

Equilibrium Phase Diagram of the Ternary 2-Nitrobenzoic acid-3-Nitrobenzoic Acid-Acetone System at 283.15 K and 313.15 K

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In this investigation, the mutual solubilities for ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system were measured at 283.15 K and 313.15 K, respectively. Two partial isothermal phase diagrams of the system were constructed on the basis of the measured solubilities, one at 283.15 K and the other at 313.15 K. The phase diagrams of the ternary system are similar at the different temperature. Two solid phases were formed and confirmed by the Schreinemaker's wet residue method, and the two were identified as 2-nitrobenzoic acid and 3-nitrobenzoic acid. The crystallization regions of 2-nitrobenzoic acid and 3-nitrobenzoic acid increase as the temperature decreases.

Keywords nitrobenzoic acid, phase diagram, phase equilibrium

1. Introduction

3-Nitrobenzoic acid is a commercially valuable intermediate for producing the widest variety of derivatives, such as pigments, dyes and pesticides, particularly for synthesis of procaine hydrochloride, procaine ammonium salts, and amino-nitrobenzoic acid.^[1] These are in general produced by nitration of benzoic acid with nitric acid in sulfuric acid.^[2-8] In the process for nitration of benzoic acid that is thus far customary, a raw reaction product is obtained which contains about 20% of 2-nitrobenzoic acid and about 1% of 4-nitrobenzoic acid as by-products to the formation of 3-nitrobenzoic acid. Pure 3-nitrobenzoic acid can be separated from the mixture of isomeric nitrobenzoic acids by repeated recrystallization from solvents, such as water, alcohol, a mixture of alcohol and water, acetone and so on, and at the cost of a large decrease of the yield of the acid. Bright and Kendall point out that 3-nitrobenzoic acid can be recovered from the isomeric nitrobenzoic acids by basifying to a pH of 8-12 and then adding an acid to reduce the pH to 1.5-3.5 to precipitate the desired compound.^[9] However it is very difficult to operate in commercial scale.

It is well known that solid-liquid phase equilibrium data is important in crystallization processes. Obviously, the separation process by crystallization in acetone is based on the phase diagram of the ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system. It is very important to

study the system and construct the phase diagram of the ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system. Although the solubility of 2-nitrobenzoic acid and 3-nitrobenzoic acid in different solvents has been investigated,^[10,11] to the best of our present knowledge, no further investigations on the solubility or phase diagram for the 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system have been reported in the literature. The objectives of this research is to generate and analyze the phase diagrams of the ternary system at 283.15 K and 313.15 K by Schreinemaker's wet residue method and demonstrate the temperature dependence of the ternary phase diagram.

2. Material Section

2.1 Materials

The C.P. 2-nitrobenzoic acid obtained from the Shanghai Shiyi Chemicals Reagent Co. Ltd. was twice crystallized from water; this yielded white crystals with only a faint tinge of yellow. Melting temperature by the capillary tube method 147.7 °C corrected. International Critical Tables give 147.5 °C. The mass fraction of 2-nitrobenzoic acid was 99.52%.

The 3-nitrobenzoic acid was provided by the Shanghai Shiyi Chemicals Reagent Co. Ltd., with a mass fraction of 98.5%. The crude material was recrystallized from CHCl₃, and again from water, giving a product which was pure white in color and which had a melting point of 142.4 °C corrected. International Critical Tables give 141.4 °C. The mass fraction of 3-nitrobenzoic acid in this study was 99.56%.

The acetone was produced by the Shanghai Sinopharm Chemical Reagent Co. Ltd., which was dried over CaCl₂ and twice distilled: the fraction used boiled at 55.9-60.0 °C at 747 mm Hg, and the mass fraction of acetone was 99.92%.

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Section I: Basic and Applied Research

The water used to prepare solutions was deionized (conductivity $< 5 \mu\text{S}/\text{cm}^1$). A water bath (Neslab, model RTE-101), with a device for rotating several bottles at a time, thermostatically controlled to $\pm 0.1 \text{ K}$, was used for equilibrating samples. In this study, the temperature water bath was enclosed in order to maintain the water temperature.

2.2 Procedure

Schreinemaker's wet residue method consists of filtering the wet solid residue from an equilibrated saturated aqueous solution and analyzing both the solid residue and the saturated liquid that passed through the filter.^[12,13] This technique was used in the present study.² Initial samples were prepared as mixtures of known amounts of 2-nitrobenzoic acid, 3-nitrobenzoic acid, and acetone with the relevant amounts being chosen to vary the 2-nitrobenzoic acid/3-nitrobenzoic acid ratio from 0 to ~ 1 . All liquid mixtures were stirred in flasks that were surrounded by a constant temperature water bath. Aliquots of the liquid phase were taken at 2 h intervals and analyzed. When the composition of the liquid became constant, this was taken to indicate that equilibration had been attained. Generally, it took about 19 h to reach equilibrium. After equilibrium was achieved, the solid and liquid phases were separated by filtration, and then both were analyzed. This procedure was repeated by varying the ratio of 2-nitrobenzoic acid and 3-nitrobenzoic acid in order to obtain different compositions of the solid and liquid phases.

2.3 Analysis

The moist solid samples and the equilibrium liquid phase were dissolved in methanol and analyzed by a Shimadzu-6A high-performance liquid-phase chromatograph (HPLC) with the Diamonsil C_{18} (150 mm \times 4.6 mm) chromatographic column.^[14] The eluent consisted of three components that were water, propanol, and acetic acid. The densities (ρ) were measured with a specific weighing bottle calibrated by the floating force of air with a precision of $\pm 0.2 \text{ mg}$. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis (precision: $\pm 0.1\%$).

3. Results and Discussion

The measured solubility and the density of equilibrium liquid phase for the ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system at 283.15 K and 313.15 K are shown in Table 1 and 2, respectively. The ternary phase diagrams are plotted in Fig. 1 and 2.

In Fig. 1 and 2, along the solubility curve S_1P or S'_2P' , linking the component points of liquid phase and moist solid phase and an extension thereof, the point of intersection of

Table 1 Solubilities of the system 2-nitrobenzoic acid (1)-3-nitrobenzoic acid (2)-acetone (3) at 283.15 K^a

| Composition of liquid phase, mass % | | Composition of solid phase, mass % | | Density of liquid phase, $\text{g} \cdot \text{mL}^{-1}$ | Equilibrium solid phase |
|-------------------------------------|-----------------|------------------------------------|-----------------|--|---|
| $100 \cdot w_1$ | $100 \cdot w_2$ | $100 \cdot w_1$ | $100 \cdot w_2$ | | |
| 0.00 | 34.39 | 0.00 | 83.43 | 0.9136 | 3-nitrobenzoic acid |
| 5.91 | 31.78 | 2.82 | 81.77 | 0.9486 | 3-nitrobenzoic acid |
| 11.01 | 29.49 | 2.55 | 70.39 | 0.9816 | 3-nitrobenzoic acid |
| 16.84 | 28.18 | 8.53 | 64.91 | 1.0096 | 3-nitrobenzoic acid |
| 21.88 | 27.76 | 11.76 | 60.50 | 1.0383 | 3-nitrobenzoic acid |
| 28.22 | 25.30 | 15.33 | 60.52 | 1.0683 | 3-nitrobenzoic acid |
| 29.57 | 24.23 | 49.53 | 31.33 | 1.0765 | 2-nitrobenzoic acid + 3-nitrobenzoic acid |
| 29.79 | 24.97 | 42.69 | 21.40 | 1.0685 | 2-nitrobenzoic acid |
| 30.46 | 19.26 | 43.36 | 15.87 | 1.0626 | 2-nitrobenzoic acid |
| 33.49 | 11.91 | 52.42 | 8.71 | 1.0346 | 2-nitrobenzoic acid |
| 36.14 | 9.06 | 51.29 | 7.25 | 0.9946 | 2-nitrobenzoic acid |
| 36.47 | 5.54 | 57.46 | 3.64 | 0.9854 | 2-nitrobenzoic acid |
| 38.89 | 2.61 | 63.13 | 1.93 | 0.9691 | 2-nitrobenzoic acid |
| 40.87 | 0.01 | 84.65 | 0.00 | 0.9546 | 2-nitrobenzoic acid |

^a w_1 , mass fraction of 2-nitrobenzoic acid; w_2 , mass fraction of 3-nitrobenzoic acid.

Table 2 Solubilities of the system 2-nitrobenzoic acid (1)-3-nitrobenzoic acid (2)-acetone (3) at 313.15 K

| Composition of liquid phase, mass % | | Composition of solid phase, mass % | | Density of liquid phase, $\text{g} \cdot \text{mL}^{-1}$ | Equilibrium solid phase |
|-------------------------------------|-----------------|------------------------------------|-----------------|--|---|
| $100 \cdot w_1$ | $100 \cdot w_2$ | $100 \cdot w_1$ | $100 \cdot w_2$ | | |
| 0.00 | 51.69 | 0.00 | 75.83 | 1.0229 | 3-nitrobenzoic acid |
| 5.42 | 46.09 | 3.55 | 64.99 | 1.0361 | 3-nitrobenzoic acid |
| 12.34 | 42.41 | 8.54 | 58.19 | 1.0547 | 3-nitrobenzoic acid |
| 16.69 | 40.16 | 10.87 | 60.30 | 1.0663 | 3-nitrobenzoic acid |
| 19.46 | 36.71 | 6.78 | 79.17 | 1.0716 | 3-nitrobenzoic acid |
| 25.03 | 36.34 | 10.58 | 74.20 | 1.0859 | 3-nitrobenzoic acid |
| 27.66 | 35.41 | 14.43 | 66.02 | 1.091 | 3-nitrobenzoic acid |
| 30.56 | 33.26 | 20.21 | 57.07 | 1.0968 | 3-nitrobenzoic acid |
| 31.06 | 32.90 | 31.86 | 47.33 | 1.0972 | 2-nitrobenzoic acid + 3-nitrobenzoic acid |
| 31.98 | 31.59 | 49.95 | 23.90 | 1.0989 | 2-nitrobenzoic acid |
| 32.35 | 29.18 | 42.82 | 24.75 | 1.0959 | 2-nitrobenzoic acid |
| 33.13 | 25.49 | 60.74 | 14.99 | 1.0929 | 2-nitrobenzoic acid |
| 36.14 | 22.69 | 56.59 | 15.02 | 1.0705 | 2-nitrobenzoic acid |
| 37.82 | 18.01 | 58.32 | 11.86 | 1.0623 | 2-nitrobenzoic acid |
| 40.00 | 12.80 | 44.26 | 11.54 | 1.0494 | 2-nitrobenzoic acid |
| 43.07 | 8.48 | 59.16 | 6.22 | 1.0383 | 2-nitrobenzoic acid |
| 46.08 | 5.12 | 55.33 | 4.37 | 1.0276 | 2-nitrobenzoic acid |
| 51.19 | 0.00 | 63.21 | 0.00 | 1.0179 | 2-nitrobenzoic acid |

^a w_1 , mass fraction of 2-nitrobenzoic acid; w_2 , mass fraction of 3-nitrobenzoic acid.

¹This is the unit for the scale on a Siemen's meter.

²This method for determining a tie-line is only valid if no mutual solubility in the solid acids exists.

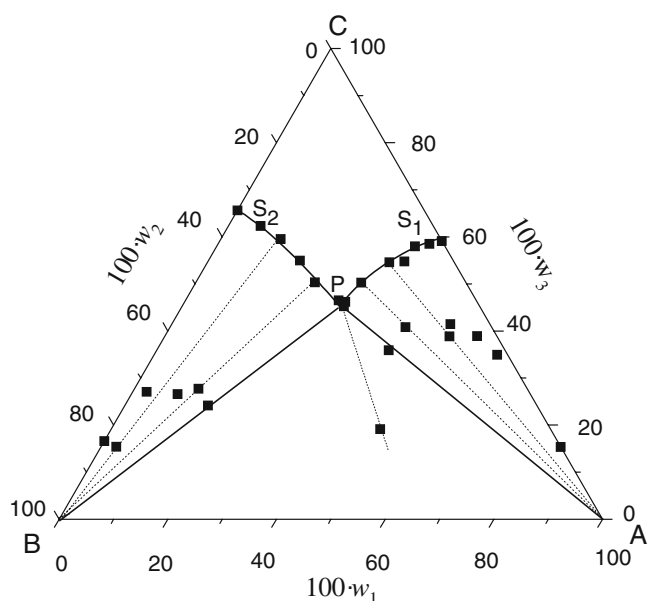


Fig. 1 Equilibrium phase diagram of the ternary 2-nitrobenzoic acid (1)-3-nitrobenzoic acid (2)-acetone (3) system at 283.15 K: A, 2-nitrobenzoic acid; B, 3-nitrobenzoic acid in acetone; C, acetone; S_1 , S_2 , solubility of 2-nitrobenzoic acid and 3-nitrobenzoic acid, respectively; P, cosaturated point; CS_2PS_1 , unsaturated region; BS_2P , crystalline region of solid 3-nitrobenzoic acid; AS_1P , crystalline region of solid 2-nitrobenzoic acid; BPA , crystalline region of solids 2-nitrobenzoic acid and 3-nitrobenzoic acid; w , mass fraction

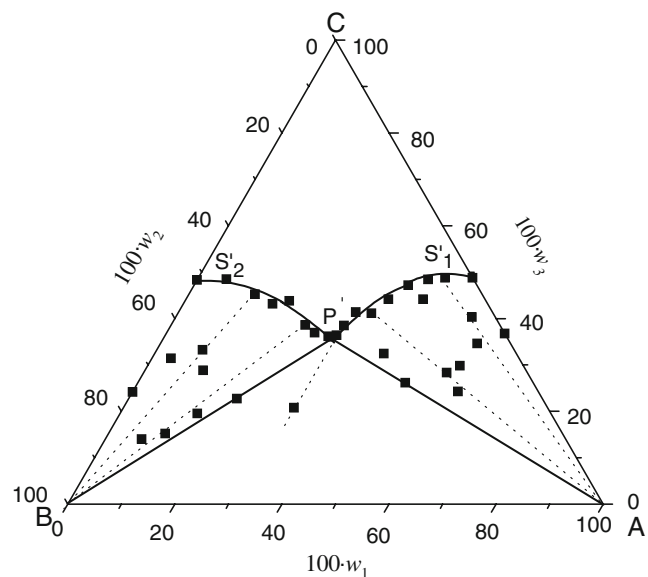


Fig. 2 Equilibrium phase diagram of the ternary 2-nitrobenzoic acid (1) - 3-nitrobenzoic acid (2) - acetone (3) system at 313.15 K: A, 2-nitrobenzoic acid; B, 3-nitrobenzoic acid in acetone; C, acetone; S'_1 , S'_2 , solubility of 2-nitrobenzoic acid and 3-nitrobenzoic acid, respectively; P' , cosaturated point; $CS'_2P'S'_1$, unsaturated region; BS'_2P' , crystalline region of solid 3-nitrobenzoic acid; AS'_1P' , crystalline region of solid 2-nitrobenzoic acid; $BP'A$, crystalline region of solids 2-nitrobenzoic acid and 3-nitrobenzoic acid; w , mass fraction

these tie-lines is approximately the solid-phase component for 2-nitrobenzoic acid on a wet basis. Along the solubility curve S_2P or S'_2P' linking the component points of liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for 3-nitrobenzoic acid. The results indicated that two solids were present in the system: one is 2-nitrobenzoic acid, and the other is 3-nitrobenzoic acid. This result is in agreement with the graph and with direct analysis after drying of the compound obtained by crystallization at the given temperatures.

In the phase diagrams as shown in Fig. 1 and 2, there are three crystallization fields: 2-nitrobenzoic acid (APS_1 in Fig. 1 and $AP'S'_1$ in Fig. 2), 3-nitrobenzoic acid (BPS_2 in Fig. 1 and $BP'S'_2$ in Fig. 2), mixture of 2-nitrobenzoic acid and 3-nitrobenzoic acid (BPA in Fig. 1 and $BP'S'_2$ in Fig. 2). The phase diagram has two invariant curves. PS_1 and $P'S'_1$ are saturation curves corresponding to the solid-phase 2-nitrobenzoic acid at 283.15 K and 313.15 K, respectively. PS_2 and $P'S'_2$ are saturation curves corresponding to the solid-phase 3-nitrobenzoic acid. P and P' are invariant points, which represent the equilibrium of the two solid phases 2-nitrobenzoic acid and 3-nitrobenzoic acid.

Figure 1 and 2 further illustrate the temperature dependence of the phase diagram for the ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system. When the temperature increases from (283.15 to 313.15) K, the solubility of 2-nitrobenzoic acid and 3-nitrobenzoic acid increases, and the co-saturated point moves upward. The phase diagrams of the ternary system are similar at different temperatures. The crystalline regions of 2-nitrobenzoic acid and 3-nitrobenzoic acid increase as the temperature decreases. No adduct is formed in the system at studied temperatures.

On the basis of data collected in Table 1 and 2, the relationship between the density of the equilibrium liquid phase and the component concentration values expressed in mass fractions (Fig. 3 and 4) are found. Results show that

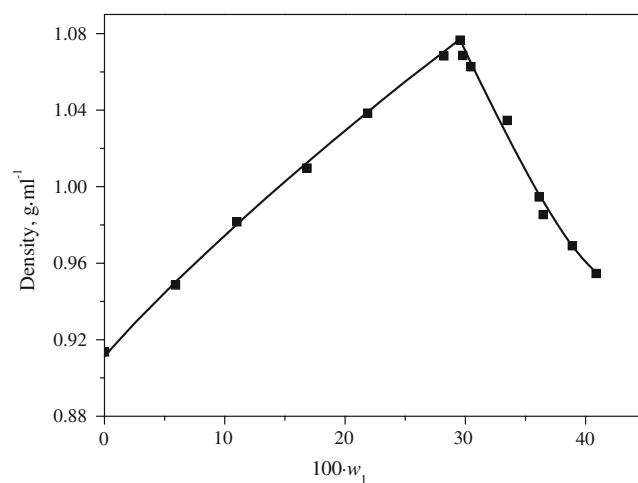


Fig. 3 Density value—composition relationship diagram for the ternary 2-nitrobenzoic acid (1)-3-nitrobenzoic acid (2)-acetone (3) system at 283.15 K. ■, experimental data point; —, experimental relationship diagram

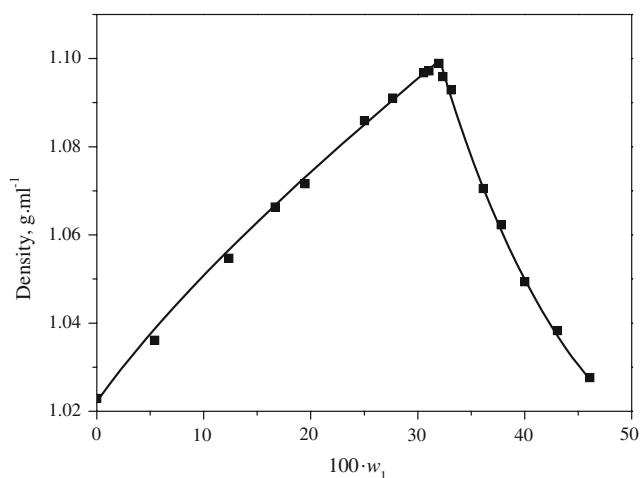


Fig. 4 Density value—composition relationship diagram for the ternary 2-nitrobenzoic acid (1)-3-nitrobenzoic acid (2)-acetone (3) system at 313.15 K. ■, experimental data point; —, experimental relationship diagram

the equilibrium solution density values increases at first and then decreases with respect to a rise in the 2-nitrobenzoic acid concentrations.

4. Conclusion

The solubility of the ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system at 283.15 K and 313.15 K was determined experimentally. The ternary phase diagram was constructed. The densities of the equilibrium liquid phase were obtained. The solid-phases were confirmed by Schreinemaker's wet residue method. At the studied temperatures, two solid phases were formed in the ternary 2-nitrobenzoic acid-3-nitrobenzoic acid-acetone system that corresponded to 2-nitrobenzoic acid and 3-nitrobenzoic acid, respectively. The phase diagram had three crystallization fields (2-nitrobenzoic acid, 3-nitrobenzoic acid, and a mixture of 2-nitrobenzoic acid and 3-nitrobenzoic acid), two invariant curves, and one invariant point at each temperature. The phase diagrams of the ternary system are similar at different temperatures. The solubility of 2-nitrobenzoic acid and 3-nitrobenzoic acid increases with increasing temperature.

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