# Solid−Liquid Equilibria of Naphthalene + Alkanediamine Mixtures

**Kamel Khimeche**[†,‡] **and Abdallah Dahmani***[,‡]

Ecole Militaire Polytechnique EMP, BP 17 Bordj-el-Bahri, Alger, Algeria, and Laboratoire de Thermodynamique et de Modélisation Moléculaire, Faculté de Chimie, USTHB, BP 32 El-Alia, 16111 Bab-Ezzouar, Alger, Algeria

A differential scanning calorimeter (DSC) was used to determine binary solid + liquid-phase equilibria (SLE) for naphthalene + diamines $NH_2-(CH_2)_n-NH_2$ ($n = 6$, 8, and 12) mixtures. The results obtained with this technique were compared with those predicted by the modified UNIFAC (Larsen and Gmehling) and ideal models. It was found out that all the systems are simple eutectic systems but there are deviations between experimental and predicted SLE.

## Introduction

Alkane-α,ω-diamines $NH_2-(CH_2)_n-NH_2$ are an important class of compounds in different fields of industry, particularly in the synthesis of numerous polymers. They also act as biochemical model compounds.[1−4] Thermodynamic properties and structural details of some alkane-α,ω-diamines have been investigated.[4−6]

For complex molecules such as biological products, the data of solid + liquid-phase equilibria (SLE) are scarce. Among the methods of SLE measurement, it was shown that differential scanning calorimetry (DSC) is a rapid and sensitive technique, broadly used for the characterization of many kinds of phase change.[7−10]

To further our systematic study of the thermodynamic properties and solid−liquid equilibrium of mixtures of diamines,[11−15] it seemed interesting to test the application of DSC to the determination of SLE of complex systems including polyaromatics and alkane-α,ω-diamines.

In this work, thermodynamic properties of mixtures containing naphthalene + alkanediamines are reported. The data obtained by DSC of SLE for naphthalene + diamines $NH_2-(CH_2)_n-NH_2$ ($n = 6$, 8, and 12) systems are compared with those predicted by the modified UNIFAC (Larsen and Gmehling) and ideal models.

## Experimental Procedures

Most of our products (hexane-1,6-diamine, octane-1,8-diamine, and naphthalene) were supplied from Merck with purity > 99 %. The dodecane-1,12-diamine (purity > 98 %) was purchased from Fluka. All these products were used without further purification. Some alkanediamines are highly hygroscopic,[4] and special care was taken to prepare fully anhydrous samples. Nevertheless some difficulties, probably due to the high level of hygroscopicity of the diamine, were found, particularly for the system hexane-1,6-diamine + naphthalene.

The naphthalene + diamine binary mixtures were prepared as follows:

The sample was heated very slowly inside a glass cell near the melting temperature of the major component. The liquefied sample with continuous stirring was solidified and kept in a desiccator with silica gel. Then a small amount of solid from (6 to 10) $10^{-3}$ g was taken and sealed in a DSC 7 Perkin-Elmer pan for the analysis. The measurements were carried out at constant heating rate of 1 K·min$^{-1}$ and under nitrogen atmosphere (20 mL·min$^{-1}$). Prior to the analysis, the DSC7 was calibrated with indium. Data acquisition (enthalpies of fusion of the pure compounds and onsets of the solid−liquid equilibria temperatures) and processing were done with Perkin-Elmer's Pyris software. The endothermic peaks were optimized for the best localization of the onset temperatures. The mass of the samples was determined with a precision ± 0.0002 g using a Mettler H31 balance. The uncertainty of mole fraction did not exceed ± 0.0005. The uncertainties of the measurements are estimated to be ± 0.20 K for the temperatures and ± 0.40 kJ·mol$^{-1}$ for the heat of fusion.

**Table 1. Melting Temperature ($T_m$) and Melting Molar Enthalpy ($\Delta_{fus}H$) of Pure Compounds**

| compound | $T_m$/K | $\Delta_{fus}H$/kJ·mol$^{-1}$ |
|---|---|---|
| hexane-1,6-diamine (HAD) | 311.60[a] | 39.38[a] |
| | 312.28[b] | 40.21[b] |
| octane-1,8-diamine (ODA) | 324.88[a] | 50.51[a] |
| | 324.79[b] | 50.98[b] |
| dodecane-1,12-diamine (DDDA) | 341.84[a] | 67.05[a] |
| | 340.53[b] | 67.10[b] |
| naphthalene | 354.69[a] | 19.55[a] |
| | 353.30[c] | 18.78[c] |

[a] Our experimental values. [b] Dall'acqua et al.[4] [c] Peng et al.[16]

## Results and Discussion

The melting points of the pure samples are in good agreement with literature data.[4,16] Physical properties of pure compounds $T_m$ (melting temperature) and $\Delta_{fus}H$ (molar enthalpy of fusion) are given in Table 1.

The systems show eutectics as the first peak that appeared at a constant temperature. The area of the eutectic peak in a DSC curve is affected by the amount of the sample and the enthalpy of the melting component. Tables 2 to 4 list the experimental SLE temperatures for the different systems. The SLE were reproducible to within 0.4 % for the system hexane-1,6-diamine + naphthalene and 0.2 % for the systems octane-1,8-diamine + naphthalene and dodecane-1,12-diamine + naphthalene. The deviations recorded in the experimental results can be attributed principally to the hydration of the diamines that can occur during

---

* Corresponding author. E-mail: Abdahmani@yahoo.fr.
[†] Ecole Militaire Polytechnique EMP.
[‡] Laboratoire de Thermodynamique et de Modélisation Moléculaire.

10.1021/je0502851 CCC: $33.50 © 2006 American Chemical Society
Published on Web 02/07/2006

**Table 2. Experimental Solid−Liquid Equilibrium Temperatures for the System Hexane-1,6-diamine (1) + Naphthalene (2)**

| $x_1$ | $T_{F1}$/K | $T_{F2}$/K | $x_1$ | $T_{F1}$/K | $T_{F2}$/K |
|---|---|---|---|---|---|
| 0.0000 | 354.69 | | 0.6511 | 307.58 | |
| 0.0439 | 350.61 | | 0.6896 | 305.73 | |
| 0.1035 | 345.64 | | 0.7912 | 301.85 | |
| 0.2001 | 338.08 | | 0.8342 | 300.15 | |
| 0.3042 | 329.13 | | 0.8741 | | 299.02 |
| 0.3989 | 322.95 | | 0.7912 | | 300.94 |
| 0.4273 | 320.65 | | 0.9345 | | 305.60 |
| 0.4955 | 316.39 | | 0.9755 | | 309.58 |
| 0.5792 | 312.06 | | 1.0000 | | 311.60 |

**Table 3. Experimental Solid−Liquid Equilibrium Temperatures for the System Octane-1,8-diamine (1) + Naphthalene (2).**

| $x_1$ | $T_{F1}$/K | $T_{F2}$/K | $x_1$ | $T_{F1}$/K | $T_{F2}$/K |
|---|---|---|---|---|---|
| 0.0000 | 354.69 | | 0.4553 | 317.65 | |
| 0.0261 | 351.05 | | 0.4823 | 316.92 | |
| 0.0520 | 348.21 | | 0.5151 | 316.12 | |
| 0.0805 | 345.00 | | 0.5434 | | 316.76 |
| 0.1063 | 345.05 | | 0.5840 | | 317.60 |
| 0.1150 | 341.07 | | 0.6355 | | 318.42 |
| 0.1760 | 336.57 | | 0.6982 | | 320.18 |
| 0.2001 | 333.21 | | 0.7492 | | 319.92 |
| 0.2437 | 328.92 | | 0.8013 | | 321.58 |
| 0.2998 | 325.25 | | 0.9002 | | 323.78 |
| 0.3294 | 322.92 | | 0.9533 | | 324.12 |
| 0.4121 | 319.10 | | 1.0000 | | 324.88 |

**Table 4. Experimental Solid−Liquid Equilibrium Temperatures for the System Dodecane-1,12-diamine (1) + Naphthalene (2).**

| $x_1$ | $T_{F1}$/K | $T_{F2}$/K | $x_1$ | $T_{F1}$/K | $T_{F2}$/K |
|---|---|---|---|---|---|
| 0.0000 | 354.69 | | 0.3503 | 328.99 | |
| 0.0192 | 352.68 | | 0.3956 | 328.43 | |
| 0.0435 | 348.80 | | 0.4502 | | 329.13 |
| 0.0609 | 346.28 | | 0.5012 | | 330.05 |
| 0.0840 | 345.23 | | 0.5863 | | 331.49 |
| 0.1007 | 342.25 | | 0.6305 | | 332.12 |
| 0.1193 | 340.06 | | 0.6675 | | 332.69 |
| 0.1495 | 337.72 | | 0.7222 | | 333.83 |
| 0.2021 | 335.36 | | 0.7882 | | 334.83 |
| 0.2261 | 333.75 | | 0.8311 | | 336.63 |
| 0.2722 | 331.77 | | 0.8884 | | 338.48 |
| 0.3012 | 331.49 | | 1.0000 | | 341.84 |

simple sealing for DSC analysis. As cited in the literature, between hexane-1,6-diamine and its hydrated form, the decrease of the fusion temperature is about 10 K.

SLE data can be used to calculate activity coefficients of the components. In the case of the studied systems, the components are not miscible in the solid phase, and all diagrams present a simple eutectic. Therefore, the activity coefficient $\gamma_i$ of the component $i$, in the liquid phase, can be calculated according to the following expression:[17−19]

$$\ln x_i\gamma_i = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\left(1-\frac{T}{T_{\mathrm{m},i}}\right)+\frac{\Delta C_{p,i}}{R}\left(\ln\frac{T}{T_{\mathrm{m},i}}+\frac{T_{\mathrm{m},i}}{T}-1\right)-\frac{\Delta H_{\mathrm{tr},i}}{RT}\left(1-\frac{T}{T_{\mathrm{tr},i}}\right) \quad (1)$$

where $\Delta_{\mathrm{fus}}H_i$, $T_{\mathrm{m},i}$, $\Delta C_{p,i}$, $\Delta H_{\mathrm{tr},i}$, and $T_{\mathrm{tr},i}$ are the molar enthalpy of fusion, the melting temperature, the molar heat capacity variation (assumed to be independent of $T$) during the fusion process, the enthalpy variation corresponding to the transition, and the transition temperature of the pure component $i$, respectively. Because of the lack of appropriate data representing $\Delta C_{p,i}$ the related terms in eq 1 was neglected. The required physical constants of the pure compounds are reported in Table 1.

The modified UNIFAC, Larsen, and Gmehling models were used for the calculation of the activity coefficients and prediction of SLE. The required geometrical and interaction parameters of our systems have been given elsewhere.[20,21]

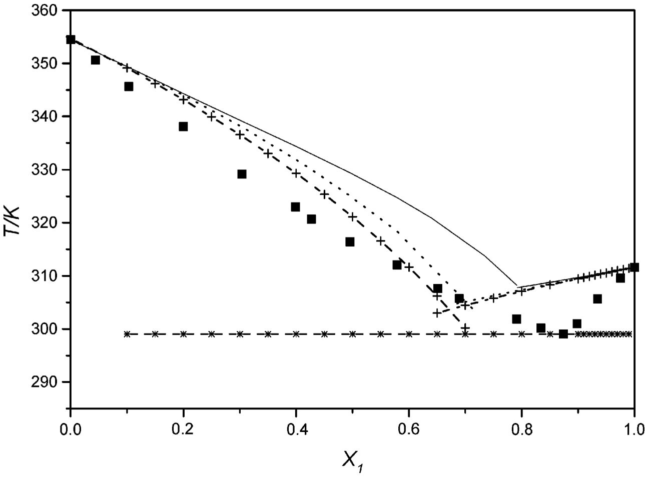

**Figure 1.** Experimental and predicted SLE phase diagrams of hexane-1,6-diamine (1) + naphthalene (2) mixture: ■, experimental results; —, Larsen; ···, Gmehling; − + −, ideal; − ∗ThinSpace−, eutectic temperature.

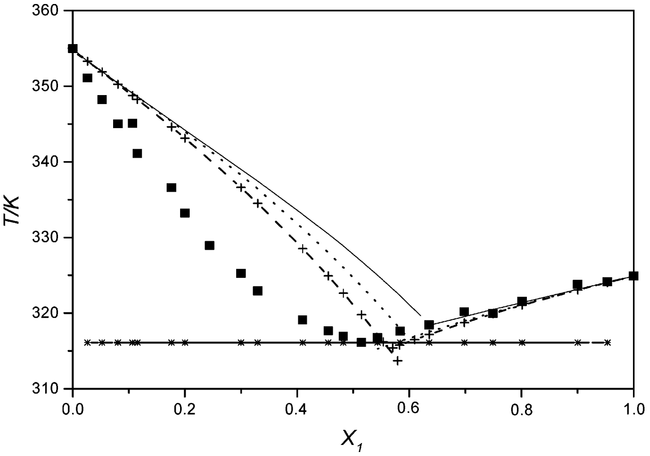

**Figure 2.** Experimental and predicted SLE phase diagrams of octane-1,8-diamine (1) + naphthalene (2) mixture: ■, experimental results; —, Larsen; ···, Gmehling; − + −, ideal; − ∗ThinSpace−, eutectic temperature.

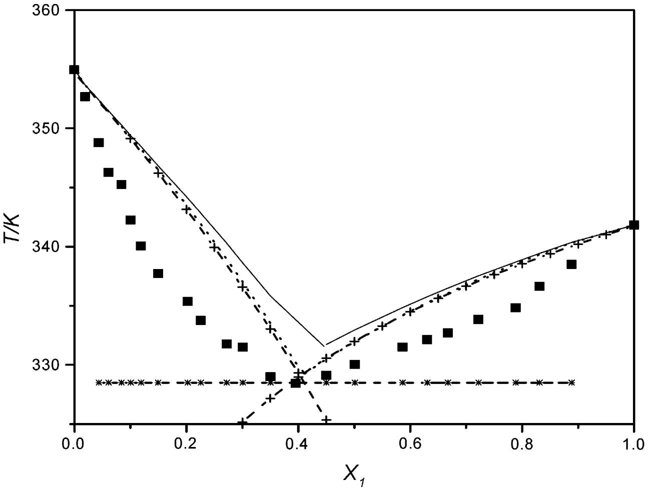

**Figure 3.** Experimental and predicted SLE phase diagrams of dodecane-1,12-diamine (1) + naphthalene (2) mixture: ■, experimental results; —, Larsen; ···, Gmehling; − + −, ideal; − ∗ThinSpace−, eutectic temperature.

Important deviations were observed between experimental and calculated SLE, as shown in Figures 1 to 3. For the binary diamines (1) $NH_2{-}(CH_2)_n{-}NH_2$ ($n$ = 6, 8, and 12) +

**Table 5. Values of the Relative Standard Deviations $\sigma^a$ and of Absolute Mean Deviations $\Delta T^b$ of Equilibrium Temperatures Obtained Using Modified UNIFAC and Ideal Models**

| | | Larsen | | Gmehling | | ideal | |
|---|---|---|---|---|---|---|---|
| system | $n^c$ | $\Delta T$/K | $\sigma$ | $\Delta T$/K | $\sigma$ | $\Delta T$/K | $\sigma$ |
| HDA + naphthalene | 18 | 4.72 | 0.0289 | 3.28 | 0.0198 | 2.55 | 0.0139 |
| ODA + naphthalene | 24 | 7.19 | 0.0330 | 4.90 | 0.0203 | 4.04 | 0.0166 |
| DDDA + naphthalene | 24 | 4.06 | 0.0151 | 2.81 | 0.0119 | 3.29 | 0.0123 |

[a] $\sigma = [1/N\sum_{i=1}^{N}((T_{i\,\mathrm{cal}} - T_{i\,\mathrm{exp}})/T_{i\,\mathrm{exp}})^2]^{1/2}$. [b] $\Delta T/\mathrm{K} = 1/N\sum_{i=1}^{N}|T_{i\,\mathrm{cal}} - T_{i\,\mathrm{exp}}|$. [c] $n$ is the number of data points.

**Table 6. Comparison of Experimental Coordinates of Eutectic Points: $T_{eu}$ and Mole Fraction, $x_{1eu}$, with Values Calculated by UNIFAC (Larsen and Gmehling versions) and Ideal Models**

| | $T_{eu}$/K | | $x_{1eu}$ | |
|---|---|---|---|---|
| system | exp. | cal. | exp. | cal. |
| HDA (1) | 299.02 | 307.90$^a$ | 0.8741 | 0.7950$^a$ |
| + naphthalene (2) | | 305.24$^b$ | | 0.6999$^b$ |
| | | 303.57$^c$ | | 0.6722$^c$ |
| ODA (1) | 316.12 | 318.48$^a$ | 0.5151 | 0.6338$^a$ |
| + naphthalene (2) | | 316.65$^b$ | | 0.5986$^b$ |
| | | 315.45$^c$ | | 0.5660$^c$ |
| DDDA (1) | 328.42 | 331.57$^a$ | 0.3956 | 0.4437$^a$ |
| + naphthalene (2) | | 329.31$^b$ | | 0.4139 |
| | | 328.97$^c$ | | 0.4046$^c$ |

[a] Calculated by UNIFAC (Larsen version). [b] Calculated by UNIFAC (Gmehling version). [c] Calculated (ideal model).

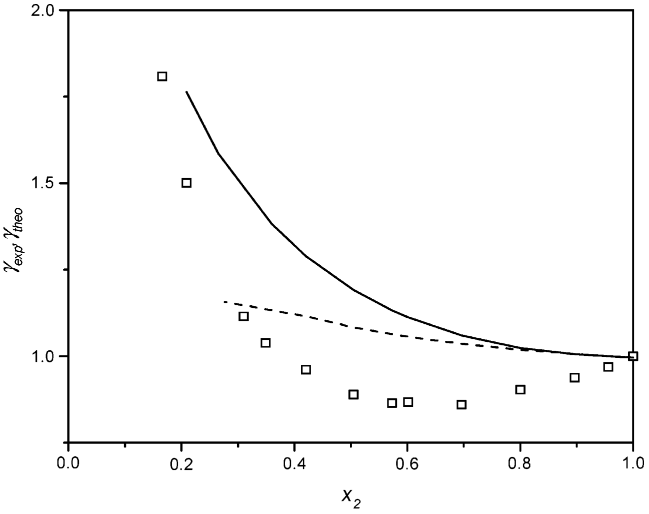

**Figure 4.** Experimental and predicted activity coefficients, $\gamma_i$, vs $x_2$ for hexane-1,6-diamine (1) + naphthalene (2) mixture: □, experimental results; —, Larsen; − −, Gmehling.

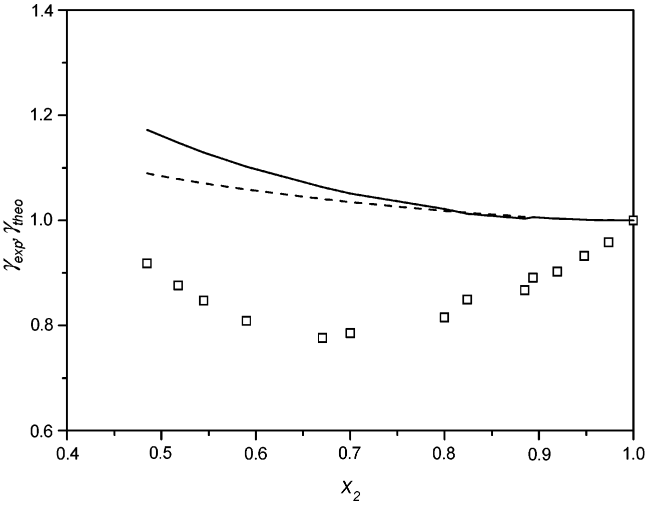

**Figure 5.** Experimental and predicted activity coefficients, $\gamma_i$, vs $x_2$ for octane-1,8-diamine (1) + naphthalene (2) mixture: □, experimental results; —, Larsen; − −, Gmehling.

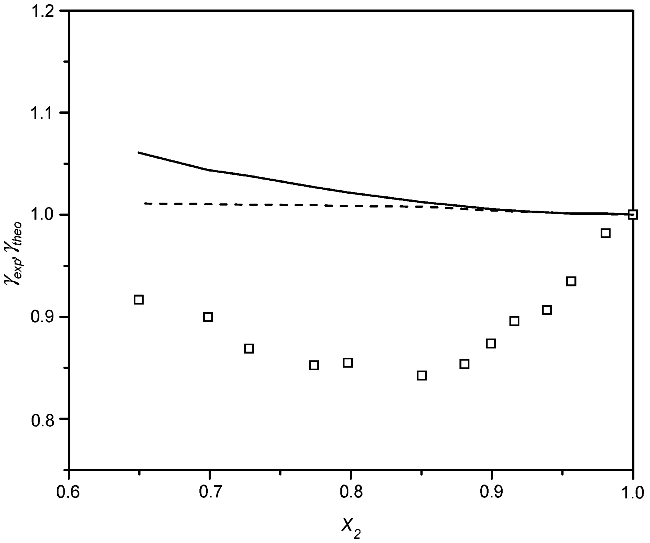

**Figure 6.** Experimental and predicted activity coefficients, $\gamma_i$, vs $x_2$ for dodecane-1,12-diamine (1) + naphthalene (2) mixture: □, experimental results; —, Larsen; − −, Gmehling.

naphthalene (2), the relative and the absolute mean deviations of the equilibrium temperatures are given in Table 5.

As shown in Table 6, the experimental values of $T_{eu}$ and $x_{1eu}$ corresponding to the eutectic points are close to those predicted by the different models and depend on the chain length of the alkanediamine. For alkane-α,ω-diamines $NH_2-(CH_2)_n-NH_2$ with $n = 6$, 8, and 12, the values of the molar fractions $x_{1eu}$ corresponding to the eutectic point of the binary alkanediamine (1) + naphthalene (2) systems decrease with the increase of $n$, the number of carbon atoms. The behavior is different for $T_{eu}$ that increases, like the melting temperature, with and increase of the chain length.

Predicted phase diagrams for the SLE investigated in this work are characterized by positive deviations from Raoult's law. Experimental SLE shows the opposite behavior. These deviations illustrated by Figures 4 to 6 could be assigned to the hydrogen bonding between an amine and aromatic electrons and possible interactions between non-bonding electron from N and an aromatic system as mentioned by Letcher and Bayles.[22]

## Conclusion

We confirm by this work that the DSC method is effective in the study of SLE. The determination of binary SLE by analyzing DSC curves for systems exhibiting simple eutectic is found to be efficient and accurate.The survey evidences the eutectic character of the binary system diamines (1) $NH_2-(CH_2)_n-NH_2$ ($n = 6$, 8, and 12) + naphthalene (2) mixtures and allows location of the eutectic point composition. The dependence of the thermodynamic parameters of fusion and SLE on the even number $n$ of carbon atoms in the alkyl chain of a series of alkyldiamines was also observed. Heat of fusion as well as the melting and eutectic temperatures increase as a function of n. But an opposite behavior is observed for the molar fraction $x_{leu}$ of the diamine corresponding to the eutectic point.

Deviations were recorded between the values of the activity coefficients given by the UNIFAC model and those resulting from the experiment. This can be explained by the weakness of the group contribution model in the description of complex systems such as polyaromatics and diamine mixtures. The presence of intramolecular effects, especially of the proximity effect, is difficult to incorporate into activity coefficient models. As already demonstrated for polyfunctional molecules, the proximity of two identical or different groups has a strong influence on the interaction parameters. Previous studies[23] have shown that the occurrence of a functional group in cycle and/or the proximity of another group may change considerably the interaction parameters.

## Literature Cited

(1) Konin, C.; Delmotte, A.; Larno, P.; Van Mele, B. Influence of polymerization conditions on melt crystallisation of partially aliphatic polyimides. *Polymer* **1998**, *39*, 3697−3702.
(2) Nagata, M. Novel regular network polyimide films from mellitic acid and aliphatic and aromatic diamines or diisocyanates. *Polymer* **1995**, *36*, 2657−2662.
(3) Fulem, M.; Ruzicka, K.; Della Gatta, G.; Badea, E.; Ruzicka, V. Vapor pressure and enthalpies of vaporization and sublimation of alkane-$\alpha,\omega$-diamines. 13 ICTAC, Italie, Sept 2004.
(4) Dall'acqua, L.; Della Gatta, G.; Nowicka, B.; Ferloni, P. Enthalpies and entropies of fusion of 10 alkane-$\alpha,\omega$-diamines $H_2N-(CH_2)_n-NH_2$ where $3 \leq n \leq 12$. *J. Chem. Thermodyn.* **2002**, *34*, 1−12.
(5) Thalladi, V. R.; Boese, R.; Weiss, H. C. The melting point alternation in $\alpha,\omega$-alkanediols and $\alpha,\omega$-alkanediamines: interplay between hydrogen bonding and hydrophobic interactions. *Angew. Chem., Int. Ed.* **2000**, *39*, 918−922.
(6) Messerly, J. F.; Finke, H. L.; Osborn, A. G.; Douslin, D. I. Low-temperature calorimetric and vapour-pressure studies on alkanediamines. *J. Chem. Thermodyn.* **1975**, *7*, 1029−1046.
(7) Matsuoka, M.; Ozawa, R. Determination of solid−liquid-phase equilibria of binary organic systems by differential scanning calorimetry. *J. Cryst. Growth* **1989**, *96*, 596−604.
(8) Shibuya, H.; Suzuki, Y.; Yamaguchi, K.; Arai, K.; Saito, S. Measurement and prediction of solid−liquid-phase equilibria of organic compound mixtures. *Fluid Phase Equilib.* **1993**, *82*, 397−405.
(9) Dalmazzone, D.; Kharrat, M.; Lachet, V.; Fouconnier, B.; Clausse, D. DSC and PVT measurements. Methane and trichloromethane hydrate dissociation equilibria. *J. Therm. Anal. Calorim.* **2002**, *70*, 493−505.
(10) Benkhenouf, M.; Khimeche, K.; Dahmani, A. Solid−liquid phase equilibria for aromatic compounds. *J. Phys. IV Fr.* **2004**, *113*, 7−9.
(11) Dahmani, A.; Ait Kaci, A.; Jose, J. Vapour pressures and excess functions of *N*,*N*,*N*′,*N*′-tetramethylalkanediamine + cyclohexane. A group contribution study of the N−N proximity effect. *Fluid Phase Equilib.* **1997**, *130*, 271−279.
(12) Dahmani, A.; Ait Kaci A.; Jose, J. Excess properties of *N*,*N*,*N*′,*N*′-tetramethylalkanediamine + *n*-heptane. A study of the N−N proximity effect. *Thermochim. Acta* **1997**, *292*, 39−44.
(13) Dahmani, A.; Ait Kaci A.; Jose, J. Vapour pressures and excess functions of 1,4-dimethylpiperazine + *n*-heptane or cyclohexane measurement and prediction. *Fluid Phase Equilib.* **1997**, *134*, 255−265.
(14) Kecira, Z.; Dahmani, A. Excess enthalpies of alkanediamines + benzene or + toluene mixtures. Prediction using group contribution models. *Thermochim. Acta* **2001**, *369*, 1−7.
(15) Allal, F.; Dahmani, A. Measurement and prediction of solid−liquid equilibria for diamine + *n*-heptane, or cyclohexane. *Fluid Phase Equilib.* **2001**, *190*, 33−45.
(16) Peng, C.; Liu, H.; Hu, Y. Solid−liquid equilibria based on an equation of state for chain fluids. *Fluid Phase Equilib.* **2001**, *180*, 299−311.
(17) Jakob, A.; Joh, R.; Rose, C.; Gmehling, J. Solid−liquid equilibria in binary mixtures of organic compounds. *Fluid Phase Equilib.* **1995**, *113*, 117−126.
(18) Dahmani, A.; AitKaci, A.; Mokbel, I.; Ghanem, G.; Jose, J. Solid−liquid phase equilibria for tetrachloromethane + *n*-alkanes. *J. Chim Phys*. **1995**, *92*, 1093−1103.
(19) Domanska, U.; Gonzalez, J. A. Solid−liquid equilibria for systems containing long-chain 1-alkanols. II. Experimental data for 1-dodecanol, 1-tetradecanol, 1-hexadecanol, 1- octadecanol or 1-eicosanol + $CCl_4$ or + cyclohexane mixtures. Characterisatization in terms of DISQUAC. *Fluid Phase Equilib.* **1996**, *123*, 167−187.
(20) Larsen, B. L.; Rasmussen, P.; Frendeslund, A. A modified UNIFAC Group −Contribution Model for prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286.
(21) Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.
(22) Letcher, T. M.; Bayles, J. W. A molecular interpretation of the thermodynamics of some binary liquid mixtures. *J. S. Afr. Chem. Inst.* **1972**, *25*, 53−59.
(23) Artal, M.; Munoz Embid, J.; Otin, S.; Velasko, I.; Kehiaian, H. V. Excess enthalpies of binary mixtures containing $\alpha,\omega$-dibromoalkanes. Measurement and analysis in terms of group contributions. *Fluid Phase Equilib.* **1991**, *70*, 267−279.

Received for review July 20, 2005. Accepted January 17, 2006.

JE0502851