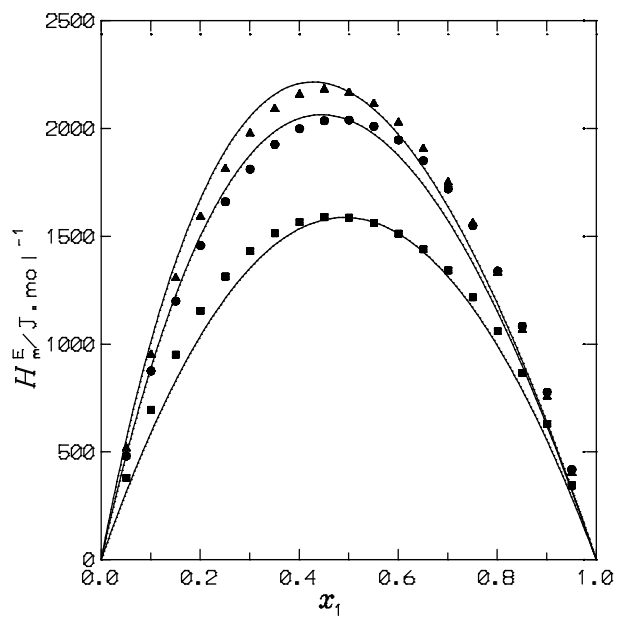


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ORIENTATIONAL EFFECTS AND RANDOM MIXING IN 1-ALKANOL + NITRILE MIXTURES

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H_m^E at 29815 K for 1-butanol(1) + ethanenitrile(2) (●), or + butanenitrile(2) (■), or for 1-decanol(1) + butanenitrile(2) (▲). Solid lines, Flory calculations

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Abstract

1-Alkanol + alkanenitrile, or + benzonitrile systems have been investigated by means of the molar excess functions: enthalpies (H_m^E), isobaric heat capacities (C_{pm}^E), volumes (V_m^E) and entropies, and using the Flory model and the concentration-concentration structure factor ($S_{CC}(0)$) formalism. From the analysis of the experimental data available in the literature, it is concluded that interactions are mainly of dipolar type. In addition, large H_m^E values contrast with rather low V_m^E values, indicating the existence of strong structural effects. H_m^E measurements have been used to evaluate the enthalpy of the hydroxyl-nitrile interactions (ΔH_{OH-CN}). They are stronger in methanol systems and become weaker when the alcohol size increases. In solutions with a given short chain 1-alkanol (up to 1-butanol), the replacement of ethanenitrile by butanenitrile weakens the mentioned interactions. Application of the Flory model shows that orientational effects exist in methanol or 1-nonanol, or 1-decanol + ethanenitrile mixtures. In the former solution, this is due to the existence of interactions between unlike molecules. For mixtures including 1-nonanol or 1-decanol, the systems at 298.15 K are close to their UCST (upper critical solution temperature), and interactions between like molecules are dominant. Orientational effects also are encountered in methanol or ethanol + butanenitrile mixtures due to self-association of the alcohol plays a more important role. Aromaticity effect seems to enhance orientational effects. For the remainder systems under consideration, the random mixing hypothesis is attained in rather large extent. Results from the application of the $S_{CC}(0)$ formalism shows that homocoordination is the dominant trend in the investigated solutions, and are consistent with those obtained from the Flory model.

KEYWORDS: 1-alkanols/ nitriles/ excess functions/ dipolar interactions/ structural effects/ random mixing.

1. Introduction

Nitriles show a large variety of applications in synthesis of plastics, cosmetics, pharmaceuticals and of other organic chemicals. They are also important as hydrogen bond acceptors.¹⁻³ Interestingly, aqueous solutions of acetonitrile are used for the separation of protein and peptides mixtures.⁴

1-Alkanol + nitrile mixtures have been studied in terms of different theories. Systems with methanol, ethanol, 1-propanol or 1-butanol and acetonitrile have been investigated by means of an association model which assumes the existence of linear and cyclic species for alcohols and acetonitrile, and only open chains for alcohol-nitrile heterocomplexes.⁵⁻⁷ In this theory, the physical contribution to the molar excess enthalpy, H_m^E , is derived from the NRTL equation.⁵⁻⁷ The model yields an accurate representation for H_m^E of the mentioned binary systems and, neglecting ternary interactions, for related ternary solutions including benzene as third component.⁵⁻⁷ The UNIQUAC association solution model has been also used for the study of the same binary solutions cited above.⁸⁻¹⁰ In this case, the physical contribution to H_m^E is obtained from the UNIQUAC equation,⁸⁻¹⁰ and only linear polymers for self-association of 1-alcohols and for alcohol-nitrile solvation are taken into account.⁸⁻¹⁰ The well-known ERAS model¹¹ and the Flory-Benson-Treszczanowicz theory¹² have been applied to some 1-alkanol + ethanenitrile, + propanenitrile, + butanenitrile or + benzonitrile mixtures.¹³⁻¹⁷

In a series of works, we have shown that the Flory model¹⁸ is an useful tool to investigate the existence of orientational effects in liquid mixtures. Systems of the type: 1-alkanol + linear or cyclic monoether,¹⁹ + linear polyether,²⁰ or + alkanone,²¹ or 1-butanol + alkoxyethanol,²² or ether + alkane,²³ + benzene, or + toluene,²⁴ or + CCl_4 ²⁵ have been investigated using this approach. As continuation, we now pay attention to orientational effects in 1-alkanol + nitrile mixtures by means of the same methodology. As far as we know, only molar excess volumes, V_m^E , of 1-alkanol + ethanenitrile systems²⁶ have been correlated by means of the Prigogine-Flory-Patterson model.^{18,27}

On the other hand, it is interesting to link thermodynamic properties of liquid mixtures with local deviations from the bulk composition. The investigation of fluctuations in a binary system²⁸⁻³⁰ can be conducted in terms of so-called Kirkwood-Buff integrals formalism^{31,32} where fluctuations in the number of molecules of each component and the cross fluctuations are taken into account. A different alternative, due to Bhatia and Thorton,³³ 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 has been used in the investigation of liquid binary alloys.^{34,35} We have applied it to mixtures involving pyridines³⁶ or to 1-alkanol + cyclic ether,³⁷ + aromatic hydrocarbon³⁸ or + alkanone²¹ systems and here is extended to 1-alkanol + nitrile solutions.

2. Theories

2.1.1 Flory model

The main hypotheses of the theory^{18,39-42} have been summarized elsewhere^{21,23} and will not be repeated here. We merely remark that random mixing is a basic assumption of the model.

The Flory equation of state is:

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

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 thermal expansion coefficients, α_{pi} , and isothermal compressibilities, κ_{Ti} , data. Expressions for reduction parameters of mixtures are given elsewhere.²³ H_m^E is determined from:

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

where all the symbols have their usual meaning.²³ In equation (2), the term which depends directly on X_{12} is commonly 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 (1). Therefore, the molar excess volume can be also calculated:

$$V_m^E = (x_1 V_1^* + x_2 V_2^*)(\bar{V} - \phi_1 \bar{V}_1 - \phi_2 \bar{V}_2) \quad (3)$$

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}

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

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

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

and that from the equation of state, $\bar{V} = \bar{V}(\bar{T})$. More details can be found elsewhere.^{19,22,23}

Equation (5) is a generalization of that previously given to calculate X_{12} from H_m^E at $x_1 = 0.5$.⁴³ Properties of nitriles ($i = 2$) at 298.15 K, molar volumes, V_i , α_{Pi} , κ_{Ti} , 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.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 $\gamma (= \alpha_p/\kappa_T)$.^{19,44} 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^{21,29,30,45}

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

with

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

In equations (6) and (7), G^M , G_m^E are the molar Gibbs energy of mixing and the molar excess Gibbs energy, respectively. D is a function closely related to thermodynamic stability.⁴⁶⁻⁴⁸ For ideal mixtures, $G_m^{E,id} = 0$; $D^{id} = 1$ and $S_{CC}(0) = x_1 x_2$. Stability conditions require that $S_{CC}(0) > 0$. Then, for a system close to phase separation, $S_{CC}(0)$ must be large and positive (∞ , when there is immiscibility). If compound formation between components appears, $S_{CC}(0)$ must be very low (0, in the limit). Therefore, $S_{CC}(0) > x_1 x_2$ ($D < 1$) implies 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.^{30,45}

3. Results

Results on H_m^E obtained from the Flory model using X_{12} values at $x_1 = 0.5$ are listed in Table 2, which also contains the interactional contribution to H_m^E at equimolar composition and, for the sake of clarity, the relative standard deviations for H_m^E calculated according to:

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

where $N (=19)$ is the number of data points, and $H_{m,\text{exp}}^E$ 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 (see Table 2). A graphical comparison between experimental and theoretical H_m^E values are shown in Figures 1 and 2. The concentration dependence of X_{12} , according to equation (4) is shown in Figure 3 for some selected systems. Table 3 lists the results obtained for the $S_{CC}(0)$ function (see also Figure 4). 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

Along this section, we are referring to the excess functions at equimolar composition and 298.15 K. On the other hand, n_{OH} stands for the number of C atoms of the 1-alkanol, and n_{CN} represents the number of C atoms of the alkyl chain attached to the CN group.

4.1 Enthalpies of the hydroxyl-nitrile interactions

If structural effects are neglected,^{46,49} H_m^E can be considered as the result of three contributions. $\Delta H_{\text{OH-OH}}$, $\Delta H_{\text{CN-CN}}$ are positive contributions and arise, respectively, from the disruption of alkanol-alkanol and nitrile-nitrile interactions during the mixing process; $\Delta H_{\text{OH-CN}}$ is a negative term related to the new OH---CN interactions created upon that process. Therefore:⁵⁰⁻⁵³

$$H_m^E = \Delta H_{\text{OH-OH}} + \Delta H_{\text{CN-CN}} + \Delta H_{\text{OH-CN}} \quad (9)$$

The $\Delta H_{\text{OH-CN}}$ term represents the enthalpy of the H-bonds between 1-alkanols and nitriles. This magnitude can be evaluated by extending the equation (9) to $x_1 \rightarrow 0$,⁵³⁻⁵⁶ and replacing, $\Delta H_{\text{OH-OH}}$ and $\Delta H_{\text{CN-CN}}$ by the corresponding $H_{\text{ml}}^{\text{E},\infty}$ values (partial excess molar enthalpy at infinite dilution of the first component) of 1-alkanol or nitrile + alkane systems. Thus,

$$\begin{aligned} \Delta H_{\text{OH-CN}} &= H_{\text{ml}}^{\text{E},\infty} (\text{1-alkanol} + \text{nitrile}) \\ &- H_{\text{ml}}^{\text{E},\infty} (\text{1-alkanol} + \text{alkane}) - H_{\text{ml}}^{\text{E},\infty} (\text{nitrile} + \text{alkane}) \end{aligned} \quad (10)$$

This procedure shows some shortcomings: (i) for 1-alkanol + nitrile systems, the $H_{\text{ml}}^{\text{E},\infty}$ data used were often calculated from H_{m}^{E} measurements over the entire mole fraction range. Nevertheless, we note that there is a fair agreement between such data and those obtained from calorimetric measurements at high dilution of the 1-alkanol⁵⁷ (Table 4) (ii) For 1-alkanol + alkane systems, it was assumed that $H_{\text{ml}}^{\text{E},\infty}$ is independent of the alcohol, a common approach when applying association theories.^{11,58-60} As in previous applications,^{20,21,53} we have used $H_{\text{ml}}^{\text{E},\infty} = 23.2 \text{ kJ}\cdot\text{mol}^{-1}$.⁶¹⁻⁶³ (iii) For nitrile + alkane systems, the alkane considered is cyclohexane as $H_{\text{ml}}^{\text{E},\infty}$ data are available in the literature for these solutions.⁵⁷ The $\Delta H_{\text{OH-CN}}$ values obtained are listed in Table 4 (Fig. 5). From their inspection, some statements can be outlined. (i) For mixtures including a given nitrile, $\Delta H_{\text{OH-CN}}$ increases with n_{OH} , which indicates that alcohol-nitrile interactions become then weaker. (ii) Interestingly, such $\Delta H_{\text{OH-CN}}$ variation is sharper for solutions with $n_{\text{CN}} = 1$, than for those with $n_{\text{CN}} = 3$ (Figure 5). This may be ascribed to the fact that 1-octanol, or 1-decanol or 1-undecanol + ethanenitrile mixtures show miscibility gaps at temperatures close to 298.15 K at the composition range (0,0.7) of the alcohol, while systems with butanenitrile do not show this behaviour.^{13,64} The coordinates ($x_{1c}, T_c/\text{K}$) of the critical points for acetonitrile mixtures are:¹³ (0.266, 282.08) (1-octanol); (0.252, 297.06) (1-decanol); (0.216, 303.26) (1-undecanol). Therefore, H_{m}^{E} values of the mixtures with 1-nonanol or 1-decanol are very large and positive (Table 2),¹⁴ which remarks that interactions between like molecules are preponderant in such solutions. (iii) Interactions between unlike molecules are stronger in mixtures with $n_{\text{OH}} = 1-4$ and $n_{\text{CN}} = 1$. (Table 4, Fig. 5). (iv) There are no relevant differences between $\Delta H_{\text{OH-CN}}$ values for systems with butanenitrile or benzonitrile.

The $\Delta H_{\text{OH-CN}}$ values reported in the literature depend on the method applied for their estimation. In the UNIQUAC associated solution model, the value $-17.0 \text{ kJ}\cdot\text{mol}^{-1}$ is used for the mixtures methanol, ethanol, or 1-propanol + ethanenitrile.⁸⁻¹⁰ In the association model with a physical term represented by the NRTL equation, solvation between alcohols and ethanenitrile molecules are considered to be of the type A_iB and A_iB_j ($A = \text{alcohol}$; $B = \text{nitrile}$) and the corresponding enthalpies are -22 and $-16.8 \text{ kJ}\cdot\text{mol}^{-1}$,⁵⁻⁷ respectively. In the framework of the ERAS model, the following values of Δh_{AB}^* (enthalpy of solvation) have been reported for 1-alkanol + butanenitrile mixtures:¹⁵ -8.9 (methanol); -1.0 (ethanol); -16.5 (1-propanol) $\text{kJ}\cdot\text{mol}^{-1}$. For ethanenitrile systems, $\Delta h_{\text{AB}}^* / \text{kJ}\cdot\text{mol}^{-1} = -17.15$ (1-nonanol); -17 (1-decanol).¹⁴ Infrared spectroscopy studies provide for the enthalpy of hydrogen bonding for alcohols with nitriles (all values in $\text{kJ}\cdot\text{mol}^{-1}$):⁶⁵ -10.88 (methanol + ethanenitrile); -8.37 (1-butanol + ethanenitrile); -10.05 (methanol + butanenitrile); -7.12 (1-butanol + butanenitrile); -8.79 (methanol + benzenitrile); -6.69 (1-butanol + benzenitrile).

4.2 Excess molar enthalpies and excess molar entropies.

H_m^E values of 1-alkanol + nitrile mixtures are large and positive (Table 2). Therefore, the main contributions to this excess function arise from the breaking of the interactions between like molecules. This means that the $\Delta H_{\text{OH-OH}}$, $\Delta H_{\text{CN-CN}}$ terms in equation 9 are higher than $|\Delta H_{\text{OH-CN}}|$. Except for methanol solutions, $H_m^E(1\text{-alkanol} + \text{nitrile}) > H_m^E(1\text{-alkanol} + \text{isomeric hydrocarbon})$. Thus, $H_m^E(1\text{-propanol})/\text{J}\cdot\text{mol}^{-1} = 1587$ ($n_{\text{CN}} = 3$)⁶⁶ > 459 (pentane);⁶⁷ 1454 (benzonitrile)¹⁵ > 880 (toluene).⁶⁸ This clearly reveals that nitriles are good breakers of the alcohol self-association. The fact that the Kirkwood correlation factor of methanol + alkanenitrile mixtures does not show a minimum at low alcohol concentrations⁶⁹ supports our conclusion. The existence of such minimum is characteristic of 1-alkanol + alkane mixtures and is ascribed to the existence of cyclic species, mainly tetramers, at the mentioned low concentrations of alcohol.^{70,71} The replacement of alkane by a nitrile leads to the breaking of the cyclic species and, consequently, the minimum vanishes. Many solutions behave similarly.^{70,72} On the other hand, in mixtures involving a given nitrile, H_m^E increases with n_{OH} and the H_m^E curves are rather symmetrical, except for mixtures containing methanol (Figures 1-2). These features indicate that interactions are essentially of dipolar type and effects related to self-association of 1-alkanols and to solvation between unlike molecules are here of minor importance. Systems where self-association of alcohols plays the dominant role, as 1-alkanol + heptane, are characterized by the following features: (i) H_m^E increases from ethanol to 1-propanol or 1-butanol and then smoothly decreases; (ii) the H_m^E curves are shifted to low mole

fractions of the alcohol,⁵³ and the corresponding H_m^E values are rather low (see above); (iii) the isobaric excess heat capacities, $C_{p,m}^E$, are large and positive (11.7 J·mol⁻¹·K⁻¹ for ethanol + heptane⁷³); (iv) in contrast, values of $TS_m^E (= H_m^E - G_m^E)$ are large and negative. For the ethanol + hexane mixture, $H_m^E = 548$,⁷⁴ $G_m^E = 1374$ ⁶² and $TS_m^E = -826$ (data in J·mol⁻¹). The corresponding values of $C_{p,m}^E$ for 1-alkanol + nitrile mixtures are much lower, and those of TS_m^E are positive (Table 3). Thus, $C_{p,m}^E (n_{CN} = 1)$ /J·mol⁻¹·K⁻¹, estimated from $\frac{\Delta H_m^E}{\Delta T}$, is 5.3 and 7.4 for the methanol and ethanol solutions, respectively.⁵ All this supports the importance of dipolar interactions in the investigated systems.

4.2.1 The effect of increasing n_{CN} in mixtures with a given 1-alcohol

H_m^E decreases at this condition, which can be ascribed to the following features. (i) Polarity of longer nitriles is weaker. As a consequence, the UCST, T_c , decreases when n_{CN} increases in mixtures with a given alkane. For example, $T_c(\text{hexane})/\text{K} = 350.2$ ($n_{CN} = 1$) > 284.2 ($n_{CN} = 2$) > 244.2 ($n_{CN} = 3$).⁷⁵ This leads to a lower ΔH_{CN-CN} contribution to H_m^E when n_{CN} is increased (Table 4), effect which is predominant over: (ii) a larger ΔH_{OH-OH} term related to the higher number of alcohol-alcohol interactions broken by nitriles with larger aliphatic surfaces. It should be kept in mind that H_m^E of 1-alkanol + n -alkane mixtures increases with the alkane size.⁷⁶ (iii) A more negative ΔH_{OH-CN} contribution for mixtures with $n_{CN} = 1$ and particularly, $n_{OH} = 1-4$.

4.2.2 The effect of increasing n_{OH} in systems with a given nitrile

Now, H_m^E increases (Table 2). This may be due to: (i) the weakening of the alcohol-nitrile interactions (larger ΔH_{OH-CN} contribution, Table 4). (ii) Increased ΔH_{CN-CN} contribution, as it is expected that more nitrile-nitrile interactions are broken by alcohols with larger aliphatic surfaces. Note that T_c of systems with a given nitrile increases with the chain length of the n -alkane. Thus, $T_c(n_{CN} = 1)/\text{K} = 350.2$ (hexane) < 358 (heptane) < 381.7 (decane) < 398.2 (dodecane) < 403.7 (tetradecane).⁷⁵ As in other studies, the H_m^E variation is steeper when replacing methanol by ethanol, than when this alcohol is replaced by 1-propanol. This underlines that interactions between unlike molecules are much important in methanol systems. Accordingly, TS_m^E is also lower for such solutions (Table 3). (iii) Alcohol-alcohol interactions are more easily broken by nitriles in the case of long chain 1-alkanols, which leads to larger

$\Delta H_{\text{OH-OH}}$ term. The increase of the TS_m^E with the alcohol size (Table 3) is consistent with this picture. Therefore, association/solvation effects become weaker with the increasing of the alcohol size, and physical interactions are predominant in systems with long chain 1-alkanols.

4.3 Excess molar volumes

There is a rather wide database on V_m^E for 1-alkanol + nitrile mixtures.^{13,66,77-92} From its examination (see Figure 6), 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 large and positive (Table 2). 1-Alkanol + alkanone²¹ or + linear polyether²⁰ mixtures behave similarly. Some numerical values follow: $V_m^E(n_{\text{CN}} = 1)/\text{cm}^3 \cdot \text{mol}^{-1} = -0.145$ (methanol);⁸⁶ -0.022 (ethanol);⁸⁶ 0.098 (1-butanol);⁸⁶ 0.194 (1-hexanol);⁸⁶ 0.280 (1-octanol);⁸² 0.340 ,⁹⁰ 0.378 ⁸⁶ (1-decanol). The H_m^E values are ranged between 1086 (methanol)⁵ and 3032 (1-decanol)¹⁴ $\text{J} \cdot \text{mol}^{-1}$. This suggests the existence of interactions between unlike molecules and/or structural effects (see below). (ii) Both magnitudes V_m^E and H_m^E of solutions with a given n_{CN} value increase with n_{OH} . Thus, the V_m^E variation can be essentially attributed to an increased contribution from the breaking of the interactions between like molecules. (iii) For mixtures with $n_{\text{OH}} = 1-3$, $V_m^E(n_{\text{CN}} = 1) < V_m^E(n_{\text{CN}} = 3)$, while an inversion in this variation is produced from $n_{\text{OH}} \geq 4$ (Figure 6). This suggests that the contributions to V_m^E from interactions between unlike molecules and from structural effects are more relevant in systems formed by ethanenitrile and shorter 1-alkanols than in those with butanenitrile. In contrast, for mixtures involving longer 1-alkanols, the interactional contribution to V_m^E from the disruption of interactions between like molecules is more relevant in ethanenitrile solutions. (iv) For $n_{\text{CN}} = 1$ and $n_{\text{OH}} \geq 4$, the V_m^E curves are skewed to higher mole fractions of the nitrile,⁸⁶ the smaller compound, which suggests that structural effects are of the free volume type. A similar trend is observed in methanol or ethanol + linear polyether mixtures.⁹³ For $n_{\text{OH}} = 2,3$, the V_m^E curves are s-shaped, with positive values at lower mole fractions of the alcohol.⁸⁶ This seems to indicate that the alkanol network is better broken in that region. For $n_{\text{OH}} = 1$, V_m^E values are negative at any alcohol composition,⁸⁶ which might be ascribed, at least in part, to the existence of interactions between unlike molecules. However, free volume effects are also present as the V_m^E curve is skewed to higher mole fractions of the alcohol (smaller compound). In the case of solutions with $n_{\text{CN}} = 3$ and longer 1-

alkanol, the V_m^E curves become more symmetrical⁸⁴ as butanenitrile size is larger than that of ethanenitrile. The s-shaped V_m^E curve of the system with $n_{OH} = 1$ can be explained in terms of a lower contribution (in absolute value) to this magnitude from the creation of alcohol-nitrile interactions. Interestingly, the V_m^E curves of benzonitrile systems are shifted to lower mole fractions of the nitrile (the larger component)^{15,88} showing, newly, the existence of free volume effects. (v) The magnitude $A_p = \left(\frac{\partial V_m^E}{\partial T} \right)_p$ is positive for mixtures formed by ethanenitrile and $n_{OH} = 1-5$,^{78,87} and becomes negative for solutions with $n_{OH} = 8,10$.⁹⁰ Thus, $A_p(n_{CN} = 1)/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.09 \cdot 10^{-3}$ ($n_{OH} = 1$);⁷⁸ $-3.8 \cdot 10^{-3}$ ($n_{OH} = 10$).⁹⁰ Positive values of A_p are encountered in solutions where association effects are preponderant; negative A_p values are found in systems where important structural effects exist. For example, $A_p = -1.2 \cdot 10^{-2} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the hexadecane + hexane mixture;⁹⁴ and for the 1-propanol + heptane solution,^{95,96} $A_p = 5.9 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The negative A_p value of the methanol + benzonitrile system ($-3.8 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ⁸⁸) may be interpreted in terms of the existence of relevant structural effects.

4.4 Results from the Flory model

We define the mean standard relative deviation of H_m^E as:

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

where N_s represents the number of systems considered. At 298.15 K, $\bar{\sigma}_r(H_m^E)$ shows close values for $n_{CN} = 1$ or $n_{CN} = 3$ (0.126 ($N_s = 6$) and 0.111 ($N_s = 10$), respectively). One can conclude that orientational effects are quite similar in both types of mixtures. However, a more detailed examination of results reveals that $\sigma_r(H_m^E)$ values of the methanol or ethanol + butanenitrile systems are larger than those of the corresponding solutions with ethanenitrile, probably because alcohol self-association plays a more important role in the former mixtures (see below). In contrast, for 1-nonanol or 1-decanol solutions, $\sigma_r(H_m^E)(n_{CN} = 1) > \sigma_r(H_m^E)(n_{CN} = 3)$ (Table 2) as orientational effects are stronger in these ethanenitrile mixtures due to the system temperature is close to the UCST. On the other hand, the rather large $\sigma_r(H_m^E)$ values of solutions containing benzonitrile indicate that the aromaticity effect leads to strengthened orientational effects. In spite of such results, remarkably $\sigma_r(H_m^E)$ is lower than 0.10 for many of the systems under study at 298.15 K, which means that the random mixing

hypothesis is attained in rather large extent (see results, e.g. for ethanol or 1-propanol or 1-butanol + ethanenitrile, or + butanenitrile, Table 2). The increase of temperature slightly weakens orientational effects ($\bar{\sigma}_r(H_m^E) = 0.108$, $N_s = 6$ for $n_{CN} = 1$, Table 2). Interestingly, H_m^E and X_{12} do not change in line with n_{OH} for a given n_{CN} value. In fact, the excess function increases with n_{OH} , while X_{12} increases up to ethanol or 1-propanol and then slowly decreases (Table 2). In the case of $n_{CN} = 3$, the very smooth variation of X_{12} with n_{OH} from 1-hexanol is remarkable. This suggests that, in the framework of the theory, mixtures with longer 1-alkanols differ mainly by size effects. Thus, the $\sigma_r(H_m^E)$ value of the 1-decanol + butanenitrile system remains unchanged when is determined using $X_{12} = 76.77 \text{ J}\cdot\text{cm}^{-3}$ (the same parameter of the 1-hexanol solution). The fact that $H_m^E/(x_1V_1^* + x_2V_2^*)$, a magnitude widely used to compare H_m^E values of solutions with compounds of very different size,^{97,98} and X_{12} change in line with n_{OH} (Figure 7) also supports our conclusion. In order to obtain quick H_m^E values for mixtures for which experimental data are not available, one could use $X_{12} = 130.71 \text{ J}\cdot\text{cm}^{-3}$ for ethanenitrile solutions with $5 \leq n_{OH} \leq 8$ and $X_{12} = 73.58 \text{ J}\cdot\text{cm}^{-3}$ for butanenitrile systems with $10 \leq n_{OH} \leq 16$. Finally, it should be mentioned that the model fails when describing V_m^E , as the theoretical results are much higher than the experimental values. The model can not represent the strong structural effects present in these systems.

4.5 $S_{CC}(0)$ results

Inspection of Table 3 shows that 1-alkanol + nitrile systems are characterized by homocoordination ($S_{CC}(0) > 0.25$). A comparison of $S_{CC}(0)$ results for solutions with $n_{CN} = 1$, or 3 becomes difficult as the corresponding G_m^E values are at different temperatures. We have used DISQUAC interaction parameters for the hydroxyl/nitrile contacts obtained by our research group (unpublished results) for calculating $S_{CC}(0)$ at 298.15 K for methanol or 1-octanol + ethanenitrile systems, and some conclusions can be drawn. (i) The large $S_{CC}(0)$ value (1.411) for the 1-octanol + ethanenitrile solution is in agreement with the proximity of the system temperature to the critical one (see above), as mixtures at this condition show very large $S_{CC}(0)$ values.⁹⁹ This is the case, e.g. of pyridine,³⁶ nitroethane⁹⁹ or 2-propanone¹⁰⁰ + alkane mixtures. (ii) Therefore, homocoordination of systems with e.g. ethanenitrile and long chain 1-alkanols is much more relevant than for corresponding solutions with butanenitrile. (iii) In the case of methanol systems, $S_{CC}(0)(n_{CN} = 1) < S_{CC}(0)(n_{CN} = 3)$, and interactions between

unlike molecules (i.e., heterocoordination) are more important in the ethanenitrile mixture. Note that, as usually, the increasing of temperature weakens homocoordination.

4.6 Comparison of 1-alkanol + butanenitrile, or + 2-butanone systems

Butanenitrile and 2-butanone are very polar compounds (their dipole moment is 3.50 and 2.76 D, respectively¹⁰¹) of similar size and shape. A comparison of their mixtures with 1-alkanols is pertinent. Interestingly, $\Delta H_{\text{OH-CO}}$ and $\Delta H_{\text{OH-CN}}$ values are rather similar (Figure 5), while homocoordination is higher in butanenitrile solutions, as 2-butanone mixtures show lower $S_{\text{CC}}(0)$ values²¹ ($S_{\text{CC}}(0) = 0.425$ (methanol); 0.403 (1-propanol), 0.420 (1-hexanol); 0.443 (1-octanol)) (see Table 4 for comparison). The larger H_{m}^{E} of systems with butanenitrile could be then explained taking into account that $\Delta H_{\text{CN-CN}} > \Delta H_{\text{CO-CO}}$ as $H_{\text{m,1}}^{\text{E},\infty} / \text{kJ}\cdot\text{mol}^{-1} = 10.2$ (butanenitrile + cyclohexane)⁵⁷ > 7.47 (2-butanone + heptane)¹⁰² and that heterocoordination is more important in 2-butanone systems. In addition, TS_{m}^{E} (2-butanone)²¹ / $\text{J}\cdot\text{mol}^{-1} = 161$ ($n_{\text{OH}} = 1$); 205 ($n_{\text{OH}} = 2$) and 725 ($n_{\text{OH}} = 3$), which are lower values than those of systems containing butanenitrile (Table 3). This could be also related to the existence of more interactions between unlike molecules in the alkanone solution. However, an opposite behaviour is observed for mixtures including longer 1-alkanols, e.g., TS_{m}^{E} (1-octanol) / $\text{J}\cdot\text{mol}^{-1} = 1172$ (2-butanone)²¹ > 1006 (butanenitrile).⁸² It is remarkable that the same trend is encountered in systems with alkanes. Thus, TS_{m}^{E} (heptane) / $\text{J}\cdot\text{mol}^{-1} = 476$ (2-butanone)^{102,103} > 270 (butanenitrile).^{104,105} An interesting result, as allows to conclude that dipolar interactions become much more important when 2-butanone or butanenitrile are mixed with 1-alkanols different to methanol or ethanol than when they are mixed with alkanes. Finally, as an average, orientational effects are very similar in 1-alkanol + 2-butanone, or + butanenitrile systems ($\bar{\sigma}_{\text{r}}(H_{\text{m}}^{\text{E}}) = 0.111$). However, such effects are more relevant in the methanol + 2-butanone mixture,²¹ ($\sigma_{\text{r}}(H_{\text{m}}^{\text{E}}) = 0.270 > 0.222$ (methanol + butanenitrile)) probably due to the existence of more interactions between unlike molecules. For the remainder solutions, orientational effects seem to be slightly weaker in those including 2-butanone: $\bar{\sigma}_{\text{r}}(H_{\text{m}}^{\text{E}}) = 0.079$ (2-butanone)²¹ < 0.099 (butanenitrile).

5. Conclusions

1-Alkanol + alkanenitrile or + benzonitrile mixtures have been investigated through the analysis of H_{m}^{E} , C_{pm}^{E} , TS_{m}^{E} and V_{m}^{E} data and using the Flory model and the $S_{\text{CC}}(0)$ formalism. The enthalpy of the hydroxyl-nitrile interactions has been evaluated. These interactions are essentially of dipolar type. Large structural effects are encountered in the studied solutions, as

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3 their high H_m^E values contrast with low V_m^E . Stronger orientational effects are encountered in
4 methanol or 1-nonanol or 1-decanol + ethanenitrile systems, or in methanol or ethanol +
5 butanenitrile mixtures. Aromaticity strengthens orientational effects. For other solutions, the
6 random mixing hypothesis is attained in large extension. $S_{CC}(0)$ results show that
7 homocoordination is the dominant trend.
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TABLE 1

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

Alkanone	$V_i /$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\alpha_p / 10^{-3} \cdot \text{K}^{-1}$	$\kappa_T / \text{TPa}^{-1}$	$V_i^* /$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$P_i^* / \text{J} \cdot \text{cm}^{-3}$
Ethanenitrile	52.87 ^b	1.35 ^b	1070 ^b	40.20	650.8
Butanenitrile	87.86 ^b	1.17 ^b	991 ^c	68.56	578.1
Benzonitrile	103.06 ^b	0.864 ^b	623 ^d	84.53	615.0

^amolar volume, V_i ; isobaric thermal expansion coefficient, α_p ; isothermal compressibility κ_T ;

^bRef 101; ^c calculated using¹⁰⁶ $\gamma = \frac{\alpha_p}{\kappa_T} = 1.18 \text{ MPa}^{-1} \cdot \text{K}^{-1}$; ^dRef. 107

TABLE 2

Molar Excess Enthalpies, H_m^E , Interactional Contribution According to the Flory's Model, $H_{m,int}^E$ and Flory's Interaction Parameter, X_{12} , for 1-Alkanol(1) + Nitrile(2) Systems at Equimolar Composition and Temperature T .

1-alkanol	T/K	$H_m^E / J \cdot mol^{-1}$	$H_{m,int}^E / J \cdot mol^{-1}$	$X_{12} / J \cdot cm^{-3}$	$\sigma_r (H_m^E)^a$
		1-alkanol(1) + ethanenitrile(2)			
Methanol	298.15	1086 ⁵	765	119.23	0.147
	308.15	1140 ⁵	785	124.17	0.135
Ethanol	298.15	1500 ⁵	1069	128.35	0.077
	308.15	1574 ⁵	1097	133.71	0.069
	318.15	1645 ¹⁰⁸	1120	138.69	0.056
1-propanol	298.15	1827 ⁶	1326	133.41	0.075
	308.15	1921 ¹⁰⁹	1366	139.39	0.071
	318.15	1983 ¹⁰⁹	1381	143.00	0.076
1-butanol	298.15	2039 ⁷	1504	131.76	0.094
1-nonanol	298.15	2671 ¹⁴	2069	120.87	0.193
	308.15	3050 ¹⁴	2321	137.33	0.159
1-decanol	298.15	3032 ¹⁴	2356	130.71	0.169
	308.15	3297 ¹⁴	2521	141.53	0.193
		1-alkanol(1) + butanenitrile(2)			
Methanol	298.15	978 ⁸⁴	713	93.43	0.220
Ethanol	298.15	1316 ⁸¹	964	95.45	0.184
1-propanol	298.15	1522 ⁶⁶	1128	92.48	0.098
1-butanol	298.15	1587 ⁸¹	1191	84.17	0.089
1-pentanol	298.15	1707 ⁸⁴	1295	81.27	0.065
1-hexanol	298.15	1762 ⁸²	1347	76.77	0.107
1-heptanol	298.15	1867 ⁸⁴	1440	75.42	0.072
1-octanol	298.15	1960 ⁸²	1522	74.14	0.112
1-nonanol	298.15	2016 ⁸⁴	1572	72.01	0.083
1-decanol	298.15	2171 ⁸⁴	1700	73.58	0.081
		1-alkanol(1) + benzonitrile(2)			
Methanol	298.15	976 ¹⁵	766	91.35	0.294
Ethanol	298.15	1209 ¹⁵	943	84.55	0.188
1-propanol	298.15	1454 ¹⁵	1133	83.98	0.166

^aRelative standard deviations for H_m^E (eq. 8)

TABLE 3

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

System	T/K	$G_m^E/J\cdot\text{mol}^{-1}$	$TS_m^E/J\cdot\text{mol}^{-1}$	$S_{CC}(0)$
Methanol(1) + ethanenitrile(2)	298.15	668 ^b	418	0.579 ^b
	328.15	619 ¹¹¹		0.432
Ethanol(1) + ethanenitrile(2)	298.15	860 ^b	640	0.793 ^b
	323.15	795 ¹¹²		0.556
	393.15	533 ¹¹³		0.364
1-propanol(1) + ethanenitrile(2)	298.15	956 ^b	871	0.666 ^b
	328.15	859 ¹¹⁴		0.599
1-butanol(1) + ethanenitrile(2)	298.15	1026 ^b	1013	0.808 ^b
	333.15	908 ¹¹⁵		0.610
1-octanol(1) + ethanenitrile(2)	298.15	1222 ^b		1.411 ^b
Methanol(1) + butanenitrile(2)	278.15	759 ⁸⁴		0.600
	298.15	733 ⁸⁴	245	0.556
	318.15	710 ⁸⁴		0.500
Ethanol(1) + butanenitrile(2)	278.15	809 ⁸¹		0.666
	298.15	774 ⁸¹	542	0.578
	323.15	733 ⁸¹		0.502
1-propanol(1) + butanenitrile(2)	278.15	839 ⁶⁶		0.516
	298.15	754 ⁶⁶	768	0.504
	323.15	702 ⁶⁶		0.472
1-butanol(1) + butanenitrile(2)	278.15	852 ⁸¹		0.738
	298.15	787 ⁸¹	800	0.605
	323.15	710 ⁸¹		0.488
1-pentanol(1) + butanenitrile(2)	298.15	834 ⁸⁴	873	0.609
1-hexanol(1) + butanenitrile(2)	298.15	854 ⁸²	908	0.663
1-heptanol(1) + butanenitrile(2)	298.15	908 ⁸⁴	959	0.934
1-octanol(1) + butanenitrile(2)	298.15	954 ⁸²	1006	0.830
1-decanol(1) + butanenitrile(2)	298.15	1049 ⁸⁴	1122	0.906

^a TS_m^E values calculated using H_m^E data from Table 2; ^bDISQUAC value

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, $\Delta H_{\text{OH-CN}}$, for 1-Alkanol(1) + Nitrile(2) Systems.

System	$H_1^{E,\infty} / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_{\text{OH-CN}} / \text{kJ}\cdot\text{mol}^{-1}$
ethanenitrile(1) + cyclohexane(2)	15.0 ^{57,a}	
butanenitrile(1) + cyclohexane(2)	10.2 ^{57,a}	
benzonitrile(1) + cyclohexane(2)	10.43 ¹¹⁰	
methanol(1) + ethanenitrile(2)	5.66 ^{57,a}	-32.5
	6.06 ^{5,b}	
ethanol(1) + ethanenitrile(2)	7.88 ^{57,a}	-30.3
	7.99 ^{5,b}	
1-propanol(1) + ethanenitrile(2)	8.84 ^{57,a}	-29.4
	9.24 ^{6,b}	
1-butanol(1) + ethanenitrile(2)	10.29 ^{57,a}	-27.9
	10.39 ^{7,b}	
1-nonanol(1) + ethanenitrile(2)	15.53 ^{14,b}	-22.7
1-decanol(1) + ethanenitrile(2)	18.98 ^{14,b}	-19.2
methanol(1) + butanenitrile(2)	4.91 ^{84,b}	-28.5
ethanol(1) + butanenitrile(2)	7.17 ^{81,b}	-26.2
1-propanol(1) + butanenitrile(2)	8.08 ^{66,b}	-25.3
1-butanol(1) + butanenitrile(2)	8.39 ^{81,b}	-25.0
1-pentanol(1) + butanenitrile(2)	8.32 ^{84,b}	-25.1
1-hexanol(1) + butanenitrile(2)	9.89 ^{82,b}	-23.5
1-heptanol(1) + butanenitrile(2)	9.86 ^{84,b}	-23.5
1-octanol(1) + butanenitrile(2)	12.32 ^{82,b}	-21.5
1-nonanol(1) + butanenitrile(2)	11.95 ^{84,b}	-21.7
1-decanol(1) + butanenitrile(2)	11.36 ^{84,b}	-22.0
methanol(1) + benzonitrile(2)	6.50 ^{15,b}	-27.1
ethanol(1) + benzonitrile(2)	8.23 ^{15,b}	-25.4
1-propanol(1) + benzonitrile(2)	9.07 ^{15,b}	-24.6

^avalue obtained from H_m^E data at high dilution; ^bvalue obtained from H_m^E data over the whole concentration range

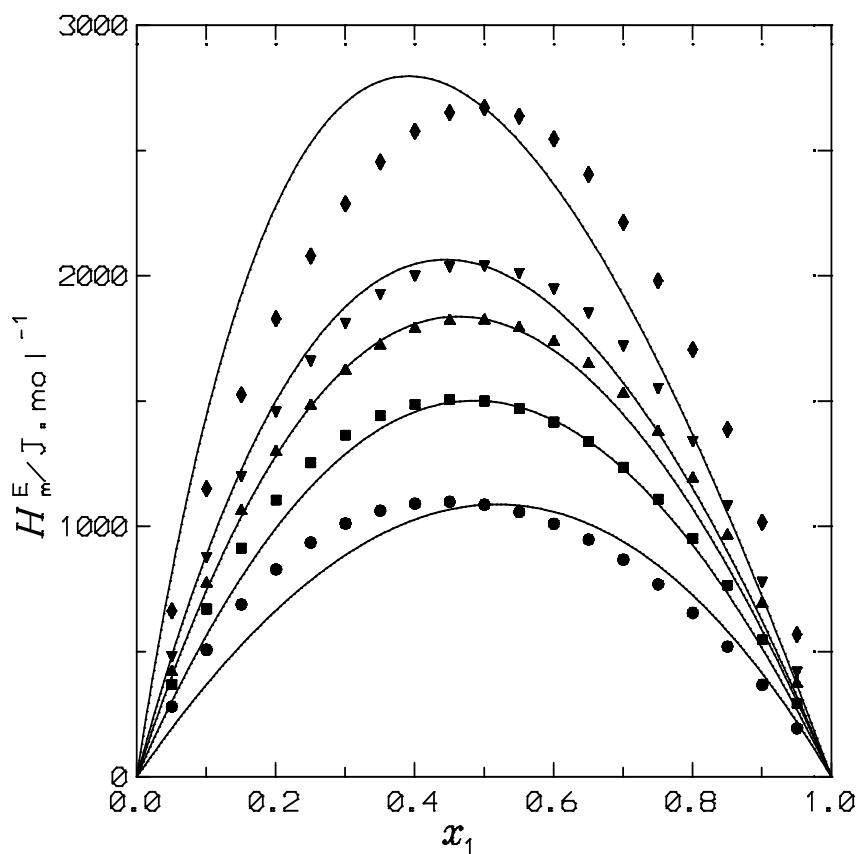


Figure 1 H_m^E of 1-alkanol(1) + ethanenitrile(2) systems at 298.15 K. Symbols, experimental results: (●), methanol;⁵ (■), ethanol;⁵ (▲), 1-propanol;⁶ (▼), 1-butanol;⁷ (◆), 1-nanol.¹⁴ Solid lines, results from the Flory model with interaction parameters listed in Table 2.

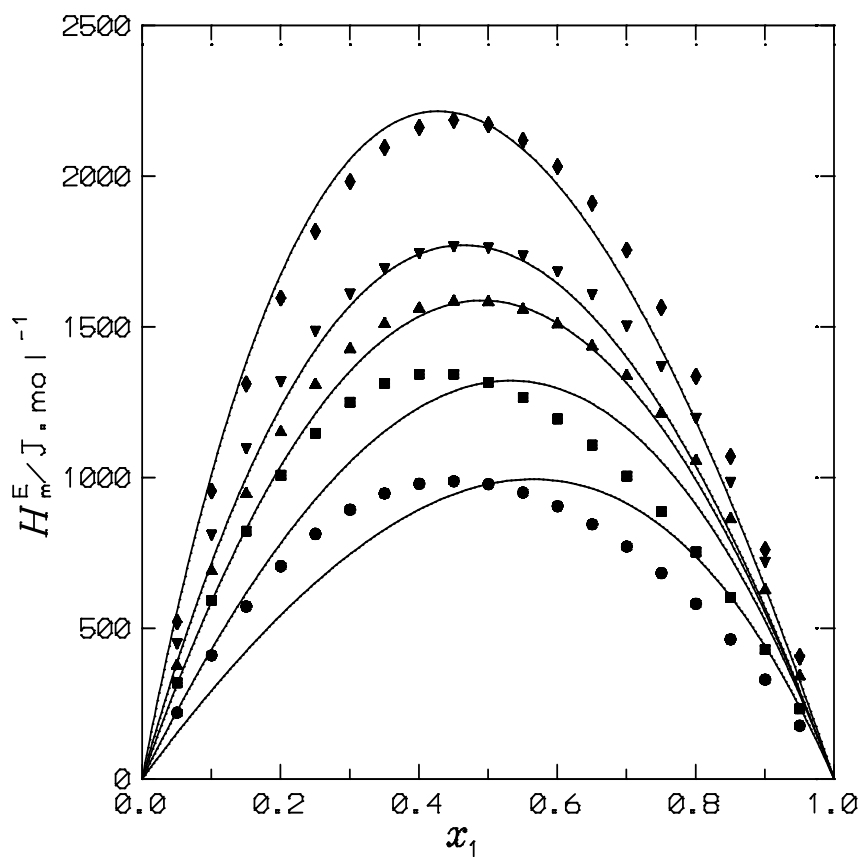


Figure 2 H_m^E of 1-alkanol(1) + butanenitrile(2) systems at 298.15 K. Symbols, experimental results: (●), methanol,⁸⁴ (■), ethanol,⁸¹ (▲), 1-butanol,⁸¹ (◆), 1-hexanol,⁸² (▼), 1-decanol.⁸⁴ Solid lines, results from the Flory model with interaction parameters listed in Table 2.

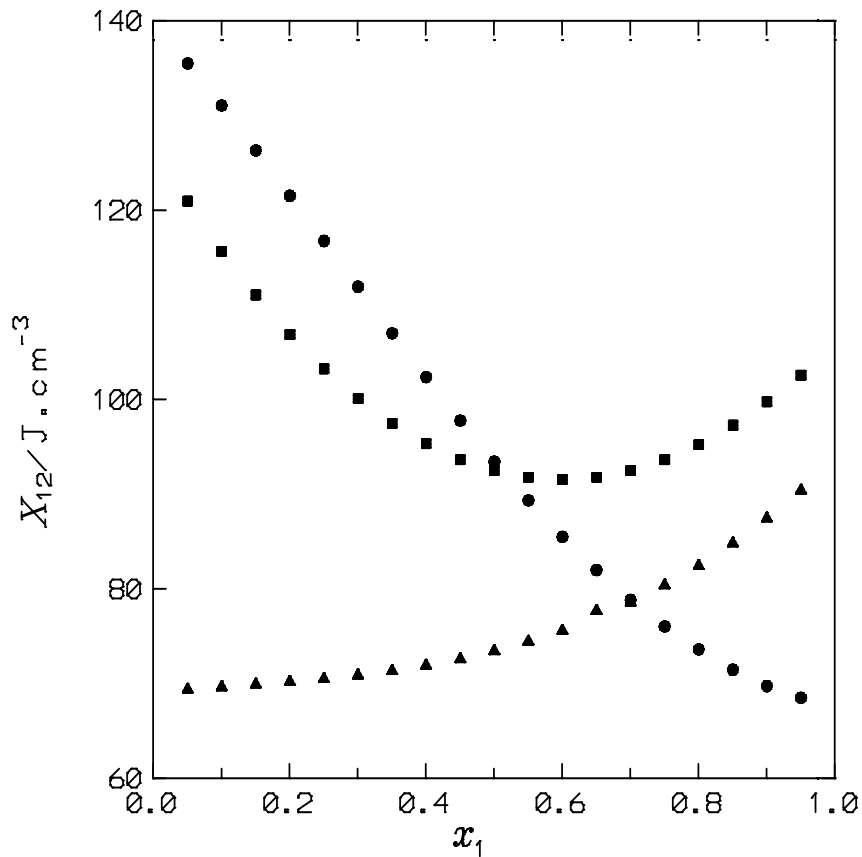


Fig. 3 Flory interaction parameters, X_{12} , for 1-alkanol(1) + butanenitrile(2) mixtures at 298.15 K. Full, symbols: (●), methanol,⁸⁴ (■), 1-propanol⁶⁶ (▲), 1-decanol.⁸⁴

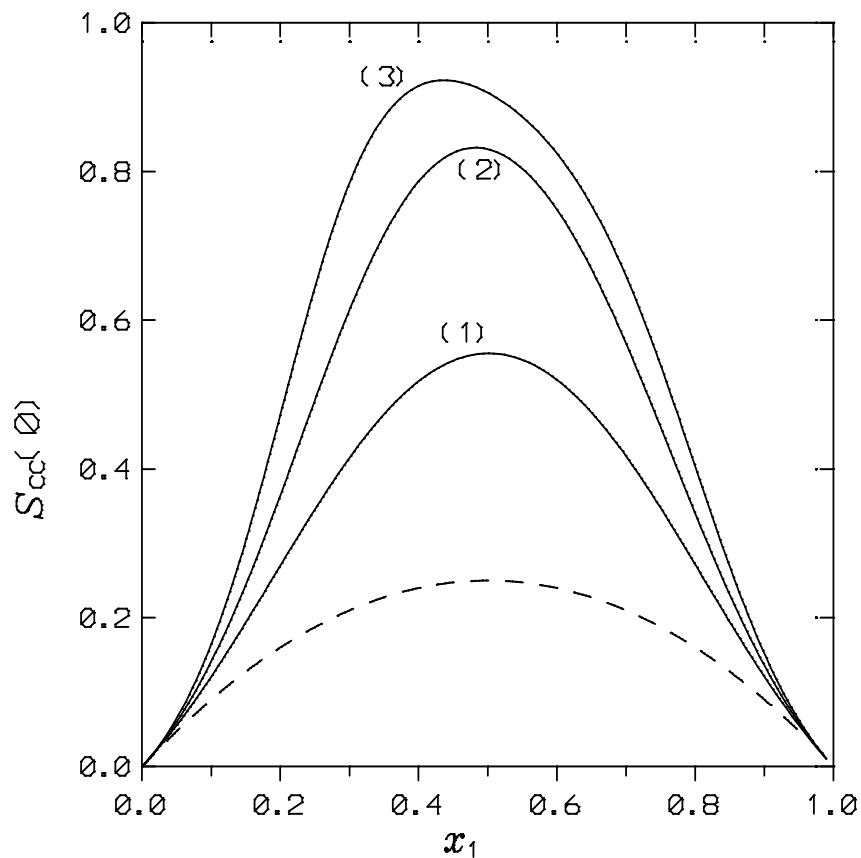


Figure 4 $S_{cc}(0)$ results for 1-alkanol(1) + butanenitrile(2) mixtures at 298.15 K: (1), methanol⁸⁴; (2), 1-octanol⁸²; (3), 1-decanol⁸⁴. Dashed line, ideal mixture

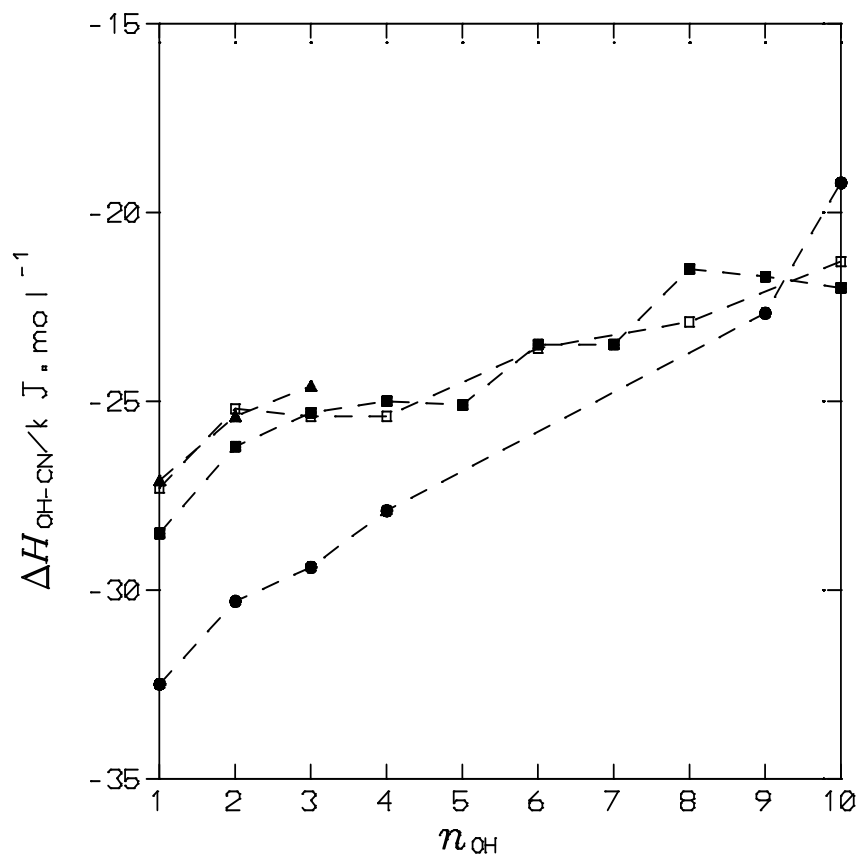


Figure 5 ΔH_{OH-CN} of hydroxyl/nitrile interactions in 1-alkanol(1) + nitrile(2) mixtures at 298.15 K. Full symbols, (●), ethanenitrile; (■), butanenitrile; (▲), benzonitrile. Open symbols correspond to the enthalpy of the hydroxyl/carbonyl interactions in 1-alkanol + 2-butanone systems.²¹

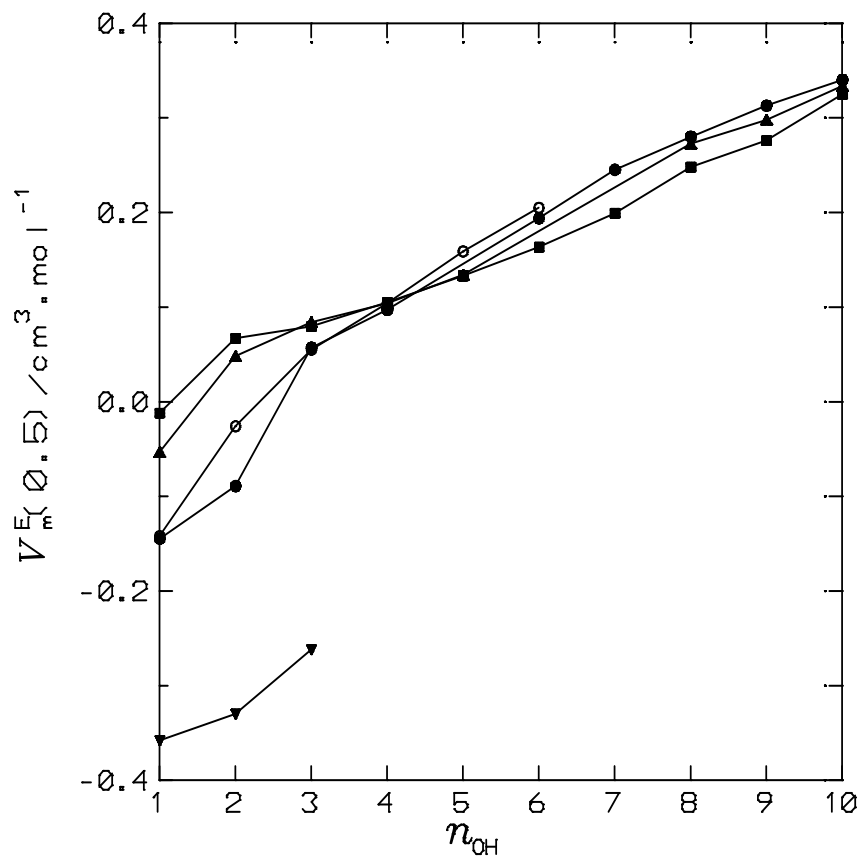


Figure 6 V_m^E of 1-alkanol(1) + nitrile(2) systems at 298.15 K. Symbols: experimental results: (●), ethanenitrile;⁸⁶ (○), ethanenitrile⁷⁸; (▲), propanenitrile;^{13,92} (■), butanenitrile;^{66,81,82,84}; (▼), benzonitrile.¹⁵

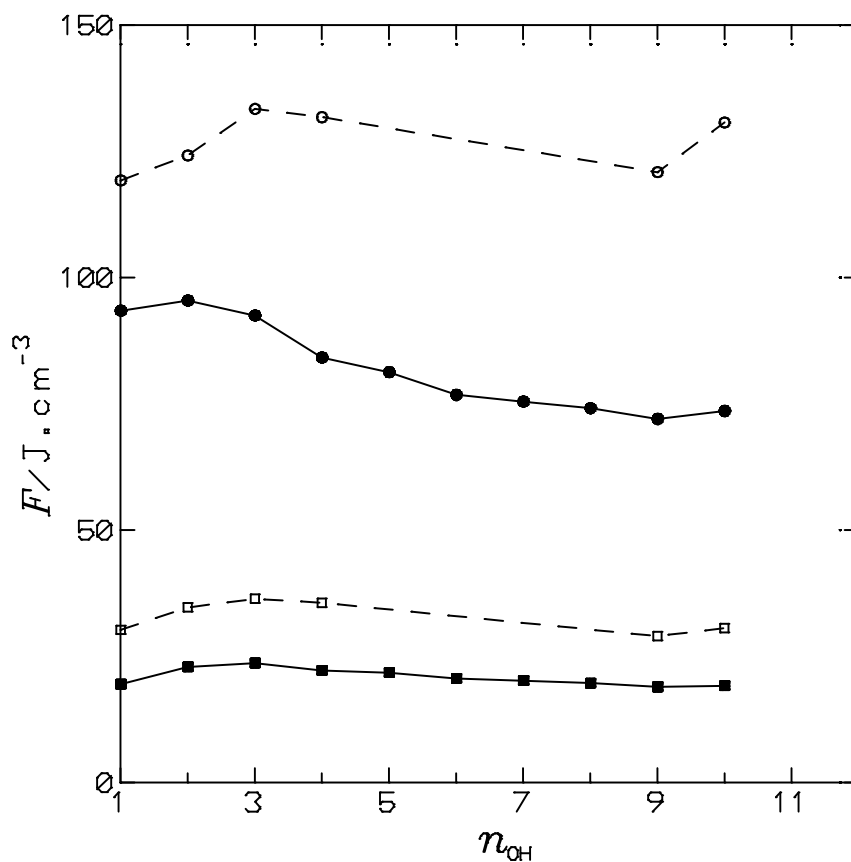


Figure 7 F property of 1-alkanol + nitrile systems at 298.15 K vs. n_{OH} , the number of C atoms of the alcohol. $F = X_{12}$: (O), $n_{CN} = 1$; (●), $n_{CN} = 3$; $F = H_m^E / (x_1V_1^* + x_2V_2^*)$: (□), $n_{CN} = 1$; (■), $n_{CN} = 3$