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# A study of nitrile group interactions in alkane solutions[1]

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## Abstract

The molar excess enthalpies, reported in a previous paper, the vapor–liquid and liquid–liquid phase equilibrium data available in the literature, the activity coefficients, the partial molar excess enthalpies at infinite dilution, and the excess molar heat capacities of *n*-alkanenitriles + *n*-alkane or cyclohexane are examined on the basis of the DISQUAC group contribution model. The quasi-chemical interaction parameters for the CN group/*n*-alkane and CN group/cyclohexane decrease with the chain length of the nitriles (steric effect). The dispersive parameters of all the alkanenitriles investigated, except ethanenitrile, remain constant. Using a unique set of parameters, the model describes consistently the thermodynamic properties. The deviations between experimental and calculated quantities are typical for alkane solutions of very polar compounds.

## LIST OF SYMBOLS

| | |
|---|---|
| c-$CH_2$ | methylene group in a cyclic compound |
| $C$ | interchange coefficient |
| $C_p$ | molar heat capacity at constant pressure |
| $G$ | molar Gibbs energy |
| $h$ | partial molar enthalpy |
| $H$ | molar enthalpy |
| $m$ | number of C atoms in alkane |
| $n$ | number of C atoms in alkanenitrile |
| $P$ | pressure |
| $q$ | relative molecular area |
| $r$ | relative molecular volume |
| $T$ | temperature |
| $x$ | mole fraction in liquid phase |
| $y$ | mole fraction in vapor phase |

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[1] This paper is a contribution to the TOM Project [1, 2].

| | |
|---|---|
| $z$ | coordination number |

*Greek letters*

| | |
|---|---|
| $\alpha$ | molecular surface fraction |
| $\gamma$ | activity coefficient |

*Superscripts*

| | |
|---|---|
| c | liquid–liquid critical property |
| dis | dispersive term |
| E | excess property |
| quac | quasi-chemical term |
| $\infty$ | property at infinite dilution |

*Subscripts*

| | |
|---|---|
| **a, c, t** | type of contact surface (group): **a**, $CH_3$, $CH_2$, CH; **c**, c-$CH_2$; **t**, CN |
| $i$ | type of molecule (component): $i = 1$, alkanenitrile; $i = 2$, alkane |
| $l$ | order of interchange coefficient: $l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity |

## INTRODUCTION

Mixtures containing short chain-length nitriles exhibit large positive deviations from ideality that are often reflected in partial miscibility. This marked evidence of high polarity on the part of the nitriles is scarcely surprising in view of the complete miscibility of enthanenitrile and water. As the chain length of the nitriles increases, the positive deviations from ideality diminish in magnitude, and total miscibility becomes more common.

The polarity of the C≡N bond may be responsible in part for the observed non-randomness in mixtures containing alkanenitrile. Therefore, the addition of an orientational contribution to the thermodynamic random-mixing functions should improve the agreement with experimental data.

We decided, therefore, to examine the properties of these mixtures in terms of DISQUAC, an extended quasi-chemical pseudo-lattice group contribution model [3, 4], according to the procedure reported in the first paper of the series in which DISQUAC was applied to a very polar group, namely the nitro group $NO_2$ [5], where we investigated the ability of the first-approximation quasi-chemical theory [6], on which the DISQUAC quasi-chemical term relies, to account for orientational effects in very polar molecules.

The purpose of this paper is to study low-pressure fluid phase equilibria and related thermodynamic excess functions (molar excess Gibbs energy $G^E$, molar excess enthalpies $H^E$, activity coefficients at infinite dilution $\gamma_1^\infty$) of binary liquid mixtures of *n*-alkane or cyclohexane with *n*-alkanenitriles in terms of the DISQUAC group contribution model.

## SURVEY OF THE EXPERIMENTAL DATA

McLure et al. [7] reported the UCST with equi-volume mixtures for binary mixtures of ethanenitrile, propanenitrile or butanenitrile with *n*-alkanes containing between 5 and 18 carbon atoms. Zieborak and Olzewski [8] reported the critical composition $x_1^c$ at the upper critical solution point for ethanenitrile + *n*-alkane mixtures; and Ott et al. [9] and Vani et al. [10] reported $x_1^c$ for ethanenitrile + cyclohexane (Table 1).

Several authors [11–22] have measured the liquid–liquid curves (LLE) of ethanenitrile + *n*-alkane or cyclohexane (Table 2).

The liquid–vapor equilibrium (VLE) of ethanenitrile + *n*-pentane at various temperatures has been investigated by Zawisza and Glowka [23] and the VLE of ethanenitrile + *n*-hexane at 313.15 K has been reported by Sugi and Katayama [24]. VLE data on ethanenitrile + *n*-heptane have been also measured by several authors: Monfort [25], Palmer and Smith [17], and Heinrich and Dojcansky [16]. A single source of liquid–vapor equilibrium data ($x$–$y$) is available for propanenitrile or butanenitrile + *n*-heptane at 298.15 K (Kikic et al. [26]) and for butanenitrile + octane at 363.15 K (Speyling and Tassios [27]). Recently, excess Gibbs energies $G^E$ and volumes $V^E$ were measured for mixtures of *n*-alkanenitriles + *n*-heptane or cyclohexane by Dernini et al. [28]. The equimolar $G^E$ values of completely miscible mixtures are listed in Table 3.

The data of Heinrich and Dojcansky [16] covered the region of dilute solutions, permitting the accurate determination of the activity coefficients at infinite dilution $\gamma_1^\infty$, in good agreement with data obtained by gas–liquid chromatography (GLC) [30]. Table 4 lists these data along with other results obtained by GLC or by differential ebulliometry.

Molar excess enthalpies $H^E$ of alkanenitrile + *n*-alkane or cyclohexane have been measured calorimetrically by several authors: Lakhanpal et al. [42], Palmer and Smith [17], Amaya [43] and Alessandrini et al. [44]. The most extensive investigations of the $H^E$ values of alkanenitrile + alkane mixtures have been published by McLure [45] and Valero et al. [46]. However, there is some discrepancy in the results reported by different authors. Molar excess enthalpies have recently been measured for mixtures of alkanenitrile with *n*-alkane or cyclohexane (Marongiu and Porcedda

TABLE 1

Liquid–liquid mixing composition $x_1^c$ and temperatures $T^c$ for alkanenitrile (1) + *n*-alkane or cyclohexane (2) mixtures. Comparison of experimental results (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}$ from Table 8 (*m* is the number of C atoms in the alkane, c-6 means cyclohexane)

| *m* | $x_1^c$ | | $T^c$/K | | Ref. |
|---|---|---|---|---|---|
| | Calc. | Exp. | Calc. | Exp. | |
| *Ethanenitrile* | | | | | |
| 5 | 0.573 | 0.688 | 335.8 | 341.2 | 7[a] |
| 6 | 0.641 | 0.714 | 348.4 | 350.2 | 7[a] |
| 7 | 0.694 | 0.736 | 358.9 | 358.0 | 7[a] |
| | | 0.360 | | 357.8 | 8[b] |
| 8 | 0.723 | 0.754 | 368.1 | 365.1 | 7[a] |
| | | 0.670 | | 364.7 | 8[b] |
| 9 | 0.771 | 0.772 | 376.2 | 374.2 | 7[a] |
| | | 0.700 | | 373.2 | 8[b] |
| 10 | 0.799 | 0.785 | 383.4 | 381.7 | 7[a] |
| | | 0.750 | | 380.7 | 8[b] |
| 11 | 0.822 | 0.798 | 390.0 | 386.2 | 7[a] |
| | | 0.770 | | 385.7 | 8[b] |
| 12 | 0.844 | 0.812 | 395.9 | 398.2 | 7[a] |
| 14 | 0.874 | 0.833 | 406.1 | 403.7 | 7[a] |
| 16 | 0.893 | 0.848 | 414.9 | 420.2 | 7[a] |
| 18 | 0.910 | 0.864 | 422.6 | 426.2 | 7[a] |
| c-6 | 0.550 | 0.517 | 350.0 | 347.6 | 9 |
| | | 0.516 | | 349.8 | 10 |
| *Propanenitrile* | | | | | |
| 5 | 0.453 | 0.622 | 271.5 | 276.2 | 7[a] |
| 6 | 0.512 | 0.651 | 282.9 | 284.2 | 7[a] |
| 8 | 0.630 | 0.696 | 301.0 | 303.7 | 7[a] |
| 10 | 0.706 | 0.732 | 315.0 | 316.2 | 7[a] |
| 12 | 0.757 | 0.763 | 326.3 | 327.7 | 7[a] |
| 14 | 0.805 | 0.789 | 335.9 | 341.2 | 7[a] |
| 16 | 0.833 | 0.807 | 343.9 | 349.2 | 7[a] |
| 18 | 0.856 | 0.826 | 350.9 | 359.2 | 7[a] |
| *Butanenitrile* | | | | | |
| 5 | 0.336 | 0.570 | 23.4 | 237.2 | 7[a] |
| 6 | 0.406 | 0.600 | 233.2 | 244.2 | 7[a] |
| 10 | 0.615 | 0.687 | 261.7 | 269.2 | 7[a] |
| 12 | 0.675 | 0.721 | 271.8 | 284.7 | 7[a] |
| 14 | 0.728 | 0.750 | 280.5 | 297.2 | 7[a] |
| 16 | 0.769 | 0.770 | 287.7 | 307.2 | 7[a] |
| 18 | 0.801 | 0.792 | 294.0 | 318.2 | 7[a] |

[a] $x^c$ is the mole fraction of nitrile in an equi-volume mixture at 298.15 K.

[b] Molar fraction is referred to the upper critical solution point.

TABLE 2

Liquid–liquid equilibrium composition, $x_1'$ and $x_1''$ for ethanenitrile (1) + alkane or cyclohexane (2) mixtures at various temperatures $T$. Comparison of experimental results (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}$ from Table 8 ($m$ is the number of C atoms in the alkane, c-6 means cyclohexane)

| $m$ | $T$/K | $x_1'$ | | $x_1''$ | | Ref. |
|---|---|---|---|---|---|---|
| | | Calc. | Exp. | Calc. | Exp. | |
| 6 | 293.15 | 0.141 | 0.090 | 0.923 | 0.934 | 11 [a] |
| | 298.15 | 0.160 | 0.092 | 0.916 | 0.933 | 11 [a] |
| | | | 0.076 | | 0.944 | 12, 17 |
| | 303.15 | 0.182 | 0.094 | 0.908 | 0.927 | 11 [a] |
| | 308.15 | 0.206 | 0.096 | 0.899 | 0.921 | 11 [a] |
| | 313.15 | 0.232 | 0.098 | 0.889 | 0.914 | 11 [a] |
| 7 | 291.15 | 0.135 | – | 0.952 | 0.966 | 13 |
| | 293.15 | 0.142 | 0.034 | 0.950 | 0.950 | 11 [a], 22 |
| | 298.15 | 0.161 | 0.063 | 0.946 | 0.961 | 14 |
| | | | 0.058 | | 0.980 | 15 |
| | | | 0.062 | | 0.962 | 15 |
| | 313.15 | 0.228 | 0.098 | 0.928 | 0.946 | 16 |
| | 318.15 | 0.254 | 0.102 | 0.921 | 0.937 | 17 |
| 8 | 298.15 | 0.163 | 0.057 | 0.963 | 0.980 | 15 |
| 9 | 291.15 | 0.143 | – | 0.978 | 0.987 | 18 |
| | 300.35 | 0.176 | – | 0.973 | 0.983 | 18 |
| | 314.65 | 0.238 | – | 0.965 | 0.976 | 18 |
| | 333.15 | 0.351 | – | 0.949 | 0.966 | 18 |
| 13 | 300.15 | 0.197 | 0.043 | 0.992 | – | 18 |
| | 303.15 | 0.154 | 0.047 | 0.995 | 0.995 | 11 [a], 18 |
| | 305.65 | 0.217 | – | 0.991 | 0.995 | 18 |
| | 313.15 | 0.253 | 0.062 | 0.990 | 0.994 | 18 |
| | 321.15 | 0.291 | – | 0.998 | 0.993 | 18 |
| | 323.15 | 0.300 | 0.086 | 0.987 | 0.993 | 18 |
| | 323.65 | 0.227 | 0.088 | 0.992 | – | 18 |
| | 333.15 | 0.266 | 0.125 | 0.991 | 0.990 | 18 |
| | 337.35 | 0.375 | 0.147 | 0.983 | – | 18 |
| | 338.15 | 0.380 | – | 0.982 | 0.988 | 18 |
| 15 | 295.15 | 0.189 | 0.054 | 0.996 | – | 18 |
| | 298.15 | 0.200 | 0.056 | 0.996 | 0.981 | 18 |
| | 303.15 | 0.221 | 0.059 | 0.995 | 0.978 | 18 |
| | 303.15 | 0.221 | – | 0.995 | 0.977 | 18 |
| | 303.65 | 0.221 | 0.059 | 0.995 | 0.996 | 18 |
| | 301.15 | 0.213 | – | 0.995 | 0.981 | 18 |
| | 330.15 | 0.267 | – | 0.995 | 0.996 | 18 |
| c-6 | 298.15 | 0.101 | 0.044 | 0.897 | 0.940 | 19 |
| | 313.15 | 0.153 | 0.079 | 0.863 | 0.896 | 20 |
| | 318.15 | 0.176 | 0.094 | 0.848 | 0.888 | 21 |
| | 323.15 | 0.202 | 0.118 | 0.830 | – | 19 |
| | 341.28 | 0.345 | 0.222 | 0.731 | 0.772 | 10 |
| | 345.97 | 0.412 | 0.279 | 0.678 | 0.709 | 10 |

[a] Smoothed data.

TABLE 3

Molar Gibbs energies $G^E(T; x_1 = 0.5)$ of alkanenitrile (1) + alkane or cyclohexane (2) mixtures at various temperatures $T$ and equimolar composition. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}$ from Table 8 ($m$ is the number of C atoms in the alkane, c-6 means cyclohexane)

| $m$ | $T$/K | $G^E(T; x_1 = 0.5)/(\text{J mol}^{-1})$ | | Ref. |
|---|---|---|---|---|
| | | Calc. | Exp. | |
| *Ethanenitrile* | | | | |
| 5 | 333.15 | 1551 | [a] | 23 |
| | 363.15 | 1528 | [a] | 23 |
| | 393.15 | 1496 | [a] | 23 |
| 6 | 313.15 | 1605 | [a] | 24 |
| 7 | 293.15 | 1648 | [a] | 22 |
| | 313.15 | 1634 | [a] | 16 |
| | 318.15 | 1629 | [a] | 17 |
| *Propanenitrile* | | | | |
| 7 | 298.15 | 1321 | 1423 [b] | 28 |
| | | | 1369 [c] | 26 |
| | 308.15 | 1313 | 1398 [c] | 26 |
| c-6 | 298.15 | 1301 | 1319 [b] | 28 |
| *Butanenitrile* | | | | |
| 7 | 298.15 | 1072 | 1060 [b] | 28 |
| | | | 1034 [c] | 26 |
| c-6 | 298.15 | 1046 | 1072 [b] | 28 |
| | 363.15 | 1022 | 938 [c] | 27 |
| *Pentanenitrile* | | | | |
| 7 | 298.15 | 927 | 930 [b] | 28 |
| c-6 | 298.15 | 880 | 848 [b] | 28 |

[a] Miscibility gap.

[b] Calculation by reduction of the original gas-chromatographic $x$–$y$ data with the Redlich–Kister equation; vapor phase non-ideality corrected in terms of the second virial coefficient estimated by the method of Hayden and O'Connell [29].

[c] Calculation (this work) by the reduction of the original isothermal $P$–$x$ data with the Redlich–Kister equation.

[47]). The experimental equimolar $H^E$ values of completely miscible mixtures are listed in Table 5.

A single source of partial molar excess enthalpies at infinite dilution $h_1^{E,\infty}$ is available for alkanenitriles + $n$-alkane or cyclohexane mixtures (Trampe and Eckert [48]) (Table 6).

As can be seen from Table 5, $H^E$ ($x_1 = 0.5$) decreases rapidly with temperature, in agreement with recent direct molar excess heat capacity $C_p^E$ measurements (Saint Victor and Patterson [49]).

TABLE 4

Logarithm of activity coefficients at infinite dilution ln $\gamma_1^\infty$ in alkanenitrile (1) + *n*-alkane or cyclohexane (2) mixtures at various temperatures. Comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}$ from Table 8 (*m* is the number of C atoms in the alkane, c-6 means cyclohexane)

| *m* | $T$/K | ln $\gamma_1^\infty$ | | ln $\gamma_2^\infty$ | | Ref. |
|---|---|---|---|---|---|---|
| | | Calc. | Exp. | Calc. | Exp. | |
| *Ethanenitrile* | | | | | | |
| 5 | 298.15 | 3.08 | – | 2.88 | 3.06 | 31 |
| | | | | | 3.00 | 32 |
| | 323.15 | 2.70 | – | 2.67 | 2.74 | 33 |
| 6 | 295.00 | 3.04 | 3.32 | 3.23 | – | 30 |
| | 298.15 | 2.99 | – | 3.20 | 3.24 | 32 |
| | | | | | 3.23 | 34 |
| | | | | | 3.42 | 31 |
| | 322.90 | 2.62 | 2.82 | 2.96 | – | 35 |
| | 332.30 | 2.49 | 2.62 | 2.88 | – | 35 |
| | 340.90 | 2.38 | 2.52 | 2.80 | – | 35 |
| 7 | 293.15 | 2.99 | 3.40 | 3.56 | – | 35 |
| | | | 3.72 | | | 36 |
| | 298.15 | 2.91 | 3.57 | 3.50 | – | 25 |
| | | | | | 3.52 | 37 |
| | | | | | 3.75 | 31 |
| | 313.15 | 2.67 | 3.18 | 3.34 | 3.48 | 16 |
| | 323.15 | 2.53 | – | 3.23 | 2.97 | 33 |
| 8 | 293.15 | 2.91 | 3.44 | 4.15 | – | 30 |
| | 298.15 | 2.83 | – | 3.78 | 4.12 | 31 |
| | | | | | 3.96 | 32 |
| 9 | 298.15 | 2.75 | – | 4.06 | 4.45 | 31 |
| 16 | 305.25 | 2.21 | 3.07 | 5.56 | – | 38 |
| | 315.35 | 2.06 | 2.87 | 5.33 | – | 38 |
| | 323.15 | 1.95 | – | 5.16 | 5.91 | 33 |
| 18 | 324.15 | 1.84 | 2.77 | 5.50 | – | 38 |
| | 334.55 | 1.70 | 2.54 | 5.25 | – | 38 |
| | 343.65 | 1.59 | 2.41 | 5.05 | – | 38 |
| | 353.15 | 1.48 | 2.27 | 4.82 | – | 39 |
| | 353.65 | 1.47 | 2.25 | 4.80 | – | 38 |
| 22 | 323.15 | 1.68 | – | 6.23 | 7.44 | 33 |
| 24 | 324.15 | 1.60 | 2.61 | 6.54 | – | 38 |
| | 333.25 | 1.48 | 2.39 | 6.25 | – | 38 |
| | 343.15 | 1.35 | 2.26 | 5.94 | – | 38 |
| | 353.45 | 1.23 | 2.11 | 5.63 | – | 38 |
| 32 | 323.15 | 1.37 | – | 7.99 | 0.86 | 33 |
| c-6 | 293.15 | 3.40 | – | 3.02 | 2.13 | 30 |
| | 298.15 | 3.30 | – | 2.96 | 3.05 | 32 |
| | | | | | 3.20 | 31 |

TABLE 4 (contd.)

| $m$ | $T$/K | $\ln \gamma_1^\infty$ | | $\ln \gamma_2^\infty$ | | Ref. |
|---|---|---|---|---|---|---|
| | | Calc. | Exp. | Calc. | Exp. | |
| *Propanenitrile* | | | | | | |
| 5 | 293.15 | 2.52 | – | 2.04 | 2.14 | 35 |
| | 298.15 | 2.45 | – | 2.01 | 2.09 | 35 |
| | | | | | 1.68 | 37 |
| 6 | 293.15 | 2.45 | – | 2.29 | 2.40 | 35 |
| | 295.00 | 2.43 | – | 2.27 | 1.81 | 37 |
| | 298.15 | 2.39 | – | 2.25 | 2.32 | 34 |
| | | | | | 2.36 | 35 |
| | 322.25 | 2.11 | 2.37 | 2.14 | – | 30 |
| | 322.90 | 2.11 | 2.61 | 2.06 | – | 30 |
| | 340.90 | 1.93 | 2.30 | 1.94 | – | 30 |
| 7 | 293.15 | 2.39 | 3.09 | 2.51 | – | 30 |
| | | | | | 3.09 | 37 |
| | | | 3.17 | | | 36 |
| | 298.15 | 2.32 | – | 2.47 | 2.50 | 36 |
| | | | | | 2.50 | 37 |
| 8 | 293.15 | 2.32 | 3.04 | 2.72 | 3.04 | 35 |
| | 298.15 | 2.26 | – | 2.67 | 2.72 | 35 |
| | | | | | 2.08 | 37 |
| 18 | 353.15 | 1.16 | 1.87 | 3.18 | – | 39 |
| c-6 | 293.15 | 2.71 | – | 2.11 | 2.13 | 35 |
| | 298.15 | 2.64 | – | 2.07 | 1.54 | 37 |
| | 336.65 | 2.19 | – | 1.80 | 1.79 | 35 |
| | 356.30 | 2.00 | – | 1.68 | 1.65 | 35 |
| *Butanenitrile* | | | | | | |
| 5 | 298.15 | 2.07 | 2.09 | 1.44 | 1.68 | 37 |
| 6 | 298.15 | 2.03 | 2.36 | 1.63 | 1.81 | 37 |
| 7 | 298.15 | 1.98 | 2.50 | 1.80 | 1.95 | 37 |
| 8 | 298.15 | 1.93 | 2.72 | 1.95 | 2.08 | 37 |
| | 363.15 | 1.37 | 1.49 | 1.52 | 1.23 | 37 |
| c-6 | 298.15 | 2.26 | – | 1.52 | 2.08 | 37 |
| *Pentanenitrile* | | | | | | |
| 6 | 298.15 | 1.86 | – | 1.28 | 1.55 | 40 |
| 7 | 323.15 | 1.60 | 2.09 | 1.31 | – | 33 |
| 24 | 349.00 | 0.76 | 1.44 | 2.04 | – | 41 |
| c-6 | 298.15 | 2.10 | – | 1.18 | 1.46 | 40 |
| *Hexanenitrile* | | | | | | |
| 6 | 298.15 | 1.71 | – | 1.03 | 1.38 | 40 |
| c-6 | 298.15 | 1.90 | – | 0.96 | 1.18 | 40 |
| *Heptanenitrile* | | | | | | |
| 6 | 298.15 | 1.57 | – | 0.84 | 1.10 | 40 |
| c-6 | 298.15 | 1.74 | – | 0.77 | 0.95 | 40 |

TABLE 4 (contd.)

| $m$ | $T$/K | $\ln \gamma_1^\infty$ |  | $\ln \gamma_2^\infty$ |  | Ref. |
|---|---|---|---|---|---|---|
|  |  | Calc. | Exp. | Calc. | Exp. |  |
| *Octanenitrile* |  |  |  |  |  |  |
| 6 | 298.15 | 1.43 | – | 0.68 | 1.00 | 40 |
| c-6 | 298.15 | 1.58 | – | 0.61 | 0.84 | 40 |
| *Nonanenitrile* |  |  |  |  |  |  |
| 6 | 298.15 | 1.30 | – | 0.55 | 0.82 | 40 |
| c-6 | 298.15 | 1.43 | – | 0.48 | 0.68 | 40 |
| *Heptadecanenitrile* |  |  |  |  |  |  |
| 5 | 343.15 | −0.03 | – | −0.20 | 0.19 | 37 |
|  | 355.15 | −0.08 | – | −0.21 | 0.21 | 37 |
|  | 362.65 | −0.10 | – | −0.21 | 0.21 | 37 |
| 6 | 343.15 | −0.02 | – | −0.15 | 0.27 | 37 |
|  | 355.15 | −0.03 | – | −0.16 | 0.25 | 37 |
|  | 364.65 | −0.06 | – | −0.17 | 0.27 | 37 |
| 7 | 343.15 | 0.23 | – | −0.04 | 0.31 | 37 |
|  | 355.15 | 0.18 | – | −0.05 | 0.32 | 37 |
|  | 364.65 | 0.15 | – | −0.06 | 0.32 | 37 |
| c-6 | 343.15 | −0.11 | – | −0.24 | 0.02 | 37 |
|  | 355.15 | −0.16 | – | −0.25 | 0.02 | 37 |
|  | 364.15 | −0.20 | – | −0.26 | 0.02 | 37 |

## THEORY

The *n*-alkanenitriles + *n*-alkane or + cyclohexane systems are regarded as possessing three types of surfaces: type **a**, $CH_3$ and $CH_2$ groups in *n*-alkanes and *n*-alkanenitriles; type **c**, c-$CH_2$ groups in cyclohexane; and type **t**, CN group in alkanenitriles.

The equations used to calculate $G^E$ and $H^E$ are the same as in other applications [4] and need not be repeated here.

The temperature dependence of the interaction parameters has been expressed in terms of the dispersive or quasi-chemical interchange coefficients $C_{\mathrm{st},l}^{\mathrm{dis}}$ and $C_{\mathrm{st},l}^{\mathrm{quac}}$, where $\mathbf{s} = \mathbf{a}$ or $\mathbf{c}$ and $l = 1$ (Gibbs energy) and $l = 2$ (enthalpy). Heat capacity coefficients, $l = 3$, were not considered.

## ASSESSMENT OF GEOMETRICAL PARAMETERS

The relative molecular volumes $r_i$, the surfaces $q_i$, and the surface fraction $\alpha_{si}$, of all the non-cyclic molecular species have been calculated on the basis of the $CH_3$, $CH_2$ and CN group volumes ($V_G$) and surfaces ($A_G$) recommended by Bondi [50], taking arbitrarily the volume $V_{CH_4}$ and the

TABLE 5

Molar excess enthalpies $H^E(T; x_1 = 0.5)$ of $n$-alkanenitrile (1) + $n$-alkane or cyclohexane (2) mixtures at various temperatures and equimolar compositions. Comparison of direct experimental result (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}$ from Table 8 ($m$ is the number of C atoms in the alkane, c-6 means cyclohexane)

| $m$ | $T$/K | $H^E(T; x_1 = 0.5)/(\mathrm{J\ mol^{-1}})$ | | Ref. |
|---|---|---|---|---|
| | | Calc. | Exp. | |
| *Ethanenitrile* | | | | |
| 6 | 300.05 | 1712 | [a] | 42 |
| | 321.30 | 1833 | [a] | 42 |
| 7 | 298.15 | 1828 | [a] | 47 |
| | 318.15 | 1950 | [a] | 17 |
| | 321.35 | 1968 | [a] | 42 |
| c-6 | 300.05 | 1865 | [a] | 42 |
| | 321.35 | 1973 | [a] | 42 |
| *Propanenitrile* | | | | |
| 5 | 298.15 | 1336 | 1236 | 45 |
| 6 | 298.15 | 1457 | 1428 | 45 |
| | | | 1456 | 47 |
| 7 | 298.15 | 1567 | 1546 | 45 |
| | | | 1553 | 44 |
| | | | 1541 | 45 |
| c-6 | 298.15 | 1507 | 1522 | 45 |
| *Butanenitrile* | | | | |
| 6 | 298.15 | 1217 | 1280 | 45 |
| | | | 1233 | 47 |
| | 303.15 | 1227 | 1306 | 46 |
| 7 | 298.15 | 1315 | 1304 | 47 |
| | | | 1232 | 44 |
| 8 | 298.15 | 1405 | 1397 | 45 |
| 12 | 298.15 | 1700 | 1554 | 45 |
| 14 | 298.15 | 1819 | 1702 | 45 |
| c-6 | 298.15 | 1266 | 1257 | 47 |
| | 303.15 | 1274 | 1331 | 46 |
| *Pentanenitrile* | | | | |
| 6 | 298.15 | 1044 | 1052 | 47 |
| 7 | 298.15 | 1134 | 1129 | 47 |
| c-6 | 298.15 | 1098 | 1101 | 47 |
| | 353.55 | 1157 | 1188 | 43 |
| *Tetradecanenitrile* | | | | |
| 6 | 303.15 | 450 | 533 | 46 |
| 14 | 303.15 | 778 | 821 | 46 |
| c-6 | 303.15 | 484 | 796 | 46 |

[a] Miscibility gap.

TABLE 6

Partial molar excess enthalpy at infinite dilution $h_i^{E,\infty}$ in alkanenitrile (1) + alkane or cyclohexane (2) mixtures at various temperatures $T$. Comparison of direct experimental result (Exp.) with values calculated (Calc.) using the coefficients $C_{st,l}$ from Table 8 ($m$ is the number of C atoms in the alkane, c-6 means cyclohexane)

| $m$ | $T$/K | $h_1^{E,\infty}$/(J mol$^{-1}$) | | $h_2^{E,\infty}$/(J mol$^{-1}$) | | Ref. |
|---|---|---|---|---|---|---|
| | | Calc. | Exp. | Calc. | Exp. | |
| *Ethanenitrile* | | | | | | |
| 5 | 298.15 | 12200 | – | 6300 | 8900 | 48 |
| 6 | 298.15 | 12200 | – | 7300 | 10300 | 48 |
| 7 | 298.15 | 12200 | – | 8300 | 12100 | 48 |
| 8 | 298.15 | 12200 | – | 9300 | 13400 | 48 |
| c-6 | 298.15 | 13400 | 15000 | 7800 | 9800 | 48 |
| *Propanenitrile* | | | | | | |
| c-6 | 298.15 | 10100 | 12600 | 5700 | – | 48 |
| *Butanenitrile* | | | | | | |
| c-6 | 298.15 | 8900 | 10200 | 4300 | – | 48 |

surface $A_{CH_4}$ of methane as unity. The c-CH$_2$ group parameters have been estimated previously [51].

Table 7 lists the geometrical parameters of all the alkanenitriles referred to in this paper.

TABLE 7

Volumes $r_i$, total surfaces $q_i$, and molecular surface fractions $\alpha_{si}$ of alkanenitriles [a]

| Alkanenitrile | $r_i$ | $q_i$ | $\alpha_{ai}$ | $\alpha_{ti}$ |
|---|---|---|---|---|
| Ethanenitrile | 1.6571 | 1.4862 | 0.4919 | 0.5081 |
| Propanenitrile | 2.2547 | 1.9517 | 0.6131 | 0.3869 |
| Butanenitrile | 2.8522 | 2.4172 | 0.6876 | 0.3124 |
| Pentanenitrile | 3.4498 | 2.8828 | 0.7380 | 0.2620 |
| Hexanenitrile | 4.0473 | 3.3483 | 0.7744 | 0.2255 |
| Heptanenitrile | 4.6449 | 3.8138 | 0.8020 | 0.1980 |
| Octanenitrile | 5.2424 | 4.2793 | 0.8235 | 0.1765 |
| Nonanenitrile | 5.8400 | 4.7448 | 0.8408 | 0.1592 |
| Decanenitrile | 6.4375 | 5.2104 | 0.8551 | 0.1449 |
| Undecanenitrile | 7.0351 | 5.6759 | 0.8670 | 0.1330 |
| Dodecanenitrile | 7.6326 | 6.1414 | 0.8770 | 0.1230 |
| Tridecanenitrile | 8.2302 | 6.6069 | 0.8857 | 0.1143 |
| Tetradecanenitrile | 8.8277 | 7.0724 | 0.8932 | 0.1068 |
| Heptadecanenitrile | 10.6201 | 8.4690 | 0.9108 | 0.0892 |

[a] For the parameters $r_i$ and $q_i$ of $n$-alkanes ($\alpha_{ai}$ = 1.0000), see ref. 52.

TABLE 8

Interchange energy coefficients $C^{\text{quac}}_{\mathbf{st},l}$ ($z = 4$) and $C^{\text{dis}}_{\mathbf{st},l}$ for contacts (**s**, **t**) (**s** = **a**, alkanes; **s** = **c**, cyclohexane) for alkanenitrile + alkane or cyclohexane mixtures; *n* represents the number of C atoms in the alkanenitrile

| $n$ | $C^{\text{quac}}_{\mathbf{st},1}$ | $C^{\text{quac}}_{\mathbf{st},2}$ | $C^{\text{dis}}_{\mathbf{at},1}$ | $C^{\text{dis}}_{\mathbf{at},2}$ | $C^{\text{dis}}_{\mathbf{ct},1}$ | $C^{\text{dis}}_{\mathbf{ct},2}$ |
|---|---|---|---|---|---|---|
| 2 | 6.10 | 7.45 | 0.40 | 0.80 | 0.72 | 1.44 |
| 3 | 5.30 | 5.80 | 0.80 | 1.70 | 1.07 | 2.16 |
| 4 | 5.00 | 5.60 | 0.80 | 1.70 | 1.07 | 2.16 |
| ≥5 | 5.00 | 5.60 | 0.80 | 1.70 | 1.07 | 2.16 |

## ESTIMATION OF INTERACTION PARAMETERS

As in previous applications, we assumed that interchange coefficients vary regularly with the molecular structure. We used the best experimental data to make a preliminary fit of the coefficients for the corresponding systems and then we tried to identify the ‘rules’ governing the structure dependence. The DISQUAC parameters $C^{\text{dis}}_{\mathbf{at},l}$ and $C^{\text{quac}}_{\mathbf{at},l}$ are listed in Table 8 and Fig. 1.

### *Alkanenitriles* + n-*alkanes*

These systems are characterized by a single type of contact (**a**, **t**). The dispersive coefficients $C^{\text{dis}}_{\mathbf{at},l}$ are the same for all the alkanenitriles: 0.8 ($l = 1$) and 1.7 ($l = 2$), except for ethanenitrile where $C^{\text{dis}}_{\mathbf{at},1} = 0.4$ and $C^{\text{dis}}_{\mathbf{at},2} = 0.8$. The quasi-chemical coefficients $C^{\text{quac}}_{\mathbf{at},l}$ decrease with increasing the chain length on the *n*-alkyl group in the alkanenitriles.

### *Alkanenitriles + cyclohexane*

These systems are characterized by three types of contact: (**a**, **c**), (**a**, **t**) and (**c**, **t**). The non-polar (**a**, **c**) contact of cyclohexane + *n*-alkane is entirely dispersive. For the short-chain alkanenitriles investigated in this paper, the interchange coefficients have been put equal to zero, i.e. $C^{\text{dis}}_{\mathbf{ac},l} = 0$. The dispersive coefficients $C^{\text{dis}}_{\mathbf{ct},l}$ are somewhat larger than the parameters of mixtures containing *n*-alkanes. The quasi-chemical coefficients for cyclohexane are the same as for *n*-alkane, i.e. $C^{\text{quac}}_{\mathbf{ct},l} = C^{\text{quac}}_{\mathbf{at},l}$.

## COMPARISON WITH EXPERIMENT

### *Excess Gibbs energies and activity coefficients at infinite dilution*

The experimental $G^{\text{E}}$ ($T; x_1 = 0.5$) values are reproduced by the DISQUAC model to better than 5% (Table 3). The values for propanenitrile + *n*-heptane calculated from the VLE ($x$–$y$) data of Dernini et al. [28] are

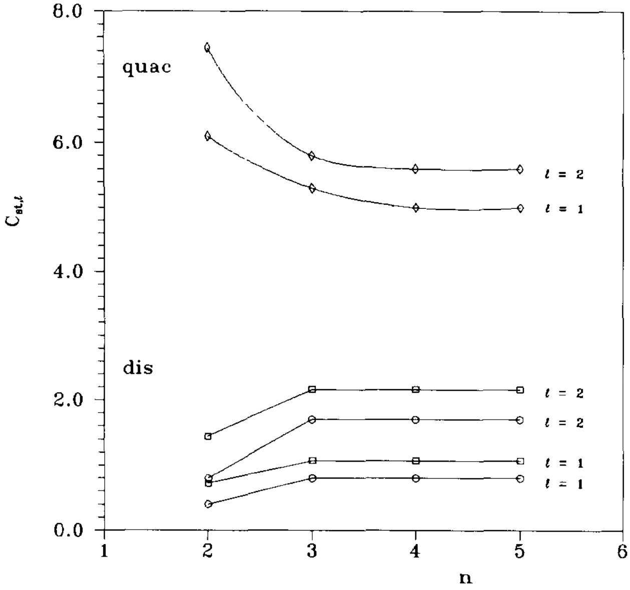

Fig. 1. Change of the dispersive $C^{\rm dis}_{{\rm st},l}$ and quasi-chemical $C^{\rm quac}_{{\rm st},l}$ ($l = 1$ or 2) coefficients of –CN groups + alkane (O, s = **a**) or cyclohexane (□, s = **c**) mixtures with the number of C atoms $n$ in the alkanenitrile. Graphical representation of the numerical data of Table 8.

approx. 7% higher. The composition dependence of $G^{\rm E}$ is well represented, except at low concentrations of alkanenitrile (Figs. 2 and 3). This is in agreement with the experimental activity coefficients at infinite dilution of alkanenitriles $\gamma_1^\infty$, which are always much larger (approx. 20%) than the calculated values (Table 4). However, the activity coefficients at infinite dilution of the alkanes $\gamma_2^\infty$ are predicted within nearly the experimental errors (Table 4).

## *Excess enthalpies and partial molar excess enthalpies at infinite dilution*

The experimental $H^{\rm E}$ ($T$; $x_1 = 0.5$) values are reproduced by DISQUAC to within 8% for alkanenitriles + lower alkane mixtures. The agreement improves significantly for the mixtures with higher alkanes (Table 5). The same holds for the composition dependence of $H^{\rm E}$. In general, the experimental curves are much flatter than predicted by DISQUAC (Figs. 4–6). Accordingly, the experimental partial molar enthalpies at infinite dilution $h_1^{{\rm E},\infty}$ are much larger than the calculated values, especially for the alkanenitriles (Table 6).

## *Liquid–liquid equilibria*

The model correctly predicts phase splitting for ethanenitrile + alkanes or cyclohexane, and for propanenitrile and butanenitrile + alkanes, using the same set of interchange parameters as for VLE and $H^{\rm E}$.

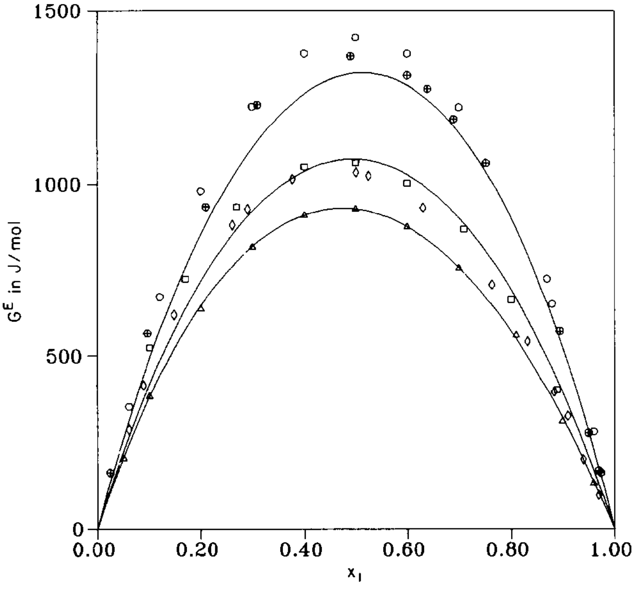

Fig. 2. Comparison of theory with experiment in plots of the molar excess Gibbs energy $G^E$ at 298.15 K of alkanenitrile (1) + heptane (2) mixtures versus the mole fraction of alkanenitrile $x_1$. Full lines, predicted values; points, experimental results: propanenitrile, ○ [28] and ⊕ [26]; butanenitrile, □ [28] and ◇ [26]; pentanenitrile, △ [28].

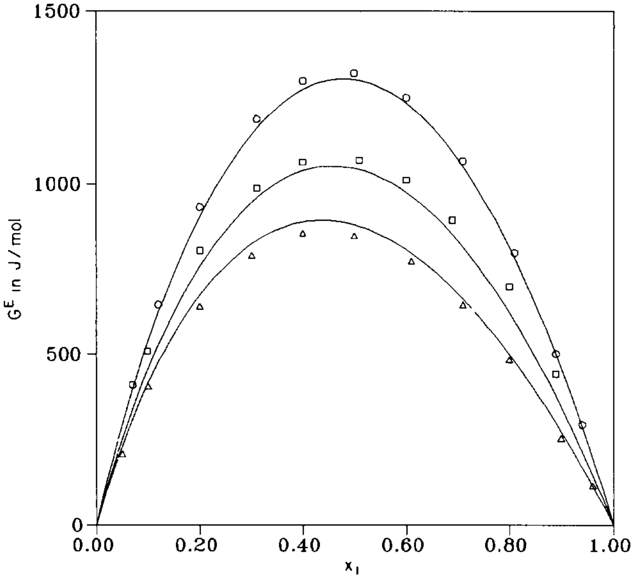

Fig. 3. Comparison of theory with experiment in plots of the molar excess Gibbs energy $G^E$ at 298.15 K of alkanenitrile (1) + cyclohexane (2) mixtures versus the mole fraction of alkanenitrile $x_1$. Full lines, predicted values; points, experimental results: propanenitrile, ○ [28]; butanenitrile, □ [28]; pentanenitrile, △ [28].

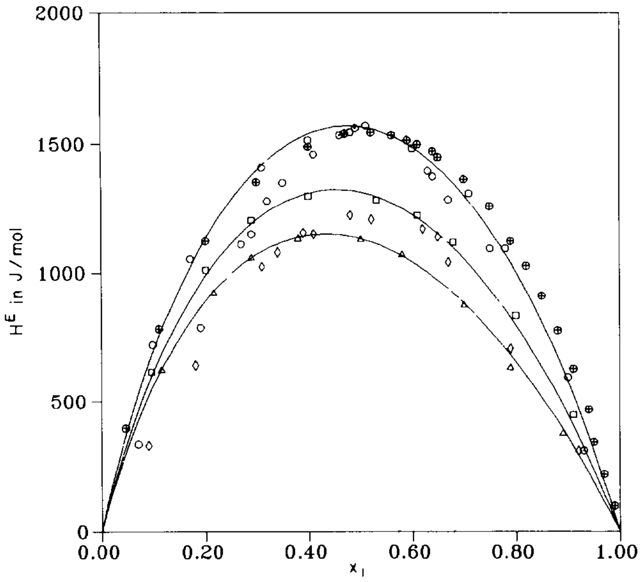

Fig. 4. Comparison of theory with experiment in plots of the molar excess enthalpy $H^E$ at 298.15 K of alkanenitrile (1) + heptane (2) mixtures versus the mole fraction of alkanenitrile $x_1$. Full lines, predicted values; points, experimental results: propanenitrile, ○ [47], ⊙ [44], and ⊕ [45]; butanenitrile, □ [47] and ◇ [44]; pentanenitrile, △ [47].

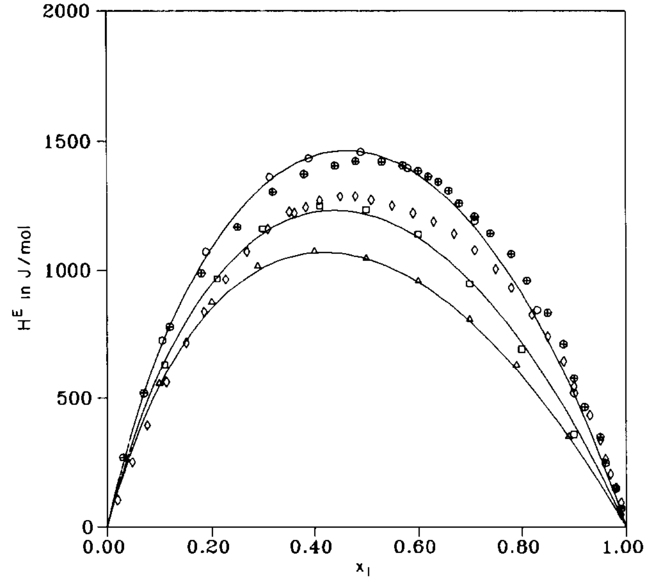

Fig. 5. Comparison of theory with experiment in plots of the molar excess enthalpy $H^E$ at 298.15 K of alkanenitrile (1) + hexane (2) mixtures versus the mole fraction of alkanenitrile $x_1$. Full lines, predicted values; points, experimental results: propanenitrile, ○ [47] and ⊕ [45]; butanenitrile, □ [47] and ◇ [44]; pentanenitrile, △ [47].

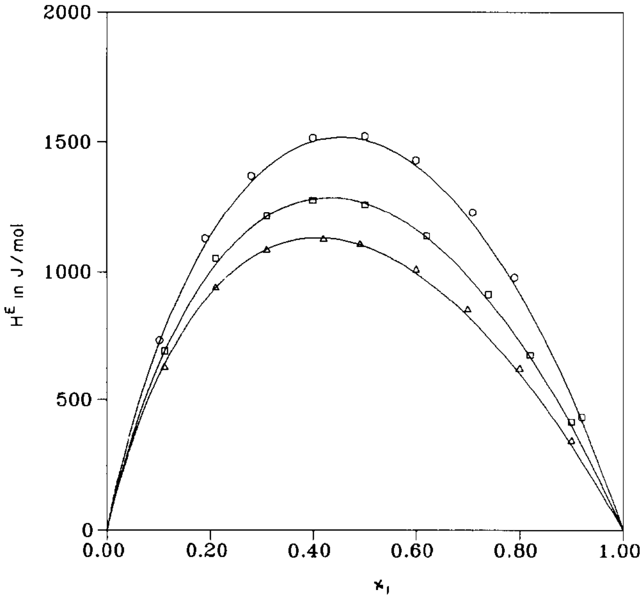

Fig. 6. Comparison of theory with experiment in plots of the molar excess enthalpy $H^E$ at 298.15 K of alkanenitrile (1) + cyclohexane (2) mixtures versus the mole fraction of alkanenitrile $x_1$. Full lines, predicted values; points, experimental results: propanenitrile, ○ [47]; butanenitrile, ○ [47]; pentanenitrile, △ [47].

The difference between the calculated and experimental upper critical solution temperatures are, in general, less than 10 K, except for butanenitrile + *n*-alkane mixtures, where the differences are much larger (20 K) (Table 2 and Fig. 7). The shape of the LLE curves is poorly represented (Table 1 and Fig. 8).

## *Excess heat capacity*

Figure 9 compares the $C_p^E$ curves of propanenitrile + cyclohexane, calculated with DISQUAC at 298.15 and 313.15 K, with the experimental points of Saint Victor and Patterson [49]. The model predicts the right order of magnitude for $C_p^E$, approx. 4 J K$^{-1}$ mol$^{-1}$ at 313.15 K, and a very weak temperature dependence. However, $C_p^E$ increases sharply with decreasing $T$, reaching approx. 11 J K$^{-1}$ mol$^{-1}$ at 288.15 K, i.e. when approaching the critical solution temperature, 285.35 K.

## DISCUSSION AND CONCLUSIONS

The decrease in the quasi-chemical interchange coefficients with the size of the alkyl radical (Fig. 1) reveals a notable steric effect in the alkanenitriles. There is no evidence for an inductive alkyl size effect: the dispersive coefficients are constant, except for ethanenitrile ($n = 2$).

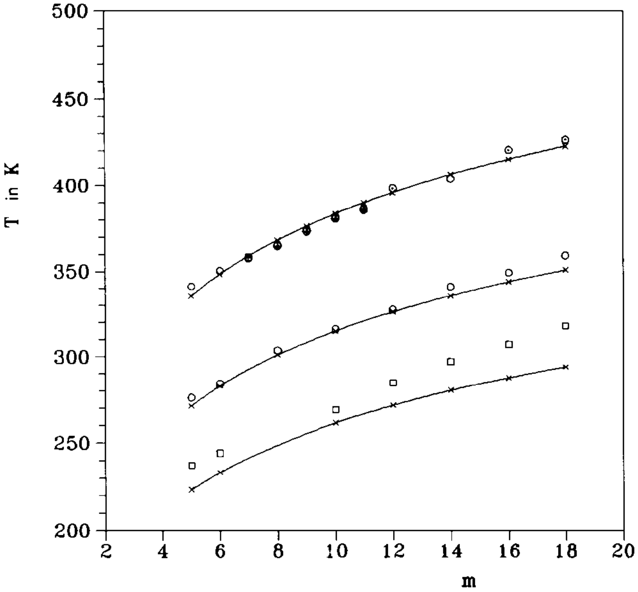

Fig. 7. Upper critical solution temperatures for *n*-alkanenitrile–*n*-alkane mixtures. The crosses (×), joined by full lines, are predicted values; the points, experimental results: ethanenitrile, ⊙ [7] and ⊕ [8]; propanenitrile, ○ [7]; butanenitrile, □ [7].

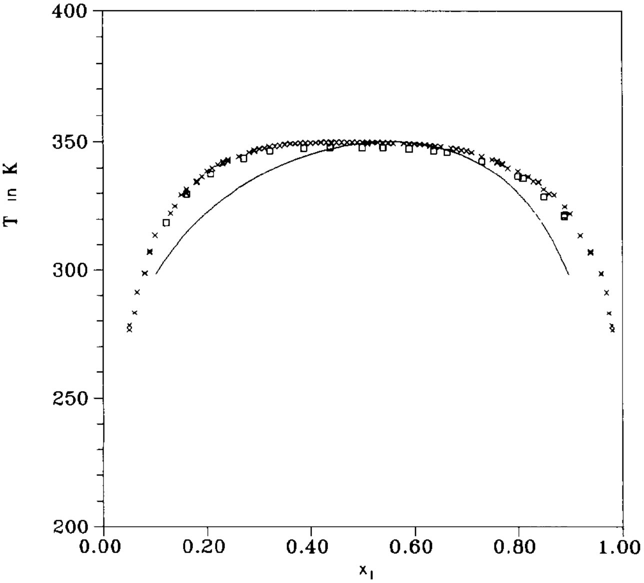

Fig. 8. Comparison of liquid–liquid phase diagrams: temperature $T$ for the ethanenitrile (1) + cyclohexane (2) mixtures versus $x_1$, the mole fraction of ethanenitrile. Full lines, predicted curve; points, experimental results: □ [9]; × [10].

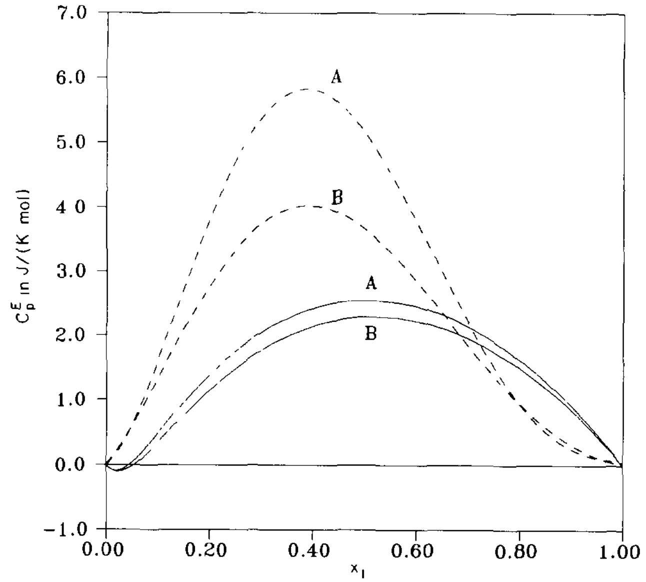

Fig. 9. Comparison of theory with experiment in plots of the excess molar heat capacity $C_p^E$ of propanenitrile (1) + cyclohexane (2) versus the mole fraction of propanenitrile $x_1$. Full lines, predicted curves; broken lines, experimental results [49]: (A) at 298.15 K; (B) at 313.15 K.

The comparison between experimental and calculated data shows that one can make useful predictions with DISQUAC, even in the case of such very polar molecules as alkanenitriles. The discrepancies are of the same type as with less polar compounds, e.g. carbonates [53], anhydrides [54] and nitroalkanes [5], but are much more important. The flattening of the $H^E$ curves, expecially at low temperatures close to the critical solution point, is a characteristic behavior. It reflects dramatically on the excess heat capacities. As expected, the first-order quasi-chemical approximation is unable to account exactly for the high degree of non-randomness in these mixtures [52].

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