Binary Solid−Liquid Equilibria of Organic Systems Containing ε-Caprolactone

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Solid−liquid equilibria (SLE) for the following seven systems have been measured by the visual technique: benzene, toluene, cyclohexane, 1-propanol, methanol, water, and 2-pentanone with ε-caprolactone. For the description of the SLE data the NRTL model and the group contribution method Modified UNIFAC (Dortmund) were used.

Introduction

Solid−liquid equilibria (SLE) are of great technical interest. A knowledge of SLE is necessary for the design and optimization of crystallization processes. Crystallization processes are used for the separation of mixtures with thermolabile components or if the separation factor a_{ij} is near unity and cannot be changed by any selective solvent. Furthermore, crystallization is also a suitable technology to obtain products of very high purity.[1] Knowledge of the solid−liquid equilibrium behavior is also important for refrigeration and pipeline design, where undesired crystallization can cause safety problems.

SLE of eutectic systems can be calculated with the following equation derived from the isofugacity criterion:[2]

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

In eq 1 x_i^L is the mole fraction in the liquid phase, γ_i^L the activity coefficient in the liquid phase, $\Delta_{fus}H_i$ the molar enthalpy of fusion, $T_{fus,i}$ the fusion temperature, $\Delta_{trs}H_i$ the molar enthalpy of transition, $T_{trs,i}$ the transition temperature of component i, T the absolute temperature, and R the universal gas constant.

If no solid−solid transition is observed, the last term in eq 1 can be neglected and eq 1 simplifies to[3]

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

Eqs 1 and 2 must be solved iteratively, because the activity coefficient in the liquid phase γ_i^L depends on the mole fraction in the liquid phase x_i^L as well as on the temperature T.

For the description of the activity coefficient the NRTL[4] model was used. The interaction parameters for the NRTL model have been fitted to the SLE data using the heat of fusion values and melting temperatures given in Table 1 assuming eutectic behavior. The objective function F has been chosen for the fitting procedure

$$F = \sum_{i=1}^{n}\left(\frac{\gamma_{calcd} - \gamma_{exptl}}{\gamma_{exptl}}\right)^2 \quad (3)$$

where n is the number of experimental data points and $\gamma_{calcd} - \gamma_{exptl}$ is the difference between calculated and experimental activity coefficients.

Furthermore, the group contribution method Modified UNIFAC (Dortmund)[5,6] was used for the prediction of the activity coefficients, whereby the available group interaction parameters of the "acyclic esters" group (COO) were applied.

Because the mixture behavior of cyclic esters differs from the behavior of acyclic ones, a new main group (cyclic esters, cy-COO-C) will be introduced into the Modified UNIFAC (Dortmund) model to be able to handle lactone systems. The solid−liquid equilibria were measured to obtain the required supporting data at low temperature[7] for the introduction of the new main group "cyclic esters". Within this project also phase equilibrium (vapor−liquid equilibria, activity coefficients at infinite dilution, azeotropic data) and excess enthalpy data of lactone systems will be measured in a wide temperature range. All of the data will be used together with the SLE data for fitting reliable temperature-dependent interaction parameters for the Modified UNIFAC (Dortmund) main group cyclic esters.

Thermodynamic data are also of importance for the various processes with ε-caprolactone. ε-Caprolactone is an important intermediate for the production of polyesters and polyurethanes. ε-Caprolactone can also be converted to ε-caprolactam with ammonia. It is produced by oxidation of cyclohexanone.[8]

Experimental Section

The chemicals were purchased from different commercial suppliers, stored over molecular sieve 3 Å, and distilled under vacuum using a Vigreux column with a height of 1.5 m. All compounds were stored under nitrogen to avoid contamination with water. The resulting purity as determined by gas chromatography, the water content obtained by Karl Fischer titration, and the pure component properties taken from the Dortmund Data Bank are listed in Table 1.
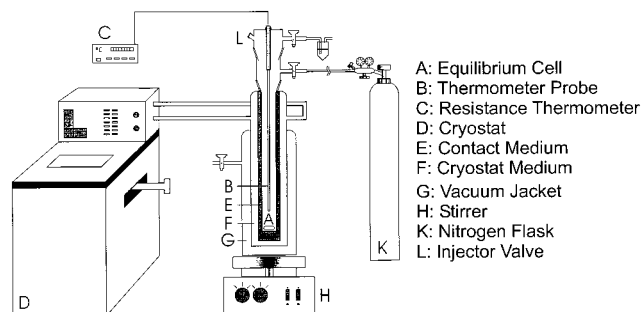
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Table 1. Suppliers, Purities, Water Contents, CAS Registry Numbers, and Pure Component Properties of the Chemicals Used (Values Taken from the Dortmund Data Bank)

compound	supplier	purity/% GC	water content/ mass ppm	CAS Registry No.	$\Delta_{fus}H$/J·mol^{-1}	T_{fus}/K
cyclohexane	Scharlau	>99.9	18	110-82-7	2630	279.75
benzene	Merck	>99.9	25	71-43-2	9951	278.68
toluene	Scharlau	>99.9	10	108-88-3	6851	178.16
methanol	Merck	>99.9	20	67-56-1	3177	175.25
1-propanol	Merck	>99.9	8	71-23-8	5195	147.05
2-pentanone	Aldrich	>99.9		107-87-9	10632	196.15
water		>99.9		7732-18-5	6000	273.15
ϵ-caprolactone	Acros	>99.9	27	502-44-3	13821	272.13

Figure 1. Static apparatus for SLE measurement.

A: Equilibrium Cell
B: Thermometer Probe
C: Resistance Thermometer
D: Cryostat
E: Contact Medium
F: Cryostat Medium
G: Vacuum Jacket
H: Stirrer
K: Nitrogen Flask
L: Injector Valve

Table 2. Experimental SLE Data for the System Benzene (1) + ϵ-Caprolactone (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.15	0.3558	253.71	0.6986	261.55
0.0482	269.93	0.4069	250.65	0.7443	264.62
0.1042	267.30	0.4528	247.93	0.8019	268.19
0.1587	264.62	0.4996	245.06	0.8434	270.43
0.2056	262.21	0.5494	249.68	0.8890	272.82
0.2537	259.74	0.6043	254.43	0.9437	275.62
0.2853	257.88	0.6495	257.99	1.0000	278.77

Table 3. Experimental SLE Data for the System Toluene (1) + ϵ-Caprolactone (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.18	0.3616	254.98	0.7019	233.61
0.0631	269.26	0.4104	252.41	0.7528	229.07
0.1041	267.40	0.4532	250.02	0.8058	223.74
0.1526	265.08	0.4961	247.63	0.8514	218.64
0.2086	262.44	0.5482	244.43	0.8991	210.83
0.2577	260.11	0.6025	240.92		
0.3122	257.42	0.6499	237.57		

Table 4. Experimental SLE Data for the System Cyclohexane (1) + ϵ-Caprolactone (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.15	0.1781	270.20	0.9713	278.33
0.0584	269.73	0.2044	273.94	0.9800	278.65
0.1076	268.15	0.2073	275.11	1.0000	279.79
0.1528	267.01	0.2196	276.90		

Table 5. Experimental SLE Data for the System 1-Propanol (1) + ϵ-Caprolactone (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.18	0.3592	258.87	0.6999	249.03
0.0796	268.66	0.4115	257.35	0.7514	247.14
0.1176	267.05	0.4532	256.10	0.8045	244.77
0.1592	265.37	0.5078	254.61	0.8524	241.93
0.2031	263.70	0.5537	253.37	0.9008	237.09
0.2511	262.19	0.6048	251.95	0.9428	228.76
0.3124	260.20	0.6538	250.51		

Table 6. Experimental SLE Data for the System Methanol (1) + ϵ-Caprolactone (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.25	0.4127	255.05	0.7541	241.06
0.0667	269.17	0.4623	253.04	0.8031	236.98
0.1355	266.22	0.5007	251.56	0.8499	233.55
0.1663	264.97	0.5599	249.15	0.8970	227.92
0.2166	262.81	0.6022	247.95	0.9504	214.25
0.2567	261.21	0.6549	245.55	0.9701	204.08
0.3188	258.76	0.6605	245.48		
0.3700	256.69	0.7031	243.62		

Table 7. Experimental SLE Data for the System Water (1) + ϵ-Caprolactone (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.18	0.4228	261.61	0.7500	266.51
0.1163	267.92	0.4706	260.99	0.7991	267.17
0.1553	266.65	0.4983	261.51	0.8484	267.80
0.1919	265.67	0.5487	262.94	0.8993	268.69
0.2440	264.50	0.5990	264.26	0.9478	270.07
0.2980	263.47	0.6493	265.41	1.0000	273.15
0.3565	262.60	0.7016	266.01		

The SLE of all systems were measured by the synthetic, visual technique.[2,9] The experimental setup is shown in Figure 1. The glass apparatus consists of a three-jacket vessel. The equilibrium cell (A) is inserted in this vessel. The volume of the sample is ∼160 cm³. Using the apparatus, measurements between 183 and 373 K can be performed. The exterior vacuum jacket prevents the condensation of water vapor on the glass surface at low temperatures so that the visual observation is not disturbed. The cryostat medium (F) flows through the central jacket and transfers the heat to the equilibrium cell via the contact medium (E). A nitrogen atmosphere in the equilibrium cell avoids contamination with water. The temperature is determined with a platinum resistance thermometer (B) (model 162 CE, Rosemount). For the conversion of the measured resistance a digital thermometer (C) (model 1506, Hart Scientific) is used. The accuracy of the melting temperature is determined to be ±0.05 K; the accuracy of the composition is ±0.005.

First the sample is supercooled in liquid nitrogen for a short time, whereby a small amount of the liquid crystallizes in the form of fine particles. Then the equilibrium cell is installed in the apparatus. The mixture is heated slowly within a defined rate (e.g., 0.3 K h^{-1}). The melting point for a given composition is determined by visual detection of the temperature at which the solid phase just disappears. By varying the composition of the mixture the liquidus line over the whole composition range can be obtained.

Results

In Tables 2−8 the experimental SLE data for the seven binary systems are given. The corresponding Figures 2−8 contain the experimental data together with the correlations using the NRTL model and the predictions of the group contribution method Modified UNIFAC (Dortmund) using the parameters for the acyclic main group. These results are compared with the predictions assuming ideal

**Table 8. Experimental SLE Data for the System
2-Pentanone (1) + ε-Caprolactone (2)**

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	272.24	0.3505	256.22	0.7005	234.27
0.0542	269.80	0.4007	253.68	0.7503	230.58
0.1127	267.17	0.4510	251.63	0.8003	224.99
0.1601	265.09	0.5011	248.54	0.8375	218.85
0.2107	262.95	0.5734	244.23	0.8890	210.11
0.2541	260.87	0.6002	242.27	0.9410	194.46
0.3018	258.73	0.6511	238.55	1.0000	196.36
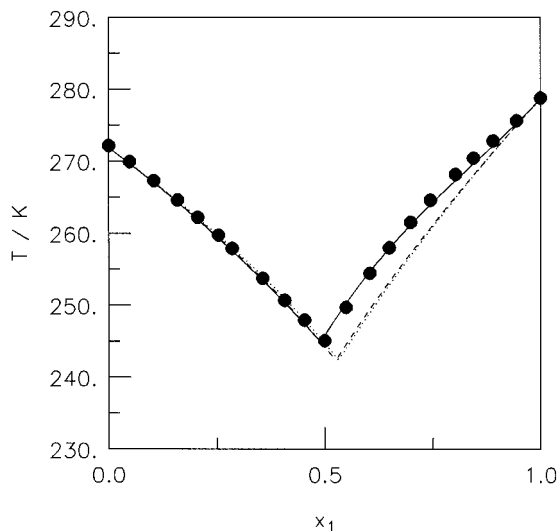
Figure 2. SLE for the system benzene (1) + ε-caprolactone (2): ●, visual method; —, NRTL; - - -, ideal; · · ·, Modified UNIFAC (Dortmund).
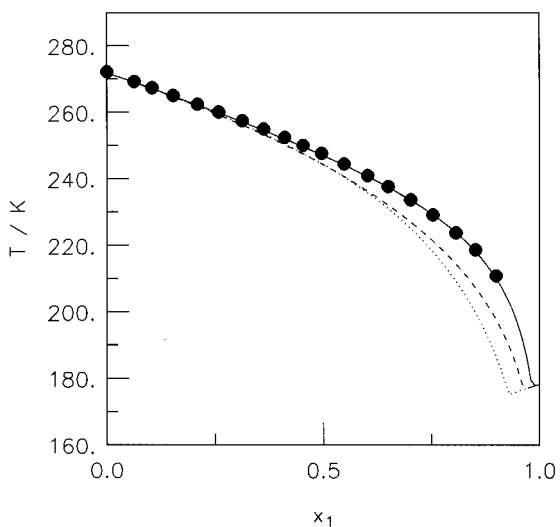
Figure 3. SLE for the system toluene (1) + ε-caprolactone (2): ●, visual method; —, NRTL; - - -, ideal; · · ·, Modified UNIFAC (Dortmund).

behavior. In all cases eutectic behavior is assumed. The binary parameters for the NRTL model Δg_{ij} as well as the nonrandomness parameters α_{ij} together with the root-mean-square deviations (RMSD) are given in Table 9. For all studied systems (except the system cyclohexane + ε-caprolactone) the obtained RMSDs are smaller than 0.6.

The systems benzene + ε-caprolactone (Figure 2) (eutectic point at $x_1 \approx 0.49$), toluene + ε-caprolactone (Figure 3), and 2-pentanone + ε-caprolactone (Figure 8) (eutectic point at $x_1 \approx 0.95$) show nearly ideal behavior. This behavior is nearly predicted with Modified UNIFAC (Dortmund) using the acyclic ester group.
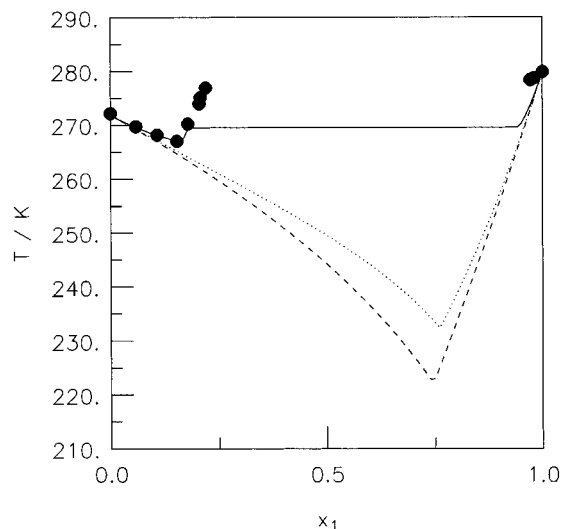
Figure 4. SLE for the system cyclohexane (1) + ε-caprolactone (2): ●, visual method; —, NRTL; - - -, ideal; · · ·, Modified UNIFAC (Dortmund).
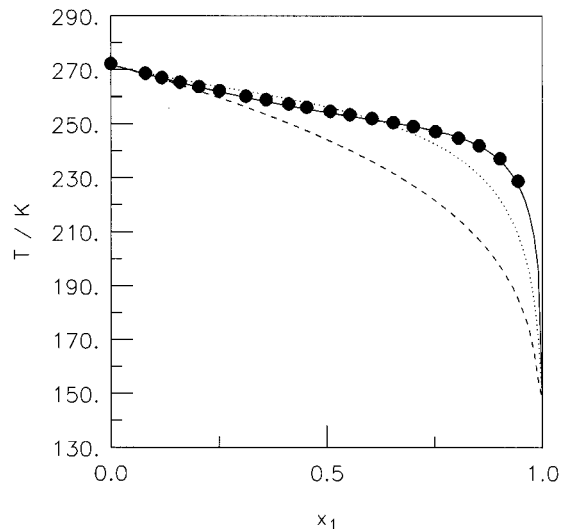
Figure 5. SLE for the system 1-propanol(1) + ε-caprolactone (2): ●, visual method; —, NRTL; - - -, ideal; · · ·, Modified UNIFAC (Dortmund).

Table 9. NRTL Interaction Parameters Fitted to SLE Data

system component (1) + component (2)	$\Delta g_{12}^o/$ J mol^{-1}	$\Delta g_{21}^o/$ J mol^{-1}	α_{12}	RMSD[a]
benzene + ε-caprolactone	4124.38	−2119.44	0.2934	0.552
toluene + ε-caprolactone	2762.14	−1203.26	0.2844	0.401
cyclohexane + ε-caprolactone	4894.21	2982.76	0.2967	3.598
1-propanol + ε-caprolactone	3639.81	214.45	0.2957	0.424
methanol + ε-caprolactone	3206.51	−293.15	0.2965	0.495
2-pentanone + ε-caprolactone	309.77	628.85	0.3017	0.593

[a]
$$\text{RMSD} = \sqrt{\frac{1}{n}\sum_n (T_{\text{exptl}} - T_{\text{calcd}})^2}$$

The experimental data for the systems 1-propanol + ε-caprolactone and methanol + ε-caprolactone are shown in Figures 5 and 6. The predictions with Modified UNIFAC (Dortmund) provide temperatures that are too low or too high. It is obvious that neglecting the real behavior in the liquid phase leads to poor results.

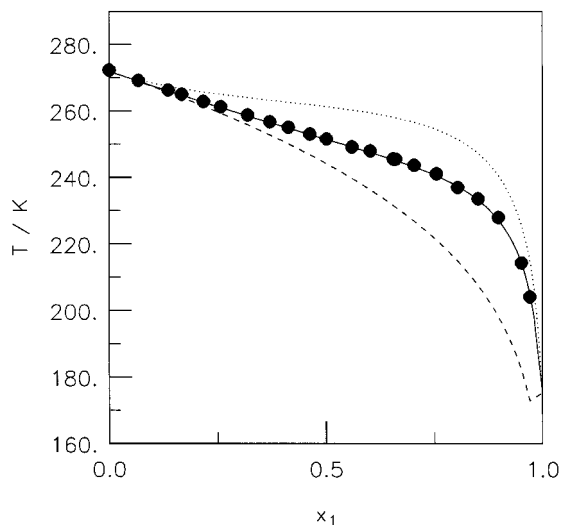The system cyclohexane + ε-caprolactone (Figure 4) (eutectic point at $x_1 \approx 0.16$) represents a solid−liquid

Figure 6. SLE for the system methanol(1) + ϵ-caprolactone (2): ●, visual method; —, NRTL; - - -, ideal; ···, Modified UNIFAC (Dortmund).
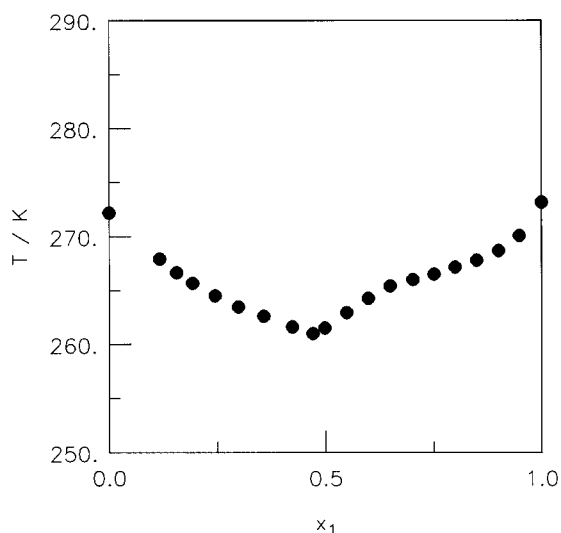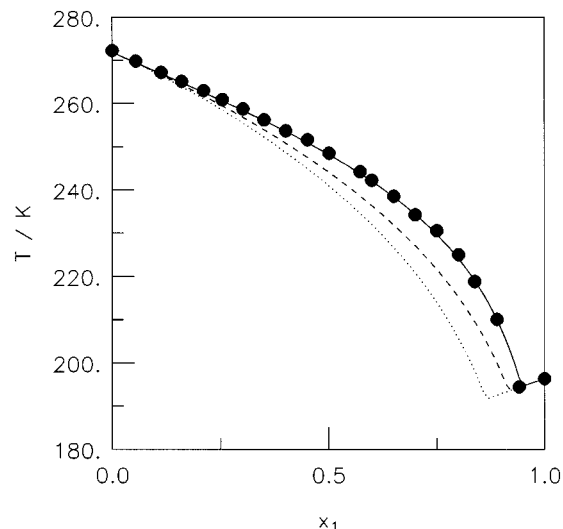

Figure 8. SLE for the system 2-pentanone (1) + ϵ-caprolactone (2): ●, visual method; —, NRTL; - - -, ideal; ···, Modified UNIFAC (Dortmund).

method. The correlations of these phase diagrams with the help of NRTL are in good agreement with the experimental data. The prediction with Modified UNIFAC (Dortmund) using the main group "acyclic esters" performs not too badly except for the system cyclohexane + ϵ-caprolactone. To improve the description of the thermodynamic behavior of systems containing cyclic esters such as ϵ-caprolactone or γ-butyrolactone with Modified UNIFAC (Dortmund), a new main group (cyclic esters, cy-COO-C) will be introduced. The measurement of the required SLE has been completed with this work. Soon further phase equilibrium and excess enthalpy data of lactone systems will be measured. These thermodynamic mixture data together with the SLE data will be used for fitting simultaneously temperature-dependent interaction parameters for the group contribution method Modified UNIFAC (Dortmund).

Figure 7. SLE for the system water (1) + ϵ-caprolactone (2): ●, visual method.

equilibrium with a miscibility gap. Solid−liquid−liquid equilibrium (SLLE) occurs in a mole fraction range between 0.22 and 0.97, within which the two liquid phases are in equilibrium with solid cyclohexane. The occurrence of the miscibility gap is calculated qualitatively only by the NRTL model, whereas the Modified UNIFAC (Dortmund) predicts nearly ideal behavior using the parameters for the acyclic ester group.

For all systems except for water + ϵ-caprolactone (Figure 7) (eutectic point at $x_1 \approx 0.47$), eutectic behavior was observed. The bend in the course of the experimental data at $x_1^L \approx 0.75$ is not caused by a solid−solid transition of water but by the formation of an incongruently melting compound (peritectic behavior). Because all calculations are based on eq 2, which is valid only for eutectic systems, the SLE behavior of the system water + ϵ-caprolactone cannot be calculated with the NRTL equation or with Modified UNIFAC (Dortmund).

Summary

The liquidus lines of seven binary systems containing ϵ-caprolactone were determined by the synthetic, visual

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