474 J. Chem. Eng. Data **1996,** *41,* 474−478

Excess Enthalpies for Various Binary Mixtures with *N*-Methylacetamide or Acetic Anhydride

André B. de Haan*

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

Jürgen Gmehling

Technische Chemie (FB9), Universität Oldenburg, Postfach 2503, D-26111 Oldenburg, Federal Republic of Germany

---

Excess enthalpy data provide information to allow a quantitative temperature extrapolation of the excess Gibbs energy model parameters or the interaction parameters in group contribution methods. In the case of amide or anhydride systems however, insufficient excess enthalpy data are available in the literature. This paper presents excess enthalpies for binary mixtures of *N*-methylacetamide with cyclohexanol, propanoic acid, hexylamine, *N*,*N*-dimethylacetamide, benzene, toluene, propyl acetate, and cyclohexanone at 90 °C and water at 50, 90, and 125 °C. Excess enthalpy data are also reported for binary mixtures of acetic anhydride with benzene, toluene, and cyclohexane at 90 °C. The results have been fitted to the Redlich−Kister expansion.

Introduction

Excess enthalpy data provide information to allow a quantitative temperature extrapolation of the excess Gibbs energy (G^E) or activity coefficients. Therefore, excess enthalpies (H^E) should be used to determine reliable G^E model parameters or the group interaction parameters for group contribution methods. In the case of amide or anhydride systems however, only very limited excess enthalpy data are available in the literature (Christensen et al., 1984; Gmehling and Holderbaum, 1989). Therefore, we have measured excess enthalpies for binary mixtures of *N*-methylacetamide with cyclohexanol, propanoic acid, hexylamine, *N*,*N*-dimethylacetamide, benzene, toluene, propyl acetate, and cyclohexanone at 90 °C and water at 50, 90, and 125 °C. Excess enthalpy data are also presented for binary mixtures of acetic anhydride with benzene, toluene, and cyclohexane at 90 °C. Of the 12 binary systems considered in this paper, data have only been published for *N*-methylacetamide + water at 35 °C (Manczinger and Kortüm, 1975) and acetic anhydride + cyclohexane at 26.9 and 48.2 °C (Campbell and Kartzmark, 1969) and 59.0 °C (Lakhanpal et al., 1973).

Experimental Section

A commercially available flow calorimeter from Hart Scientific (model 7501) was used for the measurement of the excess enthalpies (Gmehling, 1993). The calorimeter consists of two solvent pumps (ISCO, LC 2600, 260 cm^3), a thermostated flow cell, and a back pressure regulator to prevent evaporation.

The flow cell containing a pulsed heater, a calibration heater, a Peltier cooler, and a mixing tube wound around a copper cylinder (Ott et al., 1986) is located in a stainless steel cylinder which is immersed in a thermostat. Depending on the H^E values and the flow rate for the different systems, the power per pulse can be varied between 0.05 and 20 μJ. The energy per pulse is obtained by calibration using the energy dissipated from a precise resistor fixed at the cylinder of the flow cell.

Table 1. Excess Enthalpies H^E and Liquid Mole Fraction x_1 for Binary Mixtures of Water (1) + *N*-Methylacetamide (2)

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
		50 °C			
0.1062	−367.5	0.6652	−1707.3	0.9154	−827.7
0.1961	−656.5	0.7555	−1601.6	0.9488	−536.6
0.3399	−1131.9	0.8225	−1382.8	0.9766	−258.6
0.5368	−1613.2	0.8743	−1119.1		
		90 °C			
0.0514	−142.2	0.6474	−1173.9	0.9449	−343.6
0.0990	−273.9	0.7406	−1073.8	0.9747	−164.3
0.1840	−499.3	0.8107	−915.6	0.9879	−81.0
0.3225	−841.7	0.8653	−730.4		
0.5171	−1146.8	0.9090	−535.2		
		125 °C			
0.0514	−97.7	0.5171	−677.9	0.9278	−216.4
0.0990	−175.6	0.6474	−661.5	0.9449	−166.3
0.1430	−254.3	0.7406	−584.8	0.9604	−120.0
0.1840	−320.9	0.8107	−488.7	0.9747	−77.6
0.2578	−434.6	0.8107	−487.5	0.9814	−55.3
0.3225	−523.1	0.8653	−376.3	0.9940	−16.7
0.4305	−620.7	0.9090	−267.4		

A constant temperature of the flow cell is realized by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler. The temperatures of the liquid pumps and the thermostat are monitored with a Hart Scientific platinum resistance thermometer (model 1006 Micro-Therm) with an accuracy of ±0.005 K. The calibrated liquid pumps were maintained at 40 °C for all systems studied.

From the recorded frequency change of the pulsed heater and the flow rates, the molar excess enthalpies were calculated using the energy evolved per pulse, the pure component densities at 40 °C, and the molar mass of the components. The uncertainty in H^E was estimated to be less than ±1%, as shown previously (Gmehling, 1993).

Chemicals with high purity obtained from various suppliers were purified further by vacuum rectification. The purity was checked by gas chromatography and the water content by Karl Fischer titration. Except for cyclohex-

0021-9568/96/1741-0474$12.00/0

Table 2. Excess Enthalpies H^E and Liquid Mole Fraction x_1 for Binary Mixtures of *N*-Methylacetamide with Other Components at 90 °C

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
Cyclohexanol (1) + *N*-Methylacetamide (2)					
0.0181	−8.3	0.2795	−207.1	0.6837	−506.5
0.0365	−18.4	0.3245	−250.4	0.7424	−500.3
0.0741	−41.6	0.3709	−293.6	0.8033	−463.3
0.1128	−68.4	0.4188	−339.0	0.8664	−381.0
0.1526	−98.0	0.4683	−378.4	0.9319	−232.6
0.1937	−132.0	0.5194	−421.6	0.9656	−123.4
0.1937	−132.7	0.5723	−460.4		
0.2360	−168.9	0.6271	−490.2		
Propanoic Acid (1) + *N*-Methylacetamide (2)					
0.0254	−148.6	0.3535	−1445.5	0.7032	−937.6
0.0507	−284.2	0.4037	−1511.1	0.7529	−730.2
0.1014	−539.6	0.4538	−1526.9	0.8025	−524.4
0.1520	−777.1	0.5039	−1522.1	0.8520	−348.5
0.2025	−989.9	0.5538	−1411.3	0.9014	−161.5
0.2529	−1173.4	0.6037	−1286.6	0.9507	−15.5
0.3033	−1332.0	0.6535	−1125.8	0.9754	17.4
Hexylamine (1) + *N*-Methylacetamide (2)					
0.0293	−124.2	0.2763	−836.4	0.6321	−898.8
0.0598	−243.1	0.3190	−905.2	0.6961	−798.9
0.0918	−358.7	0.3641	−958.1	0.7644	−648.9
0.1252	−471.9	0.4117	−991.6	0.8375	−451.8
0.1603	−567.0	0.4620	−1007.1	0.9158	−209.7
0.1970	−665.6	0.5154	−1000.5	0.9571	−90.4
0.2357	−756.9	0.5719	−965.0		
N,*N*-Dimethylacetamide (1) + *N*-Methylacetamide (2)					
0.0413	−24.6	0.3532	−97.5	0.7107	−65.6
0.0834	−45.5	0.4012	−97.8	0.7661	−54.1
0.1263	−62.2	0.4502	−96.5	0.8227	−41.6
0.1699	−76.4	0.5002	−92.3	0.8805	−28.0
0.2144	−86.0	0.5512	−86.9	0.9396	−14.1
0.2598	−90.3	0.6033	−79.6		
0.3060	−94.8	0.6565	−72.1		
Benzene (1) + *N*-Methylacetamide (2)					
0.0215	13.5	0.3640	294.2	0.8854	508.7
0.0432	30.5	0.4620	374.6	0.9422	402.5
0.0871	65.0	0.5629	447.6	0.9710	273.8
0.1767	138.5	0.6670	508.6		
0.2690	214.8	0.7745	544.6		
Toluene (1) + *N*-Methylacetamide (2)					
0.0181	20.2	0.3241	352.2	0.8662	591.0
0.0365	40.7	0.4183	442.1	0.9318	479.8
0.0740	84.1	0.5189	522.7	0.9656	338.3
0.1524	172.1	0.6266	591.2		
0.2356	261.4	0.7420	630.3		
Propyl Acetate (1) + *N*-Methylacetamide (2)					
0.0165	18.8	0.2611	309.0	0.6049	594.2
0.0334	39.8	0.3043	356.3	0.6631	609.0
0.0680	80.6	0.3493	400.8	0.7241	613.4
0.1038	125.0	0.3962	442.2	0.7881	590.2
0.1409	168.8	0.4451	482.1	0.8552	523.3
0.1795	213.1	0.4960	525.4	0.9257	364.4
0.2195	262.8	0.5493	562.8		
Cyclohexanone (1) + *N*-Methylacetamide (2)					
0.0371	80.6	0.3278	600.0	0.6869	779.9
0.0752	160.0	0.3744	659.1	0.7453	736.4
0.1143	240.5	0.4224	705.2	0.8056	655.9
0.1546	319.7	0.4720	745.6	0.8681	525.2
0.1960	392.3	0.5232	778.0	0.9329	319.2
0.2387	466.8	0.5760	795.5	0.9661	172.9
0.2826	536.1	0.6305	798.1		

anone, purity >99.6%, all the used materials had a purity greater than 99.9%.

Results

The measured excess enthalpies for the water + *N*-methylacetamide system at 50, 90, and 125 °C are listed in Table 1. Table 2 presents the results for binary mixtures of *N*-methylacetamide with cyclohexanol, propanoic acid, hexylamine, *N*,*N*-dimethylacetamide, benzene, toluene, propyl acetate, and cyclohexanone at 90 °C. Finally the measured excess enthalpies for binary mixtures of acetic anhydride with benzene, toluene, and cyclohexane at 90 °C are given in Table 3. At present vapor−liquid or liquid−liquid equilibrium data are available in the literature only for some of the systems studied (Aucejo et al., 1993; Jones, 1962; Kortüm and Van Biedersee, 1970; Manczinger and Kortüm, 1975; Mihaila et al., 1984; Molochnikov et al., 1967). Therefore, we have used the Redlich−Kister expansion to fit the results

Table 3. Excess Enthalpies H^E and Liquid Mole Fraction x_1 for Binary Mixtures Containing Acetic Anhydride at 90 °C

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
Benzene (1) + Acetic Anhydride (2)					
0.0527	101.2	0.4134	511.2	0.7602	442.7
0.1051	190.6	0.4637	530.2	0.8087	389.7
0.1572	271.7	0.5138	532.2	0.8569	323.5
0.2090	339.2	0.5637	538.3	0.9049	236.4
0.2605	398.2	0.6132	529.9	0.9526	128.6
0.3118	447.2	0.6625	511.8		
0.3627	483.2	0.7115	483.7		
Toluene (1) + Acetic Anhydride (2)					
0.0222	63.5	0.3226	652.6	0.6736	715.1
0.0445	126.7	0.3709	704.3	0.7263	663.9
0.0895	240.1	0.4198	731.6	0.7796	593.6
0.1350	348.1	0.4693	757.0	0.8336	497.3
0.1811	442.4	0.5194	761.2	0.8884	373.7
0.2277	520.0	0.5702	767.2	0.9438	209.9
0.2748	594.0	0.6212	747.0	0.9718	108.8
Cyclohexane (1) + Acetic Anhydride (2)					
0.0437	382.7	0.3669	2089.0	0.7228	1995.6
0.0881	728.0	0.4156	2185.3	0.7766	1811.2
0.1330	1054.6	0.4650	2251.9	0.8312	1548.6
0.1785	1339.4	0.5151	2263.9	0.8866	1192.9
0.2246	1570.9	0.5659	2258.9	0.9429	692.1
0.2714	1789.7	0.6175	2216.9		
0.3188	1959.1	0.6697	2132.9		

$$\frac{H^{E}/(\mathrm{J\ mol^{-1}})}{(x_1x_2)} = \sum_{i=1}^{m} A_i(2x_1 - 1)^{i-1} \qquad (1)$$

using the following objective function (Christensen et al., 1984):

$$F = \sum\left[\frac{(H^{E} - \mathrm{H}^{E}_{\mathrm{calcd}})}{H^{E}}\right]^2 \qquad (2)$$

$$j = 1, 2, ..., n$$

where x_1 and x_2 are the liquid mole fractions of component 1 and component 2, respectively. The fitted Redlich−Kister parameters A_j and mean relative deviations (MRD) are given in Tables 4 and 5. For all studied systems the obtained MRDs are within the estimated experimental error of ±1% (Gmehling, 1993). Figures 1−5 compare the Redlich−Kister fits with the experimental results for the *N*-methylacetamide-containing systems. Figures 1−3 show that, due to hydrogen bonding, the mixtures of *N*-methylacetamide with water, cyclohexanol, propanoic acid, and hexylamine show negative excess enthalpies. The small negative excess enthalpies measured for *N*-methylacetamide + *N*,*N*-dimethylacetamide indicate that also in this system some hydrogen bonding effects occur, as illustrated by Figure 2. The other four systems, Figures 4 and 5, show large positive excess enthalpies. In the case of the *N*-methylacetamide mixtures with propanoic acid, benzene, and toluene, the excess enthalpy curves are highly asymmetric and therefore require eight Redlich−Kister parameters to obtain a good fit.

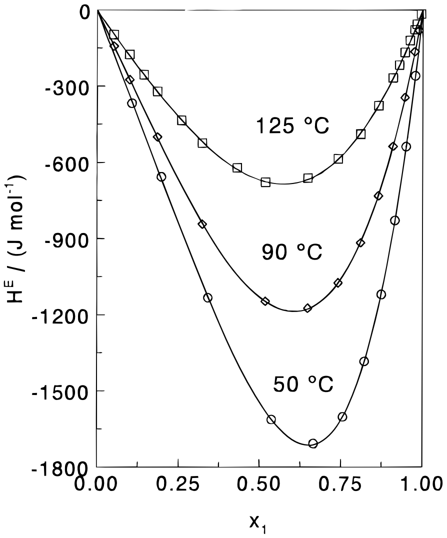

Figure 1. Experimental H^E data and Redlich–Kister fit for water (1) + *N*-methylacetamide (2) at 50 °C (□), 90 °C (◇), and 125 °C (○).

Table 4. Redlich–Kister Parameters A_j and Mean Relative Deviation (MRD) for Binary Mixtures with *N*-Methylacetamide (2) at Temperature *t*

component 1	t/°C	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	MRD/%
water	50.0	−6177.5	−4061.0	−1486.8	−185.5					0.54
	90.0	−4522.7	−2036.7	−344.1	−99.8					0.46
	125.0	−2676.6	−863.6	76.0	164.7					1.14
cyclohexanol	90.0	−1633.3	−1635.6	−687.9	−195.1					0.75
propanoic acid	90.0	−6036.4	2118.7	4643.9	1288.1	−4442.5	−4121.8	3826.7	4915.3	0.76
hexylamine	90.0	−4019.8	375.7	215.1	782.0	748.7				0.78
N,*N*-dimethyl-acetamide	90.0	−368.7	166.1	−91.5	53.8					1.67
benzene	90.0	1601.5	1427.9	1592.0	2184.8	−1808.3	−3904.1	4980.9	6346.7	1.08
toluene	90.0	2024.6	1484.4	1751.8	2154.1	−2230.7	−3721.5	5680.7	6472.1	0.90
propyl acetate	90.0	2115.0	1368.6	1000.5	1265.9	792.4				1.04
cyclohexanone	90.0	3055.4	1167.0	795.4	582.3					0.42

Table 5. Redlich–Kister Parameters A_j and Mean Relative Deviation (MRD) for Binary Mixtures with Acetic Anhydride (2) at Temperature *t*

component 1	t/°C	A_1	A_2	A_3	A_4	MRD/%
benzene	90.0	2144.2	287.1	377.9	238.7	0.58
toluene	90.0	3056.9	345.1	506.0	267.4	0.57
cyclohexane	90.0	9054.8	704.0	2345.8	1761.1	0.42

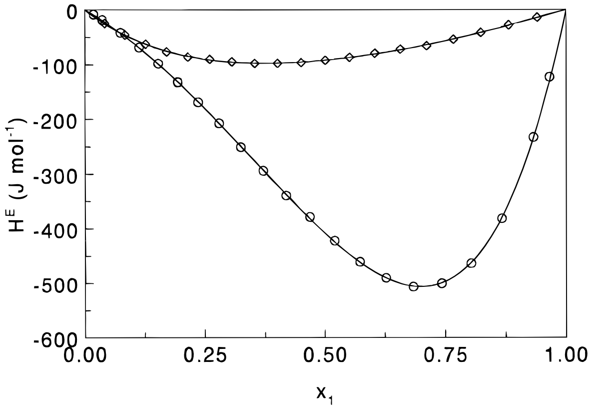

Figure 2. Experimental H^E data and Redlich–Kister fits for cyclohexanol (1) (○) and *N*,*N*-dimethylacetamide (1) (◇) + *N*-methylacetamide (2) at 90 °C.

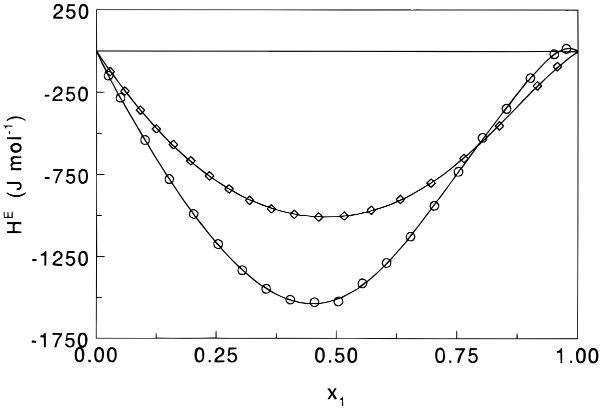

Figure 3. Experimental H^E data and Redlich–Kister fits for propanoic acid (1) (○) and hexylamine (1) (◇) + *N*-methylacetamide (2) at 90 °C.

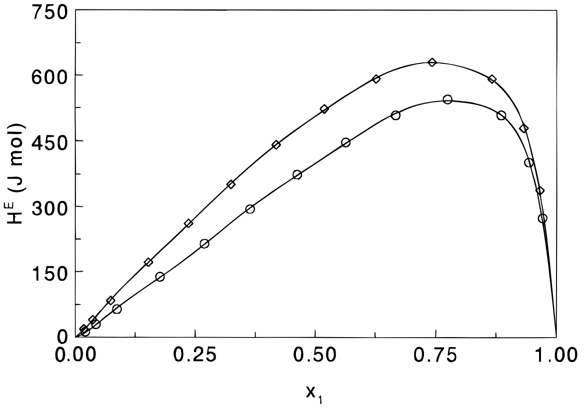

Figure 4. Experimental H^E data and Redlich–Kister fits for benzene (1) (○) and toluene (1) (◇) + *N*-methylacetamide (2) at 90 °C.

Figures 6 and 7 illustrate that large positive excess enthalpies occur in the three acetic anhydride containing systems. For acetic anhydride + cyclohexane, our results, obtained at 90 °C, are compared with the previously published data at 48.2 °C (Campbell and Kartzmark, 1969) and 59.0 °C (Lakhanpal et al., 1973) in Figure 7. The excess enthalpies obtained at 90 °C in this study are considerably lower than one would expect from extrapolation of the reported literature data. This was expected, however, because it appeared impossible to fit the excess enthalpy data reported by Campbell and Kartzmark (1969) or Lakhanpal et al. (1973) together with available vapor–liquid equilibrium data (Jones, 1962) to the UNIQUAC model. The temperature dependence of the interaction parameters required to describe the published excess enthalpies was far to high to get a good simultaneous representation of the vapor–liquid equilibrium data. However, when instead of the data of Campbell and Kartzmark (1969) or Lakhanpal et al. (1973) the excess enthalpy data measured in this study are used, an excellent simultaneous description of the vapor–liquid equilibrium data is obtained, which is illustrated in Figures 8 and 9.

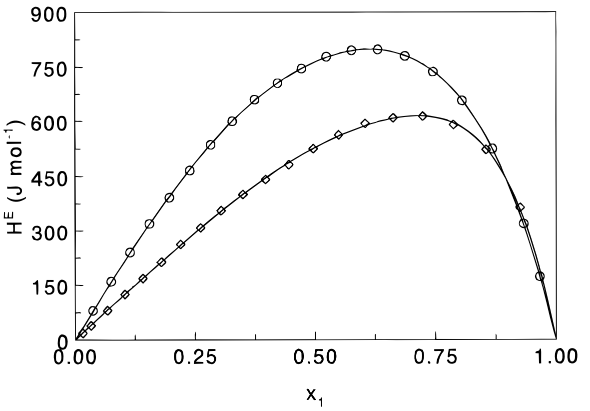

Figure 5. Experimental H^E data and Redlich−Kister fit for cyclohexanone (1) (○) and propyl acetate (1) (◇) + *N*-methylacetamide (2) at 90 °C.

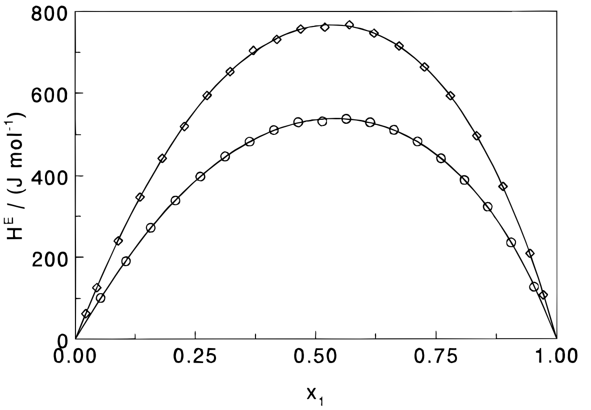

Figure 6. Experimental H^E data and Redlich−Kister fit for benzene (1) (○) and toluene (1) (◇) + acetic anhydride (2) at 90 °C.

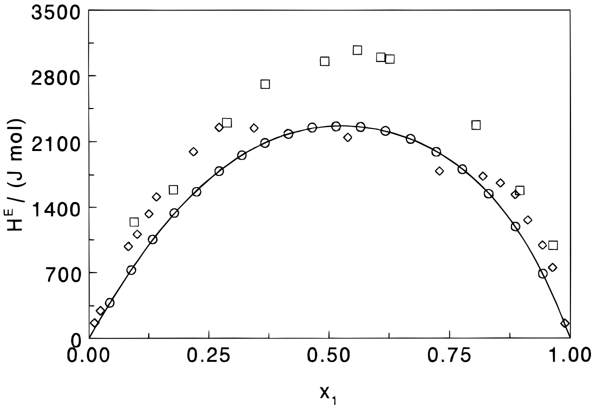

Figure 7. Comparison of experimental H^E data (○) and Redlich−Kister fit for cyclohexane (1) + acetic anhydride(2) at 90 °C with data from Campbell and Kartzmark (1969) at 48.9 °C (◇) and Lakhanpal et al. (1973) at 59.0 °C (□).

Conclusions

Excess enthalpies were measured for binary mixtures of *N*-methylacetamide with cyclohexanol, propanoic acid, hexylamine, *N*,*N*-dimethylacetamide, benzene, toluene, propyl acetate, and cyclohexanone at 90 °C and water at 50, 90, and 125 °C. Furthermore, excess enthalpy data have been presented for binary mixtures of acetic anhydride with benzene, toluene, and cyclohexane at 90 °C. Because at this moment vapor−liquid or liquid−liquid equilibrium data are only available for a part of the studied systems (Aucejo et al., 1993; Jones, 1962; Kortum and Van Biedersee, 1970; Manczinger and Kortum, 1975; Mihaila et al., 1984; Molochnikov et al., 1967), the results have been fitted to the Redlich−Kister expansion instead of a G^E model. For the other systems vapor−liquid and some liquid−liquid equilibrium data are currently being measured and will be published in two future papers (Aim and De Haan, 1996a,b).

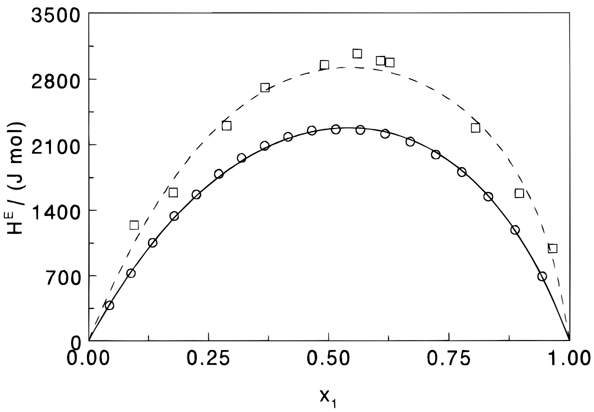

Figure 8. Results of the UNIQUAC fits, one for the experimental H^E data obtained in this study (○, 90 °C) and the other for the data published by Lakhanpal et.al. (1973) (□, 59.0 °C), both in combination with the vapor−liquid equilibrium data at 1.013 bar (Jones, 1962), for the cyclohexane (1) + acetic anhydride (2) system.

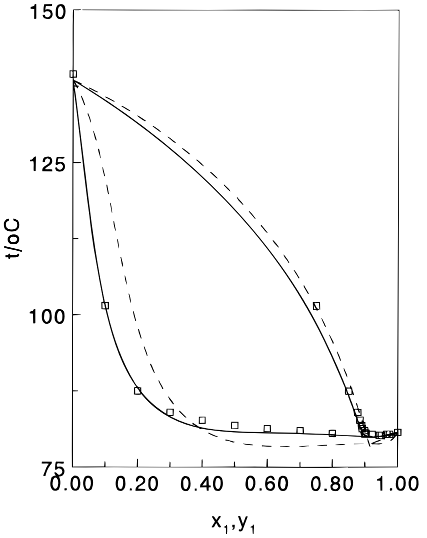

Figure 9. Comparison of vapor-−iquid equilibrium data for the cyclohexane (1) + acetic anhydride (2) system at 1.013 bar (□; Jones, 1962) as temperature, *t*, vs composition (x_1, y_1) and the UNIQUAC description using the interaction parameter temperature dependency obtained from the H^E data measured in this study (—) or the H^E data published by Lakhanpal et al. (1973) (- - -).

Acknowledgment

The authors thank Mrs. B. H. Kreutscher for carrying out the measurements.

Literature Cited

Aim, K.; De Haan, A. B. Vapor-Liquid and Liquid-Liquid Equilibria for the Benzene+N-Methyl-acetamide and Toluene+N-Methylacetamide Systems. *Fluid Phase Equilib.* **1996a**, manuscript in preparation.

Aim, K.; De Haan, A. B. Vapor-Liquid Equilibria for Binary Mixtures of N-Methylacetamide with Cyclohexanol, Propanoic Acid, Hexylamine, Propyl Acetate and *N*,*N*-Dimethylacetamide. *Fluid Phase Equilib.* **1996b**, manuscript in preparation.

Aucejo, A.; Montón, J. B.; Muñoz, R.; Sanchotello, M. Isobaric Vapor-Liquid Equilibria for the Cyclohexanone+N-Methylacetamide System. *J. Chem. Eng. Data* **1993**, *38*, 160−162.

Campbell, A. N.; Kartzmark, E. M. Heats of Mixing and Dielectric Constants of some Partially Miscible Liquid Phases. *Can. J. Chem.* **1969**, *47*, 619−623.

Christensen, C.; Gmehling, J.; Rasmussen, P.; Weidlich, U. *Heats of Mixing Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, 1984; Vol. III, Parts 1 and 2.

Gmehling, J.; Holderbaum, Th. *Heats of Mixing Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, 1989; Vol. III, Parts 3 and 4.

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

Jones, H. E. Vapor-Liquid Equilibriums for Eight Binary Mixtures. *J. Chem. Eng. Data* **1962**, *7*, 13−18.

Kortüm, G.; Van Biedersee, H. Liquid-Vapor Equilibrium Diagrams of Binary Systems of High Relative Volatility: Water+N-Methylacetamide, Water+N-Methylformamide, and N-Methylacetamide+N-Methylformamide. *Chem.-Ing.-Tech.* **1970**, *8*, 552−560.

Lakhanpal, M. L.; Kapoor, K. K.; Lal, G.; Mandal, H. G. Thermochemical Studies of some Partially Miscible Liquid Pairs of Formic Acid with Benzene, Toluene and p-Xylene, and of Acetic Anhydride and Furfural with Cyclohexane. *Indian J. Chem.* **1973**, *11*, 471−475.

Manczinger, J.; Kortüm, G. Thermodynamic Mixing Effects in the Water+N-Methylacetamide System. *Z. Phys. Chem., Neue Folge* **1975**, *95*, 177−186.

Mihaila, Gh.; Bilba, N.; Dranga, D.; Luca, C. Vapor-Liquid Equilibria at Atmospheric Pressure of the Toluene+Acetic Anhydride and Acetic Anhydride+o-Xylene Systems. *Rev. Roum. Chim.* **1984**, *29*, 261−265.

Molochnikov, M. L.; Markova, L. P.; Kogan, V. B Liquid-Vapor Equilibriums in a Benzene+Acetic Anhydride System. *Zh. Prikl. Khim.* **1967**, *40*, 2083−2084.

Ott, J. B.; Stouffer, C. E.; Cornett, G. V.; Woodfield, B. F.; Withlin, R. C.; Christensen, J. J.; Deiters, U. K. Excess Enthalpies for (Ethanol+Water) at 298.15 K and Pressures of 0.4, 5, 10, and 15 MPa. *J. Chem. Thermodyn.* **1986**, *18*, 1−12.

Received for review November 20, 1995. Accepted January 16, 1996.⊗

JE950294H

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.