(Solid + Liquid) Equilibrium of (4-Chloro-2-benzofuran-1,3-dione + 5-Chloro-2-benzofuran-1,3-dione)

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(Solid + liquid) phase equilibrium (SLE) has been measured for 4-chloro-2-benzofuran-1,3-dione anhydride and 5-chloro-2-benzofuran-1,3-dione anhydride using differential scanning calorimetry (DSC) over the whole concentration range. It was found that this system is a simple eutectic system. The eutectic point is at $T =$ 336.95 K and a mole fraction of 4-chloro-2-benzofuran-1,3-dione of 0.3482. Furthermore, the results obtained in mixtures of (4-chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione) have been compared with those predicted by the ideal model and correlated by Wilson and nonrandom two-liquid (NRTL) equations. The best modeling results were obtained using the NRTL model with the average root-mean-square deviation of $\sigma = 7.88$ K.

Introduction

The number of organic materials separated or purified by crystallization in industrial scale operations is increasing rapidly because of the low energy consumption of such processes and the possibility of obtaining products with higher purity than can be achieved by other conventional separation operations. The continued development of solution models for describing the thermodynamic properties of binary mixtures requires a large database to be available for assessing the applications and limitations of established expressions. 4-Chloro-2-benzofuran-1,3-dione (CAS Registry No. 117-21-5) and 5-chloro-2-benzofuran-1,3-dione (CAS Registry No. 118-45-6) are commercially valuable intermediates in the synthesis of a number of compounds.[1] The isomeric mixtures are formed in various proportions of 4-chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione with many synthetic methods.[2−6] To the best of the present authors' knowledge, no study has been reported on the (solid + liquid) phase equilibrium (SLE) of the binary mixture. In the present paper, the SLE has been measured for the system of 4-chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione.

Various methods have been proposed to measure the SLE.[7] Classically, SLE is often determined by sampling saturated solutions and analyzing samples by spectroscopy or gas or liquid chromatography.[8−10] Sample detection often requires a separation step and the presence of chromophores for detection. Errors can occur in sampling, particularly in systems with finely dispersed solute particles with little density difference between solid and liquid phases. Recently, methods of using output data of differential scanning calorimetry (DSC) are suggested. Of the methods of measuring SLE, it was shown that DSC is a rapid and sensitive technique, broadly used for determining the phase boundaries through the measurement of the heat effect during the phase transformation process.[11−13]

In this work, a complete data set is obtained by DSC technique for the SLE of 4-chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione. Furthermore, the results obtained have been compared with those predicted by the ideal model and correlated by Wilson and nonrandom two-liquid (NRTL) equations.

Experimental Procedures

Materials. 4-Chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione were provided from XinPeng Chemical Promoter Factory, China, with a mass fraction of 0.9952 and 0.9973, and were used without further purification. Their melting temperatures and enthalpies of fusion were measured using DSC (Netzsch DSC 204F1).

Equipment. The calorimetry experiments were performed on a Netzsch DSC 204F1 differential scanning calorimeter equipped with sample and reference standard aluminum crucibles. During the scanning operation, high-purity nitrogen gas was purged through the DSC chamber at 1 $\text{cm}^3 \cdot \text{s}^{-1}$. The measurements were carried out under a constant heating rate of 0.03 $\text{K} \cdot \text{s}^{-1}$. This scanning rate is low enough to approach the equilibrium measurement conditions. The temperature range is from (287 to 432) K. Before the analysis, the energy flow was determined by calibration with the enthalpy of fusion of an exact known quantity of indium. The temperature was measured with a nominal 100 Ω platinum resistance thermometer calibrated using a pan containing an exact known quantity of indium as well as lead and zinc in separate compartments. The uncertainties of the measurements were estimated to be ± 0.2 K for the temperature and ± 0.40 $\text{kJ} \cdot \text{mol}^{-1}$ for the enthalpy of fusion and transition.

Sample Preparation. The sample was heated very slowly inside a glass tube at near the melting temperature of the major component. The liquefied sample with continuous stirring was solidified. Then about 5 mg of solid was taken and sealed in a sample crucible for the analysis.

SLE Measurement. As described in detail previously,[14] we adopted the method in which liquidus and solidus curves were estimated from the onset and peak temperatures obtained from the measured DSC curves. Figure 1, plotting the heat flow rate versus temperature, shows a typical DSC curve of 4-chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione based on the scanning rates of (0.03 and 0.08) $\text{K} \cdot \text{s}^{-1}$ on the same

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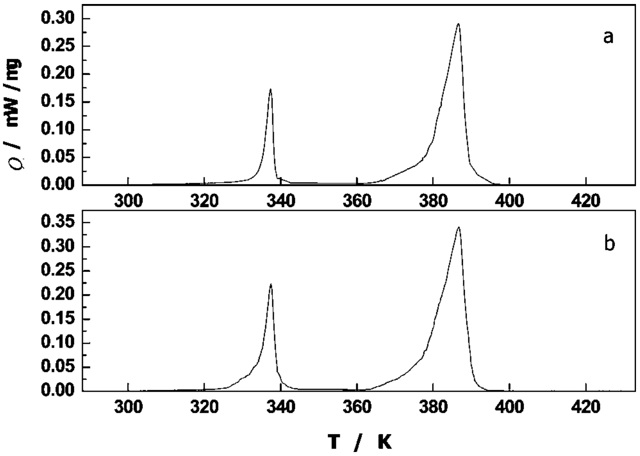

Figure 1. Typical DSC heat flux Q as a function of temperature T for (4-chloro-2-benzofuran-1,3-dione + 5-chloro-2-benzofuran-1,3-dione). Top: $dT/dt = 0.03\ \mathrm{K \cdot s^{-1}}$. Bottom: $dT/dt = 0.08\ \mathrm{K \cdot s^{-1}}$.

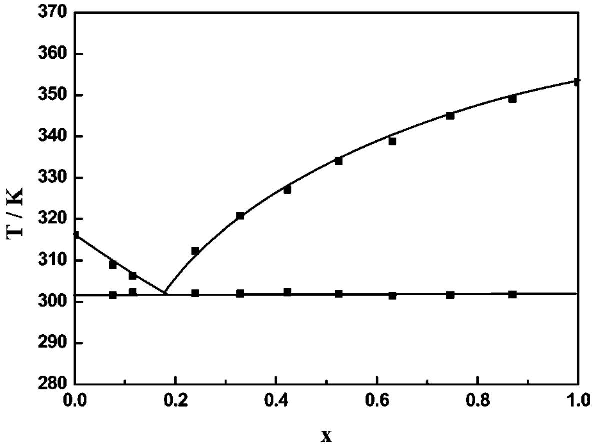

Figure 2. Temperature T as a function of mole fraction x for the SLE of (bicyclo[4.4.0]deca-1,3,5,7,9-pentene + hydroxybenzene). ■, SLE data obtained in this work with DSC; —, literature data from ref 15.

sample. The results show that the onset temperature is not affected by thermal history. The onset temperatures at each first peak almost show constant value for the eutectic temperature. The next peak temperatures are solidus temperature. This SLE measurement method was verified by comparing our results to published SLE data for the system of (bicyclo[4.4.0]deca-1,3,5,7,9-pentene + hydroxybenzene) shown in Figure 2, which shows that the results are in good agreement with literature data.[15]

Results and Discussion

Determination of the Solid—Liquid Phase Diagram. The melting temperatures and enthalpies of fusion were measured using DSC (Netzsch DSC 204F1). The melting points of the pure samples are in good agreement with literature data.[16] For the pure components the melting temperature T_m and molar enthalpy of fusion $\Delta_{fus}H$ are listed in Table 1. The equilibrium temperatures for varying mole fractions of 4-chloro-2-benzofuran-1,3-dione and 5-chloro-2-benzofuran-1,3-dione are listed in Table 2 and shown in Figure 3. It is found that it is a simple eutectic system. The eutectic point of the mixture is at $T = 336.95$ K and a mole fraction of 4-chloro-2-benzofuran-1,3-dione of 0.3482.

Table 1. Melting Temperature T_m and Melting Molar Enthalpy $\Delta_{fus}H$ of Pure Compounds

compound	T_m / K	$\Delta_{fus}H$ / $\mathrm{J \cdot mol^{-1}}$
4-chloro-2-benzofuran-1,3-dione	397.95[16]	13352.44
5-chloro-2-benzofuran-1,3-dione	367.35[16]	33061.62

Table 2. Measured SLE Temperatures T and T_E as a Function of Mole Fraction x for {4-Chloro-2-benzofuran-1,3-dione (1) + 5-Chloro-2-benzofuran-1,3-dione (2)}

x_1	T_E/K	T/K
0.0000		367.35
0.0549	336.95	362.51
0.1041	336.95	359.05
0.1472	336.95	355.59
0.1891	336.95	351.15
0.2530	336.95	345.95
0.3052	336.95	340.72
0.3482	336.95	336.95
0.4166	336.95	345.85
0.4695	336.95	351.99
0.5211	336.95	356.75
0.5549	336.95	360.55
0.6619	336.95	369.56
0.7073	336.95	374.51
0.7980	336.95	381.87
0.8728	336.95	388.15
0.9370	336.95	393.59
1.0000		397.95

Equations for Prediction of SLE. The equation of the solid equilibrium curve of a pure solid component including two first-order transitions is, for a temperature below that of phase transition[17]

$$\ln(\gamma_i x_i) = \frac{\Delta H_{m,i}}{RT}\left(\frac{T}{T_{m,i}} - 1\right) - \frac{\Delta c_{p,i}}{R}\left(\ln\frac{T_{m,i}}{T} - \frac{T_{m,i}}{T} + 1\right) \tag{1}$$

where x_i is the mole fraction and γ_i the activity coefficient of component i in the mixture at temperature T. $T_{m,i}$, $\Delta H_{m,i}$, and $\Delta c_{p,i}$, respectively, are the melting temperature, the molar enthalpy of melting in, and the difference between the molar heat capacity of the component i in the solid and liquid states, and R is the universal gas constant.

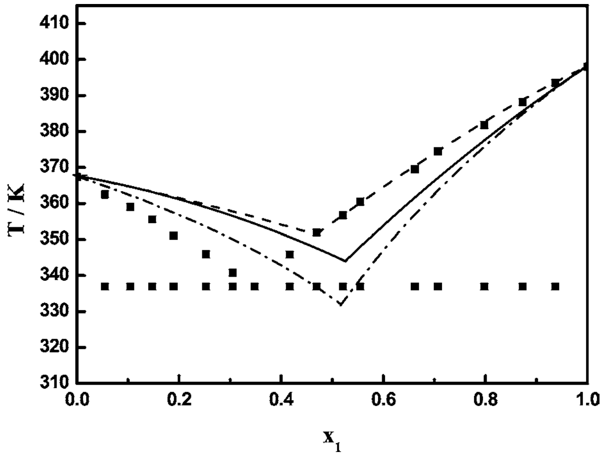

Figure 3. Temperature T as a function of mole fraction x for the SLE of {4-chloro-2-benzofuran-1,3-dione (1) + 5-chloro-2-benzofuran-1,3-dione (2)}: ■, experimental results; - - -, NRTL model; -•-•-, Wilson model; —, ideal model.

Table 3. Correlation of the Solubility Data of {4-Chloro-2-benzofuran-1,3-dione Anhydride (1) + 5-Chloro-2-benzofuran-1,3-dione Anhydride (2)} by Means of the Wilson and NRTL Equations and Ideal Models: Values of Parameters and Measures of Deviations

	parameters					σ/K		
system	Wilson		NRTL			Wilson	NRTL	ideal
	$\Delta\lambda_{12}$	$\Delta\lambda_{21}$	Δg_{12}	Δg_{21}	α_{12}	11.48	7.88	9.14
4-chloro-2-benzofuran-1,3-dione + 5-chloro-2-benzofuran-1,3-dione	74000	−5038.6	2372	57360	0.47			

In addition, in eq 1, the right-hand side term containing Δc_p is of significantly less importance than the other term. Therefore, a simplified form of this equation can be used:

$$\ln(\gamma_i x_i) = \frac{\Delta H_{\mathrm{m},i}}{RT}\left(\frac{T}{T_{\mathrm{m},i}} - 1\right) \qquad (2)$$

If the mixture can be assumed to be ideal then the activity coefficients are unity ($\gamma_i \approx 1$), and eq 2 can be rewritten as:

$$\ln x_i = \frac{\Delta H_{\mathrm{m},i}}{RT}\left(\frac{T}{T_{\mathrm{m},i}} - 1\right) \qquad (3)$$

Predicting the liquidus line can be made easier by assuming that the system is eutectic. This is because the only information needed is the liquid nonideality and the pure component properties.

In this study, two methods are used to derive the solute activity coefficient γ_1 from the Wilson and NRTL equations. The exact mathematical forms of the equations for binary systems are presented as follows.

From the Wilson equation[18] the activity coefficient is given by

$$\ln \gamma_1 = -\ln(1 - A_{2/1}x_2) + x_2\left(\frac{x_2 A_{1/2}}{1 - A_{1/2}} - \frac{x_1 A_{2/1}}{1 - A_{2/1}x_2}\right) \qquad (4)$$

where $A_{j/i}$ are the adjustable parameters, $A_{1/2} = 1 - \Lambda_{21}$, and $A_{2/1} = 1 - \Lambda_{12}$, that permits eq 4 to be cast as

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \qquad (5)$$

where

$$\Lambda_{12} = \frac{\nu_2}{\nu_1}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right)$$
$$\Lambda_{21} = \frac{\nu_1}{\nu_2}\exp\left(-\frac{\lambda_{21} - \lambda_{11}}{RT}\right) \qquad (6)$$

where ν is molar volume and x is the mole fraction. For (4-chloro-2-benzofuran-1,3-dione + 5-chloro-2-benzofuran-1,3-dione), ν_2/ν_1 is taken as 1. The Wilson equation has two adjustable parameters per binary: $\Delta\lambda_{12}$ ($= \lambda_{12} - \lambda_{11}$) and $\Delta\lambda_{21}$ ($= \lambda_{21} - \lambda_{22}$).

For the NRTL equation[19] the activity coefficient is given by

$$\ln \gamma_1 = x_2^{\,2}\left[\frac{\tau_{21}G_{21}^2}{(x_1 + G_{21}x_2)^2} + \frac{\tau_{12}G_{12}}{(G_{12}x_1 + x_2)^2}\right] \qquad (7)$$

where

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad (8)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \qquad (9)$$

The NRTL equation contains three parameters, Δg_{12} ($= g_{12} - g_{22}$), Δg_{21} ($= g_{21} - g_{11}$), and α_{12}. The third parameter α_{12} is related to the nonrandomness in the mixture and varies from 0.2 to 0.47.

Correlation of Results Based on the Wilson and NRTL Equations. The parameters of the two equations were evaluated by minimizing the following objective function, F_{obj}, between the calculated and the experimentally determined temperature:

$$F_{\mathrm{obj}} = \sum_{j=1}^{N}(\gamma_j - \gamma_j^{\mathrm{cal}})^2 \qquad (10)$$

where the summation is over of the all jth data points. The root-mean-square deviation of temperature (σ defined by eq 11) was used as a measure of goodness of the solubility correlation.

$$\sigma = \left[\frac{1}{N - 2}\sum_{j=1}^{N}(T_j - T_j^{\mathrm{cal}})^2\right]^{1/2} \qquad (11)$$

where N is the number of experimental points and 2 is the number of adjustable parameters.

Table 3 lists the results of fitting the solubility curves by the three equations used: Wilson and NRTL equations and prediction by the ideal model. For the three models presented in this work, the best description of SLE was given by the three-parameter NRTL equation with the average standard deviation of $\sigma = 7.88$ K. The results of correlations by use of the Wilson model present the worst deviation, $\sigma = 11.48$ K. The calculated results are also presented in Figure 3. The compositions calculated have been compared with those obtained experimentally.

Conclusions

The SLE for (4-chloro-2-benzofuran-1,3-dione + 5-chloro-2-benzofuran-1,3-dione) has been measured from the DSC experiments. It was shown that it is a simple eutectic system. The eutectic point of the mixture is at $T = 336.95$ K and a mole fraction of 4-chloro-2-benzofuran-1,3-dione of 0.3482.

Relatively simple mathematical models, Wilson and NRTL models and the ideal model, were used to represent the SLE temperature of (4-chloro-2-benzofuran-1,3-dione + 5-chloro-2-benzofuran-1,3-dione). The best results for the correlation of experimental points were obtained by means of the three-parameter NRTL equation with the average root-mean-square deviation of $\sigma = 7.88$ K.

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