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Solid−Liquid Equilibria for Binary Organic Systems Containing 1-Methoxy-2-propanol and 2-Butoxy Ethanol

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Solid−liquid equilibria (SLE) for the four binary systems of 1-methoxy-2-propanol and 2-butoxy ethanol with benzene and cyclohexane have been measured by a visual method. For correlating the experimental SLE data, the enthalpy of fusion for 1-methoxy-2-propanol has been measured additionally using a Tian-Calvet batch calorimeter. For the description of the SLE data, the Wilson equation has been used with good results. The SLE data were also compared with predicted data using modified UNIFAC (Dortmund).

Introduction

Solid−liquid equilibrium (SLE) data are of great technical interest, because their knowledge forms the basis for designing crystallization processes. These processes are in particular 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 with the help of selective solvents.

Besides their importance for crystallization processes, SLE of eutectic systems are also of interest for fitting reliable temperature-dependent parameters for G^E models or group contribution methods such as modified UNIFAC (Dortmund), because they are important as supporting data at low ($\vartheta < 0$ °C) temperatures.[1]

SLE can be calculated by a relation derived from the isofugacity criterion; that is, the fugacity of component i in the liquid phase must be equal to the fugacity of component i in the solid phase

$$f_i^S = f_i^L \qquad (1)$$

For eutectic systems after a few simplifications, that is, the neglect of the heat capacity differences between the solid and hypothetical liquid phase, the following equation is obtained for eutectic systems[2−5]

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

In eq 2, 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, $T_{m,i}$ the melting 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 occurs in the considered temperature range, the last term in eq 2 can be neglected and the equation simplifies to[6]

$$\ln x_i^L \gamma_i^L = -\frac{\Delta_{fus}H_i}{RT}\left(1 - \frac{T}{T_{m,i}}\right) \qquad (3)$$

Because the activity coefficients depend not only on mole fraction but also on temperature, eqs 2 and 3 must be solved iteratively. For the correlation of the activity coefficients, the Wilson equation has been used by means of the following objective function, F

$$F = \sum_n \left(\frac{\gamma_{i,calc} - \gamma_{i,exp}}{\gamma_{i,calc}}\right)^2 \qquad (4)$$

where n represents the number of the experimental points and $\gamma_{i,calc}$, $\gamma_{i,exp}$ represent the activity coefficients for component i calculated by the Wilson equation or derived from experimental data.

For the prediction of the activity coefficient, the group contribution method modified UNIFAC (Dortmund) has also been used.[7−9]

The present work represents a continuation of the project concerning phase behavior of systems containing “oxyalcohol” compounds. Azeotropic and heat of mixing data for various binary systems containing 1-methoxy-2-propanol and 2-butoxy ethanol have been presented previously.[10] In this work, solid−liquid equilibrium data for 1-methoxy-2-propanol and 2-butoxy ethanol with benzene and cyclohexane have been measured from (215 to 279) K. No experimental data for the studied systems have been found in the literature for comparison. Due to the correlation requirements for the SLE data, the missing heat of fusion $\Delta_{fus}H$ for 1-methoxy-2-propanol has been measured as well.

Experimental Section

Chemicals. Chemicals of high purity obtained from different suppliers were purified by vacuum distillation before their use. The purity was carefully checked by gas chromatography (GC) and Karl Fischer titration. Besides the supplier, the chemicals together with the pure component specifications are summarized in Table 1.

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Table 1. Suppliers, CAS Number, Purity, Water Content, Heat of Fusion ($\Delta_{fus}H$), Melting Points (T_{fus}), Heat of Transition ($\Delta_{trs}H$), and Transition Points (T_{trs}) for the Chemicals Used

					$\Delta_{fus}H$		T_{fus}		$\Delta_{trs}H$	T_{trs}
					J·mol^{-1}		K		J·mol^{-1}	K
compound	supplier	CAS number	purity (% GC)	water content (mass ppm)	DDB[a]	this work	DDB[a]	this work	DDB[a]	DDB[a]
1-methoxy-2-propanol	Adrich	107-98-2	>99.9	16.0		3607	176.45			
2-butoxy ethanol	Aldrich	111-76-2	>99.8	75.9	19100		203.15			
benzene	Fisher Chemicals	71-43-2	>99.9	6.0	9951		278.68	278.95		
cyclohexane	Aldrich	110-822-7	>99.9	9.0	2630		279.75	279.96	6740.7	185.95

[a] Dortmund Data Bank.[16]

Table 2. Experimental Solid−Liquid Equilibrium (SLE) Data for the Binary Systems 1-Methoxy-2-propanol (1) + Benzene (2) and 1-Methoxy-2-propanol (1) + Cyclohexane (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
1-Methoxy-2-propanol (1) + Benzene (2)					
0.0000	278.95	0.3029	268.35	0.5995	252.62
0.0490	276.50	0.3498	266.30	0.6501	248.09
0.1013	274.73	0.3999	264.29	0.7005	242.30
0.1497	273.32	0.4503	261.84	0.7478	236.48
0.2008	271.64	0.5000	258.92	0.7996	227.95
0.2209	271.02	0.5450	256.52	0.8500	217.10
1-Methoxy-2-propanol (1) + Cyclohexane (2)					
0.0000	279.96	0.2993	266.58	0.5992	258.36
0.0509	274.26	0.3504	265.57	0.6501	255.70
0.1002	271.65	0.3998	264.50	0.6999	251.99
0.1524	269.89	0.4508	263.14	0.7487	247.33
0.2011	268.74	0.4995	262.07	0.8000	239.93
0.2508	267.50	0.5498	260.61	0.8507	227.09

Table 3. Experimental Solid−Liquid Equilibrium (SLE) Data for the Binary Systems 2-butoxy Ethanol (1) + Benzene (2) and 2-butoxy Ethanol (1) + Cyclohexane (2)

x_1^L	T/K	x_1^L	T/K	x_1^L	T/K
2-Butoxy Ethanol (1) + Benzene (2)					
0.0000	278.95	0.2991	267.93	0.6003	246.49
0.0504	276.85	0.3509	265.51	0.6486	242.02
0.1007	275.22	0.4007	262.36	0.6996	235.59
0.1496	273.50	0.4499	259.60	0.7501	228.12
0.2010	271.60	0.4994	255.88	0.8001	220.43
0.2508	269.84	0.5504	251.55		
2-Butoxy Ethanol (1) + Cyclohexane (2)					
0.0000	279.96	0.2974	262.51	0.5532	240.34
0.0529	274.49	0.3038	262.45	0.6000	233.99
0.1021	271.72	0.3516	259.20	0.6502	225.38
0.1501	269.45	0.4009	255.85	0.6997	216.22
0.2005	267.16	0.4494	251.19		
0.2508	264.61	0.5012	246.44		

Apparatus and Procedures. The SLE data of all the systems were measured by the synthetic visual technique, which is described elsewhere.[11−13] The equilibrium cell (total volume 160 cm^3) is made of glass. It is inserted in a three-jacket vessel. The exterior jacket, kept under vacuum, prevents the condensation of water vapor from atmosphere on the glass surface at low temperatures. Therefore, the visual observation is not disturbed. The cryostat (RL6 CP Lauda model) medium (usually pure ethanol with low water content) flows through the central jacket and transfers the heat to the equilibrium cell via the contact medium (also ethanol). A dry nitrogen atmosphere in the equilibrium cell avoids contamination with water.

First, the sample inserted in the equilibrium cell is supercooled with liquid nitrogen for a short time, whereby a small amount of the liquid crystallizes in the form of fine crystals. 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 synthetically prepared, the liquidus line over the whole composition range can be measured. Using the apparatus, measurements between (193 and 280) K can be performed. The temperature was determined with a calibrated platinum resistance thermometer (model KT5614, Hart Scientific). For the conversion of the measured resistance, a digital thermometer unit (model 1560, Hart Scientific) was used. The uncertainty of the melting temperature measurement by this method for the studied mixtures was found to be of ±0.1 K. The uncertainty of the composition was ±0.005 in mole fraction.

As it has been mentioned above, for the correlation and/or prediction of SLE data for eutectic systems, besides the melting temperature, the enthalpies of fusion of the pure compounds are required. For 1-methoxy-2-propanol, no such data were available in the literature. Subsequently, it had to be determined in this work. The heat of fusion measurements have been performed by means of a Tian-Calvet heat flow batch calorimeter from SETARAM, France (model BT 2.15 II), with a temperature range from (77.15 to 473.15) K. The principle of the measurement method has been described in detail by Calvet and Prat.[14] The calorimeter consists of two thermal flux meters, each constructed by a series of 480 thermocouples surrounding a cylindrical cavity. The flux meters are arranged symmetrically around two identical cells in an aluminum block located in the cavity. The signal delivered by the power difference of the two flux meters is proportional to the heat effects occurring in the cells. The temperature of the calorimeter block can be regulated using liquid nitrogen and electrical heating and is monitored using a Pt 100 resistance thermometer located between the two cells. To account for the difference between the registered temperature and the sample temperature from the measuring cell, a calibration run was performed in advance as described elsewhere.[15] The two identical cells used for the heat of fusion measurements were standard cells (five bars) made of stainless steel with 12.5 cm^3 total volume and inlet volume of 2 cm^3 and with PTFE sealing. While one of the cells was empty, the other one was filled with a defined amount of the sample. The whole calorimeter block was evacuated properly by vacuum pump to avoid condensation effects and then liquid nitrogen was introduced to cool the system below the melting temperature of the investigated substance. After the sample was crystallized, the calorimeter was heated using a heating rate of 0.1 K·min^{-1}. The melting process was registered by the heat flow signal, and the area of the corresponding peak was converted to heat of fusion by integration. From the tangent line to the peak corresponding to the appearance of the first drop of liquid in the sample, the melting temperature was determined. According to the manufacturer's specification, the experimental uncertainty for the determination of enthalpy of fusion is ±50 J·mol^{-1}.

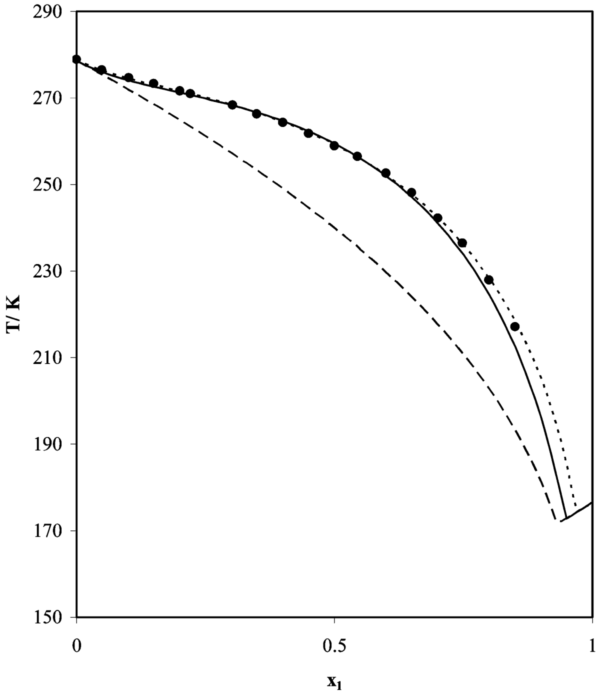

Figure 1. Solid−liquid equilibrium for the system 1-methoxy-2-propanol (1) + benzene (2): ●, visual method; - - -, ideal; ···, Wilson equation; —, modified UNIFAC (Dortmund).

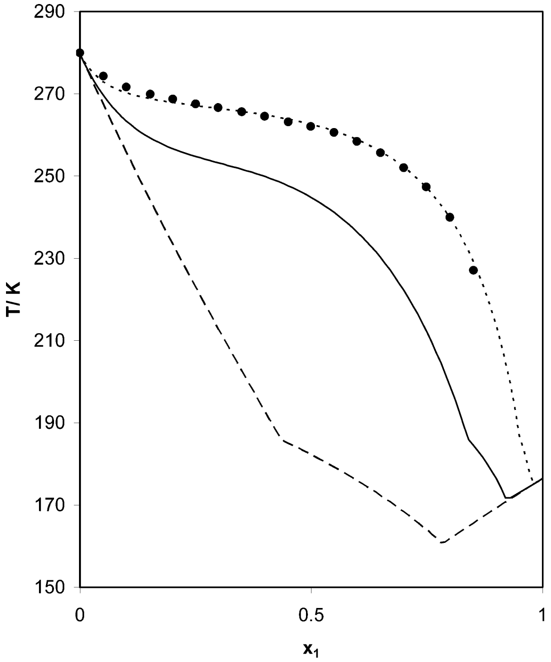

Figure 2. Solid−liquid equilibrium for the system 1-methoxy-2-propanol (1) + cyclohexane (2): ●, visual method; - - -, ideal; ···, Wilson equation; —, modified UNIFAC (Dortmund).

Results

For 1-methoxy-2-propanol, the heat of fusion has been measured by means of a Tian-Calvet heat flow batch calorimeter from SETARAM, France (model BT 2.15 II). The obtained value is given in Table 1. It has been used for the correlation or prediction of SLE data for the binary systems 1-methoxy-2-propanol + benzene and 1-methoxy-2-propanol + cyclohexane.

It must be mentioned that the measurements have been quite difficult because of the hygroscopic behavior of 1-methoxy-2-propanol and the difficulty to crystallize the sample. The measurements could only be performed successfully by adding a grain of molecular sieve in the cell.

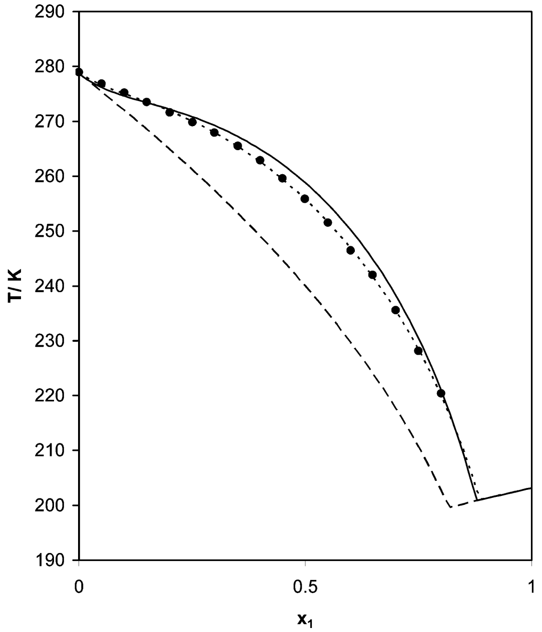

Figure 3. Solid−liquid equilibrium for the system 2-butoxy ethanol (1) + benzene (2): ●, visual method; - - -, ideal; ···, Wilson equation; —, modified UNIFAC (Dortmund).

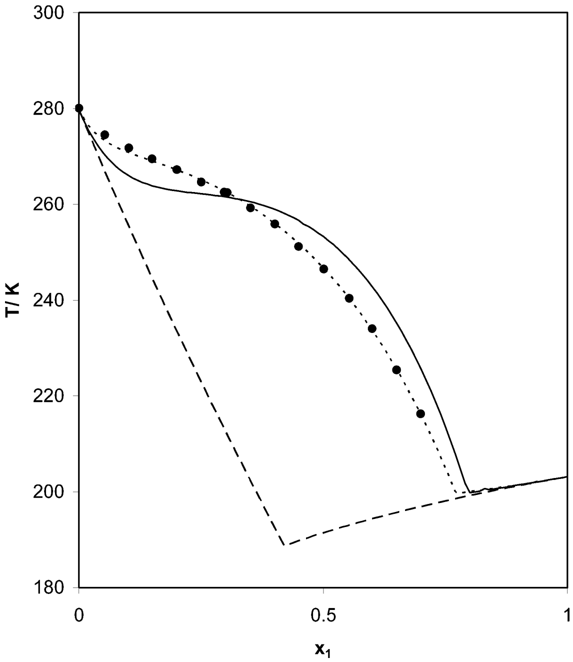

Figure 4. Solid−liquid equilibrium for the system 2-butoxy ethanol (1) + cyclohexane (2): ●, visual method; - - -, ideal; ···, Wilson equation; —, modified UNIFAC (Dortmund).

The experimental SLE data for the binary systems 1-methoxy-2-propanol + benzene and 1-methoxy-2-propanol + cyclohexane are listed in Table 2, and those for 2-butoxy ethanol + benzene and 2-butoxy ethanol + cyclohexane are given in Table 3.

Figures 1 to 4 contain the experimental data together with the correlations by means of the Wilson equation and the predictions of the group contribution method modified UNIFAC (Dortmund) using the parameters for the “oxyalcohol” main group. At the same time, the results are compared with the predictions assuming ideal behavior ($\gamma_i = 1$). In all the cases,

Table 4. Molar Volumes and Results of the Solid−Liquid Equilibrium Data Correlation by Means of the Wilson Equation

compound	molar volume/cm^3·mol^{-1}
benzene	89.41
cyclohexane	108.75
1-methoxy-2-propanol	97.79
2-butoxy ethanol	131.85

system	$\Delta\lambda_{12}$/J·mol^{-1}	$\Delta\lambda_{21}$/J·mol^{-1}
1-methoxy-2-propanol (1) + benzene (2)	4249.30	28.4842
1-methoxy-2-propanol (1) + cyclohexane (2)	6451.37	2957.00
2-butoxy ethanol (1) + benzene (2)	4610.67	−48.3680
2-butoxy ethanol (1) + cyclohexane (2)	6258.71	1168.22

eutectic behavior is assumed. The binary parameters for the Wilson equation $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are given together with the molar volumes used in Table 4.

Below 215 K, the four mixtures become quite viscous (high oxyalcohol concentration), therefore the systems could not be measured over the whole concentration range.

The investigated systems show positive deviation from ideal behavior. Except for the system 1-methoxy-2-propanol + cyclohexane, this behavior is at least qualitatively predicted by modified UNIFAC (Dortmund) using the “oxyalcohol” main group. This situation can most likely be improved by a revision of the parameters between the “oxyalcohol” group and the cyclic alkane group using the new data,[10] since for fitting the existing group interaction parameters no data at temperatures below 0 °C were taken into account.

Summary

The liquidus lines for the binary systems of 1-methoxy-2-propanol and 2-butoxy ethanol with benzene and cyclohexane were determined by a synthetic visual method. This method provides information about the real mixture behavior at low temperatures, with the range being limited only by the high viscosity of the oxyalcohols at low temperature.

The experimental SLE data have been correlated successfully using the Wilson equation. They were also compared with those predicted by the modified UNIFAC (Dortmund) model using the “oxyalcohol” groups. The results of the comparison are good for all the systems except for 1-methoxy-2-propanol + cyclohexane.

The agreement between experimental and predicted data shows that modified UNIFAC (Dortmund) in most cases allows a reliable extrapolation to low temperatures. Therefore, it is a very suitable tool for the prediction of thermophysical mixture properties, required for the synthesis and design of thermal separation (e.g., crystallization) processes.

Acknowledgment

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