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Binary Solid−Liquid Equilibria of Organic Systems Containing Different Amides and Sulfolane

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Solid−liquid equilibria of 14 binary systems containing various amides or sulfolane with organic compounds have been measured by a visual technique. The substances investigated are important and often used as selective solvents in the chemical industry, for example for extractive distillation or extraction. Assuming eutectic behavior for all systems, the experimental data are compared with the results of the Modified UNIFAC (Dortmund) model.

Introduction

A knowledge of solid−liquid equilibria is necessary in order to design and optimize crystallization processes. Crystallization is used instead of distillation, if thermolabile compounds or substances with low vapor pressures (e.g. inorganic salts) have to be separated or the separation factor α_{ij} is near unity and cannot be improved by any selective solvent (extractive or azeotropic distillation). Another application of crystallization consists of puryfing substances (Wynn, 1992). In particular, pharmaceuticals are often purified by crystallization. Measurements of solid−liquid equilibria are also important for refrigeration and pipeline design, where undesired crystallization can lead to safety risks.

Solid−liquid equilibria have been measured for the extension and further development of the group contribution method Modified UNIFAC (Dortmund) (Gmehling et al., 1993; Gmehling et al., 1998; Lohmann et al., 1998), which is a well-known model for the prediction of phase equilibria and excess properties. The further development of the group contribution methods UNIFAC and Modified UNIFAC (Dortmund) is supported by approximately 30 companies (Lohmann et al.,1998). The current status of the two parameter matrixes can be found on our research group's web site (http://www.uni-oldenburg.de/tchemie).

The calculation of solid−liquid equilibria of eutectic systems is based on the equation

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

which can be derived from the isofugacity criterion (Gmehling and Kolbe, 1992). In addition to a suitable model for the reliable calculation of the real phase behavior, the knowledge of the properties of the pure compounds (enthalpy of fusion $\Delta_{\mathrm{fus}}H_i$, enthalpy of transition $\Delta_{\mathrm{trs}}H_i$, melting temperature $T_{\mathrm{fus},i}$ and temperature of transition $T_{\mathrm{trs},i}$) is necessary. Equation 1 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. If no solid−solid transition is observed, the last term in eq 1 can be neglected.

The activity coefficient can be calculated using g^{E} models (e.g. NRTL or UNIQUAC) or a group contribution method like Modified UNIFAC (Dortmund). The use of temperature-dependent group interaction parameters allows reliable predictions in a large temperature range.

$$\Psi_{\mathrm{nm}} = \exp\left(-\frac{(a_{\mathrm{nm}} + b_{\mathrm{nm}}T + c_{\mathrm{nm}}T^2)}{T}\right) \qquad (2)$$

SLE data (T < 273 K) and h^{E} data (up to 413 K) are used as supporting data during the fitting procedures to cover a large temperature range in order to ensure the reliability of the prediction performed at these temperatures (Gmehling et al., 1998).

The measured solid−liquid equilibria were determined mainly to extend the database of reliable experimental data at low temperatures. The compounds investigated are of technical interest, since *N*,*N*-dimethylacetamide, *N*-methylformamide, and sulfolane are important as selective solvents for extraction processes; for example, sulfolane is used as a selective solvent for the separation of aromatics from aliphatics by extractive distillation (Gmehling and Brehm, 1996).

Experimental Section

All chemicals were obtained from commercial sources (Fluka, Aldrich, Scharlau) or were placed at our disposal by BASF AG and stored over 3 Å molecular sieves. *N*-methyl-formamide, *N*,*N*-dimethylacetamide, and sulfolane were distilled under vacuum using a Vigreux column with a height of 1.5 m. The other compounds were used without further purification. The purities were determined by gas chromatography, and the water content was determined by Karl Fischer titration. As the melting point of sulfolane is strongly influenced by the water content, the substance was stored under a nitrogen atmosphere to avoid contamination with ambient water vapor. The purities and pure component properties of the applied organic compounds, which were taken from the Dortmund Data Bank (Gmehling et al., 1999), are given in Table 1.

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Table 1. Purities and Pure Component Properties of the Chemicals from the Dortmund Data Bank (Gmehling et al., 1999)

compound	CAS no.	purity/%	$\Delta_{fus}H$/J·mol^{-1}	T_{fus}/K	$\Delta_{trs}H$/J·mol^{-1}	T_{trs}/K
cyclohexane	110-82-7	>99.9	2630	279.75	6741	185.95
benzene	71-43-2	>99.9	9951	278.68		
toluene	108-88-3	>99.9	6851	178.16		
water	7732-18-5	>99.9	6000	273.15		
ethanol	64-17-5	>99.9	5021	158.65		
methanol	67-56-1	>99.9	3177	175.25	641	157.35
1-propanol	71-23-8	>99.9	5195	147.05		
N-methylformamide	123-39-7	>99.9	10439[b]	270.60[a]	1231[b]	228.10[b]
N-methylacetamide	79-16-3	>99.9	10107[b]	303.72		
N,*N*-dimethylacetamide	127-19-5	>99.9	10418	251.42[a]		
sulfolane	126-33-0	>99.9	1372[b]	301.65[a]	7860[b]	288.60[b]

[a] Measured with a visual method. [b] Measured with a Tian−Calvet calorimeter.

Table 2. Experimental SLE Data

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K	x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
(a) *N*-Methylformamide (1) + Benzene (2)											
0.0000	278.67	0.2021	277.97	0.3503	275.89	0.5496	272.04	0.7007	264.09	0.9015	265.81
0.0512	277.81	0.2498	276.69	0.3995	275.28	0.6010	270.09	0.7478	260.25	0.9487	268.09
0.0998	277.41	0.2993	276.37	0.4503	274.47	0.6476	267.79	0.7951	261.81	1.0000	270.61
0.1633	277.14			0.4985	273.46			0.8479	263.78		
(b) *N*-Methylformamide (1) + Toluene (2)											
0.0230	253.42	0.2024	257.66	0.3500	257.85	0.5505	258.90	0.6982	260.70	0.8992	266.08
0.0509	255.92	0.2504	257.76	0.3985	257.93	0.6031	259.45	0.7484	261.80	0.9454	267.98
0.0989	256.76	0.3014	257.80	0.4493	258.06	0.6515	260.06	0.7980	262.95	1.0000	270.61
0.1568	257.19			0.5026	258.50			0.8458	264.30		
(c) *N*-Methylformamide (1) + Ethanol (2)											
0.0972	199.51	0.2986	226.71	0.4484	238.41	0.6498	251.31	0.7978	259.74	1.0000	270.60
0.1502	210.19	0.3479	230.89	0.5000	241.75	0.6998	254.13	0.8422	262.15		
0.2007	216.97	0.3972	234.62	0.5504	244.89	0.7500	256.63	0.8988	264.90		
0.2494	221.95			0.5931	247.43			0.9479	267.75		
(d) *N*-Methylformamide (1) + Methanol (2)											
0.1498	198.75	0.3001	219.75	0.4487	234.13	0.5909	245.06	0.7502	256.55	0.8977	265.07
0.2003	207.12	0.3497	224.94	0.5014	238.30	0.6486	249.05	0.7989	259.56	0.9413	267.50
0.2485	213.68	0.3942	229.19	0.5498	242.05	0.6982	253.18	0.8490	262.39	1.0000	270.60
(e) *N*-Methylformamide (1) + Water (2)											
0.0000	273.15	0.1490	255.24	0.5009	235.11	0.6476	249.19	0.8003	259.27	0.9501	268.03
0.0519	267.77	0.2000	246.63	0.5404	239.14	0.6929	252.59	0.8505	262.61	1.0000	270.59
0.0984	262.23	0.2497	236.70	0.6033	245.55	0.7480	256.27	0.9013	265.39		
(f) *N*-Methylformamide (1) + *N*,*N*-Dimethylacetamide (2)											
0.0000	251.41	0.2052	239.86	0.3487	230.78	0.5508	235.42	0.6995	250.55	0.9000	265.01
0.0527	248.64	0.2487	237.47	0.4046	225.57	0.5957	241.20	0.7485	254.48	0.9516	268.07
0.0990	246.14	0.3009	234.78	0.4604	225.58	0.6507	246.28	0.8006	258.45	1.0000	270.60
0.1524	243.15			0.4963	229.73			0.8493	261.74		
(g) *N*,*N*-Dimethylacetamide (1) + Benzene (2)											
0.0000	278.68	0.2043	266.84	0.3450	256.86	0.5505	237.78	0.7002	236.15	0.8960	246.37
0.0463	276.08	0.2501	263.90	0.4042	252.04	0.6017	232.06	0.7483	238.95	0.9494	249.02
0.0978	273.16	0.2999	260.36	0.4528	247.70	0.6489	234.06	0.8014	241.79	1.0000	251.42
0.1444	270.45			0.5007	243.21			0.8448	243.47		
(h) Cyclohexane (1) + *N*,*N*-Dimethylacetamide (2)											
0.0000	251.43	0.1046	250.00	0.2065	269.44	0.2202	271.15	0.2380	272.57	1.0000	279.74
0.0518	249.39	0.1495	261.02	0.2086	270.08	0.2328	272.20	0.9510	273.87		
(i) *N*,*N*-Dimethylacetamide (1) + *N*-Methylacetamide (2)											
0.0000	303.73	0.1994	286.11	0.3511	270.52	0.5497	246.25	0.7016	236.29	0.9001	246.59
0.0512	299.55	0.2523	280.88	0.4003	265.09	0.6030	239.79	0.7503	238.82	0.9500	248.81
0.0981	295.55	0.3029	275.63	0.4492	259.51	0.6525	233.73	0.7978	241.29	1.0000	251.43
0.1478	290.99			0.5090	251.61			0.8498	243.91		
(j) Sulfolane (1) + Toluene (2)											
0.0512	223.77	0.2505	255.39	0.3974	262.11	0.5959	269.25	0.7477	275.63	0.9385	286.36
0.1002	239.17	0.3006	258.01	0.4497	264.06	0.6476	271.26	0.7973	278.10	1.0000	301.65
0.1480	246.94	0.3496	260.21	0.4988	265.79	0.6980	273.39	0.8495	280.88		
0.1989	251.85			0.5456	267.44			0.9006	283.83		
(k) Methanol (1) + Sulfolane (2)											
0.0000	301.62	0.1484	280.85	0.3501	269.94	0.6001	260.93	0.7996	255.65	0.9600	239.32
0.0052	299.47	0.1975	277.89	0.3919	267.97	0.6542	259.52	0.8503	253.75	0.9700	234.47
0.0207	292.47	0.2502	274.92	0.4512	265.63	0.6986	258.36	0.9004	250.50	0.9796	227.29
0.0384	287.94	0.2973	272.51	0.5021	263.90	0.7495	257.04	0.9496	242.70		
0.1027	283.73			0.5500	262.31			0.9551	240.96		
(l) Sulfolane (1) + Ethanol (2)											
0.0589	261.82	0.2518	268.79	0.4014	269.55	0.5983	271.86	0.7508	276.40	0.9208	285.35
0.1021	266.16	0.2989	269.01	0.4490	269.87	0.6491	273.06	0.7893	278.04	1.0000	301.64
0.1471	267.84	0.3493	269.25	0.5008	270.40	0.6998	274.53	0.8478	280.98		
0.2077	268.56			0.5455	270.91			0.8960	283.87		
(m) Sulfolane (1) + 1-Propanol (2)											
0.0254	259.24	0.1018	272.80	0.5494	274.31	0.7027	276.13	0.7979	279.00	0.9493	287.04
0.0445	266.45	0.1476	273.94	0.5938	274.50	0.7393	277.04	0.8522	281.44	1.0000	301.66
0.0498	267.61			0.6486	275.15			0.8994	283.96		
(n) Water (1) + Sulfolane (2)											
0.0000	301.63	0.1035	284.06	0.2964	275.46	0.5008	268.94	0.7000	262.53	0.9004	267.80
0.0224	294.82	0.1480	281.64	0.3474	273.73	0.5507	267.33	0.7509	264.00	0.9502	269.61
0.0445	288.43	0.1968	279.34	0.4018	271.94	0.5983	265.81	0.8007	265.27	0.9601	270.11
0.0655	286.29	0.2602	276.80	0.4543	270.33	0.6517	264.07	0.8545	266.63	1.0000	301.66

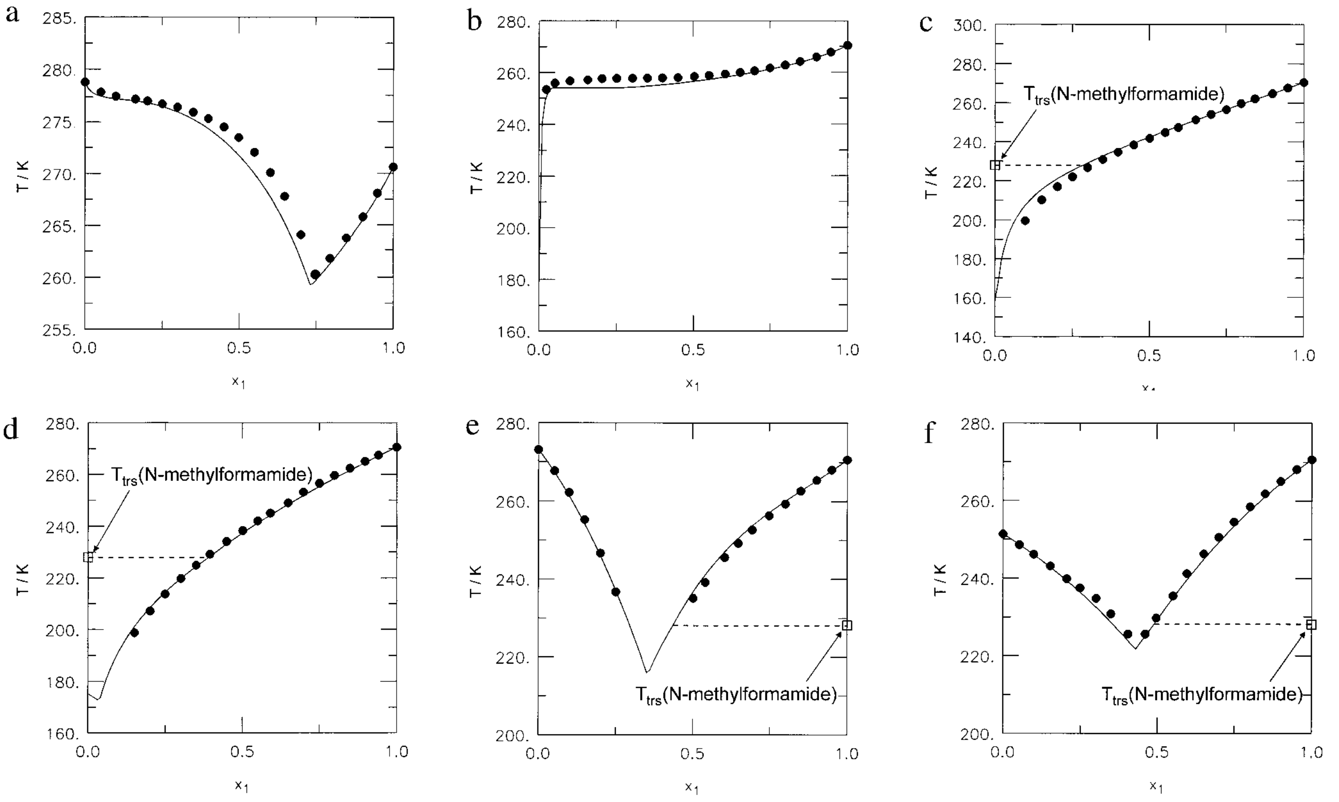

Figure 1. Solid−liquid equilibria for the systems *N*-methylformamide (1) + (a) benzene (2), (b) toluene (2), (c) ethanol (2), (d) methanol (2), (e) water (2), and (f) *N*,*N*-dimethylacetamide: (●) visual method; (—) Modified UNIFAC (Dortmund).

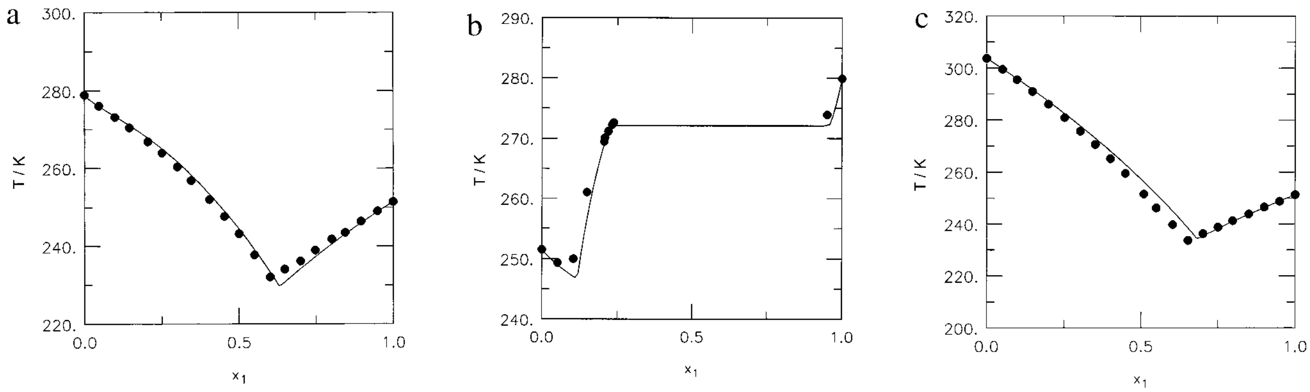

Figure 2. Solid−liquid equilibria for the systems (a) *N*,*N*-dimethylacetamide (1) + benzene (2), (b) cyclohexane (1) + *N*,*N*-dimethylacetamide (2), and (c) *N*,*N*-dimethylacetamide (1) + *N*-methylacetamide (2): (●) visual method; (—) Modified UNIFAC (Dortmund).

The synthetic, visual technique is a reliable and often described method for the determination of solid−liquid equilibria (Jakob et al., 1996; Fiege et al., 1996; Lohmann et al., 1997). The determination of the melting point for a given composition depends on visual detection of the temperature where the solid phase just disappears. The static apparatus permits measurements in the temperature range between 190 K and 373 K. The accuracy of the composition was determined to be ±0.0001; the accuracy of the melting temperature is ±0.015 K.

Since the calculation of solid−liquid equilibria also depends on pure component properties, reliable enthalpies of fusion, enthalpies of transition, and transition temperatures of sulfolane, *N*-methylformamide, and *N*-methylacetamide were measured with a SETARAM BT 2.15 II Tian-Calvet calorimeter (Calvet and Prat, 1963). According to the manufacturer's specifications, the experimental error for the determination of enthalpies amounts to ±0.5%.

Results

In Table 2 the binary experimental data of the investigated liquidus lines are given. The corresponding Figures 1−3 contain the experimental data, given by the circles, together with the predicted results using Modified UNIFAC (Dortmund). For all systems, eutectic behavior is assumed.

The system *N*-methylformamide + water (Table 2e) could not be measured completely, because of a high viscosity at temperatures below 235 K. The occurrence of a solid−solid transition of *N*-methylformamide at 228.1 K leads only to a small bend in the course of the liquidus lines (Figure 1c−f) because of the small heat of transition (see Table 1). The system *N*,*N*-dimethylacetamide + cyclohexane (Figure 2b) represents a solid−liquid equilibrium with a miscibility

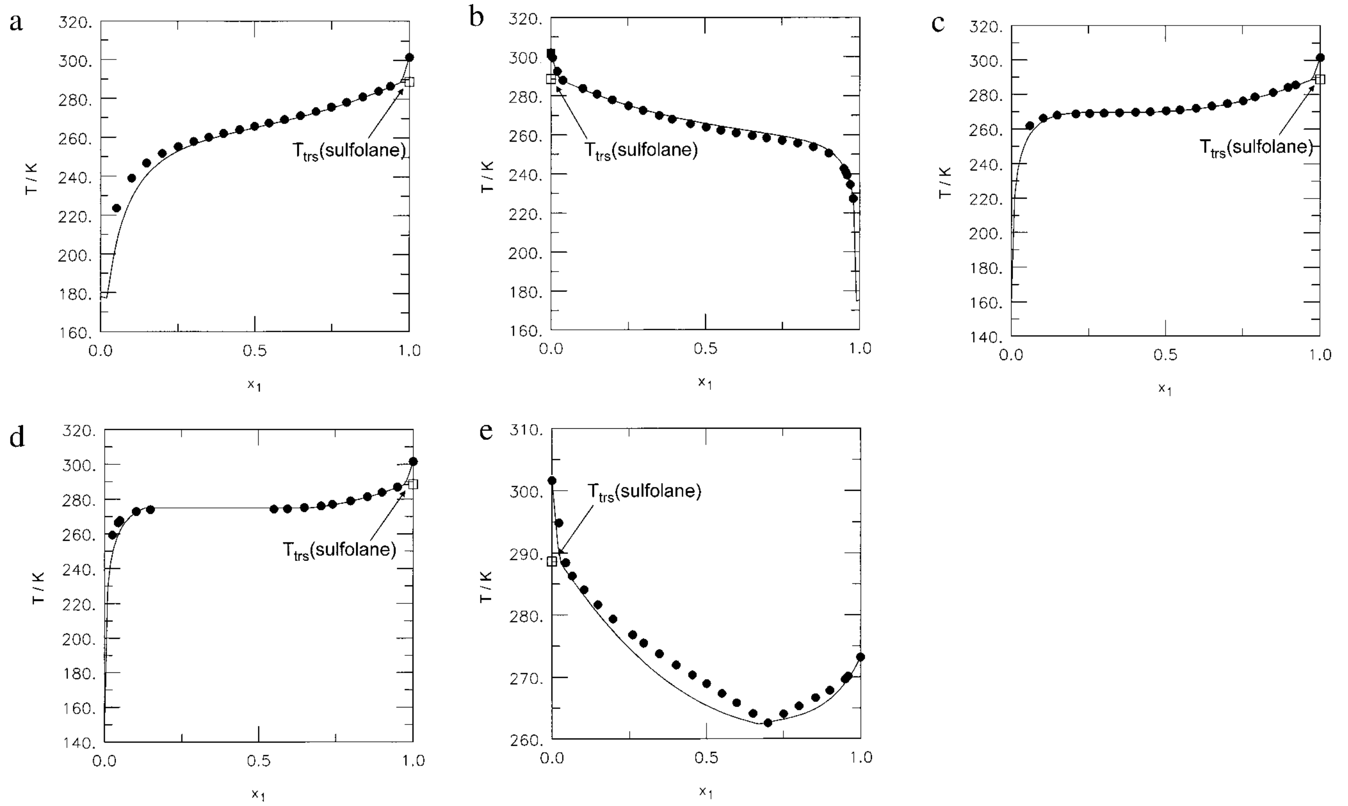

Figure 3. Solid−liquid equilibria for the systems (a) sulfolane (1) + toluene (2), (b) methanol (1) + sulfolane (2), (c) sulfolane (1) + ethanol (2), (d) sulfolane (1) + 1-propanol (2), and (e) water (1) + sulfolane (2): (●) visual method; (−) Modified UNIFAC (Dortmund).

gap. A solid−liquid−liquid equilibrium (SLLE) occurs in the mole fraction range between 0.25 and 0.95, where two liquid phases are in equilibrium with solid cyclohexane.

All liquidus lines of the systems containing sulfolane (Figure 3 and Table 2j−n) are characterized by a bend, which is caused by the solid−solid transition of sulfolane at 288.6 K. Good agreement between the predicted and experimental data can be observed. Even the occurrence of a miscibility gap for the system sulfolane + 1-propanol is predicted very well. The fitted parameters of Modified UNIFAC (Dortmund) are of great interest for the members of the UNIFAC consortium because of the importance of the investigated substances. The group interaction parameters are fitted simultaneously not only to experimental VLE data, activity coefficients at infinite dilution, liquid−liquid equilibria (LLE), and azeotropic data but also to excess enthalpies at high temperatures (up to 413 K) and SLE data to cover a wide temperature range. The given solid−liquid equilibria containing the selective solvents *N*-methylformamide, *N*,*N*-dimethylacetamide, and sulfolane are described very well by this group contribution method. The agreement between experimental and predicted data shows that Modified UNIFAC (Dortmund) is a very suitable tool to account for the real behavior (γ_i) not only at high and normal temperatures but also at low temperatures.

Summary

The liquidus lines of 14 binary systems with the compounds sulfolane, *N*-methylformamide, and *N*,*N*-dimethylacetamide were determined with a visual method. To start with reliable pure component properties required for the prediction, additionally the latent heats (heat of fusion, heat of transition) and transition temperatures for *N*-methylformamide, *N*-dimethylacetamide, and sulfolane were measured additionally using a Tian-Calvet calorimeter. The predictions of these phase diagrams with the help of Modified UNIFAC (Dortmund) are in good agreement with the experimental data.

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