

Solid–Liquid Equilibria of Several Binary Systems with Organic Compounds

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Solid–liquid equilibria of the seven binary systems benzaldehyde + benzene, benzaldehyde + dodecane, benzaldehyde + cyclohexane, cyclohexane + phenol, methylcyclohexane + tetrachloromethane, 2-butanone + water and acrylic acid + propionic acid have been measured by the visual method. Furthermore, the liquid–liquid equilibrium of the system benzaldehyde + dodecane was determined analytically using gas chromatography. The experimental data of the eutectic systems were compared with predicted results using the modified UNIFAC (Dortmund) method and in two cases correlated with the NRTL equation.

Introduction

Solid–liquid equilibria (SLE) are of great technical interest. Mainly, they are used for the development, design, and operation of crystallization processes. Crystallization processes are applied for the separation of thermolabile components or isomeric compounds with very similar vapor pressures for which the separation factor α_{ij} is approximately near unity and cannot be strongly influenced using selective solvents. Furthermore, crystallization is used in order to obtain products of very high purity (Wynn, 1992). Solid–liquid equilibria are also important considering refrigeration and pipeline design, where undesired crystallization can lead to safety problems.

It is also possible to combine crystallization with other separation processes. The resulting process is known as a hybrid process. A further alternative is the separation by extractive or adductive crystallization.

Besides all these technical applications, solid–liquid equilibria of eutectic systems are of great interest for fitting temperature-dependent g^E -model parameters or interaction parameters of group contribution methods such as modified UNIFAC (Dortmund) (Gmehling et al., 1993). In the latter case, the solid–liquid equilibria are used as supporting data at low temperatures. The use of SLE as supporting data ensures a more reliable prediction of the activity coefficients γ_i at low temperatures.

Solid–liquid equilibria of eutectic systems can be calculated by knowledge of the real behavior in the liquid phase and the pure component properties (melting point, enthalpy of fusion, transition temperature, and enthalpy of transition) using eq 1, which can be derived from the isofugacity criterion (Gmehling and Kolbe, 1992):

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

In eq 1 x_i^L is the mole fraction of component i in the liquid phase, γ_i^L the activity coefficient, $\Delta_{\text{fus}} H_i$ the molar enthalpy of fusion, $T_{\text{fus},i}$ the fusion temperature, $\Delta_{\text{trs}} H_i$ the

molar enthalpy of transition, $T_{\text{trs},i}$ the transition temperature, T the absolute temperature, and R the universal gas constant.

If a solid–solid transition does not occur, the last term of eq 1 can be neglected and eq 1 simplifies to (Gmehling et al., 1978)

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

Because the activity coefficient depends on mole fraction and temperature, eq 1 and eq 2 must be solved iteratively.

The activity coefficient can also be used in order to calculate liquid–liquid equilibria (LLE). The exact description of LLE in multicomponent systems is a more difficult task than the description of SLE, since for SLE γ_i is only a correction term, while on the other hand the composition and temperature dependence of LLE has to be described by the activity coefficient (Gmehling and Kolbe, 1992) alone:

$$x_i^A \gamma_i^A = x_i^B \gamma_i^B \quad (3)$$

In eq 3 x_i^A and x_i^B are the mole fractions of component i in phase A and phase B, respectively, and γ_i^A and γ_i^B the corresponding activity coefficients. For the description of the activity coefficient, the group contribution method modified UNIFAC (Dortmund) was used (Gmehling et al., 1993).

This paper presents the experimental SLE data for seven binary systems containing organic compounds. These data were measured for the further development of modified UNIFAC (Dortmund). In particular, they are used to extend the quantity of supporting data at low temperatures.

The systems, in which a miscibility gap was observed, are presented together with the experimental LLE data.

For two systems, for which only poor results are obtained using modified UNIFAC (Dortmund), parameters for the NRTL-model (Renon and Prausnitz, 1968) are given in addition.

Experimental Section

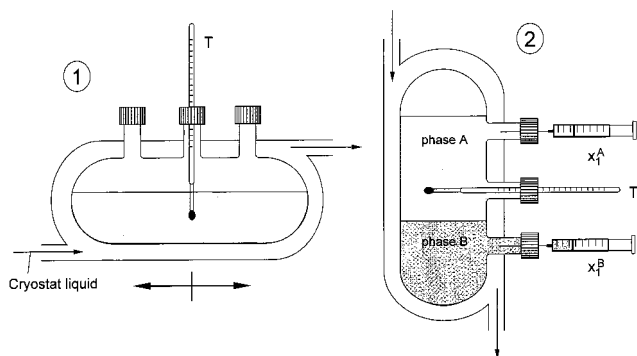
All chemicals were obtained from commercial sources (Aldrich, Fluka, Merck) and stored over molecular sieve 3

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Table 1. Purities and Pure Component Properties of the Applied Chemicals Taken from the Dortmund Data Bank (DDB)

compound	CAS number ^a	purity/%	$\Delta_{\text{fus}}H/J\cdot\text{mol}^{-1}$	T_{fus}/K	$\Delta_{\text{trs}}H/J\cdot\text{mol}^{-1}$	T_{trs}/K
benzaldehyde	[100-52-7]	99.9	9322	216.0		
dodecane	[112-40-3]	99.9	36582	263.6		
cyclohexane	[110-82-7]	99.9	2630	279.8	6741	185.95
benzene	[71-43-2]	99.9	9951	278.7		
tetrachloromethane	[56-23-5]	99.9	2530	250.8	4560	225.35
water	[7732-18-5]	99.9	6000	273.2		
phenol	[108-95-2]	99.8	11289	314.1		
acrylic acid	[79-10-7]	>99.0	11165	285.7		
propionic acid	[79-09-4]	99.8	7535	252.4		
2-butanone	[78-93-3]	99.9	8439	186.5		
methylcyclohexane	[108-87-2]	99.9	6750	146.6		

^a Supplied by authors.

**Figure 1.** Experimental apparatus for analytical measurements of liquid-liquid equilibria.

Ä. Benzaldehyde, phenol, and propionic acid were distilled under vacuum using a Vigreux column with a height of 1.5 m. All other chemicals were used without further purification. All compounds were stored under nitrogen to avoid contamination with humidity. Table 1 gives the purities (determined using gas chromatography) and the pure component properties (taken from DDB) of the applied chemicals. Various melting temperatures are available from literature, so that we assume the melting temperatures to be correct within ± 0.5 K.

All systems were measured by the established synthetic method (Jakob et al., 1995; Fiege et al., 1996), where the melting process is observed visually. The melting temperature at a given composition is determined as the temperature when the solid phase just disappears.

Using the apparatus, measurements between 190 and 373 K can be performed. The accuracy of the given composition is assumed to be ± 0.0001 . Furthermore, the degree of accuracy of the temperature using the visual method was determined to be ± 0.015 K.

The liquid-liquid equilibrium data of the system benzaldehyde + dodecane were determined analytically with the help of the apparatus shown in Figure 1. The glass apparatus consists of an equilibrium cell, which can be thermostated by a cryostat liquid flowing through the jacket. If water is used as the cryostat liquid, measurements are possible between 273.15 K and 373.15 K.

The cell is shaken automatically in order to support the mass transfer between the coexisting liquid phases ((1) in Figure 1). The phases are mixed continuously for at least 12 h. For the separation of the two phases (A and B), the equilibrium cell can be turned over ((2) in Figure 1). After the two phases have been separated (which sometimes takes several hours), samples of both phases are taken using a sampling needle. The samples are analyzed using a gas chromatograph HP 5890 with an integrator HP

Table 2. Experimental SLE Data for the System Benzaldehyde (1) + Benzene (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	278.76	0.2985	259.85	0.6009	235.47
0.0459	275.87	0.3495	256.42	0.6573	229.54
0.1011	272.43	0.3991	252.85	0.6994	224.52
0.1489	269.48	0.4497	248.94	0.7500	217.67
0.2010	266.21	0.4995	244.88	0.7995	209.64
0.2499	263.09	0.5487	240.53	1.0000	216.35

Table 3. Experimental SLE and LLE Data for the System Benzaldehyde (1) + Dodecane (2)

(a) SLE Data					
x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	263.63	0.9235	261.31	0.9951	237.59
0.0442	263.03	0.9414	260.21	0.9971	232.09
0.1055	262.38	0.9603	257.38	0.9987	223.80
0.1563	261.91	0.9800	251.57	1.0000	216.35
0.2074	261.61	0.9905	244.34		
(b) LLE Data					
T/K	x_1^A	x_1^B			
274.2	0.42	0.86			
276.2	0.46	0.85			
278.2	0.47	0.84			
279.7	0.49	0.83			
281.2	0.51	0.81			
293.2	0.54	0.78			
284.7	0.58	0.75			

3396A manufactured by Hewlett-Packard; the column used was CP-Sil-19 CB (DF-0.2, 25 m \times 0.32 mm) from Chrompack.

The absolute error in mole fraction is assumed as ± 0.01 ; the accuracy in the determination of the temperature is given by the thermometer used. In this case, the mercury thermometer used provides an accuracy of ± 0.5 K.

The experimental liquid-liquid equilibrium data of the system benzaldehyde + dodecane obtained with the apparatus described above are given in Table 3b.

Results

In Tables 2 to 8 the experimental solid-liquid equilibrium data for the seven systems investigated are given. Figures 2 to 8 present the experimental data in graphical form. The circles stand for the visually detected experimental data. If predictions with the group contribution method modified UNIFAC (Dortmund) were possible (eutectic behavior assumed for the solid-liquid equilibrium), the predicted values using group interaction parameters published before (see Table 9; Gmehling et al., 1993) and eq 2 are presented together with the corresponding binary experimental data.

Table 4. Experimental SLE Data for the System Benzaldehyde (1) + Cyclohexane (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	279.80	0.3523	260.04	0.7003	252.86
0.0506	270.86	0.4002	259.79	0.7499	248.77
0.0989	266.00	0.4503	259.41	0.7996	242.45
0.1496	263.12	0.5001	258.99	0.8501	232.65
0.1999	261.45	0.5502	258.37	0.9001	217.91
0.2485	260.91	0.6002	257.31	0.9455	214.38
0.2996	260.38	0.6498	255.62	1.0000	216.35

Table 5. Experimental SLE Data for the System Cyclohexane (1) + Phenol (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	314.11	0.3513	300.79	0.7001	298.03
0.0540	311.14	0.3985	300.31	0.7498	297.51
0.0983	308.90	0.4505	299.76	0.7999	296.83
0.1493	306.43	0.5000	299.41	0.8499	295.75
0.1985	304.53	0.5507	299.00	0.8998	293.67
0.2500	302.99	0.5993	298.71	0.9496	288.46
0.3020	301.83	0.6493	298.43	1.0000	279.79

Table 6. Experimental SLE Data for the System Methylcyclohexane (1) + Tetrachloromethane (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	250.77	0.2015	220.75	0.4516	202.53
0.0516	241.50	0.2507	217.40	0.4999	198.59
0.1012	232.61	0.3046	213.66	0.5500	193.95
0.1260	228.04	0.3496	210.44		
0.1514	224.08	0.3992	206.67		

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

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	273.15	0.6753	264.47	0.8547	252.70
0.0246	270.85	0.7011	264.07	0.8757	249.13
0.0506	268.51	0.7251	263.41	0.9036	241.07
0.0751	266.77	0.7499	262.52	0.9329	228.05
0.0977	265.84	0.7738	261.22	0.9501	216.84
0.1252	265.18	0.7997	259.43	0.9766	197.75
0.6458	264.74	0.8239	257.09		

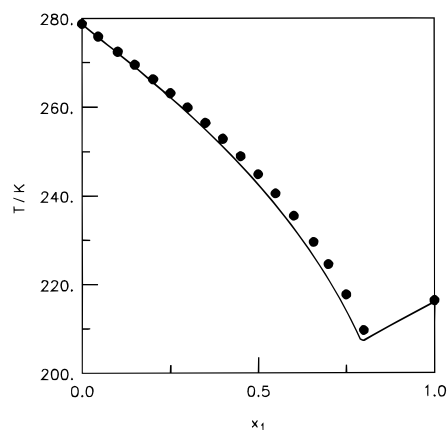
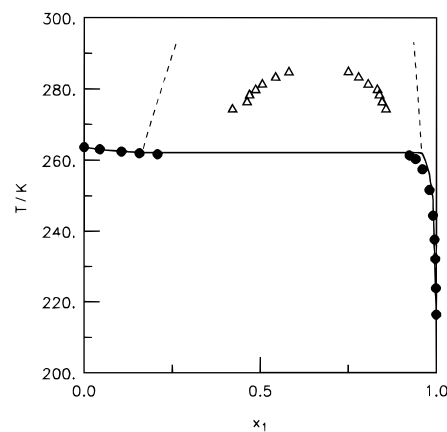
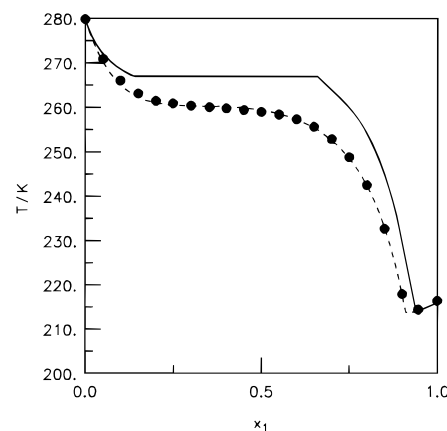
Table 8. Experimental SLE Data for the System Acrylic Acid (1) + Propionic Acid (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	253.17	0.3056	250.46	0.5998	264.35
0.0495	251.85	0.3523	252.48	0.6503	267.62
0.0559	251.62	0.3987	254.24	0.6999	270.59
0.1042	250.55	0.4007	254.33	0.7496	273.44
0.1200	250.24	0.4456	255.78	0.8008	276.21
0.1531	249.64	0.4512	256.04	0.8523	278.87
0.1767	249.34	0.5004	257.47	0.8999	281.23
0.2017	248.95	0.5011	257.51	0.9502	283.58
0.2290	248.91	0.5492	260.88	1.0000	285.87
0.2565	248.67	0.5499	260.90		

The temperature of the solid–solid transition of tetrachloromethane at 225.35 K is indicated in Figure 6. The prediction of the binary SLE data are performed using eq 1. All required pure component properties are given in Table 1.

The system benzaldehyde + benzene (Figure 2 and Table 2) shows a gap in the range $x_1 = 0.8$ to $x_1 = 1.0$. This gap cannot be filled with experimental data because the high viscosity of the mixture in this region does not allow to perform measurements using the synthetic method.

In two systems (Figures 3 and 7) a miscibility gap was observed. In these cases, experimental and predicted (also using modified UNIFAC (Do)) liquid–liquid equilibrium data are indicated in the phase diagrams.

**Figure 2.** Solid–liquid equilibrium for the system benzaldehyde (1) + benzene (2): ●, visual method; —, modified UNIFAC (Do).**Figure 3.** Benzaldehyde (1) + dodecane (2) system: SLE: ●, visual method; —, modified UNIFAC (Do); LLE: △, exptl data, this paper; ---, modified UNIFAC (Do).**Figure 4.** Solid–liquid equilibrium for the system benzaldehyde (1) + cyclohexane (2): ●, visual method; —, modified UNIFAC (Do); ---, NRTL ($\Delta g_{12} = 408.90$ K, $\Delta g_{21} = 541.16$ K, $\alpha_{12} = 0.4350$).

The good agreement between experimental and predicted LLE, SLE, and azeotropic data for the system 2-butanone + water (Figure 7) shows again the reliability of the modified UNIFAC (Do) model for the prediction of different phase equilibrium data in a wide temperature range.

On the other hand, the results for the systems benzaldehyde + dodecane and benzaldehyde + cyclohexane (Figures 3 and 4) are poor if compared with the results for other systems. Especially the predicted miscibility gap of the system benzaldehyde + dodecane is too large. The reason for this disagreement is that the predictions of the

Table 9. Modified UNIFAC (Dortmund) Interaction Parameters (Gmehling et al., 1993)

main groups		interaction parameters ^a					
<i>n</i>	<i>m</i>	<i>a_{nm}/K</i>	<i>b_{nm}</i>	<i>c_{nm}/K⁻¹</i>	<i>a_{nm}/K</i>	<i>b_{nm}</i>	<i>c_{nm}/K⁻¹</i>
1	3	114.200	0.0933	0.000 000	16.070	-0.2998	0.000 000
1	7	1391.300	-3.6156	0.001 144	-17.253	0.8389	0.000 902
1	9	433.600	0.1473	0.000 000	199.000	-0.8709	0.000 000
1	10	875.850	0.0000	0.000 000	256.210	0.0000	0.000 000
1	24	267.510	-1.7109	0.003 388	-148.070	1.0927	-0.002 416
1	42	-117.100	0.5481	-0.000 980	170.900	-0.8062	0.001 291
3	8	1356.000	-2.1180	0.000 000	2340.000	-5.0430	0.000 000
3	10	-365.500	1.8740	0.000 000	1011.000	-2.1670	0.000 000
3	42 ^b	134.600	-1.2310	0.001 488	-2.619	1.0940	-0.001 557
7	9	190.500	-3.6690	0.008 838	770.600	-0.5873	-0.003 252
8	42 ^b	391.200	-0.8799	0.000 000	3630.000	-6.2300	0.000 000
10	42 ^b	716.700	-1.5160	0.000 000	1161.000	-0.5724	0.000 000
24	42	-37.183	-0.0478	0.000 000	60.780	0.0243	0.000 000

^a $\Psi_{nm} = \exp(-(a_{nm} + b_{nm}T + c_{nm}T^2)/T)$. ^b Revised 1994.

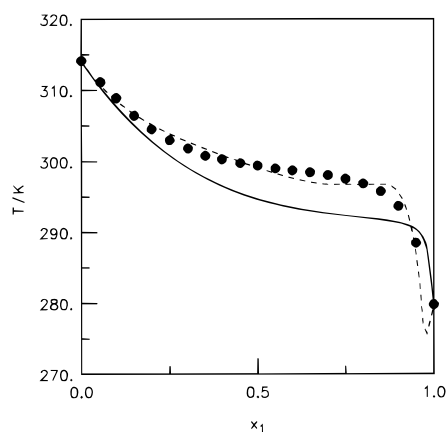


Figure 5. Solid-liquid equilibrium for the system cyclohexane (1) + phenol (2): ●, visual method; ○, modified UNIFAC (Do); ---, NRTL ($\Delta g_{12} = 744.55$ K, $\Delta g_{21} = 457.28$ K, $\alpha_{12} = 0.4691$).

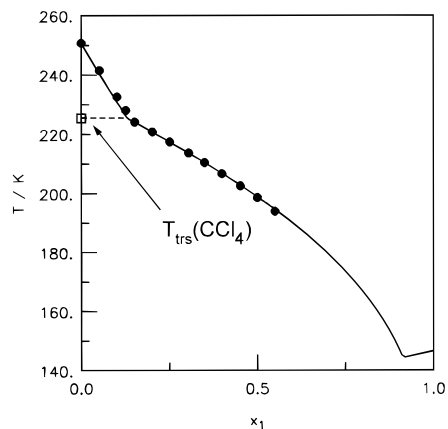


Figure 6. Solid-liquid equilibrium for the system methylcyclohexane (1) + tetrachloromethane (2): ●, visual method; ○, modified UNIFAC (Do).

systems containing benzaldehyde were performed using the main group for aliphatic aldehydes (CHO). Because the behavior of aromatic aldehydes in mixtures differs from the aliphatic ones, the introduction of a new main group (aromatic aldehydes, ACCHO) for the modified UNIFAC (Dortmund) model is planned (Lohmann et al., 1998). Another fact to be considered was the lack of supporting data at low temperatures ($T < 0$ °C) when fitting the group interaction parameters between the main groups alkanes (CH2) and cyclic alkanes (cy-CH2) with aliphatic aldehydes (CHO).

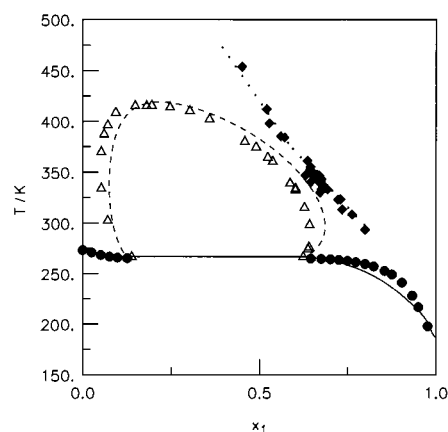


Figure 7. 2-Butanone (1) + water (2) system: SLE: ●, visual method; ○, modified UNIFAC (Do); LLE: △, exptl data (Ochi et al., 1990); ---, modified UNIFAC (Do); azeotropic points: ◆, exptl data (Gmehling et al., 1994) ... modified UNIFAC (Do).

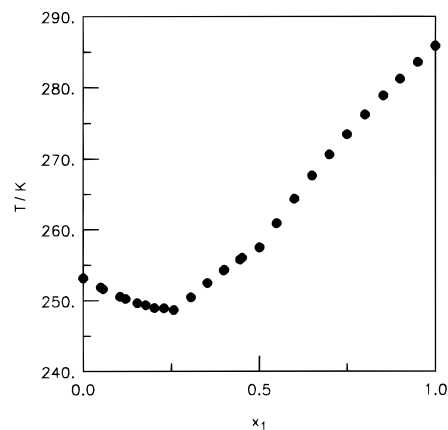


Figure 8. Solid-liquid equilibrium for the system acrylic acid (1) + propionic acid (2): ●, visual method.

Furthermore, the quite poor prediction of the systems cyclohexane + phenol (Figure 5) should be overcome refitting the group interaction parameters between the main group 8 (aromatic alcohols, ACOH) and the main group 42 (cyclic alkanes, cy-CH2) of the current parameter matrix (Gmehling et al., 1993) because again no experimental information at low temperatures (e.g SLE data of eutectic systems) was used when fitting the required group interaction parameters.

Nevertheless, most of the diagrams show that modified UNIFAC (Dortmund) is a suitable tool for the prediction of solid-liquid equilibria. This confirms investigations that

were published previously (Joh and Kreutz, 1997; Hofman et al., 1998).

For all systems except for the system acrylic acid + propionic acid, eutectic behavior was observed. The bend in the course of the experimental data at $x_1^L \approx 0.5$ is not caused by a solid–solid transition of acrylic acid, but by the formation of an incongruently melting compound of equimolar composition (peritectic behavior). This assumption is supported by the fact that calorimetric measurements of pure acrylic acid did not show any solid–solid transition. Since all calculations (fitting g^E -model parameters, predictions using group contribution methods) are based on eqs 1 or 2, which can be derived for eutectic systems, the SLE behavior of the system acrylic acid + propionic acid cannot be predicted or correlated.

Summary

The liquidus lines of seven binary systems containing organic compounds were determined by the synthetic visual method. The agreement between experimental and predicted data for most systems shows that modified UNIFAC (Dortmund) is a suitable prediction tool for solid–liquid equilibria of eutectic systems. In the cases of nonsatisfying results, the gap between experimental and predicted data should be overcome by either the introduction of a new main group (aromatic aldehydes, ACCHO) or the revision of the group interaction parameters between the main group for phenols and the main group for cyclic alkanes taking into account experimental data at low temperatures.

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