Solid–Liquid Phase Diagram of the Binary System Benzil + 2,2-Dimethoxy-1,2-diphenylethanone

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This work reports measurements of the phase diagram of the system w benzil + $(1 - w)$ 2,2-dimethoxy-1,2-diphenylethanone. The liquidus and solidus equilibrium temperatures were determined from thermal analysis using a differential scanning calorimeter. On the basis of the results, the binary mixture can be considered a simple eutectic system having a eutectic at a weight fraction of benzil of $w = 0.3$. The liquidus curve is successfully predicted assuming ideal behavior.

Introduction

The melt crystallization is one of the most effective unit operations to purify organic compounds. Furthermore, it appears particularly attractive from an economic point of view when the melting points of the organic compounds are in the range between 50 and 100 °C (*1*).

In order to define the possibility of separating a given organic mixture by melt crystallization and to determine the process operating conditions, the knowledge of solid–liquid equilibrium (SLE) data for the system is required.

This work deals with an experimental investigation on the binary system benzil + 2,2-dimethoxy-1,2-diphenylethanone. The latter compound, also called benzil dimethyl ketal (BDK), is an effective enhancer of polymerization when exposed to light. In industrial application its purity must be high (>99.5%). Its melting point is around 66 °C, and its purification from benzil, the main impurity, appears to be accomplished by crystallization from the melt.

This paper reports the measurements of the binary SLE made by differential scanning calorimetry (DSC), and compares the results with an ideal solid–liquid equilibrium model.

Experimental Section

Both compounds, supplied by Lamberti, have a purity higher than 99.7 mass %.

The benzil, also called dibenzoyl, has a temperature of melt, t_B, of 95.2 °C and an enthalpy of fusion, ΔH_B, of 92.7 J g^{-1} (*2*); there appear to be, for BDK, no measurements on the enthalpy, ΔH_{BDK}, and temperature of fusion, t_{BDK}.

The SLE of the binary system has been determined at atmospheric pressure using a DuPont DSC apparatus, model 9000.

To obtain a uniform material, mixtures of a total of 100 g (benzil + BDK) were kept molten and maintained under agitation for 1 h before two samples were withdrawn and analyzed by the DSC. All measurements were made with samples of 10 mg using a constant heating rate of 4 °C/min. The calibration coefficient of the DSC was recalculated using the benzil peak area, and its enthalpy of fusion (*2*).

The reproducibilities of the measurements of temperature and enthalpy of fusion are ±0.2 °C and ±3 J g^{-1}, respectively.

The mass of the samples was weighed with a reproducibility of ±0.1 mg.

Results and Discussion

The melting point and the enthalpy of fusion can be derived from the DSC curve. The melting point is usually assumed equal to the so-named on set point t_0, the temperature at which a temperature deviation between the sample pan and the reference pan arises. The enthalpy of fusion can be calculated by the area bound by the curve and the base line.

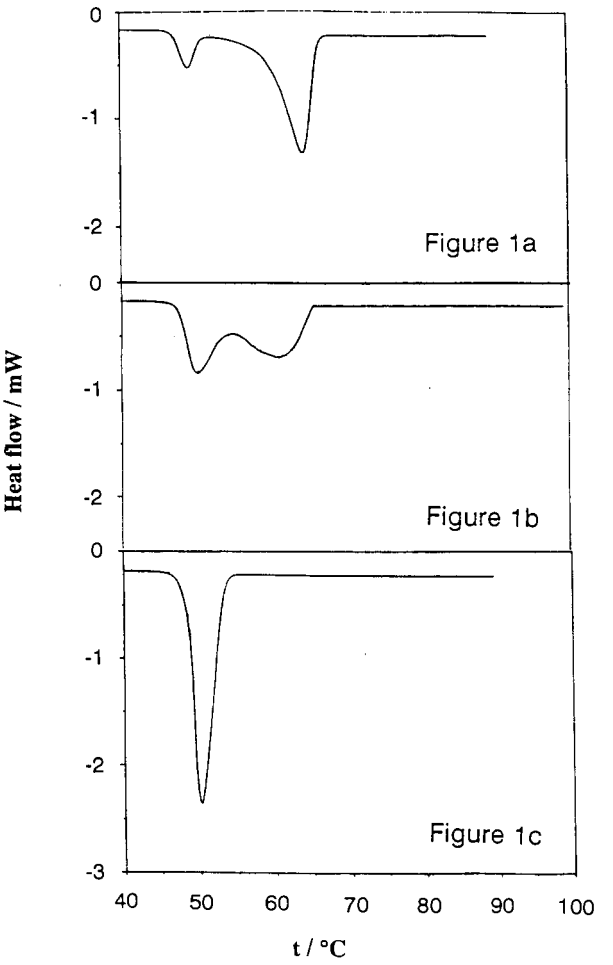

Figure 1. Typical DSC curves for a simple eutectic binary mixture: (a, b) mixtures at concentrations below the eutectic point, (c) mixture at the eutectic concentration.

The freezing point may be considered the lowest temperature at which the material is entirely molten and is assumed equal to the peak's temperature t_p during heating (*3*).

The DSC curve of the binary systems showed two peaks at each composition (except for the pure components and the

0021-9568/94/1739-0179$04.50/0

Table 1. Energy Released at the Eutetic Point, $\Delta H'$, and Total Energy Released above the Eutectic Point, $\Delta H''$, for the Binary Mixtures w Benzil + (1 − w) BDK

w	$\Delta H'$/(J g^{-1})	$\Delta H''$/(J g^{-1})	w	$\Delta H'$/(J g^{-1})	$\Delta H''$/(J g^{-1})
0.0	0.0	81.4	0.60	46.7	38.7
0.10	27.6	57.7	0.70	34.0	53.7
0.20	50.8	31.3	0.80	22.1	66.1
0.30	76.6	0.0	0.90	14.3	76.5
0.40	67.4	10.4	1.00	0.0	92.7
0.50	57.0	20.4			

eutectic mixture). The first peak, having an onset temperature in a close range of 46.0–48.7 °C, is typical of a eutectic point. The second peak's temperature, always greater than the first one, is a characteristic of the liquidus equilibrium curve (see Figure 1a,b).

For pure components one peak is present in the DSC diagram, so that the relevant fusion is still characterized by a temperature range instead of a single temperature value as expected. This discrepancy is mainly due to the finite thermal conductivity in the samples during fusion (*3*). However the onset temperature is usually assumed as the temperature of fusion.

For a mass fraction of benzil equal to 0.3, the DSC diagram shows only one peak (see Figure 1c), which has been attributed to the eutectic. The experimental reproducibility of the eutectic composition is ±0.015 by weight.

The experimental data, reported in Table 1 and Figure 2, clearly show that the system can be considered as a simple eutectic system. A temperature of 65.3 °C can be attributed to the fusion of BDK.

The small decrease in temperature at the boundaries of the solid line could be attributed to the small amount of impurities present in the two original compounds, which can slightly change the composition of the eutectic point and its melting point as well when the mass fraction of the eutectic is very small.

However, the impurities of BDK, essentially methyl benzoate, toluene, and benzil less than 0.3% by weight, do not significantly affect the SLE of the binary system. In fact by adding up to 1% of the first two impurities to mixtures of benzil and BDK, two peaks are still present in the DSC diagram, with the onset temperature of the first one nearly equal to that of the eutectic of the binary system.

The composition of the eutectic point w_{eu} has been confirmed by applying the procedure suggested by Matsuoka et al. (*4*). From the two peak areas of each DSC diagram, the amount of energy released at the eutectic point, $\Delta H'$, and the total energy released above the eutectic temperature, $\Delta H''$, were determined at various compositions (see Table 2). For $w = 0.3$, $\Delta H'$ assumes the maximum value and $\Delta H''$ is equal to zero, which means that such a composition can be considered the eutectic one.

The liquidus curve has been compared with that calculated assuming the solution as ideal and the solid and liquid heat capacities equal. In such a case the Schroder–van Laar equation (*5*) can been applied to the two branches of the liquidus curve, giving for $x < x_{eu}$

$$-\ln(1-x) = \Delta H_{BDK}/R[1/T - 1/T_{BDK}] \quad (1)$$

and for $x > x_{eu}$

$$-\ln(x) = \Delta H_B/R[1/T - 1/T_B] \quad (2)$$

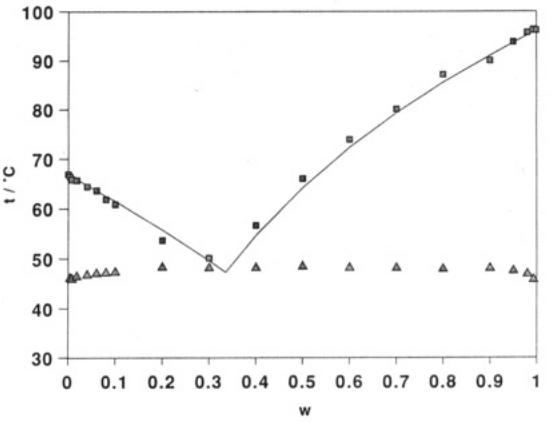

Figure 2. Solid–liquid phase diagram of the binary system w benzil + (1 − w) 2,2-dimethoxy-1,2-diphenylethanone: (▲) experimental values of solidus points, (■) experimental values of liquidus points, (—) calculated curves.

Table 2. Determination of the Melting Temperature Range of the Binary System w Benzil + (1 − w) BDK

w	t_0/°C	t_p/°C	w	t_0/°C	t_p/°C
<0.0001	65.3	66.4	0.400	48.4	56.6
0.004	46.4	66.4	0.500	48.7	66.0
0.008	46.2	65.9	0.600	48.4	73.9
0.018	46.7	65.7	0.700	48.4	80.0
0.040	47.0	64.4	0.800	48.1	87.1
0.060	47.3	63.6	0.900	48.3	90.0
0.080	47.4	61.9	0.950	47.8	93.8
0.100	47.6	60.9	0.980	47.1	95.7
0.200	48.6	53.6	0.993	46.0	96.3
0.300	48.4	50.1	>0.999	95.3	96.1

where x is the molar fraction of benzil, x_{eu} the molar fraction of the eutectic, and T the absolute temperature.

The eutectic point has been calculated by the simultaneous solution of the two above equations with $x = x_{eu}$ and $t = t_{eu}$. Values of $x_{eu} = 0.38$ (w_{eu}=0.335) and 47.3 °C for temperature results. Both calculated values are in satisfying agreement with the values derived from the experimental results.

The liquidus curve, calculated by eqs 1 and 2 compares well with the experimental values (Figure 2). The average absolute deviation between the calculated and experimental temperature is 0.8 °C.

It can be concluded that the assumption of an ideal solution is appropriate for the binary mixture primarily because of their chemical similarity.

Literature Cited

(1) Wynn, N. P. *Chem. Eng. Prog.* **1992**, *88* (3), 52.
(2) *Perry's Chemical Engineering Handbook;* McGraw-Hill: Tokyo, 1984.
(3) Nojima,H.; Akehi, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2067.
(4) Matsuoka, M.; Ozawa, R. *J. Cryst. Growth* **1989**, *96*, 596.
(5) Prausnitz, J. M. *Molecular thermodynamics of fluid-phase equilibria;* Prentice-Hall: Englewood Cliffs, NJ, 1969.

Received for review August 2, 1993. Accepted August 16, 1993.• This study was supported by the Research Project "Chimica Fine 2" of the Italian Research Council.

• Abstract published in *Advance ACS Abstracts,* November 1, 1993.