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Vapor−Liquid Equilibria and Enthalpies of Mixing for the Binary System Water + *N*-Methyl-2-pyrrolidone in the Temperature Range 80−140 °C

Oliver Noll, Kai Fischer, and Jürgen Gmehling*

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

Precise $P-x$ data have been measured for the binary system water + *N*-methyl-2-pyrrolidone (NMP) at (80 and 110) °C using a static apparatus. Furthermore, enthalpies of mixing have been determined at (90, 140, and 143) °C with an isothermal flow calorimeter. Temperature dependent NRTL parameters have been fitted simultaneously to all the experimental data. The experimental data have been compared with the predicted results of the modified UNIFAC method, for which a new flexible lactam (cyclic amide) group was defined.

Introduction

Separating mixtures containing components with similar volatilities or systems exhibiting azeotropic behavior by distillation is an important task in chemical engineering. One possibility to separate azeotropic systems is the extractive distillation process using a high-boiling entrainer to alter the separation factor of the components of interest. *N*-Methyl-2-pyrrolidone (NMP) due to its unique physical properties, such as high polarity, low volatility, miscibility with water and organic solvents, and thermal and chemical stability, is a commonly used solvent, e.g., for absorbing sour gases from crude natural gas and separating aromatics from aliphatics or alkenes from alkanes (GAF, 1972).

The applicability of an entrainer mainly depends on its selectivity and capacity. The selectivity can be expressed by the influence on the relative volatilities, and the capacity by the minimum entrainer demand. The high-boiling entrainer has to be regenerated and recycled, so the costs of the extractive distillation process also depend on the amount of entrainer needed to perform the separation.

Often NMP is used as a selective solvent in combination with small amounts of water. Because the selectivity and capacity of NMP strongly depends on the water content (Fischer and Gmehling, 1996), a serious demand for precise experimental data of the binary system exists. Moreover, the temperature dependence of the thermophysical properties of the binary mixture are requested, because of the large enthalpies of mixing and excess heat capacity. Most of the vapor−liquid equilibrium data for the system water−*N*-methyl-2-pyrrolidone from literature are isobaric (Chen et al., 1983; Golubkov et al., 1975; Gupta and Rawat, 1992; Li et al., 1986; Pavlov et al., 1967). For this type of data it is difficult to distinguish between concentration and temperature effects. Therefore isothermal data are required and have been measured to overcome this problem.

The binary system exhibits a strong temperature dependence of the excess Gibbs energy expressed by the large exothermic excess enthalpies measured for this system between (0 and 80) °C (Burgdorf, 1995; Dohnal et al., 1994; MacDonald et al., 1971; Murakami et al., 1974; Ryabtseva and Rudin, 1982; Vasilev and Novikov, 1989), as shown in Figure 1. Furthermore, large excess heat capacities were measured between (15 and 50) °C by Vasilev and Novikov (1989), as shown in Figure 2.

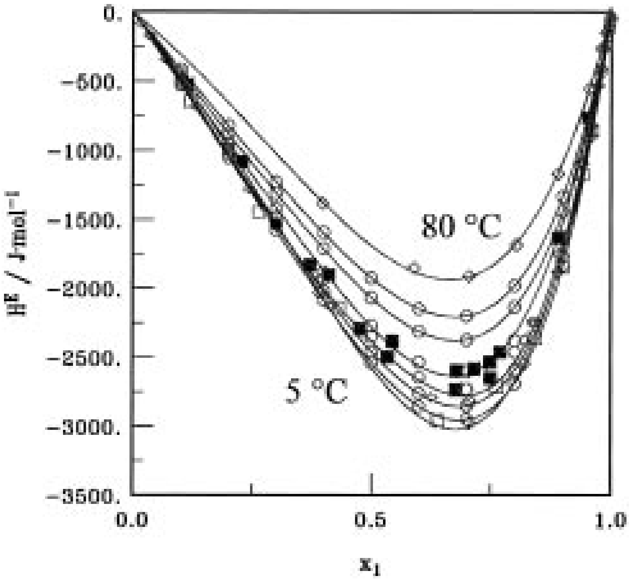

Figure 1. Experimental H^E data for the system water (1) + *N*-methyl-2-pyrrolidone (2) at different temperatures between (5 and 80) °C by (○) Vasilev and Novikov (1989) at (5, 15, 25, 35, 50, and 60) °C, (△) Dohnal et al. (1994) at 25 °C, (□) MacDonald et al. (1971) at 25 °C, (◇) Murakami et al. (1974) at 25 °C, (■) Ryabtseva and Rudin (1982) at (25 and 35) °C, and (◇) Burgdorf (1995) at (10, 25, and 80) °C.

In this paper, the behavior of binary mixtures of water and NMP has been studied experimentally by measuring isothermal $P-x$ and enthalpies of mixing data at different temperatures. In order to describe both vapor−liquid equilibria and excess enthalpies, quadratic temperature dependent NRTL parameters are fitted to the experimental data (Gmehling, 1994). The experimental data are also compared with the predicted values using the modified UNIFAC method (Gmehling et al., 1993) with a new flexible lactam group (Jakob and Gmehling, 1995). This group can also be used to describe, e.g., systems with ϵ-caprolactam.

Experimental Section

VLE Measurements. *N*-Methyl-2-pyrrolidone was supplied by BASF. NMP and water have been degassed and distilled at low pressure as described before (Fischer and

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* Corresponding author.

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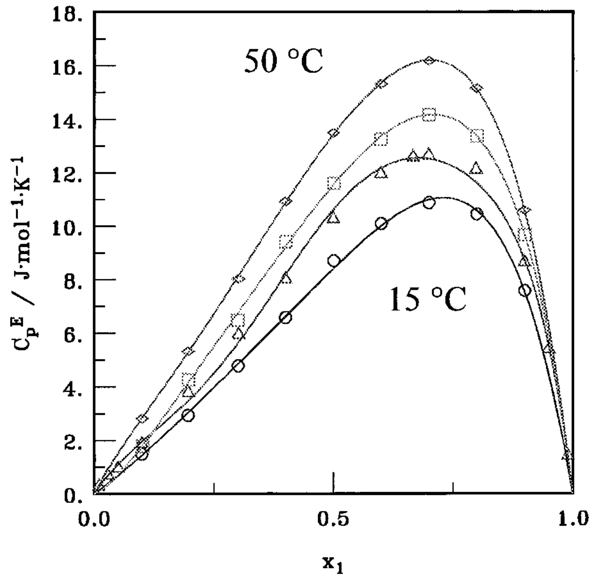

Figure 2. Experimental C_p^E data for the system water (1) + *N*-methyl-2-pyrrolidone (2) by Vasilev and Novikov (1989) at (○) $t = 15$ °C, (△) $t = 25$ °C, (□) $t = 35$ °C, and (◇) $t = 50$ °C.

Gmehling, 1994). Its final purity was found to be >99.9 mass %, as determined by gas chromatography and Karl Fischer titration.

The static apparatus used and the measurement procedure applied have been described in detail previously (Fischer and Gmehling, 1994). The principle of the VLE measurement by the static method is to determine the system pressure as a function of liquid composition. The composition of the liquid phase is not measured. But it is determined from the volumes of the compounds injected by using precise replacement pumps, taking into account the small composition changes caused by evaporation as described before (Fischer and Gmehling, 1994).

The accuracy of the replacement pumps of ±0.005 cm^3 evokes a cumulative feed composition error also depending on the relative molecular weight of both compounds and the amount of liquid within the equilibrium cell; therefore an error of ±0.5‰ considering molar quantities is assumed. The resolution of the temperature sensor (Pt100) is less than 1 mK, while the temperature deviation is ±2 mK during measurement of a single point and ±10 mK for the complete data set. The resolution of the pressure gauge is 2 Pa.

Excess Enthalpy (H^E) Measurements. An isothermal flow calorimeter from Hart Scientific has been used to measure the enthalpies of mixing data. The experimental setup has been described previously (Gmehling, 1993). With this type of calorimeter, the heat effects which occur during mixing are compensated for with the help of a pulsed heater. A Peltier cooler allows one to control the frequency of the pulsed heater and to set the baseline, so that also exothermic enthalpy of mixing effects can be measured. With the help of a back-pressure regulator the pressure is kept at a constant level so that evaporation is prevented.

Table 1. Experimental *Px* Data for the System Water (1) + *N*-Methyl-2-pyrrolidone (2) at 77.86 °C

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	1.21	0.6887	29.77	0.9102	40.47
0.0104	1.58	0.7228	31.97	0.9205	40.81
0.0246	2.06	0.7597	33.81	0.9311	41.18
0.0386	2.53	0.8072	36.18	0.9417	41.51
0.0410	2.62	0.8180	36.63	0.9521	41.83
0.0513	2.97	0.8219	36.87	0.9601	42.09
0.0941	4.25	0.8337	37.43	0.9696	42.30
0.1574	5.89	0.8425	37.80	0.9769	42.54
0.2099	7.90	0.8449	37.89	0.9823	42.71
0.2796	10.65	0.8516	38.16	0.9873	42.87
0.3501	13.66	0.8609	38.57	0.9910	42.96
0.4306	17.16	0.8706	38.96	0.9936	43.02
0.5078	20.64	0.8802	39.36	0.9961	43.11
0.5793	24.17	0.8901	39.76	0.9986	43.37
0.6354	27.06	0.9002	40.14	1.0000	43.24
0.6785	29.12				

Table 2. Experimental *Px* Data for the System Water (1) + *N*-Methyl-2-pyrrolidone (2) at 107.09 °C

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	4.64	0.7203	99.01	0.9700	126.95
0.0589	11.08	0.7599	104.37	0.9764	127.59
0.1041	16.18	0.7936	108.73	0.9815	127.95
0.1449	20.93	0.8226	112.30	0.9858	128.42
0.1886	26.15	0.8353	113.73	0.9928	129.10
0.2296	31.22	0.8664	117.45	0.9958	129.40
0.2688	36.21	0.8890	119.78	0.9969	129.64
0.3188	42.71	0.9082	121.58	0.9975	129.68
0.3703	49.59	0.9256	123.21	0.9981	129.81
0.4345	58.40	0.9377	124.19	0.9991	129.81
0.4995	67.56	0.9497	125.34	0.9994	129.88
0.5588	76.06	0.9575	125.94	0.9998	129.91
0.6197	84.79	0.9638	126.50	1.0000	130.03
0.6732	92.41				

Table 3. Activity Coefficients at Infinite Dilution for the System Water (1) + *N*-Methyl-2-pyrrolidone (2)

t/°C	γ_1^∞	γ_2^∞
77.86	0.832	1.592
107.09	0.868	2.050

Table 4. Experimental Excess Enthalpies for the System Water (1) + *N*-Methyl-2-pyrrolidone (2) at 90.00 °C and 8 bar

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0629	−190.5	0.2599	−853.7	0.3708	−1220
0.1454	−466.5	0.2599	−854.7	0.4311	−1395
0.1454	−468.6	0.2612	−859.4	0.5701	−1719
0.2182	−712.7	0.3007	−994.6		

Table 5. Experimental Excess Enthalpies for the System Water (1) + *N*-Methyl-2-pyrrolidone (2) at 140.00 °C and 21 bar

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0636	−84.74	0.4863	−695.4	0.8429	−612.6
0.1209	−163.8	0.5729	−770.3	0.8677	−542.2
0.1481	−219.2	0.6413	−801.3	0.8895	−473.7
0.1481	−216.9	0.6969	−801.4	0.9088	−402.9
0.1729	−241.7	0.7428	−773.0	0.9088	−401.5
0.2202	−314.9	0.7815	−727.4	0.9260	−337.7
0.3031	−463.5	0.8144	−670.8	0.9415	−266.2
0.3735	−556.6	0.8429	−613.4	0.9555	−204.7
0.4339	−635.5	0.8429	−611.9	0.9903	−48.15

Results

Tables 1 and 2 present the measured pressures P as a function of liquid composition x_1 at (77.86 and 107.09) °C. The quasi experimental activity coefficients at infinite dilution γ^∞ listed in Table 3 were derived with the help of a flexible Legendre polynomial, as described by Fischer and Gmehling (1994). In Tables 4−6 the experimental enthalpies of mixing H^E at (90, 140, and 143) °C are listed as a function of liquid composition. In Figures 3 and 4 graphical representations are given. It can be seen from the $P-x$ data that at high water concentrations the system shows a positive deviation from Raoult's law while at high NMP concentrations a negative deviation is obtained. Applying nonideality corrections for the vapor phase using viral coefficients gave no significant change in calculating the $P-x$ data. Usually, the vapor phase can be expected to be

Table 6. Experimental Excess Enthalpies for the System Water (1) + *N*-Methyl-2-pyrrolidone (2) at 143.00 °C and 24 bar

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0636	−93.38	0.4049	−571.5	0.9133	−368.1
0.1454	−208.2	0.4864	−665.3	0.9415	−254.5
0.1454	−207.4	0.5533	−722.1	0.9415	−255.5
0.1730	−249.7	0.6415	−768.8	0.9588	−184.4
0.2599	−378.6	0.7631	−725.5	0.9741	−115.6
0.2599	−380.8	0.8430	−586.2	0.9877	−53.95
0.2599	−378.2	0.8430	−582.2	0.9928	−31.40
0.3398	−489.7	0.8790	−487.6		

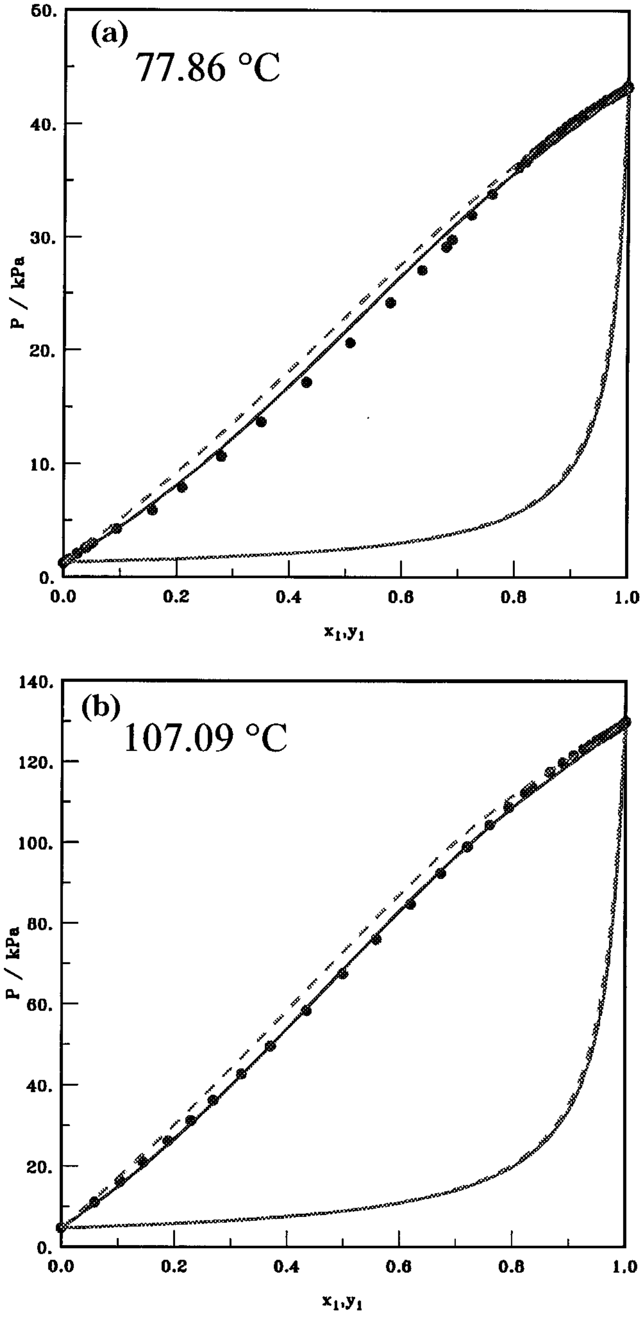

Figure 3. Experimental *Px* data (—), modified UNIFAC (Jakob and Gmehling, 1995) (— —)) for the system water (1) + *N*-methyl-2-pyrrolidone (2) at 77.86 °C (a) and 107.09 °C (b)

ideal for low-pressure systems; therefore the tables contain $P-x$ data neglecting any vapor phase reality. The exothermic enthalpies of mixing show smaller values with increasing temperature, which is in agreement with the published enthalpy of mixing and excess heat capacity data.

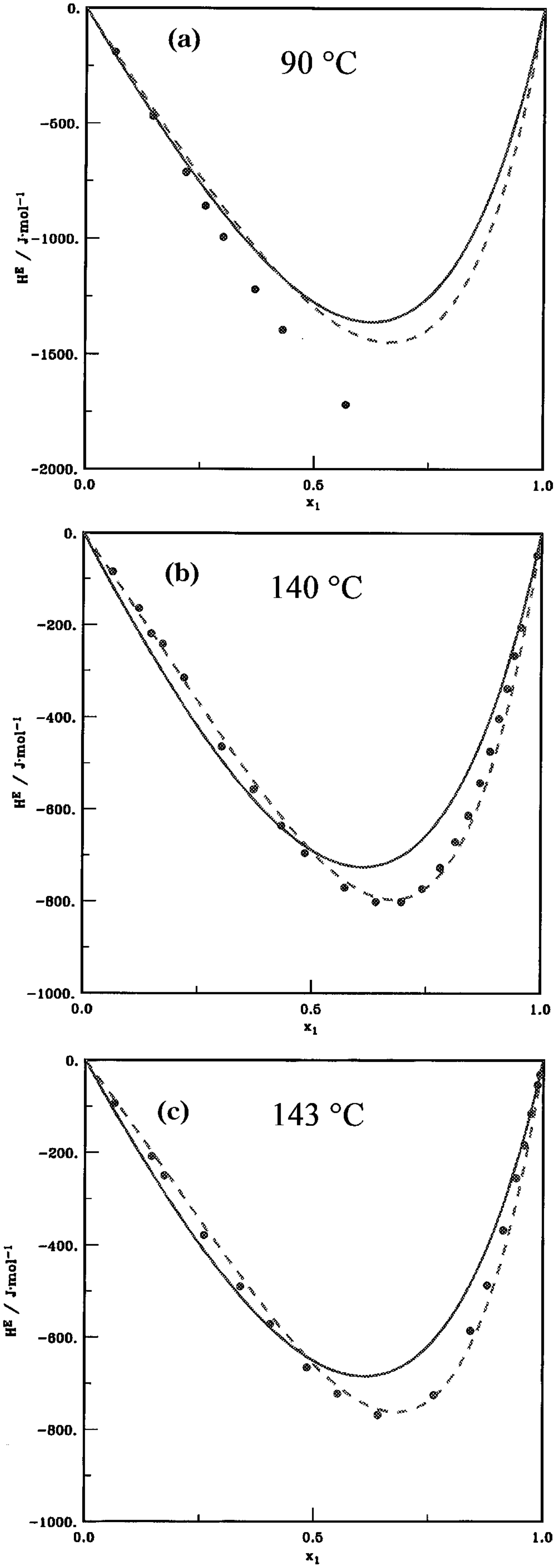

Figure 4. Experimental H^E data (●) and calculated H^E behavior (NRTL (—), modified UNIFAC (Jakob and Gmehling, 1995) (— —)) for the system water (1) + *N*-methyl-2-pyrrolidone (2) at 90 °C (a), 140 °C (b), and 143 °C (c).

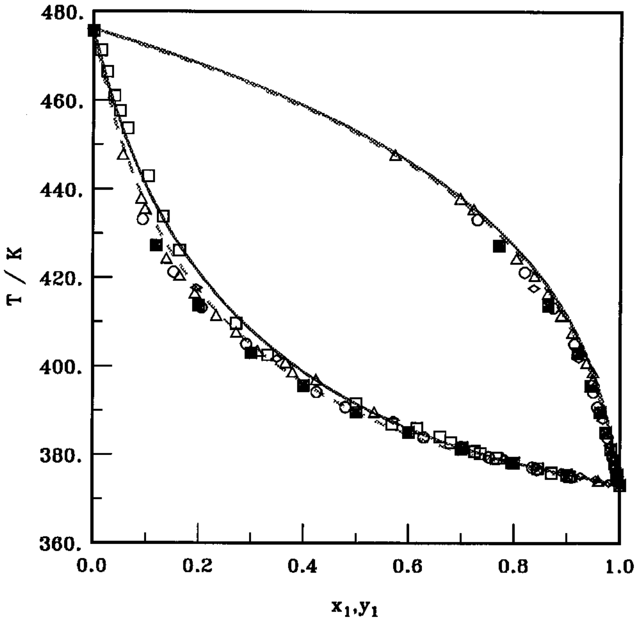

Figure 5. Experimental *Txy* data and calculated *Txy* behavior (NRTL (—), modified UNIFAC (Jakob and Gmehling, 1995) (– –)) for the system water (1) + *N*-methyl-2-pyrrolidone (2) at 101 kPa: (■) Pavlov et al. (1967); (○) Golubkov et al. (1975); (△) Chen et al. (1983); (□) Li et al. (1986); (◇) Gupta and Rawat (1992).

Table 7. NRTL Interaction Parameters Fitted Simultaneously to VLE and H^E Data

G^0_{12}	G^1_{12}	G^2_{12}	G^0_{21}	G^1_{21}	G^2_{21}	α_{12}
−6946.0	54.025	−0.036 07	−7576.0	20.607	−0.033 84	0.3020

Table 8. Modified UNIFAC Group Assignments and Volume and Surface Values

group	main group	sub group	*R*	*Q*
water	7	7	1.7334	2.4561
cyc-CH_2	42	78	0.7136	0.8635
cyc-CON-C	46	86	3.9810	3.2000

The *P*–*x* and H^E data have been used to fit simultaneously temperature dependent interaction parameters for the NRTL model, where ideal behavior of the vapor phase has been assumed and the following objective function *F* including variable weighting factors w_i and the number of experimental data n_i has been used:

$$F = w_1 \sum_{i=1}^{n_1} \left| \frac{P_i - P_{i,\mathrm{cal}}}{P_i} \right| \frac{1}{n_1} + w_2 \sum_{i=1}^{n_2} \left| \frac{H_i^E - H_{i,\mathrm{cal}}^E}{H_i^E} \right| \frac{1}{n_2}$$

The obtained NRTL interaction parameters G_{ij} (J/mol) and the nonrandomness parameter α_{ij} are given in Table 7. The temperature dependence is given by the following three-parameter equation:

$$G_{ij} = G^0_{ij} + G^1_{ij}\,(T/\mathrm{K}) + G_{ij}^{\;2}(T/\mathrm{K})^2$$

In Figures 3 and 4, the experimental data are compared with the calculated behavior using NRTL and the fitted parameters (solid lines). With the help of the NRTL model it was not possible to obtain smaller deviations between experimental and calculated data. The deviations are larger than the accuracy of the experimental data. As shown in Figure 5, the fitted temperature dependent NRTL parameters, which are based on the isothermal data, can be used also to describe the isobaric data from literature at 101 kPa.

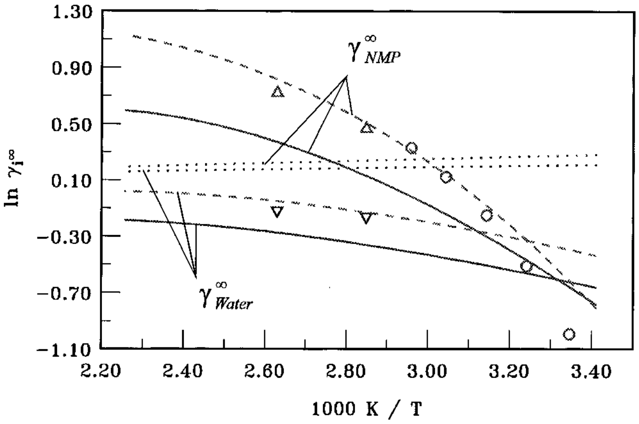

Figure 6. Experimental γ^∞ data and calculated γ^∞ behavior (NRTL using temperature dependent parameters (—), NRTL using temperature independent parameters (···), modified UNIFAC (Jakob and Gmehling, 1995) (– –)) for the system water (1) + *N*-methyl-2-pyrrolidone (2): (○) $\gamma^\infty_{\mathrm{NMP}}$, Trampe and Eckert (1993), (△) $\gamma^\infty_{\mathrm{NMP}}$, this work; (▽) $\gamma^\infty_{\mathrm{water}}$, this work.

Furthermore in Figures 3–5 the real behavior predicted by modified UNIFAC using a new flexible lactam group is included for comparison (broken lines). The required modified UNIFAC group volume and surface values are listed in Table 8, while the interaction parameters are given in Table 9 (Jakob and Gmehling, 1995). It can be seen for the system NMP + water, that the predicted results are better than the correlated results. There are other particular cases, when the introduction of the group concept results in an increased flexibility, e.g. the system 1,4-dioxane + cyclohexane (Skjold-Jørgensen et al., 1980).

It has been pointed out by Van Ness (1995), that "there is no longer any excuse for taking isobaric data in agreement with the operation at uniform pressure in distillation columns, as they were preferred in the early unsophisticated days of chemical engineering. Rigorous thermodynamic treatment of isobaric data presents problems that do not arise with isothermal data." In order to demonstrate the advantages of experimental isothermal VLE data compared with isobaric data for the correlation using g^E models, NRTL parameters have been fitted to isobaric VLE data at 101 kPa. Fitting to isobaric data only will not give a correct separation of temperature and concentration effects, especially when no H^E data are taken into account. In Figure 6 the different calculated activity coefficients at infinite dilution as a function of temperature are compared with experimental data from Trampe and Eckert (1993) (cycles) and from this work (triangles). The solid lines represent the calculated results using NRTL with temperature dependent interaction parameters from Table 7. The broken lines were predicted using modified UNIFAC. The results using constant NRTL parameters fitted to isobaric data are represented by dotted lines. It can be seen that with the help of temperature dependent parameters (modified UNIFAC and NRTL) the temperature dependence of the limiting activity coefficients is described correctly,

Table 9. Modified UNIFAC Group Interaction Parameters

assignments	a_{12}/K	a_{21}/K	b_{12}	b_{21}	$10^3\,c_{12}/\mathrm{K}^{-1}$	$10^2\,c_{21}/\mathrm{K}^{-1}$
7–42	274.37	1632.9	−0.5861	−2.8719	−0.3001	0.3455
7–46	659.22	−588.21	−1.8841	0.9707		
42–46	298.46	499.59	−0.6823	−0.8158		

whereas constant parameters give opposite results. Using modified UNIFAC, the limiting activity coefficients of both components show values larger than those calculated with NRTL using temperature dependent parameters. As mentioned above (VLE, H^E), modified UNIFAC gives better results than NRTL when compared with the experimental data.

In general, isothermal data are preferred for improving group contribution methods like UNIFAC or modified UNIFAC, because isobaric data do not allow one to obtain reliable activity coefficients at least in the case of systems with large volatility differences of the components. In this case composition and temperature effects are overlapping, and the activity coefficients are also changed by enthalpy of mixing effects.

Conclusions

Using precise experimental techniques, reliable VLE data at 77.86 and 107.09 °C and H^E data at (90, 140, and 143) °C for the system water + *N*-methyl-2-pyrrolidone have been measured. These data were used to fit simultaneously temperature dependent NRTL parameters, which allow one to describe the vapor−liquid equilibrium and excess enthalpy behavior of the binary system water−*N*-methyl-2-pyrrolidone. The differences of activity coefficients obtained from isothermal or isobaric VLE show the advantages of isothermal data.

The predicted VLE and H^E behavior using the group contribution method modified UNIFAC (Do) with a new flexible lactam group shows excellent agreement with the experimental results. Moreover the new group is flexible enough to describe also the behavior of other cyclic amide compounds like ϵ-caprolactam.

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