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Solid−Liquid Equilibria for Different Heptanones with Benzene, Cyclohexane, and Ethanol

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The liquidus lines of solid−liquid equilibria for the binary systems 2-heptanone, 3-heptanone, and 4-heptanone with benzene, cyclohexane, and ethanol were determined by means of the visual method. Furthermore enthalpies of fusion of the isomeric heptanones were measured with a Tian-Calvet calorimeter. The experimental SLE data were compared with those calculated from the modified UNIFAC (Dortmund) group contribution method.

Introduction

The knowledge of solid−liquid equilibria (SLE) is of technical and theoretical interest. As it forms the basis for any crystallization process, it is important in different parts of the chemical industry such as separation of thermolabile or isomeric compounds, refrigeration processes, pipeline design, and obtaining high-purity products (Wynn, 1992). The theoretical importance of solid−liquid equilibria is connected with the development of prediction models. The experimental data are used for fitting simultaneously temperature-dependent parameters of G^E models or group contribution methods to VLE (vapor−liquid equilibria), H^E (molar enthalpy of mixing), and SLE data in order to ensure reliable extrapolation to high and low temperatures. When the observed system exhibits eutectic behavior (which occurs in about 80% of the organic nonelectrolyte systems) and when the required pure component properties (melting point, enthalpy of fusion, transition temperature, and transition enthalpy) are available, the activity coefficient can be calculated.

This paper presents experimental solid−liquid equilibrium data for isomeric heptanones with benzene, cyclohexane, and ethanol 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). Since for the calculation of the solid−liquid equilibria of eutectic systems, the enthalpies of fusion of all involved compounds are required, the missing enthalpies of fusion were measured with the help of a Tian-Calvet calorimeter.

Chemicals

2-Heptanone (Aldrich, 98%), 3-heptanone (Aldrich, 97%), and 4-heptanone (Aldrich, 98%) were distilled under reduced pressure using a Vigreux column (1.5 m in length) in order to obtain them with a purity better than 99.5%. Benzene (Scharlau, 99.7%), cyclohexane (Scharlau, 99.7%), and ethanol (Scharlau, 99.8%) were dried with molecular sieves 3 Å (Riedel-de-Haën). The purities were checked by means of gas chromatography, and the results are shown in Table 1.

Table 1. Purities and Pure Component Properties of the Chemicals Applied

component	CAS no.[a]	purity/%	$\Delta_{fus}H$/J·mol^{-1}	T_{fus}/K
2-heptanone	[110−43−0]	99.9	19711.8[b]	237.65
3-heptanone	[106−35−4]	99.7	17531.6[b]	235.94
4-heptanone	[123−19−3]	99.8	16159.5[b]	240.15
benzene	[71−43−2]	99.9	9934.6	278.68
cyclohexane	[110−82−7]	99.9	2625.9	279.75
ethanol	[64−17−5]	99.9	5012.7	158.65

[a] Supplied by the authors. [b] Measured with a Tian-Calvet calorimeter.

Table 2. Solid−Liquid Equilibria for Isomeric Heptanones with Benzene

2-heptanone (1) + benzene (2)		3-heptanone (1) + benzene (2)		4-heptanone (1) + benzene (2)	
x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	278.67	0.0000	278.67	0.0000	278.67
0.0487	275.36	0.0508	275.33	0.0512	275.28
0.1001	271.91	0.1006	272.01	0.1021	271.86
0.1490	268.25	0.1510	268.55	0.1500	268.53
0.1999	264.52	0.2003	264.96	0.2001	264.90
0.2496	260.68	0.2495	261.23	0.2507	261.04
0.2994	256.57	0.3005	257.01	0.2996	256.74
0.3495	252.27	0.3490	252.86	0.3500	252.43
0.3995	247.73	0.3991	248.30	0.3997	247.91
0.4490	243.01	0.4486	243.51	0.4492	243.06
0.4994	237.74	0.4999	238.20	0.5013	237.60
0.5474	232.86	0.5493	232.70	0.5496	232.23
0.5991	227.79	0.6011	226.88	0.6031	226.56
0.6498	228.07	0.6487	224.72	0.6510	228.79
0.6997	229.83	0.6999	226.62	0.7002	230.88
0.7494	231.40	0.7496	228.39	0.7498	232.88
0.7994	232.93	0.7997	230.04	0.7998	234.71
0.8505	234.51	0.8493	231.77	0.8496	236.48
0.8924	235.57	0.8986	233.20	0.8997	238.13
0.9465	236.98	0.9420	234.39	0.9357	239.36
1.0000	238.40	1.0000	235.94	1.0000	241.47

Solid−Liquid Phase Equilibria

A calculation formula for solid−liquid phase equilibria can be derived 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):

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

where x_i^L is the mole fraction of component i in the liquid phase, γ_i^L is the activity coefficient of component i in the liquid phase, $\Delta_{fus}H_i$ is the enthalpy of fusion of component i, $T_{fus,i}$ is the fusion temperature of component i, T is the

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Table 3. Solid−Liquid Equilibria for Isomeric Heptanones with Cyclohexane

2-heptanone (1) + cyclohexane (2)		3-heptanone (1) + cyclohexane (2)		4-heptanone (1) + cyclohexane (2)	
x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	279.80	0.0000	279.80	0.0000	279.80
0.0505	269.49	0.0480	269.58	0.0477	269.55
0.0989	262.20	0.1006	261.08	0.0993	260.80
0.1512	255.95	0.1508	254.48	0.1494	253.88
0.1985	251.13	0.1992	248.48	0.1996	247.69
0.2497	246.30	0.2499	243.06	0.2499	242.13
0.2991	241.90	0.2998	238.07	0.2996	236.89
0.3491	237.41	0.3499	232.95	0.3498	231.69
0.3997	232.76	0.4000	227.92	0.3973	226.50
0.4502	227.50	0.4498	223.29	0.4510	226.67
0.4978	228.04	0.5009	224.20	0.4999	227.92
0.5518	228.97	0.5492	225.26	0.5490	229.19
0.6043	229.94	0.6005	226.33	0.6012	230.42
0.6523	230.83	0.6500	227.38	0.6513	231.72
0.7022	231.82	0.7011	228.52	0.7010	233.07
0.7535	232.88	0.7504	229.67	0.7540	234.47
0.8048	233.98	0.8001	230.86	0.8038	235.84
0.8515	234.94	0.8537	232.19	0.8532	237.23
0.8928	235.85	0.8998	233.36	0.9081	238.78
0.9365	236.85	0.9526	234.72	0.9521	240.07
1.0000	238.40	1.0000	235.94	1.0000	241.47

Table 4. Solid−Liquid Equilibria for Isomeric Heptanones with Ethanol

2-heptanone (1) + ethanol (2)		3-heptanone (1) + ethanol (2)		4-heptanone (1) + ethanol (2)	
x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0496	208.09	0.0497	204.05	0.0492	205.44
0.0990	216.63	0.0987	213.29	0.0992	215.91
0.1489	221.24	0.1481	218.13	0.1493	221.38
0.1988	224.01	0.1994	221.21	0.1983	224.69
0.2499	225.91	0.2491	223.35	0.2491	226.99
0.2991	227.47	0.2991	224.93	0.2989	228.87
0.3494	228.55	0.3497	226.20	0.3488	230.26
0.3991	229.59	0.4006	227.23	0.4005	231.47
0.4514	230.43	0.4508	228.13	0.4496	232.47
0.5008	231.16	0.5013	228.91	0.5021	233.41
0.5521	231.89	0.5519	229.64	0.5488	234.18
0.6006	232.52	0.6007	230.27	0.6015	235.02
0.6518	233.12	0.6511	230.87	0.6502	235.62
0.7050	233.76	0.7033	231.50	0.7010	236.32
0.7538	234.38	0.7505	232.09	0.7463	236.94
0.8003	234.98	0.7962	232.61	0.8010	237.72
0.8469	235.60	0.8485	233.30	0.8424	238.32
0.9076	236.56	0.9017	234.12	0.8967	239.22
0.9460	237.28	0.9480	234.82	0.9422	240.10
1.0000	238.40	1.0000	235.94	1.0000	241.47

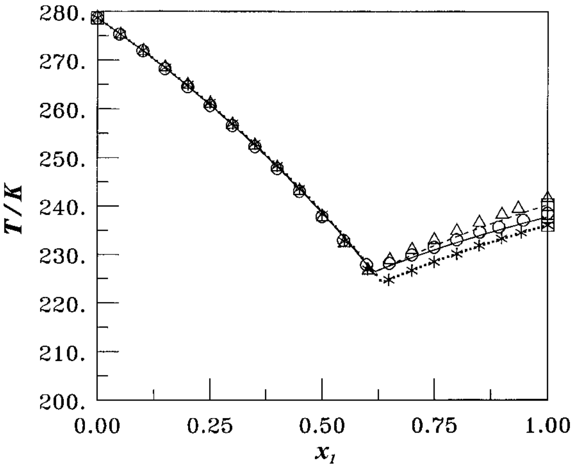

Figure 1. Solid−liquid equilibria for isomeric heptanones with benzene. 2-Heptanone (1) + benzene (2): experimental (○); modified UNIFAC (Do) (—). 3-Heptanone (1) + benzene (2): experimental (*); modified UNIFAC (Do) (···). 4-Heptanone (1) + benzene (2): experimental (△); modified UNIFAC (Do) (- - -).

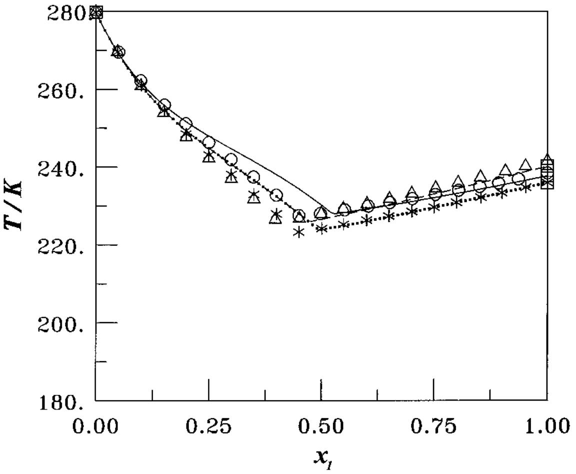

Figure 2. Solid−liquid equilibria for isomeric heptanones with cyclohexane. 2-Heptanone (1) + cyclohexane (2): experimental (○); modified UNIFAC (Do) (—). 3-Heptanone (1) + cyclohexane (2): experimental (*); modified UNIFAC (Do) (···). 4-Heptanone (1) + cyclohexane (2): experimental (△); modified UNIFAC (Do) (- - -).

absolute temperature, and R is the universal gas constant. As the activity coefficient depends on temperature as well as on concentration, eq 1 must be solved iteratively. For the calculation of the activity coefficients the modified UNIFAC (Dortmund) group contribution method was used (Gmehling et al., 1993). The necessary interaction parameters (Gmehling and Li, 1994) for the calculations with the modified UNIFAC method are shown in Table 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 solid phase just disappears. The estimated error for the equi-

Table 5. Modified UNIFAC Interaction Parameters

main groups		interaction parameters					
n	m	a_{nm}/K	b_{nm}	c_{nm}/K^{-1}	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}
1	3	114.200	0.0933		16.070	−0.2998	
1	5	2777.000	−4.6740	0.001 551	1606.000	−4.7460	0.000 918
1	9	433.600	0.1473		199.000	−0.8709	
1	42[a]	−117.100	0.5481	−0.000 980	170.900	−0.8062	0.001 291
3	5	3972.000	−13.1600	0.012 080	3049.000	−12.7700	0.014 350
3	9	146.200	−1.2370	0.004 237	−57.530	1.2120	−0.003 715
3	42[a]	134.600	−1.2310	0.001 488	−2.619	1.0940	−0.001 557
5	9	−250.000	2.8570	−0.006 022	653.300	−1.4120	0.000 954
5	42[a]	3121.000	−13.6900	0.014 460	2601.000	−1.2500	−0.006 309
9	42[a]	168.200	−0.8197		464.500	0.1542	

[a] Parameter sets for main group 42 (cy-CH_2) revised in 1994.

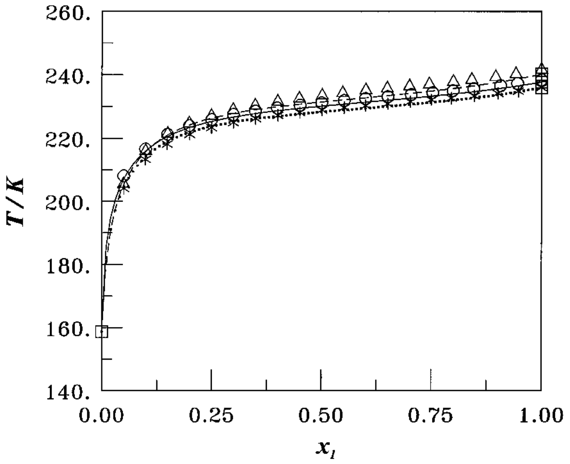

Figure 3. Solid−liquid equilibria for isomeric heptanones with ethanol. 2-Heptanone (1) + ethanol (2): experimental (○) modified UNIFAC (Do) (—). 3-Heptanone (1) + ethanol (2): experimental (*) modified UNIFAC (Do) (···). 4-Heptanone (1) + ethanol (2): experimental (△) modified UNIFAC (Do) (- - -).

librium temperature determination with this method is 0.025 K.

The liquidus lines of the following binary systems were measured: 2-heptanone + benzene, 3-heptanone + benzene, 4-heptanone + benzene, 2-heptanone + cyclohexane, 3-heptanone + cyclohexane, 4-heptanone + cyclohexane, 2-heptanone + ethanol, 3-heptanone + ethanol, 4-heptanone + ethanol.

Enthalpies of Fusion

Equation 1 shows the necessity of the enthalpies of fusion for the prediction of solid−liquid phase equilibria of eutectic systems. The accuracy of the prediction depends on the quality of the pure component properties used. Therefore calorimetric measurements were carried out to determine the missing enthalpies of fusion of the three isomeric heptanones with a SETARAM BT 2.15 II Tian-Calvet calorimeter (Calvet and Prat, 1963). According to the manufacturer's specification the experimental error for the determination of enthalpies of fusion amounts to 0.5%. A paper containing further information on measurements with the Tian-Calvet calorimeter is in preparation.

Results

Tables 2−4 contain the experimental solid−liquid equilibrium data of the isomeric heptanones. In Table 1 the enthalpy of fusion data of the heptanones obtained by the calorimetric measurements are listed. In Figures 1−3 the experimental SLE results are presented together with those calculated using the modified UNIFAC (Dortmund, Do) group contribution method. Except for the enthalpies of fusion of the heptanones, the necessary pure component properties were taken from the Dortmund Data Bank and are also presented in Table 1. The diagrams show that modified UNIFAC (Dortmund) is very suitable for the prediction of solid−liquid equilibria even for isomeric ketones. This can be attributed mainly to the fact that a large database (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 VLE, H^E, azeotropic, and SLE data.

Summary

The liquidus lines for nine binary systems containing isomeric heptanones were determined by the visual method. Additionally, the enthalpies of fusion for the different heptanones were measured with a Tian-Calvet calorimeter. Using melting points and enthalpy of fusion data the liquidus lines for the nine systems were calculated with the help of the modified UNIFAC (Dortmund) group contribution method. The results show good agreement with the experimental data.

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