot\text{s}^{-1}$.

Table 4

Refractive indices, n_D , of *N,N*-dimethylformamide (1) + amine (2) mixtures at temperature T and pressure $p = 0.1$ MPa. ^a

x_1	n_D	x_1	n_D
DMF (1) + DPA (2) ; $T/K = 293.15$ K			
0.0600	1.40543	0.5487	1.41645
0.1556	1.40725	0.6018	1.41789
0.2614	1.40952	0.7033	1.42079
0.3463	1.41140	0.8216	1.42444
0.3985	1.41266	0.8844	1.42653
0.4554	1.41402	0.9486	1.42882
DMF (1) + DPA (2) ; $T/K = 298.15$ K			
0.0626	1.40259	0.4966	1.41247
0.1083	1.40358	0.6527	1.41673
0.1544	1.40443	0.7477	1.41960
0.2541	1.40662	0.8063	1.42147
0.3148	1.40796	0.9020	1.42478
0.3609	1.40908	0.9482	1.42645
0.4077	1.41017		
DMF (1) + DPA (2) ; $T/K = 303.15$ K			
0.0453	1.39971	0.6016	1.41295
0.1034	1.40091	0.7502	1.41745
0.1963	1.40293	0.8498	1.42070
0.2582	1.40419	0.9000	1.42246
0.3559	1.40647	0.9498	1.42417
0.4099	1.40779		
DMF (1) + DBA (2) ; $T/K = 298.15$ K			
0.1038	1.41553	0.7709	1.42323
0.2076	1.41628	0.8398	1.42459
0.3608	1.41761	0.8989	1.42587
0.4897	1.41900	0.9497	1.42706
0.5933	1.42034	0.9738	1.42765
0.6880	1.42178		
DMF (1) + BA (2) ; $T/K = 293.15$ K			
0.0599	1.40222	0.5059	1.41521
0.1056	1.40348	0.6043	1.41829
0.1591	1.40498	0.6569	1.41992
0.2010	1.40619	0.6999	1.42126
0.2505	1.40760	0.7537	1.42292

0.3017	1.40911	0.8036	1.42448
0.3583	1.41079	0.8579	1.42618
0.3992	1.41200	0.9048	1.42763
0.4401	1.41322	0.9546	1.42915

DMF (1) + BA (2) ; $T/K = 298.15$ K

0.0575	1.39946	0.6005	1.41578
0.1092	1.40093	0.6608	1.41769
0.1519	1.40215	0.6934	1.41871
0.2043	1.40367	0.7572	1.42076
0.2448	1.40485	0.8056	1.42230
0.3090	1.40680	0.8546	1.42383
0.3558	1.40820	0.9076	1.42553
0.5028	1.41274	0.9553	1.42705

DMF (1) + BA (2) ; $T/K = 303.15$ K

0.0505	1.39644	0.5281	1.41094
0.1477	1.39927	0.6056	1.41337
0.2019	1.40087	0.6574	1.41502
0.2410	1.40209	0.6960	1.41625
0.3024	1.40392	0.7558	1.41820
0.3558	1.40552	0.8006	1.41964
0.3992	1.40686	0.8544	1.42138
0.4358	1.40802	0.8998	1.42282
0.5114	1.41041	0.9466	1.42431

DMF (1) + HxA (2) ; $T/K = 298.15$ K

0.0506	1.41613	0.5500	1.42107
0.1725	1.41707	0.6558	1.42257
0.2548	1.41779	0.7573	1.42411
0.3476	1.41870	0.8492	1.42564
0.4461	1.41980	0.9530	1.42747

^a The standard uncertainties, u , are: $u(x_i) = 0.0008$; $u(T) = 0.03$ K; $u(p) = 1$ kPa. The relative combined expanded standard uncertainty (0.95 level of confidence), U_{rc} , is: $U_{rc}(n_D) = 0.0030$.

Table 5

Coefficients A_i and standard deviations, $\sigma(F^E)$ (eq. 9), for the representation of the F^E property at temperature T and pressure $p = 0.1$ MPa for N,N -dimethylformamide (1) + amine (2) systems by eq. 8.

System	T/K	Property ^a F^E	A_0	A_1	A_2	A_3	A_4	$\sigma(F^E)$
DMF + DPA	293.15	V_m^E	-1.121	-0.23	-0.37			0.005
		n_D^E	0.00540	0.0033	0.0013			0.00004
	298.15	V_m^E	-1.157	-0.25	-0.30			0.004
		κ_S^E	-191.0	-84.2	-52.2	-18		0.11
		c^E	148.6	120.2	90	75	48	0.10
		α_p^E	-52.5					0.5
303.15	n_D^E	0.0056	0.0028	0.0015			0.00004	
	V_m^E	-1.192	-0.21	-0.37			0.005	
DMF + DBA	298.15	n_D^E	0.00583	0.0032	0.0020			0.00003
		V_m^E	0.071	-0.304	-0.30			0.0015
	298.15	κ_S^E	-70.7	-59.6	-38	-35	-27	0.08
		c^E	62.2	65	53	74	61	0.15
		n_D^E	0.00020	0.00109	0.0010	0.0010	0.0008	0.000004
		V_m^E	-0.978	-0.29	-0.12			0.003
DMF + BA	293.15	n_D^E	0.00527	0.00229				0.00002
		V_m^E	-1.052	-0.29	-0.24			0.003
	298.15	κ_S^E	-167.6	-36.0	-17.0			0.09
		c^E	151.2	92	48			0.3
		α_p^E	-86	56	-195	-44		0.6
		n_D^E	0.00532	0.00189				0.00001
303.15	V_m^E	-1.060	-0.23	-0.28			0.003	
	n_D^E	0.00578	0.00197				0.00002	
DMF + HxA	298.15	V_m^E	-0.084	-0.316	-0.17	-0.07		0.0010
		κ_S^E	-53.1	-38.0	-24.4	-11		0.05
		c^E	52.8	49	44	27		0.12
		n_D^E	0.00020	0.00173	0.0013			0.000014

^a $F^E = V_m^E$, units: $\text{cm}^3 \cdot \text{mol}^{-1}$; $F^E = c^E$, units: $\text{m} \cdot \text{s}^{-1}$; $F^E = \kappa_S^E$ units: TPa^{-1} ; $F^E = \alpha_p^E$, units: $10^{-6} \cdot \text{K}^{-1}$.

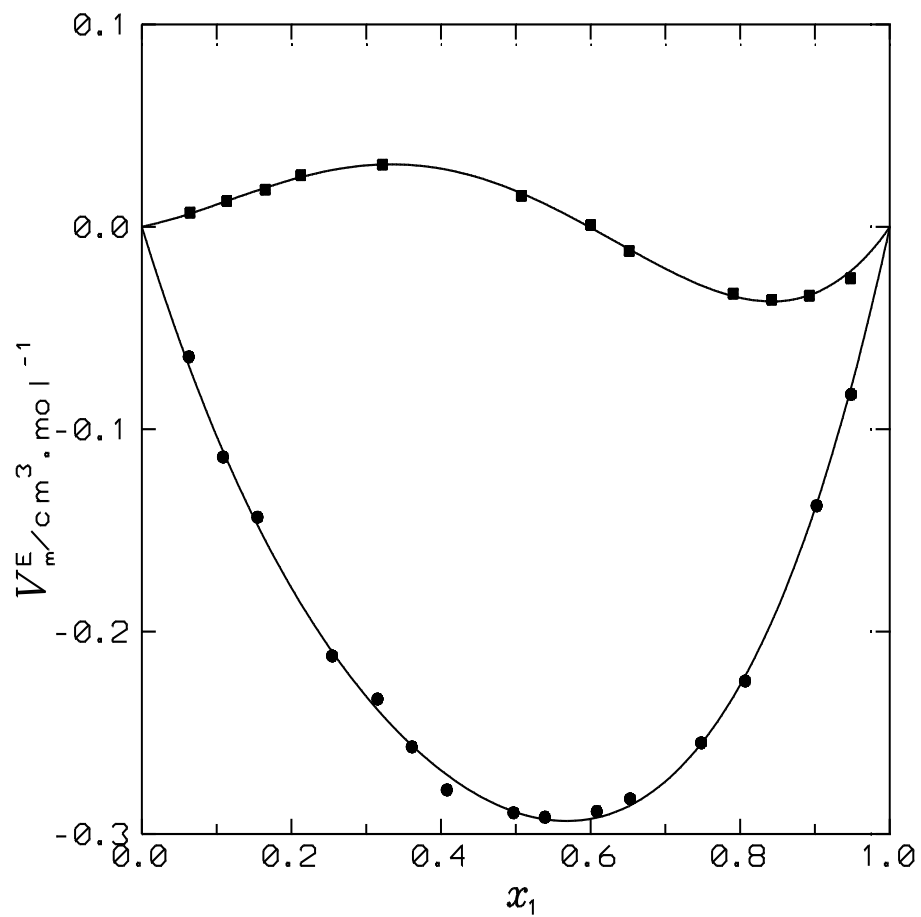


Figure 1

Excess molar volumes, V_m^E , for DMF (1) + DPA (2), or + DBA (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), DPA; (■), DBA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

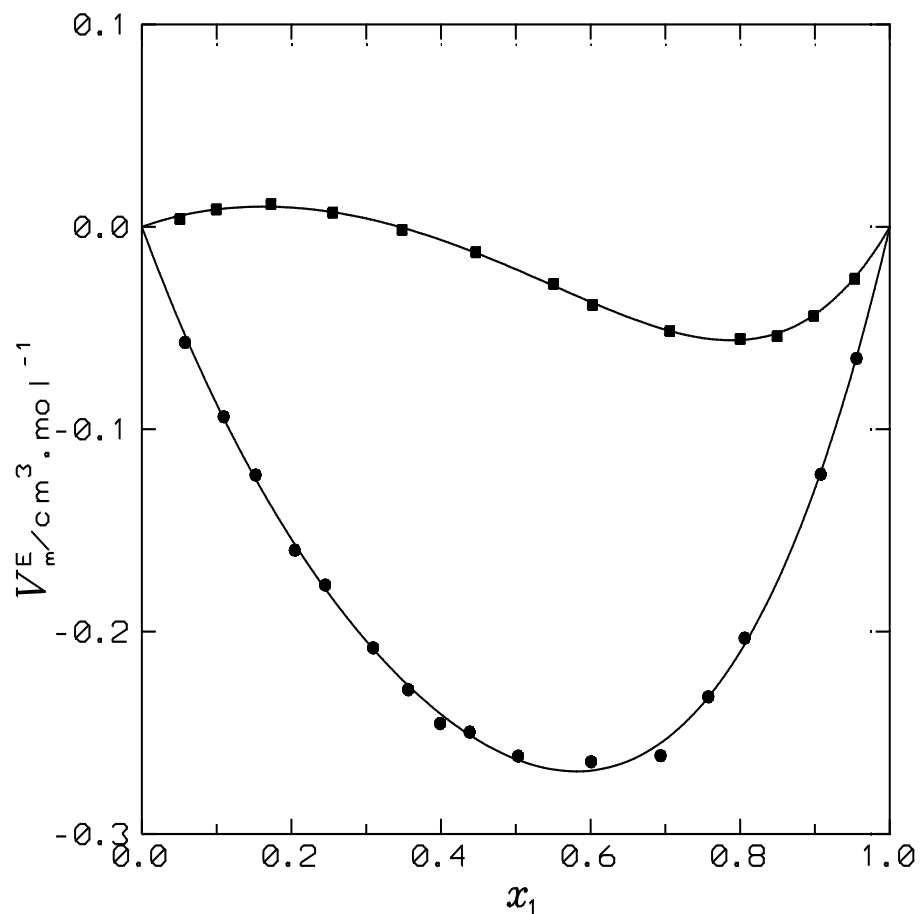


Figure 2

Excess molar volumes, V_m^E , for DMF (1) + BA (2), or + HxA (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), BA; (■), HxA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

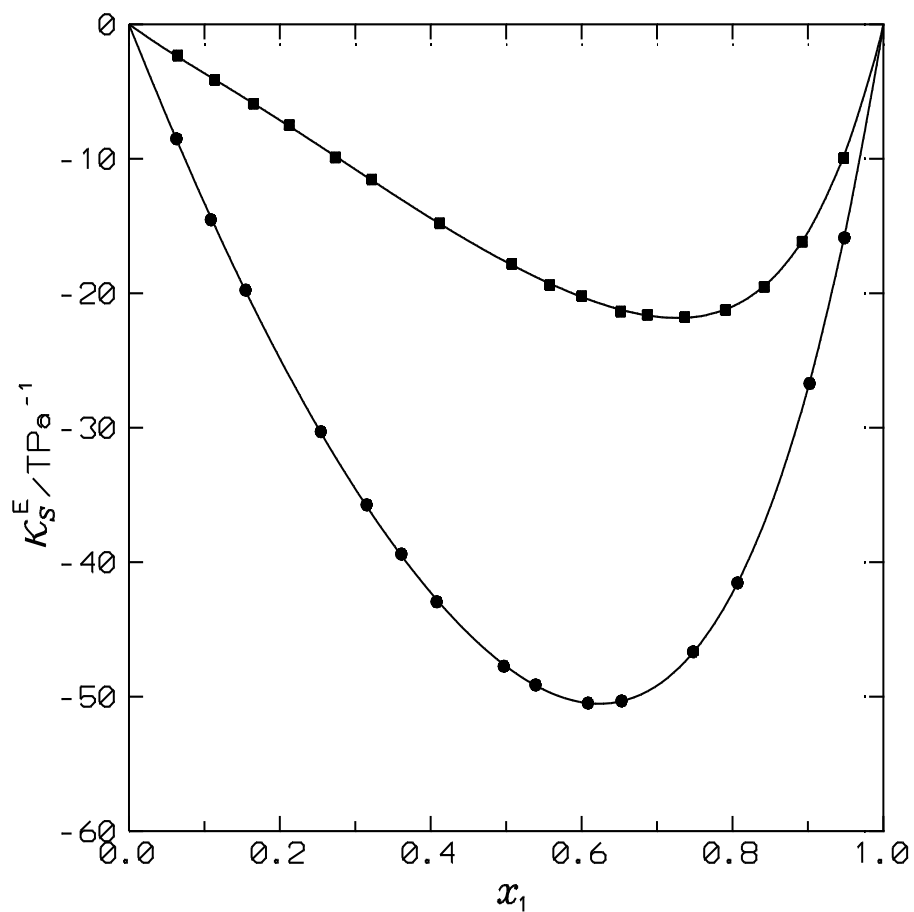


Figure 3

Excess isentropic compressibilities, κ_S^E , for DMF (1) + DPA (2), or + DBA (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), DPA; (■), DBA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

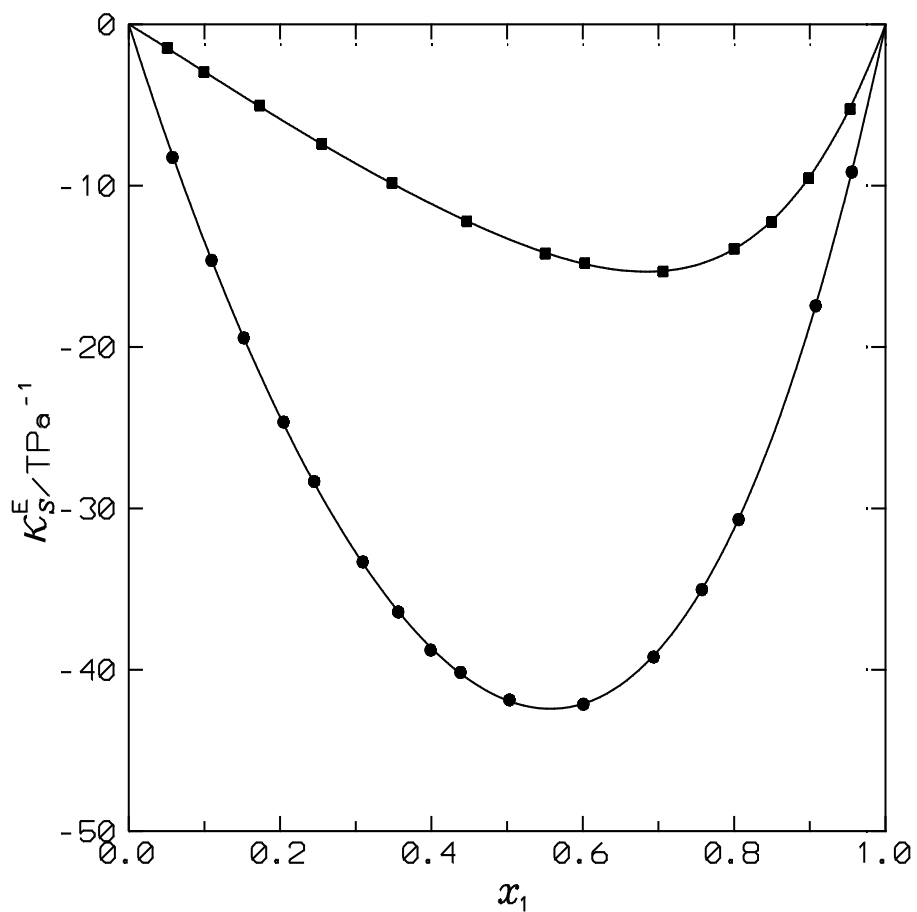


Figure 4

Excess isentropic compressibilities, κ_s^E , for DMF (1) + BA (2), or + HxA (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), BA; (■), HxA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

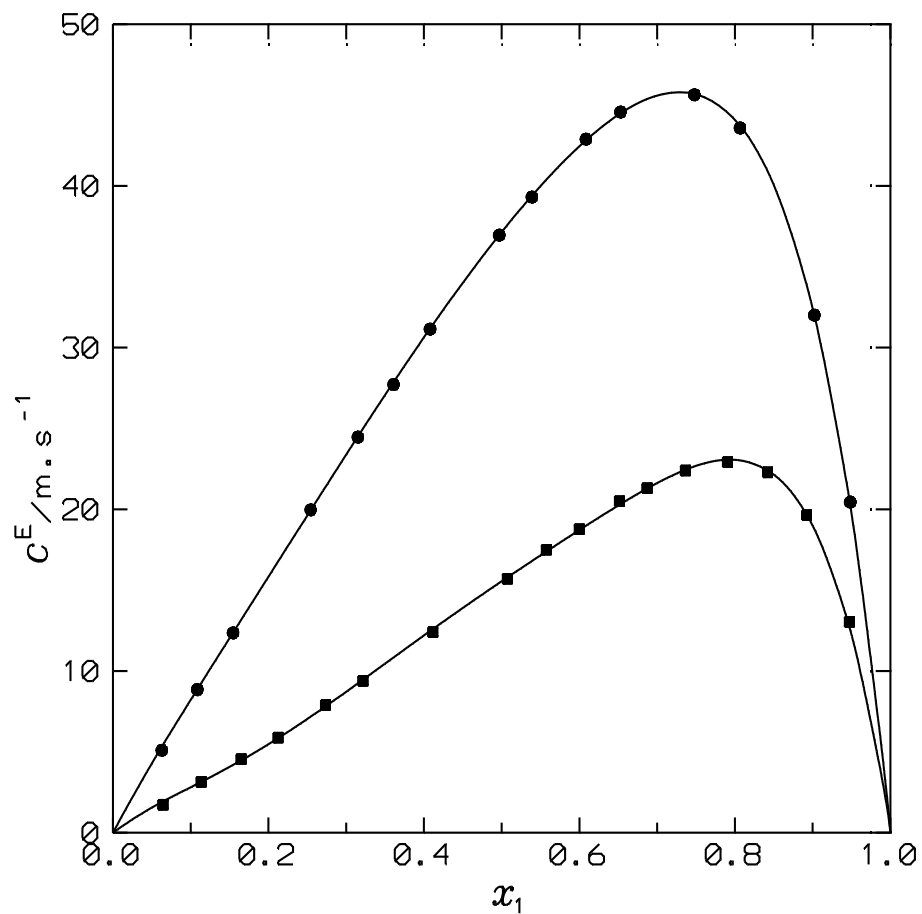


Figure 5

Excess speeds of sound, c^E , for DMF (1) + DPA (2), or + DBA (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), DPA; (■), DBA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

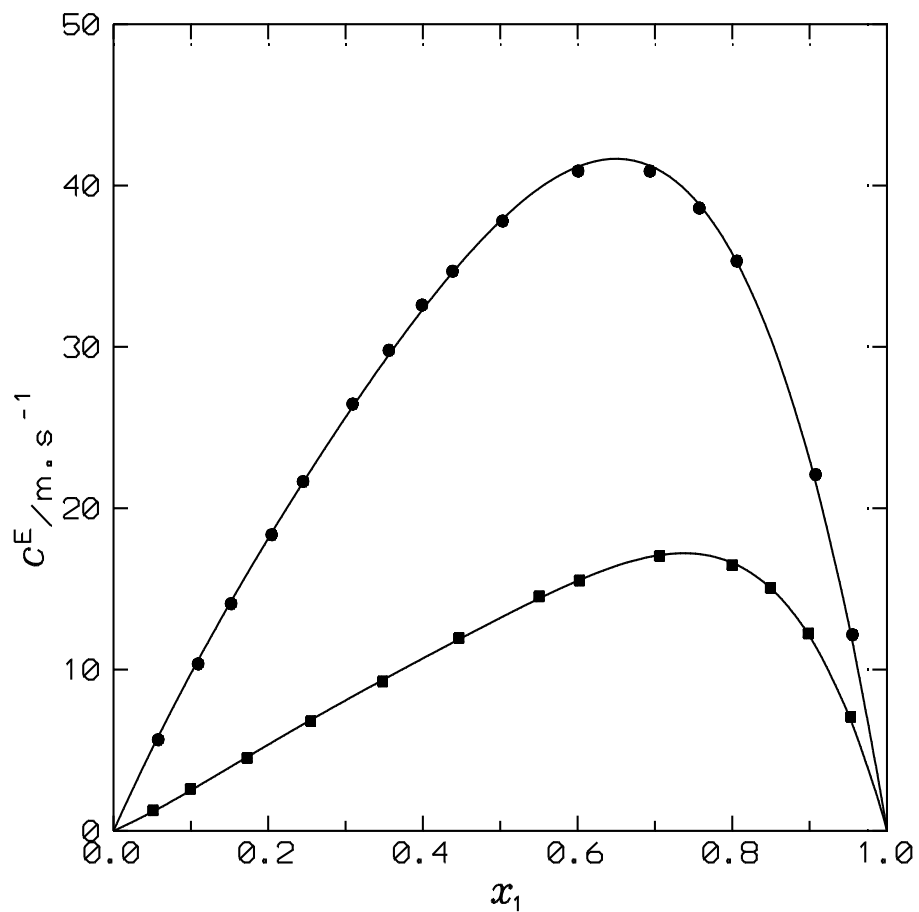


Figure 6

Excess speeds of sound, c^E , for DMF (1) + BA (2), or + HxA (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), BA; (■), HxA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

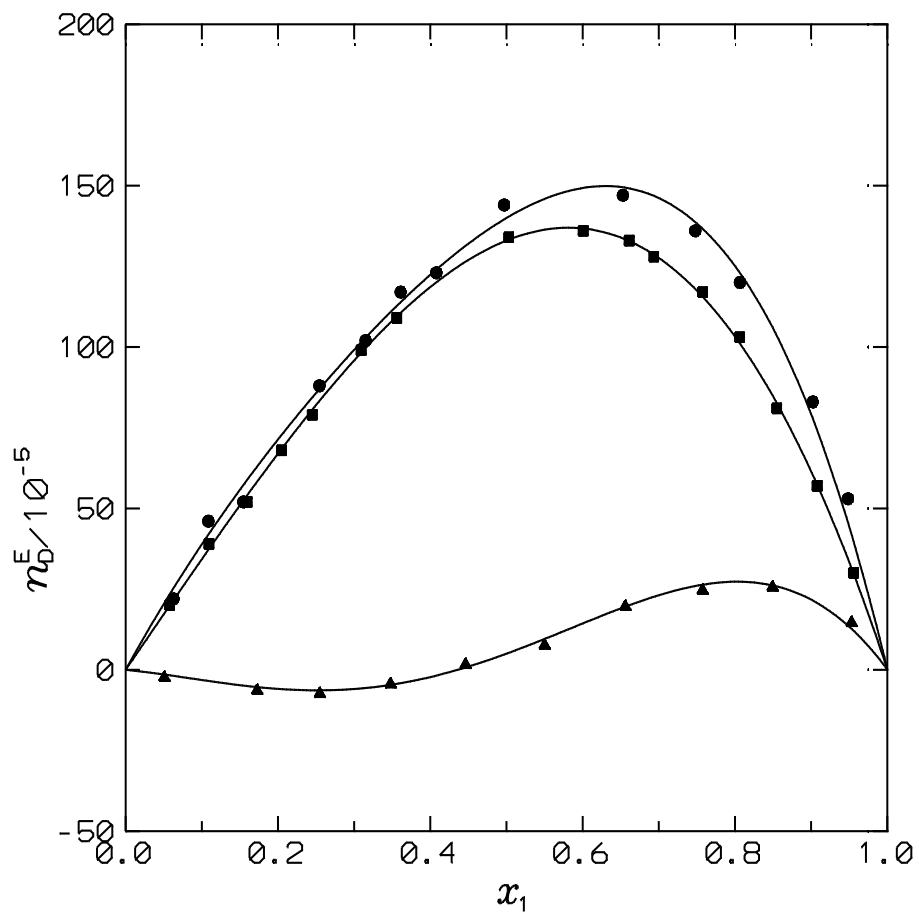


Figure 7

Excess refractive indices, n_D^E , for DMF (1) + amine (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), DPA; (■), BA; (▲), HxA. Solid lines, calculations with eq. 8 using the coefficients from Table 5.

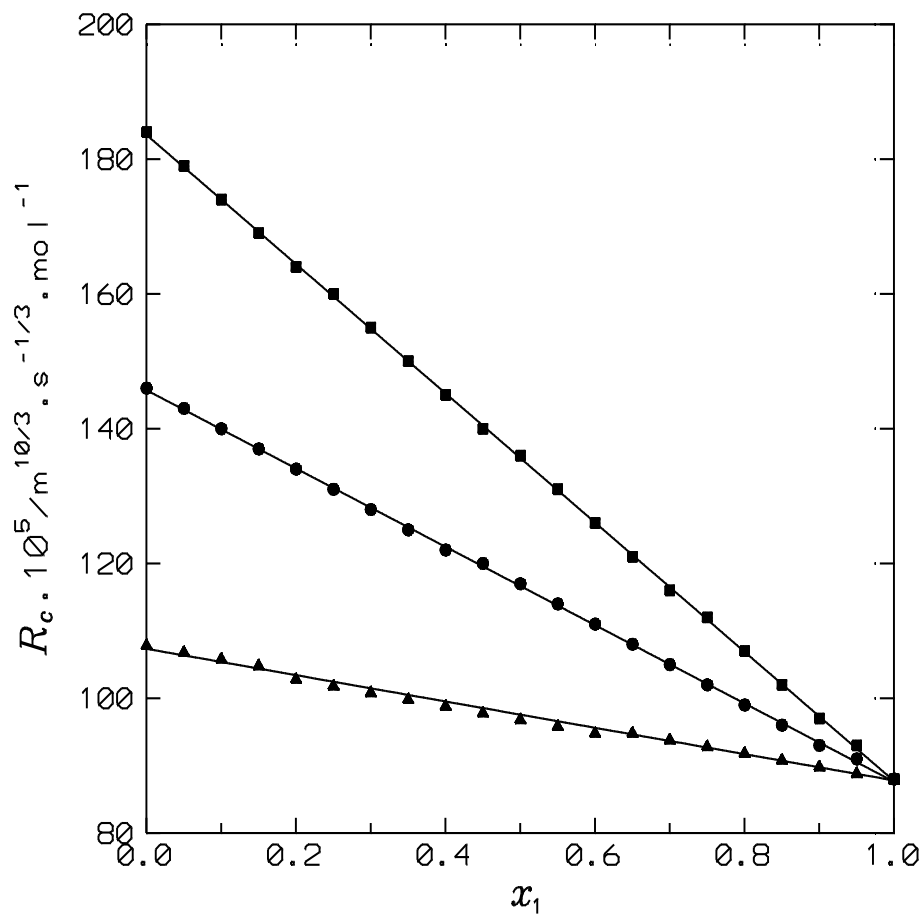
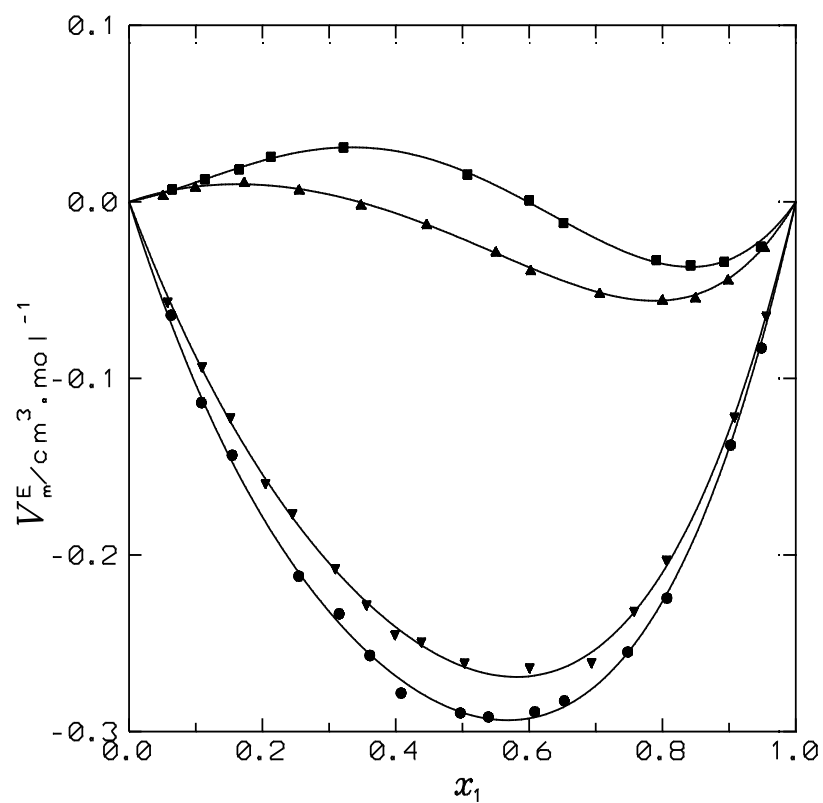


Figure 8

Rao's constant, R_c , for DMF (1) + amine (2) systems at atmospheric pressure and 298.15 K (this work): (●), DPA; (■), DBA; (▲), BA.

FOR TOC ONLY



Excess molar volumes, V_m^E , for DMF (1) + amine (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values: (\bullet), DPA; (\blacksquare), DBA; (\blacktriangledown), BA; (\blacktriangle) HxA. Solid lines, results from the Redlich-Kister fittings.

Supporting information

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

Fernando Hevia, Ana Cobos, Juan Antonio González*, Isafías García de la Fuente, Luis Felipe Sanz

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain.

*e-mail: jagl@termo.uva.es; Fax: +34-983-423136; Tel: +34-983-423757

Table S1

Excess molar volumes, V_m^E , for *N,N*-dimethylformamide (1) + amine (2) mixtures at temperature T and pressure $p = 0.1$ MPa. ^a

x_1	$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$
DMF (1) + DPA (2) ; $T/ \text{K} = 293.15$ K			
0.0600	-0.0724	0.4974	-0.2847
0.1071	-0.1116	0.5487	-0.2869
0.1560	-0.1539	0.6562	-0.2787
0.1975	-0.1765	0.7514	-0.2413
0.2490	-0.1986	0.8216	-0.2017
0.3099	-0.2341	0.8501	-0.1875
0.3463	-0.2397	0.9025	-0.1447
0.3985	-0.2621	0.9486	-0.0800
0.4480	-0.2741		
DMF (1) + DPA (2) ; $T/ \text{K} = 298.15$ K			
0.0626	-0.0642	0.5386	-0.2917
0.1083	-0.1137	0.6082	-0.2889
0.1544	-0.1435	0.6527	-0.2826
0.2541	-0.2120	0.7477	-0.2549
0.3148	-0.2333	0.8063	-0.2244
0.3609	-0.2569	0.9020	-0.1378
0.4077	-0.2782	0.9482	-0.0828
0.4966	-0.2895		
DMF (1) + DPA (2) ; $T/ \text{K} = 303.15$ K			
0.0453	-0.0626	0.5415	-0.3027
0.1034	-0.1218	0.6016	-0.2975
0.1963	-0.1857	0.6517	-0.2908
0.2582	-0.2163	0.7502	-0.2558
0.3559	-0.2677	0.8498	-0.1931
0.4099	-0.2877	0.9000	-0.1465
0.4565	-0.2954	0.9498	-0.0838
DMF (1) + DBA (2) ; $T/ \text{K} = 298.15$ K			
0.0642	0.0070	0.5996	0.0009
0.1134	0.0128	0.6514	-0.0120
0.1647	0.0184	0.7904	-0.0330
0.2121	0.0255	0.8418	-0.0360
0.3213	0.0307	0.8921	-0.0340

0.5072	0.0153	0.9471	-0.0255
DMF (1) + BA (2) ; $T/ K = 293.15 K$			
0.0599	-0.0476	0.5483	-0.2483
0.1056	-0.0798	0.6569	-0.2449
0.1591	-0.1094	0.6999	-0.2320
0.2505	-0.1610	0.7537	-0.2128
0.3017	-0.1860	0.8036	-0.1858
0.3583	-0.2066	0.8579	-0.1587
0.3992	-0.2259	0.9048	-0.1102
0.5059	-0.2465	0.9546	-0.0587
DMF (1) + BA (2) ; $T/ K = 298.15 K$			
0.0575	-0.0571	0.4381	-0.2497
0.1092	-0.0938	0.5028	-0.2615
0.1519	-0.1227	0.6005	-0.2643
0.2043	-0.1598	0.6934	-0.2613
0.2448	-0.1770	0.7572	-0.2322
0.3090	-0.2080	0.8056	-0.2033
0.3558	-0.2287	0.9076	-0.1223
0.3986	-0.2454	0.9553	-0.0651
DMF (1) + BA (2) ; $T/ K = 303.15 K$			
0.0505	-0.0522	0.5281	-0.2698
0.1477	-0.1338	0.6056	-0.2704
0.2019	-0.1675	0.6960	-0.2574
0.2410	-0.1816	0.7558	-0.2289
0.3024	-0.2108	0.8006	-0.2107
0.3558	-0.2335	0.8544	-0.1664
0.4358	-0.2533	0.8998	-0.1251
0.5114	-0.2621	0.9466	-0.0748
DMF (1) + HxA (2) ; $T/ K = 298.15 K$			
0.0506	0.0039	0.6022	-0.0387
0.0992	0.0086	0.7056	-0.0516
0.1725	0.0112	0.7996	-0.0554
0.2548	0.0070	0.8492	-0.0541
0.3476	-0.0015	0.8982	-0.0439
0.4461	-0.0126	0.9530	-0.0256
0.5500	-0.0281		

^a The standard uncertainties are: $u(x_1) = 0.0008$; $u(p) = 1 \text{ kPa}$; $u(T) = 0.02 \text{ K}$. The relative combined expanded standard uncertainty (0.95 level of confidence) is: $U_{rc}(V_m^E) = 0.025$.

Table S2

Isobaric thermal expansion coefficient, α_p , and the corresponding excess function, α_p^E , at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa, of *N,N*-dimethylformamide (1) + amine (2) mixtures. ^a

x_1	ϕ_1	$\alpha_p^b/10^{-3}\text{K}^{-1}$	$\left(\frac{\partial \rho}{\partial T}\right)_p / \text{kg m}^{-3} \text{K}^{-1}$	r^c	$\alpha_p^E/10^{-6}\text{K}^{-1}$
DMF (1) + DPA(2)					
0.0626	0.0361	1.228	-0.910953	0.999977	-4
0.1083	0.0638	1.220	-0.912081	0.999966	-5
0.1544	0.0930	1.211	-0.913352	0.999961	-7
0.2541	0.1605	1.192	-0.916600	0.999965	-11
0.3148	0.2050	1.181	-0.918932	0.999973	-11
0.3609	0.2407	1.172	-0.920886	0.999980	-12
0.4077	0.2787	1.162	-0.923030	0.999986	-13
0.4966	0.3564	1.144	-0.927515	0.999993	-13
0.5386	0.3959	1.135	-0.929800	0.999994	-13
0.6082	0.4656	1.120	-0.933767	0.999995	-12
0.6527	0.5134	1.109	-0.936379	0.999994	-12
0.7477	0.6245	1.086	-0.941942	0.999989	-9
0.8063	0.7003	1.070	-0.945181	0.999983	-8
0.9020	0.8378	1.042	-0.949609	0.999975	-4
0.9482	0.9113	1.027	-0.951097	0.999978	-2
DMF (1) + BA(2)					
0.0575	0.0452	1.283	-0.952253	1.000000	-14
0.1092	0.0868	1.262	-0.948543	0.999999	-23
0.1519	0.1219	1.248	-0.947139	0.999998	-26
0.2043	0.1660	1.232	-0.947004	0.999995	-29
0.2448	0.2008	1.221	-0.947790	0.999993	-29
0.3090	0.2574	1.205	-0.950026	0.999988	-28
0.3558	0.2998	1.193	-0.952015	0.999983	-27
0.3986	0.3394	1.183	-0.953824	0.999978	-25
0.4381	0.3767	1.173	-0.955318	0.999972	-24
0.5028	0.4394	1.156	-0.957074	0.999959	-22
0.6005	0.5382	1.128	-0.957395	0.999931	-20
0.6934	0.6368	1.098	-0.954824	0.999901	-20
0.7572	0.7074	1.076	-0.951809	0.999886	-21
0.8056	0.7626	1.059	-0.949272	0.999885	-21
0.9076	0.8839	1.027	-0.945455	0.999929	-16
0.9553	0.9431	1.014	-0.945764	0.999968	-11

^a The standard uncertainties are: $u(x_1) = 0.0008$; $u(p) = 1$ kPa; $u(T) = 0.02$ K. The relative combined expanded standard uncertainty (0.95 level of confidence) is $U_{rc}(\alpha_p^E) = 0.05$.

^b Density values at 293.15 and 303.15 K at the mole fractions reported at 298.15 K were obtained from the corresponding Redlich-Kister adjustments for V_m^E .

^c Regression coefficients (absolute values) obtained when fitting densities against temperature, assuming a linear dependence between the two quantities.

Table S3

Excess functions, at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa, for κ_S^E , adiabatic compressibility, and c , speed of sound, of N,N -dimethylformamide (1) + amine (2) mixtures. ^a

x_1	$\kappa_S^E/\text{TPa}^{-1}$	$c^E/\text{m}\cdot\text{s}^{-1}$	x_1	$\kappa_S^E/\text{TPa}^{-1}$	$c^E/\text{m}\cdot\text{s}^{-1}$
DMF (1) + DPA (2)					
0.0626	- 8.5	5.1	0.5386	- 49.1	39.3
0.1083	- 14.5	8.8	0.6082	- 50.5	42.9
0.1544	- 19.8	12.4	0.6527	- 50.3	44.6
0.2541	- 30.3	19.9	0.7477	- 46.7	45.6
0.3148	- 35.7	24.5	0.8063	- 41.5	43.6
0.3609	- 39.4	27.7	0.9020	- 26.7	32.0
0.4077	- 42.9	31.1	0.9482	- 15.9	20.4
0.4966	- 47.7	36.9			
DMF (1) + DBA (2)					
0.0642	- 2.3	1.7	0.5574	- 19.4	17.5
0.1134	- 4.1	3.1	0.5996	- 20.2	18.8
0.1647	- 5.9	4.5	0.6514	- 21.4	20.5
0.2121	- 7.5	5.9	0.6869	- 21.6	21.3
0.2734	- 9.9	7.9	0.7361	- 21.8	22.4
0.3213	- 11.5	9.4	0.7904	- 21.2	22.9
0.4114	- 14.8	12.4	0.8418	- 19.5	22.3
0.4526	- 16.2	13.9	0.8921	- 16.2	19.6
0.5072	- 17.8	15.7	0.9471	- 9.9	13.0
DMF (1) + BA (2)					
0.0575	- 8.2	5.6	0.4381	- 40.2	34.7
0.1092	- 14.6	10.3	0.5028	- 41.9	37.8
0.1519	- 19.4	14.1	0.6005	- 42.1	40.9
0.2043	- 24.6	18.4	0.6934	- 39.2	40.9
0.2448	- 28.3	21.6	0.7572	- 35.0	38.6
0.3090	- 33.3	26.5	0.8056	- 30.7	35.3
0.3558	- 36.4	29.8	0.9076	- 17.4	22.1
0.3986	- 38.8	32.6	0.9553	- 9.1	12.2
DMF (1) + HxA (2)					
0.0506	- 1.5	1.3	0.6022	- 14.8	15.5
0.0992	- 2.9	2.6	0.7056	- 15.3	17.0
0.1725	- 5.0	4.5	0.7996	- 13.9	16.5
0.2548	- 7.4	6.8	0.8492	- 12.2	15.1
0.3476	- 9.8	9.3	0.8982	- 9.5	12.2
0.4461	- 12.2	11.9	0.9530	- 5.2	7.1

0.5500	- 14.2	14.5
--------	--------	------

^a The standard uncertainties, u , are: $u(x_1) = 0.0008$; $u(p) = 1 \text{ kPa}$; $u(T) = 0.02 \text{ K}$. The combined expanded standard uncertainties (0.95 level of confidence) are: $U_{rc}(c^E) = 0.0015$; $U_{rc}(\kappa_S^E) = 0.05$.

Table S4

Excess refractive indices, n_D^E , of *N,N*-dimethylformamide (1) + amine mixtures at temperature T and pressure $p = 0.1$ MPa. ^a

x_1	n_D^E	x_1	n_D^E
DMF (1) + DPA (2) ; $T/ K = 293.15$ K			
0.0600	0.00019	0.5487	0.00142
0.1556	0.00045	0.6018	0.00146
0.2614	0.00081	0.7033	0.00143
0.3463	0.00102	0.8216	0.00115
0.3985	0.00118	0.8844	0.00089
0.4554	0.00126	0.9486	0.00056
DMF (1) + DPA (2) ; $T/ K = 298.15$ K			
0.0626	0.00022	0.4966	0.00144
0.1083	0.00046	0.6527	0.00147
0.1544	0.00052	0.7477	0.00136
0.2541	0.00088	0.8063	0.00120
0.3148	0.00102	0.9020	0.00083
0.3609	0.00117	0.9482	0.00053
0.4077	0.00123		
DMF (1) + DPA (2) ; $T/ K = 303.15$ K			
0.0453	0.00017	0.6016	0.00158
0.1034	0.00041	0.7502	0.00149
0.1963	0.00080	0.8498	0.00114
0.2582	0.00088	0.9000	0.00089
0.3559	0.00116	0.9498	0.00046
0.4099	0.00128		
DMF (1) + DBA (2) ; $T/ K = 298.15$ K			
0.1038	-0.00002	0.7709	0.00023
0.2076	-0.00003	0.8398	0.00026
0.3608	-0.00001	0.8989	0.00023
0.4897	0.00004	0.9497	0.00016
0.5933	0.00011	0.9738	0.00010
0.6880	0.00018		
DMF (1) + BA (2) ; $T/ K = 293.15$ K			
0.0599	0.00019	0.5059	0.00128
0.1056	0.00034	0.6043	0.00137
0.1591	0.00051	0.6569	0.00135
0.2010	0.00066	0.6999	0.00131
0.2505	0.00078	0.7537	0.00119

0.3017	0.00093	0.8036	0.00106
0.3583	0.00107	0.8579	0.00087
0.3992	0.00114	0.9048	0.00064
0.4401	0.00120	0.9546	0.00033
DMF (1) + BA (2) ; $T/ K = 298.15 K$			
0.0575	0.00020	0.6005	0.00136
0.1092	0.00039	0.6608	0.00133
0.1519	0.00052	0.6934	0.00128
0.2043	0.00068	0.7572	0.00117
0.2448	0.00079	0.8056	0.00103
0.3090	0.00099	0.8546	0.00081
0.3558	0.00109	0.9076	0.00057
0.5028	0.00134	0.9553	0.00030
DMF (1) + BA (2) ; $T/ K = 303.15 K$			
0.0505	0.00020	0.5281	0.00147
0.1477	0.00057	0.6056	0.00146
0.2019	0.00075	0.6574	0.00142
0.2410	0.00092	0.6960	0.00136
0.3024	0.00107	0.7558	0.00127
0.3558	0.00117	0.8006	0.00113
0.3992	0.00126	0.8544	0.00093
0.4358	0.00134	0.8998	0.00069
0.5114	0.00146	0.9466	0.00040
DMF (1) + HxA (2) ; $T/ K = 298.15 K$			
0.0506	-0.00002	0.5500	0.00008
0.1725	-0.00006	0.6558	0.00020
0.2548	-0.00007	0.7573	0.00025
0.3476	-0.00004	0.8492	0.00026
0.4461	0.00002	0.9530	0.00015

^a The standard uncertainties, u , are: $u(x_1) = 0.0008$; $u(T) = 0.03 K$; $u(p) = 1 kPa$. The relative combined expanded standard uncertainty (0.95 level of confidence), U_{rc} , is: $U_{rc}(n_D^E) = 0.04$.