

Thermodynamics of amide + ketone mixtures. 1. Volumetric, speed of sound and refractive index data for *N,N*-dimethylformamide + 2-alkanone systems at several temperatures

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Abstract

Densities, ρ , speeds of sound, c , and refractive indices, n_D , have been measured for the systems *N,N*-dimethylformamide (DMF) + propanone, + 2-butanone, or + 2-pentanone in the temperature range from 293.15 to 303.15 K and at 298.15 K for the DMF + 2-heptanone mixture. Due to the high volatility of acetone, the corresponding n_D measurements were developed at 293.15 K and 298.15 K. The direct experimental data were used to determine the excess molar volumes, V_m^E , and the excess refractive indices, n_D^E , at the working temperatures. Values of the excess functions at 298.15 K, for the speed of sound, c^E , the isentropic compressibility, κ_S^E and for the excess thermal expansion coefficient, α_p^E , were also calculated. The investigated systems are characterized by strong amide-ketone interactions, which become weaker when the alkanone size is increased. This is supported by negative V_m^E values; by the dependence on temperature and pressure of V_m^E , and by positive P_{int}^E (excess internal pressure) values. Analysis of the systems in terms of the Rao's constant indicates that there is no complex formation. In addition, negative V_m^E values also reveal the existence of structural effects, which largely contribute to the excess molar enthalpy, H_m^E . V_m^E and H_m^E values increase with the chain length of the 2-alkanone. It allows conclude that the relative V_m^E variation with the ketone size is closely related to that of the interactional contribution to this excess function. Molar refraction values, R_m , show that dispersive interactions become more relevant for the systems including longer 2-alkanones.

Keywords: DMF; 2-alkanone; ρ , c , and n_D data; interactions/structural effects

1. Introduction

Amides are interesting compounds as they are very polar solvents which can form hydrogen bonds both through the oxygen and nitrogen atoms. Particularly, *N,N*-dimethylformamide (DMF) is an aprotic protophilic solvent, with good donor-acceptor properties, capable to solve many organic substances. DMF has many practical applications. It is used in the production of acrylic fibers, plastics, pesticides or surface coatings [1], or as a highly selective extractant for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks [2]. DMF is also very effective in nanotechnology [3-5]. On the other hand, the investigation of liquid mixtures containing the amide functional group is needed for a better understanding of complex molecules of biological interest [6]. In this framework, DMF is useful as a model compound for peptides, and the aqueous solution of DMF is a simple biochemical model of biological aqueous solutions [7,8]. From a theoretical point of view, amides are also a very interesting class of compounds, as in pure state, they show a significant local order [9]. 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]. 2-Alkanones ($\text{CH}_3\text{CO}(\text{CH}_2)_{u-1}\text{CH}_3$) are polar, aprotic compounds and hydrogen bonds acceptors, used as solvents for plastics and some synthetic fibers. Acetone is used as intermediate of methyl methacrylate. Ketones are also important substances in Biochemistry, as many sugars are ketones (fructose, e.g.) and fatty acid synthesis proceeds via these compounds. On the basis of these features, the investigation of amide + ketone mixtures seems to be convenient. In this first article of the series, we pay attention to DMF + ($\text{CH}_3\text{CO}(\text{CH}_2)_{u-1}\text{CH}_3$) ($u = 1,2,3,5$) systems, reporting density, ρ , data, speeds of sound, c , and refractive indices, n_D , in the temperature range from 293.15 to 303.15 K for systems with $u = 1,2,3$ and only at 298.15 K for the mixture with $u = 5$ since the behaviour of this system is nearly ideal (see below). In the case of the propanone system, n_D measurements were conducted at 293.15 K and 298.15 K due to the high volatility of the compound. A literature survey shows that there are available density data at 298.15 K for systems with propanone or 2-butanone; excess molar volumes, V_m^E , for mixtures at 303.15 K including 2-butanone or 2-pentanone [11-13], and excess molar enthalpies, H_m^E , for mixtures at 298.15 K with $u = 1,2,3$ [14,15].

2. Experimental

Materials. Information on the source and purity of the chemicals used is given in Table 1. The compounds were used without further purification. The physical properties, ρ, c, n_D , thermal expansion coefficient, α_p , and adiabatic, κ_S , and isothermal κ_T , compressibilities of

the pure liquids are collected in Table 2. Our values are in good agreement with those from 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 kg), with all weighings corrected for buoyancy effects. The error on the final mole fraction is estimated to be lower than ± 0.0008 . Molar quantities were calculated using the relative atomic mass table of 2011 issued by IUPAC [16].

Densities and speeds of sound of both pure liquids and of the mixtures were measured by means of a vibrating-tube densimeter and sound analyser, Anton Paar model DSA-5000, automatically thermostated within ± 0.01 K. Details of the calibration of the apparatus have been reported elsewhere [17]. The repeatability of the ρ measurements is $\pm 1 \cdot 10^{-3}$ kg·m⁻³, while the relative standard uncertainty of the measurements is estimated to be $\pm 0.12\%$. The determination of the speed of sound is based on the measurement of the propagation time of short acoustic pulses (3 MHz center frequency [18]), which are repeatedly transmitted to the sample. The repeatability and relative standard uncertainty of the c measurements are respectively, ± 0.1 m·s⁻¹ and ± 0.0004

The experimental technique was checked by determining V_m^E and c^E of the standard mixture (cyclohexane + benzene) at the temperatures (293.15-303.15) K. Our results agree well with published values [19-21]. The accuracy in V_m^E is less than $\pm(0.012|V_{m,\max}^E| + 0.005)$ cm³·mol⁻¹, where $|V_{m,\max}^E|$ stands for the maximum experimental value of V_m^E with respect to the mole fraction. The c^E accuracy is estimated to be 0.8 m·s⁻¹.

Refractive indices were measured using a refractometer model RFM970 from Bellingham-Stanley. The measurement repeatability is ± 0.00004 . The measurement method is based on the optical detection of the critical angle at the wave length of the sodium D line (586.9 nm). The temperature is controlled by Peltier modulus. The temperature stability is ± 0.02 K. The refractometer was calibrated using 2,2,4-trimethylpentane and toluene at the three working temperatures following the recommendations by Marsh [22]. The relative standard uncertainty of the experimental n_D values is ± 0.0015 .

3. Equations

The thermodynamic properties derived more directly from the experimental measurements obtained by means of the densimeter and sound analyser Anton Paar DSA-5000

are: density, ρ , molar volume, V_m , coefficient of thermal expansion, $\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$ and κ_S . In this work, α_p values were obtained assuming a linear dependence of ρ with T . If the absorption of the acoustic wave is negligible, κ_S can be calculated from the Newton-Laplace's equation:

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

For an ideal mixture at the same temperature and pressure as the system under study, the values F^{id} of the thermodynamic property, F , are calculated using the equations [23-25]:

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

and

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

where C_{pm} is the isobaric molar heat capacity, $\phi_i = \frac{x_i V_{mi}^{id}}{V_m^{id}}$ the volume fraction, κ_T , the isothermal compressibility, and F_i , the F value of component i , respectively. For κ_S and c , the ideal values are calculated according to [23]:

$$\kappa_S^{id} = \kappa_T^{id} - \frac{TV_m^{id} \alpha_p^{id2}}{C_{pm}^{id}} \quad (4)$$

and

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

where $\rho^{id} = (x_1 M_1 + x_2 M_2) / V_m^{id}$ (M_i , molecular mass of the i component). For n_D , ideal values are calculated from the expression [26]:

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

The excess functions are determined using the equation:

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

4. Experimental results

Table 3 lists values, at the working temperatures, of densities, V_m^E and c vs. x_1 , the mole fraction of DMF (see Figure 1). Table 4 contains the derived quantities κ_S^E , α_p^E and c^E at 298.15 K (Figures 2-4). Results on n_D and n_D^E are shown in Table 5 (Figure 5). The data were fitted by unweighted least-squares polynomial regression to the equation:

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

where F stands for the properties cited above. The number of coefficients k used in eq. (8) for each mixture was determined by applying an F-test [27] at the 99.5 % confidence level. Table 6 lists the parameters A_i obtained in the regression and the standard deviations σ , defined by:

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

where N is the number of direct experimental values. At $x_1 = 0.5$ and 303.15 K, the V_m^E values reported in the literature, obtained using a dilatometer with Hg as confining liquid, for the systems containing 2-butanone ($-0.3103 \text{ cm}^3 \cdot \text{mol}^{-1}$ [12]) or 2-pentanone ($-0.1802 \text{ cm}^3 \cdot \text{mol}^{-1}$ [13]) are somewhat different to those obtained here: -0.3345 and $-0.2630 \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively (see Figure S1 of supplementary material). The V_m^E values derived from ρ measurements for systems with $u = 1, 2$ are very scattered (see Figure S1, supplementary material). No information is given in the original work [11], essentially concerned with conductance measurements, on the experimental technique applied for the density determination.

5. Discussion

Below, we are referring to values of the excess functions at 298.15 K and equimolar composition.

As already mentioned, DMF and ketones are very polar compounds. The dipole moment, μ , of DMF is 3.7 D [28]. The μ values of 2-alkanones are: 2.69 (acetone); 2.76 (2-butanone); 2.70 (2-pentanone); 2.59 (2-heptanone) D [29]. The impact of polarity on bulk properties is better evaluated by means of the effective dipole moment, $\bar{\mu}$, defined by [30-33]:

$$\bar{\mu} = \left[\frac{\mu^2 N_A}{4\pi\epsilon_0 V_m k_B T} \right]^{1/2} \quad (10)$$

where N_A , ϵ_0 , k_B stand for the Avogadro's number, the permittivity of the vacuum, and the Boltzmann's constant, respectively. Thus, $\bar{\mu} = 1.60$ (DMF); 1.2 (propanone); 1.11 (2-butanone); 1.0 (2-pentanone); 0.84 (2-heptanone) (values calculated with data taken from reference [29]). Remarkably, 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. DMF + alkane mixtures show miscibility gaps at rather high temperatures. For example, the upper critical solution temperatures (UCST) of the DMF + heptane, or + hexadecane systems are, respectively, 342.55 K [34], and 385.15 K [35]. Mixtures of acetone with alkanes also show miscibility gaps, but their UCST values are much lower than those containing DMF (245.22 K [36] and 300.9 K [37] for the systems with heptane or hexadecane, respectively). The excess molar enthalpies, $H_m^E/\text{J}\cdot\text{mol}^{-1}$, of 2-alkanone + alkane systems are large and positive: 1704 (propanone) [38]; 1339 (2-butanone) [39]; 886 (2-heptanone) [40]. All these features arise from the existence of strong dipolar interactions between DMF molecules or between ketone molecules in their corresponding mixtures with alkanes. It must be remarked that in systems with a given alkane, say heptane, the H_m^E and V_m^E values decrease with the increasing of u . The observed H_m^E variation (see above) [41-43] is due to a weakening of the dipolar interactions between ketone molecules [43]. On the other hand, V_m^E (heptane)/ $\text{cm}^3\cdot\text{mol}^{-1} = 1.129$ (acetone) [44]; 0.280 (2-octanone) [45]. This variation can be ascribed to the positive contribution to V_m^E related to the disruption of ketone-ketone interactions becomes lower when u increases.

DMF + 2-alkanone systems are characterized by low and positive $H_m^E/\text{J}\cdot\text{mol}^{-1}$ values: 37 (acetone) [15], 140 (2-butanone), 206 (2-pentanone) [14]. In view of the features of DMF or 2-alkanone + alkane mixtures, such values reveal the existence of strong amide-ketone interactions. The enthalpy of such interactions may be evaluated from the expression [46-48]:

$$\begin{aligned} \Delta H_{\text{NCO-CO}} &= H_{\text{ml}}^{\text{E},\infty} (\text{DMF} + 2\text{-alkanone}) \\ &- H_{\text{ml}}^{\text{E},\infty} (\text{DMF} + \text{heptane}) - H_{\text{ml}}^{\text{E},\infty} (2\text{-alkanone} + \text{heptane}) \end{aligned} \quad (11)$$

where $H_{m1}^{E,\infty}$ represents the partial excess molar enthalpy at infinite dilution of the first component. We have applied widely equation (11) for the estimation of the enthalpy of interaction between 1-alkanols and different organic solvents, or, e.g., between amines and ketones [49,50]. Details on its derivation and range of applicability can be found elsewhere [46-48]. For DMF mixtures (see Table 7), $\Delta H_{\text{NCO-CO}}/\text{kJ}\cdot\text{mol}^{-1} = -26.0$ (acetone); -24.1 (2-butanone) and -22.6 (2-heptanone). It is remarkable that these values are more or less similar to those encountered for 1-alkanol + ketone mixtures [47] ($\Delta H_{\text{OH-CO}}/\text{kJ}\cdot\text{mol}^{-1} = -28.6$ (methanol + acetone); -26 (1-propanol + acetone); -22.1 (1-propanol + 2-heptanone). Interestingly, the replacement of DMF by aniline leads to slightly stronger interactions between unlike molecules. Thus, $\Delta H_{\text{N-CO}}$ (aniline)/ $\text{kJ}\cdot\text{mol}^{-1} = -29.3$ (propanone); -24.5 (2-heptanone) [49]. Amine-ketone interactions are weaker in mixtures where secondary or tertiary amines are involved. For example, $\Delta H_{\text{N-CO}}$ (acetone)/ $\text{kJ}\cdot\text{mol}^{-1} = -21.5$ (*N*-methylaniline); -8.1 (dipropylamine); -5.9 (dibutylamine); -4.9 (*N,N,N*-triethylamine) [49,50].

H_m^E values increase with u . This is due to the contributions from: (i) the weakening of the amide-ketone interactions (less negative contribution to H_m^E); (ii) a larger number of DMF-DMF interactions broken by the longer 2-alkanones (higher positive contribution to H_m^E ; note that UCST values of DMF + n -alkane mixtures increase with the alkane size, see above) are dominant terms over that arising from the disruption of ketone-ketone interactions (lower positive contribution to H_m^E).

The excess molar internal energies at constant volume, U_{vm}^E , can be calculated from [33,51]:

$$U_{\text{vm}}^E = H_m^E - \frac{T\alpha_p V_m^E}{\kappa_T} \quad (12)$$

where $\frac{\alpha_p}{\kappa_T} T V_m^E$ is usually termed the equation of state (eos) contribution to H_m^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

$$\kappa_T = \kappa_S + \frac{T\alpha_p^2 V_m}{C_{p,m}} \quad (13)$$

assuming that $C_{pm}^E = 0$, what is a good approximation in view of the low H_m^E values of the investigated mixtures [52]. Thus, $U_{vm}^E / \text{J}\cdot\text{mol}^{-1} = 207$ (acetone); 261 (2-butanone) and 303 (2-pentanone). The large differences between U_{vm}^E and H_m^E values are remarkable, and underline, in the present case, the importance of structural effects on H_m^E .

The mixtures have been also investigated by means of the internal pressures, P_{int} [53-56]:

$$P_{\text{int}} = \frac{\alpha_p T}{\kappa_T} - p \quad (14)$$

It is known that the main contributions to P_{int} arise from dispersion forces and weak dipole-dipole interactions [55]. For the pure liquids, $P_{\text{int},i} / \text{MPa} = 456.5$ (DMF); 331.4 (acetone), 333.4 (2-butanone); 334.5 (2-pentanone) and 326.4 (2-heptanone). The cohesive energy density is defined by [55]:

$$D_{\text{ce}} = \frac{\Delta H_{\text{vap}} - RT}{V_m} \quad (15)$$

where ΔH_{vap} is the molar enthalpy of vaporization at 298.15 and R the gas constant. D_{ce} is a measure of the total molecular cohesion (per cm^3) of the liquid [55]. Using values of ΔH_{vap} from [57], $D_{\text{ce},i} / \text{MPa}$: 573.8 (DMF), 389.3 (acetone), 358.5 (2-butanone); 334.5 (2-pentanone) and 326.9 (2-heptanone). The comparison between $P_{\text{int},i}$ and $D_{\text{ce},i}$ clearly shows: (i) the existence of very strong dipolar interactions between amide molecules or between ketone molecules for acetone or 2-butanone; (ii) dipolar interactions become weaker when u increases. For the investigated systems, at $x_1 = 0.5$ and 298.15 K, $P_{\text{int}} / \text{MPa} = 396.2$ (acetone), 388.6 (2-butanone); 386.8 (2-pentanone) and 369.9 (2-heptanone). P_{int} values can be also obtained from the equation [54]:

$$P_{\text{int}} = \frac{RT}{x_1 v_{f1} + x_2 v_{f2} + V_m^E} - P \quad (16)$$

In this expression, $v_{fi} (= RT / (p + P_{\text{int},i}))$ is the free volume of component i [54]. From eq. (16), $P_{\text{int}} / \text{MPa} = 411.2$ (acetone), 404.8 (2-butanone), 401.8 (2-pentanone) and 369.9 (2-

heptanone), which differ by $\approx 4\%$ from those values obtained using eq. (14). This demonstrates the consistency of our data, and that the Van der Waals equation is hold in large extent for the current mixtures, as eq. (16) is derived from this equation of state [54]. We have also determined the excess internal pressures, $P_{\text{int}}^{\text{E}} (= P_{\text{int}} - P_{\text{int}}^{\text{id}})$, with $P_{\text{int}}^{\text{id}} = \frac{\alpha_p^{\text{id}} T}{\kappa_T^{\text{id}}} - p$ [58].

Results are shown graphically in Fig. 6. Systems where strong interactions between unlike molecules exist are characterized by large positive $P_{\text{int}}^{\text{E}}$ values. For example, in the case of the aniline + propanone system, $P_{\text{int}}^{\text{E}} = 61.35$ MPa [59] (Figure 6). Inspection of Figure 6 allows conclude that interactions between unlike molecules become weaker when u increases. The rather low $P_{\text{int}}^{\text{E}}$ value of the 2-heptanone system (7.7 MPa) may be due partially to structural effects as is similar to that for the hexane + hexadecane mixture (6.5 MPa [29,60]) (see below).

Additional information from P_{int} values can be obtained from the molar refraction, R_m , of the systems, which can be calculated using the Lorentz-Lorenz equation [61,62]:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \quad (17)$$

This magnitude is linked to dispersion forces as n_D at optical wavelengths is related to the mean polarizability [61]. As expected, R_m , increases with u . That is, at such condition, dispersive interactions become more important. On the other hand, the magnitude $P_{\text{int}} V_m$ has been proposed as a measure of the London dispersion energy, independent of the existence of strong specific interactions [63]. In fact, $P_{\text{int}} V_m$ increases linearly with R_m ($P_{\text{int}} V_m = 9.15 + 1.15 R_m$; coefficient of regression, $r = 0.997$) and decreases linearly with $\bar{\mu}$ ($P_{\text{int}} V_m = 65.16 - 29.58 \bar{\mu}$; $r = -0.999$). This confirms that dispersive interactions become more relevant when u increases. Therefore, the observed smooth variation of P_{int} may be due to the increase of dispersive interactions with u is partially counterbalanced by the weakening of the weak dipolar interactions considered within P_{int} .

The parameter $\chi = \left(\frac{c}{c^{\text{id}}}\right)^2 - 1$ is commonly used to estimate the non-ideality of a system. In fact, mixtures which show strong deviations from the ideal behaviour are characterized by high χ values. Thus, in the case of 1-alkanol + 2-pyrrolidone mixtures, $\chi = 0.8$ (methanol); 0.35 (ethanol) [64]. For DMF systems, $\chi = 0.102$ (acetone); 0.072 (2-

butanone); 0.059 (2-pentanone); 0.026 (2-heptanone). In terms of the speed of sound, the present solutions are close to the ideal behaviour.

The Rao's constant, R , [65] (or molar sound velocity, $R = V_m c^{1/3}$) is an useful magnitude to investigate molecular interactions in liquid mixtures. This magnitude depends linearly on the molar fractions of the components ($R = x_1 R_1 + x_2 R_2$) if there is no association, or if the degree of association does not change with concentration, as long as the density of the component liquids does not differ largely [65-67]. Systems characterized by complex formation or including a compound with a halogen atom show deviations from this behaviour [68]. Figure 7 shows that R of DMF + 2-alkanone mixtures varies linearly with x_1 , indicating the absence of complex formation [66,67].

It is well known that negative V_m^E values reveal the existence of interactions between unlike molecules and/or structural effects (geometrical factors as differences in size and shape between them [69-71] or interstitial accommodation [72]). For example, $V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = -0.368$ ($\text{CHCl}_3 + 1\text{-butylamine}$) [73]; -0.610 (hexadecane + hexane) [60]. The $H_m^E/\text{J}\cdot\text{mol}^{-1}$ values are -3125 ($T = 303.15\text{ K}$) [74] and 114 [75], respectively. The positive H_m^E values and those negative of V_m^E for the investigated systems suggest that the more relevant contribution to this excess function arises from structural effects [71]. Many other mixtures behave similarly. Some examples follow: $H_m^E/\text{J}\cdot\text{mol}^{-1} = 322$ (N,N,N -triethylamine + hexadecane) [76]; 34 (N,N,N -tributylamine + octane) [77]; 1780 (2,5,8,11,15-pentaoxapentadecane + pentane) [78]. In the same order, $V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = -0.098$ [79]; -0.070 [79]; -0.39 [78]. We note that the symmetry of the V_m^E curve of the 2-heptanone system is noticeably skewed to higher concentration values of DMF, the smaller component (Figure 1). This is a typical behaviour of systems with compounds which largely differ in size. A similar trend is observed for the systems cited above. Interestingly, both H_m^E and V_m^E of the DMF mixtures increase with u . Therefore, the observed V_m^E variation can be ascribed to changes in the interactional contribution to V_m^E . This means that the contributions which increase V_m^E , weakening of the amide-alkanone interactions and larger number of broken DMF-DMF interactions, are predominant over that arising from the disruption of ketone-ketone interactions, and suggests that the negative V_m^E values are partially due to the rather strong DMF-ketone interactions created upon mixing. We have determined $A_p = \left(\frac{\Delta V_m^E}{\Delta T}\right)_p = -4.2\cdot 10^{-3}$; (acetone); $-3.4\cdot 10^{-3}$ (2-

butanone) and $-2.4 \cdot 10^{-3}$ (2-pentanone) (values in $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). 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. Systems characterized by strong interactions between like molecules show positive values of A_p and α_p^E over the entire mole fraction range. Thus, $A_p / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 7.6 \cdot 10^{-3}$ (2-ethoxyethanol + octane) [80] or $2.3 \cdot 10^{-3}$ (1-pentanol + cyclohexane) [81]. For the CHCl_3 + 1-butylamine mixture, A_p is $-4.2 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ [73] and is $-1.3 \cdot 10^{-2}$ (same units) for the hexane + hexadecane mixture [60]. The pressure dependence of H_m^E can be evaluated from the expression:

$$\left(\frac{\partial H_m^E}{\partial p} \right)_T = V_m^E - T A_p \quad (18)$$

For the present systems, this magnitude is (in $\text{cm}^3 \cdot \text{mol}^{-1}$): 0.821 (acetone); 0.702 (2-butanone) and 0.465 (2-pentanone). The value of the benzene + cyclohexane mixture, characterized by dispersive interactions, is $-0.054 \text{ cm}^3 \cdot \text{mol}^{-1}$ [82]. Mixtures with strong positive deviations from the Raoult's law have more negative values: -1.54 (2-ethoxyethanol + octane); $-0.28 \text{ cm}^3 \cdot \text{mol}^{-1}$ (1-pentanol + octane) [80,81]. Values of $\left(\frac{\partial H_m^E}{\partial p} \right)_T / \text{cm}^3 \cdot \text{mol}^{-1}$ of systems where strong interactions between unlike exist may be rather large and positive: 2.07 (ClCH_3 + 1-butylamine [73]); 1.53 (aniline + acetone [83]). Our experimental results seem to support the existence of interactions between unlike molecules, in such way that the increase of pressure leads to the breaking of any type of interactions and H_m^E increases. Negative κ_S^E values are also typically ascribed to structural effects and/or to interactions between unlike molecules, while positive values are attributed to the breaking of physical interactions [84]. For example, $\kappa_S^E / \text{TPa}^{-1} = -142$ (aniline + propanone) [83]; 15.3 (2-ethoxyethanol + octane) [85]. Therefore, the negative κ_S^E values of DMF + 2-alkanone systems are in agreement with the trends mentioned above. Finally, we remark the consistency between the signs of the V_m^E , κ_S^E and c^E functions. For mixtures with acetone, 2-butanone or 2-pentanone, values of V_m^E , κ_S^E are negative, while those for c^E are positive. In addition, V_m^E , κ_S^E increase and c^E decreases when u is increased. The behaviour of the 2-heptanone systems is close to the ideal solution.

6. Conclusions

Volumetric, speeds of sound and refractive indices data have been reported, at different temperatures, for the systems DMF + acetone, + 2-butanone, + 2-pentanone, or + 2-heptanone. These mixtures are characterized by strong amide-ketone interactions, which become weaker when the alkanone size is increased. The existence of interactions between unlike molecules is supported by positive P_{int}^E values; by negative V_m^E values, as well as by the dependences on temperature and pressure of V_m^E . Analysis of the Rao's constant indicates that there is no complex formation. Negative V_m^E values also reveal the existence of structural effects, which have a large contribution to H_m^E . V_m^E and H_m^E change in line with the 2-alkanone size. Therefore, the relative V_m^E variation is due to that of the interactional contribution to this excess function. From the P_{int}^E , V_m^E and R_m values, it is possible to conclude that dispersive interactions become more relevant for the systems with longer 2-alkanones.

7. References

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TABLE 1

Sample description

Chemical	CAS number	Source	Purity ^a	Analysis method
<i>N,N</i> -dimethylformamide	68-12-2	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

^ain mass fraction; ^bgas chromatography; ^c High-performance liquid chromatography^dflash column chromatography

TABLE 2

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

Property	T/K	DMF	propanone	2-butanone	2-pentanone	2-heptanone
$\rho/g\cdot\text{cm}^3$	293.15	0.94882	0.79019	0.80506	0.80683	0.81539
		0.948922 ^b	0.790546 ^c	0.8049 ^d	0.8064 ^d	0.81537 ^d
			0.78998 ^d	0.80495 ^e	0.80626 ^e	0.815497 ^f
				0.805058 ^f		
		0.94406	0.78443	0.79978	0.80199	0.81108
		0.944163 ^b	0.7844 ^d	0.7997 ^d	0.8015 ^d	0.81123 ^d
	298.15		0.784431 ^g	0.79974 ^e	0.80142 ^e	0.81093 ^h
		0.93928	0.77863	0.79455	0.79673	0.80681
		0.939390 ^b	0.77966 ^e	0.7946 ^d	0.79658 ^e	0.806867 ^f
				0.79448 ^e		
				0.794565 ^f		
$c/\text{m}\cdot\text{s}^{-1}$	293.15	1476.7	1183.6	1212.6	1232.4	1282.1
		1477.8 ^b	1182.5 ^c	1213 ^e	1233 ^e	1281.9 ^j
			1185 ^e			
		1458.6	1163.6	1191.5	1211.9	1262.7
		1458.5 ^b	1161.7 ^g	1192 ^e	1213 ^e	1262.5 ^j
		1458.6 ^j	1163.9 ^k			
	303.15	1438.8	1139.9	1172.0	1191.7	1244.4
		1439 ^b	1140 ^e	1171 ^e	1192 ^e	1244.1 ^j
		1440.3 ^j	1139.2 ^c			
$\alpha_p/10^{-3}\text{K}^{-1}$	298.15	1.01	1.47;1.45 ^c	1.31	1.26	1.06; 1.06 ^d
		1.01 ^j	1.46 ^e	1.31 ^e	1.21 ^e	
κ_S/TPa^{-1}	293.15	483.34	903.4	844.8	816.1	746.1
		485 ^b	904.7 ^c	844 ^e	816 ^e	746.3 ^j
			900 ^e			

TABLE 2 (continued)

	298.15	497.88	941.4	880.8	849.0	773.2
		497.9 ^b	944.6 ^g	880 ^e	848 ^e	773.5 ^j
		497.6 ⁱ	941.1 ^k			
	303.15	514.28	988.4	916.3	883.8	800.4
		514 ^b	988.8 ^c	918 ^e	883.5 ^e	800.7 ^j
		512.9 ⁱ	987 ^e			
κ_T/TPa^{-1}	298.15	659.5	1323.8	1172.8	1122.8	966.6
		650 ^d	1324 ^d	1188 ^d	1092 ^e	957 ^d
		662 ^l				
$C_{p,m}/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	298.15	146.05 ^m	125.45 ⁿ	159 ^o	185.4 ^p	242.5 ^h
n_D	293.15	1.43055	1.35845	1.37872	1.39026	
		1.43047 ^d	1.35868 ^d	1.3788 ^d	1.39080 ^d	
		1.4281 ^q	1.3584 ^r			
	298.15	1.42840	1.35386	1.37605	1.38793	1.40688
		1.4280 ^l	1.35597 ^s	1.3767 ^t	1.3885 ^t	1.40655 ^d
	303.15	1.42610		1.37351	1.38523	
		1.4271 ^l		1.3740 ^u	1.38627 ^v	

^a ρ , density; c , speed of sound; α_p , isobaric thermal expansion coefficient; κ_S , adiabatic compressibility; κ_T , isothermal compressibility; $C_{p,m}$, isobaric molar heat capacity and n_D , refractive index. Relative standard uncertainties, u_r , are: $u_r(\rho) = \pm 0.0012$; $u_r(c) = \pm 0.0004$; $u_r(\alpha_p) = \pm 0.028$; $u_r(\kappa_S) = \pm 0.002$; $u_r(\kappa_T) = \pm 0.015$; $u_r(n_D) = \pm 0.0015$; standard uncertainties for temperature and pressure are $u(T) = \pm 0.01$ K (for n_D values, $u(T) = \pm 0.02$ K); and for pressure, $u(p) = \pm 1$ kPa; ^b[86] ^c[87]; ^d[29]; ^e[88]; ^f[89]; ^g[90] ^h[91] ⁱ[17]; ^j[92]; ^k[93]; ^l[94]; ^m[95]; ⁿ[96]; ^o[97]. ^p[98]; ^q[99]; ^r[100]; ^s[101]; ^t[102]; ^u[103]; ^v[104]

TABLE 3

Densities, ρ , molar excess volumes, V_m^E , and speeds of sound, c , for *N,N*-dimethylformamide (1) + 2-alkanone (2) mixtures at temperature T and 0.1 MPa.

x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V_m^E /$ $\text{cm}^3\cdot\text{mol}^{-1}$	$c/\text{m}\cdot\text{s}^{-1}$	x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V_m^E /$ $\text{cm}^3\cdot\text{mol}^{-1}$	$c/\text{m}\cdot\text{s}^{-1}$
<i>N,N</i> -dimethylformamide (1) + propanone (2) $T/\text{K}= 293.15$							
0.0503	0.799565	-0.0952	1200.1	0.5476	0.883523	-0.3944	1352.9
0.1057	0.809645	-0.1798	1218.0	0.5990	0.891359	-0.3696	1367.5
0.1529	0.818017	-0.2349	1232.9	0.6521	0.899454	-0.3486	1382.9
0.1992	0.826191	-0.2867	1247.6	0.7051	0.907302	-0.3108	1397.8
0.2475	0.834489	-0.3235	1262.6	0.7538	0.914504	-0.2803	1411.4
0.2981	0.843136	-0.3600	1278.3	0.8063	0.921993	-0.2268	1425.7
0.3458	0.851059	-0.3790	1292.6	0.8441	0.927346	-0.1879	1436.0
0.3942	0.859037	-0.3940	1307.4	0.9022	0.935518	-0.1273	1451.7
0.4516	0.868376	-0.4059	1324.6	0.9471	0.941723	-0.0739	1463.7
0.4973	0.875647	-0.4032	1338.1				
<i>N,N</i> -dimethylformamide (1) + propanone (2) $T/\text{K}= 298.15$							
0.0500	0.793781	-0.0952	1180.1	0.5490	0.878710	-0.4216	1336.2
0.1270	0.807814	-0.2116	1205.5	0.5893	0.884968	-0.4086	1348.1
0.1485	0.811673	-0.2405	1212.5	0.6413	0.892941	-0.3849	1363.3
0.1908	0.819252	-0.2963	1226.2	0.6822	0.898928	-0.3447	1374.7
0.2492	0.829349	-0.3419	1244.6	0.7435	0.908066	-0.3041	1392.3
0.2970	0.837550	-0.3763	1259.6	0.7945	0.915398	-0.2507	1406.4
0.3399	0.844898	-0.4091	1273.1	0.8342	0.921109	-0.2132	1417.5
0.3997	0.854838	-0.4314	1291.5	0.8801	0.927621	-0.1632	1430.1
0.4461	0.862361	-0.4339	1305.3	0.9377	0.935649	-0.0932	1445.8
0.4978	0.870632	-0.4308	1320.8				
<i>N,N</i> -dimethylformamide (1) + propanone (2) $T/\text{K}= 303.15$							
0.0571	0.789325	-0.1089	1159.0	0.5422	0.872357	-0.4354	1310.9
0.1075	0.798734	-0.2046	1175.8	0.6046	0.882041	-0.4074	1329.2
0.1480	0.805999	-0.2542	1188.9	0.6507	0.889133	-0.3862	1342.6
0.2001	0.815316	-0.3180	1205.7	0.6986	0.896270	-0.3460	1356.3
0.2528	0.824518	-0.3648	1222.4	0.7493	0.903843	-0.3080	1370.7
0.3003	0.832657	-0.3953	1237.3	0.7975	0.910848	-0.2590	1384.2
0.3487	0.840866	-0.4220	1252.5	0.8442	0.917613	-0.2140	1397.1
0.3920	0.848120	-0.4388	1265.8	0.8972	0.925060	-0.1448	1411.5

TABLE 3 (continued)

0.4547	0.858369	-0.4457	1284.8	0.9411	0.931137	-0.0845	1423.4
0.4991	0.865505	-0.4430	1298.1				
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2) <i>T</i> /K= 293.15							
0.0482	0.811508	-0.0493	1224.5	0.5514	0.882097	-0.2945	1354.1
0.1051	0.819281	-0.1116	1238.6	0.6017	0.889386	-0.2844	1367.5
0.1480	0.825263	-0.1614	1249.6	0.6519	0.896759	-0.2717	1381.2
0.1915	0.831169	-0.1864	1262.8	0.7023	0.904135	-0.2460	1394.9
0.2530	0.839789	-0.2364	1276.1	0.7525	0.911634	-0.2257	1408.8
0.3008	0.846349	-0.2485	1288.2	0.8002	0.918668	-0.1889	1421.7
0.3386	0.851673	-0.2663	1298.0	0.8492	0.926050	-0.1546	1435.2
0.3915	0.859222	-0.2904	1311.8	0.9032	0.934175	-0.1058	1450.2
0.4887	0.873095	-0.3023	1337.4	0.9477	0.940900	-0.0597	1462.4
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2) <i>T</i> /K= 298.15							
0.0519	0.806811	-0.0606	1204.4	0.5536	0.877384	-0.3010	1334.6
0.1048	0.814011	-0.1142	1217.5	0.5946	0.883427	-0.3002	1345.8
0.1506	0.820379	-0.1637	1229.3	0.6572	0.892579	-0.2765	1362.3
0.1948	0.826510	-0.2016	1240.5	0.7034	0.899388	-0.2555	1375.5
0.2482	0.834008	-0.2456	1254.4	0.7461	0.905863	-0.2432	1387.6
0.3032	0.841593	-0.2619	1268.4	0.7965	0.913261	-0.1990	1401.3
0.3543	0.848769	-0.2795	1281.6	0.8488	0.921083	-0.1552	1415.8
0.3962	0.854829	-0.3025	1292.8	0.8940	0.928027	-0.1235	1428.6
0.4495	0.862429	-0.3095	1306.9	0.9427	0.935405	-0.0726	1442.1
0.4916	0.868442	-0.3088	1318.0				
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2) <i>T</i> /K= 303.15							
0.0496	0.801341	-0.0665	1184.6	0.5486	0.871924	-0.3341	1315.5
0.1068	0.809288	-0.1410	1199.1	0.6028	0.879882	-0.3260	1330.1
0.1478	0.814925	-0.1780	1209.5	0.6517	0.886955	-0.2983	1343.2
0.1836	0.819800	-0.1988	1218.5	0.7023	0.894541	-0.2826	1357.4
0.2521	0.829427	-0.2550	1236.4	0.7483	0.901328	-0.2496	1369.9
0.2943	0.835351	-0.2779	1248.2	0.7995	0.908942	-0.2083	1384.1
0.3532	0.843706	-0.3038	1262.8	0.8514	0.916844	-0.1727	1399.0
0.3938	0.849516	-0.3199	1273.5	0.8982	0.923832	-0.1199	1410.9
0.4538	0.858110	-0.3283	1289.4	0.9460	0.931082	-0.0651	1425.2
0.4969	0.864319	-0.3287	1301.1				

TABLE 3 (continued)

<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2) $T/K= 293.15$							
0.1141	0.819616	-0.0909	1254.3	0.5466	0.875212	-0.2423	1350.0
0.1516	0.823961	-0.1138	1261.7	0.5987	0.882775	-0.2363	1363.1
0.2063	0.830491	-0.1497	1273.0	0.6581	0.891660	-0.2236	1378.4
0.2588	0.836933	-0.1821	1284.0	0.7528	0.906494	-0.1958	1404.2
0.3089	0.843115	-0.1930	1294.7	0.8029	0.914576	-0.1640	1418.1
0.3594	0.849625	-0.2133	1303.2	0.8461	0.921840	-0.1434	1430.7
0.4006	0.855077	-0.2283	1315.3	0.9017	0.931277	-0.0962	1446.8
0.4488	0.861489	-0.2296	1326.3	0.9496	0.939704	-0.0531	1460.9
0.4999	0.868584	-0.2398	1338.5				
<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2) $T/K= 298.15$							
0.0568	0.808267	-0.0472	1222.8	0.5570	0.871899	-0.2463	1332.9
0.1000	0.813221	-0.0883	1231.3	0.6022	0.878552	-0.2473	1344.4
0.1526	0.819250	-0.1164	1241.7	0.6448	0.884967	-0.2436	1355.5
0.1895	0.823621	-0.1408	1249.2	0.7117	0.895208	-0.2190	1373.4
0.2545	0.831549	-0.1796	1262.9	0.7504	0.901333	-0.2013	1384.0
0.3298	0.841051	-0.2154	1279.3	0.8027	0.909784	-0.1704	1398.7
0.3502	0.843666	-0.2208	1283.9	0.8490	0.917570	-0.1463	1412.1
0.3956	0.849557	-0.2279	1294.0	0.9019	0.926592	-0.1019	1427.6
0.4567	0.857796	-0.2404	1308.5	0.9429	0.933872	-0.0708	1440.1
0.5084	0.865012	-0.2502	1320.8				
<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2) $T/K= 303.15$							
0.0581	0.803204	-0.0546	1203.0	0.5407	0.864591	-0.2649	1309.0
0.1088	0.808974	-0.0954	1212.9	0.5989	0.873078	-0.2619	1323.9
0.1600	0.815007	-0.1384	1223.3	0.6467	0.880175	-0.2452	1336.3
0.2044	0.820314	-0.1673	1232.5	0.6949	0.887598	-0.2312	1349.2
0.2620	0.827319	-0.1923	1244.6	0.7518	0.896616	-0.2091	1364.8
0.3046	0.832689	-0.2136	1253.9	0.8007	0.904558	-0.1807	1378.6
0.3506	0.838634	-0.2351	1264.1	0.8527	0.913274	-0.1469	1393.6
0.4014	0.845319	-0.2496	1275.7	0.8991	0.921307	-0.1155	1407.5
0.4820	0.856310	-0.2641	1294.7	0.9485	0.929946	-0.0615	1422.2
0.5006	0.858884	-0.2638	1299.1				
<i>N,N</i> -dimethylformamide (1) + 2-heptanone (2) $T/K= 298.15$							
0.0530	0.815095	-0.0062	1268.2	0.4957	0.858130	-0.0487	1328.7
0.0936	0.818298	-0.0109	1272.9	0.5985	0.871481	-0.0567	1348.2

TABLE 3 (continued)

0.1502	0.822964	-0.0158	1279.0	0.6368	0.876894	-0.0604	1356.2
0.2011	0.827389	-0.0205	1285.3	0.6999	0.886398	-0.0641	1370.3
0.2495	0.831808	-0.0252	1291.3	0.7433	0.893368	-0.0630	1380.8
0.2960	0.836272	-0.0309	1297.5	0.8482	0.911958	-0.0508	1408.7
0.3419	0.840896	-0.0363	1304.0	0.8634	0.914867	-0.0483	1413.1
0.3963	0.846646	-0.0393	1312.2	0.8985	0.921855	-0.0412	1423.7
0.4324	0.850691	-0.0457	1318.0	0.9480	0.932305	-0.0255	1439.5

^astandard uncertainties are: $u(x_1) = \pm 0.0008$; $u(p) = \pm 1$ kPa; $u(T) = \pm 0.01$ K; and the relative combined expanded uncertainties (0.95 level of confidence) are: $U_{rc}(\rho) = \pm 0.0024$; $U_{rc}(c) = \pm 0.001$; $U_{rc}(V_m^E) = \pm 0.025$

TABLE 4

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

x_1	$\kappa_S^E/\text{TPa}^{-1}$	$c^E/\text{m}\cdot\text{s}^{-1}$	$\alpha_p^E/10^{-3}\cdot\text{K}^{-1}$	x_1	$\kappa_S^E/\text{TPa}^{-1}$	$c^E/\text{m}\cdot\text{s}^{-1}$	$\alpha_p^E/10^{-3}\cdot\text{K}^{-1}$
<i>N,N</i> -dimethylformamide (1) + propanone (2)							
0.0500	-16.5	9.9	-0.011	0.5490	-68.5	62.9	-0.047
0.1270	-37.6	24.1	-0.025	0.5893	-65.8	62.7	-0.045
0.1485	-42.4	27.7	-0.028	0.6413	-61.2	61.1	-0.042
0.1908	-50.9	34.4	-0.034	0.6822	-56.3	58.4	-0.038
0.2492	-59.4	42.2	-0.040	0.7435	-48.5	53.2	-0.033
0.2970	-64.8	47.9	-0.044	0.7945	-40.5	46.7	-0.027
0.3399	-68.4	52.4	-0.046	0.8342	-33.8	40.5	-0.023
0.3997	-71.2	57.4	-0.048	0.8801	-25.4	31.8	-0.017
0.4461	-71.4	59.9	-0.049	0.9377	-13.9	18.4	-0.009
0.4978	-70.4	61.9	-0.048				
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2)							
0.0519	-10.2	6.7	-0.007	0.5536	-49.8	46.7	-0.036
0.1048	-19.2	13.1	-0.013	0.5946	-48.6	47.1	-0.036
0.1506	-26.5	18.6	-0.018	0.6572	-44.8	45.7	-0.033
0.1948	-32.3	23.3	-0.023	0.7034	-41.9	44.5	-0.031
0.2482	-38.6	28.9	-0.027	0.7461	-38.4	42.2	-0.028
0.3032	-43.1	33.6	-0.031	0.7965	-32.6	37.6	-0.024
0.3543	-46.4	37.5	-0.033	0.8488	-25.8	31.2	-0.019
0.3962	-48.7	40.5	-0.035	0.8940	-19.2	24.3	-0.014
0.4495	-50.2	43.5	-0.036	0.9427	-11.0	14.6	-0.008
0.4916	-50.5	45.2	-0.037				
<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2)							
0.0568	-7.7	5.4	-0.0021	0.5570	-41.8	39.4	-0.0100
0.1000	-13.3	9.4	-0.0039	0.6022	-41.4	40.3	-0.0097
0.1526	-19.1	14.0	-0.0058	0.6448	-40.3	40.5	-0.0093
0.1895	-22.9	17.1	-0.0068	0.7117	-37.0	39.3	-0.0083
0.2545	-29.0	22.5	-0.0083	0.7504	-34.4	37.7	-0.0076
0.3298	-34.7	28.1	-0.0095	0.8027	-29.6	34.1	-0.0065
0.3502	-35.9	29.5	-0.0097	0.8490	-24.6	29.5	-0.0053

TABLE 4 (continued)

0.3956	-38.1	32.2	-0.0101	0.9019	-17.4	22.0	-0.0037
0.4567	-40.7	35.8	-0.0103	0.9429	-10.9	14.4	-0.0023
0.5084	-41.6	37.9	-0.0103				
<i>N,N</i> -dimethylformamide (1) + 2-heptanone (2)							
0.0530	-2.4	2.0		0.5537	-18.7	18.7	
0.0936	-4.4	3.7		0.5985	-19.3	19.7	
0.1502	-6.4	5.4		0.6368	-19.5	20.4	
0.2011	-8.6	7.4		0.6999	-19.2	20.9	
0.2495	-10.4	9.0		0.7433	-18.6	20.8	
0.2960	-12.0	10.7		0.7946	-17.0	19.9	
0.3419	-13.6	12.3		0.8482	-14.4	17.6	
0.3963	-15.3	14.1		0.8634	-13.5	16.7	
0.4324	-16.3	15.3		0.8985	-11.0	14.1	
0.4957	-17.7	17.2		0.9480	-6.5	8.7	

^astandard uncertainties are: $u(x_1) = \pm 0.0008$; $u(p) = \pm 1$ kPa; $u(T) = \pm 0.01$ K; and the relative combined expanded uncertainties (0.95 level of confidence) are: $U_{rc}(c^E) = \pm 0.04$; $U_{rc}(\kappa_S^E) = \pm 0.05$ and $U_{rc}(\alpha_p^E) = 0.05$

TABLE 5

Excess refractive indices, n_D , and the corresponding excess values, n_D^E of *N,N*-dimethylformamide (1) + 2-alkanone(2) mixtures at temperature T and 0.1 MPa.

x_1	n_D	n_D^E	x_1	n_D	n_D^E
<i>N,N</i> -dimethylformamide (1) + propanone (2) $T/K= 293.15$					
0.0503	1.36286	0.00052	0.5476	1.40156	0.00233
0.1057	1.36770	0.00112	0.5990	1.40511	0.00222
0.1529	1.37155	0.00138	0.6521	1.40867	0.00202
0.1992	1.37532	0.00165	0.7051	1.41226	0.00189
0.2475	1.37922	0.00193	0.7538	1.41537	0.00161
0.2981	1.38311	0.00205	0.8063	1.41877	0.00138
0.3458	1.38685	0.00227	0.8441	1.42113	0.00115
0.3942	1.39050	0.00236	0.9022	1.42474	0.00079
0.4516	1.39472	0.00240	0.9471	1.42742	0.00043
0.4973	1.39800	0.00237			
<i>N,N</i> -dimethylformamide (1) + propanone (2) $T/K= 298.15$					
0.0500	1.35901	0.00116	0.5490	1.39951	0.00343
0.1270	1.36640	0.00247	0.5893	1.40233	0.00328
0.1485	1.36834	0.00272	0.6413	1.40581	0.00296
0.1908	1.37223	0.00331	0.6822	1.40851	0.00268
0.2492	1.37711	0.00367	0.7435	1.41236	0.00210
0.2970	1.38103	0.00390	0.7945	1.41552	0.00161
0.3399	1.38441	0.00401	0.8342	1.41805	0.00131
0.3997	1.38893	0.00400	0.8801	1.42090	0.00092
0.4461	1.39235	0.00392	0.9377	1.42451	0.00048
0.4978	1.39595	0.00367			
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2) $T/K= 293.15$					
0.0482	1.38120	0.00028	0.5536	1.40712	0.00150
0.1051	1.38410	0.00055	0.6017	1.40972	0.00146
0.1480	1.38629	0.00072	0.6519	1.41237	0.00143
0.1915	1.38843	0.00080	0.7023	1.41495	0.00128
0.2530	1.39163	0.00105	0.7525	1.41752	0.00110
0.3008	1.39408	0.00116	0.8002	1.42009	0.00101
0.3386	1.39604	0.00126	0.8492	1.42274	0.00090
0.3915	1.39872	0.00131	0.9032	1.42553	0.00060
0.4432	1.40144	0.00141	0.9477	1.42785	0.00034

TABLE 5 (continued)

0.4887	1.40384	0.00149			
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2) <i>T/K</i> = 298.15					
0.0519	1.37886	0.00041	0.5536	1.40522	0.00186
0.1048	1.38152	0.00059	0.5946	1.40739	0.00185
0.1506	1.38397	0.00087	0.6572	1.41063	0.00170
0.1948	1.38631	0.00108	0.7034	1.41301	0.00155
0.2482	1.38913	0.00132	0.7461	1.41516	0.00133
0.3032	1.39213	0.00161	0.7965	1.41779	0.00113
0.3543	1.39479	0.00172	0.8488	1.42048	0.00084
0.3962	1.39697	0.00178	0.8940	1.42276	0.00050
0.4495	1.39982	0.00189	0.9427	1.42542	0.00031
0.4916	1.40199	0.00189			
<i>N,N</i> -dimethylformamide (1) + 2-butanone (2) <i>T/K</i> = 303.15					
0.0496	1.37623	0.00079	0.5486	1.40242	0.00419
0.1068	1.37911	0.00138	0.6028	1.40517	0.00402
0.1478	1.38113	0.00171	0.6517	1.40780	0.00394
0.1836	1.38314	0.00221	0.7023	1.41050	0.00373
0.2521	1.38686	0.00296	0.7483	1.41287	0.00337
0.2943	1.38911	0.00332	0.7995	1.41553	0.00290
0.3532	1.39202	0.00352	0.8514	1.41823	0.00231
0.3938	1.39409	0.00366	0.8982	1.42066	0.00168
0.4538	1.39728	0.00391	0.9460	1.42320	0.00097
0.4969	1.39967	0.00413			
<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2) <i>T/K</i> = 293.15					
0.0560	1.39208	0.00015	0.5466	1.41036	0.00123
0.1141	1.39408	0.00035	0.5976	1.41245	0.00122
0.1531	1.39541	0.00044	0.6581	1.41495	0.00114
0.2063	1.39735	0.00066	0.6992	1.41668	0.00106
0.2588	1.39918	0.00073	0.7528	1.41906	0.00101
0.3089	1.40106	0.00088	0.8029	1.42129	0.00088
0.3594	1.40295	0.00097	0.8461	1.42325	0.00074
0.4006	1.40453	0.00105	0.9017	1.42583	0.00053
0.4488	1.40643	0.00113	0.9496	1.42811	0.00031
0.4999	1.40845	0.00118			

TABLE 5 (continued)

<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2) $T/K= 298.15$					
0.0568	1.38979	0.00016	0.5570	1.40855	0.00126
0.1000	1.39128	0.00032	0.6022	1.41039	0.00123
0.1526	1.39310	0.00047	0.6448	1.41217	0.00119
0.1895	1.39442	0.00059	0.7117	1.41498	0.00105
0.2545	1.39670	0.00070	0.7511	1.41672	0.00098
0.3298	1.39955	0.00092	0.8027	1.41905	0.00088
0.3502	1.40029	0.00093	0.8490	1.42117	0.00073
0.3956	1.40203	0.00102	0.9019	1.42364	0.00053
0.4567	1.40441	0.00110	0.9429	1.42557	0.00032
0.5084	1.40650	0.00117			
<i>N,N</i> -dimethylformamide (1) + 2-pentanone (2) $T/K= 303.15$					
0.0681	1.38748	0.00018	0.5505	1.40580	0.00124
0.1130	1.38906	0.00035	0.5986	1.40783	0.00126
0.1576	1.39062	0.00047	0.6407	1.40954	0.00116
0.1979	1.39212	0.00064	0.6952	1.41187	0.00107
0.2343	1.39347	0.00076	0.7401	1.41378	0.00091
0.3128	1.39635	0.00091	0.7992	1.41643	0.00075
0.3603	1.39820	0.00104	0.8559	1.41908	0.00059
0.4156	1.40034	0.00112	0.8994	1.42109	0.00037
0.4485	1.40167	0.00119	0.9411	1.42312	0.00019
0.4954	1.40355	0.00123			
<i>N,N</i> -dimethylformamide (1) + 2-heptanone (2) $T/K= 298.15$					
0.0530	1.40756	0.000034	0.5537	1.41582	0.000193
0.0936	1.40811	0.000062	0.5985	1.41679	0.000193
0.1502	1.40890	0.000101	0.6368	1.41766	0.000200
0.2011	1.40962	0.000114	0.6999	1.41919	0.000207
0.2495	1.41034	0.000119	0.7433	1.42032	0.000211
0.2960	1.41107	0.000134	0.8482	1.42329	0.000182
0.3419	1.41182	0.000143	0.8634	1.42376	0.000177
0.3963	1.41276	0.000151	0.8985	1.42488	0.000169
0.4324	1.41341	0.000159	0.9480	1.42651	0.000100
0.4957	1.41462	0.000171			

^athe standard uncertainties, u , are: $u(T) = \pm 0.02 \text{ K}$; $u(p) = \pm 1 \text{ kPa}$; $u(x_1) = \pm 0.0008$; the relative standard uncertainty of n_D is $u_r(n_D) = 0.0015$; and relative combined expanded uncertainty (0.95 level of confidence) is $U_{rc}(n_D^E) = \pm 0.042$

TABLE 6

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

System ^b	T/K	Property F^E	A_0	A_1	A_2	A_3	A_4	$\sigma(F^E)$
DMF + propanone	293.15	V_m^E	-1.601	0.265	-0.079			0.003
		n_D^E	0.00955	-0.00144				0.00004
	298.15	V_m^E	-1.725	0.265				0.004
		c^E	251.1	53.9				0.6
		κ_S^E	-282.4	65.23	-14.05			0.17
		α_P^E	-192.7	42.7	0.06			0.00003
303.15	n_D^E	0.01492	-0.00880	0.00139			0.00005	
	V_m^E	-1.768	0.302	-0.081			0.003	
DMF + 2-butanone	293.15	V_m^E	-1.201	0.019				0.004
		n_D^E	0.00590	0.00079				0.00004
	298.15	V_m^E	-1.246	0.021				0.005
		c^E	181.6	69.1	26.3			0.3
		κ_S^E	-202.6	3.9				0.2
		α_p^E	-146.8	-5.3	-0.05			0.000001
303.15	n_D^E	0.00767	-0.00017	-0.00213			0.00004	
	V_m^E	-1.338	0.026				0.005	
DMF + 2-pentanone	293.15	n_D^E	0.01644	0.00271				0.00008
		V_m^E	-0.958	-0.121	-0.070			0.003
	298.15	n_D^E	0.00468	0.00152				0.00003
		V_m^E	-1.004	-0.113	-0.078			0.003
		c^E	150.1	78.8	39.3	17.2		0.1
		κ_S^E	-167.2	-31				0.3
303.15	α_p^E	-41.3	-2.4	-3.2			0.00011	
	n_D^E	0.00465	0.00155				0.00003	

TABLE 6 (continued)

	303.15	V_m^E	-1.052	-0.113	-0.078			0.003
		n_D^E	0.00498	-0.00096	-0.00213			0.00003
DMF + 2-heptanone	298.15	V_m^E	-0.2011	-0.1822	-0.1323	-0.0357		0.0010
		c^E	69.4	56.4	36.8	22.5	13.2	0.1
		κ_S^E	-71.23	-42.71	-22.39			0.11
		n_D^E	0.000688	0.000373	0.000834	0.000339		0.000006

^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: $10^{-3} \cdot \text{K}^{-1}$

TABLE 7

Partial excess molar enthalpies, $H_{m,1}^{E,\infty}$, at $T = 298.15$ K for solute(1) + organic compound (2) mixtures, and enthalpy of the amide-ketone interaction, $\Delta H_{\text{NCO-CO}}$ (eq. 11), at $T = 298.15$ K, for amide(1) + 2-alkanone(2) systems.

System	$H_1^{E,\infty} / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_{\text{NCO-CO}} / \text{kJ} \cdot \text{mol}^{-1}$
propanone(1) + heptane(2)	9.09 [90]	
2-butanone(1) + heptane(2)	7.47 [38]	
2-pentanone(1) + heptane(2)	6.35 [38]	
2-heptanone(1) + heptane(2)	5.58 [39]	
<i>N,N</i> -dimethylformamide(1)+ heptane(2)	17.1 [105]	
<i>N,N</i> -dimethylformamide(1) + propanone(2)	0.2 [14]	− 26.0
<i>N,N</i> -dimethylformamide(1) + 2-butanone(2)	0.5 [14]	− 24.1
<i>N,N</i> -dimethylformamide(1) + 2-pentanone(2)	0.86 [14]	− 22.6

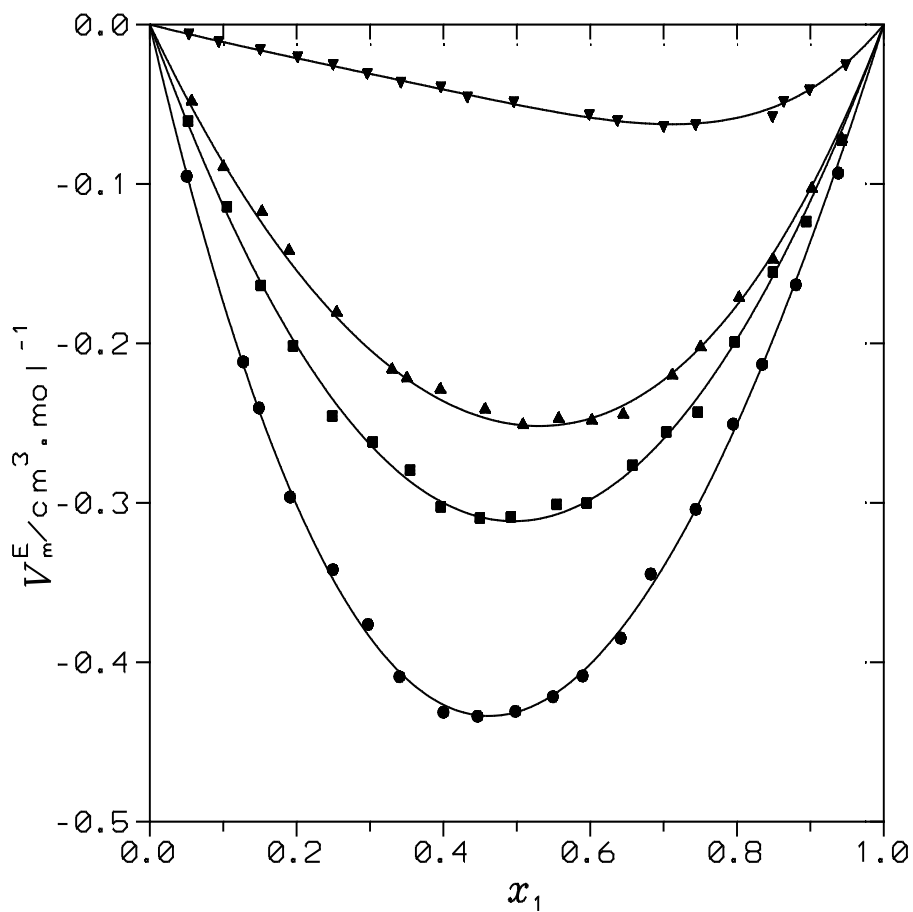


Figure 1 Excess molar volumes, V_m^E , for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), propanone; (■), 2-butanone; (▲), 2-pentanone, (▼), 2-heptanone. Solid lines, calculations with eq. 8 using the coefficients from Table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

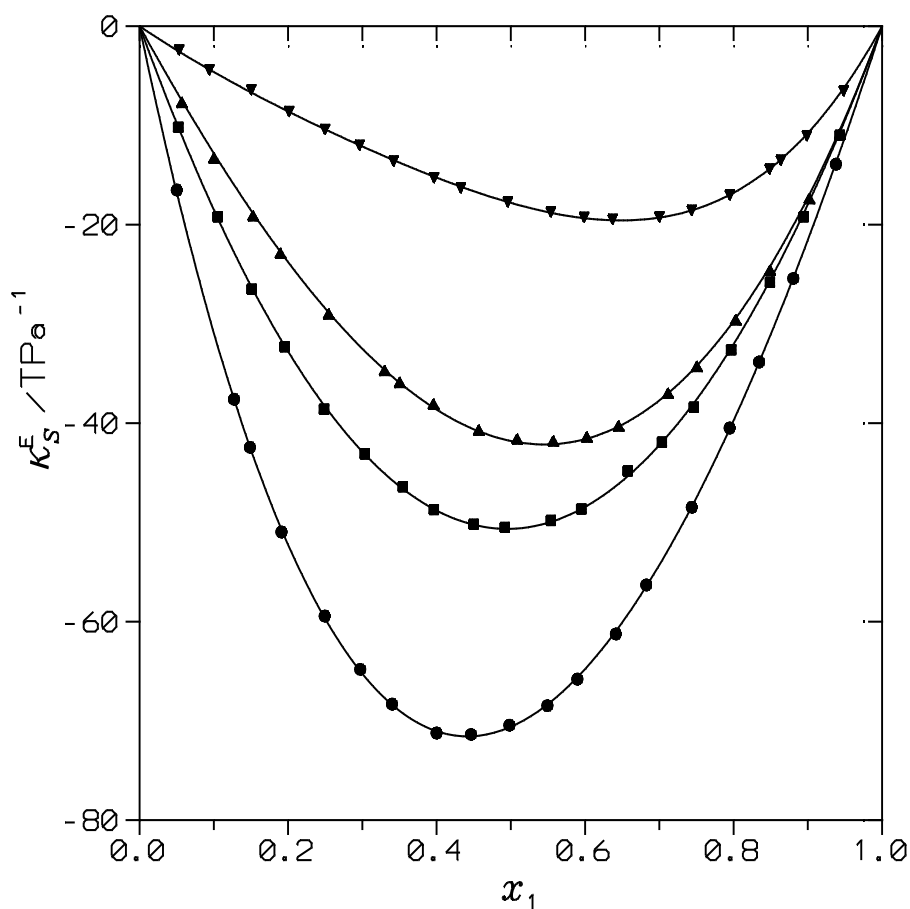


Figure 2 Excess isentropic compressibilities, κ_s^E , for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), propanone; (■), 2-butanone; (▲), 2-pentanone, (▼), 2-heptanone. Solid lines, calculations with eq. 8 using the coefficients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

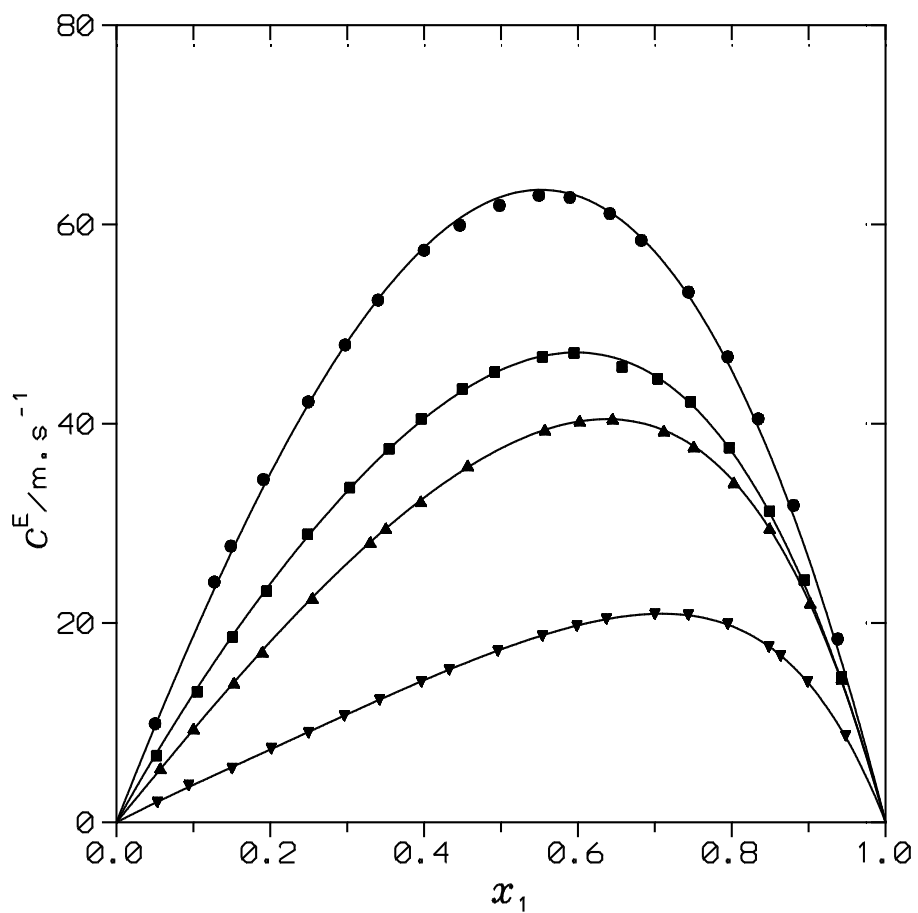


Figure 3 Excess speeds of sound, c^E , for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (\bullet), propanone; (\blacksquare), 2-butanone; (\blacktriangle), 2-pentanone, (\blacktriangledown), 2-heptanone. Solid lines, calculations with eq. 8 using the coefficients from Table 6.

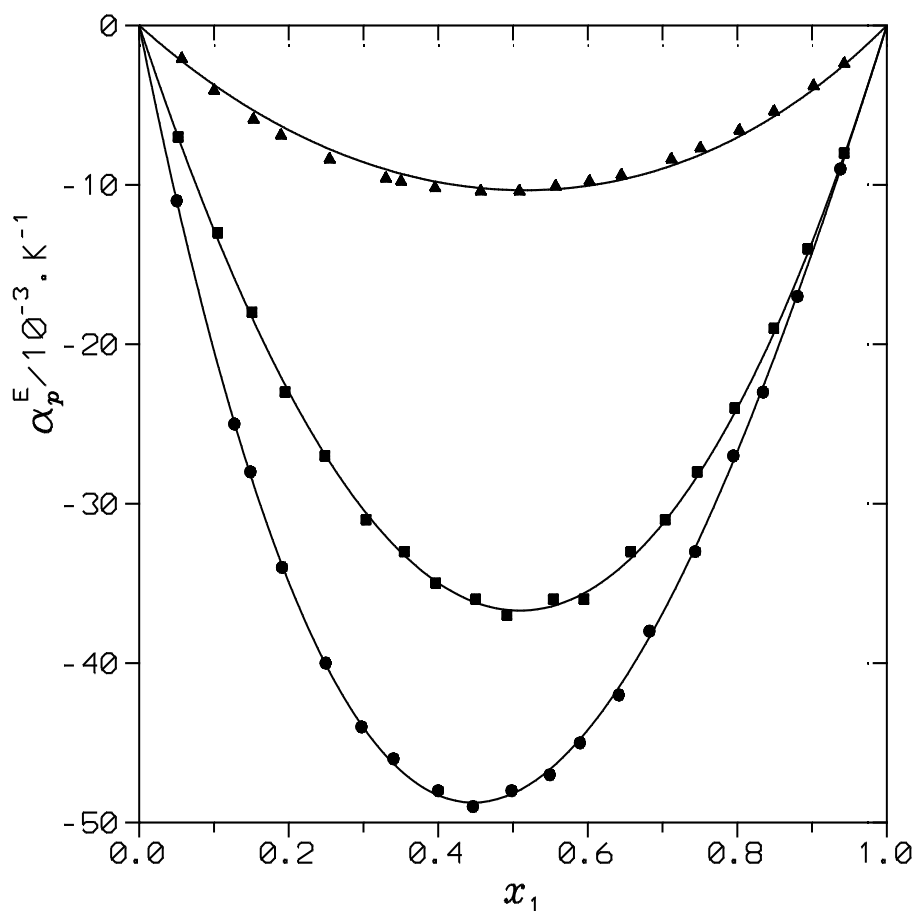


Figure 4 Excess isobaric thermal expansion coefficients, α_p^E , for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), propanone; (■), 2-butanone; (▲), 2-pentanone. Solid lines, calculations with eq. 8 using the coefficients from Table 6.

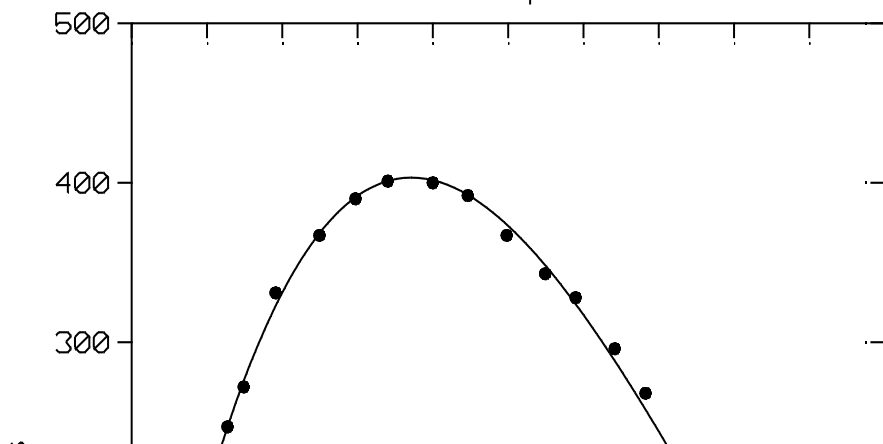
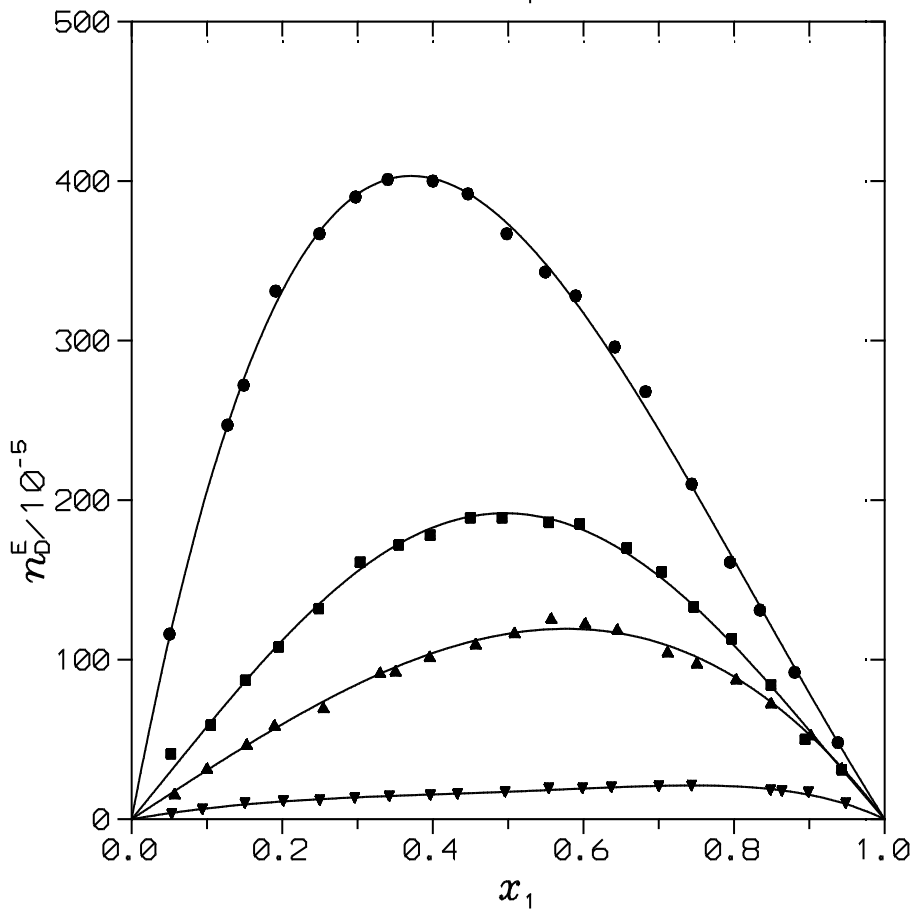
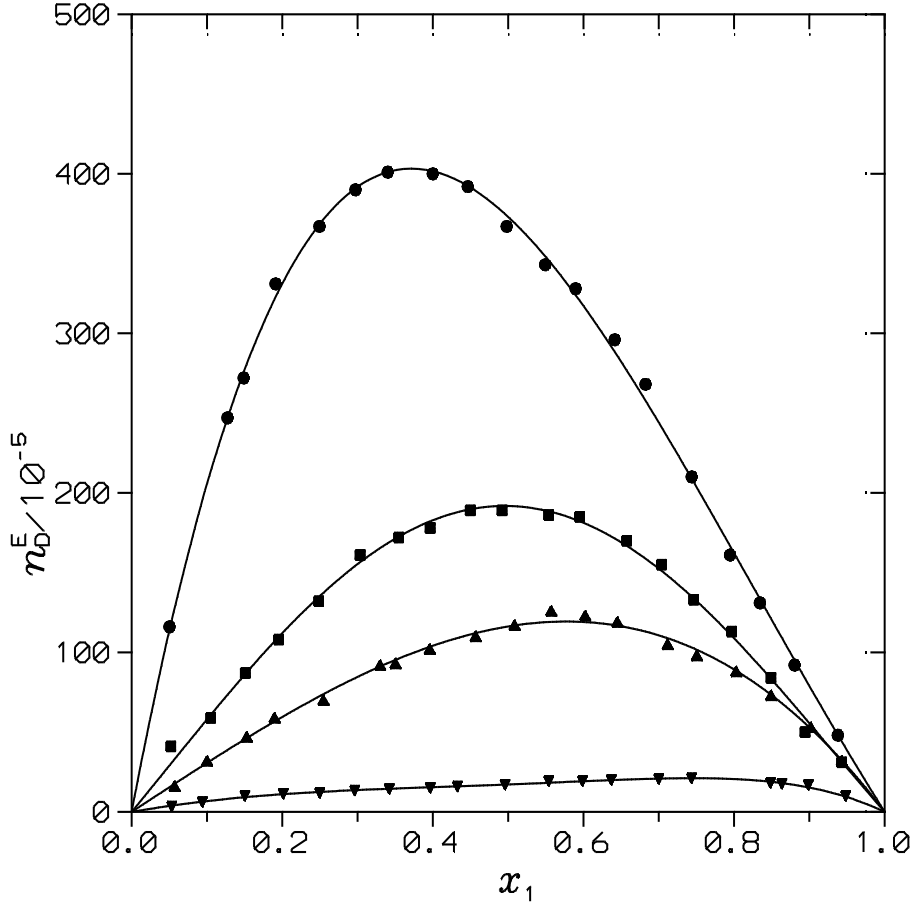


Figure 5 Excess refractive indices, n_D^E , for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Full symbols, experimental values (this work): (●), propanone; (■), 2-butanone; (▲), 2-pentanone, (▼), 2-heptanone. Solid lines, calculations with eq. 8 using the coefficients from Table 6.

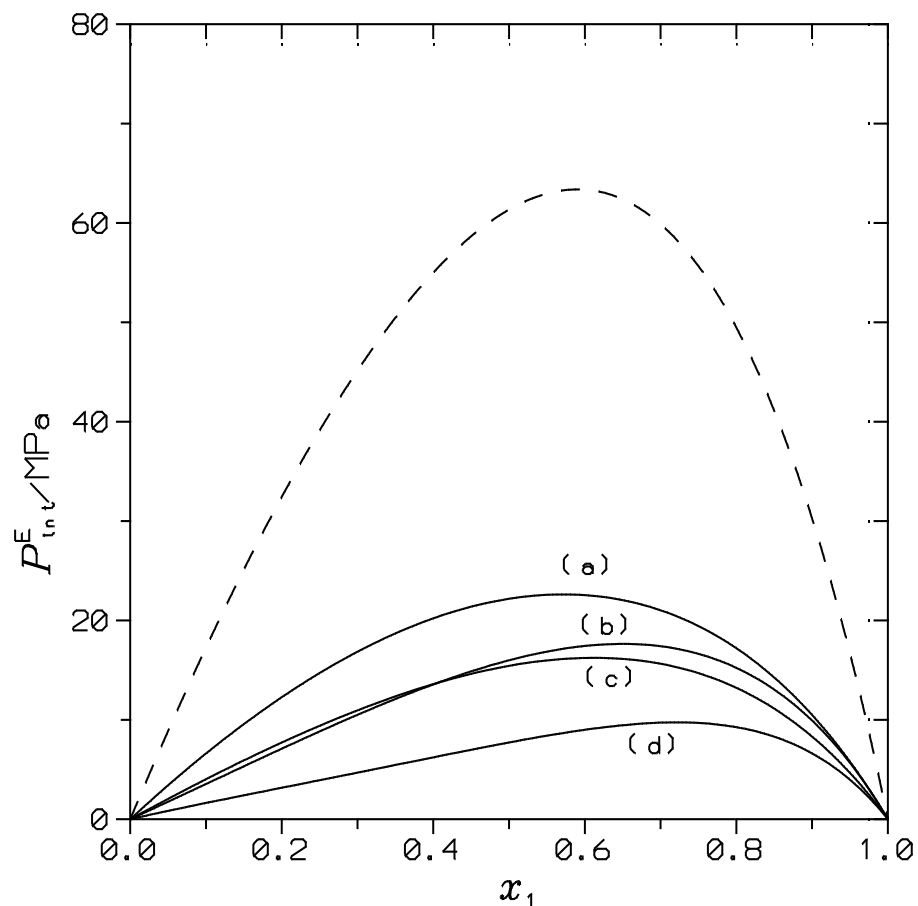


Figure 6 Excess internal pressures, P_{int}^E , for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K. Solid lines: (a) propanone; (b), 2-butanone; (c), 2-pentanone, (d), 2-heptanone. Dashed line, aniline + propanone [81]

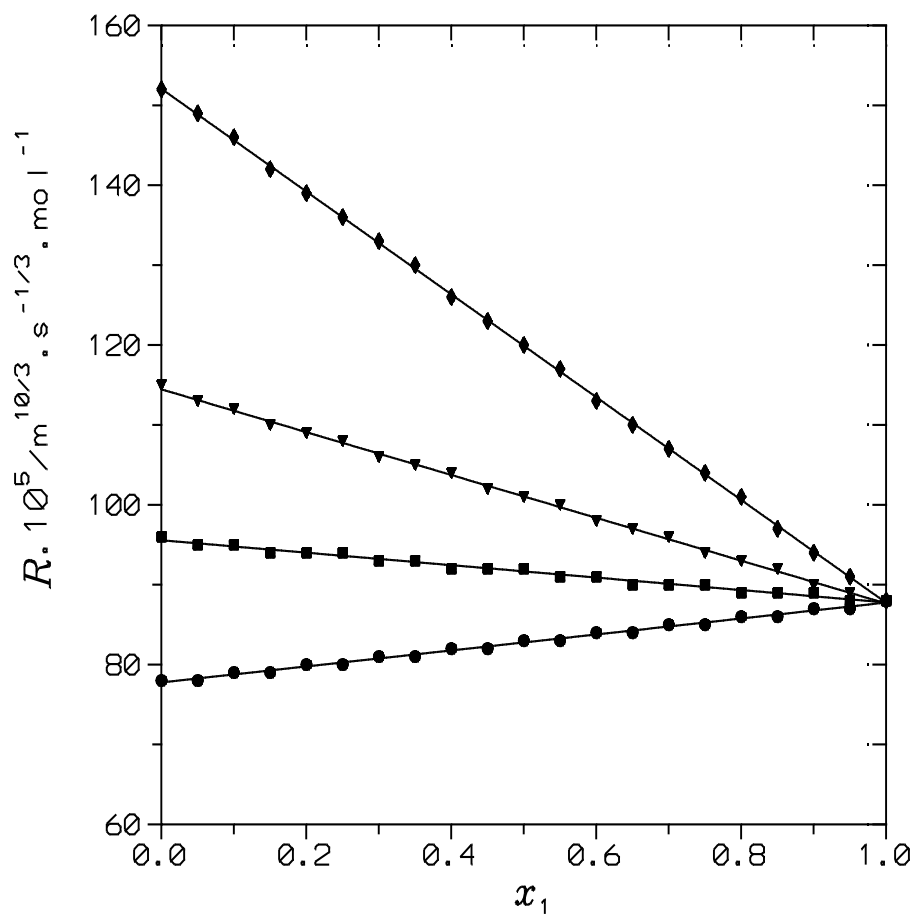


Figure 7 Rao's constant for DMF (1) + 2-alkanone (2) systems at atmospheric pressure and 298.15 K (this work): (●), propanone; (■), 2-butanone; (▲), 2-pentanone, (▼), 2-heptanone.