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Solid−Liquid Phase Equilibrium and Phase Diagram for the Ternary *o*-Nitrobenzoic Acid + *m*-Nitrobenzoic Acid + Ethanol System

Hong-Kun Zhao,* Qiu-Hong Zhang, Rong-Rong Li, Hai-Zhe Ji, Xian-Chao Meng, and Qi-Shu Qu

College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, People's Republic of China

In this investigation, the mutual solubilities for the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system were measured at (273.15, 283.15, and 293.15) K, respectively. The isothermal phase diagrams of the system were constructed on the basis of the measured solubilities. Two solid phases were formed and confirmed by the Schreinemakers wet residue method, and the two were identified as *o*-nitrobenzoic acid and *m*-nitrobenzoic acid. The solubility fields of two solid phases were observed from the phase diagram. The phase diagrams of the ternary system are similar at the different temperatures. The crystallization regions of 2-nitrobenzoic acid and 3-nitrobenzoic acid increase as the temperature decreases. The solubility data and the ternary phase diagram can provide the fundamental basis for separation of the mixture of isomeric nitrobenzoic acids.

Introduction

m-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] It is in general produced by nitration of benzoic acid with nitric acid in sulfuric acid.[2–8] In the process for the nitration of benzoic acid that is thus far customary, a raw reaction product is obtained which contains about 20 % of *o*-nitrobenzoic acid and about 1 % of *p*-nitrobenzoic acid as byproduct to the formation of *m*-nitrobenzoic acid. Pure *m*-nitrobenzoic acid can be separated from the mixture of isomeric nitrobenzoic acids by repeated recrystallization from solvents, such as water, ethanol, a mixture of ethanol 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 *m*-nitrobenzoic acid can be recovered from the isomeric nitrobenzoic acids by basifying to a pH of 8 to 12 and then adding an acid to reduce the pH to 1.5 to 3.5 to precipitate the desired compound.[9] However, it is very difficult to operate in a commercial scale.

It is well-known that solid−liquid phase equilibrium data are important in crystallization processes. Obviously, the separation process by crystallization in ethanol is based on the phase diagram of the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system. It is very important to study the system and construct the phase diagram of the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system. Although the solubilities of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in different solvents have been investigated,[10,11] to the best of our present knowledge, no further investigations on the solubility or phase diagram for the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system were made in the literature. The objective of this research is to generate and analyze the phase diagrams of the ternary system at (273.15, 283.15, and 293.15) K by the Schreinemakers wet residue method[12,13] and demonstrate the temperature dependence of the ternary phase diagram.

Material Section

Materials. The C.P. *o*-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 temperatures were determined by the DSC method (Netzsch STA 409PC Luxx simultaneous TG-DSC) with the heating rate of 1.5 $K\cdot min^{-1}$ in nitrogen, which is 420.2 K. The *CRC Handbook of Chemistry and Physics* gave (420.1 to 421.1) K.[14] The mass fraction of *o*-nitrobenzoic acid was 99.84 %.

The *m*-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 $CHC1_3$ and again from water, giving a product which was pure white in color and which had a melting point of 414 K. The *CRC Handbook of Chemistry and Physics* gave (413.1 to 415.1) K.[14] The mass fraction of *m*-nitrobenzoic acid was 99.82 %.

Absolute ethanol, provided by the Shanghai Shiyi Chemicals Reagent Co., Ltd., was refluxed with lime, distilled, dried with sodium, and redistilled twice. Its purity was 99.95 %.

The water used to prepare solutions was deionized (conductivity < 5 $\mu S\cdot cm^{-1}$). A water bath (Neslab, model RTE-101), with a device for rotating several bottles at a time, thermostatically controlled to ± 0.1 K, was used for equilibrating samples.

Procedure. Schreinemakers wet residue method[12,13] 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. This technique was used in the present study. Initial samples were prepared as mixtures of known amounts of *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, and ethanol with the relevant amounts being chosen to vary the *o*-nitrobenzoic acid/*m*-nitrobenzoic acid ratio from 0 to ∼1. All liquid mixtures were stirred in flasks that were surrounded by a constant-temperature water bath, and the fluctuation of the temperature was less than ± 0.01 K. A

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* Corresponding author. E-mail: hkzhao@zzu.edu.cn. Tel.: +86 514 87975568. Fax: +86 514 87975244.

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Table 1. Mass Fraction Solubilities of the Ternary System *o*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 273.15 K[a]

liquid phase		moist solid phase		
100 w_1	100 w_2	100 w_1	100 w_2	equilibrium solid phase
0	25.59	0	54.45	*m*-nitrobenzoic acid
2.74	24.13	2.2	41.8	*m*-nitrobenzoic acid
5.66	23.08	3.64	50.99	*m*-nitrobenzoic acid
8.25	21.93	5.93	44.69	*m*-nitrobenzoic acid
9.58	21.47	5.36	52.15	*m*-nitrobenzoic acid
11.81	21.28	8.53	39.79	*m*-nitrobenzoic acid
13.74	20.52	26.63	44.39	*m*-nitrobenzoic acid + *o*-nitrobenzoic acid
14.13	16.64	45.29	10.78	*o*-nitrobenzoic acid
14.48	14.33	25.76	13.08	*o*-nitrobenzoic acid
14.5	13.29	38.11	9.92	*o*-nitrobenzoic acid
15.56	8.87	51.61	5.02	*o*-nitrobenzoic acid
16.69	4.82	42.12	3.88	*o*-nitrobenzoic acid
17.93	0	65.41	0	*o*-nitrobenzoic acid

[a] w_1, mass fraction of *o*-nitrobenzoic acid; w_2, mass fraction of *m*-nitrobenzoic acid.

condenser was connected to the flask to prevent the ethanol from evaporating. The ethanol was stirred using a Teflon-coated magnetic stirring bar. Thirty minutes prior to sampling, stirring was ceased to allow any solid phase to settle. Attainment of equilibrium was verified both by repetitive measurements after a minimum of 2 additional days and by approaching equilibrium from supersaturation by preequilibrating the solutions at a higher temperature. 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, and then both were analyzed. This procedure was repeated by varying the ratio of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid to obtain different compositions of the solid and liquid phases.

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 × 4.6 mm) chromatographic column.[15] The eluent consisted of three components that were water, propanol, and acetic acid. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis. The average value of three measurements was considered as the final value of the analysis (precision: ± 0.1 %).

Results and Discussion

The measured solubilities of the equilibrium liquid phase for the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at (273.15, 283.15, and 293.15) K are shown in Tables 1, 2, and 3, respectively. The ternary phase diagrams are plotted in Figures 1, 2, and 3.

In Figures 1, 2, and 3, along the solubility curve S_1C_1, S_2C_2, or S_3C_3, linking the composition points of the 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 *o*-nitrobenzoic acid on a wet basis. Along the solubility curve $C_1S'_1$, $C_2S'_2$, or $C_3S'_3$, linking the composition points of the liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase composition for *m*-nitrobenzoic acid. The results indicated that two solids were present in the system: one is *o*-nitrobenzoic acid, and the other is *m*-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.

Table 2. Mass Fraction Solubilities of the Ternary System *o*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 283.15 K[a]

liquid phase		moist solid phase		
100 w_1	100 w_2	100 w_1	100 w_2	equilibrium solid phase
0	31.66	0	74.99	*m*-nitrobenzoic acid
2.98	29.94	1.02	71.17	*m*-nitrobenzoic acid
7.03	29.64	5.32	45.51	*m*-nitrobenzoic acid
10.47	27.34	3.14	76.55	*m*-nitrobenzoic acid
14.54	25.89	6.39	67.42	*m*-nitrobenzoic acid
19.69	24.74	11.09	55.77	*m*-nitrobenzoic acid
22.71	24.46	16.9	45.79	*m*-nitrobenzoic acid
23.34	24.17	46.5	30.12	*m*-nitrobenzoic acid + *o*-nitrobenzoic acid
23.56	23.59	46.1	17.24	*o*-nitrobenzoic acid
24.21	20.71	37.08	16.96	*o*-nitrobenzoic acid
25.5	14.94	53.61	9.46	*o*-nitrobenzoic acid
28.29	8.02	66.49	3.69	*o*-nitrobenzoic acid
29.14	4.28	49.54	3.12	*o*-nitrobenzoic acid
31.94	0	61.35	0	*o*-nitrobenzoic acid

[a] w_1, mass fraction of *o*-nitrobenzoic acid; w_2, mass fraction of *m*-nitrobenzoic acid.

Table 3. Mass Fraction Solubilities of the Ternary System *o*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 293.15 K[a]

liquid phase		moist solid phase		
100 w_1	100 w_2	100 w_1	100 w_2	equilibrium solid phase
0	38.56	0	75.24	*m*-nitrobenzoic acid
3.91	36.08	2.76	54.46	*m*-nitrobenzoic acid
5.87	34.65	3.06	61.35	*m*-nitrobenzoic acid
9.16	33.22	6.8	48.13	*m*-nitrobenzoic acid
12.43	31.93	6.05	69.73	*m*-nitrobenzoic acid
15.58	30.34	9.64	58.45	*m*-nitrobenzoic acid
20.25	28.76	14.26	50.13	*m*-nitrobenzoic acid
24.32	27.64	18.57	44.97	*m*-nitrobenzoic acid
28.79	26.48	42.71	42.67	*m*-nitrobenzoic acid + *o*-nitrobenzoic acid
29.28	23.83	47.03	17.96	*o*-nitrobenzoic acid
30.61	20.33	40.12	17.63	*o*-nitrobenzoic acid
31.29	16.54	49.88	12.74	*o*-nitrobenzoic acid
32.76	11.57	60.31	6.49	*o*-nitrobenzoic acid
34.53	7.49	62.49	4.31	*o*-nitrobenzoic acid
37.78	0	64.08	0	*o*-nitrobenzoic acid

[a] w_1, mass fraction of *o*-nitrobenzoic acid; w_2, mass fraction of *m*-nitrobenzoic acid.

In the phase diagrams as shown in Figures 1, 2, and 3, there are three crystallization fields: crystalline region of solid *o*-nitrobenzoic acid (OS_1C_1 in Figure 1, OS_2C_2 in Figure 2, and OS_3C_3 in Figure 3), crystalline region of solid *m*-nitrobenzoic acid (MS'_1C_1 in Figure 1, MS'_2C_2 in Figure 2 and MS'_3C_3 in Figure 3), crystalline region of mixture of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid (MC_1O in Figure 1, MC_2O in Figure 2, and MC_3O in Figure 3). The phase diagram has two invariant curves. C_1S_1, C_2S_2, and C_3S_3 are saturation curves corresponding to the solid-phase *o*-nitrobenzoic acid at (273.15, 283.15, and 293.15) K, respectively. $C_1S'_1$, $C_2S'_2$, and $C_3S'_3$ are saturation curves corresponding to the solid-phase *m*-nitrobenzoic acid. C_1, C_2, and C_3 are invariant points, which represent the equilibrium of the two solid phases *o*-nitrobenzoic acid and *m*-nitrobenzoic acid.

Figures 1, 2, and 3 further illustrate the temperature dependence of the phase diagram for the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system. When the temperature increases from (273.15 to 293.15) K, the solubility of *o*-

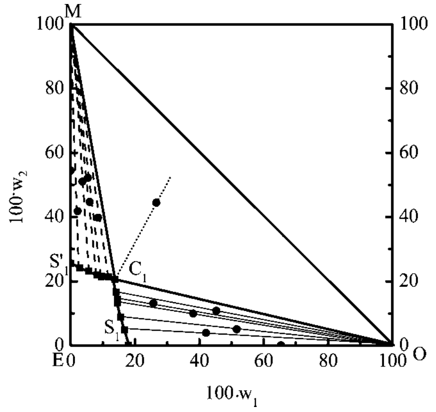

Figure 1. Equilibrium phase diagram of the ternary *o*-nitrobenzoic acid (1) + *m*-nitrobenzoic acid (2) + ethanol (3) system at 273.15 K: O, *o*-nitrobenzoic acid; M, *m*-nitrobenzoic acid in ethanol; E, ethanol; S_1,S_1', solubility of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol at 273.15 K, respectively; C_1, cosaturated point; $ES_1C_1S_1'$, unsaturated region; $MS_1'C_1$, crystalline region of solid *m*-nitrobenzoic acid; OS_1C_1, crystalline region of solid *o*-nitrobenzoic acid; MC_1O, crystalline region of solids *o*-nitrobenzoic acid and *m*-nitrobenzoic acid; dashed line (-----), the tie-lines linking the composition points of liquid phase and moist solid phase inside the crystalline region of *m*-nitrobenzoic acid; short dot (. . . . . .), the tie-lines linking the composition points of the liquid phase and moist solid phase inside the crystalline region of *m*-nitrobenzoic acid and *o*-nitrobenzoic acid; solid line (—), the tie-lines linking the composition points of the liquid phase and moist solid phase inside the crystalline region of *o*-nitrobenzoic acid; *w*, mass fraction.

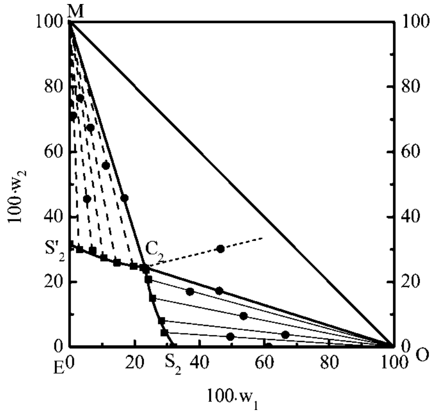

Figure 2. Equilibrium phase diagram of the ternary *o*-nitrobenzoic acid (1) + *m*-nitrobenzoic acid (2) + ethanol (3) system at 283.15 K: O, *o*-nitrobenzoic acid; M, *m*-nitrobenzoic acid in ethanol; E, ethanol; S_2,S_2', solubility of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol at 283.15 K, respectively; C_2, cosaturated point; $ES_2C_2S_2'$, unsaturated region; $MS_2'C_2$, crystalline region of solid *m*-nitrobenzoic acid; OS_2C_2, crystalline region of solid *o*-nitrobenzoic acid; MC_2O, crystalline region of solids *o*-nitrobenzoic acid and *m*-nitrobenzoic acid; dashed line (-----), short dot (•••••••), solid line (—), and *w* have the same meaning as described in Figure 1.

nitrobenzoic acid and *m*-nitrobenzoic acid increases, and the cosaturated point moves upward. The phase diagrams of the ternary system are similar at different temperatures. The crystalline regions of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid increase as the temperature decreases. No adduct is formed in the system at the studied temperature.

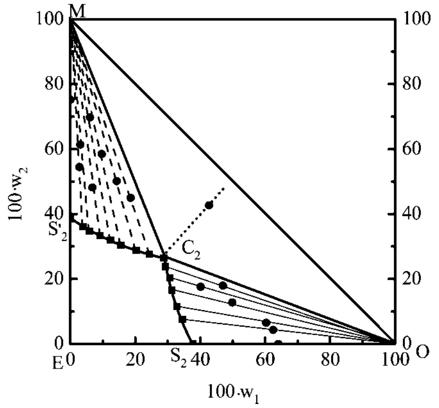

Figure 3. Equilibrium phase diagram of the ternary *o*-nitrobenzoic acid (1) + *m*-nitrobenzoic acid (2) + ethanol (3) system at 293.15 K: O, *o*-nitrobenzoic acid; M, *m*-nitrobenzoic acid in ethanol; E, ethanol; S_3,S_3', solubility of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol at 293.15 K, respectively; C_3, cosaturated point; $ES_3C_3S_3'$, unsaturated region; $MS_3'C_3$, crystalline region of solid *m*-nitrobenzoic acid; OS_3C_3, crystalline region of solid *o*-nitrobenzoic acid; MC_3O, crystalline region of solids *o*-nitrobenzoic acid and *m*-nitrobenzoic acid; dashed line (-----), short dot (•••••••), solid line (—), and *w* have the same meaning as described in Figure 1.

Table 4. Mass Fraction Solubilities of *o*-Nitrobenzoic Acid and *m*-Nitrobenzoic Acid in Ethanol

		solubility/wt %	
name	temp/K	ref 10 values	this work values
o-nitrobenzoic acid	273.15	23.3	17.69
	283.15		31.94
	293.15		37.78
	295.15	42.7	
m-nitrobenzoic acid	273.15	33.6	25.59
	283.15		31.66
	292.15		42.3
	293.15		38.56
	294.65	43.9	

Table 4 gives the solubilities of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol reported in the literature[10,11] and measured in this work. It can be seen from Table 4 that the equilibrium solubility of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol is smaller than those reported in the literature. In order to illustrate the difference of solubility data, we determine again the solubility of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol by a synthetic method described in ref 11. The solubilities of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol at 273.15 K are 23.41 % (mass fraction) and 33.69 % (mass fraction), respectively. The experimental solubility shows good agreement with the results reported in ref 12. However, when the saturated solutions are placed in a thermostat at 273.15 K, 6 h later, crystals appear in the system. The *o*-nitrobenzoic acid content in the liquid phase is 17.95 % (mass fraction) and *m*-nitrobenzoic acid, 25.58 % (mass fraction), respectively, which agree well with those of the present work. It can be seen that a supersaturated solution is formed during experiments by the synthetic method.

Conclusion

The solubilities of the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at (273.15, 283.15, and 293.15) K were determined experimentally. The ternary phase diagrams were constructed. The solid phases were confirmed by Schreinemaker's wet residue method. The phase diagrams of the ternary system are similar at different temperatures. The solubility of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid increases with increasing temperature. The solubility data and the ternary phase diagram can provide the fundamental basis for separation of the mixture of isomeric nitrobenzoic acids.

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