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ORIENTATIONAL EFFECTS AND RANDOM MIXING IN 1-ALKANOL + ALKANONE MIXTURES

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Abstract

1-Alkanol + alkanone systems have been investigated through the data analysis of molar excess functions, enthalpies, isobaric heat capacities, volumes and entropies, and using the Flory model and the formalism of the concentration-concentration structure factor ($S_{CC}(0)$). The enthalpy of the hydroxyl-carbonyl interactions has been evaluated. These interactions are stronger in mixtures with shorter alcohols (methanol-1-butanol) and 2-propanone, or 2-butanone. However, effects related to the self-association of alcohols and to solvation between unlike molecules are of minor importance when are compared with those which arise from dipolar interactions. Physical interactions are more relevant in mixtures with longer 1-alkanols. The studied systems are characterized by large structural effects. The variation of the molar excess enthalpy with the alcohol size along systems with a given ketone, or with the alkanone size in solutions with a given alcohol are discussed in terms of the different contributions to this excess function. Mixtures with methanol show rather large orientational effects. The random mixing hypothesis is attained in large extent for mixtures with 1-alkanols $\neq$ methanol and 2-alkanones. Steric effects and cyclization lead to stronger orientational effects in mixtures with 3-pentanone, 4-heptanone or cyclohexanone. The increase of temperature weakens orientational effects. Results from $S_{CC}(0)$ calculations show that homocoordination is predominant and support conclusions obtained from the Flory model,

1.   Introduction

It is well known that ketones are proton acceptors due to their characteristic carbonyl group, and that 1-alkanols are self-associated compounds via hydrogen bonds. In mixtures with alcohols or amines, ketones can form hydrogen bonds with these compounds.[1-6] The research of the mentioned interactions is important for a better understanding of the hydrogen-bond properties of complex molecules with carbonyl groups such as acids, or proteins, which, on the other hand, are of evident biological interest.

Different theories have been applied to the study of 1-alkanol + n-alkanone mixtures. Systems containing methanol, ethanol or 1-propanol and 2-propanone, or 2-butanone have been investigated in terms of an association model which assumes the existence of linear and cyclic species for alcohols, and only open chains for alcohol-alkanone heterocomplexes.[1-4] In this theory, the physical contribution to the molar excess enthalpy, $H_{\mathrm{m}}^{\mathrm{E}}$. is derived from the NRTL equation by application of the Gibbs-Duhem equation.[1-4] The model describes accurately $H_{\mathrm{m}}^{\mathrm{E}}$ of the mentioned binary systems. $H_{\mathrm{m}}^{\mathrm{E}}$ values of related ternary solutions, including benzene as third compound, are also correctly predicted by the model neglecting ternary interactions.[1-4] In the UNIQUAC association solution model, the physical contribution to $H_{\mathrm{m}}^{\mathrm{E}}$ is obtained from the UNIQUAC equation,[7-10] and only   linear polymers for the self-association of 1-alcohols and for the alcohol-ketone solvation are considered.[7-10] The model provides good $H_{\mathrm{m}}^{\mathrm{E}}$ results for mixtures involving shorter 1-alkanols and 2-propanone.[7-10] A theory based on hydrogen-bond configuration extended to mixtures including molecules with proton acceptors has been used to describe solid-liquid equilibria and $H_{\mathrm{m}}^{\mathrm{E}}$ of 1-alkanol + 2-propanone or + 2-butanone mixtures.[11] Hydrogen bond between methanol and 2-propanone has been characterized by means of a distributed multipole analysis combined with intermolecular perturbation theory calculations.[12] The group contribution Nitta-Chao model[13] has been very shortly applied to 1-alkanol + 2-alkanone mixtures. Differences between experimental and calculated $H_{\mathrm{m}}^{\mathrm{E}}$ values are 15% or lower, but the model largely fails when representing $V_{\mathrm{m}}^{\mathrm{E}}$.[14] The purely physical model DISQUAC[15] has been successfully applied to 1-alkanol (from methanol to 1-decanol) + n-alkanone (from 2-propanone to 2-heptanone) systems.[16] Assuming interaction parameters which are dependent of the molecular structure of the mixture components, DISQUAC provides theoretical values for vapor-liquid equilibria, VLE, and $H_{\mathrm{m}}^{\mathrm{E}}$ in very good agreement with the experimental measurements.[16] The average deviations between experimental results and theoretical calculations are 2% and 6% for VLE and $H_{\mathrm{m}}^{\mathrm{E}}$, respectively. DISQUAC predictions on these thermodynamic properties of related ternary mixtures compare also well with the experimental values.[17]

In previous works, we have shown that the Flory model[18] is a useful tool to investigate orientational effects in liquid mixtures. Systems such as 1-alkanol + linear or cyclic monoether,[19] or + linear polyether,[20] or 1-butanol + alkoxyethanol,[21] or ether + alkane[22], + benzene, or + toluene[23], or + CCl_4[24] have been investigated using this approach. As continuation, here we study orientational effects in 1-alkanol + ketone mixtures by means of the same methodology. As far as we know, only 1-alkanol + 2-heptanone mixtures[25] have been treated using the Prigogine-Flory-Patterson model.[26]

On the other hand, it is interesting to link thermodynamic properties of liquid mixtures with local deviations from the bulk composition. There are at least two ways of looking at the fluctuations in a binary mixture.[27-29] Thus, it is possible to consider fluctuations in the number of molecules of each component and the cross fluctuations. This is the so-called Kirkwood-Buff integrals formalism.[30,31] A different alternative, developed by Bhatia and Thorton[32] and used in the investigation of liquid binary alloys[33,34] on the basis of the Bhatia-Thorton partial structure factors, is concerned with the study of fluctuations in the number of molecules regardless of the components, the fluctuations in the mole fraction and the cross fluctuations. This approach was generalized to link the asymptotic behaviour of the ordering potential to the interchange energy parameters in the semi-phenomenological theories of thermodynamic properties of liquid solutions.[35-38] We have applied this formalism to mixtures involving pyridines[39] or to 1-alkanol + cyclic ether systems,[40] and now is extended to 1-alkanol + 2-alkanone systems.

2. Theories

2.1.1 Flory model

The main hypotheses of the theory[18,41-44] are briefly summarized. (i) Molecules are divided into segments (arbitrarily chosen isomeric portions of a molecule). (ii) The mean intermolecular energy per contact is proportional to $-\eta / v_s$ (η is a positive constant which characterizes the energy of interaction for a pair of neighbouring sites; v_s is the segment volume). (iii) The configurational partition function is stated taking the number of external degrees of freedom of the segments lower than 3. This is necessary to take into account restrictions on the precise location of a given segment by its neighbours in the same chain. (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). In the case of very large total number of contact sites, 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 given by:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{V}\bar{T}} \tag{1}$$

where $\bar{V} = V/V^*$; $\bar{P} = P/P^*$ and $\bar{T} = T/T^*$ are the reduced volume, pressure and temperature, respectively. Equation (1) is valid for pure liquids and liquid mixtures. For pure liquids, the reduction parameters, V_i^*, P_i^* and T_i^* are obtained from densities, ρ_i, isobaric expansion coefficients, α_{P_i}, and isothermal compressibilities, κ_{T_i}, data. The corresponding expressions for reduction parameters for mixtures are given elsewhere.[22] H_m^E is determined from

$$H_m^E = \frac{x_1 V_1^* \theta_2 X_{12}}{\bar{V}} + x_1 V_1^* P_1^* \left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}}\right) + x_2 V_2^* P_2^* \left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}}\right) \tag{2}$$

All the symbols have their usual meaning.[22] In this expression, the term which depends directly on X_{12} is usually named 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 (2) is obtained from the equation of state. Therefore, the molar excess volume can be also calculated:

$$V_m^E = (x_1 V_1^* + x_2 V_2^*)(\bar{V} - \varphi_1 \bar{V}_1 - \varphi_2 \bar{V}_2) \tag{3}$$

2.1.2 Estimation of the Flory interaction parameter

X_{12} is determined from a H_m^E measurement at given composition from:[19,21,22]

$$X_{12} = \frac{x_1 P_1^* V_1^* (1 - \frac{\bar{T}_1}{\bar{T}}) + x_2 P_2^* V_2^* (1 - \frac{\bar{T}_2}{\bar{T}})}{x_1 V_1^* \theta_2} \tag{4}$$

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

$$H_m^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2} + \frac{1}{\bar{V}\bar{T}} (x_1 P_1^* V_1^* \bar{T}_1 + x_2 P_2^* V_2^* \bar{T}_2) \tag{5}$$

and that from the equation of state, $\bar{V} = \bar{V}(\bar{T})$. More details have been given elsewhere.[19,21,22] Equation (5) is a generalization of that previously given to calculate X_{12} from H_m^E at $x_1 = 0.5$.[45] Properties of alkanones ($i = 2$) at 298.15 K, molar volumes, V_i, α_{P_i}, κ_{T_i}, and the

corresponding reduction parameters, P_i^* and V_i^*, needed for calculations are listed in Table 1. For 1-alkanols (i = 1), values have been taken from the literature.[19,20] At $T \neq 298.15$ K, the mentioned properties were estimated using the same equations as in previous applications for the temperature dependence of ρ, α_p and γ (= α_p/κ_T)[19,46] X_{12} values determined from experimental H_m^E data at $x_1 = 0.5$ are collected in Table 2

2.2 *The concentration-concentration structure factor*

Mixture structure can be studied using the $S_{CC}(0)$ function[28,29,35,36,47]

$$S_{CC}(0) = \frac{RT}{(\partial^2 G^M / \partial x_1^2)_{P,T}} = \frac{x_1 x_2}{D} \tag{6}$$

with

$$D = \frac{x_1 x_2}{RT}(\partial^2 G^M / \partial x_1^2)_{P,T} = 1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G_m^E}{\partial x_1^2}\right)_{P,T} \tag{7}$$

In these equations, G^M, G_m^E stand for the molar Gibbs energy of mixing and the molar excess Gibbs energy, respectively. D is a function closely related to thermodynamic stability.[48-50] For ideal mixtures, $G_m^{E,id} = 0$ (excess Gibbs energy of the ideal mixture); $D^{id} = 1$ and $S_{CC}(0) = x_1 x_2$. As stability conditions require, $S_{CC}(0) > 0$. Thus, for a system close to phase separation, $S_{CC}(0)$ must be large and positive (∞, when the mixture presents a miscibility gap). If compound formation between components appears, $S_{CC}(0)$ must be very low (0, in the limit). Therefore, $S_{CC}(0) > x_1 x_2$ ($D < 1$) indicates that the dominant trend in the system is the homocoordination (separation of the components), and the mixture is less stable than the ideal. If $0 < S_{CC}(0) < x_1 x_2 = S_{CC}(0)^{id}$, ($D > 1$), the fluctuations in the system have been removed, and the dominant trend in the solution is heterocoordination (compound formation). In such case, the system is more stable than ideal. In summary, $S_{CC}(0)$ is an useful magnitude to evaluate the non-randomness in the mixture.[29,47]

3. Results

Results on H_m^E obtained from the Flory model using X_{12} values at $x_1 = 0.5$ are listed in Tables 2, which also contains the interactional contribution to H_m^E at equimolar composition.

Experimental and theoretical values for H_m^E are compared graphically in Figures. 1-5. For

clarity, Table 2 also includes the relative standard deviations for H_m^E defined as

$$\sigma_r(H_m^E) = \left[\frac{1}{N} \sum \left(\frac{H_{m,exp}^E - H_{m,calc}^E}{H_{m,exp}^E} \right)^2 \right]^{1/2} \tag{8}$$

where $N\,(=19)$ is the number of data points, and $H_{m,exp}^E$ stands for the smoothed H_m^E values

calculated at $\Delta x_1 = 0.05$ in the composition range [0.05, 0.95] from polynomial expansions,

previously checked, given in the original works. The concentration dependence of X_{12},

according to equation (4) is shown in Figure 6 for some selected systems. Table 3 lists the

results obtained for the $S_{CC}(0)$ function (see also Figure 7). D values were calculated from G_m^E

functions represented by means of equations of the Redlich-Kister type with parameters

determined from isothermal vapour-liquid equilibria available in the literature.

4.   Discussion

4.1 Enthalpies of the hydroxyl-carbonyl interactions

It is well known that if structural effects are neglected,[48,51] H_m^E is the result of three

contributions: two of them are positive, $\Delta H_{OH-OH}, \Delta H_{CO-CO}$, and are related to the breaking of

alkanol-alkanol and ketone-ketone interactions upon mixing, respectively; ΔH_{OH-CO} is a

negative contribution due to the new OH---CO interactions created during the mixing process.

That is:[52-55]

$$H_m^E = \Delta H_{OH-OH} + \Delta H_{CO-CO} + \Delta H_{OH-CO} \tag{9}$$

The ΔH_{OH-CO} term represents the enthalpy of the H-bonds between 1-alkanols and alkanones, and

may be evaluated by extending the equation (9) to $x_1 \to 0$.[55-57] In such case, ΔH_{OH-OH} and

ΔH_{CO-CO} can be replaced by $H_{m1}^{E,\infty}$ (partial excess molar enthalpy at infinite dilution of the first

component) of 1-alkanol or alkanone + heptane systems. Thus,

$$\Delta H_{OH-O} = H_{m1}^{E,\infty}(1-\text{alkanol} + \text{alkanone})$$
$$-H_{m1}^{E,\infty}(1-\text{alkanol} + \text{heptane}) - H_{m1}^{E,\infty}(\text{alkanone} + \text{heptane}) \tag{10}$$

This is a rough estimation of $\Delta H_{\text{OH-CO}}$ due to: i) $H_{\text{m1}}^{\text{E},\infty}$ data used were calculated from H_{m}^{E} measurements over the entire mole fraction range. Nevertheless, it should be remarked that the value $H_{\text{m1}}^{\text{E},\infty}$ (ethanol + 2-propanone)[1] = 5.54 kJ·mol^{-1} used here is in reasonable agreement with that available in the literature[58] obtained from calorimetric measurements at high dilution (5.12 kJ·mol^{-1}). ii) For 1-alkanol + n-alkane systems, it was assumed that $H_{\text{m1}}^{\text{E},\infty}$ is independent of the alcohol, a common approach when applying association theories.[59-62] We have used in this work, as in previous applications,[20,55] $H_{\text{m1}}^{\text{E},\infty}$ = 23.2 kJ·mol^{-1}.[63-65] Values of $\Delta H_{\text{OH-CO}}$ are collected in Table 4. From inspection of the results for $CH_3(CH_2)_{n-1}OH + CH_3CO(CH_2)_{m-1}CH_3$ mixtures, we note: (i) interactions between unlike molecules are stronger in solutions with shorter 1-alkanols (n = 1-4) and 2-propanone or 2-butanone (m =1,2). (ii) For a given n value, $\Delta H_{\text{OH-CO}}$ smoothly increases with m. From $n > 2$, this magnitude remains practically constant for $m \geq 3$. (iii) The variation of $\Delta H_{\text{OH-CO}}$ with n for a given m value is similar to that described above. In practice, $\Delta H_{\text{OH-CO}}$ may be assumed constant for $n > 2; m \geq 3$. The average value is -22.2 kJ·mol^{-1}. In the case of cyclohexanone mixtures, alkanol-ketone interactions are also stronger in the methanol solution, and $\Delta H_{\text{OH-CO}}$ is constant from ethanol. When comparing $\Delta H_{\text{OH-CO}}$ values for systems with 2-hexanone or cyclohexanone, or 2-pentanone or 3-pentanone, or including 2-heptanone or 4-heptanone, $\left|\Delta H_{\text{OH-CO}}\right|$ is slightly higher for 2-alkanone solutions. That is, steric effects related to the position of the CO group in the alkanone (2-pentanone/3-pentanone; 2-heptanone/4-heptanone) or with the ketone shape (2-hexanone/cyclohexanone) do not change largely the $\Delta H_{\text{OH-CO}}$ values.

A variety of $\Delta H_{\text{OH-CO}}$ values can be found in the literature, depending of the method applied for their estimation. Intermolecular perturbation theory calculations give[12] -24.7 kJ·mol^{-1} for the methanol + 2-propanone mixture. In the UNIQUAC association solution model the value -21.0 kJ·mol^{-1} is used for the mixtures methanol, ethanol, or 1-propanol + 2-propanone,[8,9] while the corresponding system with 1-butanol[10] is characterized by -14.0 kJ·mol^{-1}. Methods based in infrared spectroscopy provide -15.9 and -15.1 kJ·mol^{-1} for methanol + 2-propanone, or + 2-butanone, respectively.[66]

It is interesting the comparison of the enthalpy of the 1-alkanol-oxaalkane interactions, $\Delta H_{\text{OH-O}}$, determined previously following the same approach,[20,55] with the $\Delta H_{\text{OH-CO}}$ values obtained in the present work. In the case of mixtures with linear polyethers,[20] $\Delta H_{\text{OH-O}}$ (methanol) /kJ·mol^{-1} = -26.5 (2,5-dioxahexane); -28.6 (2,5,8-trioxanonane); -34.2 (2,5,8,1,1,14-pentaoxapentadecane), and $\Delta H_{\text{OH-O}}$ (1-heptanol)/kJ·mol^{-1} = -22.2 (2,5,-

dioxahexane); -24.6 (2,5,8-trioxanonane). Interactions between unlike molecules in solutions including 2,5-dioxahexane are quite similar to those in the corresponding mixtures with a ketone of similar size (2-heptanone, e.g). Interactions between unlike molecules are stronger in solutions with 2,5,8-trioxanone, or the pentaether. In the case of mixtures with linear monoethers,[55] ΔH_{OH-O} (methanol)/ kJ·mol^{-1} $=-21.1$ (diethyl ether); -19.1 (dipropylether), or -17.3 kJ·mol^{-1} for the 1-hexanol + dipropyl ether systems. Interactions between unlike molecules are weaker in this class of solutions.

Below, we are referring to thermodynamic properties at equimolar composition and 298.15 K.

4.2   *Excess molar enthalpies and excess molar entropies.*

H_m^E values of 1-alkanol + alkanone mixtures are positive (Table 2). Consequently, the dominant contributions to this excess function come from the breaking of the interactions between like molecules, i.e., the $\Delta H_{OH-OH}, \Delta H_{CO-CO}$ terms in equation 9 are higher than $\left|\Delta H_{OH-CO}\right|$. Except for methanol systems, H_m^E (1-alkanol + alkanone) $>$ H_m^E (1-alkanol + isomeric alkane). Thus, H_m^E (1-propanol)/J·mol^{-1} $=$ 1251 (2-heptanone)[25] $>$ 673 (octane),[67] 597 (heptane).[68] This indicates that alkanones are good breakers of the alcohol self-association. On the other hand, in solutions with a given 2-alkanone, H_m^E increases with the chain length of the 1-alcohol, and the H_m^E curves are rather symmetrical, except for mixtures containing methanol (Figures 1-5). These features reveal that interactions are mainly of dipolar type and that self-association of 1-alkanols and solvation effects are of minor importance. 1-Alkanol + heptane mixtures, where self-association of alcohols plays the dominant role, behave somewhat differently: H_m^E increases from ethanol to 1-propanol or 1-butanol and then smoothly decreases, the H_m^E curves are skewed to low mole fractions of the alcohol,[55] and the corresponding H_m^E values are rather low (see above). These systems also show large positive excess heat capacities at constant pressure, $C_{p,m}^E$ (11.7 J·mol^{-1}·K^{-1} for ethanol + heptane[69]) while $C_{p,m}^E$ (ethanol)/J·mol^{-1}·K^{-1}, estimated from $\dfrac{\Delta H_m^E}{\Delta T}$, is 5 for the solution with 2-propanone[70] and 5.9 or 5 for that with 2-butanone.[71,72] The importance of dipolar interactions in the investigated mixtures is confirmed by their $TS_m^E (= H_m^E - G_m^E)$ values (Table 3), which are much higher than those for 1-alkanol + alkane systems.[55] For example, for the ethanol + hexane mixture, $H_m^E =$ 548;[73] $G_m^E = 1374$[62] and $TS_m^E = -826$ (values in J·mol^{-1}).

4.2.1   The effect of increasing the chain length or the 2-alkanone in mixtures with a given 1-alcohol

The H_m^E variation depends on the alcohol considered. H_m^E of systems with 1-alkanols longer than 1-butanol decreases with the increasing of the ketone size (Table 2). 2-Alkanone + alkane mixtures behave similarly. Thus, H_m^E (heptane)/J·mol^{-1} = 1676 (2-propanone)[74] > 1339 (2-butanone)[75] > 1135 (2-pentanone)[75] > 1055 (2-hexanone)[76] > 886 (2-heptanone).[77] Such variation has been mainly ascribed to the decreasing polarity of longer 2-alkanones,[78] and means a lower ΔH_{CO-CO} contribution to H_m^E in equation (9). This effect predominates over those which lead to increased H_m^E values: (i) the smooth increasing of ΔH_{OH-CO} (see above). (ii) The larger ΔH_{OH-OH} term due to a higher number of OH-OH interactions broken by ketones with larger aliphatic surfaces. Note that H_m^E of 1-alkanol + *n*-alkane mixtures increases with the alkane size.[79]   (iii) Stronger steric hindrances, which make more difficult the formation of interactions between unlike molecules when longer 2-alkanones are involved. Dielectric relaxation studies confirm this behaviour in methanol solutions.[80] On the other hand, solvation effects are more important in methanol mixtures (see below) and H_m^E smoothly increases with the ketone size (Table 2), indicating that the different contributions to H_m^E are nearly counterbalanced. H_m^E of 1-propanol mixtures decreases when replacing 2-propanone by 2-butanone, and then remains constant (Table 2)

TS_m^E values decrease with the increasing of the alkanone size (Table 3), probably due to the lower number of ketone-ketone interactions broken upon mixing. In the case of methanol solutions with longer 2-alkanones, the difference in size between the mixture components, which contributes negatively to TS_m^E, must be also taken into account.

4.2.2   The effect of increasing the chain length of the 1-alkanol in systems with a given ketone

At such condition, H_m^E increases (Table 2). This is partially due to the smooth increasing of ΔH_{OH-CO} (Table 4). We note that H_m^E values are much lower for methanol mixtures and that the H_m^E variation is steeper when replacing this alcohol by ethanol than when ethanol is substituted by 1-propanol. On the other hand, it should be also kept in mind that methanol + alkane mixtures show miscibility gaps at 298.15 K and equimolar composition.[81] This remarks that effects related to interactions between unlike molecules are much relevant in methanol systems. Such effects are also relatively important in ethanol + 2-butanone, or + 2-pentanone, as the following H_m^E/J·mol^{-1} values suggest: 496 (ethanol + pentane)[82] < 1071

(ethanol + 2–butanone)[72]; 866 (ethanol + 2-pentanone)[83] < 1160 (2-butanone + pentane)[75]; 966 (2-pentanone + pentane).[75] The same trend is observed in 1-alkanol + 2-propanone mixtures (Table 2), as their H_m^E values, up to 1-hexanol, are lower than those of 2-propanone + alkane systems. Some data follow for comparison, H_m^E(2-propanone)/J·mol^{-1} = 1285 (butane, T = 263.15 K);[84] 1458 (pentane, T = 293.15 K);[84] 1676 (heptane);[74] 1967 (decane).[85] This variation reveals that the number of ketone-ketone interactions disrupted upon mixing increases with the aliphatic surface of the 1-alcohol, giving a larger $\Delta H_{CO\text{-}CO}$ term in equation (9). For the remainder systems, H_m^E values are higher than those of the 1-alkanol or 2-alkanone + alkane mixtures. For example, H_m^E/J·mol^{-1} = 673 (1-propanol + octane);[67] 886 (2-heptanone + heptane);[77] 1251 (1-propanol + 2-heptanone);[25] 534 (1-heptanol + octane);[86] 1427 (1-heptanol + 2-heptanone).[25] Alcohol-alcohol interactions are more easily broken by alkanones in the case of long chain 1-alkanols, which means a larger $\Delta H_{OH\text{-}OH}$ contribution. The increase of the TS_m^E with the alcohol size (Table 3) is consistent with this picture. Interestingly, $C_{p,m}^E$(2-butanone)[71]/ J·mol^{-1}·K^{-1} = 4.9 (ethanol); 5.9 (1-butanol); 3 (1-hexanol); -0.15 (1-octanol); -1.45 (1-decanol). This clearly indicates that association/solvation effects become weaker with the increasing of the alcohol size, and that physical interactions are predominant in systems with long 1-alkanols. Note that $C_{p,m}^E$ of the benzene + heptane mixture,[87] characterized by dispersive interactions, is -3.34 J·mol^{-1}·K^{-1} .

4.2.3 Steric effects

Differences between H_m^E values of 1-alkanol + 2-pentanone, or + 3-pentanone mixtures may be explained in similar terms. For methanol, or ethanol + 2-pentanone solutions, H_m^E is lower than for the systems with 3-pentanone, probably due to a higher $\left|\Delta H_{OH\text{-}CO}\right|$ contribution in the former mixtures, and to CO group is more sterically hindered in 3-pentanone. The opposite trend is observed in solutions with longer 1-alkanols. This may be ascribed to a decreasing of the $\Delta H_{CO\text{-}CO}$ term is slightly now predominant in the case of 3-pentanone systems (H_m^E(heptane)/J·mol^{-1} = 1135 (2-pentanone) > 1078 (3-pentanone).[75] Note that the difference between these values is similar to those encountered for the corresponding systems with 1-hexanol (88 J·mol^{-1}) or 1-heptanol (93 J·mol^{-1}) (see Table 2).

On the other hand, for methanol or ethanol solutions, H_m^E(cyclohexanone) > H_m^E(2-hexanone) as $\Delta H_{OH\text{-}CO}$ is more negative for the systems with the linear ketone (Table 4) and $\Delta H_{OH\text{-}OH}$ is expected to be higher in cyclohexanone solutions due to cyclic molecules break

more easily the alcohol self-association (H_m^E(1-pentanol)/J·mol^{-1} = 598 (cyclohexane)[88] > 494

(hexane)[88]). Cyclization seems to have no influence on H_m^E of the 1-pentanol mixture.

4.3   *Excess molar volumes*

In spite of the few V_m^E data available,[14,25,71,89-91] some general trends can be outlined. (i)

V_m^E values are rather low and even negative, while the corresponding H_m^E results are usually

large and positive. Thus, V_m^E (2-butanone)/cm^3·mol^{-1} = -0.0298 (1-propanol);[89] 0.1611 (1-

octanol)[71] and H_m^E/J·mol^{-1} = 1237 (1-propanol);[4] 1711 (1-octanol)[71] Similarly, V_m^E of the

ethanol + cyclohexanone mixture is[90] -0.226 cm^3·mol^{-1} (T = 293.15 K) while H_m^E is[92] 1199

J·mol^{-1}.   This reveals the existence of large structural effects. Methanol solutions are

characterized by lower negative V_m^E values (-0.2675 cm^3·mol^{-1} for the 2-butanone mixture),[89]

which can also be ascribed in part to stronger solvation effects in this type of systems. (ii) Both

magnitudes V_m^E and H_m^E (Table 2) increase with the 1-alcohol size in solutions with a given 2-

alkanone.   For example, V_m^E (2-pentanone)/cm^3·mol^{-1} = -0.2183 (methanol)[89] < -0.0475

(ethanol)[89] < -0.0183 (1-propanol)[89] < 0.004 (1-pentanol)[14] < 0.0295 (1-hexanol)[14] < 0.0823 (1-

octanol).[14] Therefore, the V_m^E variation can be attributed to increased values of the interactional

contribution to this excess function. (iii) For fixed 1-alkanol (from 1-hexanol) + 2-alkanone

mixtures, V_m^E and H_m^E (Table 2) decrease with the increasing of the ketone size (V_m^E (1-

hexanol)/cm^3·mol^{-1} = 0.0762 (2-butanone)[71] > 0.0295 (2-pentanone)[14] > 0.0153 (2-

heptanone)[25]). This reveals a lowering of the interactional contribution to V_m^E .

4.4   *Results from the Flory model*

Let's define, the mean standard relative deviation of H_m^E as:

$$\bar{\sigma}_r(H_m^E) = \frac{1}{N_S}\sum \sigma_r(H_m^E) \qquad\qquad (11)$$

where N_S stands for the number of systems considered. Now, we can compare mean results for

mixtures containing a given 1-alkanol. In this case, $\bar{\sigma}_r(H_m^E)$ = 0.245 (methanol); 0.088

(ethanol); 0.098 (1-propanol), 0.044 (1-butanol); 0.073 (1-pentanol); 0.069 (1-hexanol); 0.056

(1-heptanol); 0.057 (1-octanol); 0.042 (1-nonanol), 0.070 (1-decanol). This indicates that strong

orientational effects exist in mixtures with methanol, and that the random mixing hypothesis is

attained in large extent for the remainder systems. However, from a more detailed inspection of

the results listed in Table 2 some conclusions can be remarked. (i) Mixtures with methanol or 1-

propanol are characterized by orientational effects which increase with the size of the 2-

alkanone. For the remainder mixtures such effects are more or less independent of the system components. (ii) Mixtures with 2-pentanone or 2-heptanone usually show weaker orientational effects than those with 3-pentanone or 4-heptanone. (iii) The increasing of temperature weakens orientational effects.

It is interesting compare results obtained from the Flory model for 1-alkanol + alkanone, or + linear monoether, or + linear polyether mixtures. In the case of alkanone solutions, $\bar{\sigma}_r(H_m^E) = 0.245$ (methanol, $N_S = 13$), 0.074 (1-alkanols $\neq$ methanol; $N_S = 66$). Orientational effects are stronger in the systems methanol or ethanol + linear monoethers[19] ($\bar{\sigma}_r(H_m^E) = 0.456$; $N_S = 8$) or + linear polyethers[20] ($\bar{\sigma}_r(H_m^E) = 0.438$; $N_S = 7$). For mixtures containing longer 1-alkanols, $\bar{\sigma}_r(H_m^E) = 0.281$ ($N_S = 18$, linear monoethers[19]) and $\bar{\sigma}_r(H_m^E) = 0.059$ ($N_S = 25$, linear polyethers[20]), and the random mixing hypothesis is also valid for the latter solutions.

Model calculations lead to very large V_m^E values (1.237 cm^3·mol^{-1} for the 1-propanol + 2-butanone system), which means that structural effects are not properly represented by the theory. The interaction parameter X_{12} decreases with the increasing of the size of the 2-alkanone in mixtures with a given 1-alkanol, and shows a maximum at ethanol or 1-propanol in solutions with a given 2-alkanone (Table 2). As previously described, the corresponding H_m^E variations are somewhat different. However, X_{12} and $H_m^E/(x_1V_1^* + x_2V_2^*)$ of mixtures with 2-alkanones change in line. It is worthwhile that this behavior is not observed for cyclohexanone systems as X_{12} decreases with the increasing of the chain length of the alcohol and $H_m^E/(x_1V_1^* + x_2V_2^*)$ presents a maximum for the ethanol solution. This might be due to structural effects are even stronger in such mixtures, while the model largely overestimates the interactional contribution to V_m^E (yields 0.642 cm^3·mol^{-1} for ethanol + cyclohexanone) and, consequently, also overestimates the equation of state contribution term to H_m^E.

4.5 $S_{CC}(0)$ results

$S_{CC}(0)$ values are higher than 0.25 (Table 3) and, therefore, homocoordination is the dominant trend in the investigated systems. Nevertheless, $S_{CC}(0)$ results are rather low, which suggests that effects related to non-randomness are weak. Interestingly, the $S_{CC}(0)$ values of 2-propanone + alkane mixtures are higher (0.984 (pentane[93]); 0.960 (heptane[93] at $T = 323.15$ K)) due to these systems show miscibility gaps at relatively high temperatures (the critical temperature of the heptane solution is 245.22 K[94]). As it is expected, the increasing of the alkanone size in mixtures with, say heptane, weakens homocoordination (0.553 for the 2-

butanone system[95] at 323.15 K). Inspection of Table 3 allows state the following features: (i) $S_{CC}(0)$ increases with the ketone size in methanol solutions. i.e., homocoordination is strengthened when the aliphatic surface of the ketone increases. In terms of the Flory model, $\sigma_r(H_m^E) = 0.178$ (2-propanone), 0.347 (2-heptanone) (Table 2). (ii) Non-randomness effects are rather similar along the series 1-alkanol + 2-butanone, as $S_{CC}(0)$ is practically independent of the alcohol (Table 3). (iii) $S_{CC}(0)$ decreases with increased T values. That is, orientational effects become weaker at higher temperatures, in agreement with results from the Flory model.

5.   Conclusions

1-Alkanol + alkanone mixtures have been investigated through the analysis of H_m^E, C_{pm}^E, V_m^E and TS_m^E data and using the Flory model and the $S_{CC}(0)$ formalism. The enthalpy of the hydroxyl-carbonyl interactions has been evaluated. Effects related to the self-association of alcohols and to solvation between unlike molecules are of minor importance. It is shown that interactions are mainly of dipolar type, and that physical interactions are more relevant in mixtures with longer 1-alkanols. The investigated systems are characterized by large structural effects. Methanol solutions show rather large orientational effects. The random mixing hypothesis is attained for mixtures with 1-alkanols ≠ methanol and 2-alkanones. Steric effects and cyclization lead to stronger orientational effects in mixtures with 3-pentanone, 4-heptanone or cyclohexanone. These effects decrease when temperature is increased. $S_{CC}(0)$ calculations show that homocoordination is predominant in the studied mixtures and support conclusions obtained from the Flory model,

6.   References

(1)   Nagata I.; Ksiazczak A. Excess enthalpies for (ethanol + propanone) and (ethanol + propanone + benzene) at the temperature 298.15 K. *J. Chem Thermodyn.* **1994,** *26,* 165.

(2)   Nagata I. Excess molar enthalpies for methanol + acetone and methanol + acetone + benzene mixtures at 298.15 K. *Thermochim. Acta* **1994**, *236*, 23.

(3)   Nagata I.; Takeuchi K. Excess molar enthalpies for 1-propanol + acetone and 1-propanol + acetone + benzene mixtures at 298.15 K. *Thermochim. Acta* **1994,** *242,* 103.

(4)   Tamura K.; Nagata I. Excess molar enthalpies of (propan-1-ol + butan-2-one) and of (propan-1-ol or propan-2-ol + butan-2-one + benzene) at the temperature 298.15. *J. Chem. Thermodyn.* **1991,** *23,* 359.

(5)   González, J.A., Alonso, I.; García de la Fuente, I.; Cobos, J.C. Thermodynamics of ketone + amine mixtures. Part IX. Excess molar enthalpies at 298.15 K for dipropylamine, or dibutylamine + 2-alkanone systems and modelling of linear or aromatic amine + 2-alkanone mixtures in terms of DISQUAC. *Fluid Phase Equilib.* **20**13, *343*, 1.

(6)   Zaitseva, K.V.; Varfolomeev; Solomonov, B.N. Thermodynamics of hydrogen bonding of weak bases in alcohol solutions: calorimetry of solution, IR-spectroscopy and vapour pressure analysis. *J. Mol. Struct*. **2012**, *1018*, 14.

(7)   Nagata, I. Excess molar enthalpies of (methanol + aniline + propanone) at the temperature 298.15 K. *J. Chem. Thermodyn*. **1994**, *26*, 1015.

(8)   Nagata I. Thermodynamics of associated solutions. Correlation of ternary excess molar enthalpies for aniline + alkanol + benzene or acetone using the UNIQUAC association-solution model. *Thermochim*. Acta **1994**, *244*, 21.

(9)   Nagata, I.; Ksiazczak, A. Excess enthalpies of (ethanol or propan-2-ol + aniline + propanone) at the temperature 298.15 K. *J. Chem. Thermodyn*. **1995**, *27*, 1235.

(10)   Nagata, I.; Tamura, K; Kataoka, H.; Ksiazczak, A. Excess molar enthalpies of ternary systems butan-1-ol or butan-2-ol + aniline + propanone and of binary systems butan-1-ol or butan-2-ol + propanone at the temperature 298.15 K. *J. Chem. Eng. Data* **1996,** *41,* 593.

(11)   Seki, T.; Nakajima, R.; Naoki, M. Theoretical analysis of phase diagrams and mixing heats of systems of ketone/1-alcohol. *Chem. Lett*. **2010**, *39*, 541.

(12)   Lommserse, J.P.M.; Price S.L.; Taylor, R. Hydrogen bonding of carbonyl, ether and ester oxygen atoms with alkanol hydroxyl groups. *J. Comp. Chem*. **1997**, *18*, 757.

(13)   Nitta, T.; Turek, E.A.; Greenkorn, R.A.; Chao, K.C. A group contribution molecular model of liquids and solutions. *Am. Inst. Chem. Eng*. **1977**, *23*, 144.

(14)   Prieto, G.; Nogueira, P.; Bravo, R.; Sarmiento, F.; Paz Andrade, M. I. Excess enthalpies and excess volumes of (pentan-2-one + an *n*-alkan-1-ol) at the temperature 298.15 K. *J. Chem. Thermodyn*. **1992,** *24,* 905.

(15)   Kehiaian, H.V. Group contribution methods for liquid mixtures: a critical review. *Fluid Phase Equilib.* **1983**, *13*, 243.

(16)   González, J.A. Thermodynamics of mixtures containing the CO and OH groups. I. Estimation of the DISQUAC interchange coefficients for 1-alkanols + *n*-alkanones systems. *Can. J. Chem*. **1997**, *75,* 1412.

(17)   González, J.A.; García de la Fuente, I.; Cobos, J.C. Thermodynamics of mixtures containing the CO and OH groups. II. DISQUAC predictions of VLE and H^E for ternary mixtures containing 1-alkanols, *n*-alkanones and one organic solvent. *Can. J. Chem.* **1997**, *75* 1424.

(18)   Flory, P.J. Statistical thermodynamics of liquid mixtures. *J. Am. Chem. Soc.* **1965**, *87*, 1833.

(19)   González, J.A.; Riesco, N.; Mozo, I.; García de la Fuente, I.; Cobos, J.C. Application of the Flory theory and of the Kirkwood-Buff formalism to the study of orientational effects in 1-alkanol + linear o cyclic monoether mixtures. *Ind. Eng. Chem. Res*. **2009**, *48*, 7417.

(20)   González, J.A.; Mediavilla, A.; García de la Fuente, I.; Cobos, J.C. Thermodynamics of 1-alkanol + linear polyether mixtures. *J. Chem. Thermodyn*. **2013**, *59*, 195.

(21)   González, J.A.; Riesco, N.; Mozo, I.; García de la Fuente, I.; Cobos, J.C. Thermodynamics of mixtures containing alkoxyethanols. Part XXI. Application of the Flory theory to the study of orientational effects in systems with dibutyl ether or 1-butanol. *Ind. Eng. Chem. Res*. **2007**, *46*, 1350.

(22)   González, J.A. Thermodynamics of mixtures containing oxaalkanes. 4. Random mixing and orientational effects in ether + alkane systems. *Ind. Eng. Chem. Res*. **2010**, *49* 9511.

(23)   González, J.A.; García de la Fuente, I.; Cobos, J.C.; Mozo, I.; Alonso, I. Thermodynamics of mixtures containing oxaalkanes. 6. Random mixing in ether + benzene, or + toluene systems. *Thermochim. Acta* **2011,** *514*, 1.

(24)   González, J.A.; García de la Fuente, I.; Cobos, J.C.; Riesco, N.;   Thermodynamics of mixtures containing oxaalkanes. 7. Random mixing in ether + CCl$_4$ systems. *Ind. Eng. Chem. Res*. **2012**, *51*, 5108.

(25)   Nogueira, P.; Prieto, G.; Sarmiento, F.; Bravo, R.; Paz Andrade, M. I. Thermodynamics of the binary mixtures of 2-heptanone with an *n*-alkanol at 298.15 K. *Phys. Chem. Liq.* **1994,** *27,* 149.

(26)   Tra, H.V.; Patterson, D. Volumes of mixing and the P^* effect: Part I. Hexane isomers with normal and branched hexadecane. *J. Solution Chem*. **1982**, *11*, 793.

(27)   Landau, L.D.; Lifshitz, E.M. Física Estadística, Reverté, Barcelona, **1969**.

(28)   Cobos, J.C. An exact quasi-chemical equation for excess heat capacity with W-shaped concentration dependence. *Fluid Phase Equilib*. **1997**, *133*, 105.

(29)   Rubio, R.G.; Cáceres, M.; Masegosa, R.M.; Andreoli-Ball, L.; Costas, M.; Patterson, D. Mixtures with W-shape C_p^E curves. A light scattering study. *Ber. Bunsenges. Phys. Chem*. **1989,** *93*, 48.

(30)   Kirkwood, J.G., Buff, F.P. The statistical mechanical theory of solutions. 1. *J. Chem. Phys*. **1951**, *19*, 774.

(31)   Ben-Naim, A. Inversion of the Kirkwood-Buff theory of solutions: application to the water-ethanol system. *J. Chem. Phys*. **1977**, *67*, 4884.

(32)   Bhatia, A.B.; Thornton, D.E. Structural aspects of the electrical resistivity of binary alloys. *Phys. Rev. B2* **1970,** 3004.

(33)   Ruppersberg, H.; Egger, H. Short-range order in liquid Li-Pb alloy. *J. Chem. Phys*. **1975,** *63*, 4095.

(34)   Gallego, L.J.; López, J.M.; Alonso, J.A. Concentration-dependence of the heat of formation of binary-liquid alloys. *Physica B & C* **1983**, *122*, 23.

(35)   Young, W.H. Structural and thermodynamic properties of NFE liquid metals and binary alloys. *Rep. Prog. Phys*. **1992**, *55*, 1769.

(36)   Karaoglu, B.; Young, W.H. Simple generalised Bhatia-March-Flory formula for concentration fluctuations in liquid mixtures. *Phys. Chem, Liq*. **1995**, *30*, 187.

(37)   Gallego, L.J.; Somoza, J.A.; Alonso, J.A. On the concentration dependence of the ordering potential in liquid Li-Pb alloys. *Phys. Chem. Liq*. **1987**, *16*, 249.

(38)   Gallego, L.J.; Somoza, J.A.; Alonso, J.A. Theory of the thermodynamic properties of binary mixtures of organic molecules with size mismatch. *Chem. Phys*. **1985,** *99*, 35.

(39)   González, J.A.; Cobos, J.C.; García de la Fuente, I.; Mozo, J.C. Thermodynamics of mixtures containing amines. IX. Application of the concentration-concentration structure factor to the study of binary mixtures containing pyridines. *Thermochim. Acta*. **2009**, *494*, 54.

(40)   González, J.A.; Mozo, I.; García de la Fuente, I.; Cobos, J.C.; Durov, V.A. Thermodynamics of 1-alkanol + cyclic ether molecules**.** *Fluid Phase Equilib*. **2006**, *245*, 168.

(41)   Abe, A.; Flory, P.J. The thermodynamic properties of mixtures of small, nonpolar molecules. *J. Am. Chem. Soc*. **1965**, *87*, 1838.

(42)   Flory, P.J.; Orwoll, R.A.; Vrij, A. Statistical thermodynamics of chain molecule liquids. I. An equation of state for normal paraffin hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3507.

(43)   Flory, P.J.; Orwoll, R.A.; Vrij, A. Statistical thermodynamics of chain molecule liquids. II. Liquid mixtures of normal paraffin hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3515.

(44)   Orwoll, R.A.; Flory, P.J. Thermodynamic properties of binary mixtures of *n*-alkanes. *J. Am. Chem. Soc.* **1967**, *89*, 6822.

(45)   Howell, P.J.; Skillerne de Bristowe, B.J.; Stubley, D. Enthalpies of mixing of carbon tetrachloride with some methyl-substituted benzenes. Part III. Analysis of the results by use of Flory's theory of liquid mixtures. *J. Chem. Soc. A* **1971**, 397.

(46)   Allen, G.; Chai, Z.; Chong, C.L. ; Higgins, J.S.; Tripathi. J. Thermodynamics of oligomeric binary mixtures of polyethylene glycol and polypropylene glycol methylethers. *Polymer* **1984**, *25*, 239.

(47)   Trejo, L.M.; Costas, M.; Patterson, D. Effect of molecular size on the W-shaped excess heat capacities: oxaalkane-alkane systems. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3001.

(48)   Rowlinson, J.S.; Swinton, F.L. *Liquids and Liquid Mixtures*, Butterworths 3th Ed., London, **1982**.

(49)   Kehiaian, H.V. Studies on liquid-liquid equilibrium. 1. Binary systems with upper and lower critical solubility temperatures. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1962**, *10*, 569.

(50)   Karaoglu, B.; Young, W.H. Conformal mixtures with concentration-dependent interactions. Application to liquid Li-Mg. *Phys. Chem, Liq.* **1991**, *24*, 43.

(51)   Kalali, H.; Kohler, F.; Svejda, P. Excess properties of binary mixtures of 2,2,4-trimethylpentane with one polar component. *Fluid Phase Equilib.* **1985**, *20* ,75.

(52)   Diogo, H.P.; Minas de Piedade, M.E.; Moura Ramos, J.; Simoni, J.; Martinho Simoes, J.A. Intermolecular forces in solution and lattice energies of ionic crystals. *J. Chem. Educ.* **1993**, *70*, A227

(53)   Letcher, T.M.; Govender, U.P. Excess molar enthalpies of an alkanol + a cyclic ether at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1097.

(54)   Calvo, E.; Brocos, P.; Piñeiro, A.; Pintos, M.; Amigo, A.; Bravo, R.; Roux, A.H.; Roux.-Desgranges, G. Heat capacities, excess enthalpies, and volumes of binary mixtures containing cyclic ethers. 4. Binary systems 1,4-dioxane + 1-alkanols. *J. Chem. Eng. Data* **1999**, *44*, 948.

(55)   González, J.A.; Mozo, I.; García de la Fuente, I.; Cobos, J.C.; Riesco, N. Thermodynamics of (1-alkanol + linear monoether) systems. *J. Chem. Thermodyn.* **2008**, *40*, 1495.

(56)   Letcher, T.M.; Bricknell, B.C. Calorimetric investigation of the interactions of some hydrogen-bonded systems at 298.15 K. *J. Chem. Eng. Data* **1996,** *41*, 166.

(57)   González, J.A.; García de la Fuente, I.; Cobos, J.C. Thermodynamics of mixtures containing oxaalkanes. 5. Ether + benzene, or + toluene systems. *Fluid Phase Equilib.* **2011**, *301*, 145.

(58)   Pfeffer, T.; Löwen, B.; Schulz, S. Calorimetric measurement of the partial molar excess enthalpy at infinite dilution $h_i^{E,\infty}$ and its meaning for the calculation of the concentration and temperature dependence of the molar excess enthalpy h^E. *Fluid Phase Equilib.* **1995**, *106*, 139.

(59)   Heintz, A. A new theoretical approach for predicting excess properties of alkanol/alkane mixtures. *Ber. Bunsenges. Phys. Chem*. **1985**, *89*, 172.

(60)   Brandani, V.; Prausnitz, J.M. A free-volume, non-random mixing theory for liquid mixtures. *Fluid Phase Equilib.* **1981**, *7*, 233.

(61)   Liu, A.; Kohler, F.; Karrer, L.; Gaube, J.; Spelluci, P. A model for the excess properties of 1-alkanol + alkane mixtures containing chemical and physical terms. *Pure & Appl. Chem*. **1989**, *61*, 1441.

(62)   Renon, H.; Prausnitz, J.M.   On the thermodynamics of alcohol-hydrocarbon solutions. *Chem. Eng. Sci*. **1967,** *22*, 299.

(63)   Stokes, R.H.; Burfitt, C. Enthalpies of dilution and transfer of ethanol in non-polar solvents. *J. Chem. Thermodyn*. **1973**, *5*, 623.

(64)   O'Shea, S.J.; Stokes, R.H. Activity coefficients and excess partial molar enthalpies for (ethanol + hexane) from 283 to 318 K. *J. Chem. Thermodyn*. **1986**, *18*, 691.

(65)   Van Ness, H.C.; Van Winkle, J.; Richtol, H.H.; Hollinger, H.B. Infrared spectra and the thermodynamics of alcohol-hydrocarbon systems. J. *Phys. Chem*. **1967,** *71*, 1483

(66)   Vedernikova, E.V.; Gafurov, M.M.; Ataev, M.B. Estimation of the thermodynamic parameters of hydrogen bonding in alcohol solutions by the method of infrared spectroscopy. *Russ. Phys. J.* **2011**, *53***,** 843

(67)   Zhu, S.; Shen. S.; Benson, G.C.; Lu, B.C.-Y.   Excess enthalpies of (ethanol or 1-propanol) + methyl *tert*-butyl ether + *n*-octane ternary mixtures at 298.15 K. *Fluid Phase Equilib*. **1994**, *94*, 217.

(68)   Keller, M.; Schnabel, S.; Heintz, A. Thermodynamics of the ternary mixture propan-1-ol + tetrahydrofuran + *n*-heptane at 298.15 K. Experimental results and ERAS model calculations of G^E, H^E and V^E. *Fluid Phase Equilib*. **1995**, *110*, 231.

(69)   Tanaka, R.; Toyama, S.; Murakami, S. Heat capacities of $\{xC_nH_{2n+1}OH + (1 - x)C_7H_{16}\}$ for $n = 1$ to 6 at 298.15 K. *J. Chem. Thermodyn*. **1986**, *18*, 63.

(70)   Lietzmann, A.; Loewen, B.; Schulz, S. Excess molar enthalpies of propanone + heptane, propanone + ethanol, ethanol + heptane, and 2-propanol + water at 283.15, 298.15, 323.15, 343,15 and 363.15 K. *J. Chem. Eng. Data* **1994**, 39, 785.

(71)   Iñarrea, J.; Valero, J.; Pérez, P.; Gracia, M.; Gutiérrez Losa, C. H_m^E and V_m^E of some (butanone or dipropylether + an alkanol) mixtures. *J. Chem. Thermodyn*. **1988,** *20,* 193.

(72)   Nagata, I. Excess enthalpies of binary 2-butanone + some normal alkanol (C_1-C_4) mixtures. *Int. DATA Ser., Sel. Data Mixtures, Ser. A*. **1984,** *2,* 81.

(73)   Wang, L.; Benson, G.C. ; Lu, B.C.-Y. Excess enthalpies of (ethanol + hexane + decane or + dodecane) at the temperature 298.15 K. *J. Chem. Thermodyn*. **1992**, *24*, 1135.

(74)   Akamatsu, Y.; Ogawa, H.; Murakami, S. Molar excess enthalpies, molar excess volumes and molar isentropic compressions of mixtures of 2-propanone with heptane, benzene and trichloromethane at 298.15 K. *Thermochim. Acta* **1987,** *113,* 141.

(75)   Kiyohara, O.; Handa, Y.P.; Benson, G.C. Thermodynamic properties of binary mixtures containing ketones. III Excess enthalpies of *n*-alkanes + some aliphatic ketones. *J. Chem. Thermodyn*. **1979**, *11*, 453.

(76)   Legido, J.L.; Bravo, R.; Paz Andrade, M.I.; Romaní, L.; Sarmiento, F.; Ortega, J. Excess enthalpies of five examples of (2-hexanone + an *n*-alkane) and five of (2-hexanone + an *n*-alkanol) at 298.15 K. *J. Chem. Thermodyn*. **1986,** *18,* 21.

(77)   Urdaneta, O.; Handa, Y.P.; Benson, G.C. Thermodynamic properties of binary mixtures containing ketones. V. Excess enthalpies of an isomeric heptanone + *n*-heptane. *J. Chem. Thermodyn*. **1979**, *11*, 857.

(78)   González, J.A.; Alonso, I.; Alonso-Tristán, C.; García de la Fuente, I.; Cobos, J.C. Thermodynamics of alkanone + aromatic hydrocarbon mixtures. *Fluid Phase Equilib*. **2013**, *337,* 125

(79)   González, J.A.; García de la Fuente, I.; Cobos, J.C.; Casanova, C. A characterization of the aliphatic/hydroxyl interactions using a group contribution model (DISQUAC). *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 1658.

(80)   Madhurima; V.; Viswanathan, B.; Murthy, V.R.K. Effect of steric hindrance of ketones in the dielectric relaxation of methanol + ketone systems. *Phys. Chem. Liq*. **2006**, *44*, 563.

(81)   González, J.A.; García de la Fuente, I.; Cobos, J.C. DISQUAC behaviour close to critical points. Application to methanol + alkane mixtures. *Ber. Bunsenges. Phys. Chem*. **1997**, *101*, 21.

(82)   Collins, S.G.; Christensen, J.J.; Izatt, R.M.; Hanks, R.W. The excess enthalpies of 10 (*n*-pentane + *n*-alkanol) mixtures at 298.15 K. *J. Chem. Thermodyn*. **1980**, *12*, 609.

(83)   Letcher, T.M.; Nevines, J.A. Excess enthalpies of ketone + alkanol at the temperature 298.15 K. *J. Chem. Eng. Data* **1995,** *40,* 995.

(84)   Schäfer, K.; Rohr, F.J. Kalorische untersuchungen an mischungen von acetone mit normal-kohlenwasserstoffen. 2. *Phys. Chem. N.F.* **1960**., *24*, 130.

(85)   Messow, U.; Doye, U.; Kuntzsch, S.; Kuchenbecker, D., 1977. Thermodynamische untersuchungen an Lösungsmittel/n-paraffin-systemen. V. Die systeme aceton/n-decan,aceton/n-dodecan, aceton/n-tetradecan und aceton/n-hexadecan. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 90.

(86)   Amigo, A.; Legido, J.L.; Bravo, R.; Paz Andrade, M.I. Excess molar enthalpies of (heptan-1-ol + an *n*-alkane) at 298.15 and 308.15 K. *J. Chem. Thermodyn.* **1989**, *21*, 1207.

(87)   Grolier, J.-P.E.; Abolhassan, F.; Kehiaian, H.V. Calorimetric effects of short-range orientational order in solutions of benzene or *n*-alkylbenzenes in *n*-alkanes. *Thermochim. Acta* **1982**, *53*, 157.

(88)   González Posa, C.; Núñez, L.; Villar. Enthalpies of mixing: 1-pentanol + *n*-hexane, 1-pentanol + cyclohexane, 1-pentanol + *n*-hexane + cyclohexane at 25 ºC. *J. Chem. Thermodyn.* **1972**, *4*, 275.

(89)   Letcher, T.M.; Nevines, J.A. Excess volumes of (ketone + alkanol) at the temperature 298.15 K. *J. Chem. Eng. Data* **1995,** *40,* 293.

(90)   Tsierkezos, N.G.; Molinou, I.E.; Filippou, A.C. Thermodynamic properties of binary mixtures of binary mixtures of cyclohexanone with *n*-alkanols (C_1-C_5) at 293.15 K. *J. Solution Chem.* **2005**, *34*, 1371.

(91)   Rao, M.V.P.; Naidu, P.R. Excess volumes and isentropic compressibilities of binary mixtures of alcohol + cyclohexanone. Part II. *J. Chem. Thermodyn.* **1976**, *8*, 96.

(92)   Chao J.P.; Dai M. Excess enthalpies of (an alkan-1-ol + tetrahydrofuran or cyclohexanone) at 298.15 K. *J. Chem. Thermodyn.* **1989,** *21,* 977.

(93)   Loehe, J.R.; Van Ness, H.C. Excess Gibbs energy and liquid-vapor equilibrium in 2-propanone + normal alkane (C_5, C_6, C_7, C_9) binary mixtures. *Int. DATA Ser., Sel. Data Mixtures, Ser. A*. **1979,** *1,* 45.

(94)   Spinolo, G.; Riccardi, R. *Int. DATA Ser. Sel. Data Mixtures*, *Ser. A* **1977**, 91

(95)   Benson, G.C. Excess Gibbs energy and liquid-vapor equilibrium in 2-butanone + normal alkane (C_6-C_8, C_{12}, C_{16}) binary mixtures. *Int. DATA Ser., Sel. Data Mixtures, Ser. A.* **1980,** *1,* 31.

(96)   Riddick, J.A.; Bunger, W.B.; Sakano T.K. *Organic solvents*. In: A. Weissberger (Ed.), *Techniques of Chemistry*, Vol. II, Wiley, N.Y., **1986.**

(97)   Alonso, I.; Alonso, V.; Mozo, I.; García de la Fuente, I.; González, J.A.; Cobos, J.C**.** Thermodynamics of ketone + amine mixtures. I. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for 2-propanone + aniline, + *N*-methylaniline, or + pyridine systems. *J. Chem. Eng. Data* **2010,** *55*, 2505.

(98)   Alonso, I.;   Mozo, I.; García de la Fuente, I.; González, J.A.;   Cobos, J.C**.** Thermodynamics of ketone + amine mixtures. III. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for 2-butanone + aniline, + *N*-methylaniline, or + pyridine systems. *J. Chem. Eng. Data* **2010,** *55*, 5400.

(99)   Alonso, I.;   Mozo, I.; García de la Fuente, I.; González, J.A.;   Cobos, J.C**.** Thermodynamics of ketone + amine mixtures 7. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for 2-pentanone + aniline, + *N*-methylaniline, or + pyridine systems. *J. Molecular Liq*. **2011**, *160*, 180.

(100) Malhotra, R.; Price, W.E.; Woolf, L.A. Thermodynamic properties of pentan-3-one at temperatures from 278 K to 338 K and pressures from 0.1 MPa to 380 MPa. *J. Chem. Thermodyn*. **1993**, *25*, 361.

(101) Malhotra, R.; Woolf, L.A. Volumetric measurements of liquid pentan-2-one, hexan-2-one, and 4-methylpentan-2-one at temperatures from 278.15 K to 338.13 K and pressures in the range from 0.1 MPa to 386 MPa. *J. Chem. Thermodyn*. **1996**, *28*, 1411.

(102) Alonso, I.; Mozo, I.; García de la Fuente, I.; González, J.A.; Cobos, J.C. Thermodynamics of ketone + amine mixtures Part V. Volumetric and speed of sound data at (293.15, 298.15 and 303.15) K for mixtures of 2-heptanone with aniline, *N*-methylaniline or pyridine. *J. Solution Chem*. **2011**, *40*, 2057.

(103) Domanska, U.; Lachwa, J.; Letcher, T.M. Densities, excess molar volumes, and excess molar enthalpies of (*N*-methyl-2-pyrrolidinone + ketone) at *T* = 298.15 K *J. Chem. Eng. Data* **2002**, *47*, 1446.

(104) Ohomuro, K.;   Tamura, K.; Murakami, S. Excess volumes and isentropic compressibilities of the binary mixtures of cyclohexanone with globular species at *T* = 298.15 K. *J. Chem. Thermodyn***. 1997,** *29*, 287.

(105)   Nagata, I.; Tamura, K. Excess enthalpies of binary and ternary mixtures of methanol with acetone, chloroform, benzene, and tetrachloromethane. *Fluid Phase Equilib*. **1983,** *15,* 67.

(106) Coomber, B.A.; Wormald, C.J. A stirred flow calorimeter. The excess enthalpies of acetone + water and of acetone + some normal alcohols. *J. Chem. Thermodyn*. **1976**, *8,* 793.

(107) Garriga, R.; Sánchez, F.; Pérez, P.; Gracia, M. Vapour pressures at six temperatures between 278.15 K and 323.15 K and excess molar functions at *T* = 298.15 K of (butanone + methanol or ethanol). *J. Chem. Thermodyn*. **1996**, *28,* 567.

(108) Colino, E.; Coto, B.; Cabañas, A.; Pando, C.; Renuncio, J.A.R. Excess enthalpies of binary mixtures of methanol with heptanone isomers at 298.15 and 323.15 K. *J. Chem. Eng. Data* **1997,** *42,* 735.

(109)   Nicolaides, G.L.; Eckert, C.A. Experimental heats of mixing of some miscible and partially miscible nonelectrolyte systems. *J. Chem. Eng. Data* **1978,** *23,*152.

(110)   Takami, M.; Murakami, S.; Fujishiro, R. Heats of mixing for binary mixtures. II. The 1,3-butanediol-methylethylketone system. *Bull. Chem. Soc. Jpn.* **1965,** *38,* 291.

(111)   Garriga, R.; Sánchez, F.; Pérez, P.; Gracia, M. Excess Gibbs free energies at seven temperatures and excess enthalpies and volumes at 298.15 K of butanone with 1-propanol or 2-propanol. *Fluid Phase Equilib.* **1996,** *124,* 123.

(112)   López, M.; Legido, J.L.; Romaní, L.; Carballo, E.; Pérez Martell, E.; Jímenez, E.; Paz Andrade, M.I. Excess molar enthalpies for (propan-1-ol + pentan-3-one + hexane) at the temperature 298.15 K. *J. Chem. Thermodyn*. **1992**, *24,* 205.

(113)   Paz-Andrade, M.I.; Casas, M.I. An. Quim. **1970,** *66,* 709. (cf. 114)

(114)   Christensen, J.J.; Hanks, R.W.; Izatt, R.M. *Handbook of heat of mixing*. Wiley, New York, **1982**

(115)   Murakami, S.; Fujishiro, R. The heats of mixing for binary mixtures. III. The intermolecular energy of hydrogen bonding between alcohol and several other polar molecules. *Bull. Chem. Soc. Jpn*. **1966,** *39,* 720

(116)   Chao, J.P; Dai, M. Studies of thermodynamic properties of binary mixtures containing an alcohol. XVI. Excess molar enthalpies of each of (one of the four butanols + methyl ethyl ketone or methyl isobutyl ketone) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1991,** *23,* 117.

(117)   Paz Andrade, M.I.; Jiménez, E.; López García, D. *An. Quim*. **1973,** *69,* 283 (cf. 114)

(118)   López, M.; Legido, J.L.; Romaní, L.; Peleteiro, J.; Paz Andrade, M.I. Excess molar enthalpies of binary and ternary mixtures for 1-propanol + 3-pentanone + 1-hexanol or + 1-heptanol at 298.15 K. *J. Chem. Eng. Data* **1993,** *38,* 238

(119)   Liao, W.-Ch.; Lin, H.; Lee, M.-J. Excess molar enthalpies of binary systems containing 2-octanone, hexanoic acid, or octanoic acid at T = 298.15 K. *J. Chem. Thermodyn*. **2012**, *44*, 51.

(120)   Tamir, A.; Apelblat, A.; Wagner, M. An evaluation of thermodynamic analyses of the vapour-liquid equilibria in the ternary systems acetone-chloroform-methanol and its binaries. *Fluid Phase Equilib*. **1981**, *6*, 113.

(121)   Van Ness, H.C.; Abbott, M.M. *Int. DATA Ser., Sel. Data Mixtures, Ser. A*. **1978,** *1,* 65.

(122)   Wilsak, R.A.; Campbell, S.W.; Thodos, G. Vapor-liquid equilibrium measurements for the methanol-acetone system at 372.8, 397.7 and 422.6 K. *Fluid Phase Equilib*. **1986**, *28*, 13.

(123)   Rubio, R.G.; Renuncio, J.A.R.; Díaz Peña, M. Vapour-liquid equilibrium of (methanol + a heptanone) at 298.15 K. *J. Chem. Thermodyn*. **1983**, *15*, 779.

(124)   Rhim, J.N.; Park, S.S. Hwahak Konghak, **1975**, *13*, 147 (cf. 125)

(125) Gmehling, J.; Onken U.; *Vapor-liquid equilibrium data collection*. Vol. I. Part 2a. Dechema, **1977**.

(126) Campbell, S.W.; Wilsak, R.A.; Thodos, G. Vapor-liquid equilibrium measurements for the ethanol-acetone system at 372.7, 397.7 and 422.6 K. *J. Chem. Eng. Data* **1987**, *32*, 357.

(127) Garriga, R.; Sánchez, F.; Pérez, P.; Gracia, M. Isothermal vapor-liquid equilibrium of butanone + butan-1-ol at eight temperatures between 278.15 and 323.15 K. *J. Chem. Eng. Data* **1996**, *41*, 451.

(128) Garriga, R.; Sánchez, F.; Pérez, P.; Gracia, M. Excess Gibbs free energies at several temperatures of butanone with 1-hexanol or 1-octanol. *J. Chem. Eng. Data* **1996**, *41*, 1091.

(129) Abbas, R.; Gmehling, J. Vapour-liquid equilibria, azeotropic data, excess enthalpies, activity coefficients at infinite dilution and solid-liquid equilibria for binary alcohol-ketone mixtures. *Fluid Phase Equilib*. **2008**, *267*, 119.

(130) Tamura, K.; Murakami, S.; Fujishiro, R. Excess enthalpies of (cyclohexanone + aromatic hydrocarbon), (methyl cyclohexane + aromatic hydrocarbon), and (methyl cyclohexane + cyclohexanone) at 298.15 K. *J. Chem. Thermodyn*. **1981**, *13*, 47.

TABLE 1

Physical Constants[a] and Reduction Parameters for Volume, V_i^*, and Pressure, P_i^*, Calculated According to the Flory Theory, for Ketones Used in this Work

Alkanone	V_i / cm^3·mol^{-1}	α_P/10^{-3}·K^{-1}	κ_T /TPa^{-1}	V_i^* / cm^3·mol^{-1}	P_i^* /J·cm^{-3}
2-propanone	74.04[b]	1.56[c]	1374[c]	54.75	619
2-butanone	90.17[b]	1.31[d]	1170[d]	68.94	571
2-pentanone	107.46[b]	1.198[e]	1099[e]	83.50	538
3-pentanone	106.41[b]	1.2[f]	1073[f]	82.66	553
2-hexanone	124.16[b]	1.04[g]	1012[b]	98.86	483
2-heptanone	140.76[b]	1.06[h]	969[h]	111.73	518
4-heptanone	140.79[b]	1.05[i]	932[i]	111.93	532
2-octanone	157.45[b]	1.03[b]	899[b]	125.57	537
Cyclohexanone	104.21[b]	0.955[j]	695[j]	84.15	628

[a]molar volume, V_i; isobaric thermal expansion coefficient, α_P; isothermal compressibility, κ_T; [b]Ref 96; [c]Ref 97; [d]Ref. 98; [e]Ref. 99; [f]Ref. 100; [g]Ref. 101; [h]Ref. 102; [i]Ref. 103; [j]Ref. 104

TABLE 2

Molar Excess Enthalpies, H_m^E, Interactional Contribution According to the Flory's Model, $H_{m,int}^E$ and Flory's Energetic Parameter for 1-Alkanol(1) + Alkanone (2) Systems at Equimolar Composition and Temperature T. $\sigma_r\left(H_m^E\right)$ Denotes the Relative Standard Deviations for H_m^E

Alkanone	T/K	H_m^E / J·mol^{-1}	$H_{m,int}^E$ / J·mol^{-1}	X_{12} / J·cm^{-3}	$\sigma_r\left(H_m^E\right)$[a]	Ref.
		methanol(1) + alkanone(2)				
2-propanone	298.15	686	479	69.09	0.190	105
	298.15	699	488	70.37	0.178	106
	298.15	693	485	69.88	0.191	2
2-butanone	298.15	708	507	67.18	0.270	72
	298.15	679	487	64.44	0.266	107
	308.15	744	522	69.76	0.262	72
2-pentanone	298.15	686	501	62.49	0.260	83
3-pentanone	298.15	725	529	66.18	0.300	83
2-heptanone	298.15	745	560	64.43	0.347	108
	323.15	923	664	78.72	0.240	108
4-heptanone	298.15	721	543	62.40	0.269	108
	323.15	905	657	77.44	0.146	108
Cyclohexanone	298.15	952	730	88.27	0.260	92
		ethanol(1) + alkanone(2)				
2-propanone	283.15	1046	765	81.92	0.066	70
	298.15	1150	814	89.26	0.083	106
	298.15	1105	784	85.84	0.034	70
	298.15	1124	797	87.29	0.080	1
	298.15	1113	789	86.45	0.058	109
	323.15	1271	850	96.84	0.021	70
		1236	828	94.25	0.038	109
	343.15	1307	834	97.89	0.022	70
	363.15	1222	747	90.04	0.069	70
2-butanone	298.15	1193	861	86.16	0.147	110
	298.15	1071	771	77.42	0.141	72
	298.15	1028	744	74.33	0.105	71
	308.15	1121	794	80.51	0.116	72

TABLE 2 (continued)

		1077	764	77.38	0.110	71
2-pentanone	298.15	886	651	60.86	0.064	83
3-pentanone	298.15	987	987	67.96	0.183	83
cyclohexanone	298.15	1199	916	83.24	0.166	92
1-propanol(2) + alkanone(2)						
2-propanone	298.15	1365	991	90.12	0.038	106
		1395	1012	92.05	0.062	3
2-butanone	298.15	1251	921	76.06	0.068	4
		1237	911	75.21	0.034	111
	308.15	1317	951	79.63	0.045	72
2-pentanone	298.15	1286	954	73.60	0.113	14
		1209	899	69.22	0.085	83
3-pentanone	298.15	1160	862	66.64	0.130	83
		1232	915	70.74	0.101	112
2-heptanone	298.15	1259	951	66.54	0.162	25
4-heptanone	298.15	1121	849	59.25	0.230	56
Cyclohexanone	298.15	1321	1013	75.95	0.109	92
1-butanol(1) + alkanone(2)						
2-propanone	298.15	1537	1139	89.49	0.015	106
		1770	1302	102.59	0.043	10
		1405	1046	82.06	0.047	113,114
		1372	1023	80.21	0.059	115
2-butanone	298.15	1324	990	70.47	0.039	71
		1421	1061	75.55	0.033	116
	308.15	1473	1081	77.97	0.019	72
		1383	1017	73.29	0.048	71
Cyclohexanone	298.15	1351	1042	67.24	0.096	92
1-pentanol(1) + alkanone(2)						
2-propanone	298.15	1603	1212	84.64	0.119	117,114
		1685	1271	88.80	0.034	106
2-pentanone	298.15	1451	1103	64.65	0.051	14
2-heptanone	298.15	1339	1027	54.15	0.080	25
Cyclohexanone	298.15	1378	1065	60.96	0.083	92
1-hexanol(1) + 2-alkanone(2)						
2-propanone	298.15	1672	1281	81.32	0.116	117
		1781	1359	86.39	0.072	106
2-butanone	298.15	1512	1158	66.34	0.078	71

TABLE 2 (continued)

	308.15	1542	1167	67.53	0.066	71
2-pentanone	298.15	1523	1166	61.93	0.048	14
3-pentanone	298.15	1435	1101	58.62	0.075	118
2-hexanone	298.15	1430	1105	54.63	0.053	76
2-heptanone	298.15	1389	1071	50.96	0.055	25
2-octanone	298.15	1223	946	43.24	0.060	119
1-heptanol(1) + 2-alkanone(2)						
2-pentanone	298.15	1603	1240	60.32	0.031	14
3-pentanone	298.15	1510	1170	57.11	0.082	118
2-hexanone	298.15	1479	1151	52.05	0.049	76
2-heptanone	298.15	1427	1109	48.20	0.060	25
1-octanol(1) + 2-alkanone(2)						
2-butanone	298.15	1711	1335	65.32	0.079	71
	308.15	1709	1318	65.18	0.075	71
2-pentanone	298.15	1676	1306	58.95	0.040	14
2-hexanone	298.15	1545	1208	50.66	0.055	76
2-heptanone	298.15	1494	1167	46.96	0.045	25
2-octanone	298.15	1346	1053	40.63	0.047	119
1-nonanol(1) + 2-alkanone(2)						
2-hexanone	298.15	1611	1263	49.65	0.042	76
1-decanol(1) + 2-alkanone(2)						
2-butanone	298.15	1844	1455	63.15	0.094	71
	308.15	1829	1441	62.64	0.086	71
2-hexanone	298.15	1688	1329	49.20	0.029	76

[a]eq. 8

TABLE 3

Molar Excess Gibbs Energies, G_m^E, $TS_m^E (= H_m^E - G_m^E)$, and Concentration-Concentration Structure Factor, $S_{CC}(0)$, for 1-Alkanol(1) + Alkanone(2) Mixtures at Equimolar Composition and Temperature T.

System	T /K	G_m^E / J·mol^{-1}	TS_m^E / J·mol^{-1}	$S_{CC}(0)$	Ref.
methanol + 2-propanone	298.15	448	251	0.391	120
	323.15	431		0.368	121
	372.8	382		0.332	122
	422.6	308		0.303	122
methanol + 2-butanone	298.15	547	161	0.425	107
methanol + 2-heptanone	298.15	748	-3	0.591	123
ethanol + 2-propanone	298.15	510	595	0.425	124,125
	323.15	525	746	0.379	121
	372.7	346		0.322	126
	426.6	257		0.293	126
ethanol + 2-butanone	298.15	566	205	0.460	107
1-propanol + 2-butanone	298.15	512	725	0.403	111
1-butanol + 2-butanone	298.15	512	812	0.410	127
1-hexanol + 2-butanone	298.15	525	987	0.420	128
1-hexanol + 2-octanone	323.15	471		0.386	129
	363.15	320		0.317	129
1-octanol + 2-butanone	298.15	539	1172	0.443	128

TABLE 4

Partial Molar Excess Enthalpies,[a] $H_1^{E,\infty}$**, at** $T = 298.15$ **K at Atmospheric Pressure for Solute(1) + Organic Solvent(2) Mixtures, and Hydrogen Bond Enthalpies,** $\Delta H_{OH\text{-}CO}$**, for 1-Alkanol(1) + Alkanone(2) Systems.**

System	$H_1^{E,\infty}$ /kJ·mol^{-1}	$\Delta H_{OH\text{-}CO}$ /kJ·mol^{-1}
2-propanone(1) + heptane(2)	9.09 [74]	
2-butanone(1) + heptane(2)	7.47 [75]	
2-pentanone(1) + heptane(2)	6.35 [75]	
2-hexanone(1) + heptane(2)	6.56 [76]	
2-heptanone(1) + heptane(2)	5.58 [77]	
2-octanone(1) + heptane(2)	5.4[b]	
3-pentanone(1) + heptane(2)	5.91 [75]	
4-heptanone(1) + heptane(2)	4.76 [77]	
cyclohexanone(1) + methylcyclohexane(2)	6.22 [130]	
methanol(1) + 2-propanone(2)	3.69 [2]	−28.6
methanol(1) + 2-butanone(2)	3.39 [107]	−27.3
methanol(1) + 2-pentanone(2)	3.12 [83]	−26.4
methanol(1) + 2-heptanone(2)	3.18 [108]	−25.6
methanol(1) + 3-pentanone(2)	4.29 [83]	−24.8
methanol(1) + 4-heptanone(2)	3.17 [108]	−24.8
methanol(1) + cyclohexanone(2)	5.14 [92]	−24.4
ethanol(1) + 2-propanone(2)	5.54 [1]	−26.7
ethanol(1) + 2-butanone(2)	5.51 [72]	−25.2
ethanol(1) + 2-pentanone(2)	3.11 [83]	−26.5
ethanol(1) + 3-pentanone(2)	5.59 [83]	−23.5
ethanol(1) + cyclohexanone(2)	6.76 [92]	−22.7
1-propanol(1) + 2-propanone(2)	6.28 [3]	−26.0
1-propanol(1) + 2-butanone(2)	5.26 [111]	−25.4
1-propanol(1) + 2-pentanone(2)	6.61 [14]	−22.9
1-propanol(1) + 3-pentanone(2)	6.97 [83]	−22.1
1-propanol(1) + 2-heptanone(2)	6.72 [25]	−22.1
1-propanol(1) + 4-heptanone(2)	6.56 [56]	−21.4
1-propanol(1) + cyclohexanone(2)	6.85 [92]	−22.6
1-butanol (1) + 2-propanone(2)	6.75 [106]	−25.5
1-butanol(1) + 2-butanone(2)	5.29 [116]	−25.4

TABLE 4 (continued)

1-butanol(1) + cyclohexanone(2)	7.16 [92]	−22.3
1-pentanol(1) + 2-propanone(2)	7.57 [106]	−24.7
1-pentanol(1) + 2-pentanone(2)	6.87 [14]	−22.7
1-pentanol(1) + 2-heptanone(2)	6.32 [25]	−22.5
1-pentanol(1) + cyclohexanone(2)	7.10 [92]	−22.3
1-hexanol(1) + 2-propanone(2)	8.99 [106]	−23.3
1-hexanol(1) + 2-butanone(2)	7.06 [71]	−23.6
1-hexanol(1) + 2-pentanone(2)	7.15 [14]	−22.4
1-hexanol(1) + 3-pentanone(2)	7.86 [118]	−21.3
1-hexanol(1) + 2-hexanone(2)	6.76 [76]	−23.0
1-hexanol(1) + 2-heptanone(2)	6.46 [25]	−22.3
1-hexanol(1) + 2-octanone(2)	6.28 [119]	−22.3
1-heptanol(1) + 2-pentanone(2)	7.51 [14]	−22.0
1-heptanol(1) + 3-pentanone(2)	8.97 [118]	−20.1
1-heptanol(1) + 2-hexanone(2)	7.18 [76]	−22.6
1-heptanol(1) + 2-heptanone(2)	7.00 [25]	−21.8
1-octanol(1) + 2-butanone(2)	7.77 [71]	−22.9
1-octanol(1) + 2-pentanone(2)	7.88 [14]	−21.7
1-octanol(1) + 2-hexanone(2)	7.32 [76]	−22.4
1-octanol(1) + 2-heptanone(2)	7.11 [25]	−21.7
1-octanol(1) + 2-octanone(2)	6.06 [119]	−22.5
1-nonanol(1) + 2-hexanone(2)	7.66 [76]	−22.1
1-decanol(1)+ 2-butanone(2)	9.37 [71]	−21.3
1-decanol(1) + 2-hexanone(2)	8.14 [76]	−21.6

[a]values obtained from H_m^E data over the whole concentration range; [c]value obtained from the application of the DISQUAC model with interaction parameters available in the literature[16]
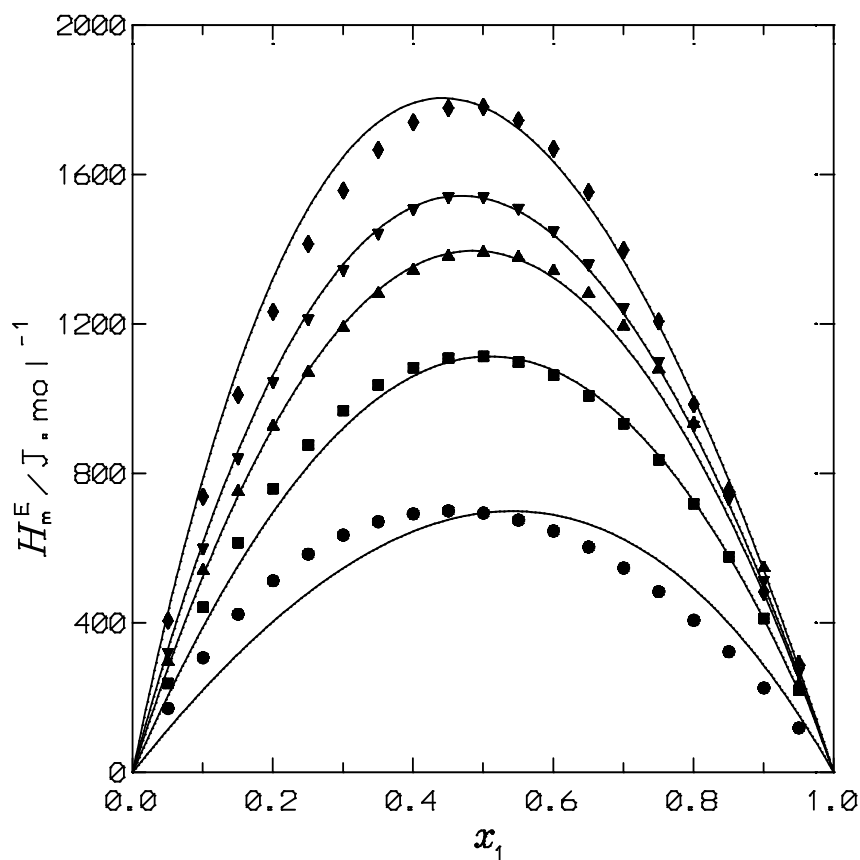
Figure 1　H_m^E of 1-alkanol(1) + 2-propanone(2) systems at 298.15 K. Symbols, experimental results: (●), methanol;[2] (■), ethanol;[70] (▲), 1-propanol;[3] (▼), 1-butanol;[106] (◆), 1-hexanol.[106] Solid lines, results from the Flory model with interaction parameters listed in Table 2.
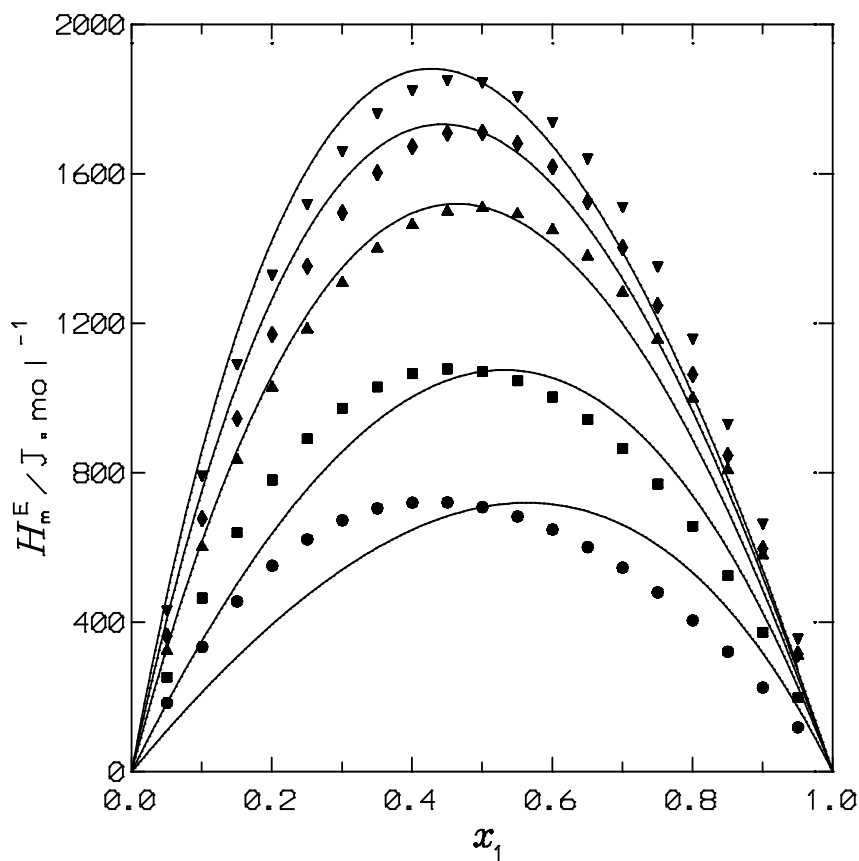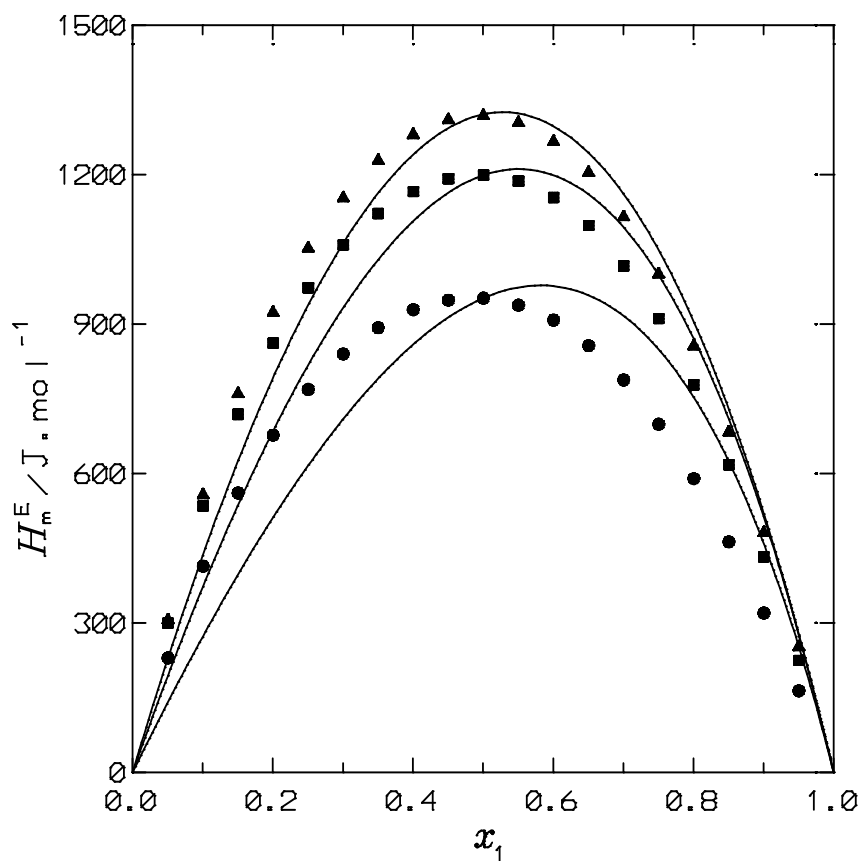
Figure 2 H_m^E of 1-alkanol(1) + 2-butanone(2) systems at 298.15 K. Symbols, experimental results: ($\bullet$), methanol;[72] ($\blacksquare$), ethanol;[72] ($\blacktriangle$), 1-hexanol;[71] ($\blacklozenge$), 1-octanol;[71] ($\blacktriangledown$), 1-decanol.[71] Solid lines, results from the Flory model with interaction parameters listed in Table 2.
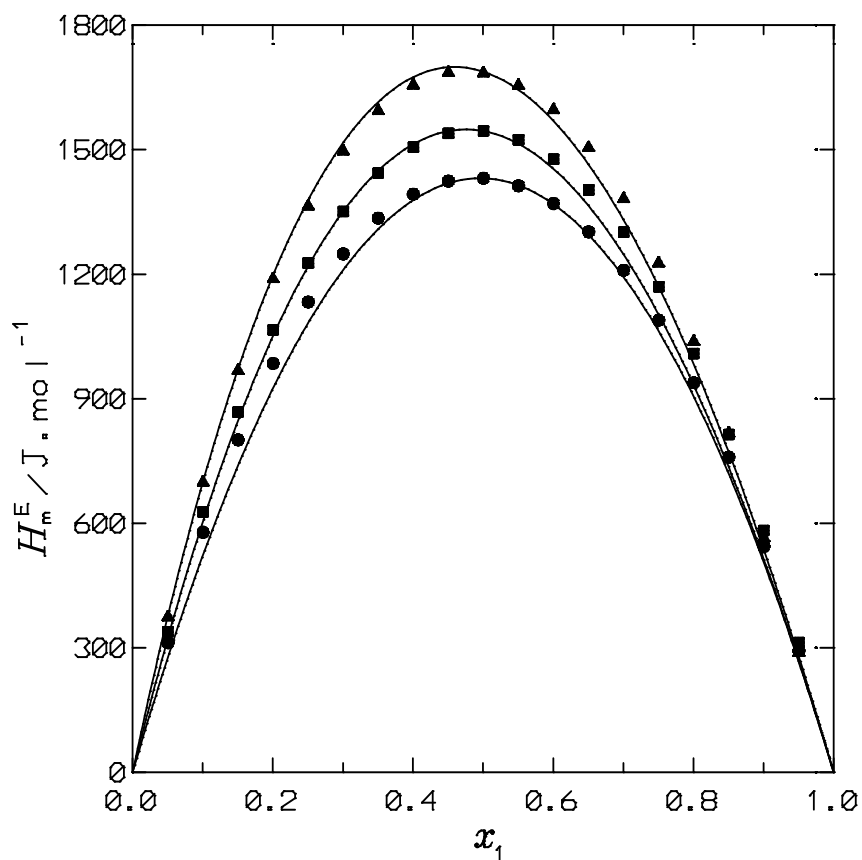
Figure 3 H_m^E of 1-alkanol(1) + 2-hexanone(2) systems at 298.15 K. Symbols, experimental results:[76] (●), 1-hexanol; (■), 1-octanol; (▲), 1-decanol. Solid lines, results from the Flory model with interaction parameters listed in Table 2.
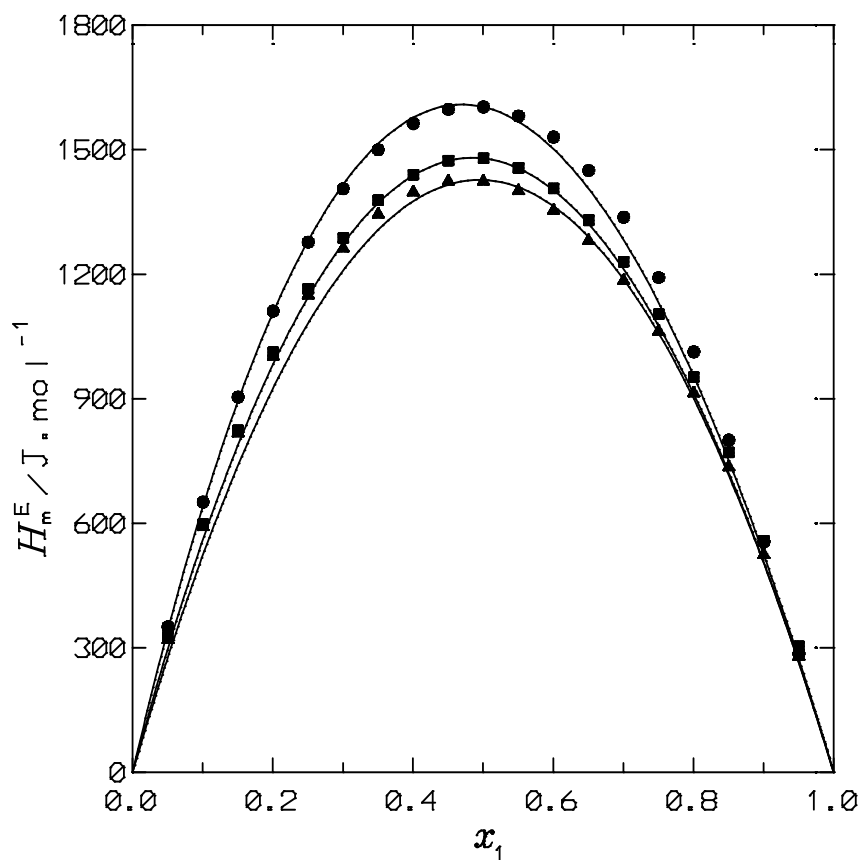
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Figure 4 H_m^E of 1-alkanol(1) + cyclohexanone(2) systems at 298.15 K. Symbols, experimental results:[92] (●), methanol; (■), ethanol; (▲), 1-propanol. Solid lines, results from the Flory model with interaction parameters listed in Table 2.

Figure 5 H_m^E of 1-heptanol(1) + 2-alkanone(2) systems at 298.15 K. Symbols, experimental results:[92] (●), 2-pentanone;[14] (■), 2-hexanone;[76] (▲), 2-heptanone.[25] Solid lines, results from the Flory model with interaction parameters listed in Table 2.
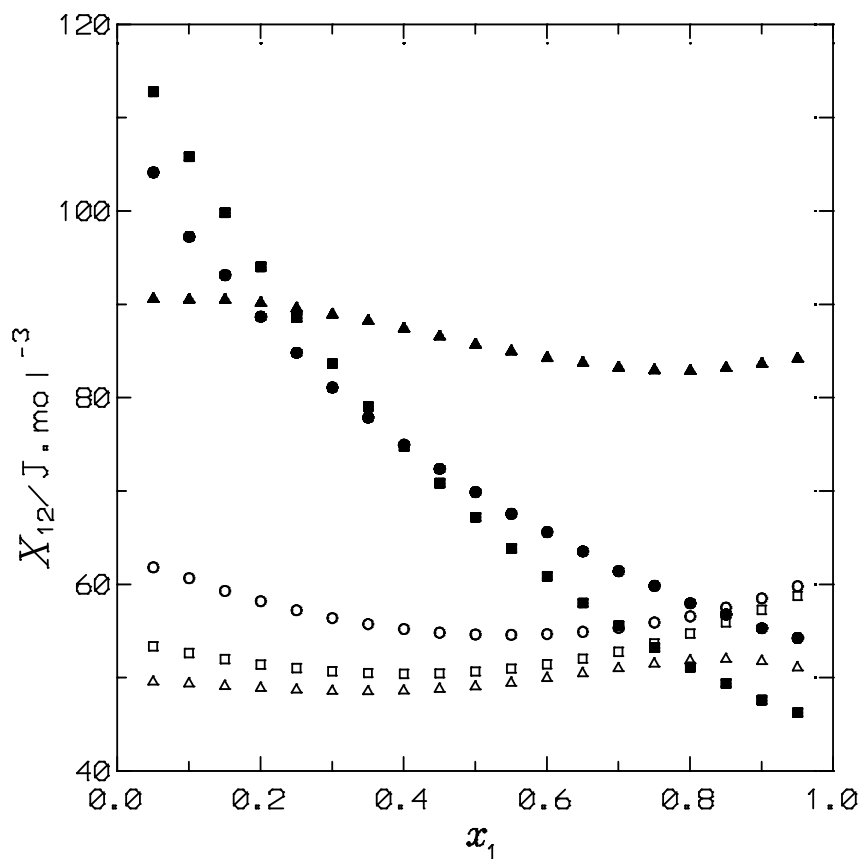
Figure 6 Flory interaction parameters, X_{12}, for 1-alkanol(1) + 2-alkanone(2) mixtures at 298.15 K. Full, symbols: (●), methanol(1) + 2-propanone(2);[2] (■), methanol(1) + 2-butanone(2);[72] (▲), ethanol(1) + 2-propanone(2).[70] Open symbols, systems with 2-hexanone:[76] (O), 1-hexanol; (□), 1-octanol; (Δ), 1-decanol.
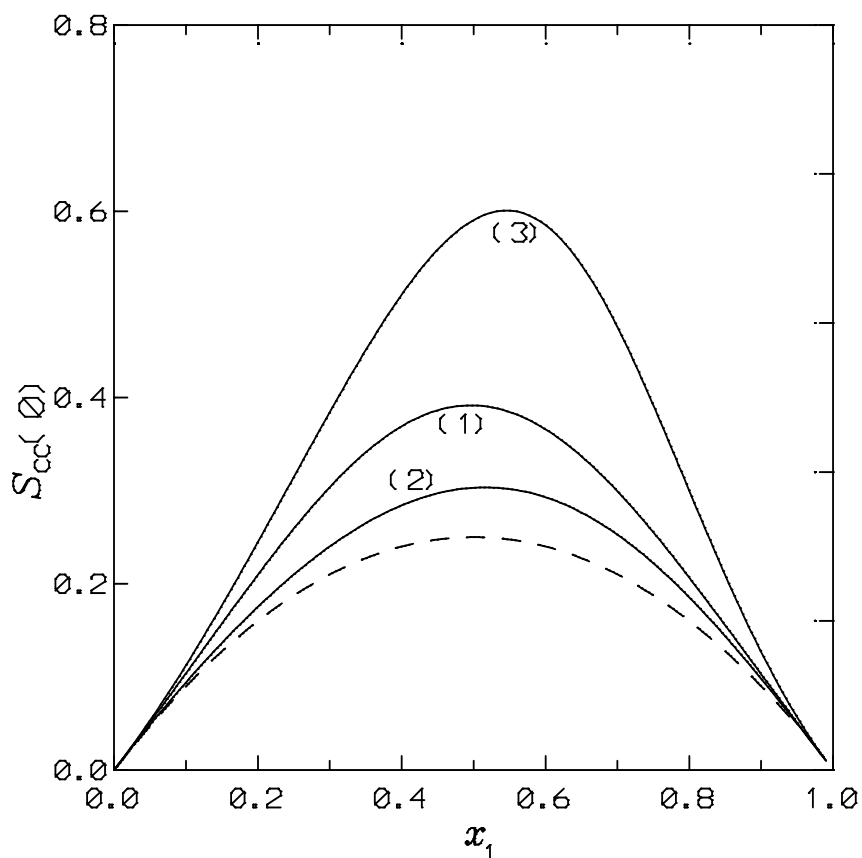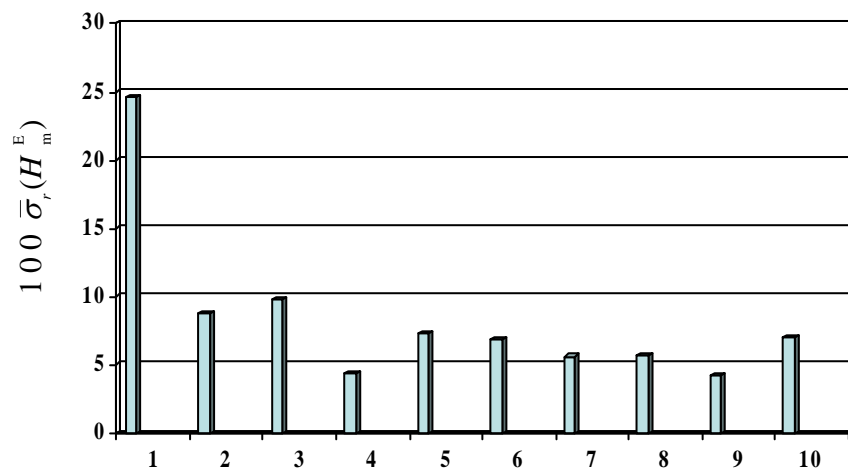
Figure 7 $S_{CC}(0)$ results for methanol(1) + 2-alkanone(2) mixtures at temperature T: (1), 2-propanone[120] ($T = 298.15$ K); (2), 2-propanone[122] ($T = 422.6$ K); (3) 2-heptanone[123] ($T = 298.15$ K). Dashed line, ideal mixture

Number of C atoms in 1-alkanol