Solid−Liquid Equilibria of Viscous Binary Mixtures with Alcohols

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Solid−liquid equilibria of the following 11 alcohol systems have been measured by the visual method: cyclohexanol + dodecane, cyclohexanol + cyclohexane, cyclohexanol + benzene, cyclohexanol + tetrachloromethane, 1-butanol + water, 2-butanol + water, 2-methyl-1-propanol + water, 2-pentanol + tetrachloromethane, 1-pentanol + cyclohexane, 2-pentanol + cyclohexane, and 3-pentanol + cyclohexane. For all systems, with the exception of the system cyclohexanol + cyclohexane, eutectic behavior is assumed. With the visual technique not all systems can be determined over the whole concentration range because the mixtures become very viscous at low temperatures and high alcohol concentrations. Therefore the systems cyclohexanol + benzene, 2-butanol + water, and 2-pentanol + cyclohexane were also studied by an analytical method, which is introduced in this paper. The experimental data of the eutectic systems were compared with predicted values using the modified UNIFAC (Dortmund) group contribution method.

Introduction

Solid−liquid equilibria (SLE) are of great technical interest, because they form the basis for crystallization processes. The crystallization process is used for the separation of mixtures with thermolabile components or isomeric compounds with very similar vapor pressures for which the separation factor α_{ij} is approximately unity and cannot be influenced strongly by selective solvents. Futhermore, crystallization is used to obtain products of very high purity (Wynn, 1992). Solid−liquid equilibria are also of importance for refrigeration and pipeline design where undesired crystallization can cause safety problems. It is also possible to combine crystallization with other separation methods. The resulting process is known as a hybrid process. A further alternative is separation by extractive or adductive crystallization. Besides these technical applications, solid−liquid equilibria of eutectic systems are also of interest for fitting reliable temperature-dependent parameters for g^E-models or group contribution methods like modified UNIFAC (Dortmund). The activity coefficient γ_i can be calculated by a knowledge of pure component properties (melting point, enthalpy of fusion, transition temperature, and enthalpy of transition). The properties used were taken from the Dortmund Data Bank (DDB) and shown in Table 2.

Solid−liquid equilibria can be calculated by a formula derived from the isofugacity criterion (Gmehling and Kolbe, 1992). After some simplifications the following equation is obtained

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

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

If solid−solid transition does not occur below the melting point of the pure solid, the last term in eq 1 can be neglected and eq 1 simplifies to (Gmehling et al., 1978):

Table 1. Measured Solid−Liquid Equilibria and Determination Methods

system	determination method
cyclohexanol + dodecane	visual
cyclohexanol + cyclohexane	visual
cyclohexanol + benzene	visual and analytical
cyclohexanol + tetrachloromethane	visual
1-butanol + water	visual
2-butanol + water	visual and analytical
2-methyl-1-propanol + water	visual
2-pentanol + tetrachloromethane	visual
1-pentanol + cyclohexane	visual
2-pentanol + cyclohexane	visual and analytical
3-pentanol + cyclohexane	visual

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

Because the activity coefficients depend on mole fraction and temperature, eqs 1 and 2 must be solved iteratively. For the description of the activity coefficient, the group contribution method modified UNIFAC (Dortmund) was used (Gmehling et al., 1993). The binary parameters used for the predictions are given in Table 3 except the parameters used for the calculations of the butanol + water systems. These systems have been predicted with a new type of group assignment. The new group interaction parameters used and some results will be published (Joh and de Haan, in preparation).

This paper presents the experimental SLE data for 11 binary mixtures listed in Table 1. All systems contain alcohol and were measured by the 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.

The viscosity of long chain alcohols (butanols and higher, C_{4+}) increases strongly near the melting point. Some systems cannot be determined by the visual method in the range of high viscosities (low temperatures and high alcohol concentrations). Even rapid stirring causes only a poor homogenization of the mixture. Large gradients of concentration and temperature must be assumed. For this reason, an alternative, isothermal analytical method for

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Table 2. Purities and Pure Component Properties of the Applied Chemicals Taken from the Dortmund Data Bank (DDB)

compound	CAS number	purity/%	$\Delta_{fus}H$/J·mol^{-1}	T_{fus}/K	$\Delta_{trs}H$/J·mol^{-1}	T_{trs}/K
cylohexanol	[108-93-0]	99.8	1756	298.61		
dodecane	[112-40-3]	99.9	36582	263.59		
cyclohexane	[110-82-7]	99.9	2630	279.75	6741	185.95
benzene	[71-43-2]	99.9	9951	278.68		
tetrachloromethane	[56-23-5]	99.9	3276	250.77	4560	225.35
water	[7732-18-5]	99.9	6000	273.15		
1-butanol	[71-36-3]	99.9	9282	183.35		
2-butanol	[78-92-2]	99.9	5971	158.50		
2-methyl-1-propanol	[78-83-1]	99.9	6322	165.20		
1-pentanol	[71-41-0]	99.8	9829	194.25		
2-pentanol	[6032-29-7]	99.8	8480	200.00		
3-pentanol	[584-02-1]	99.8	9080	204.15		

Table 3. Modified UNIFAC (Dortmund) Interaction Parameters

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}
1	5	2777.000	−4.6740	0.001 551	1606.000	−4.7460	0.000 918
1	24	267.510	−1.7109	0.0033 88	−148.070	1.0927	−0.002 416
1	42	−117.100	0.5481	−0.000 980	170.900	−0.8062	0.0012 91
3	5	3972.000	−13.1600	0.0120 80	3049.000	−12.7700	0.0143 50
3	42	134.600	−1.2310	0.0014 88	−2.619	1.0940	−0.001 557
5	24	925.600	−2.0270		3139.000	−5.9640	
5	42	3121.000	−13.6900	0.0144 60	2601.000	−1.2500	−0.006 309
24	42	−37.183	−0.0478		60.780	0.0243	

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

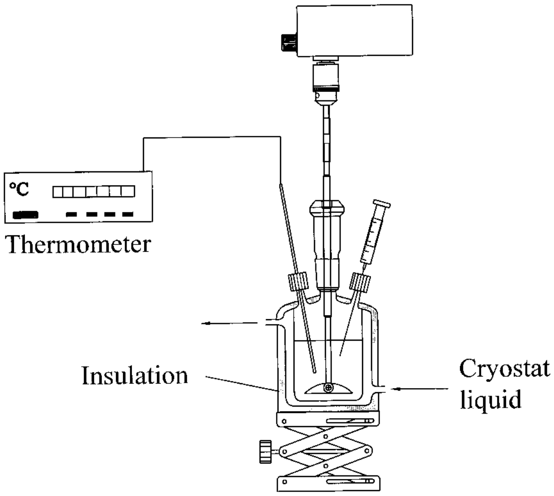

Figure 1. Apparatus used for analytical measurements of solid−liquid equilibria.

the determination of solid−liquid equilibria was tested for the systems cyclohexanol + benzene, 2-butanol + water, and 2-pentanol + tetrachloromethane. With this new method solid−liquid equilibria can also be determined in regions of high viscosity without significant problems.

Experimental Section

Table 1 shows the measured systems as well as the experimental technique applied.

All chemicals were obtained by commercial sources (Aldrich, Fluka, Gruessing). Cyclohexanol and the pentanols were distilled under vacuum using a Vigreux column with a height of 1.5 m and are stated to be of a purity greater than 99.8%. The remaining chemicals were delivered with purities greater than 99.9% and were used without further purification. Table 2 gives the purities and pure component properties of the applied chemicals.

The experimental apparatus used for the analytical determination of SLE is shown in Figure 1. The glass apparatus consists of a vessel, which can be thermostated by a cryostat liquid flowing through the jacket. Measurements are possible between 183.15 and 373.15 K. The kind of cryostat liquid depends on the desired temperatures. Usually ethanol is taken, which is replaced by water at temperatures above 333.15 K because of safety reasons. The equilibrium cell is covered by an insulation jacket to avoid undesired condensation of humidity.

The mixture is homogenized by an electric stirrer, which is more powerful than a magnetic stirrer. Temperatures are measured using a Rosemount platinum resistance temperature sensor calibrated according to ITS-90. The metrology thermometer (Model 1506) manufactured by Hart Scientific was used for the conversion of the measured resistance and display of the corresponding temperature. The accuracy is given as ±0.005 K.

The basis of the analytical isothermal method is the examination of the liquid phase composition at a given temperature. The liquidus lines were measured in the following way: A stirred binary mixture is cooled to a temperature lower than the expected liquidus line. If the temperature is low enough and no subcooling occurs, crystals precipitate. Eutectic behavior assumed, the crystals only consist of one pure compound. The mother liquor is depleted in this component, and therefore its composition varies along the liquidus line. To determine the composition of the remaining liquid phase, samples are taken by using a sampling needle. The samples are analyzed using a gas chromatograph HP 5890 with an integrator HP 3396A manufactured by Hewlett Packard. The composition is determined with a flame ionization detector (FID) for the systems cyclohexanol + benzene and 2-pentanol + cyclohexane, and with a thermal conductivity detector (TCD) for the system 2-butanol + water.

Some problems occured concerning the choice of a suitable cannula. On one hand, a cannula with a large diameter leads to crystals being sucked into the injector. On the other hand, a cannula with a small diameter does not allow to take samples of very viscous liquids. Finally we used a cannula of the dimensions 120 × 0.6 mm for the systems cyclohexanol + benzene and 2-pentanol +

Table 4. Experimental SLE Data for the System Cyclohexanol (1) + Dodecane (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	263.68	0.4001	262.36	0.7992	261.20
0.0516	263.42	0.4483	262.25	0.8514	260.45
0.1003	263.24	0.5002	262.16	0.8765	261.72
0.1523	262.99	0.5502	262.06	0.8995	265.81
0.2046	262.83	0.5989	261.94	0.9243	270.35
0.2507	262.72	0.6494	261.82	0.9516	277.83
0.3012	262.57	0.7014	261.71	0.9685	282.71
0.3502	262.48	0.7504	261.53	1.0000	297.58

Table 5. Experimental SLE Data for the System Cyclohexanol (1) + Cyclohexane (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	280.01	0.2284	280.98	0.5996	283.79
0.0204	279.73	0.2563	281.03	0.6502	284.44
0.0377	279.91	0.2770	281.23	0.7002	285.25
0.0615	280.11	0.3036	281.29	0.7459	286.15
0.0807	280.16	0.3280	281.56	0.7982	287.32
0.1070	280.23	0.3494	281.63	0.8440	288.69
0.1307	280.37	0.4009	282.05	0.8980	290.43
0.1535	280.53	0.4509	282.43	0.9454	293.26
0.1805	280.68	0.4997	282.81	1.0000	297.76
0.1995	280.74	0.5499	283.24		

Table 6. Experimental SLE Data for the System Cyclohexanol (1) + Benzene (2) (Visual and Analytical Methods)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
(a) Visual Method					
0.0000	278.84	0.3530	269.99	0.6941	253.81
0.0451	276.89	0.4006	268.69	0.7443	249.08
0.1059	275.45	0.4505	267.18	0.7964	242.57
0.1538	274.43	0.5008	265.42	0.8410	244.10
0.2041	273.38	0.5507	263.32	0.8962	258.80
0.2524	272.29	0.5992	261.13	0.9449	276.44
0.3010	271.18	0.6431	257.74	1.0000	297.86
(b) Analytical Method					
0.5038	265.34	0.7492	247.57	0.9032	258.32
0.5309	263.22	0.7704	244.75	0.9033	258.41
0.5981	260.35	0.7940	242.60	0.9147	264.89
0.6383	257.56	0.7994	241.04	0.9170	268.69
0.6729	255.53	0.8357	245.45	0.9376	275.27
0.7081	252.36	0.8544	250.10	0.9753	283.89
0.7433	247.63	0.8845	254.63		

Table 7. Experimental SLE Data for the System Cyclohexanol (1) + Tetrachloromethane (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	250.75	0.1903	240.20	0.3957	226.06
0.0479	248.40	0.2538	235.86	0.4309	224.79
0.0937	246.06	0.2957	233.17	1.0000	297.77
0.1438	243.17	0.3432	229.49		

Table 8. Experimental SLE Data for the System 1-Butanol (1) + Water (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	273.15	0.6915	260.22	0.8757	212.26
0.5535	269.28	0.7586	251.37	0.8942	199.89
0.5943	267.57	0.8016	241.77		
0.6406	264.76	0.8468	227.40		

Table 9. Experimental SLE Data for the System 2-Butanol (1) + Water (2) (Visual and Analytical Methods)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
(a) Visual Method					
0.0000	273.15	0.3520	266.27	0.5891	260.05
0.0244	270.71	0.4061	265.73	0.6460	256.55
0.0496	267.66	0.4600	264.78	0.6959	252.30
0.0751	266.63	0.4958	263.89	0.7443	246.76
0.3031	266.46	0.5440	262.20	0.7924	240.16
(b) Analytical Method					
0.6188	259.27	0.7670	245.59	0.8698	215.48
0.6203	259.28	0.7727	240.66	0.8968	215.51
0.6711	254.53	0.8295	230.58		
0.7166	249.89	0.8340	235.01		

Table 10. Experimental SLE Data for the System 2-Methyl-1-propanol (1) + Water (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	273.15	0.6953	264.11	0.8528	236.58
0.0255	270.63	0.7461	258.59	0.8810	225.27
0.5965	269.69	0.7749	254.17		
0.6502	267.04	0.8171	247.09		

Table 11. Experimental SLE Data for the System 2-Pentanol (1) + Tetrachloromethane (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	250.77	0.1976	239.04	0.4018	225.90
0.0544	247.19	0.2451	236.01	0.4518	224.51
0.0936	245.04	0.2997	232.46	0.5019	222.78
0.1455	242.20	0.3482	229.15	0.5426	221.19

Table 12. Experimental SLE Data for the System 1-Pentanol (1) + Cyclohexane (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	280.07	0.2482	266.85	0.4999	248.89
0.0509	276.78	0.3021	264.01	0.5505	241.33
0.1060	274.20	0.3499	261.10	0.5995	232.89
0.1521	271.56	0.4017	257.03	0.6495	222.21
0.2084	268.86	0.4498	253.07		

cyclohexane as well as a cannula of the dimensions 150 × 0.4 mm for the system 2-butanol + water.

The sampling was repeated until the measured composition was constant. This means the two phases of the mixture are in phase equilibrium.

The main disadvantage of the analytical method was the excessive time required to measure a binary system, which was caused by the preparation (calibration curves for the GC) and the long time required to reach phase equilibrium. In order to determine mixtures of high viscosity, it sometimes took about 75 h until constant results were obtained.

Therefore, it is hard to give an uncertainty for this method to determine solid−liquid equilibria, because there are some factors (e.g. sampling) that influence the quality of the results. The best results were obtained by taking samples directly from the stirred heterogenous mixture. The absolute error in the concentration caused by this newly introduced method is estimated to be about 5%.

Results

Tables 4−14 give the experimental solid−liquid equilibrium data for the 11 systems. In Table 2 the pure component properties are given. In Figures 2−12 the experimental values are presented. The circles stand for the visual detected data, the triangles represent the results of the analytical technique, and the squares stand for melting temperatures of the the pure components taken from the Dortmund Data Bank. If predictions with modified UNIFAC (Dortmund) were possible (eutectic behavior assumed), the calculated values are presented together with the corresponding experimental data. The diagrams show that the modified UNIFAC (Dortmund) is a suitable tool for the prediction of solid−liquid equilibria. This confirms investigations that will be published (Joh and Kreutz, 1997).

Not all of the systems could be measured over the whole concentration range. The resulting gaps are caused by two reasons: (1) the high viscosity of the mixtures at low

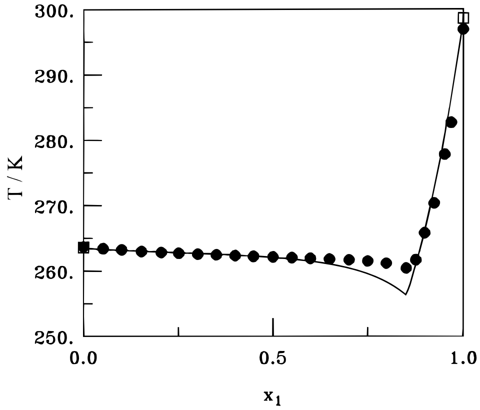

Figure 2. Solid−liquid equilibrium for the system cyclohexanol (1) + dodecane (2): ● visual method, — mod. UNIFAC (Do), ☐ melting points of the pure components [DDB].

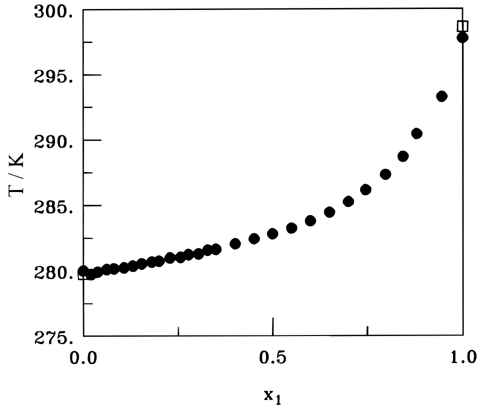

Figure 3. Solid−liquid equilibrium for the system cyclohexanol (1) + cyclohexane (2): ● visual method, ☐ melting points of the pure components [DDB].

Table 13. Experimental SLE Data for the System 2-Pentanol (1) + Cyclohexane (Visual and Analytical Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
		(a) Visual Method			
0.0000	279.86	0.2989	259.74	0.5020	244.59
0.0583	275.22	0.3502	256.22	0.5530	239.19
0.1134	271.83	0.4005	252.69	0.6014	232.59
0.1634	268.76	0.4493	249.11	0.6524	223.46
0.1956	266.25	0.4999	244.50		
0.2562	261.96	0.5020	244.61		
		(b) Analytical Method			
0.6480	222.94	0.7286	203.88	0.7576	197.30
0.6837	213.34	0.7540	195.49	0.9703	198.51

Table 14. Experimental SLE Data for the System 3-Pentanol (1) + Cyclohexane (2) (Visual Method)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
0.0000	279.99	0.2536	260.94	0.4983	242.23
0.0544	275.16	0.3010	256.98	0.5500	237.60
0.1033	271.99	0.3505	252.95	0.6010	231.58
0.1494	268.84	0.3995	249.36	0.6493	224.79
0.2009	265.03	0.4503	245.82	0.7005	214.79

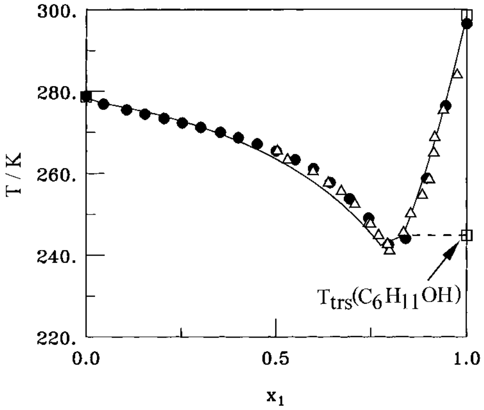

Figure 4. Solid−liquid equilibrium for the system cyclohexanol (1) + benzene (2): ● visual method, — mod. UNIFAC (Do), △ analytical method, ☐ melting points of the pure components [DDB].

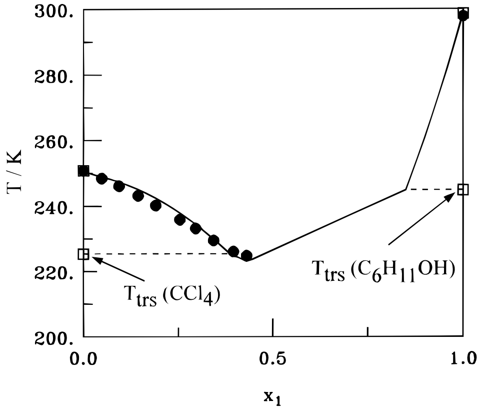

Figure 5. Solid−liquid equilibrium for the system cyclohexanol (1) + tetrachloromethane (2): ● visual method, — mod. UNIFAC (Do), ☐ melting points of the pure components [DDB].

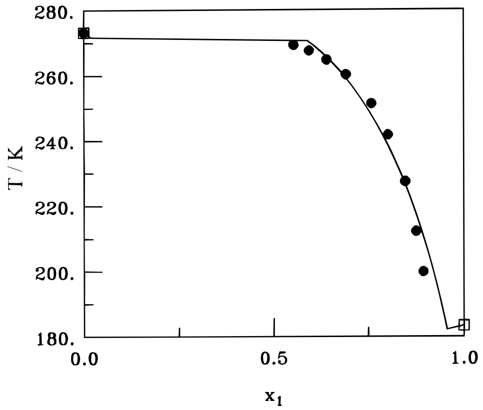

Figure 6. Solid−liquid equilibrium for the system 1-butanol (1) + water (2): ● visual method, — mod. UNIFAC (Do), ☐ melting points of the pure components [DDB].

temperatures and high alcohol concentrations and (2) for the butanol + water systems the miscibility gap in the water-rich region.

For all systems eutectic behavior is assumed except for the system cyclohexanol + cyclohexane. Gas chromatographic investigations showed that the solid phase of this system consisted of two compounds. The composition of the solid phase depends on the temperature; e.g., cooling to 283 K gave crystals of nearly equimolar composition. The simultaneous appearance of a minimum in the liquidus line and miscibility in solid phase leads to the assumption that the system cyclohexanol + cyclohexane shows dystectic behavior.

According to the literature (Kelley, 1929; Adachi et al., 1968), cyclohexanol shows three modifications of the solid phase, the solid−solid transitions are crystal-III → crystal-I at 244.8 K with $\Delta_{trs}H_i$ = 8640 J·mol^{-1} and crystal-II → crystal-I at 263.5 K with $\Delta_{trs}H_i$ = 8827 J·mol^{-1}. DSC measurements showed that due to the supercooling to 240 K the solid−solid transition crystal-III → crystal-I occurs.

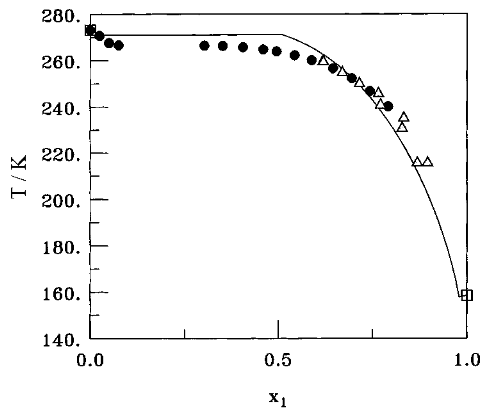

Figure 7. Solid−liquid equilibrium for the system 2-butanol (1) + water (2): ● visual method, — mod. UNIFAC (Do), △ analytical method, □ melting points of the pure components [DDB].

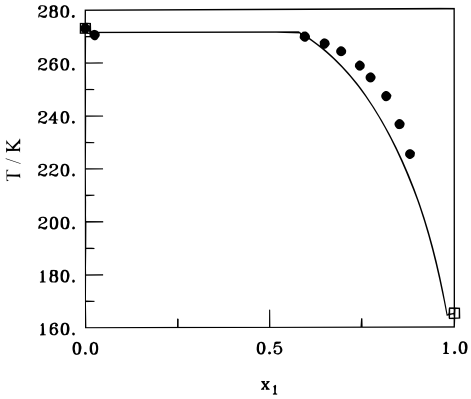

Figure 8. Solid−liquid equilibrium for the system 2-methyl-1-propanol (1) + water (2): ● visual method, — mod. UNIFAC (Do), □ melting points of the pure components [DDB].

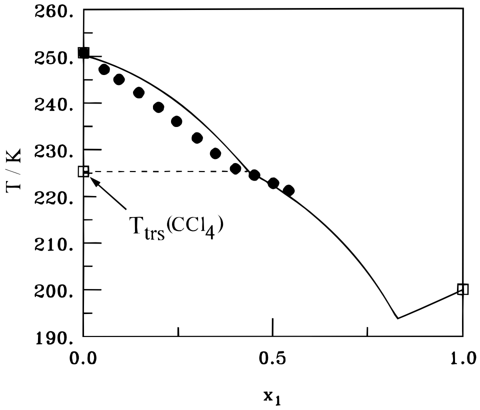

Figure 9. Solid−liquid equilibrium for the system 2-pentanol (1) + tetrachloromethane (2): ● visual method, — mod. UNIFAC (Do), □ melting points of the pure components [DDB].

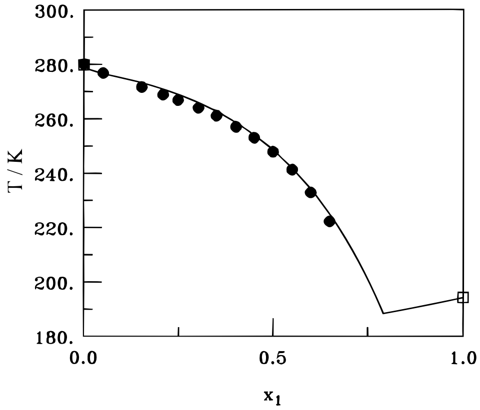

Figure 10. Solid−liquid equilibrium for the system 1-pentanol (1) + cyclohexane (2): ● visual method, — mod. UNIFAC (Do), □ melting points of the pure components [DDB].

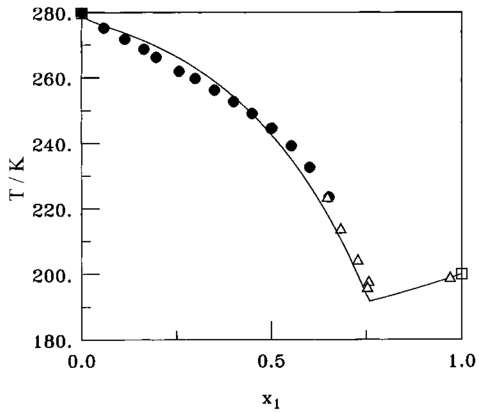

Figure 11. Solid−liquid equilibrium for the system 2-pentanol (1) + cyclohexane (2): ● visual method, — mod. UNIFAC (Do), △ analytical method, □ melting points of the pure components [DDB].

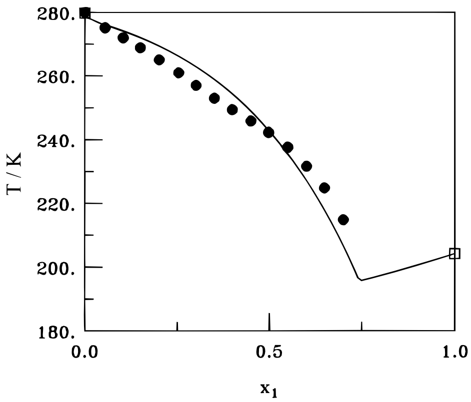

Figure 12. Solid−liquid equilibrium for the system 3-pentanol (1) + cyclohexane (2): ● visual method, — mod. UNIFAC (Do), □ melting points of the pure components [DDB].

Summary

The liquidus lines of 11 binary systems containing higher alcohols (C_{4+}) were determined by the synthetic method. Because of the high viscosities of the mixtures at low temperatures and high alcohol concentrations, a few systems were also measured with the analytical method. The comparison between the two methods showed that the analytical determinations of solid−liquid equilibria in regions of high viscosity are possible, but the quality of the results is not as high as that for data obtained by the visual method. Furthermore the agreement between experimental and calculated data shows that modified UNIFAC (Dortmund) allows a safe extrapolation to low temperatures and therefore it is a suitable tool for the prediction of solid−liquid equilibria.

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