Binary Solid−Liquid Equilibria of *N*,*N*-Dimethylacetamide with 1,2-Dichloroethane, Dichloromethane, and 1-Propanol

Z. Atik,[†] J. Ahlers, J. Lohmann, and J. Gmehling*

Lehrstuhl für Technische Chemie (FB9), Carl von Ossietzky Universität Oldenburg, Postfach 2503, D-26111 Oldenburg, Germany

Solid−liquid phase equilibria (SLE) of binary mixtures of *N*,*N*-dimethylacetamide with 1,2-dichloroethane, dichloromethane, and 1-propanol were measured using the visual method at atmospheric pressure. The system *N*,*N*-dimethylacetamide was correlated by the NRTL equation. While the phase diagram $(T, x)_P$ of *N*,*N*-dimethylacetamide with 1-propanol is well represented by modified UNIFAC (Dortmund) assuming eutectic behavior, *N*,*N*-dimethylacetamide with dichloromethane forms a distinct compound with a melting point at equimolar composition.

Introduction

Crystallization is an important separation process in several industrial fields such as the food, biological, petrochemical, and pharmaceutical industries and leads to products of high purity. For the design and optimization of crystallization processes in chemical production plants, reliable phase diagrams of the binary and multicomponent mixtures are required. For fitting the required temperature-dependent parameters of g^E-models and group contribution methods, solid−liquid equilibria data of eutectic systems can be used to cover the low-temperature range. Therefore, solid−liquid equilibrium measurements contribute successfully to the development of software tools used for the synthesis of separation processes.[1−3]

Thermodynamic properties of mixtures formed by *N*,*N*-dimethylacetamide are poorly studied, and their experimental data are scarce in the literature. To interpret the chemical and physical properties of these mixtures, to extend the SLE database, and for the further development of the group contribution method modified UNIFAC (Dortmund), this paper reports experimental solid−liquid equilibrium data of *N*,*N*-dimethylacetamide with 1,2-dichloroethane, dichloromethane, and 1-propanol.

Solid−liquid equilibria of eutectic systems without phase transitions in the solid phase can be calculated using the following simplified thermodynamic relation

$$\ln x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}} = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\left(1 - \frac{T}{T_{\mathrm{fus},i}}\right) \qquad (1)$$

where $\Delta_{\mathrm{fus}}H_i$ and $T_{\mathrm{fus},i}$ are the enthalpy of fusion and melting temperature of the pure component i, T is the absolute temperature of the mixture, and x_i^{L} is the solubility of component i in the liquid phase.[4] Since the activity coefficient γ_i^{L} depends on composition as well as temperature, eq 1 must be solved iteratively.

Experimental Section

Materials. Each commercial substance was stored over molecular sieves (4 Å effective pore size) to remove any traces of water. The purity, detected by GC (FID), and the water content, determined by Karl Fischer titration, of each substance are given in Table 1.

The solid−liquid equilibrium measurements of the pure components and all binary mixtures were performed visually by a static apparatus, which has been described in detail previously.[5,6] The cooling was achieved by a Lauda cryostat (model RUK 90W), which controls the temperature within 50 mK. With the help of the cooling liquid ethanol, the mixing vessel could be cooled to temperatures down to 183 K. The temperature was measured by a Rosemount platinum resistance thermometer calibrated according to ITS-90 and was read by a Hart Scientific temperature bridge (model 1506) with an accuracy of 5 mK. The accuracy of the melting temperature was determined to be ±0.015 K; the accuracy of the composition is ±0.0001. Below 195 K, mixtures of dichloromethane and respectively 1-propanol with *N*,*N*-dimethylacetamide become quite viscous, resulting in poor visibility and limiting the reproducibility of the results. Therefore, these data were not included in the tables.

Results

The physical properties needed for all calculations were taken from the Dortmund Data Bank (Table 1). The results of the solid−liquid equilibrium measurements of $H_3CCON(CH_3)_2$ + 1,2-$C_2H_4Cl_2$, $H_3CCON(CH_3)_2$ + CH_2Cl_2, and $H_3CCON(CH_3)_2$ + 1-C_3H_7OH are listed in Table 2, and their phase diagrams are represented in Figures 1−3. Figure 1 shows the experimental results of the system $H_3CCON(CH_3)_2$ + 1,2-$C_2H_4Cl_2$ together with the correlation of the NRTL[7] equation (NRTL parameters: $\Delta g_{12} = -1979.7$ J/mol, $\Delta g_{21} = -18.754$ J/mol, $\alpha_{12} = 0.3050$).

In Figure 3 the experimental results of the solid−liquid equilibrium of $H_3CCON(CH_3)_2$ + 1-C_3H_7OH are represented together with the predicted data using the thermodynamic model modified UNIFAC (Dortmund) assuming eutectic behavior. Besides vapor−liquid equilibria at 363.15 K,[9] two excess enthalpy data sets at 298.15 K[10] and 313.15 K[11] were included for fitting the group interaction param-

---

[†] Research Guest, Institute of Chemistry, University of Sciences and Technology Houari Boumediene, P.O. Box 32, El-Alia, 16111 Bab-Ezzouar, Algeria.

* To whom correspondence should be addressed. E-mail: gmehling@tech.chem.uni-oldenburg.de. Internet: http://www.uni-oldenburg.de/tchemie.

10.1021/je010063c CCC: $20.00

Table 1. Purities and Pure Component Properties of the Applied Chemicals Taken from the Dortmund Data Bank (DDB)

compound	supplier	CAS number	purity/%	water content/ppm	$\Delta_{fus}H$/J·mol^{-1}	T_{fus}/K
N,*N*-dimethylacetamide	BASF	127-19-5	>99.9	46.1	10418	251.42[a]
1,2-dichloroethane	Riedel de Häen	107-06-2	>99.9	13.5	8843	237.65
dichloromethane	Riedel de Häen	75-09-2	>99.9	3.3	6002	178.01
1-propanol	Aldrich	71-23-8	>99.9	83.8	5195	147.05

[a] Measured by the visual method.

Table 2. Solid−Liquid Equilibria of *N*,*N*-Dimethylacetamide + 1,2-Dichloroethane, + Dichloromethane, + 1-Propanol

$H_3CCON(CH_3)_2$ (1) + 1,2-$C_2H_4Cl_2$ (2)		$H_3CCON(CH_3)_2$ (1) + CH_2Cl_2 (2)		$H_3CCON(CH_3)_2$ (1) + 1-C_3H_7OH (2)	
x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	237.67	0.2014	198.52	0.4587	210.60
0.0528	234.73	0.2469	206.11	0.5033	216.08
0.1207	230.25	0.2927	212.31	0.5453	220.30
0.1499	227.97	0.3500	217.67	0.6068	225.98
0.2090	222.80	0.3946	220.56	0.6469	229.65
0.2557	218.48	0.4534	222.69	0.6838	232.94
0.3067	212.71	0.4985	223.29	0.7481	236.92
0.3478	207.64	0.5528	222.54	0.8002	240.35
0.3986	200.92	0.6011	220.97	0.8496	243.50
0.4486	202.85	0.6250	218.96	0.9045	246.58
0.5010	210.64	0.6767	225.88	0.9500	248.75
0.5462	215.91	0.7476	234.97	1.0000	251.40
0.5964	221.74	0.7991	240.21		
0.6462	226.62	0.8501	243.26		
0.6980	231.50	0.8987	246.07		
0.7483	235.72	0.9513	248.92		
0.7887	238.80	1.0000	251.40		
0.8451	242.91				
0.8962	246.11				
0.9397	248.44				
1.0000	251.41				

Table 3. New Modified UNIFAC (Dortmund) Interaction Parameters[a]

n	m	a_{nm}/K	b_{nm}	$10^2 c_{nm}$/K^{-1}	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}
1	48	1529.52	−6.2025	0.9754	82.60	−0.6150	-0.623×10^{-3}
5	48	1627.81	−5.8598	0.5497	−808.40	3.8321	-0.587×10^{-2}

[a] Main groups: $n = 1$, CH_2; $n = 5$, OH; $m = 48$, $CONR_2$ (dialkylated amides).

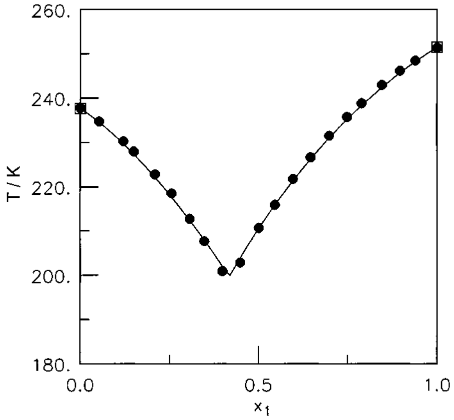

Figure 1. Solid−liquid equilibrium for the system *N*,*N*-dimethylacetamide (1) + 1,2-dichloroethane (2): ●, experimental data; —, NRTL data; □, melting points taken from the Dortmund Data Bank.

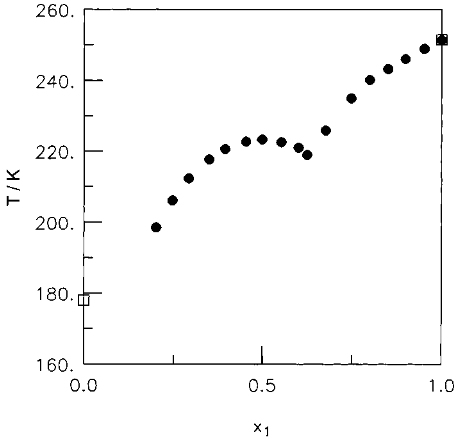

Figure 2. Solid−liquid equilibrium for the system *N*,*N*-dimethylacetamide (1) + dichloromethane (2): ●, experimental data; □, melting points taken from the Dortmund Data Bank.

eters, which are listed in Table 3. The correlation of the results using the NRTL equation and the modified UNIFAC Dortmund prediction[8] are in good agreement with the experimental data.

The SLE data of the system $H_3CCON(CH_3)_2$ + CH_2Cl_2 cannot be predicted using eq 1 because it does not show eutectic behavior. The phase diagram is characterized by the formation of a stable, equimolar compound $H_3CCON(CH_3)_2 \cdot CH_2Cl_2$ with a melting point of about 223.5 K. The strong interactions between the two compounds are underlined by the fact that this system shows large and negative excess enthalpies < −2000 J·mol^{-1} at equimolar composition. An intermolecular hydrogen bond between the hydrogen atoms of the dichloromethane molecule and the free electron pair of the amide function of *N*,*N*-dimethylacetamide may be responsible for the observed phenom-

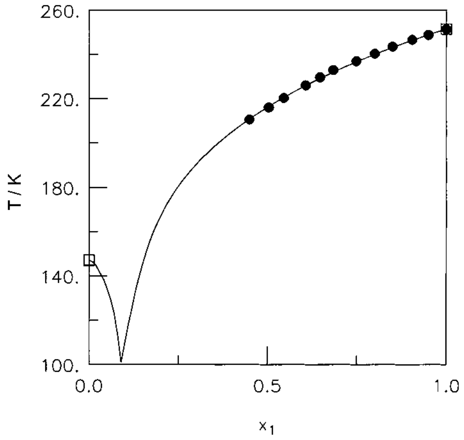

Figure 3. Solid−liquid equilibrium for the system *N*,*N*-dimethylacetamide (1) + 1-propanol (2): ●, experimental data; −, modified UNIFAC (Dortmund) data; □, melting points taken from the Dortmund Data Bank.

enon. Since the electron-attracting effect of the chloro atoms is smaller for 1,2-dichloroethane than for dichloromethane, the hydrogen bonds between 1,2-dichloroethane and *N*,*N*-dimethylacetamide should be weaker and therefore no formation of a stable adduct is observed in the solid−liquid phase diagram. This explanation is also confirmed by a smaller negative excess enthalpy of about −500 J·mol^{-1} at equimolar composition for this system.

Literature Cited

(1) Gmehling, J.; Möllmann, C. Synthesis of Distillation Processes Using Thermodynamic Models and the Dortmund Data Bank. *Ind. Eng. Chem. Res.* **1998**, *37*, 3112−3123.
(2) 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.
(3) Gmehling, J.; Lohmann, J.; Jakob, A.; Li, J.; Joh, R. A Modified UNIFAC (Dortmund) Model. Revision and Extension. *Ind. Eng. Chem. Res.* **1998**, *37*, 4876−4882.
(4) Gmehling, J.; Anderson, T. F.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 269−273.
(5) Jakob, A.; Joh, R.; Rose, C.; Gmehling, J. Solid−Liquid Equilibria in Binary Mixtures of Organic Compounds. *Fluid Phase Equilib.* **1995**, *113*, 117−126.
(6) Ahlers, J.; Lohmann, J.; Gmehling, J. Binary Solid−Liquid Equilibria of Organic Systems Containing Different Amides and Sulfolane. *J. Chem. Eng. Data* **1999**, *44*, 727−730.
(7) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135−144.
(8) Wittig, R.; Lohmann, J.; Joh, R.; Horstmann, S.; Gmehling, J. Vapor-Liquid Equilibria and Enthalpies of Mixing in a Temperature Range from 298.15 K to 413.15 K for the Further Development of Modified UNIFAC (Dortmund). *Ind. Eng. Chem. Res.*, submitted.
(9) Kietz, E.; Bittrich, H.-J.; Hauthal, W. H. *Z. Phys. Chem. (Leipzig)* **1985**, *226*, 281−288.
(10) Oba, M.; Murakami, S.; Fujishiro, R. *J. Chem. Thermodyn.* **1977**, *9*, 407−414.
(11) Pikkarainen, L. *J. Solution Chem.* **1986**, *15*, 473−479.

Received for review February 26, 2001. Accepted May 22, 2001. We are grateful to the Algerian Ministry of Higher Education for financial support of Dr. Z. Atik.

JE010063C