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Vapor−Liquid Equilibria and Enthalpies of Mixing for Binary Mixtures of *N*-Methylacetamide with Aniline, Decane, Ethylene Glycol, Naphthalene, Phenol, and Water

André de Haan

DSM-Research, Department Base Chemicals and Hydrocarbons, Section Reaction Engineering and Unit Operations, P.O. Box 18, 6160 MD Geleen, The Netherlands

Kai Fischer, Michael Haacke, Oliver Aufderhaar, Martin Petri, and Jürgen Gmehling*

Universität Oldenburg, Technische Chemie, Fachbereich 9, Postfach 2503, 26111 Oldenburg,
Federal Republic of Germany

Isothermal $P-x$ data, isobaric $T-x-y$ data, and enthalpies of mixing were measured for the binary systems of *N*-methylacetamide + aniline, decane, naphthalene, phenol, water, or ethylene glycol using a static apparatus, a Swietoslawski-ebulliometer, an isothermal flow calorimeter, and a Tian-Calvet batch calorimeter. The experimental data were correlated with the help of the NRTL or the UNIQUAC model, for which temperature dependent interaction parameters were fitted simultaneously to VLE and H^E data.

1. Introduction

The present work represents a continuation of a series of experimental studies on vapor−liquid equilibria and excess enthalpies for binary systems containing *N*-methylacetamide. (Aim and de Haan, 1996; de Haan et al., 1995; de Haan and Gmehling, 1996; de Haan et al., 1997).

For the binary systems of *N*-methylacetamide with aniline, decane, ethylene glycol, naphthalene, and phenol, no experimental vapor−liquid equilibrium data have been published up to now. Only for *N*-methylacetamide + water, isobaric (at 1 atm) and isothermal (at 60, 80, and 100 °C) data are available (Kortuem and Van Biedersee, 1970; Manczinger and Kortuem, 1975). Also enthalpy of mixing data are available only for the system *N*-methylacetamide + water at 35 °C (Manczinger and Kortuem, 1975; Zaichikov and Golubinsky, 1996).

2. Experimental Section

2.1. P−x Measurements. The $P-x$ measurements were performed in the static apparatus that had been developed and described by Kolbe and Gmehling (1985) and Fischer and Gmehling (1994). The experimental technique applied is a synthetic one as proposed by Gibbs and Van Ness (1972). No sampling and no analytical methods are required, because the system pressure is measured as a function of liquid composition, which is established by the injection of precisely known amounts of pure, degassed, compressed liquids with the help of precise displacement pumps. A vapor phase correction is taken into account for the liquid composition as described in detail previously (Fischer and Gmehling, 1994). Every isothermal $P-x$ data set consists of two parts, each starting with the injection of a pure substance. After the determination of its vapor pressure, the second component is stepwise injected and the system pressure is measured after every injection, until phase equilibrium is reached after about 30 min. For the isothermal data set *N*-methylacetamide + water at 90 °C, a similar but computer-driven static apparatus was used, which had been described in detail by Rarey and Gmehling (1993).

N-methylacetamide, aniline, decane, ethylene glycol, and water were degassed and purified using the vacuum rectification procedure as described by Fischer and Gmehling (1994). Because of the higher melting points of phenol and naphthalene, they were purified by recrystallization. Furthermore, for these components the procedure of degassing and measurement was modified as follows:

The pure high-melting component was directly weighed into the equilibrium cell. After assembling the apparatus at room temperature, the gas phase was removed from the equilibrium chamber using a vacuum pump. Then the cell was heated up to a temperature above the melting point. After the substance was crystallized by cooling approximately to room temperature, the gas phase was removed again. Several cycles were necessary, before the vapor pressure of the high-melting component remained unchanged at a given temperature indicating complete degassing.

When the measurement was started with the second component, a stepwise injection of the high-melting substance was realized using the piston injectors, charged with a degassed solution of the solid in the second liquid substance. The solution was prepared by degassing the molten solids directly in glass containers with a valve. The amount was determined by weighing after degassing. Then the second component was degassed and directly distilled under vacuum into the container. After weighing, the composition of the degassed mixture (solvent plus dissolved solid) was known.

The accuracy of the obtained data was ±0.0001 for the liquid phase mole fraction, ±0.02 K for the temperature constancy and accuracy, and ±(0.02 kPa + 0.0001 P) for the total pressure.

2.2. T−x−y Measurements. For the system *N*-methylacetamide + ethylene glycol at temperatures above 120 °C, an increase of the pressure with time was observed. This effect was caused by a slow but apparent condensation reaction of ethylene glycol, whereby water was formed. This effect was also observed with pure ethylene glycol. To reduce the residence time a Swietoslawski-ebulliometer was used to determine isobaric $T-x-y$ data as described

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* Corresponding author.

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Table 1. Experimental $P-x$ Data for the Binary System Aniline (1) + N-Methylacetamide (2) at 413.54 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	11.61	0.0980	13.17	0.7692	24.74
0.0082	11.75	0.1159	13.46	0.8269	25.56
0.0119	11.81	0.1615	14.29	0.8718	26.21
0.0154	11.88	0.1704	14.45	0.9074	26.74
0.0200	11.96	0.2663	16.17	0.9373	27.16
0.0231	11.99	0.3121	17.09	0.9591	27.50
0.0286	12.07	0.3422	17.66	0.9690	27.65
0.0344	12.16	0.4562	19.62	0.9790	27.72
0.0398	12.23	0.5092	20.54	0.9850	27.82
0.0474	12.35	0.5757	21.60	0.9924	27.94
0.0574	12.51	0.6204	22.33	0.9977	28.03
0.0684	12.69	0.6533	22.92	1.0000	28.05
0.0810	12.90	0.7181	23.91		

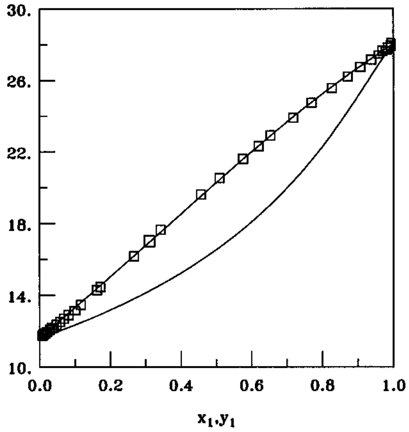

Figure 1. Aniline (1) + N-methylacetamide (2), (□) exptl $P-x$ data and calculated $P-x-y$ behavior using the UNIQUAC equation at 413.54 K.

previously (de Haan et al., 1996). The reaction was also indicated, because the temperature was decreasing with time, but after ca. 15 min samples were taken from both phases and analyzed, whereby also the small water content was determined. This information was used to roughly correct the measured boiling temperature with the help of Raoults law, and the $x-y$ data are given without consideration of the small amounts of water. For each point, a fresh mixture was charged into the ebulliometer in order not to accumulate the water during the measurements.

The accuracy of the obtained data was ±0.002 for the liquid and vapor phase mole fractions, ±0.05 K for the temperature readings (±0.1 K after the correction of the water content), and ±0.05 kPa for the total pressure constancy and accuracy.

2.3. Excess Enthalpies Using an Isothermal Flow Calorimeter. A commercially available computer-driven isothermal flow calorimeter from Hart Scientific (model 7501) was used to measure the excess enthalpies at isothermal and isobaric conditions. The principle of measurement is to compensate the enthalpy of mixing effects with the help of constant cooling and controlled pulsed heating in the nearly adiabatic flow cell. The mixture composition can be varied and measured by setting the flow rates of two calibrated solvent pumps. A back-pressure regulator allows the system to work at higher pressure and thus to prevent evaporation and degassing. The calorimeter and the experimental procedure were described earlier (Gmehling, 1993). The accuracy of H^E is estimated to be better than 1%.

2.4. Excess Enthalpies Using a Tian-Calvet Batch Calorimeter. Because the use of the flow-calorimetric setup requires working with fluids, and neither the pumps nor the back-pressure regulator can be kept at elevated temperatures (present limitation: 40 °C), a Tian-Calvet heat flow batch calorimeter from SETARAM, France (model BT215) was used to determine the excess enthalpies for the systems including phenol and naphthalene. The principle of measurement had been described by Calvet and Prat (1963).

Table 2. Experimental $P-x$ Data for the Binary System n-Decane (1) + N-Methylacetamide (2) at 413.49 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	11.88	0.1090	48.36	0.9298	48.48
0.0004	12.19	0.1387	48.83	0.9395	48.16
0.0029	13.96	0.1810	49.26	0.9496	47.81
0.0071	16.80	0.2206	49.45	0.9596	47.08
0.0100	18.68	0.2583	49.41	0.9663	46.65
0.0124	20.12	0.2681	49.24	0.9736	45.75
0.0147	21.45	0.2757	49.50	0.9803	44.64
0.0170	22.69	0.3342	49.18	0.9859	43.52
0.0193	23.90	0.4566	49.22	0.9910	42.23
0.0231	25.75	0.6313	49.19	0.9932	41.43
0.0263	27.22	0.7745	49.25	0.9959	40.71
0.0307	29.09	0.8627	49.22	0.9986	39.73
0.0433	33.68	0.8806	49.17	1.0000	39.39
0.0591	38.13	0.8992	48.99		
0.0805	42.50	0.9169	48.77		

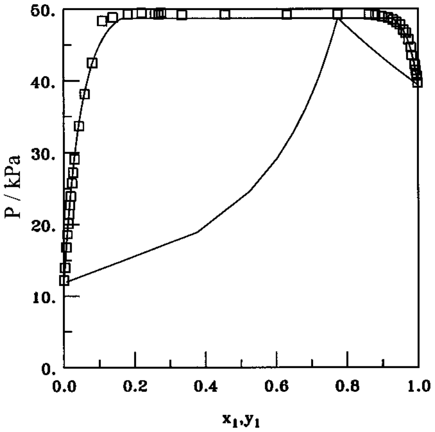

Figure 2. n-Decane (1) + N-methylacetamide (2), (□) exptl $P-x$ data and calculated $P-x-y$ behavior using the NRTL equation at 413.49 K.

The calorimeter consists of two thermal fluxmeters, each constructed by a series of 480 thermocouples surrounding a cylindrical cavity. The fluxmeters are mounted symmetrically around the two cells in an aluminium block. At isothermal conditions, the electrical signal delivered by the power difference of the two fluxmeters is proportional to the thermal power occurring in the cells. It was calibrated with the help of electrical resistance heaters inside the cells. The temperature of the calorimeter block can be regulated using a cold nitrogen gas flow and electrical heating. The temperature is monitored using a Pt 100 resistance thermometer located between the two cells. The temperature is computer controlled, and the signals (temperature and heat flux) are automatically recorded.

Two different types of cells were used, all made of stainless steel with VITON A fittings. For measurements in the high-concentration range, cells with a total volume of approximately 10 cm^3, separated in two chambers (3.8 cm^3 and 5.8 cm^3) by a intermediate bottom, were used. For the low-concentration range, the separated volumes were 0.4 cm^3 and 9.5 cm^3, respectively. After the chambers were charged with the pure compounds, the cells were immersed into the calorimeter. At one time, two cells of the same type charged with different amounts of components were simultaneously used. The cells were thermostated at a given temperature above the melting point of the high-

Table 3. Experimental $T-x-y$ Data for the Binary System Ethylene Glycol (1) + N-Methylacetamide (2) at 9.99 kPa[a]

x_1	y_1	t/°C	x_1	y_1	t/°C
0.0000	0.0000	136.2	0.5231	0.5759	134.2
0.0915	0.0987	135.9	0.6168	0.6657	133.7
0.1697	0.1827	135.7	0.6958	0.7388	133.2
0.2681	0.2954	135.4	0.7801	0.8155	132.8
0.3483	0.3858	135.1	0.8926	0.9083	132.5
0.4372	0.4843	134.7	1.0000	1.0000	132.3

[a] Measured with the help of a Swietoslawski-ebulliometer.

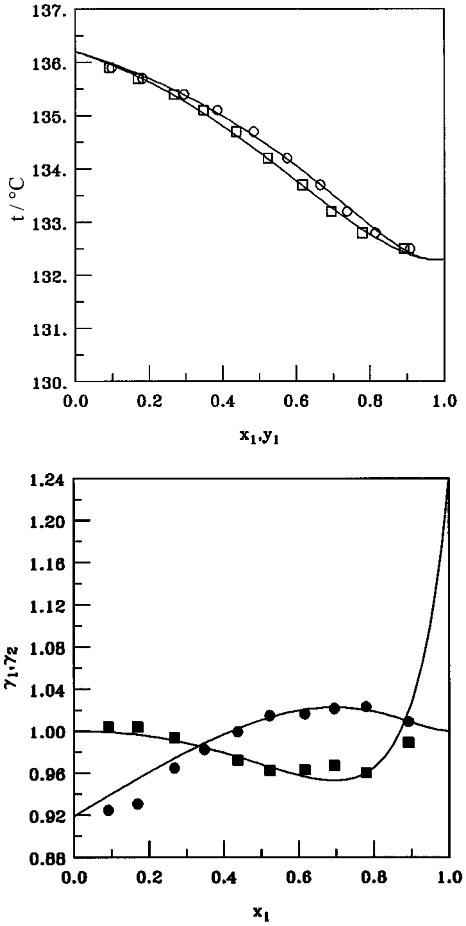

Figure 3. (a, top) Ethylene glycol (1) + N-methylacetamide (2), (□, ○) exptl $T-x-y$ data and calculated $T-x-y$ behavior using the UNIQUAC equation at 9.99 kPa. (b, bottom) Ethylene glycol (1) + N-methylacetamide (2), (●, ■) exptl γ data and calculated behavior using the UNIQUAC equation at 9.99 kPa.

melting substance, which took about 6 h. The constancy of the temperature was better than 0.01 K during the measurement. Afterward the components were mixed by removing the intermediate bottom of the cells from outside the apparatus by lowering it with a metal pole. The calorimeter is equipped with a reversing mechanism, in order to force the mixing process by turning the whole apparatus. The accuracy of the measurement is estimated to be about 3% in H^E.

3. Results

3.1. P−x and T−x−y Data. The iterative procedure applied to perform the vapor phase corrections to derive the liquid mole fractions from the feed composition was described earlier (Fischer and Gmehling, 1994). Because a large number of $P-x$ measurements was made, a flexible Legendre polynomial can be used with a variable number of adjustable parameters to describe the $P-x$ behavior of any complexity within the experimental uncertainty. This allows to determine the slope of the $P-x$ data, which contains the complete information on the activity coefficients. Therefore, (a) especially in the dilute composition range, several points were always measured, which provide precise experimental activity coefficients at infinite dilution; (b) the vapor phase correction does not introduce a model, because the vapor phase composition used is based exclusively on the $P-x$ data.

Table 4. Experimental $P-x$ Data for the Binary System N-Methylacetamide (1) + Naphthalene (2) at 413.51 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	11.74	0.3258	16.39	0.8944	14.00
0.0071	12.17	0.3726	16.51	0.8986	13.86
0.0156	12.59	0.3870	16.57	0.9060	13.74
0.0287	13.18	0.4003	16.62	0.9176	13.54
0.0421	13.67	0.4167	16.64	0.9305	13.31
0.0588	14.16	0.5760	16.56	0.9492	12.91
0.0802	14.65	0.6969	16.16	0.9711	12.40
0.1042	15.03	0.7826	15.62	0.9870	11.99
0.1285	15.35	0.8483	15.02	0.9931	11.81
0.1559	15.61	0.8878	14.45	0.9972	11.68
0.1886	15.84	0.8901	14.19	1.0000	11.60

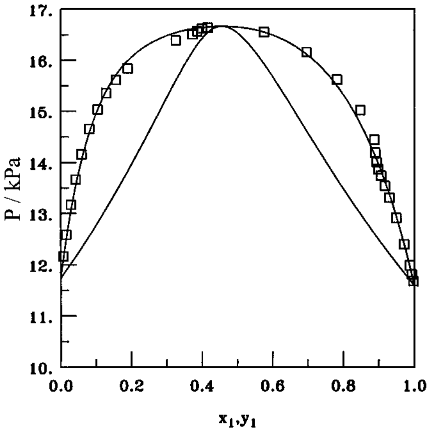

Figure 4. N-Methylacetamide (1) + naphthalene (2), (□) exptl $P-x$ data and calculated $P-x-y$ behavior using the UNIQUAC equation at 413.51 K.

Table 5. Experimental $P-x$ Data for the Binary System Phenol (1) + N-Methylacetamide (2) at 413.54 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	11.75	0.2129	10.09	0.7459	18.31
0.0091	11.62	0.2399	9.96	0.7923	20.46
0.0175	11.54	0.2658	9.89	0.8444	22.57
0.0269	11.47	0.3058	9.69	0.8901	24.34
0.0315	11.42	0.3497	9.60	0.9247	25.53
0.0368	11.39	0.4044	9.59	0.9531	26.37
0.0444	11.38	0.4728	9.89	0.9711	26.93
0.0624	11.17	0.5099	10.40	0.9813	27.15
0.0837	10.97	0.5416	10.96	0.9892	27.34
0.1080	10.74	0.5757	11.78	0.9949	27.50
0.1317	10.59	0.6137	12.87	0.9979	27.62
0.1576	10.45	0.6531	14.33	1.0000	27.72
0.18701	10.27	0.68946	15.79		

Table 1 lists and Figure 1 shows the $P-x$ results for the system aniline (1) + N-methylacetamide (2). Because the system exhibits only slight nonideality, it is zeotropic. On the contrary, the system decane (1) + N-methylacetamide (2) shows a strong deviation from Raoults law, with a pressure maximum heterogeneous azeotropic point at $x_1 = 0.78$, $T = 413.49$ K, and $P = 49.2$ kPa. The $P-x$ data are listed in Table 2. From the graphical representation in Figure 2, it can be seen that a miscibility gap is indicated in the composition range between $x_1 = 0.18$ and $x_1 = 0.89$. However, up to now no liquid−liquid equilibrium data have been published. The $T-x-y$ data for the system ethylene

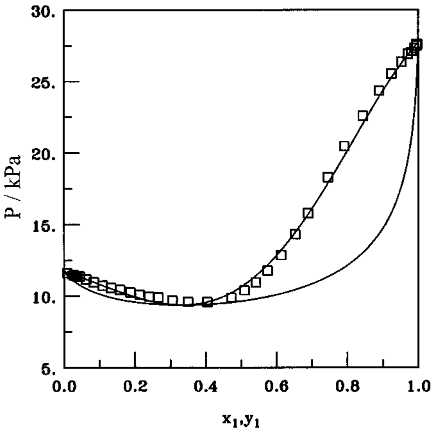

Figure 5. Phenol (1) + *N*-methylacetamide (2), (□) exptl $P-x$ data and calculated $P-x-y$ behavior using the UNIQUAC equation at 413.54 K.

Table 6. Experimental $P-x$ Data for the Binary System Water (1) + *N*-Methylacetamide (2) at 363.15 K[a]

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	1.17	0.0781	6.19	0.4606	34.66
0.0214	2.55	0.1099	8.22	0.5634	42.76
0.0354	3.43	0.1617	11.77	0.6655	50.47
0.0498	4.36	0.2464	17.95	0.7288	54.94
0.0641	5.28	0.3536	26.16	0.7765	57.72

[a] Measured with a computer-driven static apparatus.

Table 7. Experimental $P-x$ Data for the Binary System Water (1) + *N*-Methylacetamide (2) at 413.53 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	11.68	0.2820	117.60	0.4935	202.62
0.0544	30.85	0.3125	129.97	0.5379	220.10
0.0953	46.37	0.3402	141.08	0.5861	238.47
0.1387	61.97	0.3652	151.27	0.6434	259.19
0.1781	76.94	0.3899	161.29	0.7218	285.82
0.2146	91.02	0.4207	173.81	0.8088	312.56
0.2509	105.36	0.4602	189.45		

glycol (1) + *N*-methylacetamide (2) are given in Table 3 and plotted in Figure 3a. The experimental $T-x$ data suggest a S-shaped form of the curve. The system is almost ideal, and the $x-y$ data provide a slight but complex behavior of the activity coefficients with a maximum of $\gamma_1 = 1.02$ at $x_1 = 0.8$ and a minimum of $\gamma_1 = 0.95$ at $x_1 = 0.6$, as shown in Figure 3b. Since a chemical reaction takes place, the accuracy of the data is much lower than for all other data given in this paper.

In Table 4 and Figure 4, the $P-x$ data of the system *N*-methylacetamide (1) + naphthalene (2) are presented. A homogeneous pressure maximum azeotropic point at $x_1 = 0.456$, $T = 413.51$ K, and $P = 16.665$ kPa is observed. A homogeneous pressure minimum azeotrope is observed for the system phenol (1) + *N*-methylacetamide (2) at $x_1 = 0.4$, $T = 413.54$ K, and $P = 9.59$ K. The $P-x$ data are given in Table 5 and plotted in Figure 5. In Tables 6 and 7, the $P-x$ data for the zeotropic system water (1) + N-methylacetamide (2) for two temperatures are given. The diagrams are shown in Figure 6.

For all the systems for which $P-x$ data have been measured, they were used to derive quasi-experimental activity coefficients at infinite dilution with the help of a flexible Legendre polynomial as explained above. The results are given in Table 18. Furthermore the limiting activity coefficients derived from the already published $P-x$ data (de Haan et al., 1997) for the systems *N*-methylacetamide + 1-octene or dipropylamine or triethylamine or pyridine or methanol are added to Table 18.

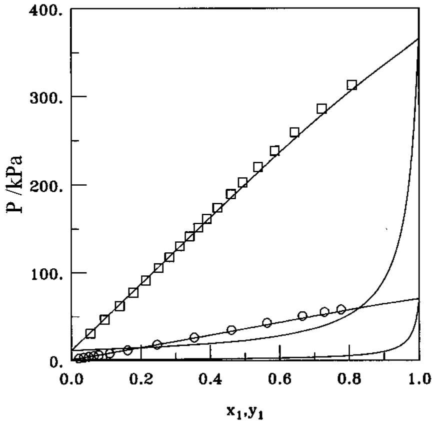

Figure 6. Water (1) + *N*-methylacetamide (2), exptl $P-x$ data and calculated $P-x-y$ behavior using the UNIQUAC equation at 363.15 K (○) and at 413.53 K (□).

Table 8. Experimental H^E Data for the Binary System Aniline (1) + *N*-Methylacetamide (2) at 413.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0211	−77.32	0.3117	−649.46	0.6625	−522.78
0.0424	−154.50	0.3593	−675.96	0.7162	−460.31
0.0855	−274.75	0.4077	−684.78	0.7709	−379.94
0.1293	−379.88	0.4569	−685.53	0.8266	−291.75
0.1738	−473.75	0.5069	−667.53	0.8833	−199.61
0.2190	−545.86	0.5579	−628.77	0.9411	−103.94
0.2650	−604.25	0.6097	−586.84	0.9704	−54.89

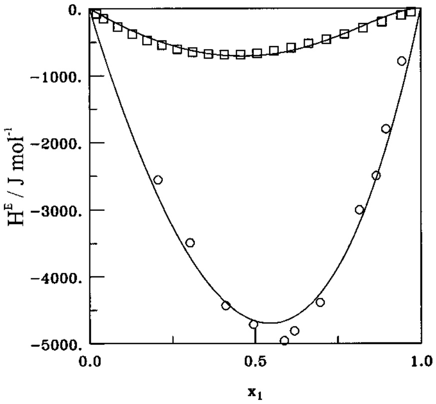

Figure 7. Experimental H^E data and calculated H^E behavior using the UNIQUAC equation at 413.15 K for the systems aniline (1) + *N*-methylacetamide (2) (□) and phenol (1) + *N*-methylacetamide (2) (○).

Table 9. Experimental H^E Data for the Binary System *n*-Decane (1) + *N*-Methylacetamide (2) at 413.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0100	74.54	0.1744	928.38	0.6108	1077.88
0.0202	148.44	0.2073	937.50	0.7330	1126.01
0.0418	297.14	0.2818	963.35	0.8817	1170.76
0.0647	439.61	0.3241	976.18	0.9097	1102.51
0.0893	575.68	0.3953	1000.86	0.9687	682.54
0.1156	708.33	0.4779	1031.61		
0.1439	834.71	0.5406	1053.83		

3.2 H^E Data. The enthalpy of mixing results for the system aniline (1) + *N*-methylacetamide (1) (Table 8 and Figure 7) show exothermic mixing. For the endothermic system decane (1) + *N*-methylacetamide (2) (Table 9 and Figure 8), the miscibility gap is definitively found as indicated by the straight line connecting the same liquid−liquid equilibrium compositions as already given above and derived from the $P-x$ data. Since G^E-models are not able to describe VLE and LLE with the same set of parameters, the calculated miscibility gap is not in perfect agreement

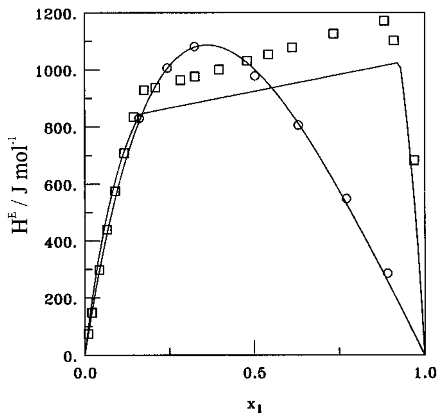

Figure 8. Experimental H^E data and calculated H^E behavior using the UNIQUAC equation at 413.15 K for the systems *n*-decane (1) + *N*-methylacetamide (2) (□) and *N*-methylacetamide (1) + naphthalene (2) (○).

Table 10. Experimental H^E Data for the Binary System Ethylene Glycol (1) + *N*-Methylacetamide (2) at 413.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0342	−25.58	0.3152	−130.96	0.8055	−35.04
0.1007	−67.63	0.4531	−122.45	0.9062	−13.87
0.1648	−97.82	0.5800	−96.00		
0.2566	−125.36	0.6971	−65.72		

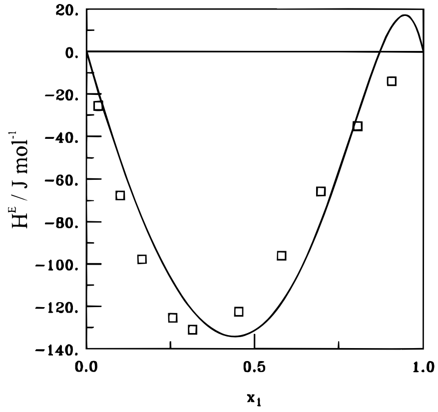

Figure 9. Ethylene glycol (1) + *N*-methylacetamide (2), (□) exptl H^E data and calculated H^E behavior using the UNIQUAC equation at 413.15 K.

Table 11. Experimental H^E Data for the Binary System *N*-Methylacetamide (1) + Naphthalene (2) at 413.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.1598	830.62	0.5017	978.71	0.8911	285.38
0.2428	1006.09	0.6291	806.32		
0.3232	1081.69	0.7708	548.53		

Table 12. Experimental H^E Data for the Binary System Phenol (1) + *N*-Methylacetamide (2) at 413.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.2067	−2555.63	0.5878	−4957.79	0.8655	−2496.87
0.3031	−3489.84	0.6187	−4810.75	0.8951	−1802.31
0.4111	−4431.27	0.6962	−4386.18	0.9432	−786.25
0.4949	−4712.99	0.8150	−3000.85		

Table 13. Experimental H^E Data for the Binary System Water (1) + *N*-Methylacetamide (2) at 323.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0990	−342.50	0.6474	−1661.85	0.9090	−822.06
0.1840	−616.06	0.7406	−1570.23	0.9449	−534.34
0.3225	−1073.99	0.8107	−1363.02	0.9747	−258.12
0.5171	−1554.39	0.8653	−1107.69		

Table 14. Experimental H^E Data for the Binary System Water (1) + *N*-Methylacetamide (2) at 363.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0514	−142.23	0.6474	−1173.90	0.9449	−343.56
0.0990	−273.85	0.7406	−1073.84	0.9747	−164.30
0.1840	−499.34	0.8107	−915.60	0.9879	−81.00
0.3225	−841.70	0.8653	−730.41		
0.5171	−1146.75	0.9090	−535.18		

Table 15. Experimental H^E Data for the Binary System Water (1) + *N*-Methylacetamide (2) at 398.15 K

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0514	−97.74	0.5171	−677.85	0.9278	−216.43
0.0990	−175.63	0.6474	−661.48	0.9449	−166.30
0.1430	−254.32	0.7406	−584.81	0.9604	−119.98
0.1840	−320.87	0.8107	−488.71	0.9747	−77.62
0.2578	−434.63	0.8107	−487.53	0.9814	−55.31
0.3225	−523.08	0.8653	−376.33		
0.4305	−620.69	0.9090	−267.36		

Table 16. Pure Components Properties[a]

component	*r*	*q*	*A*	*B*	*C*
aniline	3.7165	2.8160	7.47484	1840.790	216.923
decane	7.1974	6.0160	6.95769	1503.568	194.738
ethylene glycol	2.4088	2.2480	7.72333	1818.591	178.650
N-methylacetamide	3.1061	2.7320	7.9809	2183.100	221.320
naphthalene	4.9808	3.4400	8.09713	2603.260	282.769
phenol	3.5517	2.6800	6.92855	1382.650	159.493
water	0.9200	1.4000	8.0177	1715.700	234.268

[a] r = relative van der Waals volume, q = relative van der Waals surface area, and A, B, C = constants for the Antoine equation $\log P^s = A - [B/(t + C)]$; P in mmHg, t in °C.

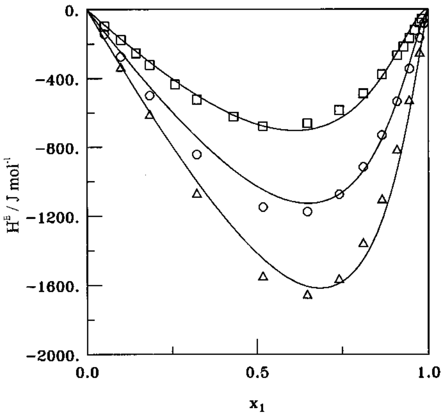

Figure 10. Water (1) + *N*-methylacetamide (2), exptl H^E data at 323.15 K (△), at 363.15 K (○), and at 398.15 K (□) and calculated H^E behavior using the UNIQUAC equation.

with the experimental one. The system ethylene glycol (1) + *N*-methylacetamide (2) (Table 10 and Figure 9) is slightly exothermic. The excess enthalpies for the endothermic mixture of naphthalene (1) + *N*-methylacetamide (2) are given in Table 11 and Figure 8. Those for the strong exothermic mixture of phenol (1) + *N*-methylacetamide (2) are given in Table 12 and Figure 7. In Tables 13−15, the enthalpy of mixing data for the system water (1) + *N*-methylacetamide (2) is given. The system shows a strong exothermic behavior, and, as shown in Figure 10, the enthalpy of mixing show a strong temperature dependence, indicating a large excess heat capacity.

3.3 Modeling. Temperature dependent interaction parameters for all the binary systems have been fitted simultaneously to the $P-x$ and H^E data for the UNIQUAC model, except in the case of the heterogeneous system decane + *N*-methylacetamide, for which the NRTL model was applied. The Simplex-Nelder-Mead nonlinear search

Table 17. Fitted UNIQUAC or NRTL Parameters

	UNIQUAC or NRTL interaction parameters				
	g_{12}^0/J mol^{-1}	g_{12}^0/J mol^{-1}	g_{12}^1/J mol^{-1}1 K^{-1}	g_{21}^1/J mol^{-1} K^{-1}	α_{12}
aniline (1) + *N*-methylacetamide (2)[a]	6915.73	−3513.68	−8.235	2.801	
n-decane (1) + *N*-methylacetamide (2)[b]	20455.6	10254.1	−28.15	−7.301	0.4102
ethylene glycol (1) + *N*-methylacetamide (2)[a]	2357.97	−1048.93	3.267	−3.219	
N-methylacetamide (1) + naphthalene (2)[a]	−720.98	3869.78	−1.439	−1.023	
phenol (1) + *N*-methylacetamide (2)[a]	−1725.61	−3867.18	1.981	4.578	
water (1) + *N*-methylacetamide (2)[a]	9835.30	−3557.12	−12.58	0.5261	

[a] UNIQUAC. [b] NRTL.

Table 18. Activity Coefficients at Infinite Dilution

		quasi-experimental Legendre polynomial		calculated			
				NRTL		UNIQUAC	
system	*t*/°C	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
aniline (1) + *N*-methylacetamide (2)	140.39	0.94	1.19	0.99	1.22	1.02	1.26
n-decane (1) + *N*-methylacetamide (2)	140.34	19.20	33.78	20.09	31.55	15.66	13.08
dipropylamine (1) + *N*-methylacetamide (2)	125.38	4.31	12.77	4.46	11.19	3.94	8.38
methanol (1) + *N*-methylacetamide (2)	125.40	0.64	0.45	0.62	0.43	0.62	0.43
N-methylacetamide (1) + naphthalene (2)	140.36	6.34	3.20	6.04	3.71	5.68	3.58
1-octene (1) + *N*-methylacetamide (2)	125.41	9.96	34.95	10.53	28.60	9.08	13.11
phenol (1) + *N*-methylacetamide (2)	140.39	0.13	0.10	0.12	0.07	0.11	0.07
pyridine (1) + *N*-methylacetamide (2)	125.36	1.54	2.02	1.48	1.97	1.52	2.06
triethylamine (1) + *N*-methylacetamide (2)	125.36	6.70	31.20	6.95	21.01	6.02	12.98
water (1) + *N*-methylacetamide (2)	90.00	0.90	1.81	0.89	1.95	0.88	1.83
water (1) + *N*-methylacetamide (2)	140.38	1.00	1.76	0.98	1.95	0.99	1.97

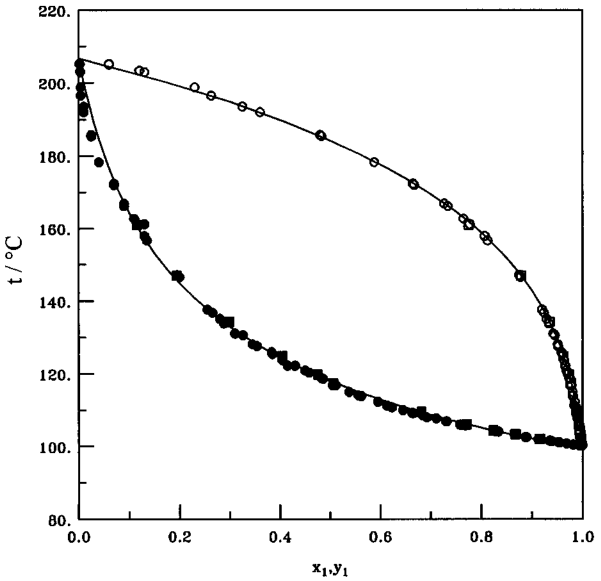

Figure 11. Water (1) + *N*-methylacetamide (2), exptl *T*−*x*−*y* data from the literature at 101.325 kPa K. Dew points (○) and bubble points (●) from Kortuem and Van Biedersee (1970); dew points (□) and bubble points (■) from Manczinger and Kortuem (1975); calculated VLE behavior using the UNIQUAC equation with the interaction parameters fitted in this work.

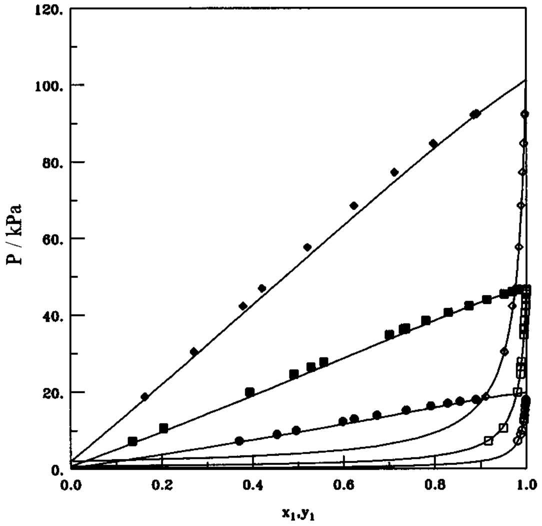

Figure 12. Water (1) + *N*-methylacetamide (2), exptl *P*−*x*−*y* data from Manczinger and Kortuem (1975). (●) at 333.15 K, (■) at 353.15 K, (◆) at 373.15 K, full symbols, bubble points; open symbols, dew points; calculated VLE behavior using the UNIQUAC equation with the interaction parameters fitted in this work.

algorithm (Nelder and Mead, 1965) was combined with the following objective function:

$$F = \sum[(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}]^2 + \sum[(H_{\text{exp}}^{\text{E}} - H_{\text{cal}}^{\text{E}})/H_{\text{exp}}^{\text{E}}]^2 \quad (1)$$

The temperature dependence of the parameters is given by the following equation:

$$g_{ij} = g_{ij}^0 + g_{ij}^1 \cdot T[\text{K}] \quad (2)$$

The obtained parameters are listed in Table 17. They have been used to calculate the pressure, vapor composition, and excess enthalpy. For all the systems investigated, the calculated results are plotted in Figures 1−10 together with the experimental data. In all cases, a satisfactory agreement between experimental and calculated results was achieved. The required Antoine constants for the vapor pressure calculations and the van der Waals parameters required for the UNIQUAC model for the components included in this study are given in Table 16. Furthermore the calculated activity coefficients at infinite dilution are listed in Table 18 together with the quasi-experimental values derived from the *P*−*x* data using a flexible Legendre polynomial. For all systems, the calculation was performed using both the NRTL and the UNIQUAC models. In general, the two models give similar results, except for the strong real systems with decane or 1-octene. For these systems, the correlation using the more flexible NRTL model is preferred.

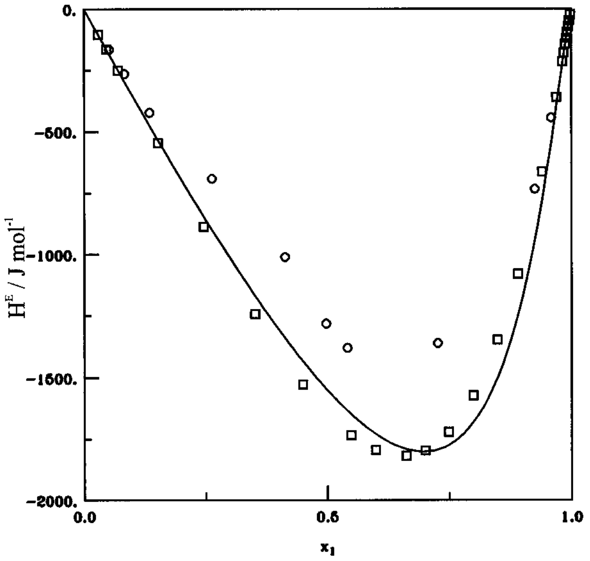

Figure 13. Water (1) + *N*-methylacetamide (2), exptl H^E data from the literature at 308.15 K from Manczinger and Kortuem (1975) (○) and from Zaichikov and Golubinsky (1996) (□); calculated H^E behavior using the UNIQUAC equation with the interaction parameters fitted in this work.

4. Discussion and Conclusions

Phase equilibrium data and excess enthalpies were measured for six binary mixtures containing *N*-methylacetamide. The experimental data were correlated with the help of the UNIQUAC or NRTL model, whereby generally good agreement between experimental and calculated results was obtained. Since for the system water + *N*-methylacetamide literature data are available, they have been compared in Figures 11−13 with the calculation provided by the UNIQUAC interaction parameters fitted only to the experimental data from this work. Good agreement is observed, except for the enthalpy of mixing data of Manczinger and Kortuem (1975) at 35 °C. But Zaichikov and Golubinsky published H^E data for the same temperature, which are consistent with all the other experimental information and thus more reliable.

The experimental data from this work will be used to fit the interaction parameters for monoalkyl amides of the modified UNIFAC model (Gmehling et al., 1993).

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