Solid−Liquid Equilibria for Seven Binary Systems

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Solid−liquid equilibria (SLE) for the following seven systems have been measured by the visual technique in a temperature range from 210 to 330 K: 2-butanol + cyclohexane, cyclohexane + methanol, 1-propanol + 1,4-dioxane, 1,4-xylene + toluene, benzonitrile + benzene, benzonitrile + toluene, and *N*-methylace-tamide + naphthalene. The predicted SLE data of all systems are in a good agreement with the experimental results using the group contribution method modified UNIFAC (Dortmund) assuming eutectic behavior.

Introduction

Solid−liquid equilibria (SLE) are of great technical interest, because they form the basis for designing crystallization processes. These processes are used for the separation of mixtures with thermolabile components or isomeric compounds with very similar vapor pressures for which the separation factor α_{ij} is approximately unity and cannot be influenced with the help of selective solvents.

Besides their importance for crystallization processes, SLE of eutectic systems are also of interest for fitting reliable temperature-dependent parameters for G^E models or group contribution methods such as modified UNIFAC (Dortmund), because they are important as supporting data at low ($\vartheta < 0$ °C) temperatures (Lohmann and Gmehling, 1999).

SLE can be calculated by a relation derived from the isofugacity criterion; i.e., the fugacity of component *i* in the liquid phase must be equal to the fugacity of component *i* in the solid phase:

$$f_i^s = f_i^L \tag{1}$$

After some simplifications [In eq 2, the contributions of the heat capacities are neglected. This simplification leads for nearly all systems to satisfying results (Jakob, 1995).], the following equation is obtained (Weimer and Prausnitz, 1965; Domanska, 1987; Lohmann, 2000):

$$\ln x_i^L \gamma_i^L = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\left(1 - \frac{T}{T_{\mathrm{fus},i}}\right) - \frac{\Delta_{\mathrm{trs}}H_i}{RT}\left(1 - \frac{T}{T_{\mathrm{trs},i}}\right) \tag{2}$$

where x_i^L is the mole fraction in the liquid phase, γ_i^L the activity coefficient in the liquid phase, $\Delta_{\mathrm{fus}}H_i$ the molar enthalpy of fusion, $T_{\mathrm{fus},i}$ the melting temperature, $\Delta_{\mathrm{trs}}H_i$ the molar enthalpy of transition, $T_{\mathrm{trs},i}$ the transition temperature of component *i*, *T* the absolute temperature, and *R* the universal gas constant.

If no solid−solid transition occurs in the considered temperature range, the last term in eq 2 can be neglected and eq 2 simplifies to (Gmehling et al., 1978)

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$$\ln x_i^L \gamma_i^L = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\left(1 - \frac{T}{T_{\mathrm{fus},i}}\right) \tag{3}$$

Because the activity coefficients depend not only on mole fraction but also on temperature, eqs 2 and 3 must be solved iteratively. For the description of the activity coefficient, the group contribution method modified UNIFAC (Dortmund) was used (Gmehling et al., 1993, 1998; Gmehling, 2000).

The SLE measurements of the systems containing benzonitrile were carried out to extend the database for aromatic nitriles (main group AC−CN) at lower temperatures for the further development of modified UNIFAC (Dortmund). Benzonitrile is a very powerful solvent. It even dissolves polymers such as poly(vinyl chloride) (PVC), poly-(vinyl acetate) resins, polystyrene, polymethacrylate, and nitrocellulose but not polyethylene (PE), polyamide (PA), poly(vinyl alcohol) (PVA), or fluoropolymers. It is produced by vapor-phase oxidation of toluene in the presence of ammonia (Ullmann, 1999). The corresponding experimental vapor−liquid equilibrium (VLE) and H^E data for the system toluene + benzonitrile were published earlier (Wilhelm et al., 1998; Horstmann et al., 1999); the SLE data given in this paper cover the low-temperature range.

The remaining systems were measured to check the results of modified UNIFAC (Dortmund) at low temperatures; the system *N*-methyacetamide + naphthalene was determined to extend the database for the introduction of the new main group CONR (monoalkylated amides), a class of compounds which are applied as selective solvents.

Experimental Section

All systems were measured by the synthetic method (Jakob et al., 1995; Fiege et al., 1996), where the melting process is observed visually. The melting temperature at a given composition (liquidus line) is determined as the temperature when the last crystal just disappears. Temperatures are measured in a range from 183 to 373 K using a Rosemount platinum resistance temperature sensor calibrated according to ITS-90. The metrology thermometer (model 1506) manufactured by Hart Scientific was used for the conversion of the measured resistance and display of the corresponding temperature. The uncertainty in the temperature is given as ±0.02 K and the uncertainty in the mole fraction as ±0.005.

Table 1. CAS Numbers, Suppliers, and Pure-Component Properties of the Applied Chemicals in Alphabetical Order [Mean Values Taken from the Dortmund Data Bank (DDB)][a]

compound	supplier	CAS no.	$\Delta_{fus}H$/J·mol^{-1}	T_{fus}/K	$\Delta_{trs}H$/J·mol^{-1}	T_{trs}/K
benzene	Scharlau	71-43-2	9951	278.68		
benzonitrile	Acros	100-47-0	10873	259.85		
2-butanol	Aldrich	78-92-2	5971	158.50		
cyclohexane	Scharlau	110-82-7	2630	279.75	6741	185.95
1,4-dioxane	Riedel de Haen	123-91-1	12550	284.85	2350	272.85
methanol	Scharlau	67-56-1	3177	175.25	641	157.35
N-methylacetamide	Aldrich	79-16-3	10100[b]	303.72		
naphthalene	Fluka	91-20-3	19110	353.35		
1-propanol	Merck	71-23-8	5195	147.05		
toluene	Scharlau	108-88-3	6851	178.16		
1,4-xylene	Aldrich	106-42-3	959	286.35		

[a] The purities were found to be at least 99.9 mol %. [b] Measured with the help of a Tian-Calvet microcalorimeter (SETARAM).

Table 2. Experimental SLE Data for the System 2-Butanol (1) + Cyclohexane (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.000	279.76	0.299	259.74	0.502	244.60
0.058	275.22	0.350	256.22	0.550	240.28
0.113	271.84	0.401	252.69	0.553	239.19
0.163	268.76	0.449	249.11	0.601	232.59
0.196	266.25	0.500	244.50	0.652	223.46
0.256	261.96	0.502	244.59		

Table 3. Experimental SLE Data for the System Cyclohexane (1) + Methanol (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.048	246.78	0.951	277.43	0.980	278.31
0.096	272.16	0.958	277.67	1.000	279.75

Table 4. Experimental SLE Data for the System 1-Propanol (1) + 1,4-Dioxane (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.000	285.06	0.399	269.94	0.802	255.73
0.077	281.19	0.478	267.86	0.883	247.88
0.157	277.66	0.561	265.66	0.961	228.68
0.239	274.63	0.641	263.22		
0.319	272.11	0.722	260.19		

Table 5. Experimental SLE Data for the System 1,4-Xylene (1) + Toluene (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.100	214.59	0.450	257.82	0.801	277.97
0.151	225.38	0.501	261.43	0.845	279.98
0.200	233.35	0.549	264.60	0.892	282.00
0.253	240.01	0.600	267.65	0.944	284.17
0.301	245.09	0.648	270.22	1.000	286.36
0.351	248.76	0.701	273.06		
0.401	253.99	0.755	275.75		

The chemicals were received from different commercial suppliers (Table 1), carefully degassed, and distilled using a 1.5 m Vigreux column (Fischer and Gmehling, 1994). The resulting purities were determined by gas chromatography, and the water content was determined by Karl Fischer titration. The purities of the chemicals used were found to be at least 99.9 mol %.

The pure-component properties of the chemicals applied are given in Table 1. Since the enthalpy of fusion for *N*-methylacetamide was not available, it was measured by differential scanning calorimetry using a Tian-Calvet microcalorimeter manufactured by SETARAM with an accuracy of ±50 J·mol^{-1}.

Results

Tables 2−8 give the experimental SLE data for the seven binary systems; the corresponding phase diagrams are

**Table 6. Experimental SLE Data for the System Benzontrile (1) + Benzene (2)**

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.000	278.68	0.353	255.67	0.701	243.46
0.051	275.59	0.405	251.72	0.733	245.32
0.107	272.17	0.452	247.76	0.800	249.14
0.152	269.39	0.503	243.36	0.849	251.92
0.200	266.34	0.550	238.85	0.899	254.59
0.257	262.61	0.596	236.99	0.951	257.35
0.301	259.52	0.639	239.64	1.000	259.85

**Table 7. Experimental SLE Data for the System Benzonitrile (1) + Toluene (2)**

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.249	205.24	0.551	234.15	0.843	251.39
0.300	211.64	0.594	236.96	0.897	254.43
0.351	217.26	0.639	239.81	0.941	256.66
0.401	222.23	0.696	243.30	1.000	259.85
0.449	226.40	0.750	246.35		
0.501	230.43	0.796	248.96		

**Table 8. Experimental SLE Data for the System *N*-Methylacetamide (1) + Naphthalene (2)**

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.700	331.31	0.850	312.50	1.000	303.74
0.750	326.72	0.900	299.76		
0.800	320.65	0.955	299.72		
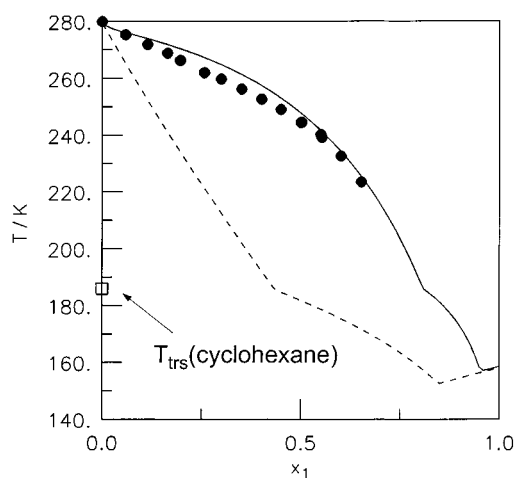
Figure 1. SLE for the system 2-butanol (1) + cyclohexane (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal; (□) transition temperature of cyclohexane.

presented in Figures 1−7. The circles represent the experimental visually detected data, the solid lines are the results of predictions carried out with modified UNIFAC (Dortmund), and the dashed lines show the results of predictions assuming ideal behavior ($\gamma_i = 1$). It is obvious
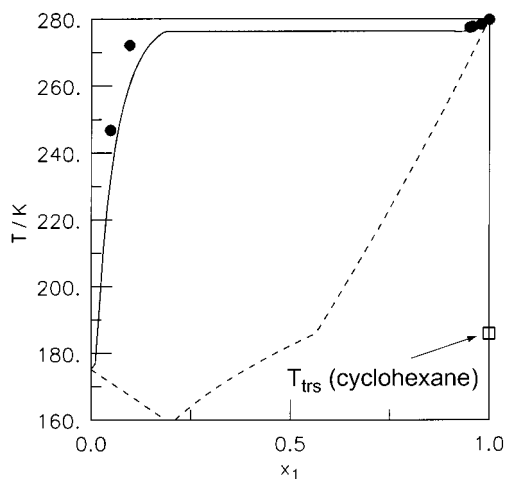
Figure 2. SLE for the system cyclohexane (1) + methanol (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal; (□) transition temperature of cyclohexane.
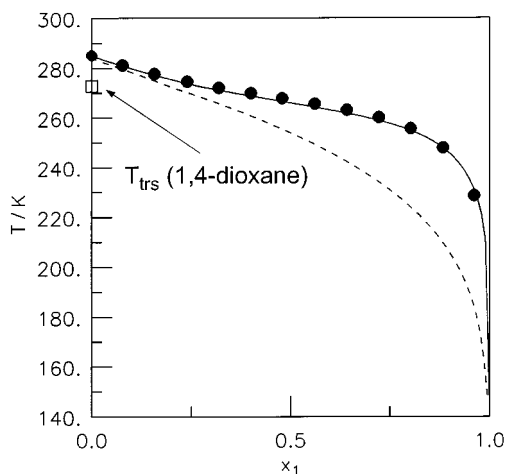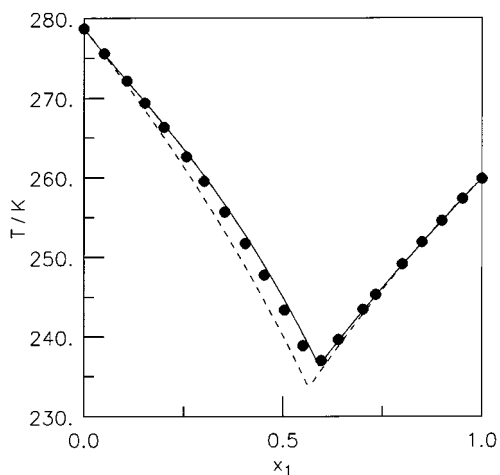

Figure 3. SLE for the system 1-propanol (1) + 1,4-dioxane (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal; (□) transition temperature of 1,4-dioxane.
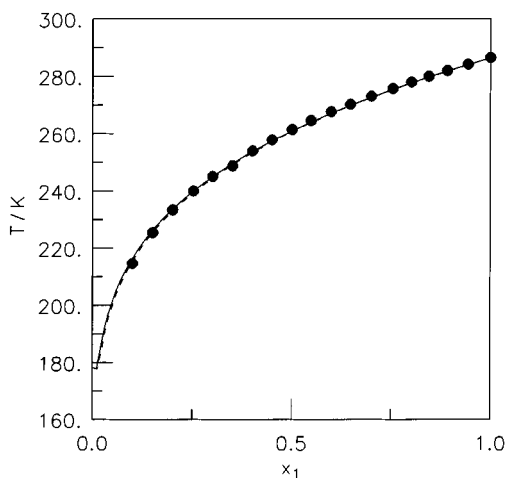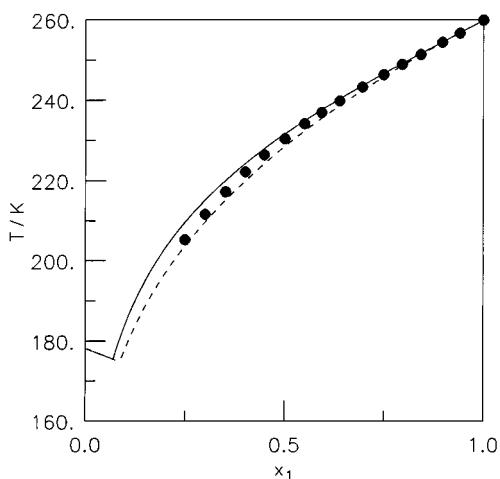

Figure 4. SLE for the system 1,4-xylene (1) + toluene (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal.

Figure 5. SLE for the system benzonitrile (1) + benzene (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal.

Figure 6. SLE for the system benzonitrile (1) + toluene (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal.

Figure 7. SLE for the system N-methylacetamide (1) + naphthalene (2): (●) visual method; (—) modified UNIFAC (Dortmund); (- - -) ideal.

that, with the exception of the nearly ideal systems 1,4-xylene + toluene and benzonitrile + toluene (Figures 4 and 6), neglecting the real phase behavior leads to poor results.
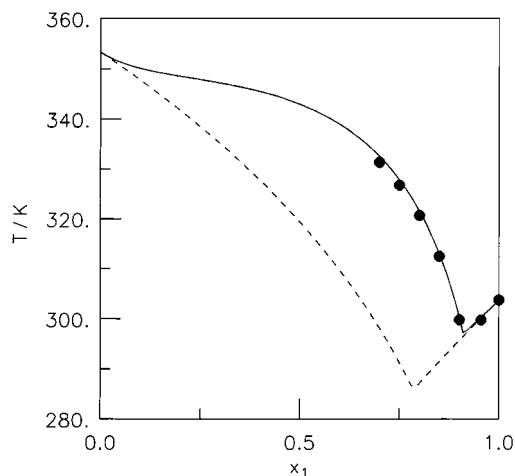
On the other hand, the diagrams show that the modified UNIFAC (Dortmund) is a suitable model for the prediction of SLE, i.e., thermophysical mixture data at low temper-

atures. For the system cyclohexane + methanol (Figure 2), also the miscibility gap in the liquid phase is predicted accurately. This accuracy shows the necessity of using SLE data as supporting data at low temperatures; i.e., the systematic experimental determination of SLE data should be continued.

The good agreement between experimental and predicted data sets confirms investigations which have been published earlier (Lohmann et al., 1997; Lohmann, 2000). In these papers the reliable results of modified UNIFAC (Dortmund) were found not only for a large number of SLE data but also for VLE, azeotropic points, excess enthalpies, and activity coefficients at infinite dilution.

Summary

The liquidus lines of seven binary SLE systems were determined by the synthetic visual method. The agreement between experimental and predicted data shows that modified UNIFAC (Dortmund) allows a reliable extrapolation to low temperatures. Therefore, it is a very suitable tool for the prediction of thermophysical mixture properties, i.e., the synthesis and design of thermal separation (e.g., crystallization) processes.

Acknowledgment

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