Isothermal Vapor−Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Water + Sulfolane and Methanol + *N*-Methyl-2-pyrrolidone[†]

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Isothermal vapor−liquid equilibrium (VLE) and excess enthalpy (H^E) data for the two binary systems water + sulfolane and methanol + *N*-methyl-2-pyrrolidone (NMP) were measured by means of a static technique and an isothermal flow calorimeter, respectively. The experimental data are presented using temperature-dependent interaction parameters for the nonrandom two-liquid model, which were fitted simultaneously to all experimental data from this work and from the literature, and allow us to compare the measured data with the data of the other authors. Furthermore, the experimental results from this work are compared to predictions using the Mod. UNIFAC (Do) group contribution method.

Introduction

For the synthesis, design, and optimization of separation processes, thermodynamic models (G^E models, equations of state, and group contribution methods) can be applied. For the development of these methods, a reliable knowledge of the phase equilibrium behavior is required, and consequently, a systematic extension of the existing database is desirable.

The investigated systems water + sulfolane and methanol + *N*-methyl-2-pyrrolidone are solvent mixtures that are typical for industrial gas absorption processes. Such solvent blends can be designed to achieve desired solvent properties such as capacity and selectivity for the compounds to be separated, viscosity, vapor pressure, etc.

For the binary systems water + sulfolane and methanol + *N*-methyl-2-pyrrolidone, experimental information such as vapor−liqiud equilibria (VLE) data, H^E data, and activity coefficients at infinite dilution are available in the literature. Since these data cover only a temperature range from (288 to 362 K), further measurements were performed at higher temperatures in this investigation. The isothermal *P*−*x* data for both systems were measured with the help of a computer-operated static apparatus. Additionally, excess enthalpy data were measured at the same temperatures with a commercial isothermal flow calorimeter.

Excess enthalpy data are important to describe the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation

$$\left(\frac{\partial \ln \gamma_i}{\partial \, 1/T}\right)_{P,x} = \frac{\bar{H}_i^{\,E}}{R} \qquad (1)$$

The experimental data of this work are presented in comparison to the results of the other authors,[1−16] calculations using the parameters for the nonrandom two-liquid (NRTL) model[17] obtained by a simultaneous correlation of

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Table 1. Supplier, Purity, and Water Content of the Chemicals Used

component	supplier	purity/% GC	water content/ mass ppm
sulfolane	Merck	>99.9	15
methanol	Riedel de Haen	>99.9	45
N-methyl-2-pyrrolidone	Riedel de Haen	>99.9	20

Table 2. Experimental *P*−*x* Data for the System Water (1) + Sulfolane (2) at 413.18 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	1.34	0.53329	258.05	0.90289	339.46
0.04898	32.25	0.55568	264.72	0.93461	345.25
0.11521	71.05	0.59614	276.62	0.95827	349.95
0.13149	81.07	0.63068	285.51	0.97436	353.81
0.22663	131.91	0.64573	289.53	0.98518	356.71
0.23344	135.56	0.70032	302.14	0.99253	358.93
0.28660	161.86	0.76127	314.66	0.99664	360.16
0.33469	183.89	0.80874	323.47	0.99815	360.72
0.34589	188.23	0.81478	324.62	0.99935	361.40
0.45093	230.22	0.85032	330.64	1.00000	361.75
0.45861	233.03	0.86206	332.60		

Table 3. Experimental H^E Data for the System Water (1) + Sulfolane (2) at 413.15 K and 1.82 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0621	405	0.6915	1676	0.9243	638
0.1183	712	0.7380	1546	0.9401	524
0.2159	1188	0.7772	1409	0.9544	412
0.3676	1696	0.8395	1140	0.9674	304
0.4800	1855	0.8648	1010	0.9792	199
0.5667	1861	0.8870	883	0.9900	97
0.6355	1789	0.9067	758		

all experimental data (VLE, H^E, and activity coefficients at infinite dilution), and the predictions using the group contribution method Mod. UNIFAC (Do).[18−20]

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Experimental Part

Chemicals. All chemicals except water, which was distilled twice, were purchased from commercial suppliers and dried over a molecular sieve. For the VLE measure-

Table 4. Experimental $P-x$ Data for the System Methanol (1) + N-Methyl-2-pyrrolidone (2) at 393.19

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	7.72	0.58874	303.58	0.94340	597.62
0.04404	21.62	0.62144	330.42	0.96702	616.26
0.10590	42.14	0.66244	361.12	0.98359	629.09
0.18745	72.84	0.73531	421.52	0.99276	636.02
0.27877	114.52	0.80457	480.84	0.99614	638.47
0.38069	169.49	0.86303	531.06	0.99870	640.52
0.48783	237.43	0.90964	569.98	1.00000	641.42

Table 5. Experimental H^E Data for the System Methanol (1) + N-Methyl-2-pyrrolidone (2) at 393.15 K and 1.79 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0576	−148	0.5619	−766	0.8475	−405
0.1114	−275	0.6136	−740	0.8772	−342
0.2093	−471	0.6609	−700	0.9050	−273
0.2959	−612	0.7043	−656	0.9310	−204
0.3732	−703	0.7443	−597	0.9554	−135
0.4425	−755	0.7813	−536	0.9784	−67
0.5051	−771	0.8156	−473	0.9893	−35

Table 6. NRTL Interaction Parameters Fitted Simultaneously to Isothermal $P-x$ and H^E Data

component 1	component 2	i j	a_{ij}/ J·mol^{-1}	b_{ij}/ J·mol^{-1}·K^{-1}	c_{ij}/ J·mol^{-1}·K^{-1}
water	sulfolane	1 2	−6746.32	40.7743	
		2 1	8570.34	−30.1684	
			$\alpha_{12} = 0.20$		
methanol	N-methyl-2-pyrrolidone	1 2	1491.73	−16.4425	0.04192075
		2 1	−1430.37	0.9620	−0.01350399
			$\alpha_{12} = 0.47$		

Table 7. Pure-Component Parameters: Antoine Coefficients A_i, B_i, and C_i

component	A_i	B_i/K	C_i/K
water	7.19621	1730.63	−39.724
sulfolane	6.53290	2255.47	−61.757
methanol	7.20587	1582.27	−33.424
N-methyl-2-pyrrolidone	6.67316	1979.68	−50.988

ments, the chemicals were distilled and degassed as described by Fischer and Gmehling.[21] For the H^E measurements, the compounds were used without degassing. The final purity and water content of the components were checked by gas chromatography and Karl Fischer titrations, respectively, and are given in Table 1.

Apparatus and Procedure. The isothermal $P-x$ data were measured with a computer-driven static apparatus. The experimental procedure for the determination of the VLE data is based on that proposed by Gibbs and Van Ness (1972),[22] where the total pressure P for different overall compositions is measured at constant temperature. The apparatus used in this work is similar to that described previously.[23] It can be used at temperatures between 278 K and 423 K and pressures up to 2.5 MPa.

The thermostated, purified, and degassed compounds are charged into the VLE cell, which was evacuated before and kept in a thermostatic oil bath. The pressure inside the cell is monitored with the help of an oil-filled pressure-transmitter system, which is connected to a pressure sensor (Model 1400A, Paroscientific) outside the thermostat. The temperature is measured with a Pt100 resistance thermometer (Model 1560, Hart Scientific). The overall compositions are determined from the known quantities of liquids injected into the equilibrium cell by stepping motor-driven injection pumps and valves. The liquid-phase composition is obtained by solving mass and volume balance equations which also account for the VLE. The experimental uncertainties of this apparatus are $\sigma(T) = 0.03$ K, $\sigma(P) = 50$ Pa + 0.0001 (P/Pa), and $\sigma(x_i) = 0.0001$.
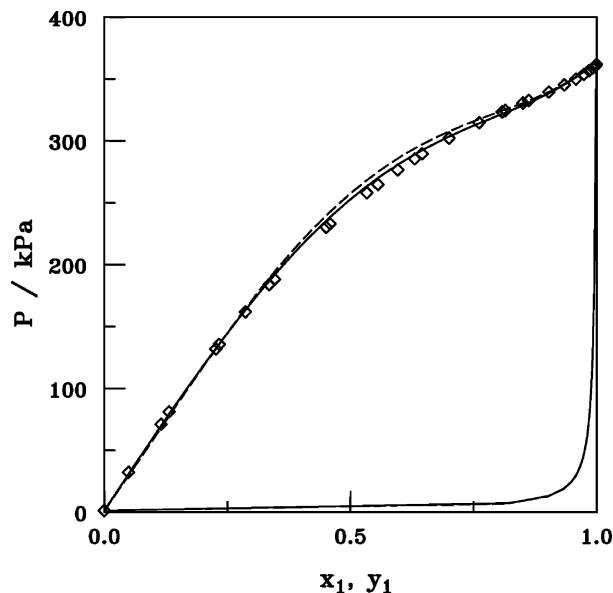
Figure 1. Experimental and predicted $P-x(y)$ behavior of the system water (1) + sulfolane (2): ◇, this work at 413.18 K; solid line, NRTL; dashed line, Mod. UNIFAC (Do).
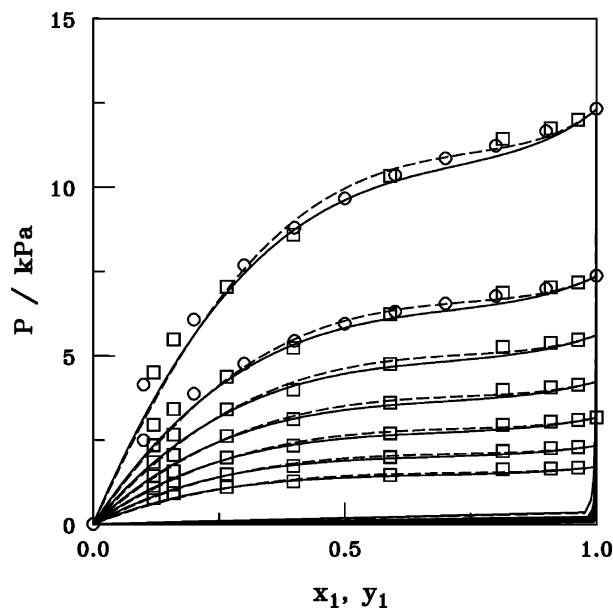
Figure 2. Experimental and predicted $P-x(y)$ behavior of the system water (1) + sulfolane (2): ○, Benoit and Choux[1] at (313.15 and 323.15) K; □, Tommila et al.[15] at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K; solid line, NRTL; dashed line, Mod. UNIFAC (Do).

The commercial isothermal flow calorimeter (Model 7501, Hart Scientific) used for the determination of the excess enthalpy data was described previously by Gmehling (1993).[24] In this apparatus, two syringe pumps (Model LC-2600, ISCO) provide a flow of constant composition through a thermostated calorimeter cell equipped with a pulsed heater and a Peltier cooler. The Peltier cooler is working at constant power producing a constant heat loss from the calorimeter cell. This allows the measurement of endothermal as well as exothermal heat effects. A back-pressure regulator serves to keep the pressure at a level at which evaporation and degassing effects can be prevented. The experimental uncertainties of this device are $\sigma(T) = 0.03$ K, $\sigma(H^E) = 2$ J mol^{-1} + 0.01 (H^E/J mol^{-1}), and $\sigma(x_i) = 0.0001$.
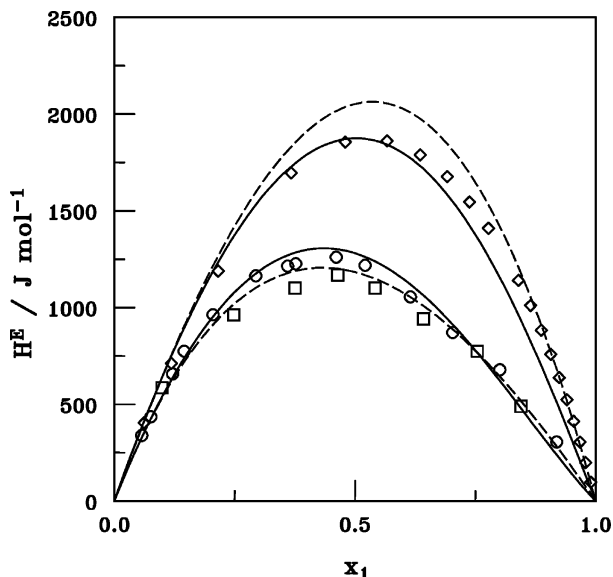
Figure 3. Experimental and predicted excess enthalpy data for the system water (1) + sulfolane (2): ◇, this work at 413.15 K; ○, Benoit and Choux[1] at 303.15 K; □, Tommila et al.[15] at 303.15 K; solid line, NRTL; dashed line, Mod. UNIFAC (Do).
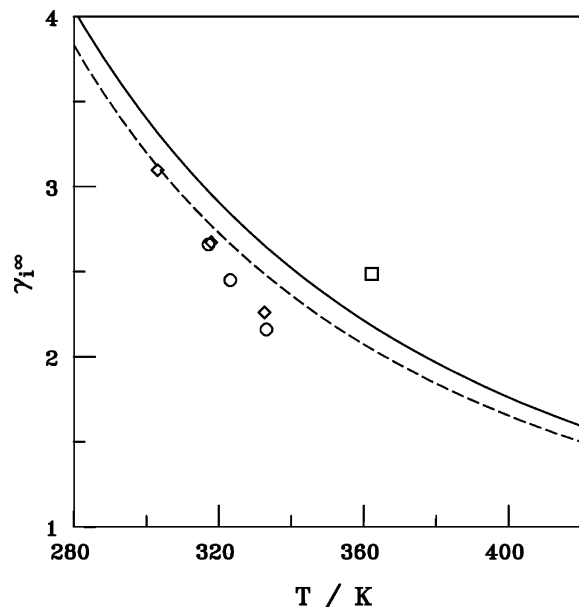

Figure 4. Experimental and predicted activity coefficients at infinite dilution of water in sulfolane: ◇, Möllmann and Gmehling;[8] ○, Lichotkin and Shaposhnikov;[6] □, Hongqin;[4] solid line, NRTL; dashed line, Mod. UNIFAC (Do).

Results

The experimental $P-x$ and H^E data for the investigated systems are listed in Tables 2−5. For both systems, temperature-dependent NRTL parameters were simultaneously fitted to the experimental data from this work and from the literature. The sum of quadratic relative deviations between all experimental and calculated data points was used as objective function. Therefore, all VLE, H^E data, and activity coefficients at infinite dilution (γ_i^∞) were considered, whereby for VLE data, the deviations in pressure were calculated in case of $PT-x$ data, and the deviations in the activity coefficients were calculated for complete $PT-xy$ data sets. To describe the temperature
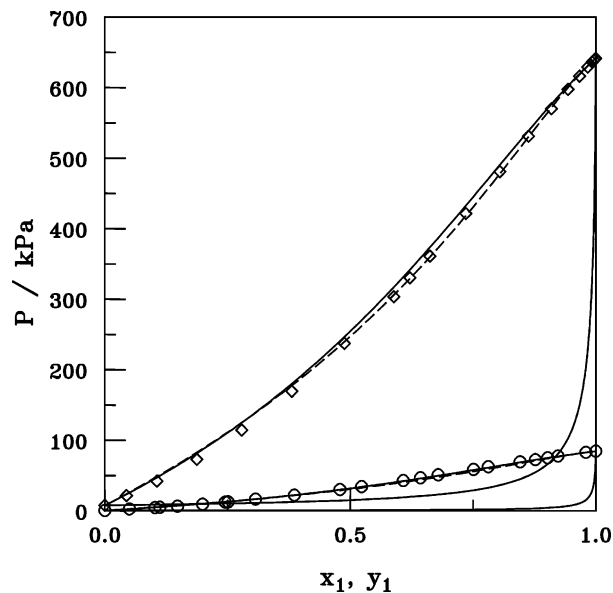

Figure 5. Experimental and predicted $P-x(y)$ behavior of the system methanol (1) + N-methyl-2-pyrrolidone (2): ◇, this work at 393.19 K; ○, Bittrich and Eckert[2] at 333.15 K; solid line, NRTL; dashed line, Mod. UNIFAC (Do).

dependence of the interaction parameters, the following expression was used

$$\Delta g_{ij}/\text{J mol}^{-1} = a_{ij} + b_{ij}(T/\text{K}) + c_{ij}(T/\text{K})^2 \quad (2)$$

The obtained parameters are given in Table 6. The required constants of the Antoine equation

$$\log (P_i^s/\text{kPa}) = A_i - \frac{B_i}{C_i + T/\text{K}} \quad (3)$$

were taken from the Dortmund Data Bank (DDB 2003) and are listed in Table 7. To account only for the excess Gibbs energy, the coefficients A_i of the Antoine equation were adjusted to the experimental vapor pressures of the pure components during the fitting procedure.

A graphical representation of experimental VLE data, H^E data, and activity coefficients at infinite dilution for both systems is given in Figures 1−7 together with the values calculated with the NRTL equation. For the system water + sulfolane, the VLE and H^E data from this work and from other authors can be described using linear temperature-dependent NRTL parameters. Also, the temperature dependence of the activity coefficients at infinite dilution can be described using these parameters. For the system methanol + N-methyl-2-pyrrolidone, quadratic temperature-dependent parameters were necessary to describe all these properties. However, for this system, the experimental activity coefficients at infinite dilution from the different authors show a large scattering, which is a hint for the low quality of the experimental results of some authors. In the diagrams, predictions using the Mod. UNIFAC (Do) group contribution model are also included. With this model, similar results as with the NRTL model are obtained for both systems, although the new data were not included in the parameter regression for Mod. UNIFAC (Do).
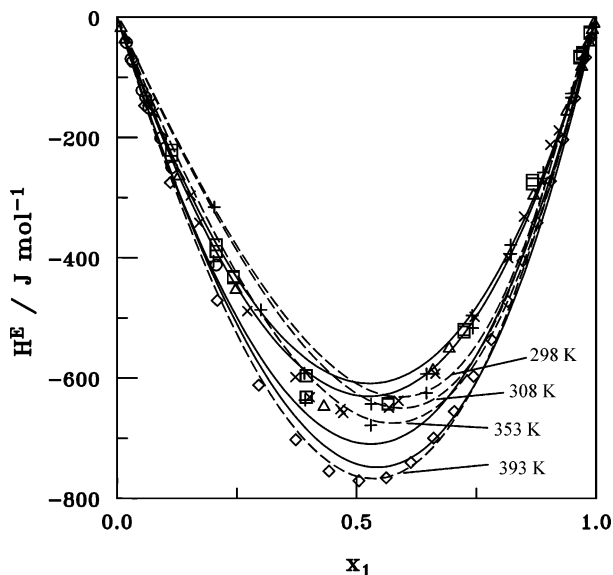
Figure 6. Experimental and predicted excess enthalpy data for the system methanol (1) + *N*-methyl-2-pyrrolidone (2): ◇, this work at 393.15 K; ○, Sitnyakovsky et al.[14] at 298.15 K; □, Joly and Mermet-Dupin[5] at (298.15 and 308.15) K; △, Murakami et al.[9] at 298.15 K; +, Burgdorf[3] at (298.15 and 353.15) K; ×, Lopez et al.[7] at 298.15 K; solid line, NRTL; dashed line, Mod. UNIFAC (Do).
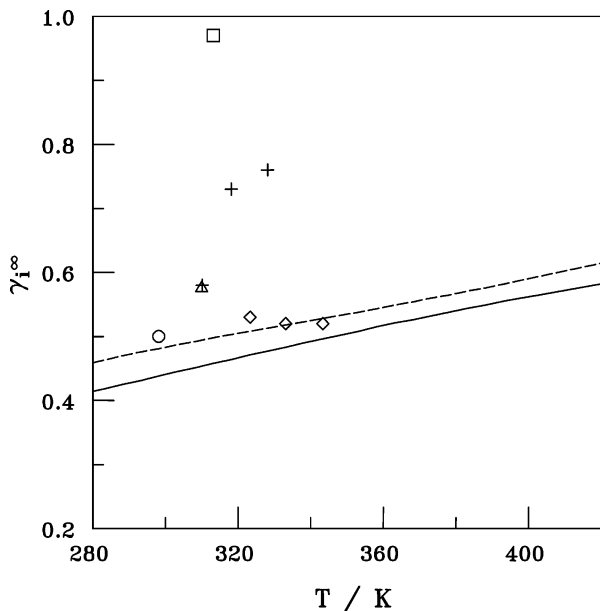

Figure 7. Experimental and predicted activity coefficients at infinite dilution of methanol in *N*-methyl-2-pyrrolidone: ◇, Weidlich et al.;[16] ○, Sitnyakovsky et al.;[13] □, Shaposhnikov and Lichotkin;[12] △, Rajeshwar Rao and Bhagat;[10] +, Rajeshwar Rao and Bhagat;[11] solid line, NRTL; dashed line, Mod. UNIFAC (Do).

Conclusions

Isothermal *P*−*x* data were measured for the binary systems water + sulfolane and methanol + *N*-methyl-2-pyrrolidone using the static technique. Additionally, H^E data were measured with a commercial isothermal flow calorimeter. From these data and experimental data taken from the literature, temperature-dependent NTRL parameters were fitted. VLE and H^E data as well as activity coefficients at infinite dilution predicted with these parameters are in good agreement with experimental data. Only the activity coefficients of some authors seem to be of lower quality and do not agree. Also, the predictions using Mod. UNIFAC (Do) show comparable results. Because of these results, the NRTL parameters given in Table 6 can be recommended for the investigated systems.

Literature Cited

(1) Benoit, R. L.; Choux, G. Reactions in Sulfolane. III. Study of the Interactions between Water and Sulfolane. *Can. J. Chem.* **1968**, *46*, 3215−3219.

(2) Bittrich, H.-J.; Eckert, R. Vapor-Liquid Phase Equilibrium of Binary Mixtures with Methanol or Ethanol as a Component. *Z. Phys. Chem., New Series* **1992**, *175*, 217−234.

(3) Burgdorf, R. Investigation of the Thermophysical Properties of Selected Organic Liquid Mixtures. Thesis, University, Berlin, 1995.

(4) Hongqin, L. The Application and Measurement of Infinite Dilution Activity Coefficients. *J. Chem. Ind. Eng.* **1995**, *12*, 14−20.

(5) Joly, R.-D.; Mermet-Dupin, M. Enthalpies of Mixtures for the Binary *N*-Methylpyrrolidone-Methanol at 25 and 35°C. *C. R. Acad. Sci. Ser. C* **1975**, *280*, 1363−1365.

(6) Lichotkin, E. S.; Shaposhnikov, Yu. K. Gas Chromatographic Study of Physicochemical Properties of Solubility of Organic Substances in Sulfolane. *Tr. Khim. Khim. Tekhnol.* **1970**, *1*, 119−122.

(7) Lopez, E. R.; Garcia, J.; Fernández, J. Excess Properties of Some Methanol + Amide Systems Proposed as Working Fluids for Adsorption Machines. *J. Chem. Eng. Data* **1999**, *44*, 309−313.

(8) Möllmann, C.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution Using Gas−Liquid Chromatography. 5. Results for *N*-Methylacetamide, *N,N*-Dimethylacetamide, *N,N*-Dibutylformamide, and Sulfolane as Stationary Phases. *J. Chem. Eng. Data* **1997**, *42*, 35−40.

(9) Murakami, S.; Tanaka, R.; Fujishiro R. Thermodynamics of Aqueous Solutions of Nonelectrolytes. I. Enthalpies of Transfer of 1-Methyl-2-pyrrolidinone from Water to Aqueous Methanol. *J. Solution Chem.* **1974**, *3*, 71−79.

(10) Rajeshwar Rao, B.; Bhagat, S. D. Evaluation of Solute−Solvent Interactions of Some Nonelectrolytes with *N*-Methylpyrrolidone by Gas−Liquid Partition Chromatography. *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* **1990**, *29*, 652−655.

(11) Rajeshwar Rao, B.; Bhagat, S. D. Thermodynamics of Solution of Some Nonelectrolyte Solutes at Infinite Dilution in *N*-Methylpyrrolidone Stationary Phase by Gas−Liquid Partition Chromatography. *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* **1991**, *30*, 751−755.

(12) Shaposhnikov, Yu. K.; Lichotkin, E. S. Study of Solubility of Some Organic Substances in *N*-Methylpyrrolidone by a Gas Chromatographic Method. *Neftekhimiya* **1970**, *10*, 616−619.

(13) Sitnyakovskii, I. B.; Gaile, A. A.; Semenov, L. V. Selectivity of Solvents in Separation of Mixtures of Oxygen-Containing Organic Compounds. *Zh. Prikl. Khim.* **1989**, *62*, 2765−2768.

(14) Sitnyakovsky, I. B.; Semenov, L. V.; Gaile, A. A.; Koldobovskaya, L. L. Intermolecular Interactions of *N*-Methylpyrrolidone with Oxygen-Containing Organic Substances. *Zh. Prikl. Khim.* **1990**, *63*, 898−902.

(15) Tommila, E.; Lindell, E.; Virtalaine, M.-L.; Laakso, R. Densities, Viscosities, Surface Tensions, Dielectric Constants, Vapour Pressures, Activities, and Heats of Mixing of Sulpholane-Water, Sulpholane-Methanol, and Sulpholane-Ethanol Mixtures. *Suom. Kemistil. B* **1969**, *42*, 95−104.

(16) Weidlich, U.; Roehm, H.-J.; Gmehling, J. Measurement of γ^∞ Using GLC. 2. Results for the Stationary Phases *N*-Formylmorpholine and *N*-Methylpyrrolidone. *J. Chem. Eng. Data* **1987**, *32*, 450−453.

(17) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

(18) Weidlich, U.; Gmehling, J. A Modified UNIFAC Model. 1. Prediction of VLE, h^E and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372−1381.

(19) Gmehling, J.; Li, Jiding; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

(20) Gmehling, J.; Lohmann, J.; Jakob, A.; Li, Jiding; Joh, R. A Modified UNIFAC (Dortmund) Model. 3. Revision and Extension. *Ind. Eng. Chem. Res.* **1998**, *37*, 4876−4882.

(21) Fischer, K.; Gmehling, J. *P-x* and γ^∞ Data for the Different Binary Butanol-Water Systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309−315.

(22) Gibbs, R. E.; Van Ness, H. C. Vapor-Liquid Equilibria from Total-Pressure Measurements. A New Apparatus. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410−413.

(23) Rarey, J.; Gmehling, J. Computer-Operated Differential Static Apparatus for the Measurement of Vapor-Liquid Equilibrium Data. *Fluid Phase Equilib.* **1993**, *83*, 279−287.

(24) Gmehling, J. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.