

**THERMODYNAMICS OF MIXTURES CONTAINING A VERY
STRONGLY POLAR COMPOUND. 11. 1-ALKANOL +
ALKANENITRILE SYSTEMS**

JUAN ANTONIO GONZÁLEZ*⁽¹⁾, FERNANDO HEVIA⁽¹⁾, ANA COBOS⁽¹⁾, ISAÍAS
GARCÍA DE LA FUENTE⁽¹⁾, AND CRISTINA ALONSO TRISTÁN⁽²⁾

⁽¹⁾ G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de
Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain,

⁽²⁾ Dpto. Ingeniería Electromecánica. Escuela Politécnica Superior. Avda. Cantabria s/n. 09006
Burgos, (Spain)

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

ABSTRACT

1-Alkanol + alkanenitrile systems have been studied by means of the DISQUAC, ERAS and UNIFAC (Dortmund) models. DISQUAC and ERAS parameters for the alkanol/nitrile interactions are reported. DISQUAC describes a whole set of thermodynamic properties: phase equilibria, vapour-liquid (VLE), liquid-liquid (LLE) and solid-liquid (SLE) equilibria, molar excess functions, Gibbs energies, G_m^E , and enthalpies, H_m^E , and partial excess molar enthalpies at infinite dilution, $H_{mi}^{E,\infty}$ using the same set of interaction parameters for each solution. The dependence on the molecular structure of the interaction parameters is similar to that observed in other previous applications to mixtures formed by 1-alkanols and a strongly polar compound, in such way that the quasichemical interchange coefficients can be kept constant from 1-propanol. However, methanol and ethanol solutions behave differently. From the analysis of experimental data for H_m^E , $TS_m^E (= H_m^E - G_m^E)$, and molar excess volumes, V_m^E , it is concluded that the studied systems are characterized by dipolar interactions and strong structural effects. The former are more relevant in acetonitrile solutions. Association effects are more important in butanenitrile mixtures. DISQUAC improves H_m^E results from the ERAS model. ERAS results on H_m^E for systems containing acetonitrile are also improved by UNIFAC. This remarks the importance of dipolar interactions in the investigated mixtures. ERAS describes the variation of $V_m^E (x_1=0.5)$ with the 1-alkanol size for mixtures with a given nitrile, but the concentration dependence of this excess function is poorly represented.

KEYWORDS: DISQUAC; ERAS; UNIFAC, 1-alkanols; nitriles; dipolar interactions; structural effects.

1. INTRODUCTION

Nitriles are important chemicals in the production of plastics, cosmetics or pharmaceuticals [1]. Nitriles are also good hydrogen bond acceptors [2,3]. For example, many hydrogen bonds are between the nitrile and aminoacids such as serine or arginine [1]. On the other hand, the high polarity of nitriles allows them to act as hydroxyl or carboxyl isosteres. The acetonitrile + water system is used as mobile phases in reversed phase high performance liquid chromatography, which is commonly the final step in protein purification [4].

1-Alkanol + alkanenitrile mixtures have been studied in terms of a variety of theories. Systems formed by methanol, ethanol, 1-propanol or 1-butanol and acetonitrile have been investigated using different association models including physical interactions by means of the UNIQUAC or NRTL equations [5-10]. The latter model assumes the existence of linear and cyclic species for alcohols and acetonitrile, and only open chains for alcohol-nitrile complexes [5-7]. The association theory what includes the UNIQUAC equation is applied taking into consideration only linear polymers for 1-alcohol self-association and for alcohol-nitrile solvation [8-10]. The ERAS model [11] has been used for the correlation of molar excess volumes of this type of systems assuming that acetonitrile is either a self-associated [12] or a non self-associated [13] compound. However, there are very limited studies on the simultaneous representation of both H_m^E and V_m^E of 1-alkanol + nitrile mixtures [14,15]. Interaction parameters for the hydroxyl/nitrile interactions are available [16] in the framework of UNIFAC (Dortmund version) [17]. In order to gain a deeper insight into the interactions and structure of these solutions, we apply now the DISQUAC [18] and ERAS models for the characterization of 1-alkanol + alkanenitrile mixtures. Interestingly, alkanenitriles are compounds with very high dipole moments (e.g., 3.53 D and 3.50 D for acetonitrile or butanenitrile, respectively [19]), and 1-octanol or 1-decanol + acetonitrile systems show miscibility gaps at temperatures close to 298.15 K. In fact, the upper critical solution temperature (UCST) of such mixtures is 282.7 and 297.05 K, respectively [15]. Thus, one can expect that the studied systems show strong positive deviations from the Raoult's law. Previously, we have investigated other solutions formed by 1-alkanols and a highly polar compound, as sulfolane [20], amides [21-23] or dimethylsulfoxide [24].

2. MODELS

2.1 DISQUAC

The DISQUAC group contribution model [18] is based on the rigid lattice theory developed by Guggenheim [25]. Some important features of the model are the following. (i) The total molecular volumes, r_i , surfaces, q_i , and the molecular surface fractions, α_{si} , of the compounds present in the solution are calculated additively using the group volumes R_G and surfaces Q_G recommended by Bondi [26]. As volume and surface units, the volume R_{CH_4} and

surface Q_{CH_4} of methane are taken arbitrarily [27]. The geometrical parameters for the groups referred to in this work are available in the literature [27-29] (ii) The partition function is factorized into two terms, and the excess functions are calculated as the sum of two contributions. The dispersive (DIS) term represents the contribution from the dispersive interactions. The quasichemical (QUAC) term is related to the anisotropy of the field forces created by the solution molecules. In the case of the Gibbs energy, G_m^E , a combinatorial term, $G_m^{E,\text{COMB}}$, represented by the Flory-Huggins equation [27,30] must be also taken into account. Thus,

$$G_m^E = G_m^{E,\text{DIS}} + G_m^{E,\text{QUAC}} + G_m^{E,\text{COMB}} \quad (1)$$

$$H_m^E = H_m^{E,\text{DIS}} + H_m^{E,\text{QUAC}} \quad (2)$$

(iii) It is assumed that the interaction parameters depend on the molecular structure; (iv) The value $z = 4$ for the coordination number is used for all the polar contacts. This is an important shortcoming of the model, partially removed via the hypothesis of considering structure dependent interaction parameters. (v) The mixing process takes place without change in volume.

The equations used to calculate the DIS and QUAC contributions to G_m^E and H_m^E in the framework of DISQUAC are given elsewhere [28,31]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [31], $C_{st,l}^{\text{DIS}}; C_{st,l}^{\text{QUAC}}$ where $s \neq t$ are two contact surfaces present in the mixture and $l = 1$ (Gibbs energy; $C_{st,1}^{\text{DIS/QUAC}} = g_{st}^{\text{DIS/QUAC}}(T_o) / RT_o$); $l = 2$ (enthalpy, $C_{st,2}^{\text{DIS/QUAC}} = h_{st}^{\text{DIS/QUAC}}(T_o) / RT_o$), $l = 3$ (heat capacity, $C_{st,3}^{\text{DIS/QUAC}} = c_{\text{pst}}^{\text{DIS/QUAC}}(T_o) / R$). $T_o = 298.15$ K is the scaling temperature and R , the gas constant. The equations are [31]:

$$g_{st}^{\text{DIS/QUAC}} / RT = C_{st,1}^{\text{DIS/QUAC}} + C_{st,2}^{\text{DIS/QUAC}} \left(\frac{T_o}{T} - 1 \right) + C_{st,3}^{\text{DIS/QUAC}} \left[\ln \left(\frac{T_o}{T} \right) - \left(\frac{T_o}{T} \right) + 1 \right] \quad (3)$$

$$h_{st}^{\text{DIS/QUAC}} / RT = C_{st,2}^{\text{DIS/QUAC}} \left(\frac{T_o}{T} \right) - C_{st,3}^{\text{DIS/QUAC}} \left[\left(\frac{T_o}{T} \right) - 1 \right] \quad (4)$$

$$c_{\text{pst}}^{\text{DIS/QUAC}} / R = C_{st,3}^{\text{DIS/QUAC}} \quad (5)$$

DISQUAC calculations for the coexistence curves for the LLE curves were conducted taking into account that the values of the mole fraction x_1 of component 1 (x_1', x_1'') relating to the two phases in equilibrium are such that the functions $G_m^M, G_m^{M''}$ ($G_m^M = G_m^E + G_m^{\text{ideal}}$) have a

common tangent [32]. On the other hand, the SLE curve of a pure solid component 1 is represented by the expression [33]:

$$-\ln x_1 = \frac{\Delta H_{m1}}{R} \left[\frac{1}{T} - \frac{1}{T_{m1}} \right] - \frac{\Delta C_{pm1}}{R} \left[\ln \left(\frac{T}{T_{m1}} \right) + \frac{T_{m1}}{T} - 1 \right] + \ln \gamma_1 \quad (6)$$

Conditions at which eq. (6) is valid have been specified in previous works [30]. In eq. (6), x_1 is the mole fraction and γ_1 the activity coefficient of component 1 in the solvent mixture, at temperature T . In this work, DISQUAC is used to calculate γ_1 . The remaining symbols $\Delta H_{m1}, T_{m1}, \Delta C_{pm1}$ have their usual meaning [15]. Values needed for calculations were taken from [15].

2.2 Modified UNIFAC (Dortmund version)

Modified UNIFAC [16,17] differs from the original UNIFAC [34] by the combinatorial term and the temperature dependence of the interaction parameters. The equations used to calculate G_m^E and H_m^E are obtained from the fundamental equation for the activity coefficient γ_i of component i:

$$\ln \gamma_i = \ln \gamma_i^{COMB} + \ln \gamma_i^{RES} \quad (7)$$

where $\ln \gamma_i^{COMB}$ and $\ln \gamma_i^{RES}$ stand for the combinatorial and residual term, respectively. Equations can be found elsewhere [31]. In this version of UNIFAC, two main groups, OH and CH₃OH, are defined for the prediction of thermodynamic properties of mixtures containing alkanols. The main group OH is subdivided in three subgroups: OH(p), OH(s) and OH(t) for the representation of primary, secondary and tertiary alkanols, respectively. The CH₃OH group is a specific group for methanol solutions. Alkanenitriles are represented by only one main group, CCN, subdivided in two subgroups, CH₃CN and CH₂CNH₂. The subgroups have different geometrical parameters, but the subgroups within the same main group are assumed to have identical group energy-interaction parameters. On the other hand, the geometrical parameters, the relative van der Waals volumes and the relative van der Waals surfaces are not calculated from molecular parameters like in the original UNIFAC, but fitted together with the interaction parameters to the experimental values of the thermodynamic properties considered. The geometrical and interaction parameters were taken from literature and used without modifications [16].

2.3 ERAS

In the ERAS model [11], the excess functions are determined as the sum of two contributions. The chemical contribution, $X_{m,\text{chem}}^E$, arises from hydrogen-bonding effects. The physical contribution, $X_{m,\text{phys}}^E$, is related to non-polar van der Waals' interactions and free volume effects. The excess functions are written as:

$$X_m^E = X_{m,\text{phys}}^E + X_{m,\text{chem}}^E \quad (8)$$

where $X_m^E = H_m^E, V_m^E, G_m^E$. The resulting expressions for these functions are given elsewhere [35]. In addition, only consecutive linear association is assumed, which is described by a chemical equilibrium constant (K_A) independent of the chain length of the associated species (1-alkanols), according to the equation:



with m ranging from 1 to ∞ . The cross-association between a self-associated species A_m (1-alkanols) and a non self-associated compound B (nitriles) is represented by



The association constants (K_{AB}) of equation (10) are also assumed to be independent of the chain length. Equations (9) and (10) are characterized by Δh_i^* , the enthalpy of the reaction that corresponds to the hydrogen-bonding energy, and by the volume change (Δv_i^*) related to the formation of the linear chains.

$X_{m,\text{phys}}^E$ is derived from the Flory's equation of state [36], which is assumed to be valid not only for pure compounds but also for the mixture [37,38].

$$\frac{\bar{P}_i \bar{V}_i}{\bar{T}_i} = \frac{\bar{V}_i^{1/3}}{\bar{V}_i^{1/3} - 1} - \frac{1}{\bar{V}_i \bar{T}_i} \quad (11)$$

where $i = A, B$ or M (mixture). In equation (11), $\bar{V}_i = V_i / V_i^*$; $\bar{P}_i = P / P_i^*$; $\bar{T}_i = T / T_i^*$ are the reduced volume, pressure and temperature respectively. The pure component reduction

parameters V_i^* , P_i^* , T_i^* are determined from P - V - T data (density, ρ , isobaric expansion coefficient, α_p , and isothermal compressibility, κ_T), and association parameters [37,38]. The reduction parameters for the mixture P_M^* and T_M^* are calculated from mixing rules [37,38]. The total relative molecular volumes and surfaces of the compounds were calculated additively using the Bondi's method (see above) [26].

3. ADJUSTMENT OF MODEL PARAMETERS

3.1 DISQUAC

In the framework of DISQUAC, 1-alkanol + alkanenitrile mixtures are regarded as possessing the following three types of surface: (i) type a, aliphatic (CH_3 , CH_2 , in 1-alkanols and nitriles); (ii) type h, hydroxyl (OH in 1-alkanols); (iii) type n, (CN in alkanenitriles)

The investigated solutions are built by three contacts: (a,h), (a,n), and (h,n). The DIS and QUAC interaction parameters for the (a,h) and (a,n) contacts are known from the study of 1-alkanol [28,39] or alkanenitrile [29] + n -alkane mixtures, respectively. Thus, only the DIS and QUAC interaction parameters of the (h,n) contacts must be fitted to VLE and H_m^E data of the studied systems. The general procedure applied in the estimation of the interaction parameters has been explained in detail elsewhere [22,31]. Final values of the fitted parameters in this work are collected in Table 1.

3.2 ERAS

Values of V_i , V_i^* and P_i^* at $T = 298.15$ K of 1-alkanols have been taken from a previous work [40]. At 298.15 K, such parameters for acetonitrile are: $V_i = 52.87 \text{ cm}^3 \cdot \text{mol}^{-1}$; $V_i^* = 40.20 \text{ cm}^3 \cdot \text{mol}^{-1}$; $P_i^* = 650.8 \text{ J} \cdot \text{cm}^{-3}$ (values determined using ρ , α_p , and κ_T data from [19]); and for butanenitrile, $V_i = 87.86 \text{ cm}^3 \cdot \text{mol}^{-1}$; $V_i^* = 68.56 \text{ cm}^3 \cdot \text{mol}^{-1}$; $P_i^* = 578.1 \text{ J} \cdot \text{cm}^{-3}$ (values determined using ρ , α_p , and κ_T data from [19,41]). In the present case, as cross-association between components exists, the binary parameters to be fitted to the H_m^E and V_m^E data available in the literature for 1-alkanol + alkanenitrile mixtures are K_{AB} , Δh_{AB}^* , Δv_{AB}^* and X_{AB} . K_A , Δh_A^* ($= -25.1 \text{ kJ} \cdot \text{mol}^{-1}$) and Δv_A^* ($= -5.6 \text{ cm}^3 \cdot \text{mol}^{-1}$) for 1-alkanols are known from H_m^E and V_m^E data for the corresponding systems with alkanes [37,38,40,42]. Adjusted ERAS parameters for the binary mixtures investigated are collected in Table 2.

4. THEORETICAL RESULTS

Theoretical results from DISQUAC and UNIFAC models for VLE, G_m^E and H_m^E are listed in Tables 3 and 4. For the sake of clarity, relative deviations for the pressure (P) and H_m^E defined as:

$$\sigma_r(P) = \left\{ \frac{1}{N} \sum \left[\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right]^2 \right\}^{1/2} \quad (12)$$

and

$$\text{dev}(H_m^E) = \left\{ \frac{1}{N} \sum \left[\frac{H_{m,\text{exp}}^E - H_{m,\text{calc}}^E}{H_{m,\text{exp}}^E(x_1 = 0.5)} \right]^2 \right\}^{1/2} \quad (13)$$

are included in Tables 3 and 4, respectively. DISQUAC results for SLE are collected in Table 5. Deviations for the equilibrium temperatures, listed in Table 5, are calculated from the equations:

$$\sigma_r(T) = \left\{ \frac{1}{N} \sum \left[\frac{T_{\text{exp}} - T_{\text{calc}}}{T_{\text{exp}}} \right]^2 \right\}^{1/2} \quad (14)$$

$$\Delta(T) / K = \frac{1}{N} \sum |T_{\text{exp}} - T_{\text{calc}}| \quad (15)$$

Table 6 compares experimental coordinates of the critical points for 1-octanol or 1-decanol + acetonitrile mixtures with values determined from DISQUAC. Table 7 shows a comparison between experimental measurements and DISQUAC calculations for partial excess molar enthalpies at infinite dilution, $H_{mi}^{E,\infty}$. ERAS results on H_m^E and V_m^E are shown in Tables 4 and 8. Theoretical calculations for different thermodynamic properties are shown graphically, for some selected systems, along Figures 1-6. In view of the present results, one can conclude that DISQUAC describes properly VLE, SLE, LLE, G_m^E and H_m^E of 1-alkanol + alkanenitrile mixtures over a wide range of temperature.

5. DISCUSSION

H_m^E values of 1-alkanol + alkanenitrile mixtures are large and positive (Table 4), indicating that the main contributions to this excess function come from the disruption of interactions between like molecules. Interestingly, $TS_m^E (= H_m^E - G_m^E)$ values are also large and positive. For butanenitrile solutions, $TS_m^E / \text{J} \cdot \text{mol}^{-1} = 245$ (methanol); 542 (ethanol); 768 (1-

propanol); 908 (1-hexanol); 1006 (1-octanol); 1122 (1-decanol) (values determined from those listed in Tables 3 and 4 for G_m^E and H_m^E). In addition, $\frac{\Delta H_m^E}{\Delta T}$ values of methanol or ethanol + acetonitrile mixtures are 5.3 and 7.4 J·mol⁻¹·K⁻¹, respectively [5]. On the basis of such features, one can conclude that interactions in the investigated systems are essentially of dipolar type. 1-Alkanol + alkane mixtures, characterized by alcohol self-association, show large and positive isobaric excess heat capacities, $C_{p,m}^E$, (11.7 J·mol⁻¹·K⁻¹ for ethanol + heptane [43]), and large and negative TS_m^E values. For the ethanol + hexane system, $H_m^E = 548$ [44]; $G_m^E = 1374$ [45] and $TS_m^E = -826$ (data in J·mol⁻¹). On the other hand, H_m^E values of mixtures containing, say, heptane, are rather low and increase from ethanol to 1-propanol or 1-butanol and then smoothly decrease. It is remarkable that the H_m^E curves are shifted to low mole fractions of the alcohol [28,40,44]. We note that H_m^E values of mixtures with a given nitrile increase with the chain length of the alcohol (Table 4). This can be ascribed to: (i) alcohols with larger aliphatic surfaces break more easily interactions between nitrile molecules. Accordingly, H_m^E values of nitrile + alkane mixtures increase with the alkane size. For example, H_m^E (butanenitrile)/J·mol⁻¹= 1304 (heptane) [46], 1554 (dodecane) [47]; 1702 (tetradecane) [47]. (ii) Interactions between unlike molecules become less probable for longer alcohols as the hydroxyl group is more sterically hindered. The replacement of acetonitrile by butanenitrile in mixtures with a given 1-alkanol leads to decreased H_m^E values (Table 4). This may be due to the positive contribution to H_m^E from the breaking of nitrile-nitrile interactions is lower in the case of butanenitrile mixtures. In fact, dipolar interactions between acetonitrile molecules are stronger, as it is indicated by: (i) the existence of miscibility gaps at temperatures close to 298.15 K for systems formed by this nitrile and long chain 1-alkanols (Table 6, [15]); (ii) the much higher upper critical solutions temperatures (UCST) of acetonitrile + alkane mixtures compared to those of butanenitrile solutions. Thus, UCST(hexane)/K = 350.2 (acetonitrile) > 244.2 (butanenitrile) [48]. Many other systems show a similar behavior. Some examples follow: H_m^E (*N,N*-dimethylformide)/J·mol⁻¹= -103 (methanol) [49]; 968 (1-butanol) [49]; H_m^E (*N,N*-dimethylacetamide)/J·mol⁻¹= -737 (methanol) [50]; 367 (1-butanol) [51]; H_m^E (1,4-dioxane)/J·mol⁻¹= 1134 (methanol) [52]; 1979 (1-butanol) [53]; H_m^E (tetrahydropyran)/J·mol⁻¹= 683 (methanol) [52]; 922 (1-butanol) [54]; or H_m^E (1-butanol)/J·mol⁻¹= 2356 (dimethyl carbonate) [55]; 1944 (diethyl carbonate) [56].

From the application of the ERAS model, some interesting statements can be provided.

i) The large X_{AB} values and the low K_{AB} values obtained for systems with 1-alkanols \geq 1-propanol remark the importance of physical interactions in these solutions. Note that, as a trend, DISQUAC meaningfully improves ERAS results on H_m^E (Table 4). (ii) The replacement of acetonitrile by butanenitrile in systems with a given 1-alkanol (\neq methanol) leads to much lower X_{AB} values (Table 2). This may be interpreted as a proof that physical interactions are more relevant in acetonitrile mixtures and that association effects become more relevant in systems with butanenitrile. Interestingly, H_m^E results for acetonitrile solutions from UNIFAC are also better than those provided by ERAS (Table 4). (iii) The large $|\Delta v_{AB}^*|$ values obtained for systems with 1-alkanols \geq 1-propanol (Table 2) point out to the existence of strong structural effects. This is supported by the lower V_m^E values which contrast with the corresponding large positive H_m^E data. Thus for the 1-butanol + acetonitrile system, $V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = 0.1045$ [57]; $H_m^E/\text{J}\cdot\text{mol}^{-1} = 2039$ [7].

ERAS describes correctly the relative variation of V_m^E (Table 8), but fails when representing the V_m^E curves. Our results are similar to those provided in previous works when applying ERAS only to the description of V_m^E .

Comparison of our ERAS parameters for the 1-alkanol-nitrile interactions with those available in the literature becomes rather difficult as different values for the Δh_A^* and Δv_A^* parameters of 1-alkanols were used [14,58]. For example, in a previous ERAS treatment of 1-nonanol, or 1-decanol + acetonitrile systems [58], the values of $\Delta h_A^*/\text{kJ}\cdot\text{mol}^{-1} = -18.57$ and of $\Delta v_A^*/\text{cm}^3\cdot\text{mol}^{-1} = -5.6$ were used for 1-decanol, reporting for the mixture: $K_{AB} = 0.3$; $\Delta h_{AB}^*/\text{kJ}\cdot\text{mol}^{-1} = -17.1$, $\Delta v_{AB}^*/\text{cm}^3\cdot\text{mol}^{-1} = -1.2$; $X_{AB}/\text{J}\cdot\text{cm}^{-3} = 146$ and $dev(H_m^E) = 0.091$. The model predicts $V_m^E = 1.89 \text{ cm}^3\cdot\text{mol}^{-1}$, which is far from the experimental value ($0.340 \text{ cm}^3\cdot\text{mol}^{-1}$ [59]). That is, structural effects are not considered.

In terms of DISQUAC, we must remark that the interaction parameters for the (h,n) contacts in methanol or ethanol solutions are very different to those of the remaining mixtures. Along our investigations on 1-alkanol + alkanone [60], + linear alkanolate [61], + linear organic carbonate [62], + cyclic ether [63], + alkoxyethanol [64], + dimethylsulfoxide [24], + amide [21,22], or + amine [31,65] mixtures, we have shown that at least the $C_{sh,1}^{QUAC}$ ($l=1,3$) coefficients, and often also the $C_{sh,2}^{QUAC}$ parameter, can be kept constant along each homologous

series. Thus, the present dependence on the molecular structure of the interaction parameters is rather anomalous. This might be related to the different behaviour of methanol or ethanol solutions, but also to certain experimental inaccuracies. Note the very different results available in the literature for ethanol or 1-propanol + butanenitrile systems (Table 4).

As usually, the model describes consistently a whole set of thermodynamic properties, VLE, SLE, LLE, G_m^E and H_m^E of a given solution using the same set of interaction parameters. The theoretical results obtained for the simultaneous representation of SLE and LLE of 1-octanol or 1-decanol + acetonitrile mixtures (Figure 6) must be underlined. Similar results have been obtained for, e.g, crown ether + alkane systems [66]. Deviations between experimental and theoretical results on LLE (Figure 6) are typically encountered when mean field theories, as DISQUAC, are used. In fact thermodynamic properties close to the critical points are expressed in terms of power laws, while for LLE, DISQUAC calculations are developed assuming erroneously that G_m^E is an analytical function close to the critical point. The instability of a system is given by $(\partial^2 G_m^M / \partial x_1^2)_{p,T}$ and represented by the critical exponent $\gamma > 1$ in the critical exponents theory [67]. According to this theory, mean field models ($\gamma = 1$) provide LLE curves which are too high at the UCST and too low at the LCST [67] (lower critical solution temperature). For this reason, the $C_{ak,1}^{DIS/QUAC}$ coefficients must be ranged between certain limits in order to provide not very high calculated UCSTs. On the other hand, in mean field theories, $\beta = 0.5$ and LLE curves are more rounded close to the UCST (Figure 6), as fluctuations of the order parameter due to the rapid increase of the correlation length are not taken into account. The same trends are observed e.g., for sulfolane [24], crown ether [66], amide [21,22] or pyridine [65] + alkane mixtures. The larger deviations obtained for H_m^E of 1-nonanol or 1-decanol + acetonitrile mixtures (Table 4) may be due, at least in part, to the proximity of the critical point.

6. CONCLUSIONS

The DISQUAC, UNIFAC and ERAS models have been applied to 1-alkanol + alkanenitrile mixtures. The DISQUAC and ERAS parameters for the alkanol/nitrile interactions are reported. The studied systems are characterized by dipolar interactions and strong structural effects. The former are more relevant in acetonitrile solutions. Association effects are more important in butanenitrile mixtures. DISQUAC improves H_m^E results from the ERAS model. For mixtures containing acetonitrile, UNIFAC also improves such ERAS results. This remarks the importance of dipolar interactions in the investigated mixtures.

7. REFERENCES

- [1] F.F. Fleming, L. Yao, P.C. Ravikumar, L. Funk, B.C. Shook. Nitrile-containing pharmaceuticals: efficacious roles of the nitrile pharmacophore. *J. Med. Chem.* 25 (2010) 7902-7917.
- [2] J.-Y. Le Questel, M. Berthelot, C. Laurence. Hydrogen-bond acceptor properties of nitriles: a combined crystallographic and ab initio theoretical investigation. *J. Phys. Org. Chem.* 13 (2000) 347-358.
- [3] A. Allerhand, P. von Rague Schleyer. Nitriles and isonitriles as proton acceptors in hydrogen bonding: correlation of $\Delta\nu_{\text{OH}}$ with acceptor structure. *J. Am. Chem. Soc.* 85 (1963) 866-891.
- [4] K. Gekko, E. Ohmae, K. Kameyana, T. Takagi, Acetonitrile-protein interactions: amino acid solubility and preferential solvation. *Biochim. Biophys. Acta* 1387 (1998) 195-205.
- [5] I. Nagata, K. Tamura. Excess enthalpies of binary and ternary mixtures of acetonitrile with methanol, ethanol and benzene. *Fluid Phase Equilib.* 24 (1985) 289-306.
- [6] I. Nagata, K. Tamura. Excess molar enthalpies of (propan-1-ol or propan-2-ol + acetonitrile), (propan-1-ol or propan-2-ol + chlorobenzene), and (propan-1-ol or propan-2-ol + acetonitrile + chlorobenzene) at 298.15 K. *J. Chem. Thermodyn.* 20 (1988) 87-93.
- [7] I. Nagata, K. Tamura. Excess molar enthalpies of (butan-1-ol or 2-methylpropan-1-ol + acetonitrile), (2-methylpropan-1-ol + benzene), and (butan-1-ol or 2-methylpropan-1-ol + acetonitrile + benzene) at 298.15 K. *J. Chem. Thermodyn.* 20 (1988) 1101-1107.
- [8] I. Nagata. Isothermal vapor—liquid equilibrium of ternary mixtures formed by 1-propanol, acetonitrile and benzene. *Fluid Phase Equilib.* 24 (1985) 279-306.
- [9] I. Nagata, K. Tamura. Isothermal (vapour + liquid) equilibria of (methanol or ethanol + butan-2-ol + acetonitrile + benzene). *J. Chem. Thermodyn.* 28 (1996) 559-565.
- [10] I. Nagata. Isothermal vapor-liquid equilibria for binary and ternary mixtures formed by 1-butanol, acetonitrile and benzene. *Thermochim. Acta*, 112 (1987) 187-195.
- [11] A. Heintz. A new theoretical approach for predicting excess properties of alkanol/alkane mixtures. *Ber. Bunsenges. Phys. Chem.* 89 (1985) 172-181.
- [12] C.G. Pina, A.Z. Francesconi. New applications of the ERAS model: excess volumes of binary liquid mixtures of 1-alkanols with acetonitrile. *Fluid Phase Equilib.* 143 (1998) 143-152.
- [13] R.B. Torres, A.Z. Francesconi, P.L.O. Volpe. Experimental study and modeling using the ERAS-model of the excess molar volume of acetonitrile-alkanol mixtures at different temperatures and atmospheric pressure. *Fluid Phase Equilib.* 210 (2003) 287-306.

- [14] T.M. Letcher, P.K. Naicker. Excess molar enthalpies and excess molar volumes of (an alkanol + nitrile compound) at $T = 298.15$ K and $p = 0.1$ MPa. *J. Chem. Thermodyn.* 33 (2001) 1035-1047.
- [15] U. Domanska, M. Marciniak. Experimental (solid-liquid) equilibria and excess molar volumes of alkanol + acetonitrile, propanenitrile, and butanenitrile mixtures. *J. Chem. Eng. Data* 50 (2005) 2035-2044.
- [16] J. Gmehling, J. Li, M. Schiller. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.*, 32 (1993) 178-193.
- [17] U. Weidlich, J. Gmehling, A modified UNIFAC model. 1. Prediction of VLE, h^E and γ^∞ . *Ind. Eng. Chem. Res.*, 26 (1987) 1372-1381.
- [18] H.V. Kehiaian. Group contribution methods for liquid mixtures: a critical review. *Fluid Phase Equilib.*, 13 (1983) 243-252.
- [19] J.A. Riddick, W.B. Bunger, T.K. Sakano *Organic solvents*. In: A. Weissberger (Ed.), *Techniques of Chemistry*, Vol. II, Wiley, N.Y., **1986**.
- [20] J.A. González, U. Domanska. Thermodynamics of mixtures containing a very strongly polar compound. Part I. Experimental phase equilibria (solid-liquid and liquid-liquid) for sulfolane + alkan-1-ols systems. Analysis of some mixtures including sulfolane in terms of DISQUAC. *Phys. Chem. Chem. Phys.*, 3 (2001) 1034-1042.
- [21] J.A. González, U. Domanska, J. Lachwa. Thermodynamics of mixtures containing a very strongly polar compound. Part 3. DISQUAC characterization of NMP + organic solvent mixtures. *Can. J. Chem.*, 81 (2004) 1451-1461.
- [22] J.A. González, J.C. Cobos, I. García de la Fuente. Thermodynamics of liquid mixtures containing a very strongly polar compound. Part 6. DISQUAC characterization of *N,N*-dialkylamides. *Fluid Phase Equilib.*, 224 (2004) 169-183.
- [23] J.A. González. Thermodynamics of mixtures containing a very strongly polar compound. V. Application of the Extended Real Association Solution model to 1-alkanol + secondary amide mixtures. *Phys. Chem. Liq.*, 42 (2004) 159-172.
- [24] J.A. González, S. Villa, N. Riesco, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing a very strongly polar compound. IV. Application of the DISQUAC, UNIFAC and ERAS models to DMSO + organic solvent systems. *Phys. Chem. Liq.*, 41 (2003) 583-597.
- [25] E.A. Guggenheim, *Mixtures*, Oxford University Press, Oxford, **1952**.
- [26] A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York, **1968**.

- [27] H.V. Kehiaian, J.-P.E. Grolier, G.C. Benson. Thermodynamics of organic mixtures. A generalized quasichemical theory in terms of group surface interactions *J. Chim. Phys.*, 75 (1978) 1031-1048.
- [28] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova. A characterization of the aliphatic/hydroxyl interactions using a group contribution model (DISQUAC). *Ber. Bunsenges. Phys. Chem.*, 95 (1991) 1658-1668.
- [29] B. Marongiu, B. Pittau, S. Porcedda. A study of nitrile group interactions in alkane solutions. *Thermochim. Acta*, 221 (1993) 143-162.
- [30] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, A. Ait-Kaci. Application of the zeroth approximation of the DISQUAC model to cyclohexane + *n*-alkane mixtures using different combinatorial entropy terms. *Fluid Phase Equilib.*, 112 (1995) 63-87.
- [31] J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 4. Application of the DISQUAC model to mixtures of 1-alkanols with primary or secondary amines. Comparison with Dortmund UNIFAC and ERAS results. *Fluid Phase Equilib.*, 168 (2000) 31-58.
- [32] I. Prigogine, R. Defay, *Chemical Thermodynamics*, Longmans, Green and Co., Norwich, **1954**.
- [33] J.M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice-Hall, Englewood Cliffs, N.J., **1969**.
- [34] A. Fredenslund, R.L. Jones, J.M. Prausnitz. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.*, 21 (1975) 1086-1099.
- [35] J.A. González, S. Villa, N. Riesco, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing alkoxyethanols: Part XVII. ERAS characterization of alkoxyethanol + alkane systems. *Can. J. Chem.*, 81 (2003) 319-329.
- [36] P.J Flory. Statistical thermodynamics of liquid mixtures. *J. Am. Chem. Soc.*, 87 (1965) 1833-1838.
- [37] A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestorf. Thermodynamics of alkanol + amine mixtures. Experimental results and ERAS model calculations of the heat of mixing. *Ber. Bunsenges. Phys. Chem.*, 102 (1998) 953-959.
- [38] A. Heintz, D. Papaioannou. Excess enthalpies of alcohol + amine mixtures. Experimental results and theoretical description using the ERAS model. *Thermochim. Acta*, 310 (1998) 69-76.
- [39] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova. DISQUAC predictions of phase equilibria, molar and standard partial molar excess quantities for 1-alkanol + cyclohexane mixtures. *J. Solution Chem.*, 23 (1994) 399-420.

- [40] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, N. Riesco. Thermodynamics of (1-alkanol + linear monoether) systems. *J. Chem. Thermodyn.*, 40 (2008) 1495-1508.
- [41] I.A. McLure, J.L. Arriaga-Colina. Thermal pressure coefficients of ethanenitrile, and butanenitrile in the region 295-395 K. *Int. J. Thermophys.*, 5 (1984) 291.
- [42] H. Funke, M. Wetzell, A. Heintz. New applications of the ERAS model. Thermodynamics of amine + alkane and alcohol + amine mixtures. *Pure Appl. Chem.* 61 (1989) 1429–1439.
- [43] R. Tanaka, S. Toyama, S. Murakami, 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.*, 18 (1986) 63-73.
- [44] L. Wang, G.C. Benson, B.C.-Y Lu. Excess enthalpies of (ethanol + hexane + decane or + dodecane) at the temperature 298.15 K. *J. Chem. Thermodyn.* 24(1992) 1135-1143.
- [45] S.J. O'Shea, R.H. Stokes. Activity coefficients and excess partial molar enthalpies for (ethanol + hexane) from 283 to 318 K. *J. Chem. Thermodyn.* 18 (1986) 691-696.
- [46] B. Marongiu, S. Porcedda. Thermodynamics of binary mixtures containing alkanenitriles. 1. Excess enthalpies of some n -alkanenitriles + n -alkane or + cyclohexane mixtures. *J. Chem. Eng. Data* 35 (1990) 172-174.
- [47] I.A. McLure, *Int. DATA Ser., Ser. A, Sel. Data Mixtures*, 3 (1984) 154-171.
- [48] I.A. McLure, A.T. Rodriguez, P.A. Ingham, J.F. Steele. Phase equilibria for binary n -alkanenitrile- n -alkane mixtures I. Upper liquid-liquid coexistence temperatures for ethanenitrile, propanenitrile and n -butanenitrile with some C_5 - C_{18} n -alkanes. *Fluid Phase Equilib.* 8 (1982) 271-284.
- [49] J.P. Chao, M. Dai, Y.X. Wang. Studies of thermodynamic properties of binary mixtures containing an alcohol. XII. Excess molar enthalpies of an (alkan-1-ol + N,N -dimethylformamide or dimethyl sulfoxide) at 298.15 K. *J. Chem. Thermodyn.* 21 (1989) 1169-1175.
- [50] M. Oba, S. Murakami, R. Fujishiro. Excess enthalpies and volumes for N,N -dimethylacetamide + n -alcohols at 298.15 K. *J. Chem. Thermodyn.* 9 (1977) 407-414.
- [51] J.P. Chao, Y.X. Wang, M. Dai. Studies of thermodynamic properties of binary mixtures containing an alcohol. XVII. Excess molar enthalpies of each of (one of the four butanols + N,N -dimethylacetamide, N,N -dimethylformamide or dimethyl sulfoxide) at the temperature 298.15 K. *J. Chem. Thermodyn.* 23 (1991) 163-168.
- [52] T.M. Letcher, P.U. Govender. Excess molar enthalpies of an alkanol + a cyclic ether at 298,15 K. *J. Chem. Eng. Data* 40 (1995) 1097-1100.
- [53] E. Calvo, P. Brocos, A. Piñeiro, M. Pintos, A. Amigo, R. Bravo, A.H. Roux, G. Roux-Desgranges. Heat capacities, excess enthalpies, and volumes of mixtures containing ethers. 4. Binary systems 1,4-dioxane + 1-alkanols. *J. Chem. Eng. Data* 44 (1999) 948-954.

- [54] C. Vallés, E. Pérez, M. Cardoso, M. Domínguez, A.M. Mainar. Excess enthalpy density, viscosity, and speed of sound for the mixture tetrahydropyran +1-butanol at (283.15,298.15 and 313.15) K. *J. Chem. Eng. Data* 49 (2004) 1460-1464.
- [55] R. Francesconi, F. Comelli. Excess molar enthalpies and excess molar volumes of binary mixtures containing dimethylcarbonate + four butanol isomers a (288.15, 298.15 and 313.15) K. *J. Chem. Eng. Data* 44 (1999) 44-47.
- [56] R. Francesconi, F. Comelli. Excess molar enthalpies, densities, and excess molar volumes of diethyl carbonate in binary mixtures with seven *n*-alkanols at 298.15 K. *J. Chem. Eng. Data* 42 (1997) 45-48.
- [57] I. Cibulka, V.D. Nguyen, R.M. Holub. Excess molar volumes of {an alkanol + acetonitrile} at 298.15 and 308.15 K. *J. Chem. Thermodyn.* 16 (1984) 159-164.
- [58] A.Z. Francesconi, D.H. Lanfredi Viola. Measurement and correlation of the excess molar enthalpy of (1-nonanol, or 1-decanol + acetonitrile) mixtures at (298.15, 303.15, and 308.15) K and atmospheric pressure. *J. Chem. Thermodyn.* 47 (2012) 28-32.
- [59] S.R. Aznarez, M.A. Postigo. Excess molar volumes of binary mixtures of acetonitrile with alkanols at 25° C. *J. Solution Chem.* 27 (1998) 1045-1053.
- [60] J.A. González 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.*, 75 (1997) 1412-1423.
- [61] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos. Thermodynamics of 1-alkanol + linear alkanoate mixtures. *Phys. Chem. Liq.*, 43 (2005) 175-194.
- [62] J.A. González, M. Szurgocinska, U. Domanska. Thermodynamics of mixtures containing organic carbonates. Part XIII. Solid-liquid equilibria of long-chain 1-alkanol + dimethyl or diethyl carbonate systems. DISQUAC and ERAS analysis of the hydroxyl/carbonate interactions. *Fluid Phase Equilib.*, 200 (2002) 349-374.
- [63] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, V.A. Durov. Thermodynamics of 1-alkanol + cyclic ether mixtures. *Fluid Phase Equilib.*, 245 (2006) 168-184.
- [64] J.A. González, J.C. Cobos, I. Mozo, I. García de la Fuente. Thermodynamics of binary mixtures containing alkoxyethanols. XIX. Systems with linear monoethers or 1-alkanols. *J. Mol. Liq.*, 126 (2006) 99-110.
- [65] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos. Thermodynamics of binary mixtures containing amines. V. Systems with pyridines. *Thermochim. Acta*, 441 (2006) 53-68.
- [66] U. Domanska, J.A. González. Solid-liquid and liquid-liquid equilibria for 1,3,5-trioxane or 1,4,7,10,13,16-hexaoxacyclooctadecane + selected *n*-alkane mixtures. Analysis in terms of DISQUAC. *Fluid Phase Equilib.*, 205 (2003) 317-338.

- [67] J.S. Rowlinson, F.L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed., Butterworths, London, **1982**.
- [68] I. Nagata, K. Katoh, J. Koyabu. Liquid-liquid equilibria for ternary systems containing acetonitrile. *Thermochim. Acta*, 47 (1981) 225-233.
- [69] O. Muthu, P.J. Maher, B.D. Smith. Vapor-liquid equilibrium for the binary systems propionitrile + ethylbenzene and acetonitrile + ethyl acetate, + ethyl alcohol, and + toluene. *J. Chem. Eng. Data*, 25 (1980) 163-170.
- [70] S.R. Wilson, R.B. Patel, M.M. Abbott, H.C. Van Ness. Excess thermodynamic functions for ternary systems. 4. Total-pressure data and G^E for acetonitrile-ethanol-water at 50 °C. *J. Chem. Eng. Data*, 24 (1979) 130-132
- [71] T. Ohta, T. Kinoshita, I. Nagata. Isothermal vapor-liquid equilibria for six binary mixtures. *J. Chem. Eng. Data* 28 (1983) 36-39.
- [72] R. Garriga, J. Ilarza, P. Pérez, M. Gracia. Excess functions at $T = 298.15$ K of {butanenitrile + methanol, + pentan-1-ol, + heptan-1-ol, + nonan-1-ol, or + decan-1-ol}. *J. Chem. Thermodyn.* 28 (1996) 233-243.
- [73] R. Garriga, I. Putze, P. Pérez, M. Gracia. Vapour pressures at several temperatures T and excess functions at $T = 298.15$ K of {butanenitrile + ethanol or butan-1-ol}. *J. Chem. Thermodyn.* 27 (1995) 481-491.
- [74] R. Garriga, F. Sánchez, P. Pérez, M. Gracia. Vapour pressures at several temperatures T and excess functions at $T = 298.15$ K of {butanenitrile + propan-1-ol or propan-2-ol}. *J. Chem. Thermodyn.* 27 (1995) 887-895.
- [75] F. Mato, J. Coca, *An. Quim.* 65 (1969) 1-7 (cf. 81)
- [76] J. Prados, *Act. Salmant, Cienc.* 7 (1967-1968) 9-39 (cf. 81).
- [77] V. Dohnal, F. Vesely, R. Holub, J. Pick. Liquid-vapor equilibrium. 93. Liquid-vapor equilibrium and heats of mixing in the ethanol-acetonitrile system. *Collect. Czech. Chem. Commun.*, 47 (1982) 3177-3187.
- [78] V. Dohnal, F. Vesely, J. Vins. Liquid-vapor equilibrium. 94. Liquid-vapor equilibrium and heats of mixing in the 1-propanol-acetonitrile system. *Collect. Czech. Chem. Commun.*, 47 (1982) 3188-3198.
- [79] P. Garriga, P. Pérez, M. Gracia. Vapour pressures at several temperatures T and excess functions at $T = 298.15$ K of {butanenitrile + hexan-1-ol or octan-1-ol}. *J. Chem. Thermodyn.*, 27 (1995) 1057-1066.
- [80] M. Trampe, C.A. Eckert. Calorimetric measurement of partial molar excess enthalpies at infinite dilution. *J. Chem. Eng. Data* 36 (1991) 112-118.
- [81] J.J. Christensen, R.W. Hanks, R.M. Izatt, *Handbook of heat of mixing*. Wiley, New York, **1982**

TABLE 1

Dispersive (DIS) and quasichemical (QUAC) interchange coefficients, $C_{hn,l}^{\text{DIS}}$ and $C_{hn,l}^{\text{QUAC}}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) for (h,n) contacts^a in $\text{CH}_3(\text{CH}_2)_{u-1}\text{OH} + \text{CH}_3(\text{CH}_2)_{v-1}\text{CN}$ mixtures.

(u,v)	$C_{hn,1}^{\text{DIS}}$	$C_{hn,2}^{\text{DIS}}$	$C_{hn,3}^{\text{DIS}}$	$C_{hn,1}^{\text{QUAC}}$	$C_{hn,2}^{\text{QUAC}}$	$C_{hn,3}^{\text{QUAC}}$
(1,1)	8.6	14.1	-1	-2	-3	3
(2,1)	6.35	15.8	-1	-0.2	-3	3
(3,1)	-2	6.6	-1	6	1	3
(4,1)	-1.5	8.2	-1	6	1	3
(8,1)	3.3	13.4	-1	6	1	3
(9,1)	5.1	17.3	-1	6	1	3
(10,1)	7.8	17.3	-1	6	1	3
(1,3)	1.9	-6.7	-1	2	7.6	3
(2,3)	2.7	-5.1	-1	2	7.6	3
(3,3)	-3	8	-1	6	1	3
(4,3)	-2.5	8.4	-1	6	1	3
(5,3)	-1.6	9.6	-1	6	1	3
(6,3)	-0.4	10.4	-1	6	1	3
(7,3)	1.15	12	-1	6	1	3
(8,3)	2.8	13.4	-1	6	1	3
(9,3)	5.1	17.3	-1	6	1	3
(10,3)	7.8	17.3	-1	6	1	3

^atype h, OH in 1-alkanols, type n, CN in alkanenitriles

TABLE 2

ERAS parameters for 1-alkanol(1) + alkanenitrile(2) mixtures at 298.15 K

System	K_{AB}	$\Delta h_{AB}^* /$ kJ·mol ⁻¹	$\Delta v_{AB}^* /$ cm ³ ·mol ⁻¹	$X_{AB} /$ J·cm ⁻³
Methanol + acetonitrile	66	-14	-8	14
ethanol + acetonitrile	45	-14	-8.6	34
1-propanol + acetonitrile	20	-14	-12	71.5
1-butanol + acetonitrile	11	-14	-16.3	88
1-decanol + acetonitrile	4	-14	-23	130
Methanol + butanenitrile	50	-14	-6.5	14
ethanol + butanenitrile	40	-14	-10.3	14
1-propanol + butanenitrile	5.8	-14	-16	53
1-butanol + butanenitrile	3	-14	-23	54.4
1-decanol + butanenitrile	1.9	-14	-23	64.3

^a K_{AB} , association constant of component A with component B; Δh_{AB}^* , association enthalpy of component A with component B; Δv_{AB}^* , association volume of component A with component B; X_{AB} , physical parameter

TABLE 3

Molar excess Gibbs energies, G_m^E , at equimolar composition and temperature T for
 $\text{CH}_3(\text{CH}_2)_{u-1}\text{OH} + \text{CH}_3(\text{CH}_2)_{v-1}\text{CN}$ mixtures.

(u,v)	T/K	N^a	$G_m^E/\text{J}\cdot\text{mol}^{-1}$		$\sigma_r(P)^b$			Ref.
			Exp.	DQ	Exp.	DQ	UNIF	
(1,1)	328.15	13	623	618	0.003	0.006	0.003	68
(2,1)	293.15	13	852	850	0.001	0.021	0.016	69
	323.15	12	795	773	0.003	0.017	0.019	70
	343.15	13	727	715	0.0007	0.014	0.011	69
	393.15	13	533	567	0.0006	0.011	0.007	69
(3,1)	328.15	10	859	855	0.005	0.017	0.037	71
(4,1)	333.15	8	908	888	0.003	0.036	0.063	10
(1,3)	278.15	11	759	750	0.004	0.028	0.027	72
	298.15	11	733	740	0.003	0.025	0.012	72
	318.15	11	710	721	0.001	0.025	0.009	72
(2,3)	278.15	11	809	808	0.004	0.011	0.027	73
	298.15	11	774	778	0.002	0.008	0.035	73
	323.15	11	732	727	0.006	0.009	0.041	73
(3,3)	278.15	10	839	804	0.009	0.034	0.050	74
	298.15	10	754	756	0.005	0.020	0.025	74
	323.15	10	702	682	0.001	0.018	0.023	74
(4,3)	278.15	10	852	844	0.016	0.029	0.060	73
	298.15	10	787	794	0.002	0.021	0.031	73
	323.15	10	710	718	0.002	0.021	0.019	73
(5,3)	298.15	11	834	836	0.010	0.047	0.086	72
(6,3)	298.15	10	854	969	0.033	0.070	0.130	72
(7,3)	298.15	10	908	918	0.014	0.050	0.120	72
(8,3)	298.15	13	954	943	0.019	0.044	0.130	72
(10,3)	298.15	9	1049	1045	0.007	0.077	0.180	72

^anumber of data points; ^beq. (12)

TABLE 4

Molar excess enthalpies, H_m^E , at equimolar composition and temperature T for $\text{CH}_3(\text{CH}_2)_{u-1}\text{OH}$ + $\text{CH}_3(\text{CH}_2)_{v-1}\text{CN}$ mixtures.

(u,v)	T/K	N^a	$H_m^E/\text{J}\cdot\text{mol}^{-1}$		$dev(H_m^E)^b$			Ref.
			Exp.	DQ	Exp.	DQ	UNIF/ERAS	
(1,1)	298.15	14	1086	1104	0.001	0.035	0.013/0.065	5
		9	1113			0.029	0.022	75
		23	1102		0.005	0.030	0.023	76
	308.15	14	1140	1152	0.001	0.038	0.018	5
(2,1)	298.15	13	1500	1542	0.002	0.025	0.028/0.087	5
		20	1496		0.003	0.025	0.031	77
	308.15	14	1574	1602	0.001	0.025	0.034	5
		20	1571		0.006	0.025	0.040	77
	318.15	20	1645	1654	0.005	0.022	0.073	77
(3,1)	298.15	20	1827	1841	0.002	0.022	0.022/0.105	6
		24	1844		0.007	0.026	0.019	78
	308.15	22	1921	1919	0.003	0.020	0.017	78
		22	1983	1995	0.002	0.013	0.043	78
(4,1)	298.15	17	2037	2075	0.004	0.012	0.054/0.122	7
		9	2067		0.0006	0.017	0.057	75
		25	2090		0.007	0.009	0.045	76
(9,1)	298.15	20	2717	2678	0.0003	0.055	0.171	58
	308.15	20	3050	2789	0.007	0.066	0.057	58
(10,1)	298.15	20	3032	2773	0.0005	0.049	0.106/0.202	58
	308.15	20	3297	2883	0.009	0.094	0.055	58
(1,3)	298.15	17	979	953	0.007	0.026	0.169/0.046	72
		11	936			0.072	0.143	14
(2,3)	298.15	11	1319	1305	0.006	0.059	0.186/0.051	73
		12	1185		0.003	0.118	0.143	14
(3,3)	298.15	12	1513	1541	0.011	0.039	0.229/0.090	74
		12	1389		0.006	0.129	0.180	14
(4,3)	298.15	12	1589	1608	0.005	0.027	0.201/0.112	73
(5,3)	298.15	14	1707	1732	0.010	0.016	0.237	72
(6,3)	298.15	19	1767	1805	0.003	0.022	0.208	79
(7,3)	298.15	13	1867	1906	0.009	0.018	0.208	72
(8,3)	298.15	11	1970	1985	0.006	0.025	0.192	79

TABLE 4 (continued)

(9,3)	298.15	13	2018	2109	0.005	0.030	0.201	72
(10,3)	298.15	18	2171	2170	0.004	0.011	0.118/0.111	72

^anumber of data points; ^beq. (13)

TABLE 5

Solid-liquid equilibria for $\text{CH}_3(\text{CH}_2)_{u-1}\text{OH} + \text{CH}_3(\text{CH}_2)_{v-1}\text{CN}$ mixtures [15].

(u,v)	N^a	$\Delta(T)^b/\text{K}$	$\sigma_r(T)^c$
(8,1)	34	1.1	0.006
(9,1)	32	1.1	0.006
(10,1)	26	1.3	0.005
(8,2)	22	1.1	0.007
(9,2)	23	0.98	0.005
(10,2)	18	0.96	0.004
(8,3)	28	0.9	0.006
(9,3)	30	1.3	0.010
(10,3)	27	1.5	0.007

^anumber of data points; ^beq. (15); ^ceq. (14)

TABLE 6

Coordinates of the critical points, composition (x_{1c}) and temperature (T_c) for 1-alkanol(1) + acetonitrile(2) mixtures [15]

1-alkanol	x_{1c}		T_c/K	
	Exp.	DQ.	Exp.	DQ
1-octanol	0.271	0.250	282.07	284.8
1-decanol	0.244	0.193	297.05	301.7

TABLE 7

Partial excess molar enthalpies at infinite dilution, $H_{mi}^{E,\infty}$, of 1-alkanol(1) + alkanenitrile(2) mixtures at 298.15 K.

System	$H_{m1}^{E,\infty} / \text{kJ}\cdot\text{mol}^{-1}$		$H_{m2}^{E,\infty} / \text{kJ}\cdot\text{mol}^{-1}$		Ref.
	Exp.	DISQUAC	Exp.	DISQUAC	
Methanol(1) + acetonitrile(2)	5.66	5.37	4.34	5.19	80
	6.1 ^a		4.1 ^a		5
Methanol(1) + butanenitrile(2)			3.81	4.68	80
	4.9 ^a	5.93	3.6 ^a		72
Ethanol(1) + acetonitrile(2)	7.88	7.37		5.26	80
	8.0 ^a		6.3 ^a		5
1-propanol(1) + acetonitrile(2)	8.84	9.47		10.16	80
	9.2 ^a		8.1 ^a		6
1-butanol(1) + acetonitrile(2)	10.29	11.21		10.55	80
	10.4 ^a		9.2 ^a		7

^avalue obtained from H_m^E data over the whole concentration range

TABLE 8

Molar excess volumes, V_m^E , at equimolar composition and 298.15 K for 1-alkanol + alkanenitrile mixtures.

System	$V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$		Ref.
	Exp.	ERAS	
methanol + acetonitrile	-0.1424	-0.148	57
ethanol + acetonitrile	-0.0258	-0.027	57
1-propanol + acetonitrile	0.0544	0.057	57
1-butanol + acetonitrile	0.1045	0.110	57
1-decanol + acetonitrile	0.340	0.331	59
methanol + butanenitrile	-0.0124	-0.014	72
ethanol + butanenitrile	0.0573	0.066	73
1-propanol + butanenitrile	0.0796	0.065	74
1-butanol + butanenitrile	0.1044	0.110	73
1-decanol + butanenitrile	0.3244	0.328	72

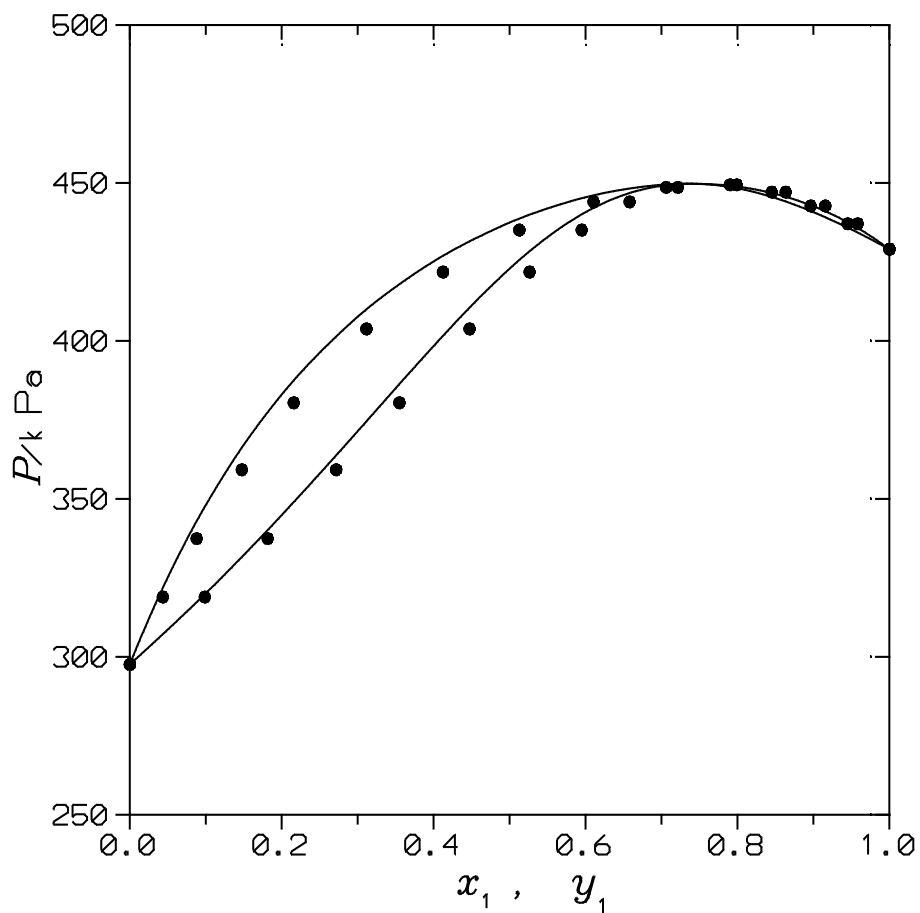


Figure 1. VLE phase diagram for the ethanol(1) + acetonitrile(2) system at 393.15 K. Points, experimental results [69]. Solid lines DISQUAC calculations with interaction parameters listed in Table 1.

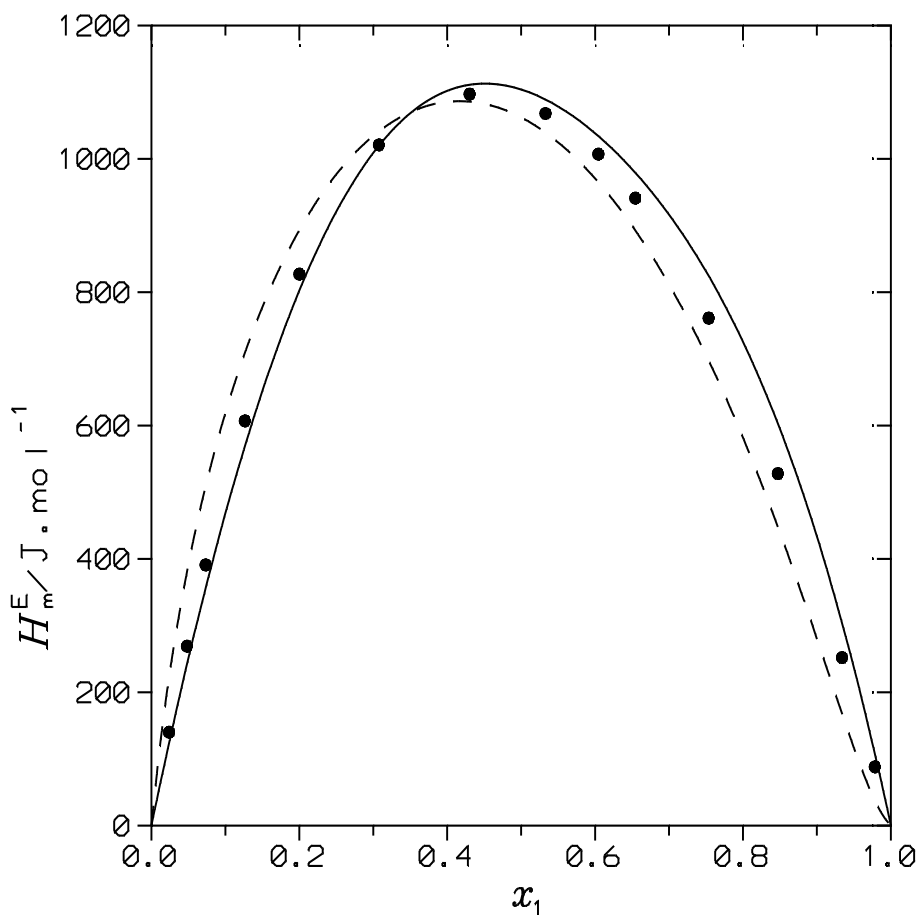


Figure 2. H_m^E for the methanol(1) + acetonitrile(2) system at 298.15 K. Points, experimental results [5]. Solid line, DISQUAC calculations with interaction parameters listed in Table 1. Dashed line, ERAS results with parameters collected in Table 2

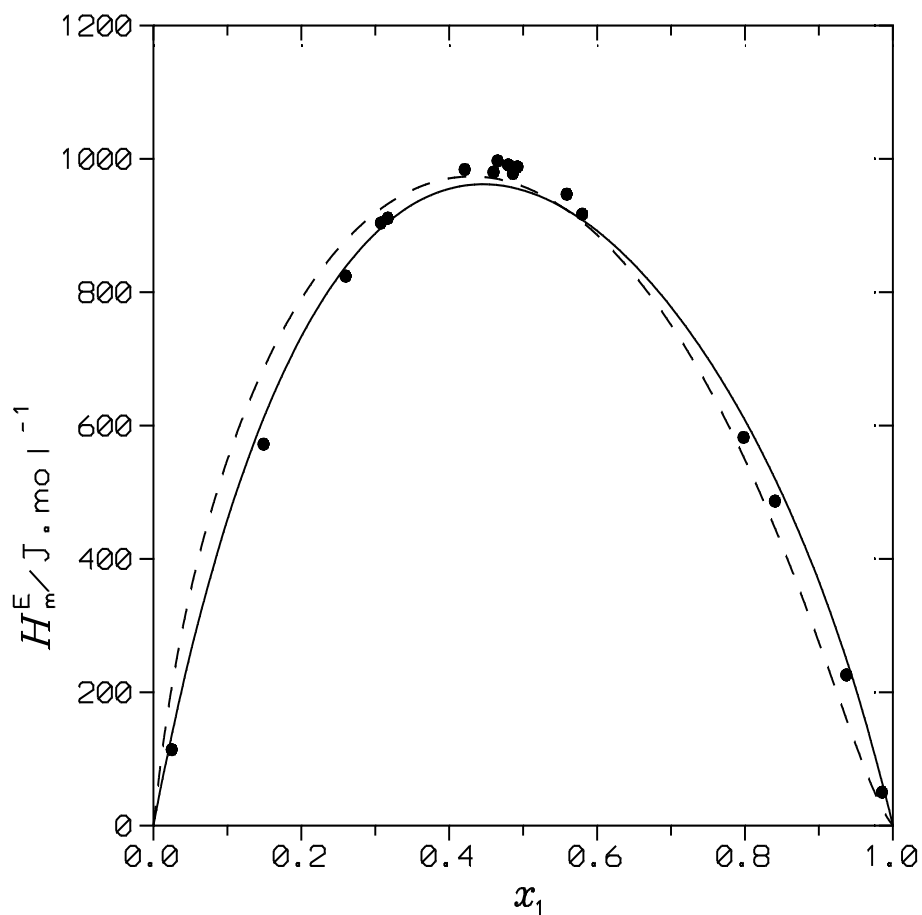


Figure 3. H_m^E for the methanol(1) + butanenitrile(2) system at 298.15 K. Points, experimental results [72]. Solid line, DISQUAC calculations with interaction parameters listed in Table 1. Dashed line, ERAS results with parameters collected in Table 2.

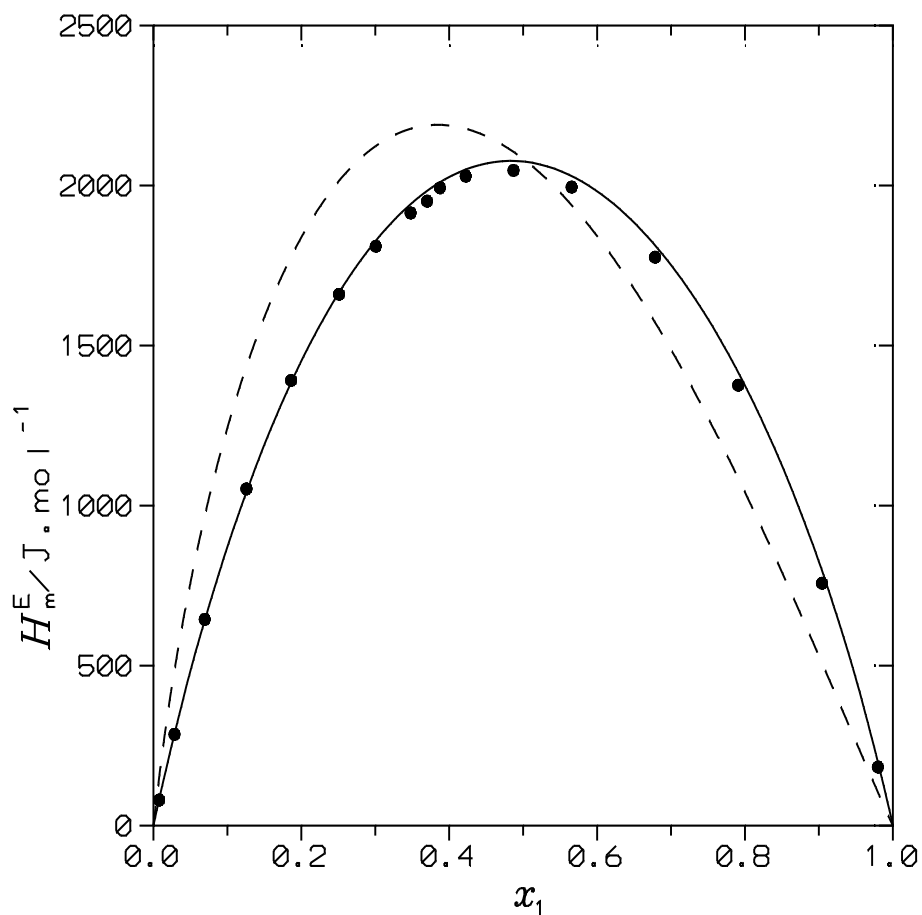


Figure 4. H_m^E for the 1-butanol(1) + acetonitrile(2) system at 298.15 K. Points, experimental results [7]. Solid line, DISQUAC calculations with interaction parameters listed in Table 1. Dashed line, ERAS results with parameters collected in Table 2

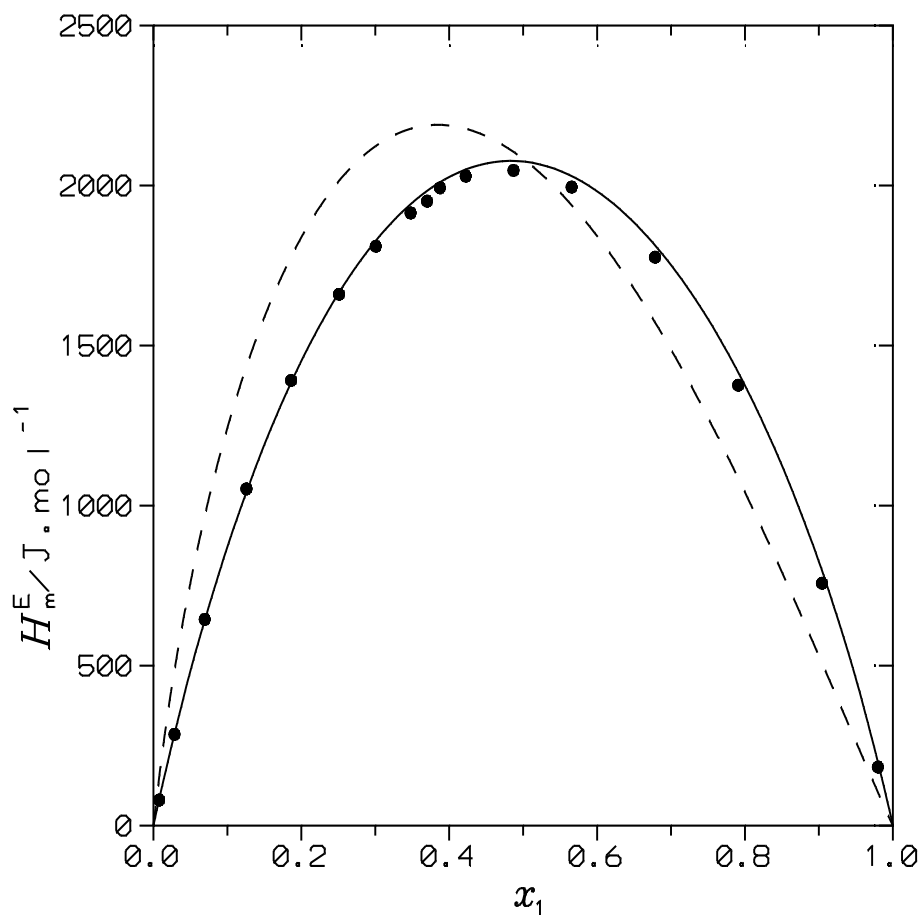


Figure 5 H_m^E for the 1-decanol(1) + butanenitrile(2) system at 298.15 K. Points, experimental results [72]. Solid line, DISQUAC calculations with interaction parameters listed in Table 1. Dashed line, ERAS results with parameters collected in Table 2

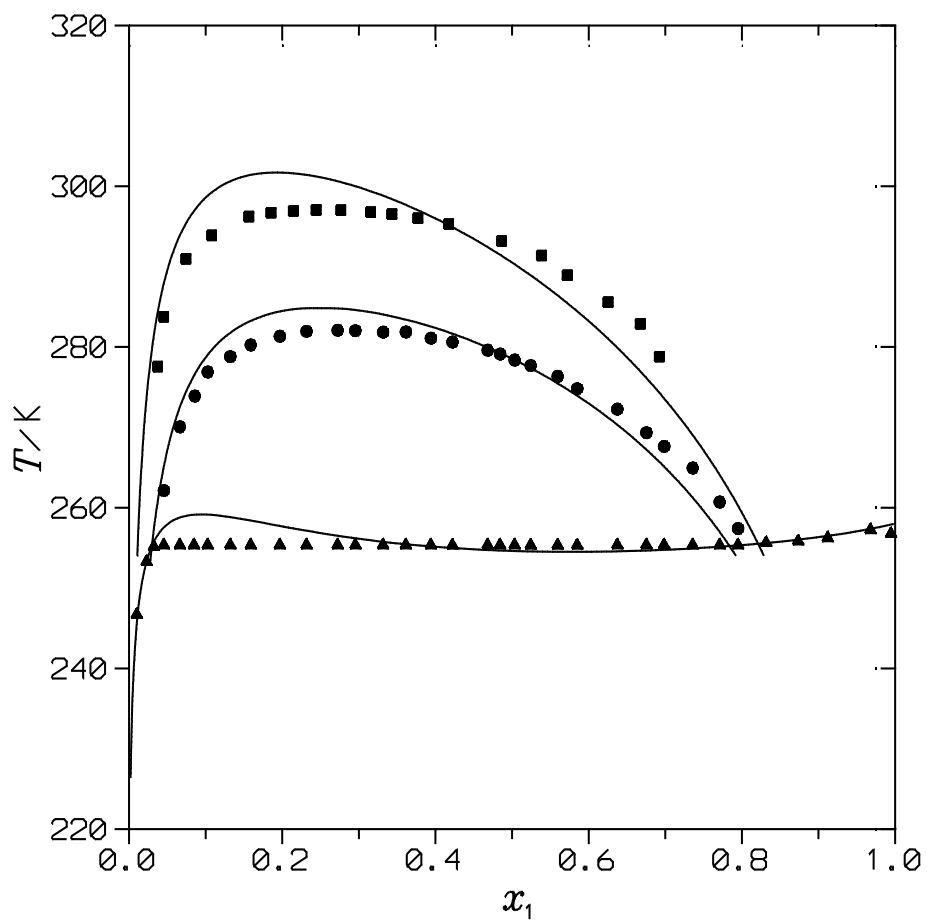


Figure 6. LLE and SLE phase diagrams for 1-alkanol(1) + acetonitrile(2) system. Points, experimental results [15]: (●), LLE for the 1-octanol mixture; (■), LLE for the 1-decanol solution; (▲), SLE for the 1-octanol system. Solid lines DISQUAC calculations with interaction parameters listed in Table 1.