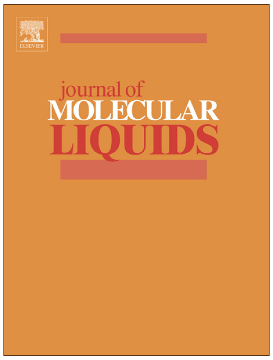

Thermodynamics of amide+ketone mixtures. 2. Volumetric, speed of sound and refractive index data for N,N-dimethylacetamide+2-alkanone systems at several temperatures. Application of Flory's model to tertiary amide+n-alkanone systems

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Thermodynamics of amide + ketone mixtures. 2. Volumetric, speed of sound and refractive index data for *N,N*-dimethylacetamide + 2-alkanone systems at several temperatures. Application of Flory's model to tertiary amide + *n*-alkanone systems

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Abstract

Data on density, ρ, speed of sound, *c*, and refractive index, n_D, have been reported at (293-303.15) K for the *N*,*N*-dimethylacetamide (DMA)+ $CH_3CO(CH_2)_{u-1}CH_3$ (u = 1,2,3) systems, and at 298.15 K for the mixture with u = 5. These data have been used to compute excess molar volumes, V_m^E, excess adiabatic compressibilities, κ_S^E, and excess speeds of sound c^E. Negative V_m^E values indicate the existence of structural effects and interactions between unlike molecules. From molar excess enthalpies, H_m^E, available in the literature for *N*,*N*-dimethylformamide (DMF), or *N*-methylpyrrolidone (NMP) + *n*-alkanone systems, it is shown: (i) amide-ketone interactions are stronger in DMF systems than in those with NMP; (ii) they become weaker when u increases in mixtures with a given amide. Structural effects largely contribute to H_m^E and are more relevant in mixtures containing NMP. The application of the Flory's model reveals that the random mixing hypothesis is valid in large extent for DMF solutions, while NMP systems are characterized by rather strong orientational effects. From values of molar refraction and of the product $P_{int}V_m$ (where P_{int} is the internal pressure and V_m the molar volume), it is concluded that dispersive interactions increase with u, or when DMF is replaced by DMA in mixtures with a fixed ketone.

KEYWORDS: amides; *n*-alkanones; thermophysical properties; Flory; random mixing

1. Introduction

Tertiary amides are aprotic solvents of high polarity, with very good donor-acceptor properties, capable to solve many organic substances. They have many applications as selective extractants of aromatic and saturated hydrocarbons and of nitrogen compounds in the fuel industry [1, 2]. These amides are also useful for the production of acrylic or fibers, plastics, pesticides or surface coatings, in nanotechnology [3-5], or in pharmaceutical industry [6, 7]. In addition, the research of liquid mixtures containing the amide group is suitable for a deeper understanding of complex molecules of biological interest [8]. For example, the water + *N,N*-dimethylformamide (DMF) system may be considered as a simple biochemical model of biological aqueous solutions [9,10]. On the other hand, the significant local order shown by pure amides makes also very interesting their theoretical study [11]. In the case of *N,N*-dialkylamides, due to the lack of hydrogen-bonds, this has been attributed to the existence of strong dipolar interactions [10,12].

2-Alkanones, ($CH_3CO(CH_2)_{u-1}CH_3$) are polar, aprotic compounds and hydrogen bonds acceptors, used as solvents for plastics and some synthetic fibers or as intermediates in the obtention of very important compounds (e.g., methyl methacrylate). They have also an essential role in biochemistry, as many sugars are ketones, and fatty acid synthesis proceeds via these compounds. These features make suitable the study of amide + alkanone mixtures, which must be taken into account within a general experimental and theoretical research of liquid mixtures containing the functional groups carbonyl, amine or amide. In a previous work, we have provided data on density, ρ, speeds of sound, c, and refractive indices, n_D, at (293.15-303.15) K for DMF systems with u = 1,2,3 and at 298.15 K for the solution with u = 5 [13]. As a continuation of this research, we report now similar data for binary mixtures containing *N,N*-dimethylacetamide (DMA) and the same 2-alkanones over the same temperature range. In order to complete our study, data available in the literature on *N*-methylpyrrolidone (NMP) + *n*-alkanone systems are also considered [14-17]. This allows examine the dependence of thermophysical properties on the size and shape of the amide in systems with a given *n*-alkanone, or on the chain length of the *n*-alkanone in mixtures with a given amide. Finally, amide + *n*-alkanone mixtures are treated in terms of the Flory model [18-20], in order to explore the validity of the random mixing hypothesis for such solutions. We have widely used this approach to investigate orientational effects in liquid mixtures, such as 1-alkanol + linear or cyclic monoether [20], or + polyether [21], or ether + benzene, or + toluene [22].

2. Experimental

2.1 Materials

Information regarding the source and the purity of the compounds considered is shown in Table 1. All the chemicals have been used without further purification. Table 2 lists experimental values of ρ, c, n_{D}, thermal expansion coefficient, α_p, isentropic compressibility, κ_S, and isothermal compressibility, κ_T, for the pure compounds. Our values are in good agreement with data from the literature.

2.2 Apparatus and procedure

Binary mixtures have been prepared by mass in small vessels (≈ 10 cm^3) using an analytical balance Sartorius MSU125p (weighing accuracy 0.01 mg), with all weighings corrected for buoyancy effects. The standard uncertainty in the final mole fraction is estimated to be 0.0001. Molar quantities were determined on the basis of the relative atomic mass Table of 2015 issued by the CIAAW (IUPAC) [23]. Temperatures were measured by means of Pt-100 resistances. Their calibration was conducted according to the ITS-90 scale of temperature, against the triple point of the water and the fusion point of Ga. The standard uncertainty of the equilibrium temperature measurements is 0.01 K and 0.02 K. for ρ and n_{D} measurements, respectively. A vibrating-tube densimeter and sound analyser DSA5000 from Anton Paar, automatically thermostated within $0.01\,\mathrm{K}$, has been used for the measurements of ρ and c values. Details about the device calibration can be found elsewhere [24]. The repeatability of the ρ measurements is $0.005\,\mathrm{kg \cdot m^{-3}}$, whereas their overall uncertainty is $1 \cdot 10^{-2}$ kg·m^{-3}. Speed of sound is determined measuring the time of propagation of short acoustic pulses (central frequency, 3 MHz) [25], transmitted repeatedly through the sample. The repeatability of the c measurements is $0.1\,\mathrm{m \cdot s^{-1}}$ and their standard uncertainty is $0.2\,\mathrm{m \cdot s^{-1}}$.

The molar excess volume, $V_{\mathrm{m}}^{\mathrm{E}}$, and the excess speed of sound, c^{E}, of the system cyclohexane + benzene have been measured at (293.15-303.15) K to check the experimental technique. Our experimental results are in good agreement with published values [26-28]. The standard uncertainty of $V_{\mathrm{m}}^{\mathrm{E}}$ is $(0.010\left|V_{\mathrm{m,max}}^{\mathrm{E}}\right| + 0.005)$ cm^3·mol^{-1}, where $\left|V_{\mathrm{m,max}}^{\mathrm{E}}\right|$ stands for the maximum absolute experimental value of $V_{\mathrm{m}}^{\mathrm{E}}$ respect to the composition. The standard uncertainty of c^{E} is estimated to be $0.4\,\mathrm{m \cdot s^{-1}}$. A refractometer RFM970 from Bellingham+Stanley has been used for the n_{D} measurements. The technique is based on the optical detection of the critical angle at the wavelength of the sodium D line (589.3 nm). The temperature is controlled by means of Peltier modules and its stability is $0.02\,\mathrm{K}$. The refractometer was calibrated using 2,2,4-trimethylpentane and toluene at (293.15-303.15) K, as recommended by Marsh [29]. The repeatability of the measurements is 0.00004, and the standard uncertainty is 0.00008.

3. Equations

The Anton Paar DSA5000 apparatus allows to obtain rather directly experimental values of ρ, molar volume, V_{m}, α_p, and κ_S. The values of $\alpha_p = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p$ have been determined assuming that ρ depends linearly on T in the range of temperatures considered. In addition, as long as it is possible to neglect the dispersion and absorption of the acoustic wave, κ_S can be obtained using the Newton-Laplace equation:

$$\kappa_S = \frac{1}{\rho c^2} \tag{1}$$

The values F^{id} of a magnitude, F, for an ideal mixture at the same temperature and pressure as the investigated solution are calculated from the relations [30-32]:

$$F^{\mathrm{id}} = x_1 F_1 + x_2 F_2 \qquad \left(F = V_{\mathrm{m}}, C_{p\mathrm{m}}\right) \tag{2}$$

$$F^{\mathrm{id}} = \phi_1 F_1 + \phi_2 F_2 \qquad \left(F = \alpha_p, \kappa_T\right) \tag{3}$$

where F_i^* denotes the property for the pure component i, $C_{p\mathrm{m}}$ is the molar heat capacity at constant pressure, and $\phi_i = x_1 V_{\mathrm{m}i} / V_m^{\mathrm{id}}$ represents the ideal volume fraction. For κ_S and c, the following expressions are used [30]:

$$\kappa_S^{\mathrm{id}} = \kappa_T^{\mathrm{id}} - \frac{T V_{\mathrm{m}}^{\mathrm{id}} \left(\alpha_p^{\mathrm{id}}\right)^2}{C_{p\mathrm{m}}^{\mathrm{id}}} \tag{4}$$

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

being $\rho^{\mathrm{id}} = \left(x_1 M_1 + x_2 M_2\right) / V_{\mathrm{m}}^{\mathrm{id}}$ the ideal density, and M_i the molar mass of the pure component i. The ideal values of n_{D} are obtained from [33]:

$$n_{\mathrm{D}}^{\mathrm{id}} = \left[\phi_1 \left(n_{\mathrm{D1}}\right)^2 + \phi_2 \left(n_{\mathrm{D2}}\right)^2\right]^{1/2} \tag{6}$$

The excess properties, F^{E}, are then obtained using the relation:

$$F^{\mathrm{E}} = F - F^{\mathrm{id}} \qquad \left(F = V_{\mathrm{m}}, \kappa_S, c, \alpha_p, n_{\mathrm{D}}\right) \tag{7}$$

4. Experimental results

Values of ρ, c, and $V_{\mathrm{m}}^{\mathrm{E}}$, at the considered temperatures, as functions of x_1, the mole fraction of DMA, are included in Table 3 (Figure 1). For the 2-heptanone mixture, the measurements were made at 298.15 K only due to: (i) the very low $|V_{\mathrm{m}}^{\mathrm{E}}|$ values encountered for this system; (ii) the weak temperature dependence of $V_{\mathrm{m}}^{\mathrm{E}}$ encountered for the remaining mixtures. The corresponding results of κ_S^{E}, c^{E}, and α_p^{E} at 298.15 K are given in Table 4 (Figures 2, 3). The n_{D} values and their corresponding excess functions, $n_{\mathrm{D}}^{\mathrm{E}}$, are collected in Table 5 (Figure 4).

The data have been fitted by an unweighted linear least-squares regression to a Redlich-Kister equation:

$$F^{\mathrm{E}} = x_1(1-x_1)\sum_{i=0}^{k-1} A_i (2x_1-1)^i \qquad \left(F = V_{\mathrm{m}}, \kappa_S, c, \alpha_p, n_{\mathrm{D}}\right) \tag{8}$$

For each system and property, the number, k, of necessary coefficients for the regression has been determined by applying an F-test of additional term [34] at 99.5% confidence level. Table 6 includes the parameters A_i obtained, and the standard deviations $\sigma\left(F^{\mathrm{E}}\right)$, defined by:

$$\sigma\left(F^{\mathrm{E}}\right) = \left[\frac{1}{N-k}\sum_{j=1}^{N}\left(F_{\mathrm{cal},j}^{\mathrm{E}} - F_{\mathrm{exp},j}^{\mathrm{E}}\right)^2\right]^{1/2} \tag{9}$$

where the index j = 1, N (number of experimental data $F_{\mathrm{exp},j}^{\mathrm{E}}$), and $F_{\mathrm{cal},j}^{\mathrm{E}}$ is the corresponding value of the excess property F^{E} calculated from equation (8).

5. Flory model

5.1. Hypotheses and equations

A short summary of the main hypotheses of the theory foloows [18,19,35-37]. (i) Molecules are formed by segments, which are arbitrarily chosen isomeric portions of a molecule. (ii) The mean intermolecular energy per contact is assumed to be proportional to $-\eta / v_s$ (where η (>0) is a constant characterizing the energy of interaction for a pair of neighbouring sites and v_s is the segment volume). (iii) Restrictions on the precise location of a given segment by its neighbours in the same chain are taken into account, when the configurational partition function is determined, assuming that the number of external degrees of freedom of the segments is lower than 3. (iv) Random mixing is assumed. The probability of having species of kind *i* neighbours to any given site is equal to the site fraction (θ_i). If the total number of contact sites is very large, the probability of formation of an interaction between contacts sites belonging to different liquids is $\theta_1\theta_2$. Under these hypotheses, the Flory equation of state is:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3}-1} - \frac{1}{\bar{V}\bar{T}} \qquad (10)$$

where $\bar{V} = V/V^*$; $\bar{P} = P/P^*$ and $\bar{T} = T/T^*$ are the reduced volume, pressure and temperature, respectively. Equation (10) is valid for pure liquids and liquid mixtures. For pure liquids, the reduction parameters, V_i^*, P_i^* and T_i^* are obtained from data on ρ_i, $\alpha_{P\mathrm{i}}$, $\kappa_{T\mathrm{i}}$. The corresponding expressions for reduction parameters for mixtures are given elsewhere [20]. H_m^E is determined from,

$$H_\mathrm{m}^\mathrm{E} = \frac{x_1 V_1^* \theta_2 X_{12}}{\bar{V}} + x_1 V_1^* P_1^* \left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}}\right) + x_2 V_2^* P_2^* \left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}}\right) \qquad (11)$$

All the symbols have their usual meaning [22]. In equation (11), the term which depends directly on X_{12} is the interaction contribution to H_m^E. The remaining terms are the so-called equation of state contribution to H_m^E. The reduced volume of the mixture, $\bar{V}$, in equation (11) is obtained from the equation of state. Therefore, the molar excess volume can be also calculated:

$$V_\mathrm{m}^\mathrm{E} = (x_1 V_1^* + x_2 V_2^*)(\bar{V} - \varphi_1 \bar{V}_1 - \varphi_2 \bar{V}_2) \qquad (12)$$

5.2 Estimation of the Flory interaction parameter

X_{12} is determined from a H_m^E measurement at given composition from [20-22]:

$$X_{12} = \frac{x_1 P_1^* V_1^* \left(1 - \frac{\bar{T}_1}{\bar{T}}\right) + x_2 P_2^* V_2^* \left(1 - \frac{\bar{T}_2}{\bar{T}}\right)}{x_1 V_1^* \theta_2} \qquad (13)$$

For the application of this expression, we note that $\overline{V}\overline{T}$ is a function of H_m^E:

$$H_\mathrm{m}^\mathrm{E} = \frac{x_1 P_1^* V_1^*}{\overline{V}_1} + \frac{x_2 P_2^* V_2^*}{\overline{V}_2} + \frac{1}{\overline{V}\overline{T}}(x_1 P_1^* V_1^* \overline{T}_1 + x_2 P_2^* V_2^* \overline{T}_2) \tag{14}$$

and that from the equation of state, $\overline{V} = \overline{V}(\overline{T})$. More details have been given elsewhere [20-22]. Equation (13) generalizes of that previously given to calculate X_{12} from H_m^E at x_1 = 0.5 [38] and allows to investigate the concentration dependence of X_{12}. Systems characterized by a behaviour close to that of random mixing show a weak concentration dependence of X_{12} [21,22]. Properties of tertiary amides and *n*-alkanones molar volumes, V_i, α_{Pi}, κ_{Ti}, and the corresponding reduction parameters, P_i^* and V_i^*, needed for calculations are collected in Table S1 (supplementary material). Table 7 lists X_{12} values determined from experimental H_m^E data at x_1 = 0.5.

5.3 Results

Results on H_m^E obtained from the Flory model are collected in Table 7 (see Figures 5-6). This Table includes the interactional contribution to H_m^E, $H_\mathrm{m,int}^\mathrm{E}$, and the relative standard deviations for H_m^E defined as:

$$\sigma_r(H_\mathrm{m}^\mathrm{E}) = \left[\frac{1}{N}\sum\left(\frac{H_\mathrm{m,exp}^\mathrm{E} - H_\mathrm{m,calc}^\mathrm{E}}{H_\mathrm{m,exp}^\mathrm{E}}\right)^2\right]^{1/2} \tag{15}$$

where *N* (=19) is the number of data points, and $H_\mathrm{m,exp}^\mathrm{E}$ stands for the smoothed H_m^E values calculated at Δx_1 = 0.05 in the composition range [0.05, 0.95] from polynomial expansions, previously checked, given in the original works. Figure S1 (supplementary material) shows the concentration dependence of X_{12} for some systems.

6. Discussion

Hereafter, we are referring to values of the excess functions and of thermophysical properties at $T = 298.15\mathrm{K}$ and equimolar composition.

The amides and ketones considered along the work are very polar compounds. Thus, the dipole moment, μ, of the amides are (in D): 3.7 (DMF); 3.81 (DMA) [39]; 4.09 (NMP) [40]. For 2-alkanones, μ/D = 2.69 (acetone); 2.76 (2-butanone); 2.70 (2-pentanone); 2.59 (2-heptanone) [40]. However, the impact of polarity on bulk properties is better evaluated by means of the effective dipole moment, $\overline{\mu}$ [41-43]:

$$\bar{\mu} = \left[\frac{\mu^2 N_A}{4\pi\varepsilon_0 V_m \kappa_B T} \right]^{1/2} \tag{16}$$

where N_A, ε_0, κ_B stand for the Avogadro's number, the permittivity of the vacuum, and the Boltzmann's constant, respectively. The $\bar{\mu}$ values are: 1.60 (DMF); 1.51 (DMA); 1.59 (NMP); 1.20 (2-propanone); 1.11 (2-butanone); 1.00 (2-pentanone); 0.83 (2-heptanone). It is to be noted that, for a given homologous series (2-alkanones), μ varies only slightly with the chain length of the compound, while the $\bar{\mu}$ variation is much greater.

Mixtures of tertiary amides with *n*-alkanes show miscibility gaps at 298.15 K. In fact, the upper critical solution temperature, UCST/K, of heptane systems changes in the order: 342.55 (DMF) [44] > 326.05 (NMP) [45] > 309.8 (DMA) [46]. This reveals that dipolar interactions between amide molecules become weaker in the same sequence. Results for excess molar enthalpies at infinite dilution of the amide, $H_{m,1}^{E,\infty}$ in systems with heptane or cyclohexane at 298.15 K also support this conclusion as it is indicated by the following values (in kJ·mol^{-1}): 17.1 (DMF + heptane) [47]; 12.0 (NMP + heptane); 11.7 (NMP + cyclohexane) [48]. If one takes into account the similar $\bar{\mu}$ values for DMF (V_m =77.42 cm^3·mol^{-1} [13]) and NMP (V_m = 96.63 cm^3·mol^{-1} [40]), this means that dipolar interactions are not only determined by $\bar{\mu}$ values. Effects related to the size and shape of the molecules must also be considered. In fact, the rather large difference between UCST values of mixtures with NMP or DMA (V_m = 93.04 cm^3·mol^{-1}) should be ascribed essentially to the different shape of these amides.

2-Alkanone + *n*-alkane systems are characterized by large and positive H_m^E values, accordingly with their rather large $\bar{\mu}$ values. For example, H_m^E(heptane)/J·mol^{-1} = 1704 (2-propanone) [49]; 1339 (2-butanone) [50]; 886 (2-heptanone) [51]. We note that H_m^E decreases with the decreasing of $\bar{\mu}$, indicating that the observed H_m^E variation is related to a weakening of the dipolar interactions between ketone molecules [52]. This also leads to a lower contribution to V_m^E from the disruption of ketone-ketone interactions and to decreased V_m^E (heptane)/cm^3·mol^{-1} values in the sequence: 1.129 (acetone) [53] > 0.280 (2-octanone) [54].

6.1 Calorimetric data

Tertiary amide + *n*-alkanone mixtures are characterized by low and even negative H_m^E values. Thus, H_m^E(DMF)/J·mol^{-1} = 34 (2-propanone) [16]; 142 (2-butanone), 206 (2-pentanone) [17], and for NMP mixtures: -165 (2-butanone) [14]; 226 (4-heptanone); 362 (5-nonanone) [15]. On the basis of the features previously discussed for tertiary amide or *n*-alkanone + alkane mixtures, these low $H_{\mathrm{m}}^{\mathrm{E}}$ values underline the existence of strong amide-alkanone interactions in the systems under investigation. In a previous work [13], we evaluated the enthalpy of the mentioned interactions, $\Delta H_{\text{NCO-CO}}$, for DMF solutions. The procedure applied is now briefly explained. It is well known that if structural effects are neglected [43,55], $H_{\mathrm{m}}^{\mathrm{E}}$ is the result of three contributions: two of them are positive, $\Delta H_{\text{NCO-NCO}}, \Delta H_{\text{CO-CO}}$, and are related to the breaking of amide-amide and ketone-ketone interactions upon mixing, respectively; $\Delta H_{\text{NCO-CO}}$ is a negative contribution due to the new NCO---CO interactions created along the mixing process. That is [56-58]:

$$H_{\mathrm{m}}^{\mathrm{E}} = \Delta H_{\text{NCO-NCO}} + \Delta H_{\text{CO-CO}} + \Delta H_{\text{NCO-CO}} \tag{17}$$

Equation (17) may be extended to $x_1 \to 0$ [56,58] to evaluate $\Delta H_{\text{NCO-CO}}$. In such a case, $\Delta H_{\text{NCO-NCO}}$ and $\Delta H_{\text{CO-CO}}$ can be replaced by $H_{\mathrm{m}1}^{\mathrm{E},\infty}$ (partial excess molar enthalpy at infinite dilution of the first component) of tertiary amide or *n*-alkanone + heptane systems. Thus,

$$\begin{aligned} &\Delta H_{\text{NCO-CO}} = H_{\mathrm{m}1}^{\mathrm{E},\infty}(\text{amide } + n\text{-alkanone}) \\ &-H_{\mathrm{m}1}^{\mathrm{E},\infty}(\text{amide } + \text{heptane}) - H_{\mathrm{m}1}^{\mathrm{E},\infty}(n\text{-alkanone} + \text{heptane}) \end{aligned} \tag{18}$$

The values (in kJ·mol^{-1}) determined for DMF systems were [13]: -26.0 (2-propanone); -24.0 (2-butanone); -22.6 (2-pentanone). These results show: (i) DMF-2-alkanone interactions are rather strong. Note that the value typically used in the ERAS model for the enthalpy of the self-association of 1-alkanols is -25.1 kJ·mol^{-1} [41, 59-61]; (ii) the enthalpy of the mentioned interactions become weaker when *u* is increased, probably due to the carbonyl group becomes then more sterically hindered. For NMP systems, we have obtained (Table S2, supplementary material) $\Delta H_{\text{NCO-CO}}$/kJ·mol^{-1}: -20.0 (2-butanone); -16.2 (4-heptanone). This means that amide-alkanone interactions are stronger in DMF solutions. The higher $H_{\mathrm{m}}^{\mathrm{E}}$ values of DMF systems can be explained assuming that the positive difference $\Delta H_{\text{NCO-NCO}}$(DMF) − $\Delta H_{\text{NCO-NCO}}$(NMP) is predominant over the negative $\Delta H_{\text{NCO-CO}}$(DMF) − $\Delta H_{\text{NCO-CO}}$(NMP) term.

A more exact treatment should take into the contribution from structural effects to $H_{\mathrm{m}}^{\mathrm{E}}$. For this purpose, the excess molar internal energy at constant volume, $U_{\mathrm{Vm}}^{\mathrm{E}}$, is an useful magnitude. It is calculated from [43, 55]:

$$U_{V\mathrm{m}}^{\mathrm{E}} = H_{\mathrm{m}}^{\mathrm{E}} - \frac{T\alpha_p V_{\mathrm{m}}^{\mathrm{E}}}{\kappa_T} \tag{19}$$

where $\frac{\alpha_p}{\kappa_T} T V_m^{\mathrm{E}}$ is the so-called equation of state (eos) contribution to $H_{\mathrm{m}}^{\mathrm{E}}$, and α_p and κ_T stand for the isobaric thermal expansion coefficient and isothermal compressibility of the mixture, respectively. Along calculations, the needed κ_T data were obtained from:

$$\kappa_T = \kappa_S + \frac{T\alpha_{\mathrm{p}}^2 V_{\mathrm{m}}}{C_{p,\mathrm{m}}} \tag{20}$$

assuming that $C_{p\mathrm{m}}^{\mathrm{E}}$ = 0,what is a good approximation in view of the low $H_{\mathrm{m}}^{\mathrm{E}}$ values of the investigated mixtures [62]. Thus, $U_{V\mathrm{m}}^{\mathrm{E}}$ (DMF)/J·mol^{-1} = 201 (acetone); 262 (2-butanone) and 303 (2-pentanone) [13], and $U_{V\mathrm{m}}^{\mathrm{E}}$ (NMP)/J·mol^{-1} = 26 (2-butanone); 351 (4-heptanone) (Table 8). The large differences between $U_{V\mathrm{m}}^{\mathrm{E}}$ and $H_{\mathrm{m}}^{\mathrm{E}}$ values must be remarked, as clearly show, in the present case, the importance of structural effects on $H_{\mathrm{m}}^{\mathrm{E}}$. Thus, the negative $H_{\mathrm{m}}^{\mathrm{E}}$ value of the NMP + 2-butanone mixture is due to the mentioned effects; it does not mean that interactions between unlike molecules are preponderant. Note that the positive $U_{V\mathrm{m}}^{\mathrm{E}}$ values obtained indicate that dominant contribution to this excess function arises from the breaking of interactions between like molecules.

6.2 Volumetric data

It is well known that negative $V_{\mathrm{m}}^{\mathrm{E}}$ values reveal the existence of interactions between unlike molecules and/or structural effects (geometrical factors as differences in size and shape between them [63-65] or interstitial accommodation [64]).

Interestingly, the excess functions $U_{V\mathrm{m}}^{\mathrm{E}}$ and $V_{\mathrm{m}}^{\mathrm{E}}$ for tertiary amide + *n*-alkanone systems show opposite signs. This shows that the main contribution to $V_{\mathrm{m}}^{\mathrm{E}}$ comes from structural effects [63]. On the other hand, for a given tertiary amide, both $U_{V\mathrm{m}}^{\mathrm{E}}$ (or $H_{\mathrm{m}}^{\mathrm{E}}$) and $V_{\mathrm{m}}^{\mathrm{E}}$ change in line, as these magnitudes increase with *u*. In consequence, the observed $V_{\mathrm{m}}^{\mathrm{E}}$ variation can be attributed to changes in the interactional contribution to $V_{\mathrm{m}}^{\mathrm{E}}$. This means that the contributions which increase $V_{\mathrm{m}}^{\mathrm{E}}$, weakening of the amide-alkanone interactions and larger number of broken amide-amide interactions, are predominant over that arising from the disruption of ketone-ketone interactions, and suggests that the negative $V_{\mathrm{m}}^{\mathrm{E}}$ values may be also ascribed to the rather strong amide-ketone interactions formed along the mixing process. The symmetry of the $V_{\mathrm{m}}^{\mathrm{E}}$ curves may be discussed in terms of the difference in size between the mixture components. For DMA or NMP + 2-propanone systems, the $V_{\mathrm{m}}^{\mathrm{E}}$ curves are shifted to larger mole fractions of the ketone, the smaller component (this work, Figure 1, [15]). The same behaviour is observed when u increases in systems with a given tertiary amide as the $V_{\mathrm{m}}^{\mathrm{E}}$ curves become skewed towards increasing values of amide concentration (smaller compound). This is particularly remarkable for the DMF + 2-heptanone mixture [13]. However, others effects are also present. Both components are of similar size in the DMF + 2-propanone mixture, and the $V_{\mathrm{m}}^{\mathrm{E}}$ curve is also shifted to lower mole fractions of the amide [13]. This may be interpreted assuming that interactions between unlike molecules are more probable in that concentration range. For a given 2-alkanone, say 2-pentanone, $V_{\mathrm{m}}^{\mathrm{E}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$ changes in the order: -0.243 (DMA) > -0.251 (DMF) [13] > -0.573 (NMP) [15]. The lower $V_{\mathrm{m}}^{\mathrm{E}}$ value of the DMF system compared to that of the DMA solution may be due to interactions between unlike molecules are more important when DMF is involved, as the amide group is less sterically hindered. The $V_{\mathrm{m}}^{\mathrm{E}}$ value of the NMP mixture is noticeably lower than the corresponding value of the DMF solution and underlines the importance of structural effects in NMP systems.

Both $A_p = (\frac{\Delta V_{\mathrm{m}}^{\mathrm{E}}}{\Delta T})_p$ and α_p^{E} are negative for the studied systems (Table 4). Thus, A_p(DMA)/$\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1} = -4.6\cdot10^{-3}$; (acetone); $-2.7\cdot10^{-3}$ (2-butanone) and $-3.6\cdot10^{-3}$ (2-pentanone). These values are very similar to those encountered for DMF mixtures [13]. Negative A_p and α_p^{E} values indicate that the structures are more difficult to be broken in the mixtures than in the pure liquids, which may be ascribed to the existence of interactions between unlike molecules and/or structural effects. For example, the 2-ethoxyethanol + octane, or 1-pentanol + cyclohexane systems, characterized by strong interactions between like molecules, show positive A_p values over the entire mole fraction range ($7.6\cdot10^{-3}$ [66] and $2.3\cdot10^{-3}$ [67], respectively (values in $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$). Interactions between unlike molecules are dominant in the $\mathrm{CHCl_3}$ + 1-butylamine mixture ($H_{\mathrm{m}}^{\mathrm{E}}/\mathrm{J}\cdot\mathrm{mol}^{-1}$ values are -3125; T = 303.15 K) [68]), and A_p is negative, $-4.2\cdot10^{-3}$ $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$ [65]. This magnitude is also negative for the hexane + hexadecane system characterized by structural effects and A_p is $-1.3\cdot10^{-2}$ (same units) for the hexane + hexadecane mixture [69].

Negative κ_S^E values have been also explained in terms of structural effects and/or interactions between unlike molecules, while positive values are considered to be due to the breaking of physical interactions [70]. The negative κ_S^E values of DMA + 2-alkanone systems (-62.0 (2-propanone); -42.8 (2-butanone); -34.1 (2-pentanone) and -14.9 (2-heptanone)) fit well within the trends stated above. DMF +2-alkanone systems behave similarly [13]. The signs of the excess functions $V_\mathrm{m}^\mathrm{E}, \kappa_S^E, c^\mathrm{E}$ are consistent between them. Thus, for a given *N*,*N*-dialkylamide, $V_\mathrm{m}^\mathrm{E}, \kappa_S^E$ values are negative, while c^E values are positive. In addition, $V_\mathrm{m}^\mathrm{E}, \kappa_S^E$ increase and c^E decreases when *u* is increased.

5.3 Internal pressures

We have also determined the internal pressures of the mixtures, P_int [71-73]:

$$P_\mathrm{int} = \frac{\alpha_P T}{\kappa_T} - p \qquad (21)$$

The main contributions to P_int arise from dispersion forces and weak dipole-dipole interactions [73]. For pure the liquids under study, $P_{\mathrm{int},i}\,/\,\mathrm{MPa}$ = 470.2 (NMP); 456.5 (DMF): 449.4 (DMA); 330.7 (acetone); 333.2 (2-butanone); 325.7 (2-pentanone) and 326.7 (2-heptanone). Some interesting information can be obtained from the comparison of these values with the corresponding results for the cohesive energy density (D_ce), which is measure of the total molecular cohesion (per cm^3) of the liquid [73]. The magnitude is defined as [73]:

$$D_\mathrm{ce} = \frac{\Delta H_\mathrm{vap} - RT}{V_m} \qquad (22)$$

where ΔH_vap is the molar enthalpy of vaporization at 298.15 K and R the gas constant. Using values of ΔH_vap from [74], the values $D_{\mathrm{ce},i}$/MPa obtained are: 573.8 (DMF); 521.8 (NMP); 512.8 (DMA); 389.3 (acetone); 358.5 (2-butanone); 334.3 (2-pentanone) and 326.9 (2-heptanone). From the $P_{\mathrm{int},i}$ and $D_{\mathrm{ce},i}$ values, we can state: (i) the existence of very strong dipolar interactions between amide or ketone molecules in the case of 2-propanone or 2-butanone; (ii) Interactions between amide molecules become weaker in the sequence: DMF > NMP > NMA, as is has been previously shown. However, it seems that dispersive interactions are stronger in NMP. (iii) Dipolar interactions become weaker when the chain length of the 2-alkanone increases. For the DMA systems, $P_\mathrm{int}\,/\,\mathrm{MPa}$ = 384.9 (acetone); 383.1 (2-butanone); 371.8 (2-pentanone) and 370.9 (2-heptanone), which are very close to those obtained for DMF solutions [13]. On the other hand, P_int can be also calculated with the equation [72]:

$$P_\mathrm{int} = \frac{RT}{x_1 v_{f1} + x_2 v_{f2} + V_\mathrm{m}^\mathrm{E}} - p \qquad (23)$$

where $v_{fi}(=RT/(p+P^{*}_{\mathrm{int},i}))$ is the free volume of the component i [72]. The P_{int} / MPa values calculated for DMA solutions determined from equation (23) are: 405.3 (acetone); 398.0 (2-butanone); 392.2 (2-pentanone) and 379.0 (2-heptanone). The differences with the experimental values are 5.3%, 3.9%, 5.5% and 2.2%, respectively. In the case of mixtures containing DMF, these differences are: 3.8 %, 4.2%, 3.9 and 0.0%. This demonstrates, apart from the consistency of our data, that the van der Waals equation holds in rather large extent for the investigated solution as equation (23) is derived from this equation of state. That is, the present mixtures are characterized in large extent by dispersive interactions.

6.4 Speeds of sound

The parameter $\chi=\left(\frac{c}{c^{\mathrm{id}}}\right)^{2}-1$ is widely used to estimate the non-ideality of a system. High χ values characterize mixtures which show strong deviations from the ideal behavior, as the methanol + 2-pyrrolidone mixture ($\chi=0.8$ [75]). For DMA systems: $\chi=0.090$ (acetone); 0.062 (2-butanone); 0.050 (2-pentanone); 0.023 (2-heptanone). These solutions are close to the ideal behavior in terms of the speed of sound.

Molecular interactions in liquid mixtures can be examined by means of the Rao's constant, R , [76] (also termed, molar sound velocity, $R\ =V_{\mathrm{m}}c^{1/3}$). If there is no association or if the degree of association is independent of the concentration, the Rao's constant shows a linear dependence on the molar fractions of the components ($R=x_1R_1+x_2R_2$) [76-78]. Systems characterized by complex formation show deviations from this behaviour [79]. For DMA solutions, the Rao's constant changes linearly with x_1 (Figure S2, supplementary material), and this suggests that association/solvatation effects can be neglected. The same occur in mixtures containing DMF.

6.5 Refractive indices

It is well known that n_{D} values of a liquid mixture can be used to calculate the molar refraction, R_{m} , of the system from the Lorentz-Lorentz equation [80, 81]:

$$R_{\mathrm{m}}=\frac{{n_{\mathrm{D}}}^{2}-1}{{n_{\mathrm{D}}}^{2}+2}V_{\mathrm{m}} \qquad (25)$$

This magnitude is closely related to the dispersion forces of the system under study, as n_{D} at optical wavelengths is related to the mean polarizability [81]. For pure amides, the values (in $\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1}$) are: 26.8 (NMP) > 24.3 (DMA) > 19.9 (DMF), and dispersive interactions decrease in the same order. For 2-alkanones, R_{m} /$\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1}$ = 16.1 (2-propanone) < 20.7 (2-butanone < 34.6 (2-heptanone). That is dispersive ketone-ketone interactions become more relevant when the 2-alkanone size is increased. Accordingly with these results: R_{m} also increases with u in DMF or DMA systems (Figure S3, supplementary material). Thus, R_{m} (DMA)/cm^3·mol^{-1} = 20.3 (2-propanone) < 22.5 (2-butanone) < 24.9 (2-pentanone) < 29.5 (2-heptanone), and R_{m} (DMF)/cm^3·mol^{-1} = 18.1 (2-propanone) < 20.4 (2-butanone) < 22.6 (2-pentanone) < 27.4 (2-heptanone). We also note that dispersive interactions are more relevant in DMA solutions than in those including DMF. Interestingly, the magnitude $P_{\mathrm{int}}V_{\mathrm{m}}$ has been proposed as a measure of the London dispersion energy, independently of the existence of strong specific interactions [82]. For DMA + 2-alkanone mixtures, $P_{\mathrm{int}}V_{\mathrm{m}}$ increases linearly with R_{m} (at equimolar composition), as $P_{\mathrm{int}}V_{\mathrm{m}} = 7.31 + 1.22R_{\mathrm{m}}$; ($r = 0.997$). In addition, $P_{\mathrm{int}}V_{\mathrm{m}}$ linearly decreases with $\bar{\mu}$ of 2-alkanones $P_{\mathrm{int}}V_{\mathrm{m}} = 68.57 - 30.56\bar{\mu}$; ($r = 0.986$). DMF mixtures show the same behavior [13] and one can conclude that that dispersive interactions become stronger when u is increased in the investigated systems.

6.5 Results from the Flory model

In spite of the few $H_{\mathrm{m}}^{\mathrm{E}}$ data available for the investigated systems, some interesting conclusions can be provided from the model application. (i) X_{12} increases with the chain length of the 2-alkanone in systems with a given amide (Table 7). In this theory, X_{12} is proportional to $\Delta\eta / v_s^*$, where v_s^* stands for the reduction volume for segment and $\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12}$. The η_{ij} magnitudes are positive and characterize the energy of interaction for a pair of neighbouring sites. As η_{11} remains constant, the mentioned X_{12} increase may be ascribed to η_{12} decreases more sharply than η_{22} does when u increases. The former is linked to a weakening of interactions between unlike molecules, the latter reflects a weakening of ketone-ketone interactions. (ii) Interestingly, the mean relative standard deviation for $H_{\mathrm{m}}^{\mathrm{E}}$ for DMF systems (0.052) is much lower than the value for NMP solutions (0.368). That is, it seems that orientational effects are much more relevant in the latter systems, while the random mixing hypothesis is held, in large extent, for mixtures including DMF. Accordingly, the concentration dependence of X_{12} is much weaker for DMF systems than for NMP solutions (Figure S1). (iii) As a trend, the model yields calculated $V_{\mathrm{m}}^{\mathrm{E}}$ values larger than the experimental values (Table 8), which may be due to the interactional contribution to this excess function is overestimated. Nevertheless, the variation of $V_{\mathrm{m}}^{\mathrm{E}}$ with u is correctly represented (Table 8). In fact, the model correctly correlates the $V_{\mathrm{m}}^{\mathrm{E}}$ data using X_{12} values determined from such measurements. (iv) $V_{\mathrm{m}}^{\mathrm{E}}$ data can be better examined by means of the Prigogine-Flory-Patterson model (PFP) [83], where $V_{\mathrm{m}}^{\mathrm{E}}$ is the result of the sum of three contributions: an interactional contribution, a curvature term and the so-called P^* term. The second one depends on $-(\bar{V}_1-\bar{V}_2)^2$ and is always negative. The latter depends on $(P_1^*-P_2^*)(\bar{V}_1-\bar{V}_2)$. For all the systems considered here, $P_1^*>P_2^*$; $\bar{V}_1<\bar{V}_2$ and the P^* term is always negative. Results included in Table 8 remarks the importance of structural effects in the investigated systems.

6.6 Comparison with other systems

Some volumetric data are available in the literature on *N*-alkylamide + 2-alkanone systems. Thus, $V_\mathrm{m}^\mathrm{E}(T$ = 303.15 K)/cm^3·mol^{-1} $= -$ 0.524 (*N*-methylformamide + 2-butanone) [84]; $-$ 0.499 (*N*-methylformamide + 2-pentanone) [85]; $-$ 0.434 (*N*-methylacetamide + 2-butanone) [86]. These values are lower than the corresponding results for systems with DMF or DMA and can be ascribed to the existence solvatation effects. Note that secondary amides are self-associated species and can form H-bonds with 2-alkanones [87].

Conclusions

Data on ρ, c, n_D, at have been reported, at different temperatures, for the systems DMA + $CH_3CO(CH_2)_{u-1}CH_3$ (u = 1,2,3,5). From these data, the excess functions $V_\mathrm{m}^\mathrm{E}, \kappa_S^E$ and c^E have been determined. Negative V_m^E values reveal the existence of structural effects and interactions between unlike molecules. From calorimetric data available in the literature, it is shown that the mentioned interactions are stronger in systems with DMF than in NMP solutions, and become weaker when u increases in systems with a given amide. Structural effects largely contribute to H_m^E. They are more relevant in mixtures containing NMP. The application of the Flory's model shows that the random mixing hypothesis is valid in large extent for DMF solutions, while NMP systems are characterized by rather strong orientational effects. From the $P_\mathrm{int}V_\mathrm{m}$ and R_m values, it is concluded that dispersive interactions become more relevant for the systems with longer 2-alkanones, or when DMF is replaced by DMA in mixtures with a given ketone.

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TABLE 1

Sample description

Chemical	CAS number	Source	Purity[a]	Analysis method
N,*N*-dimethylacetamide	127-19-5	Sigma-Aldrich	≥ 0.995	GC[b]
Propanone	67-64-1	Sigma-Aldrich	≥ 0.998	HPLC[c]
2-butanone	78-93-3	Fluka	≥ 0.995	GC[b]
2-pentanone	107-87-9	Sigma-Aldrich	≥ 0.98	FCC[d]
2-heptanone	110-43-0	Sigma-Aldrich	≥ 0.99	GC[b]

[a] in mass fraction; [b] gas chromatography; [c] High-performance liquid chromatography [d] flash column chromatography

TABLE 2

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

Property/T	N,N-dimethylacetamide	2-propanone	2-butanone	2-pentanone	2-heptanone
ρ/g cm^{-3}					
T/K=293.15	0.94101 0.9410[88]	0.79018 0.790546[89] 0.78998[40]	0.80512 0.80495[90] 0.8049[40] 0.805058[92]	0.80654 0.806322[91] 0.8064[40] 0.80626[90]	0.81557 0.81537[40]
T/K=298.15	0.93639 0.93634[93]	0.78441 0.784431[54] 0.7844[40]	0.79977 0.79974[90] 0.7997[40]	0.80166 0.801522[91] 0.8015[40] 0.80142[90]	0.81119 0.81123[40] 0.81093[94]
T/K=303.15	0.93173 0.93166[93] 0.93162[95]	0.77876 0.77966[90] 0.77863[13]	0.79465 0.79448[90] 0.7946[40] 0.794565[92]	0.79688 0.796723[91] 0.79658[90]	0.80698 0.806827[24]
c/m s^{-1}					
T/K=293.15	1475.3 1478.98[93]	1182.0 1182.5[89] 1185[90]	1212.1 1212.3[96] 1213[90]	1232.5 1231.65[91] 1233[90]	1282.3 1281.92[24]
T/K=298.15	1456.0 1455.91[93] 1456.42[95] 1458[97]	1164.2 1162.0[96] 1161.7[54] 1163.9[98]	1190.8 1191.6[96] 1192[90]	1211.8 1211.17[91] 1213[90]	1263.0 1262.49[24]
T/K=303.15	1435.9 1435.55[93]	1139.3 1139.2[89] 1140[90]	1170.9 1171[90]	1192.3 1191.79[91] 1192[90]	1244.7 1244.14[24]
α_p/10^{-3}K^{-1}					
T/K=298.15	0.98 0.960[99]	1.46 1.45[89] 1.46[92]	1.31 1.31[90]	1.2 1.22[40] 1.21[92]	1.06 1.06[40]

TABLE 2 (continued)

κ_S/TPa^{-1}					
T/K=293.15	488.34	905.81 904.66[89] 900[92]	845.40 844[90]	816.21 816[90]	745.69 746.26[24]
T/K=298.15	503.68 503.85[93]	940.64 946[100] 944.6[50] 941.1[98]	881.77 880[90]	849.47 849[90] 848[92]	772.76 773.48[24]
T/K=303.15	520.25 516[101]	989.28 988.80[89]	917.88 917.9[102] 918[90]	882.75 884[90]	799.91 800.71[24]
κ_T/TPa^{-1}					
T/K=298.15	656.7 671[103]	1315.7 1324[40]	1171.9 1175.9[102] 1188[36]	1098.3 1092[40]	967.2 957[40]
$C_{p,\mathrm{m}}$/J mol^{-1} K^{-1}					
T/K=298.15	175.5[104]	125.45[90]	159[105]	185.4[106]	242.54[94]
n_D					
T/K=293.15	1.43845 1.4384[40]	1.35854 1.35868[40] 1.3584[107]	1.37839 1.3788[40]	1.39016 1.39080[40]	
T/K=298.15	1.43621 1.4357][108] 1.4359[112] 1.4364[113]	1.35386 1.35597[109]	1.37612 1.3764[110] 1.3767[111]	1.38773 1.3885[111]	1.40688 1.40655[40]
T/K=303.15	1.43367 1.4342[113]	1.35323	1.37351 1.3740[114]	1.38530	

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[a] ρ, density; c, speed of sound; α_p, isobaric thermal expansion coefficient; κ_S, adiabatic compressibility; κ_T, isothermal compressibility; $C_{p,\mathrm{m}}$, isobaric molar heat capacity and n_D, refractive index of pure components. Relative standard uncertainties, u_r, are: $u_r(\rho^*) = 0.0012$; $u_r(c^*) = 0.0004$; $u_r(\alpha_p) = 0.028$; $u_r(\kappa_S^*) = 0.002$; $u_r(\kappa_T^*) = 0.015$; $u_r(n_D^*) = 0.0015$; standard uncertainties for temperature and pressure are $u(T) = 0.02\mathrm{K}$ $u(T) = 0.02\mathrm{K}$ (for n_D values, $u(T) = 0.02\mathrm{K}$); and $u(\rho) = 1\mathrm{kPa}$.

TABLE 3

Densities, ρ, speeds of sound, c, adiabatic compressibility, κ_S , and molar excess volumes, $V_m{}^E$,

for *N*,*N*-dimethylacetamide (1) + 2-alkanone (2) mixtures at temperature T and 0.1 MPa.

x_1	ρ / gcm^{-}3	c / ms^{-1}	κ_S / TPa^{-1}	$V_m{}^E$ / cm^{3}mol^{-1}	x_1	ρ / gcm^{-}3	c / ms^{-1}	κ_S / TPa^{-1}	$V_m{}^E$ / cm^{3}mol^{-1}
N,*N*-dimethylacetamide (1) + 2-propanone (2) T/K= 293.15									
0.0000	0.79018	1182.0	905.81	0.0000	0.5524	0.88569	1358.0	612.24	– 0.3588
0.0558	0.80177	1201.8	863.55	– 0.1066	0.5974	0.89201	1370.9	596.51	– 0.3458
0.1019	0.81090	1217.7	831.67	– 0.1740	0.6502	0.89910	1385.2	579.65	– 0.3151
0.1470	0.81947	1232.9	802.81	– 0.2239	0.7022	0.90595	1399.4	563.65	– 0.2881
0.2021	0.82962	1251.1	770.08	– 0.2778	0.7502	0.91209	1412.3	549.68	– 0.2592
0.2523	0.83856	1267.4	742.40	– 0.3194	0.8004	0.91813	1425.0	536.37	– 0.2057
0.2991	0.84651	1282.2	718.55	– 0.3398	0.8538	0.92453	1438.6	522.64	– 0.1609
0.3525	0.85539	1298.9	692.92	– 0.3650	0.8980	0.92965	1449.7	511.83	– 0.1177
0.3991	0.86282	1313.2	672.08	– 0.3739	0.9468	0.93513	1461.6	500.58	– 0.0643
0.4452	0.86994	1327.1	652.68	– 0.3759	1.0000	0.94091	1474.2	489.03	0.0000
0.4994	0.87804	1342.8	631.63	– 0.3709					
N,*N*-dimethylacetamide (1) +2-propanone (2) T/K= 298.15									
0.0000	0.78441	1164.2	940.64	0.0000	0.5547	0.88094	1343.9	628.55	– 0.3716
0.0549	0.79597	1184.2	895.93		0.6113	0.88889	1360.2	608.10	– 0.3519
0.1023	0.80533	1200.5	861.54	– 0.1789	0.6531	0.89464	1372.1	593.73	– 0.3378
0.1573	0.81599	1219.6	823.94	– 0.2573	0.7026	0.90105	1385.4	578.21	– 0.2963
0.2021	0.82421	1234.6	795.95	– 0.2964	0.7528	0.90760	1399.3	562.68	
0.2522	0.83319	1251.2	766.65	– 0.3387	0.7985	0.91314	1411.1	549.99	– 0.2225
0.2989	0.84118	1266.2	741.47	– 0.3595	0.8470	0.91890	1423.5	537.09	– 0.1699
0.3512	0.84993	1283.0	714.74	– 0.3842	0.9009	0.92523	1437.2	523.25	– 0.1179
0.3995	0.85775	1298.0	692.00	– 0.3991	0.9441	0.93022	1448.2	512.56	– 0.0790
0.4457	0.86490	1312.1	671.63	– 0.3977	1.0000	0.93625	1461.5	500.05	0.0000

TABLE 3 (continued)

0.4963	0.87248	1327.0	650.88	– 0.3890					

N,*N*-dimethylacetamide (1) + 2-propanone (2) T/K= 303.15

0.0000	0.77876	1139.3	989.28	0.0000	0.5524	0.87586	1318.9	656.36	– 0.4060
0.0558	0.79051	1159.5	940.92	– 0.1146	0.5974	0.88221	1331.7	639.17	– 0.3854
0.1019	0.79982	1175.6	904.67	– 0.1922	0.6502	0.88949	1346.4	620.17	– 0.3605
0.1470	0.80859	1191.3	871.42	– 0.2536	0.7022	0.89635	1360.5	602.73	– 0.3220
0.2021	0.81888	1209.9	834.22	– 0.3112	0.7502	0.90252	1373.7	587.16	– 0.2844
0.2523	0.82795	1226.8	802.51	– 0.3559	0.8004	0.90870	1386.4	572.54	– 0.2319
0.2991	0.83609	1241.7	775.74	– 0.3851	0.8538	0.91523	1400.3	557.22	– 0.1866
0.3525	0.84512	1258.7	746.86	– 0.4140	0.8980	0.92050	1411.7	545.12	– 0.1470
0.3991	0.85263	1273.1	723.63	– 0.4206	0.9468	0.92597	1423.5	532.95	– 0.0801
0.4452	0.85985	1287.2	701.92	– 0.4222	1.0000	0.93173	1436.0	520.48	0.0000
0.4994	0.86808	1303.4	678.09	– 0.4176					

N,*N*-dimethylacetamide (1) + 2-butanone (2) T/K= 293.15

0.0000	0.80512	1212.1	845.40	0.0000	0.5510	0.88334	1358.1	613.77	– 0.2290
0.0585	0.81389	1227.8	815.04	– 0.0625	0.5993	0.88979	1370.6	598.26	– 0.2195
0.1098	0.82153	1241.6	789.61		0.6556	0.89724	1385.4	580.69	– 0.2043
0.1550	0.82802	1253.3	768.86	– 0.1343	0.7049	0.90371	1398.3	565.94	– 0.1880
0.2085	0.83580	1267.5	744.73	– 0.1715	0.7570	0.91041	1411.9	551.00	– 0.1596
0.2537	0.84222	1279.4	725.37	– 0.1884	0.8008	0.91605	1423.4	538.80	– 0.1385
0.3022	0.84912	1292.3	705.19	– 0.2098	0.8488	0.92223	1436.1	525.76	– 0.1175
0.3501	0.85581	1305.3	685.81	– 0.2197	0.9052	0.92940	1450.9	511.12	– 0.0866
0.3997	0.86270	1318.0	667.28	– 0.2282	0.9469	0.93449	1461.5	500.99	– 0.0448
0.4566	0.87053	1333.1	646.38	– 0.2330	1.0000	0.94103	1475.3	488.24	0.0000
0.5019	0.87670	1344.9	630.62	– 0.2324					

TABLE 3 (continued)

N,*N*-dimethylacetamide (1) + 2-butanone (2) *T*/K= 298.15

0.0000	0.79977	1190.8	881.77	0.0000	0.5412	0.87713	1335.1	639.60	− 0.2450
0.0551	0.80810	1205.7	851.25	− 0.0641	0.6016	0.88529	1351.1	618.78	− 0.2376
0.1073	0.81591	1219.8	823.72	− 0.1176	0.6560	0.89249	1365.4	601.00	− 0.2184
0.1536	0.82269	1232.1	800.70	− 0.1505	0.7067	0.89915	1378.8	585.01	− 0.1979
0.2041	0.83005	1245.7	776.37	− 0.1843	0.7524	0.90509	1390.8	571.19	− 0.1751
0.2536	0.83718	1258.8	753.82	− 0.2103	0.8052	0.91194	1404.8	555.65	− 0.1500
0.2936	0.84287	1269.4	736.28	− 0.2250	0.8521	0.91791	1417.0	542.58	− 0.1183
0.3473	0.85044	1283.6	713.67	− 0.2395	0.9056	0.92466	1431.0	528.13	− 0.0788
0.4052	0.85850	1299.0	690.31	− 0.2471	0.9459	0.92971	1441.5	517.63	− 0.0475
0.4522	0.86500	1311.5	672.12	− 0.2510	1.0000	0.93641	1455.6	504.02	0.0000
0.4958	0.87095	1323.0	655.97	− 0.2479					

N,*N*-dimethylacetamide (1) + 2-butanone (2) *T*/K= 303.15

0.0000	0.79465	1170.9	917.88	0.0000	0.5418	0.87242	1330.1	647.90	− 0.2543
0.0549	0.80298	1189.2	880.61	− 0.0657	0.6085	0.88143	1347.5	624.82	− 0.2418
0.1048	0.81039	1205.2	849.55	− 0.1089	0.6488	0.88677	1356.1	613.20	− 0.2253
0.1512	0.81725	1219.9	822.24	− 0.1472	0.7015	0.89370	1369.5	596.60	− 0.2006
0.2033	0.82482	1235.7	793.99	− 0.1773	0.7563	0.90092	1382.7	580.57	− 0.1792
0.2506	0.83166	1249.6	770.04	− 0.2029	0.7981	0.90631	1392.1	569.35	− 0.1526
0.3050	0.83950	1265.6	743.68	− 0.2315	0.8467	0.91259	1402.5	557.08	− 0.1252
0.3451	0.84521	1276.9	725.64	− 0.2465	0.8954	0.91874	1414.2	544.23	− 0.0855
0.3958	0.85231	1291.4	703.53	− 0.2546	0.9441	0.92489	1423.6	533.50	− 0.0481
0.4492	0.85976	1306.2	681.72	− 0.2624	1.0000	0.93187	1436.2	520.25	0.0000
0.4871	0.86497	1315.7	667.86	− 0.2612					

TABLE 3 (continued)

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 293.15

0.0000	0.80654	1232.5	816.21	0.0000	0.5550	0.87800	1356.7	618.78	− 0.1797
0.0530	0.81307	1243.3	795.65	− 0.0402	0.6075	0.88514	1369.6	602.28	− 0.1713
0.1061	0.81966	1254.5	775.22	− 0.0735	0.6513	0.89116	1380.8	588.55	− 0.1624
0.1551	0.82579	1264.9	756.86	− 0.0997	0.6982	0.89763	1393.2	573.95	
0.2004	0.83149	1274.7	740.16	− 0.1190	0.7407	0.90361	1403.8	561.58	− 0.1365
0.2552	0.83848	1287.0	720.03	− 0.1401	0.7992	0.91192	1419.5	544.22	− 0.1178
0.3070	0.84515	1298.3	701.97	− 0.1567	0.8532	0.91960	1434.0	528.81	− 0.0884
0.3637	0.85253	1311.2	682.26	− 0.1706	0.9004	0.92645	1447.1	515.44	− 0.0664
0.4083	0.85837	1321.5	667.10	− 0.1763	0.9439	0.93271	1459.1	503.60	− 0.0319
0.4566	0.86477	1333.0	650.79	− 0.1802	1.0000	0.94101	1475.2	488.32	0.0000
0.5013	0.87074	1343.6	636.17	− 0.1813					

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 298.15

0.0000	0.80166	1211.8	849.47	0.0000	0.5497	0.87265	1335.5	642.50	− 0.2002
0.0540	0.80832	1223.0	827.11	− 0.0414	0.6041	0.88007	1348.9	624.49	− 0.1930
0.1037	0.81457	1233.6	806.72	− 0.0834	0.6373	0.88465	1357.5	613.41	− 0.1879
0.1497	0.82034	1243.5	788.34	− 0.1100	0.6983	0.89309	1373.1	593.88	− 0.1686
0.2016	0.82693	1254.7	768.16	− 0.1386	0.7431	0.89936	1384.9	579.74	− 0.1519
0.2553	0.83381	1266.3	747.93	− 0.1629	0.7979	0.90714	1399.3	562.99	− 0.1312
0.2990	0.83945	1276.3	731.31	− 0.1781	0.8446	0.91383	1412.2	548.71	− 0.1095
0.3427	0.84513	1286.4	715.03	− 0.1895	0.8957	0.92124	1426.3	533.59	− 0.0842
0.3951	0.85199	1298.6	696.01	− 0.1978	0.9392	0.92753	1438.4	521.09	− 0.0518
0.4452	0.85862	1310.3	678.36	− 0.2027	1.0000	0.93639	1455.5	504.10	0.0000
0.4986	0.86576	1323.0	659.91	− 0.2041					

TABLE 3 (continued)

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 303.15

0.0000	0.79688	1192.3	882.75	0.0000	0.5495	0.86798	1316.5	664.74	− 0.2150
0.0535	0.80355	1203.6	859.06	− 0.0512	0.5945	0.87410	1327.4	649.28	− 0.2070
0.0989	0.80923	1213.4	839.31	− 0.0865	0.6408	0.88047	1339.2	633.28	− 0.1976
0.1528	0.81603	1225.0	816.62	− 0.1232	0.6965	0.88823	1353.4	614.64	− 0.1843
0.2015	0.82226	1235.4	796.85	− 0.1556	0.7468	0.89529	1366.7	597.98	− 0.1661
0.2532	0.82887	1247.2	775.61	− 0.1773	0.7993	0.90273	1380.4	581.34	− 0.1427
0.3051	0.83556	1258.7	755.40	− 0.1935	0.8450	0.90926	1393.0	566.77	− 0.1181
0.3498	0.84140	1269.2	737.80	− 0.2072	0.9015	0.91740	1408.4	549.53	− 0.0820
0.3969	0.84757	1280.2	719.89	− 0.2136	0.9476	0.92407	1421.3	535.70	− 0.0451
0.4491	0.85446	1292.2	700.89	− 0.2151	1.0000	0.93173	1435.9	520.55	0.0000
0.4998	0.86125	1304.3	682.52	− 0.2164					

N,*N*-dimethylacetamide (1) + 2-heptanone (2) *T*/K= 298.15

0.0000	0.81119	1263.0	772.76	0.0000	0.5571	0.86810	1345.0	636.81	− 0.0051
0.0578	0.81613	1270.0	759.67	− 0.0087	0.6080	0.87466	1354.9	622.76	− 0.0067
0.1069	0.82044	1276.0	748.62	− 0.0109	0.6492	0.88020	1363.6	611.03	− 0.0107
0.1570	0.82502	1282.3	737.10	− 0.0161	0.6981	0.88699	1374.2	597.00	− 0.0092
0.2088	0.82984	1289.1	725.13	− 0.0071	0.7499	0.89455	1386.2	581.78	− 0.0115
0.2529	0.83418	1295.1	714.67	− 0.0126	0.8011	0.90234	1398.8	566.42	− 0.0092
0.3080	0.83970	1303.0	701.38	− 0.0052	0.8520	0.91047	1412.1	550.79	− 0.0082
0.3485	0.84399	1309.3	691.17	− 0.0114	0.9015	0.91879	1426.0	535.22	− 0.0104
0.4006	0.84961	1317.4	678.14	− 0.0050	0.9516	0.92755	1440.7	519.40	− 0.0035
0.4484	0.85472	1324.8	666.58		1.0000	0.93646	1456.0	503.68	0.0000
0.5048	0.86163	1335.1	651.09						

Uncertainties are: $u(x_1) = 0.0001$; $u(p) = 1\text{kPa}$; $u(T) = 0.01\text{K}$; and the combined expanded uncertainties (0.95 level of confidence) are: $U_{rc}(\rho) = 0.020\text{kgm}^{-3}$; $U_{rc}(c) = 0.2\text{ms}^{-1}$; $U_{rc}(\kappa_S) = 0.02\text{TPa}^{-1}$; $U_{rc}(V_m{}^E) = (0.02\,|V_{\text{m,max}}{}^{\text{E}}| + 0.005)\,\text{cm}^3\ \text{mol}^{-1}$.

TABLE 4

Isobaric thermal expansion coefficient, α_p, and excess functions, at 298.15 K and 0.1 MPa, for adiabatic compressibility, κ_S, speed of sound, c, and isobaric thermal expansion coefficient, α_p^{E}, of *N*,*N*-dimethylacetamide (1) + 2-alkanone (2) mixtures.

x_1	α_p / 10^{-3} K^{-1}	κ_S^{E} / TPa^{-1}	c^{E} / ms^{-1}	α_p^{E} / 10^{-3} K^{-1}	x_1	α_p / 10^{-3} K^{-1}	κ_S^{E} / TPa^{-1}	c^{E} / ms^{-1}	α_p^{E} / 10^{-3} K^{-1}
N,*N*-dimethylacetamide (1) + 2-propanone (2) *T*/K= 298.15									
0.0000	1.46	0.0	0.0	0.000	0.5547	1.12	− 58.7	55.8	− 0.050
0.0549	1.41	− 19.1	11.6	− 0.019	0.6113	1.09	− 54.4	54.4	− 0.047
0.1023	1.37	− 31.4	19.9	− 0.029	0.6531	1.08	− 50.6	52.4	− 0.044
0.1573	1.33	− 43.5	29.0	− 0.037	0.7026	1.06	− 44.8	48.5	− 0.041
0.2021	1.30	− 50.7	35.2	− 0.043	0.7528	1.04	− 39.1	44.1	− 0.036
0.2522	1.27	− 56.9	41.4	− 0.047	0.7985	1.03	− 32.5	38.3	− 0.031
0.2989	1.24	− 60.6	46.0	− 0.050	0.8470	1.01	− 25.3	31.1	− 0.026
0.3512	1.21	− 63.5	50.5	− 0.052	0.9009	1.00	− 16.9	21.7	− 0.018
0.3995	1.19	− 64.4	53.4	− 0.052	0.9441	0.99	− 10.0	12.0	− 0.011
0.4457	1.17	− 64.0	55.4	− 0.052	1.0000	0.98	0.0	0.0	0.000
0.4963	1.14	− 62.1	56.2	− 0.052					
N,*N*-dimethylacetamide (1) + 2-butanone (2) *T*/K= 298.15									
0.0000	1.31	0.0	0.0	0.000	0.5412	1.10	− 42.0	40.1	− 0.027
0.0551	1.29	− 10.7	7.1	− 0.004	0.6016	1.08	− 39.8	39.8	− 0.024
0.1073	1.27	− 19.4	13.3	− 0.007	0.6560	1.07	− 36.7	38.3	− 0.021
0.1536	1.25	− 25.5	18.1	− 0.011	0.7067	1.06	− 33.2	36.1	− 0.017
0.2041	1.23	− 31.3	23.2	− 0.015	0.7524	1.05	− 29.4	33.2	− 0.013
0.2536	1.20	− 35.6	27.3	− 0.019	0.8052	1.03	− 24.5	28.8	− 0.009
0.2936	1.19	− 38.4	30.3	− 0.022	0.8521	1.02	− 19.3	23.7	− 0.005
0.3473	1.17	− 41.0	33.7	− 0.026	0.9056	1.01	− 12.9	16.6	− 0.002
0.4052	1.15	− 42.7	36.7	− 0.028	0.9459	1.00	− 7.6	9.9	− 0.001
0.4522	1.13	− 43.2	38.4	− 0.028	1.0000	0.98	0.0	0.0	0.000
0.4958	1.12	− 42.9	39.5	− 0.028					

TABLE 4 (continued)

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 298.15

0.0000	1.20	0.0	0.0	0.000	0.5497	1.06	−33.8	32.5	−0.030
0.0540	1.18	−6.9	4.9	−0.008	0.6041	1.05	−32.6	32.6	−0.030
0.1037	1.16	−12.8	9.2	−0.016	0.6373	1.04	−31.8	32.6	−0.030
0.1497	1.15	−17.5	13.0	−0.022	0.6983	1.03	−29.0	31.2	−0.029
0.2016	1.14	−22.0	16.8	−0.026	0.7431	1.02	−26.4	29.4	−0.028
0.2553	1.12	−25.6	20.2	−0.029	0.7979	1.01	−22.2	25.9	−0.026
0.2990	1.11	−28.5	23.1	−0.030	0.8446	1.00	−18.4	22.2	−0.023
0.3427	1.10	−30.8	25.7	−0.030	0.8957	1.00	−13.2	16.7	−0.018
0.3951	1.09	−32.8	28.3	−0.030	0.9392	0.99	−8.1	11.6	−0.012
0.4452	1.08	−33.8	30.1	−0.030	1.0000	0.99	0.0	0.0	0.000
0.4986	1.07	−34.1	31.6	−0.030					

N,*N*-dimethylacetamide (1) + 2-heptanone (2) *T*/K= 298.15

0.0000	1.06	0.0	0.0		0.5571		−15.3	15.8	
0.0578		−2.9	2.3		0.6080		−15.3	16.2	
0.1069		−4.8	4.1		0.6492		−15.1	16.5	
0.1570		−6.8	5.7		0.6981		−14.5	16.3	
0.2088		−8.4	7.4		0.7499		−13.4	15.7	
0.2529		−9.8	8.7		0.8011		−11.9	14.4	
0.3080		−11.3	10.3		0.8520		−9.8	12.4	
0.3485		−12.5	11.6		0.9015		−7.3	9.6	
0.4006		−13.5	12.8		0.9516		−3.9		
0.5048		−14.8	14.9		1.0000	0.98	0.0	0.0	

Uncertainties are: $u(x_1) = 0.0001$; $u(\rho) = 1\text{kPa}$; $u(T) = 0.01\text{K}$; and the combined expanded uncertainties (0.95 level of confidence) are: $U_{rc}(\kappa_S{}^{\text{E}}) = 0.04\,|\,\kappa_S{}^{\text{E}}\,|$, $U_{rc}(c^{\text{E}}) = 0.030\,|\,c^{\text{E}}\,|$ and $U_{rc}(\alpha_p{}^{\text{E}}) = 0.005 \cdot 10^{-3}\,\text{K}^{-1}$.

TABLE 5

Excess refractive indices, n_{D}, and the corresponding excess values, $n_{\mathrm{D}}^{\mathrm{E}}$ of *N,N*-dimethylacetamide (1) + 2-alkanone(2) mixtures at temperature *T* and 0.1 MPa.

x_1	n_{D}	$n_{\mathrm{D}}^{\mathrm{E}}$	x_1	n_{D}	$n_{\mathrm{D}}^{\mathrm{E}}$
N,N-dimethylacetamide (1) + 2-propanone (2) *T*/K= 293.15					
0.0000	1.35854	0.00000	0.5524	1.40923	0.00188
0.0558	1.36466	0.00047	0.5974	1.41257	0.00184
0.1019	1.36946	0.00074	0.6502	1.41638	0.00179
0.1470	1.37405	0.00102	0.7022	1.41997	0.00167
0.2021	1.37947	0.00132	0.7502	1.42313	0.00148
0.2523	1.38417	0.00149	0.8004	1.42638	0.00131
0.2991	1.38840	0.00161	0.8538	1.42966	0.00105
0.3525	1.39306	0.00170	0.8980	1.43235	0.00087
0.3991	1.39704	0.00181	0.9468	1.43514	0.00057
0.4452	1.40083	0.00185	1.0000	1.43787	0.00000
0.4994	1.40517	0.00190			
N,N-dimethylacetamide (1) + 2-propanone (2) *T*/K= 298.15					
0.0000	1.35386	0.00000	0.5547	1.40776	0.00254
0.0549	1.36261	0.00112	0.6113	1.41169	0.00220
0.1023	1.36813	0.00195	0.6531	1.41456	0.00199
0.1573	1.37400	0.00254	0.7026	1.41776	0.00163
0.2021	1.37850	0.00286	0.7528	1.42098	0.00133
0.2522	1.38334	0.00315	0.7985	1.42383	0.00104
0.2989	1.38759	0.00327	0.8470	1.42680	0.00076
0.3512	1.39211	0.00328	0.9009	1.43002	0.00045
0.3995	1.39607	0.00319	0.9441	1.43258	0.00024
0.4457	1.39965	0.00300	1.0000	1.43584	0.00000
0.4963	1.40353	0.00284			

TABLE 5 (continued)

N,*N*-dimethylacetamide (1) + 2-propanone (2) *T*/K= 303.15					
0.0000	1.35323	0.00000	0.5524	1.40488	0.00222
0.0558	1.35961	0.00067	0.5974	1.40820	0.00211
0.1019	1.36462	0.00111	0.6502	1.41197	0.00195
0.1470	1.36938	0.00150	0.7022	1.41546	0.00167
0.2021	1.37479	0.00174	0.7502	1.41864	0.00145
0.2523	1.37966	0.00202	0.8004	1.42186	0.00119
0.2991	1.38411	0.00230	0.8538	1.42521	0.00094
0.3525	1.38875	0.00231	0.8980	1.42797	0.00078
0.3991	1.39281	0.00244	0.9468	1.43070	0.00036
0.4452	1.39655	0.00238	1.0000	1.43370	0.00000
0.4994	1.40081	0.00229			
N,*N*-dimethylacetamide (1) + 2-butanone (2) *T*/K= 293.15					
0.0000	1.37839	0.00000	0.5510	1.41334	0.00123
0.0585	1.38245	0.00038	0.5993	1.41615	0.00117
0.1098	1.38591	0.00063	0.6556	1.41937	0.00108
0.1550	1.38890	0.00081	0.7049	1.42219	0.00101
0.2085	1.39238	0.00099	0.7570	1.42511	0.00090
0.2537	1.39528	0.00111	0.8008	1.42752	0.00077
0.3022	1.39832	0.00118	0.8488	1.43016	0.00065
0.3501	1.40127	0.00121	0.9052	1.43319	0.00044
0.3997	1.40432	0.00126	0.9469	1.43532	0.00020
0.4566	1.40775	0.00127	1.0000	1.43814	0.00000
0.5019	1.41045	0.00126			
N,*N*-dimethylacetamide (1) + 2-butanone (2) *T*/K= 298.15					
0.0000	1.37612	0.00000	0.5412	1.41035	0.00099
0.0551	1.37995	0.00035	0.6016	1.41383	0.00088
0.1073	1.38349	0.00062	0.6560	1.41693	0.00076
0.1536	1.38656	0.00081	0.7067	1.41979	0.00064

TABLE 5 (continued)

0.2041	1.38982	0.00093	0.7524	1.42236	0.00054
0.2536	1.39299	0.00105	0.8052	1.42531	0.00041
0.2936	1.39551	0.00112	0.8521	1.42792	0.00031
0.3473	1.39882	0.00115	0.9056	1.43088	0.00018
0.4052	1.40231	0.00112	0.9459	1.43311	0.00011
0.4522	1.40512	0.00110	1.0000	1.43609	0.00000
0.4958	1.40768	0.00103			

N,*N*-dimethylacetamide (1) + 2-butanone (2) *T*/K= 303.15

0.0000	1.37351	0.00000	0.5948	1.41061	0.00057
0.0672	1.37816	0.00041	0.6587	1.41429	0.00046
0.1269	1.38214	0.00064	0.6964	1.41644	0.00038
0.1810	1.38566	0.00079	0.7447	1.41921	0.00031
0.2406	1.38944	0.00088	0.7940	1.42201	0.00023
0.2933	1.39272	0.00092	0.8307	1.42411	0.00019
0.3526	1.39633	0.00089	0.8727	1.42649	0.00013
0.3955	1.39891	0.00086	0.9140	1.42882	0.00008
0.4485	1.40206	0.00080	0.9545	1.43111	0.00004
0.5031	1.40527	0.00072	1.0000	1.43368	0.00000
0.5410	1.40749	0.00066			

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 293.15

0.0000	1.39016	0.00000	0.5550	1.41614	0.00069
0.0530	1.39259	0.00016	0.6075	1.41871	0.00068
0.1061	1.39501	0.00027	0.6513	1.42087	0.00066
0.1551	1.39726	0.00037	0.6982	1.42319	0.00062
0.2004	1.39936	0.00046	0.7407	1.42532	0.00060
0.2552	1.40190	0.00053	0.7992	1.42826	0.00052
0.3070	1.40431	0.00058	0.8532	1.43100	0.00043
0.3637	1.40698	0.00064	0.9004	1.43339	0.00032
0.4083	1.40909	0.00066	0.9439	1.43560	0.00020

TABLE 5 (continued)

0.4566	1.41140	0.00069	1.0000	1.43845	0.00000
0.5013	1.41354	0.00069			

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 298.15

0.0000	1.38773	0.00000	0.5497	1.41368	0.00083
0.0540	1.39022	0.00017	0.6041	1.41634	0.00081
0.1037	1.39252	0.00030	0.6373	1.41799	0.00081
0.1497	1.39466	0.00042	0.6983	1.42102	0.00077
0.2016	1.39707	0.00052	0.7431	1.42326	0.00071
0.2553	1.39958	0.00060	0.7979	1.42601	0.00063
0.2990	1.40163	0.00066	0.8446	1.42837	0.00053
0.3427	1.40371	0.00072	0.8957	1.43095	0.00040
0.3951	1.40621	0.00077	0.9392	1.43314	0.00025
0.4452	1.40862	0.00081	1.0000	1.43621	0.00000
0.4986	1.41120	0.00083			

N,*N*-dimethylacetamide (1) + 2-pentanone (2) *T*/K= 303.15

0.0000	1.38530	0.00000	0.5495	1.41121	0.00087
0.0535	1.38778	0.00019	0.5945	1.41343	0.00088
0.0989	1.38990	0.00034	0.6408	1.41571	0.00086
0.1528	1.39242	0.00049	0.6965	1.41847	0.00082
0.2015	1.39467	0.00058	0.7468	1.42099	0.00077
0.2532	1.39708	0.00066	0.7993	1.42364	0.00071
0.3051	1.39952	0.00074	0.8450	1.42596	0.00063
0.3498	1.40164	0.00080	0.9015	1.42877	0.00044
0.3969	1.40386	0.00082	0.9476	1.43108	0.00027
0.4491	1.40636	0.00085	1.0000	1.43367	0.00000
0.4998	1.40880	0.00087			

TABLE 5 (continued)

N,*N*-dimethylacetamide (1) + 2-heptanone (2) *T*/K= 298.15

0.0000	1.40691	0.00000	0.5571	1.42057	0.00031
0.0578	1.40811	0.00005	0.6080	1.42209	0.00030
0.1069	1.40917	0.00010	0.6492	1.42337	0.00030
0.1570	1.41027	0.00013	0.6981	1.42495	0.00029
0.2088	1.41146	0.00017	0.7499	1.42668	0.00027
0.2529	1.41250	0.00020	0.8011	1.42846	0.00024
0.3080	1.41384	0.00023	0.8520	1.43031	0.00020
0.3485	1.41485	0.00024	0.9015	1.43218	0.00014
0.4006	1.41621	0.00028	0.9516	1.43416	0.00008
0.4484	1.41749	0.00029	1.0000	1.43615	0.00000
0.5048	1.41905	0.00030			

Uncertainties are: $u(T) = 0.02\mathrm{K}$; $u(p) = 1\mathrm{kPa}$; $u(x_1) = 0.0001$; $u(n_\mathrm{D}) = 0.00002$; the combined expanded uncertainty (0.95 level of confidence) is $U_{rc}(n_\mathrm{D}{}^\mathrm{E}) = 0.02 n_\mathrm{D}{}^\mathrm{E}$.

TABLE 6

Coefficients A_i and standard deviations, $\sigma(F^{\mathrm{E}})$ Eq. (9) for representation of the $F^{\mathrm{E,a}}$ property at 298.15 K and 0.1 MPa for *N*,*N*-dimethylacetamide (1) + 2-alkanone (2) systems by Eq. (7).

System	T / K	Property F^{E}	A_0	A_1	A_2	A_3	$\sigma(F^{\mathrm{E}})$
DMA + 2-propanone	293.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 1.484	0.345	– 0.137		0.003
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.00751	0.00033	0.00193		0.00004
	298.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 1.561	0.391	– 0.15		0.004
		c^{E}	225.3	15.4	7.3		0.3
		$\kappa_{\mathrm{S}}^{\mathrm{E}}$	– 248.0	94.2	– 30.4		0.2
		α_p^{E}	– 0.2047	0.0467	– 0.0786	0.0387	0.0007
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.01127	– 0.00960	0.00269		0.00003
	303.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 1.668	0.369	– 0.185		0.004
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.00938	– 0.00300			0.00005
DMA + 2-butanone	293.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 0.928	0.108	– 0.101		0.003
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.005025	– 0.000981	0.001119		0.000017
	298.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 0.9996	0.1589	– 0.1164		0.0018
		c^{E}	158.34	34.09	11.00		0.08
		$\kappa_{\mathrm{S}}^{\mathrm{E}}$	– 171.37	29.17	– 8.01	4.27	0.06
		α_p^{E}	– 0.1117	0.0302	0.0988		0.0004
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.004172	– 0.00268	0.00028		0.00001
	303.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 1.037	0.140			0.003
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.002905	– 0.003135	0.001074		0.000005
DMA + 2-pentanone	293.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 0.7277	0.0294			0.0019
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.002760	0.000336	0.000766		0.000008
	298.15	$V_{\mathrm{m}}^{\mathrm{E}}$	– 0.8137	0.0781	– 0.0833	– 0.1273	0.0017
		c^{E}	126.3	48.5	20.3		0.3
		$\kappa_{\mathrm{S}}^{\mathrm{E}}$	– 136.53	– 1.91	– 3.18		0.14
		α_p^{E}	– 0.1218	0.0104	– 0.1050	– 0.0352	0.0007
		$n_{\mathrm{D}}^{\mathrm{E}}$	0.003295	0.000575	0.000730		0.000006

TABLE 6 (continued)

	303.15	V_m^E	− 0.8703	0.0553	− 0.1347		0.0016
		n_D^E	0.003474	0.000629	0.001500		0.000012
DMA + 2-heptanone	298.15	V_m^E	− 0.046	0.007			0.005
		c^E	59.36	35.51	23.12	7.62	0.08
		κ_S^E	− 59.44	− 19.44	− 10.04		0.08
		n_D^E	0.001198	0.000388	0.000172		0.000005

$F^E = V_m^E$, units: cm^3mol^{-1}; $F^E = c^E$, units: ms^{-1}; $F^E = \kappa_S^E$ units: TPa^{-1}; $F^E = \alpha_p^E$, units: $10^{-3} K^{-1}$.

TABLE 7

Molar excess enthalpies, H_m^{E}, at equimolar composition and 298.15 K for tertiary amide(1) + *n*-alkanone(2) mixtures. The interaction parameters, X_{12}, calculated from H_m^{E} values at equimolar composition and the interactional contribution, $H_{\mathrm{m,int}}^{\mathrm{E}}$, to H_m^{E} are also included.

System	$H_{\mathrm{m}}^{\mathrm{E}}$ /J·mol^{-1}	X_{12} /J·cm^{-3}	$H_{\mathrm{m,int}}^{\mathrm{E}}$ /J·mol^{-1}	$\sigma_{\mathrm{r}}(H_{\mathrm{m}}^{\mathrm{E}})$ [a]
DMF + 2-propanone	34[16]	3.97	46	0.050
DMF + 2-butanone	143[17]	9.35	117	0.071
DMF + 2-pentanone	206[17]	11.93	160	0.082
DMF + 3-pentanone	257[17]	14.84	199	0.006
NMP + 2-butanone	– 165[14]	– 6.14	– 93	0.487
NMP + 4-heptanone	226[15]	10.42	186	0.266
NMP + 5-nonanone	362[15]	15.00	288	0.352

[a] relative standard deviation (eq. 15)

TABLE 8

Excess molar volumes, V_m^E, and isochoric excess molar internal energies, $U_{V,\mathrm{m}}^\mathrm{E}$, for tertiary amide(1) + *n*-alkanone(2) mixtures at 298.15 K and equimolar composition. The contributions to V_m^E from the *P** and curvature terms, according to the Prigogine-Flory-Patterson model, and the equation of state contribution to H_m^E (Eos, see equation 19) are also included.

n-Alkanone	V_m^E /cm^3·mol^{-1}				$\left\|(V_\mathrm{m,cur}^\mathrm{E} + V_\mathrm{m,P^*}^\mathrm{E})/V_\mathrm{m,exp}^\mathrm{E}\right\|$	Eos/ J·mol^{-1}	$U_\mathrm{V,m}^\mathrm{E}$ /J·mol^{-1a}
	Exp.	Flory	Curv. term	*P** term			
			DMF + *n*-alkanone				
2-propanone	− 0.4313[11]	− 0.345	− 0.154	− 0.235	0.90	− 167	204
2-butanone	− 0.3115[11]	− 0.192	− 0.082	− 0.212	0.94	− 119	262
2-pentanone	− 0.2510[11]	− 0.088	− 0.038	− 0.188	0.90	− 97	303
3-pentanone			− 0.038	− 0.171			
2-heptanone	− 0.0503[11]		− 0.003	− 0.066	1.37	− 19	
			DMA + *n*-alkanone				
2-propanone	− 0.3903[b]		− 0.192	− 0.222	1.06	− 150	
2-butanone	− 0.2499[b]		− 0.109	− 0.215	1.30	− 95	
2-pentanone	− 0.2034[b]		− 0.056	− 0.210	1.31	− 75	
2-heptanone	− 0.0115[b]		− 0.009	− 0.105	9.91	− 4	
			NMP + *n*-alkanone				
2-propanone	− 0.7190[13]		− 0.349	− 0.310	0.92	− 273	
2-butanone	− 0.6010[13]	− 0.638	− 0.242	− 0.332	0.96	− 224	59
2-pentanone	− 0.5728[13]		− 0.166	− 0.370	0.94	− 212	
3-pentanone	− 0.4975[13]		− 0.165	− 0.334	1.00	− 187	
2-hexanone	− 0.4678[13]		− 0.106	− 0.319	0.90	− 174	
4-heptanone	− 0.3910[13]	− 0.233	− 0.072	− 0.276	0.89	− 146	372
5-nonanone	− 0.2143[13]	− 0.004	− 0.024	− 0.183	0.97	− 80	442

[a] eq. (19); [b] this work;

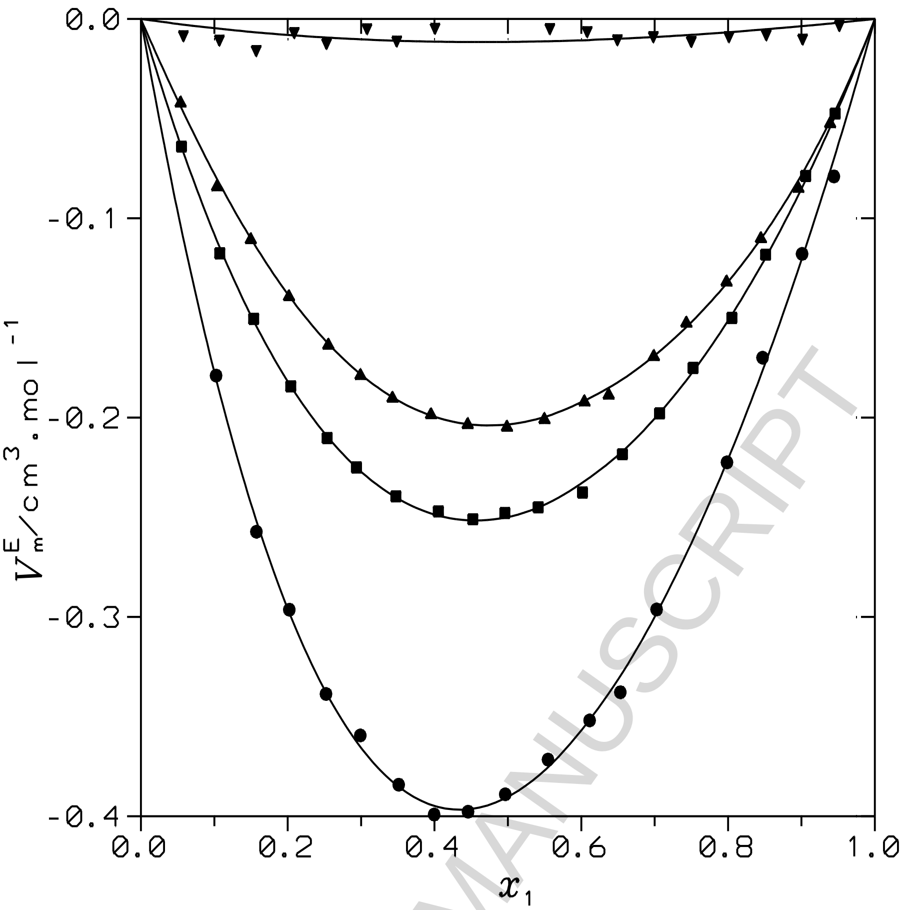


Figure 1 Excess molar volumes, V_m^E, for DMA (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), 2-propanone; (■), 2-butanone; (▲), 2-pentanone, (♦), 2-heptanone. Solid lines, calculations with equation (8) using coefficients from Table 6.

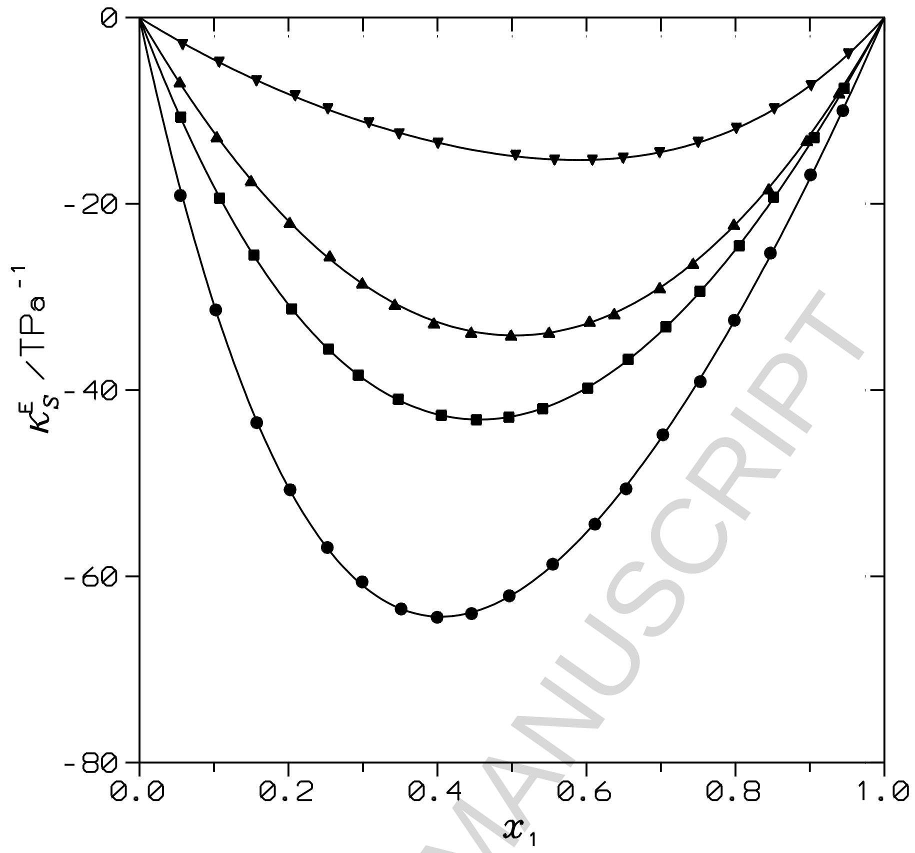


Figure 2 Excess isentropic compressibilities, κ_S^{E}, for DMA (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), 2-propanone; (■), 2-butanone; (▲), 2-pentanone, (♦), 2-heptanone. Solid lines, calculations with equation (8) using coefficients from Table 6.

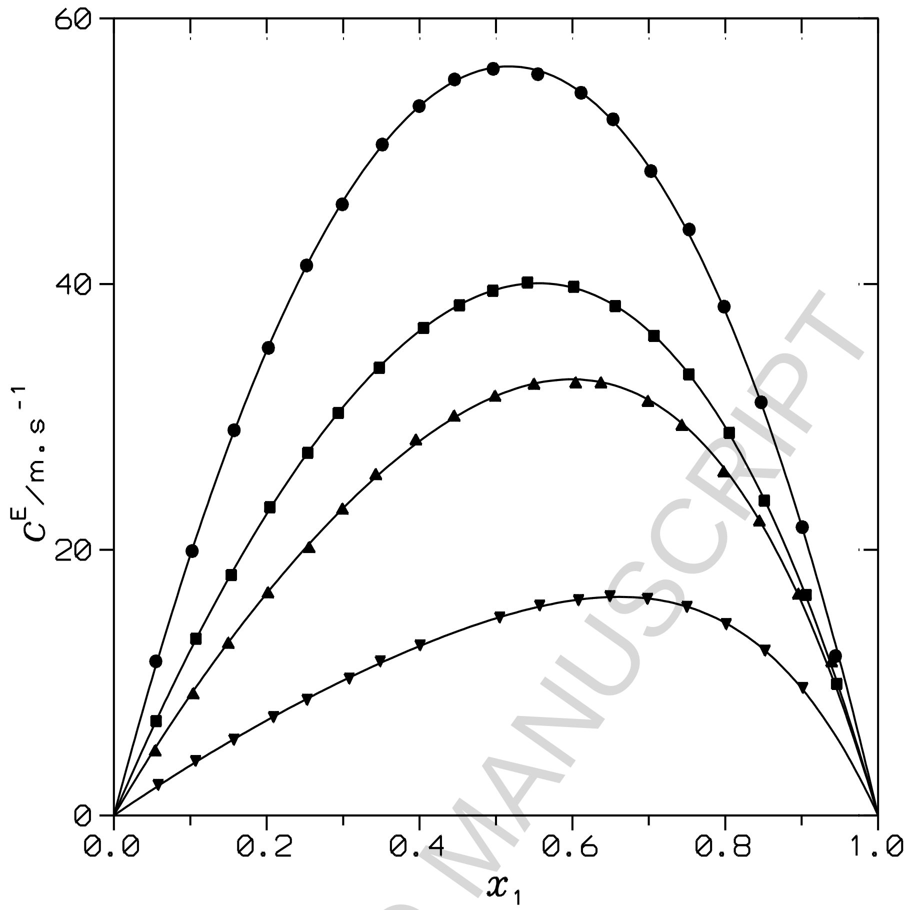


Figure 3 Excess speeds of sound, c^E, for DMA (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), 2-propanone; (■), 2-butanone; (▲), 2-pentanone, (♦), 2-heptanone. Solid lines, calculations with equation (8) using coefficients from Table 6.

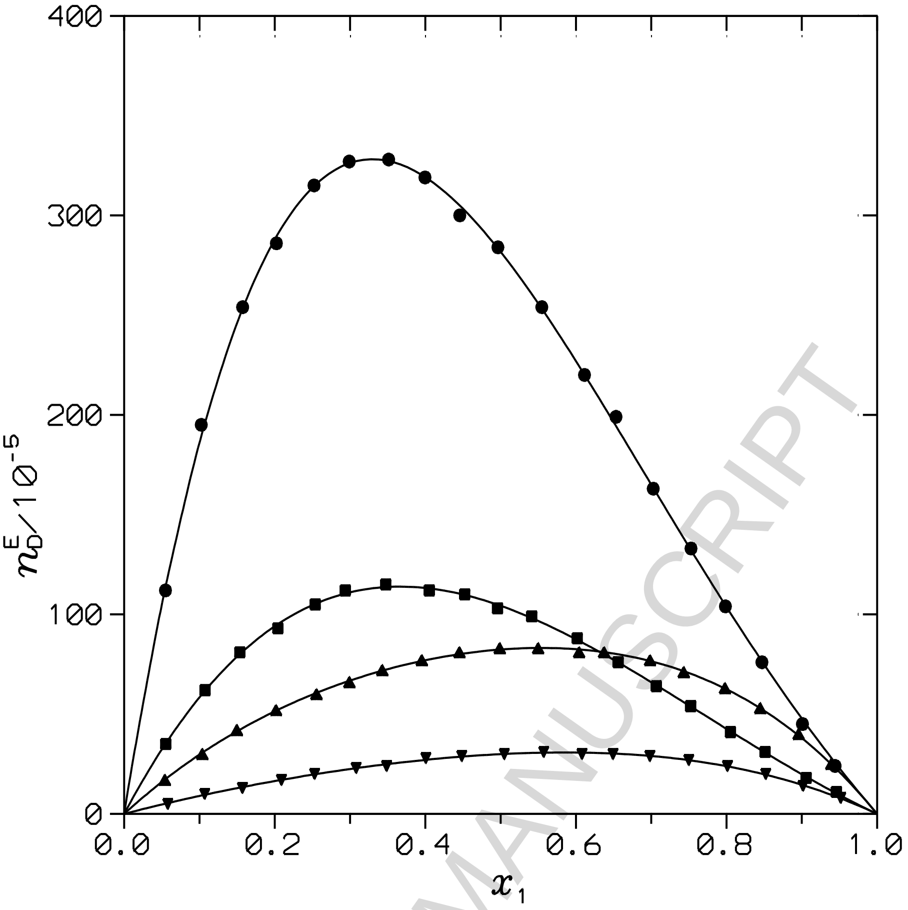


Figure 4 Excess refractive indices, n_D^E, for DMA (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), 2-propanone; (■), 2-butanone; (▲), 2-pentanone, (♦), 2-heptanone. Solid lines, calculations with equation (8) using coefficients from Table 6.

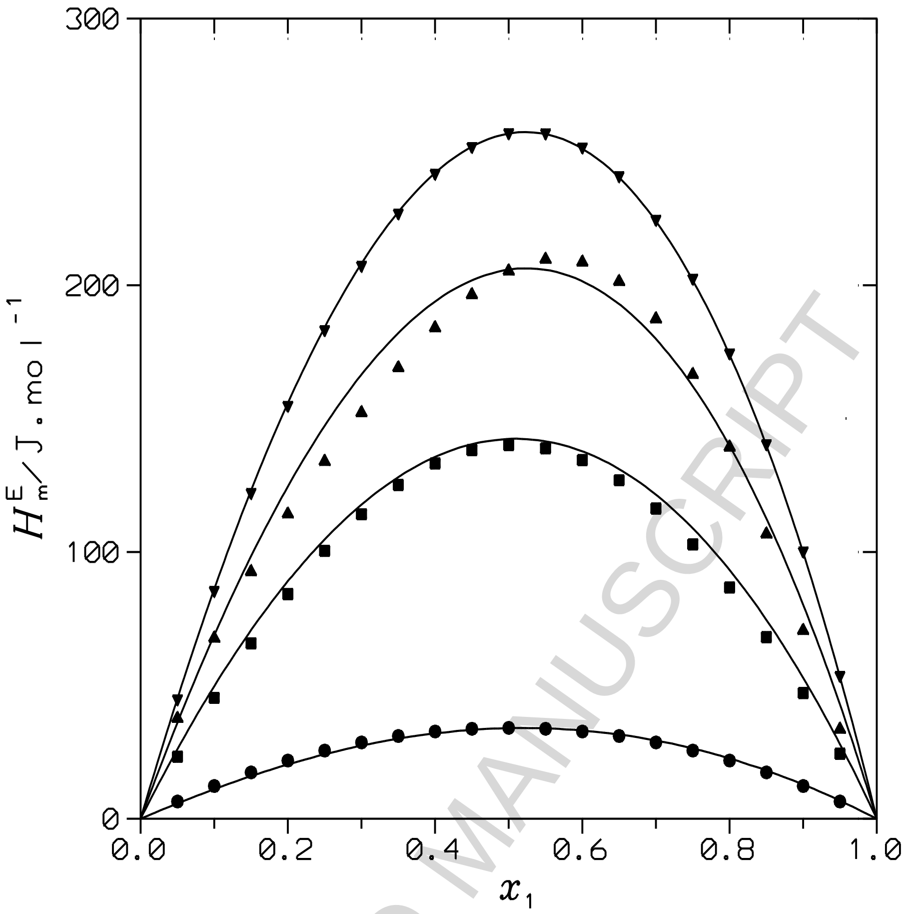


Figure 5 Excess molar enthalpies, H_m^E, for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental results: (⬣), 2-propanone [16]; (■), 2-butanone [17]; (▲), 2-pentanone [17], (♦), 3-pentanone [17]. Solid lines, results from the Flory model using interaction parameters listed in Table 7.

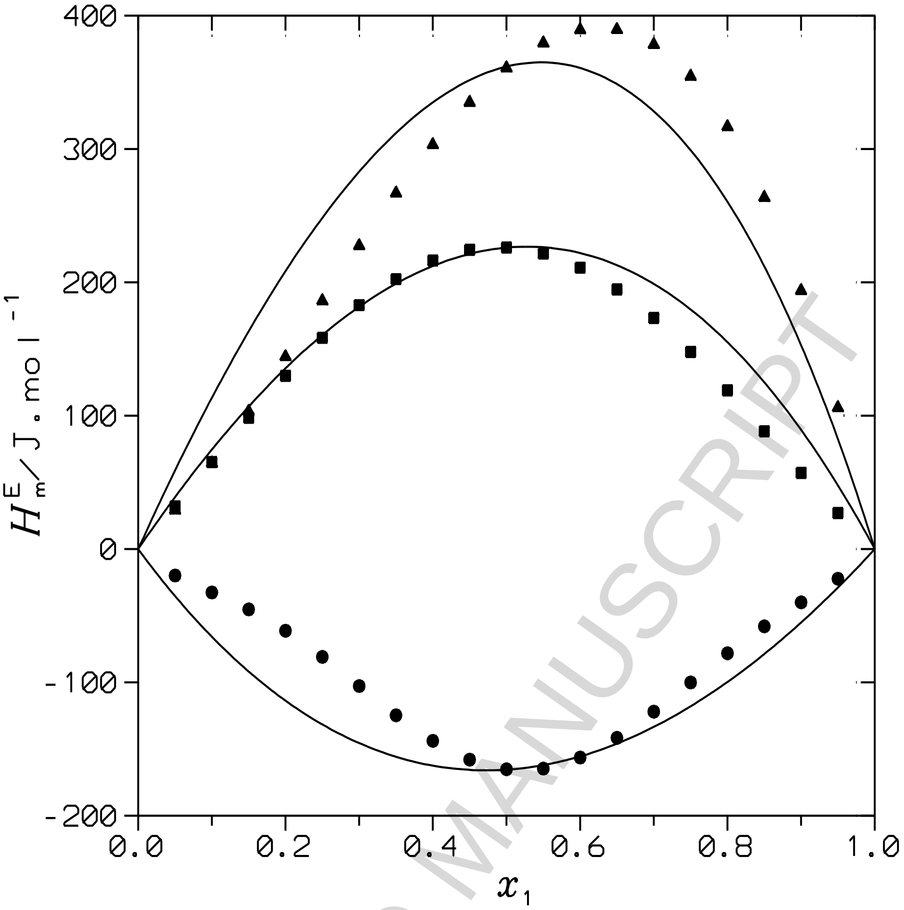


Figure 6 Excess molar enthalpies, H_m^E, for NMP (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental results: (●), 2-butanone [14]; (■), 4-heptanone [15]; (▲), 5-nonanone [15]. Solid lines, results from the Flory model using interaction parameters listed in Table 7.

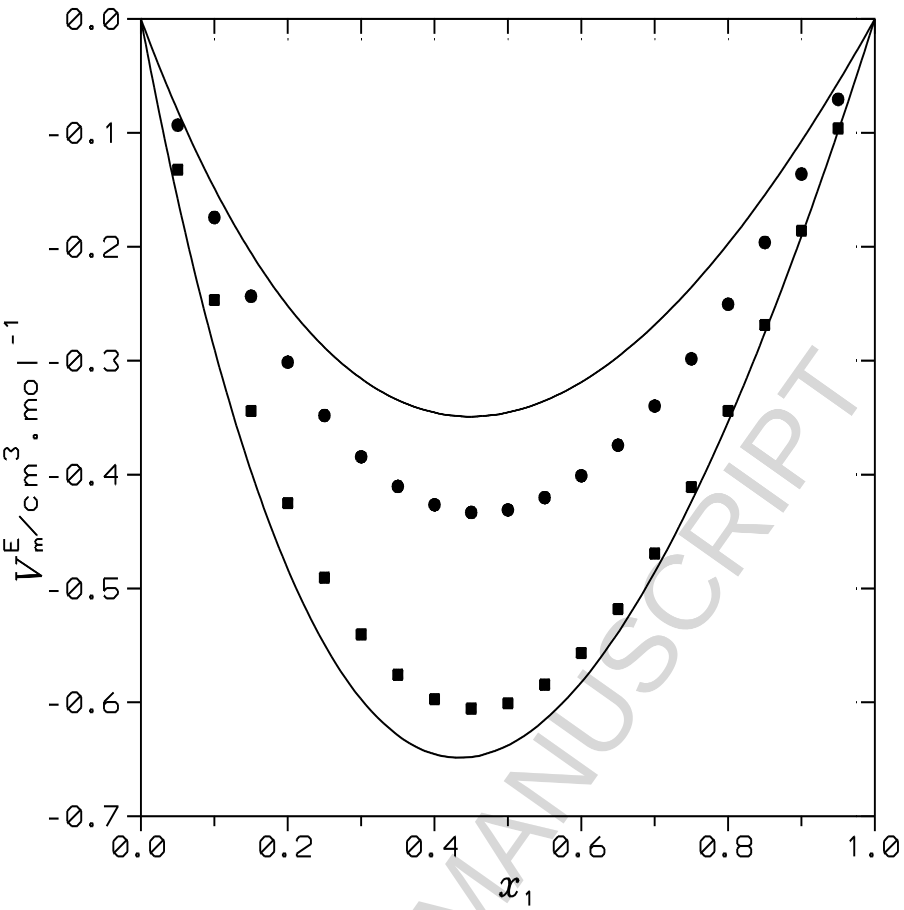
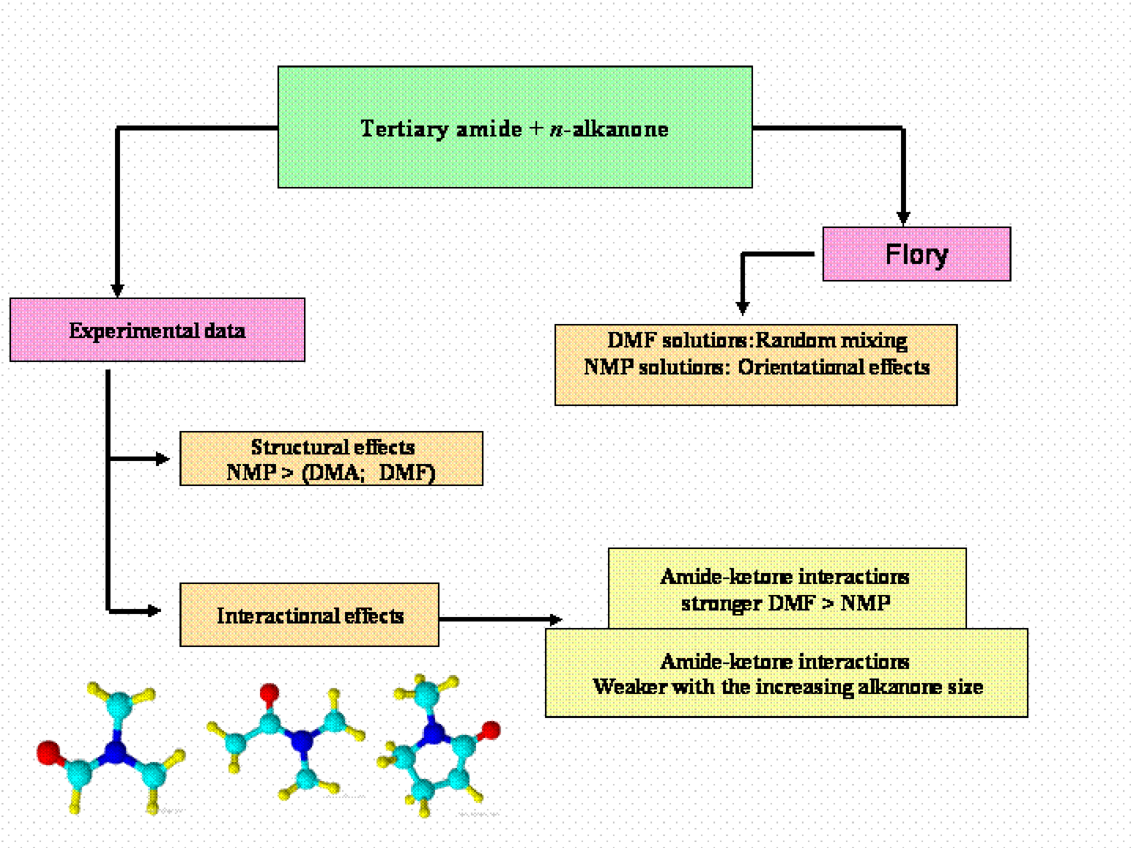


Figure 7 Excess molar volumes, V_m^E, for DMF (1) + 2-propanone (2) and NMP (1) + 2-butanone systems at atmospheric pressure and 298.15 K. Full symbols, experimental values: (●), DMF + 2-propanone [13]; (■), NMP + 2-butanone [15]. Solid lines, results from the Flory model using interaction parameters listed in Table 7.



Graphical Abstract

Highlights

- ➨Data on ρ ,c, n_D are provided for DMA+$CH_3CO(CH_2)_{u-1}CH_3$ (u = 1,2,3,5) at different temperatures
- ➨Structural effects and amide-ketone interactions lead to negative V_m^E values for tertiary amide solutions
- ➨From H_m^E data, it is shown that amide-ketone interactions are stronger in DMF systems than in those with NMP
- ➨Application of Flory’s model reveals that the random mixing hypothesis is valid for DMF solutions
- ➨NMP systems are characterized by strong orientational and structural effects