Measurement and Prediction of Ternary Solid−Liquid Equilibria

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Solid−liquid equilibria (SLE) and liquidus lines for the ternary systems cyclohexane + benzene + 2-heptanone and acetonitrile + benzene + chloroform were determined by means of the synthetic visual method. The phase diagrams are represented in different graphical forms. The experimental SLE data were compared with results obtained by the modified UNIFAC (Dortmund) method. The prediction of ternary solid−liquid equilibria with the help of a reliable group contribution method is a suitable way for choosing selective solvents for extractive crystallization processes. A model comparison (original UNIFAC, modified UNIFAC (Dortmund), modified UNIFAC (Lyngby), and ASOG) for the prediction of about 325 ternary SLE systems taken from the Dortmund Data Bank shows superior results for mod. UNIFAC (Do) in comparison to the other methods.

Introduction

Crystallization shows great advantages compared to other separation techniques, in particular when high-purity products are required. In the case of binary eutectic systems, only one theoretical stage is sufficient. However, there is the great disadvantage of simple crystallization that only one pure product can be obtained and the remaining mother liquor of nearly eutectic composition contains a significant amount of the desired product. This disadvantage can be overcome by extractive, adductive, or pressure swing crystallization or hybrid processes. For the selection of suitable solvents for extractive or adductive crystallization, a reliable knowledge of the solid−liquid equilibria (SLE) of ternary systems is required. Besides thermodynamic models for the calculation of SLE, a large data base of experimental data can be helpful for the synthesis of special crystallization processes. Especially adductive crystallization demands experimental data since the formation of adducts in a mixture cannot be predicted.

This paper presents experimental solid−liquid equilibrium data for the ternary systems benzene + cyclohexane + 2-heptanone and acetonitrile + benzene + chloroform obtained by the visual method. The experimental data are compared with predicted results using the modified UNIFAC (Dortmund) group contribution method (Gmehling et al., 1993). Necessary pure component properties were taken from the DDB (Dortmund Databank).

Experimental Section

2-Heptanone (Aldrich, 98%) was distilled under reduced pressure using a Vigreux column (1.5 m in length) in order to obtain a purity better than 99.5%. Benzene (Scharlau, 99.7%), cyclohexane (Scharlau, 99.7%), and acetonitrile (Aldrich, 99.7%) were dried using molecular sieves 3 Å (Riedel-de- Haën). Chloroform (Merck, 99%) was shaken with concentrated sulfuric acid, washed with water, and dried over calcium chloride. Final distillation gives chloroform with a purity better than 99.5%

The experimental determination of the solid−liquid phase equilibria was carried out with a static apparatus for visual SLE measurements described by Jakob et al. (1995). With this method, the melting process is observed visually and the melting temperature was determined at a given composition as the temperature when the last crystals just disappear. The estimated error for the determination of the equilibrium temperature with this method is ±0.025 K. The composition accuracy is ±0.01 mol %.

Calculation of Solid−Liquid Phase Equilibria

A relation for the calculation of solid−liquid phase equilibria can be derived starting from the isofugacity criterion (Gmehling and Kolbe, 1992). With some useful simplifications it leads to the following formula which was described elsewhere (Jakob et al., 1995)

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

where x_i^{L} is the mole fraction in the liquid phase, γ_i^{L} is the activity coefficient, $\Delta_{\mathrm{fus}}H_i$ is the molar enthalpy of fusion, $T_{\mathrm{fus},i}$ is the melting temperature of component *i*, *T* is the absolute temperature, and *R* is the universal gas constant. If a solid phase transition occurs, the molar enthalpy of transition $\Delta_{\mathrm{trs}}H_i$ must be considered below the transition temperature $T_{\mathrm{trs},i}$ by the second term on the right side of eq 1.

Since the activity coefficient depends on temperature as well as on concentration, eq 1 must be solved iteratively. From eq 1 either the mole fraction (calculation of temperature contour lines as shown in Figures 1b and 2b) or the temperature (calculation of solubility planes given in Figures 1a and 2a) can be calculated.

Whereas the eutectic point of a binary system can be easily derived from the point of intersection of the two solubility curves, for ternary systems eq 1 has to be fulfilled for each component and eqs 2−4 have to be solved simultaneously e.g. by the Gaussian method (Press et al., 1968) in order to find the eutectic temperature T_{eut} and the eutectic composition x_1^{L}, x_2^{L}, x_3^{L}.

$$\ln \gamma_1^{\mathrm{L}} x_1^{\mathrm{L}} = f(T_{\mathrm{eut}}, \Delta_{\mathrm{fus}} H_1, T_{\mathrm{fus},1}, ...) \quad (2)$$

$$\ln \gamma_2^{\mathrm{L}} x_2^{\mathrm{L}} = f(T_{\mathrm{eut}}, \Delta_{\mathrm{fus}} H_2, T_{\mathrm{fus},2}, ...) \quad (3)$$

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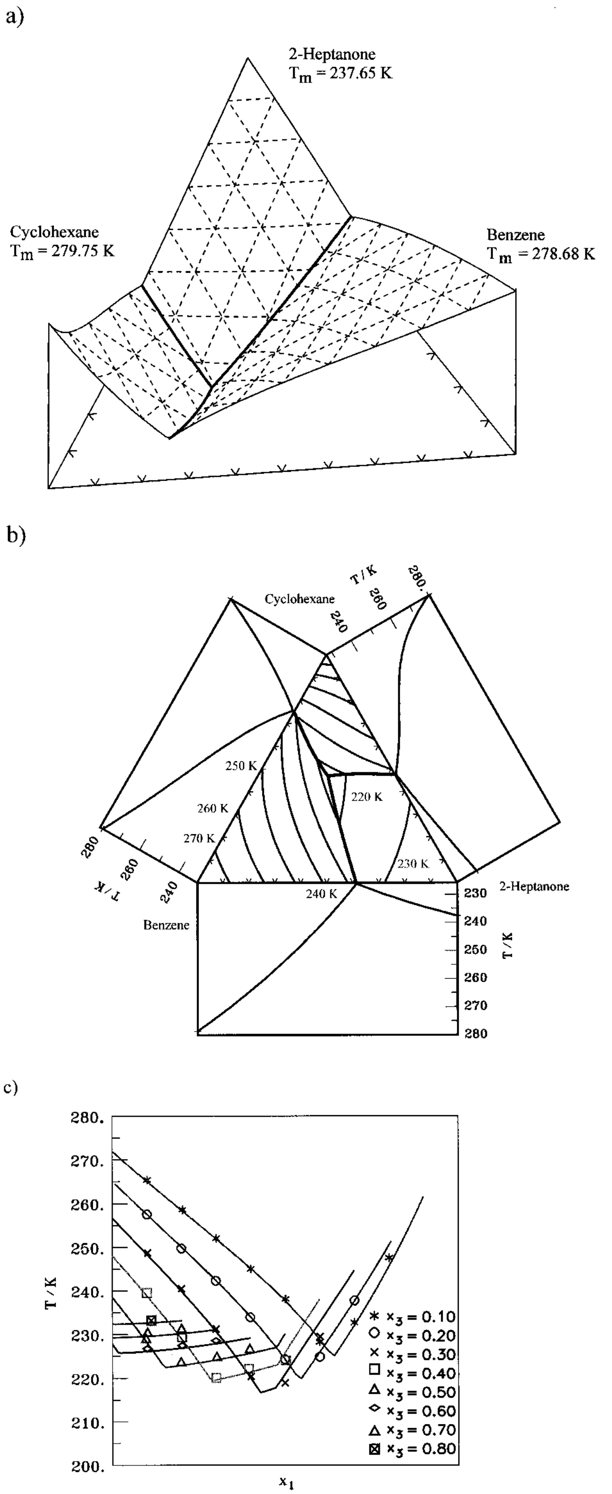

Figure 1. (a) Three-dimensional presentation of the SLE behavior for the system cyclohexane + benzene + 2-heptanone; - - - liquidus planes and — eutectic lines predicted with mod. UNIFAC (Do). (b, c) Two-dimensional presentations of the system cyclohexane + benzene + 2-heptanone predicted with mod. UNIFAC (Do): (b) temperature contour lines; (c) liquidus lines and experimental data of cyclohexane (1) + benzene (2) at constant mole fractions of 2-heptanone (3).

$$\ln \gamma_3^{L} x_3^{L} = f(T_{\text{eut}}, \Delta_{\text{fus}}H_3, T_{\text{fus},3}, ...) \qquad (4)$$

For the calculation of each point of the eutectic lines for a ternary SLE system, it is also possible to use the Gaussian method to calculate the intersection of two solubility planes for a given mole fraction of the third component.

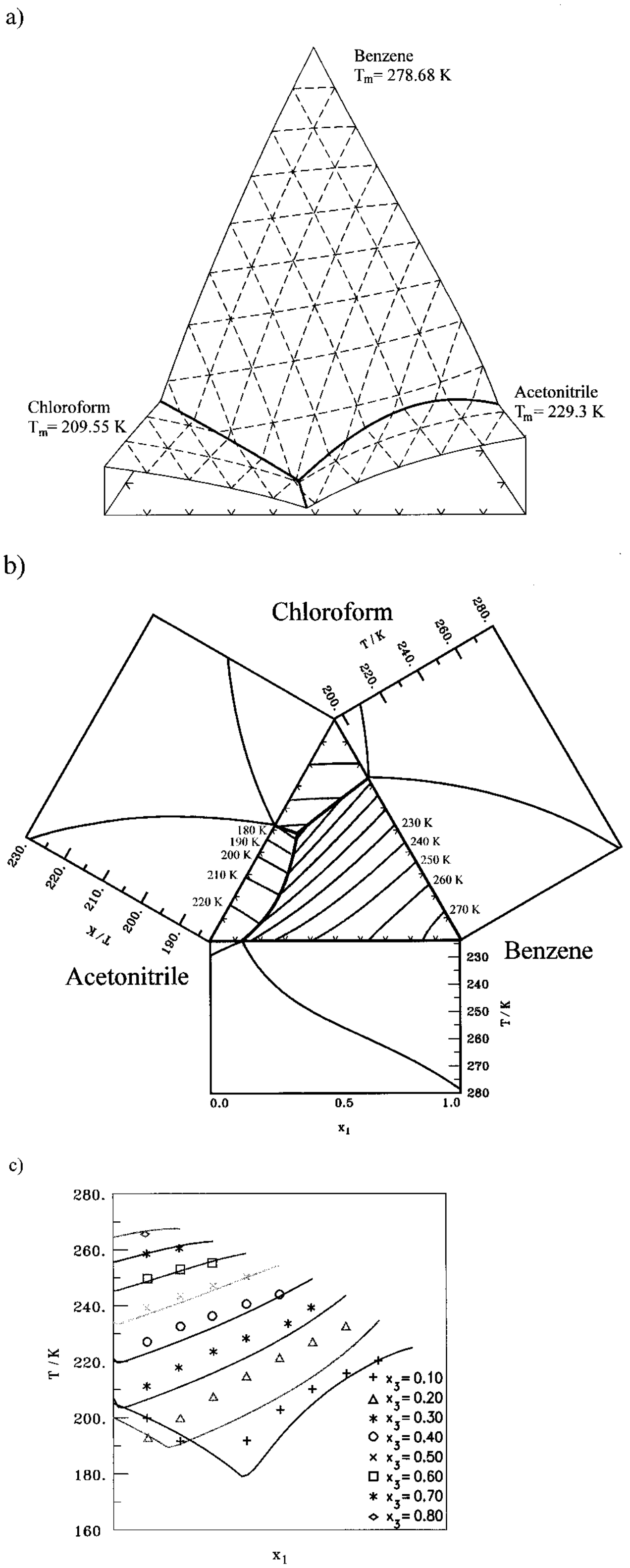

Figure 2. (a) Three-dimensional presentation of the SLE behavior for the system acetonitrile + benzene + chloroform; - - - liquidus planes and — eutectic lines predicted with mod. UNIFAC (Do). (b, c) Two-dimensional presentations of the system acetonitrile + benzene + chloroform predicted with mod. UNIFAC (Do): (b) temperature contour lines; (c) liquidus lines and experimental data of acetonitrile (1) + benzene (2) at constant mole fractions of benzene (3).

For the calculation of the required activity coefficients the mod. UNIFAC (Dortmund) method was used (Gmehling et al., 1993). The necessary interaction parameters (Gmehling and Li, 1994) for the calculations

Table 1. Pure Component Data[a]

	fusion		transition	
component	temperature/K	enthalpy/J mol^{-1}	temperature/K	enthalpy/J mol^{-1}
acetonitrile	229.30	8904.00	217.20	899.00
benzene	278.68	9944.10		
chloroform	209.55	8794.00		
cyclohexane	279.75	2628.40	185.95	6740.70
2-heptanone	237.65	19730.50		

[a] Source: Dortmund Data Bank.

Table 2. Experimental Data for the System Cyclohexane (1) + Benzene (2) + 2-Heptanone (3)

x_1^L	x_2^L	T/K	x_1^L	x_2^L	T/K
0.1116	0.1005	233.18	0.2996	0.4004	231.22
0.1011	0.2015	230.19	0.2987	0.5002	242.30
0.1002	0.2987	226.71	0.2997	0.5999	252.09
0.0970	0.4026	228.76	0.3972	0.0991	226.46
0.0991	0.5001	239.50	0.3943	0.1969	222.13
0.1020	0.5974	248.77	0.4011	0.2997	220.44
0.0999	0.6969	257.54	0.3987	0.4013	233.90
0.1004	0.8008	265.43	0.4005	0.4989	245.05
0.1994	0.0985	231.08	0.5014	0.0991	224.07
0.2011	0.1988	227.45	0.4995	0.2002	218.95
0.1982	0.3007	223.44	0.4987	0.3010	224.34
0.2000	0.3989	229.41	0.5009	0.3995	238.12
0.1994	0.5001	240.53	0.6014	0.0984	229.57
0.1991	0.5956	249.78	0.6003	0.1999	224.88
0.2030	0.6982	258.60	0.5995	0.2998	228.25
0.2990	0.1033	228.56	0.7010	0.0988	237.74
0.3016	0.1991	224.65	0.7003	0.1997	232.67
0.3002	0.2991	220.07	0.8010	0.0984	247.58

Table 3. Experimental Data for the System Acetonitrile (1) + Benzene (2) + Chloroform (3)

x_1^L	x_2^L	T/K	x_1^L	x_2^L	T/K
0.1000	0.0997	199.85	0.2999	0.5005	247.20
0.1037	0.1999	192.30	0.2973	0.5974	255.25
0.0996	0.2993	211.21	0.4007	0.0994	191.81
0.1014	0.4003	227.08	0.4002	0.2002	214.22
0.1003	0.4996	239.39	0.3991	0.2999	228.29
0.1025	0.5986	249.72	0.4003	0.4003	240.59
0.0991	0.7001	258.55	0.4012	0.5022	250.29
0.0963	0.7981	265.58	0.5017	0.1012	202.78
0.2001	0.1001	191.61	0.5000	0.2002	220.86
0.2004	0.2003	199.34	0.5255	0.2829	233.58
0.1957	0.2972	217.86	0.5004	0.3996	244.02
0.2014	0.4014	232.57	0.5989	0.0997	210.16
0.2005	0.4975	243.37	0.6000	0.2001	226.53
0.2008	0.5979	252.98	0.5953	0.3030	239.29
0.1980	0.6980	260.48	0.7011	0.1001	215.74
0.3001	0.2005	206.94	0.7000	0.2001	232.14
0.3005	0.3001	223.56	0.7967	0.0989	220.35
0.2973	0.3988	236.26			

with the modified UNIFAC (Dortmund) method are given in Table 4.

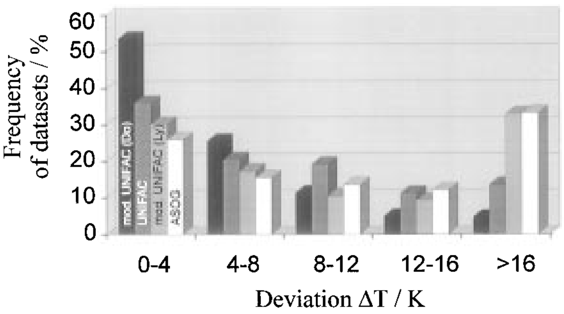

Figure 3. Frequency of the deviation ΔT for the prediction of ternary SLE using different group contribution methods.

Results

Figures 1 and 2 show the results for the systems benzene + cyclohexane + 2-heptanone and acetonitrile + benzene + chloroform in graphical form. Besides a three-dimensional presentation, the results are given in two different two-dimensional presentations. The solvent-free based projections (Figure 1c and 2c) are most suitable to show the agreement between experimental and calculated results.

Tables 2 and 3 contain the experimental solid−liquid equilibrium data. The necessary pure component properties were taken from the Dortmund Data Bank and are presented in Table 1. The prediction with mod. UNIFAC (Dortmund) provides good agreement with the experimental data for the system benzene + cyclohexane + 2-heptanone. The predicted results for the system acetonitrile + benzene + chloroform are not completely satisfactory. A revision of these parameters is planned.

Besides the measurement of ternary systems, also the quality of different group contribution methods for the prediction of solid−liquid equilibria was checked using 325 ternary SLE data sets stored in the Dortmund Data Bank. Table 5 shows the deviations for the group contribution methods ASOG (Kojima and Tochigi, 1979; Tochigi et al., 1990), UNIFAC (Fredenslund et al., 1975; Hansen et al., 1991), mod. UNIFAC (Lyngby) (Larsen et al., 1987), and mod. UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993). Figure 3 shows the frequency of data sets dependent on their calculated deviations.

The deviations were calculated for the predicted temperature at a given mole fraction. It is worth mentioning, that due to the shape of the liquidus curves also a fairly good description of a system can result from a comparatively large temperature deviation. Figure 4 shows an example for this case. The calculated absolute deviation for this system is 6.91 K (modified UNIFAC (Dortmund)). This relatively high value is mainly caused by a very small concentration shift.

Table 4. Group Interaction Parameters for the Mod. UNIFAC (Dortmund) Method

main groups		interaction parameters[a]					
n	m	a_{nm}/K	b_{nm}	c_{nm}/K^{-1}	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}
CH_2	ar-CH	114.200	0.0933		16.070	−0.2998	
CH_2	CH_2−CO−	433.600	0.1473		199.000	−0.8709	
CH_2	−CH_2−CN	593.070	0.7335		293.810	−1.3979	
CH_2	cy-CH_2[b]	−117.100	0.5481	−0.000 98	170.900	−0.8062	0.001 291
ar-CH	−CH_2−CO−	146.200	−1.2370	0.004 237	−57.530	1.2120	−0.003 715
ar-CH	−CH_2−CN	−17.440	0.9437		111.800	−0.5959	
ar-CH	cy-CH_2*	134.600	−1.2310	0.001 488	−2.619	1.0940	−0.001 557
−CH_2−CO−	−CH_2−CN	−191.000	0.6835		79.080	−0.3808	
−CH_2−CO−	cy-CH_2*	168.200	−0.8197		464.500	0.1542	
−CH_2−CN	cy-CH_2*	256.200	−1.5260	0.001 118	1336.000	−3.3950	0.004 586

[a] $\Psi_{nm} = \exp[-(a_{nm}/T + b_{nm} + c_{nm}T)]$. [b] Revised parameter sets for main group 42 (cy-CH_2) (Gmehling and Li, 1994).

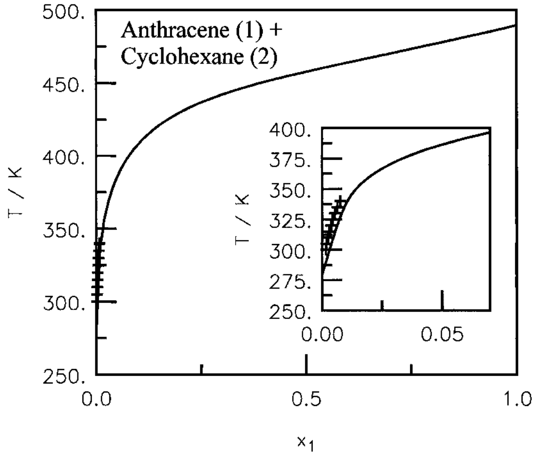

Figure 4. Binary SLE of anthracene (1) + cyclohexane (2): —, modified UNIFAC (Do); +, Somayajulu and Palit (1954).

Table 5. Mean Deviations for 325 Ternary SLE Systems

group contribution method	mean absolute deviation ΔT/K	mean relative deviation/%
mod. UNIFAC (Do)	5.30	1.71
UNIFAC	8.15	2.66
mod. UNIFAC (Ly)	12.33	4.04
ASOG	15.17	5.13

The comparison of the group contribution methods shows the superiority of mod. UNIFAC (Dortmund) for the prediction of multicomponent solid−liquid equilibria. This can be attributed mainly to the fact that a large data base (provided by the Dortmund Data Bank) (Gmehling, 1995; Gmehling et al., 1995) covering a wide temperature range is used for fitting the required group interaction parameters simultaneously to binary VLE, h^E, γ^∞, azeotropic, and SLE data.

Summary

Solid−liquid equilibrium data for two ternary systems were determined by the visual method. Different graphical presentations were used to compare experimental and predicted results. A model comparison using 325 ternary SLE data sets of the Dortmund Data Bank (DDB) shows the superior results for modified UNIFAC (Dortmund) and confirms this method as an ideal tool for the design of crystallization processes.

Literature Cited

Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086.

Gmehling, J. From UNIFAC to Modified UNIFAC to PSRK with the Help of DDB. *Fluid Phase Equilib.* **1995**, *107*, 1.

Gmehling, J.; Kolbe, B. *Thermodynamik*; VCH: Weinheim, 1992.

Gmehling, J.; Li, J. Private communication 1994.

Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178.

Hansen, H. K.; Rasmussen, P.; Fredenslund, Aa.; Schiller, M.; Gmehling, J. Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352.

Jakob, A.; Joh, R.; Rose, C.; Gmehling, J. Solid-Liquid Equilibria in Binary Mixtures of Organic Compounds. *Fluid Phase Equilib.* **1995**, *113*, 117.

Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by the ASOG-Method*; Kodansha-Elsevier: Tokyo, 1979.

Larsen, B.; Rasmussen, P.; Fredenslund, Aa. A Modified UNIFAC Group-Contribution Model for the Prediction of Phase Equilibria. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274.

Press, W. H.; Flannery, B. P.; Turkolsky, S. A.; Veffering, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, 1968.

Somayajulu, G. R.; Palit, S. R. Studies on Cosolvence. V. Lewis Acid Character of Iodo Compounds in Enhancing the Solubility of Anthracene in Hydrocarbon Solvents. *J. Phys. Chem.* **1954**, *58*, 417.

Tochigi K.; Tiegs D.; Gmehling J.; Kojima K.; Determination of New ASOG Parameters. *J. Chem. Eng. Jpn.* **1990**, *23* (4), 453.

Weidlich U.; Gmehling J.; A Modified UNIFAC Model. 1. Prediction of VLE, h^E and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372.

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