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Liquid−Liquid Equilibrium and Excess Enthalpies in the Binary System 2-Methylpentane + *N*,*N*-Dimethylformamide

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Liquid−liquid equilibrium and excess enthalpies were measured for the binary system 2-methylpentane + *N*,*N*-dimethylformamide. Equilibrium data were obtained at different temperatures by the direct analytical and volume methods; points of the binodal curve in the vicinity of the upper critical solution temperature of this system were acquired by means of the cloud-point method. Excess enthalpies were measured at 298.15 K and 313.15 K. Binary data were correlated by the modified Wilson equation. To estimate the critical composition and the upper critical solution temperature, the liquid-phase behavior data were also described by the extended scaling-law equation proposed by Ewing et al.[5] The liquid−liquid equilibrium and excess enthalpies in the binary system were predicted by the modified UNIFAC (Dortmund) model so that the prediction could be compared to the experimentally achieved data.

Introduction

One of the reasons for the study of thermodynamic properties in mixtures of alkanes with *N*,*N*-dimethylformamide is the fact that they tend to show isorefractivity and thus could be used as mixed solvents in the study of polymer properties (e.g., diffusion coefficients, mol weights, etc.) by optical methods. The present work is a part of a broader study concerning thermodynamic properties of liquid mixtures of alkanes, *N*,*N*-dimethylformamide, and methanol.[1] No literature values have been found for the system investigated in this work.

The experimental liquid−liquid equilibrium and excess enthalpy data in the binary system were correlated by the modified Wilson equation.[2−4] The liquid−liquid equilibrium data were described by an extended scaling-law equation proposed by Ewing et al.[5] The liquid−liquid equilibrium and excess enthalpies were also predicted by the modified UNIFAC (Dortmund) contribution model.[6]

Experimental Section

N,*N*-dimethylformamide (anhydrous) [C_3H_7NO (*N*,*N*-DMF)] was supplied by Sigma-Aldrich and was used as received; 2-methylpentane [C_6H_{14}] was also supplied by Sigma-Aldrich and was dried over molecular sieves before use; *n*-hexane (Sigma-Aldrich, gas chromatography (GC) grade) was used as the internal standard in the GC determination of 2-methylpentane and *N*,*N*-DMF in the equilibrium samples; 1-butanol (Lachema) was used as GC solvent. Purities determined by GC analysis and the water contents in substances used in the experiments are listed in Table 1. The content of water in the studied compounds was determined using the Karl Fischer titration. Densities of the chemicals were measured at 298.15 K using an Anton Paar DMA 5000 Density Meter and are compared with literature values in Table 1.

Table 1. Purity, Water Content, and Density of the Measured Compounds

			ρ/g·cm^{-3} at 298.15 K	
compound	GC purity mass %	water content mass %	this work	literature data
2-methylpentane[b]	99.98%	0.004	0.64845	0.64852[8]
N,*N*-DMF[a]	99.96%	0.006	0.94381	0.9439[8]

[a] Sigma-Aldrich anhydrous compound. [b] Sigma-Aldrich dried over molecular sieves.

Liquid−Liquid Equilibrium Measurement. To determine the liquid−liquid equilibrium in the studied system, three experimental methods were used. Points of the binodal curve in the critical region were obtained by the cloud-point method, and compositions of the equilibrium phases (tie lines) at several temperatures were determined by the direct analytical method and the volume method. All the equilibrium measurements were carried out at atmospheric pressure.

Determining the compositions of the equilibrium phases by the volume method[7] consists of measuring volumes of the individual phases; see our previous work[1] for the description of the apparatus used in the measurements. Relations based on the mass balance were used to obtain the compositions of the equilibrium phases from the global composition of the mixture and from the ratios of volumes of the individual phases.[10]

The direct analytical method is based on analyzing samples of the equilibrium phases. To take samples, an equilibrium cell designed by Řehák et al.,[11] which allows obtaining samples of the lower phase without contaminating them with the upper phase, was used.

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The content of 2-methylpentane and N,N-DMF in samples of the equilibrium phases was determined with an HP 6890 gas chromatograph equipped with an HP-5 cross-linked (5%-phenyl)-methylpolysiloxane capillary column (30 m × 0.32 mm × 0.25 μm).

The chromatograph was calibrated with 1-butanol solutions of known concentrations of 2-methylpentane, N,N-DMF, and n-hexane, which was utilized as the internal standard.

By the cloud-point method, the binodal curve in the vicinity of the critical solution of a binary system is determined as the temperature at which, in a mixture of a known composition, the second phase appears. An apparatus designed at our department[3] after a work by Ochi et al.[9] was used to carry out the measurements.

A mixture of a known composition was prepared in a thermostated measurement cell and brought to a temperature at which it was homogeneous. Then, using a temperature programmer, the temperature was decreased at a constant rate to establish the narrowest possible temperature interval at which the second phase appears, i.e., at which the mixture becomes turbid. The change in turbidity was detected through measuring the intensity of the laser-diode light scattered by the mixture using a photodiode connected to an amplifier. The temperature in the cell was measured by a Pt-resistance thermometer connected to an ASL resistance bridge. The temperature and the intensity of the light were monitored during the measurements using a PC.

Experimental uncertainties for the cloud-point method were found to be better than ±0.0002 mole fraction. The temperature in these experiments was measured with a Pt-100 resistance thermometer and was obtained with an uncertainty of ±0.01 K. Experimental uncertainties evaluated from the acquired data for the GC determination of 2-methylpentane and of N,N-DMF were ±0.002 mole fraction units. The uncertainty of the volume method measurements was found to be ±0.005 mole fraction units. In both the direct analytical and volume methods, the temperature was controlled within ±0.01 K with a Lauda RC6 CP thermostat.

Excess Enthalpy Measurement. Excess enthalpies for the system 2-methylpentane + N,N-DMF were determined at 298.15 K and 313.15 K using a Hart 4410 microcalorimeter with modified continuous-flow mixing cells (model 4442) and high-pressure HPP 5001 pumps from Laboratorní přístroje. The calorimeter was calibrated by measuring the excess enthalpy for the reference systems hexane + cyclohexane and methanol + water. The composition uncertainty was found to be ±0.0005 mole fraction and the enthalpy uncertainty was ±2%. Fenclová et al.[12] gives a detailed description of the instrument and its calibration. Because of the hydrostatic pressure created by the column of the sample liquid in the pipes, the pressure in the apparatus was slightly higher than atmospheric. The total pressure depends on densities of the sample liquids and was estimated to be in the range of 115 to 120 kPa.

Results and Discussion

The experimental binodal-curve and liquid−liquid equilibrium data are summarized in Table 2 and Table 3 and presented in Figure 1. Good agreement was observed between the results obtained by the three experimental methods utilized in this work; although the acquired experimental uncertainties show different values, the reliability intervals of the individual methods largely overlap.

Table 2. Binodal-Curve Mole Fractions for the System 2-Methylpentane (1) + N,N-DMF (2)

x_1	T/K	x_1	T/K	x_1	T/K
0.2483	328.72	0.4107	337.32	0.6154	337.21
0.2749	331.42	0.4230	337.29	0.6620	336.25
0.3134	334.21	0.4590	337.62	0.7118	334.23
0.3518	335.90	0.5016	337.69	0.7924	328.28
0.3763	336.70	0.5523	337.66	0.8063	326.91

Table 3. Liquid−Liquid Equilibrium Phase Mole Fractions for the System 2-Methylpentane (1) + N,N-DMF (2)

	solvent phase	alkane phase	deviation of the modified Wilson model[a]		
T/K	x_1'	x_1''	ΔT/K	$\Delta x_1'$	$\Delta x_1''$
		Direct Analytical Method			
283.15	0.070	0.959	0.50	-4.9×10^{-3}	4.2×10^{-3}
288.15	0.081	0.959	0.67	-2.4×10^{-3}	9.5×10^{-3}
293.15	0.096	0.941	−0.14	1.7×10^{-3}	-0.1×10^{-3}
298.15	0.102	0.932	0.19	-2.5×10^{-3}	-0.7×10^{-3}
303.15	0.119	0.921	−0.14	0.9×10^{-3}	-0.4×10^{-3}
308.15	0.142	0.900	−1.18	0.1×10^{-3}	-4.9×10^{-3}
313.15	0.154	0.885	−0.64	-0.7×10^{-3}	-4.9×10^{-3}
		Volume Method			
293.15	0.098	0.945	−0.08	4.2×10^{-3}	4.3×10^{-3}
298.15	0.104	0.935	0.25	-0.9×10^{-3}	2.3×10^{-3}
303.15	0.123	0.913	−0.90	2.1×10^{-3}	-6.8×10^{-3}
308.15	0.142	0.906	−0.88	5.9×10^{-3}	-0.5×10^{-3}
313.15	0.158	0.888	−0.73	2.9×10^{-3}	-1.6×10^{-3}
318.15	0.178	0.869	−0.25	1.4×10^{-3}	0.3×10^{-3}
323.15	0.204	0.838	−0.06	-1.6×10^{-3}	-1.7×10^{-3}

[a] Δ = (experimental − calculated value).

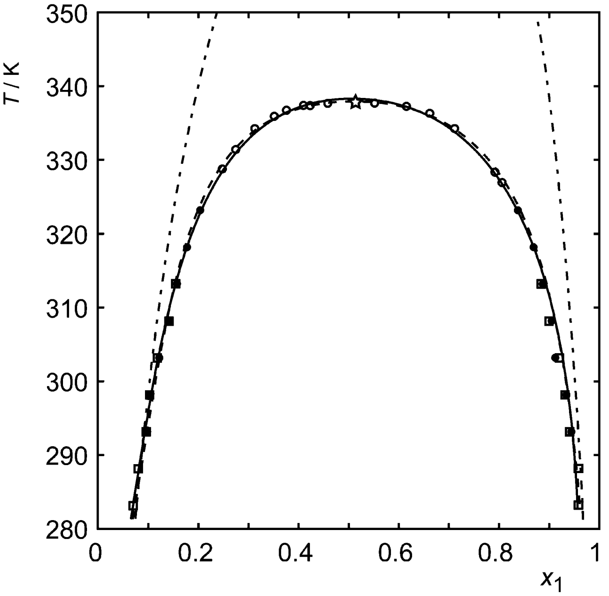

Figure 1. Liquid−liquid equilibrium in the system 2-methylpentane (1) + N,N-DMF (2). ○, cloud-point method; ■, direct analytical method; □, volume method; ☆, upper critical solution point; solid line, the modified Wilson equation; dashed line, extended scaling-law equation; dot-dashed line, the modified UNIFAC (Dortmund) method.

Excess enthalpy data for the binary system were obtained at 298.15 K and 313.15 K. The results are listed in Table 4 and displayed in Figure 2. A lower weight was attributed in subsequent correlations to data acquired in the heterogeneous region where the results obtained in the heterogeneous region may be slightly less reliable than in the homogeneous region. This is because in a flow-mixing cell heterogeneous mixtures exhibit a substantial liquid−liquid interface with a nonzero interfacial tension.

Table 4. Excess Enthalpy Data for the System 2-Methylpentane (1) + *N,N*-DMF (2)

x_1	H^E/J·mol^{-1}	ΔH^E/J·mol^{-1} [b]
	T = 298.15 K	
0.0300	230.4	6.0
0.0611	438.6	1.1
0.0613	441.0	3.5
0.0940	645.2	−1.2
0.1281[a]	743.5	34.9
0.2012[a]	737.7	41.5
0.3701[a]	699.3	32.0
0.3702[a]	703.9	36.5
0.5781[a]	654.0	22.0
0.8410[a]	578.0	−9.2
0.9178[a]	541.6	−32.5
0.9462	467.2	−0.3
	T = 313.15 K	
0.0300	230.7	0.4
0.0611	448.5	−0.1
0.0613	451.3	2.6
0.0940	656.5	−5.7
0.1281	845.8	−18.1
0.1638[a]	961.2	−33.1
0.2012[a]	982.3	−6.3
0.3702[a]	974.4	11.9
0.5781[a]	925.3	−5.1
0.8410[a]	862.8	−27.0
0.9178	728.5	26.5
0.9462	473.0	−15.2
0.9469	461.4	−18.7

[a] Data obtained in the heterogeneous region. [b] Δ = (experimental value − calculated value).

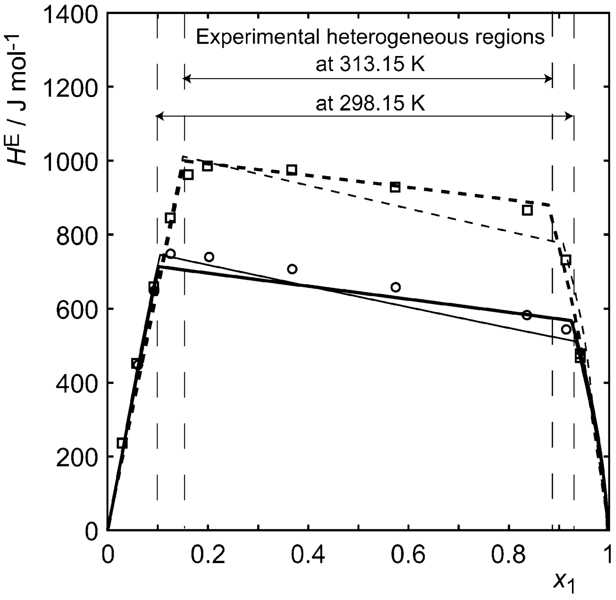

Figure 2. Excess enthalpy in the system 2-methylpentane (1) + *N,N*-DMF (2). ○, 298.15 K; □, 313.15 K; solid line, calculated data at 298.15 K; dashed line, calculated data at 313.15 K (bold lines, the modified Wilson equation; thin lines, the modified UNIFAC method).

Correlation of Experimental Data

Extended Scaling-Law Equation. One of the problems encountered in precisely representing binary liquid−liquid equilibria is the description of data in the critical region. According to modern theories,[13] the Gibbs energy cannot be expressed analytically in the vicinity of the critical point because of the long-range composition fluctuations; it can, however, be scaled in the critical region.[10,14] The original scaling equation[13] is valid for temperatures not far from the critical point ($\theta = 1 - T/T_c < 10^{-3}$). Corrections were introduced to extend its validity over the whole temperature range.[15] Ewing et al.[5] describe the coexistence (binodal) curve as follows

Table 5. Parameters of Extended Scaling-Law Equation in the System 2-Methylpentane (1) + *N,N*-DMF (2)

Critical Composition and Temperature	
x_{c1}	0.5130 (±0.002) [a]
T_c/K	337.69 [b]
Parameters	
B_1	1.7238 (±0.018)
B_2	0.5704 (±0.15)
A_1	0.3967 (±0.14)
B_3	−2.2584 (±0.30)
A_2	−0.7804 (±0.30)
total standard error of estimate in composition	s = ±0.005

[a] Determined from the extended scaling-law equation. [b] Experimental value.

$$x_i = x_{ci} \pm (B_1/2)|\theta|^{\beta} \pm (B_2/2)|\theta|^{\beta+w} + A_1|\theta| \pm (B_3/2)|\theta|^{\beta+2w} + A_2|\theta|^{1-\alpha+w} \quad (1)$$

where x_i is the mole fraction of the ith component, x_{ci} is its critical composition, $\beta = 0.329$ is the universal critical index, $\alpha = 0.11$ is the second critical index, $w = 0.5$ is the first Wegner correction term, and B_1, B_2, B_3, A_1, and A_2 are adjustable constants.[16] In this work, eq 1 was used to correlate the experimental binodal curve and to obtain the critical composition for the 2-methylpentane + *N,N*-DMF binary system (see Table 5). The upper critical solution temperature (UCST) was determined experimentally as the maximum temperature on the binodal curve. Treating the UCST as an adjustable parameter resulted in an insignificant change of the order of mK. The critical values were subsequently used in the correlation of our results by the modified Wilson equation. The results of the calculation are compared to the experimental data in Figure 1. Note that the scaling equation describes the liquid−liquid equilibrium appropriately over the whole temperature range and even in the critical region.

Modified Wilson Equation. The scaling equation permits the description of the liquid−liquid equilibrium only, giving no information about the Gibbs energy. The experimental data were therefore correlated using the modified Wilson equation[2−4] to fit simultaneously the results for liquid−liquid and excess enthalpy data. To correlate data obtained in binary systems, the model combines the original Wilson and the Redlich−Kister equation

$$Q = \frac{G^E}{RT} = Q_W + Q_{RK} \quad (2)$$

$$Q_W = -\sum_{i=1}^{N} x_i \ln \sum_{j=1}^{N} x_j (V_j/V_i) \exp(-a_{ij}/T^*) \quad (3)$$

$$Q_{RK} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} x_i x_j \sum_{k=1}^{n_{ij}} B_{ijk}(x_i - x_j)^{k-1} \quad (4)$$

where Q is the dimensionless excess Gibbs energy, Q_W is the Wilson term, Q_{RK} the Redlich−Kister term, and V_i and x_i are the ith component molar volume and mole fraction, respectively. The number of parameters, n_{ij}, in the Redlich−Kister term depends on the system to be correlated. The

Table 6. Parameters of the Modified Wilson Equation for the System 2-Methylpentane (1) + *N*,*N*-DMF (2)[a]

$\alpha_{12} = 1.7935$	$\beta_{12} = -0.6333$
$\alpha_{21} = 4.8778$	$\beta_{21} = -2.1154$
$\alpha_{121} = -2.3869$	$\gamma_{121} = 2.8604$
$\alpha_{122} = -0.3174$	$\gamma_{122} = 0.3146$
molar volumes	
$V_{m1} = 132.9\ \mathrm{cm^3 \cdot mol^{-1}}$	$V_{m2} = 77.49\ \mathrm{cm^3 \cdot mol^{-1}}$

[a] Reference 17.

temperature dependence of the model parameters were assumed to be in the forms

$$a_{ij} = \alpha_{ij} + \beta_{ij} T^* \tag{5}$$

$$B_{ijk} = \alpha_{ijk} + \gamma_{ijk}/T^* \tag{6}$$

where α_{ij}, β_{ij}, α_{ijk}, and γ_{ijk} are temperature-independent binary parameters. A dimensionless temperature $T^* = T/T_{\mathrm{ref}}$ with $T_{\mathrm{ref}} = 300$ K was introduced to improve the numerical stability of calculation.

The parameters of the correlation model equation were obtained using the correlation procedure (Řehák et al.)[4] based on the maximum-likelihood method for equilibrium data and the least-squares method for the excess enthalpy data[17] to minimize the following objective function

$$F = \sum_i \sum_j \left(\frac{\nu_j^{\mathrm{exp}} - \nu_j^{calc}}{\sigma_{\nu j}} \right)_i^2 \tag{7}$$

where ν_j^{exp} and ν_j^{calc} are the *j*th variable experimental and calculated value, respectively, $\sigma_{\nu j}$ is the *j*th variable estimated standard deviation, and the subscript *i* stands for the experimental data point. The summation comprises all the available variables (e.g., temperature, composition of equilibrium phases, pressure, and heat of mixing) and all the experimental points. The principal advantage of this method lies in its ability to correlate simultaneously all available results, including the excess enthalpy data acquired in heterogeneous regions. Examples of successful correlations may by found in our preceding work.[1,11] The large number of correlated experimental data sets allows a relatively large number of parameters to be calculated with high confidence. With regard to future studies and to obtain an appropriate description of the upper critical solution point, an eight-parameter variant of the model was applied in this work. The model parameters are given in Table 6.

Model calculations are qualitatively compared to experimental data in Figures 1 and 2 and quantitatively in Tables 3 and 4. The model describes appropriately the liquid−liquid equilibrium in the system under study. The calculated critical temperature and mole fraction of 2-methylpentane are $T_c = 337.94$ K and $x_{1c} = 0.5097$, respectively. These values differ insignificantly from those obtained from the extended scaling-law equation in Table 5. Obtaining a good description of excess enthalpy by simultaneous correlation of various thermodynamic data with an excess Gibbs energy model appears to be difficult. As good agreement between model calculation and measured data indicates, the correlation approach to the excess enthalpy used in this work is a reasonable alternative.

Figures 1 and 2 also present data obtained by the modified UNIFAC (Dortmund) group contribution method. The estimate of excess enthalpy at experimental temperatures fits well the experimental data. However, the estimated value of the upper critical temperature for the liquid−liquid equilibrium is approximately 30 K higher than the experimental value.

Conclusions

Liquid−liquid equilibrium in the 2-methylpentane + *N*,*N*-DMF binary system was determined by three different experimental methods: the cloud-point method, the volume method, and the direct analytical method. The excess enthalpies were obtained at 298.15 K and 313.15 K. The results are in excellent mutual agreement.

The extended scaling-law equation proposed by Ewing et al.[5] fits binary liquid−liquid equilibrium data, including the critical region, very well, yielding the critical values that are only hardly attainable experimentally; however, it does not furnish the description of the Gibbs energy.

The modified Wilson equation allowed a successful simultaneous correlation of the excess enthalpy and liquid−liquid equilibrium data, yielding an excellent fit based on thermodynamically consistent description.

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