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

Gan-Bing Yao*

College of Chemistry and Chemical Engineering, YangZhou University, Yangzhou, Jiangsu, 225002, P. R. China

Solubility data for the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system were measured at 273.1 K, 283.1 K, and 313.1 K, respectively. Three isothermal phase diagrams of the system were constructed on the basis of the measured solubilitities. Two solid phases, *m*-nitrobenzoic acid and *p*-nitrobenzoic acid, were formed and confirmed by Schreinemaker's wet residue method. The crystallization regions of *m*-nitrobenzoic acid and *p*-nitrobenzoic acid increase as the temperature decreases. At different temperature, the crystallization region of *p*-nitrobenzoic acid is larger than that of *m*-nitrobenzoic acid.

Introduction

m-Nitrobenzoic acid is an important intermediate which is widely used in the chemical field of agricultural chemicals, pharmaceuticals, dyes, and particularly for synthesis of procaine hydrochloride, procaine ammonium salts, and amino-nitrobenzoic acid.[1−3] Many processes for preparation of *m*-nitrobenzoic acid have been reported in the literature.[3−11] Generally, it can be prepared by the nitration of benzoic acid by means of nitric acid, a mixture of nitric and sulfuric acids, or mixtures of nitrates and sulfuric acid. All these methods lead to the production of a mixture containing principally the *m*-nitrobenzoic acid with a smaller proportion of the ortho and percent of the para isomer as a byproduct to the formation of *m*-nitrobenzoic acid. Pure *m*-nitrobenzoic acid can be separated from the mixture of isomeric nitrobenzoic acids by repeated crystallization from solvents,[3,12] 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.

It is well-known that solid−liquid phase equilibrium data are important in crystallization processes. Obviously, during the crystallization process of *m*-nitrobenzoic acid from its isomeric mixtures, the mutual solubility of isomeric mixtures in one solvent is needed. The separation process by crystallization in ethanol is based on the phase diagram of the quaternary system of *m*-nitrobenzoic acid + *o*-nitrobenzoic acid + *p*-nitrobenzoic acid + ethanol. It is very important to study the system and construct the phase diagram of the *m*-nitrobenzoic acid + *o*-nitrobenzoic acid + *p*-nitrobenzoic acid + ethanol system. The solubility of *m*-nitrobenzoic acid, *o*-nitrobenzoic acid, and *p*-nitrobenzoic acid in different solvents was investigated in the literature.[13,14] Recently, the solubility data of systems *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol,[15] *o*-nitrobenzoic acid + *p*-nitrobenzoic acid + acetone,[16] and *m*-nitrobenzoic acid + *o*-nitrobenzoic acid + acetone[17] were reported. The objective of this research is to generate and analyze the phase diagrams of the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at 273.1 K, 283.1 K, and 313.1 K by Schreinemaker's wet residue method[18] and demonstrate the temperature dependence of the ternary phase diagram.

In a ternary system involving at least one solid and one liquid phase, the composition of the solid phase is often determined indirectly, to avoid separating the crystals and completely removing the adhering mother liquor from them. Extrapolation is made by Schreinemakers' method of wet residues.[18] Equilibrium solid adhering some equilibrium liquid is called a "wet" residue. The method is based on the following: The tie line joining the composition of the pure solid and of the saturated liquid in equilibrium with it is the locus of all intermediate compositions corresponding to varying amounts of solid and liquid phases. This includes the composition of the liquid phase and of crystals wet with mother liquor. A straight line drawn through a pair of points representing such compositions on a phase diagram is a segment of the tie line and therefore passes through the composition of the pure solid. The lines drawn through several such pairs of compositions, each corresponding to a different original mixture, have a common intersection at the composition of the pure solid phase. The composition of the common intersection is in agreement with direct analysis obtained by crystallization. In this work, Schreinemaker's wet residue method was employed to study the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system.

Materials Section

Materials. *m*-Nitrobenzoic acid was purchased from Changzhou Hubin Medicine Raw Materials Co. Ltd., China, with a mass fraction of 0.991. The crude material was recrystallized from $CHCl_3$, and again from water, giving a product which was pure white in color. The contents of the crystalline *m*-nitrobenzoic acid were determined in our laboratory by HPLC, which has a mass fraction purity of 0.998.

Analytically pure grade *p*-nitrobenzoic acid was provided by the Shanghai Shiyi Chemicals Reagent Co. Ltd., China, with a mass fraction of 0.992. It was dissolved in a dilute solution of NaOH and precipitated by the addition of HCl. The material thus obtained was twice crystallized from water, giving fluffy crystals light yellow in color. The mass fraction purity of the crystalline *p*-nitrobenzoic acid is 0.999.

---

* Corresponding author. E-mail: gbyao@yzu.edu.cn. Tel.: + (86) 514 82089702. Fax: + (86) 514 87975244.

10.1021/je900364y CCC: $40.75

The analytically grade ethanol, with mass fraction purity of ethanol 0.999, was produced by Nanjing Chemical Reagent Co. Ltd., China. It was used in the experiment without further purification. The water used to prepare solutions was deionized (conductivity < 5 $\mu S \cdot cm^{-1}$).

Procedure. The solubility was determined employing the method of isothermal solution saturation.[19] The solid phases were determined by Schreinemaker's wet residue method[18] and rechecked by an X-ray diffraction method. The experimental saturated solutions were prepared by adding an excess solute, *p*-nitrobenzoic acid, and/or *m*-nitrobenzoic acid to glass vessels containing the ethanol. The components were taken in such proportions that the composition of the resulting saturated solution fell in the desired portion of the solubility curve. Solubilities were determined by equilibrating the solute with ethanol in a water-jacketed vessel with motor stirring in a constant-temperature water bath for at least 3 days. The temperature is controlled by a constant-temperature water bath (Neslab, model RTE-101) recirculated through a copper coil in the water bath. The actual temperature in the water bath was monitored by a resistance thermometer (type, TES1300; accuracy, ± 0.1 K). A condenser is connected to the flask to prevent the solvent from evaporating. Attainment of equilibrium was verified by both repetitive measurement of *p*-nitrobenzoic acid and *m*-nitrobenzoic acid after a minimum of three additional days and approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. When the composition of the liquid phase became constant, this was taken to indicate that equilibration had been attained. Generally, it took about 23.5 h to reach equilibrium. After equilibrium was achieved, the liquid phase and the solid phases with a little of the saturated liquid were taken out and then quantitatively analyzed. The equilibrium solid phases were dried in a desiccator at room temperature pestled into powder and then analyzed by an X-ray diffraction analyzer. This procedure was repeated by varying the ratio of *p*-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.[20,21] The eluent consisted of 20 (mL)/80 (mL)/0.4 (mL) 2-propanol/water/acetic acid. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis (precision: ± 0.1 %).

Table 1. Mass Fraction Solubilities of the Ternary System *p*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 273.1 K[a]

liquid phase			wet residue			
w_1	w_2	w_3	w_1	w_2	w_3	equilibrium solid phase
0.0393	0	0.9607	0.8537	0	0.1463	*p*-$C_7H_5NO_4$
0.0367	0.0418	0.9215	0.8188	0.009	0.1722	*p*-$C_7H_5NO_4$
0.0369	0.0677	0.8954	0.7745	0.0164	0.2091	*p*-$C_7H_5NO_4$
0.0351	0.1056	0.8593	0.7909	0.0236	0.1855	*p*-$C_7H_5NO_4$
0.0354	0.1392	0.8254	0.7559	0.0368	0.2073	*p*-$C_7H_5NO_4$
0.0346	0.1710	0.7944	0.8038	0.0347	0.1615	*p* $C_7H_5NO_4$
0.0341	0.2072	0.7587	0.7892	0.0459	0.1649	*p*-$C_7H_5NO_4$
0.0336	0.2362	0.7302	0.7706	0.0550	0.1744	*p*-$C_7H_5NO_4$
0.0322	0.2673	0.7005	0.8058	0.0514	0.1428	*p*-$C_7H_5NO_4$
0.0307	0.2912	0.6781	0.8242	0.0513	0.1245	*p*-$C_7H_5NO_4$
0.0304	0.3024	0.6672	0.5051	0.3573	0.1376	*p*-$C_7H_5NO_4$+ *m*-$C_7H_5NO_4$
0.0255	0.3101	0.6644	0.0063	0.8546	0.1391	*m*-$C_7H_5NO_4$
0.0216	0.3127	0.6657	0.0040	0.8179	0.1781	*m*-$C_7H_5NO_4$
0.0147	0.3145	0.6708	0.0013	0.7831	0.2156	*m*-$C_7H_5NO_4$
0	0.3365	0.6635	0	0.8038	0.1962	*m*-$C_7H_5NO_4$

[a] w_1: mass fraction of *p*-nitrobenzoic acid; w_2: mass fraction of *m*-nitrobenzoic acid; w_3: mass fraction of ethanol.

Table 2. Mass Fraction Solubilities of the Ternary System *p*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 283.1 K[a]

liquid phase			wet residue			
w_1	w_2	w_3	w_1	w_2	w_3	equilibrium solid phase
0.03310	0	0.9669	0.8317	0	0.1683	*p*-$C_7H_5NO_4$
0.0296	0.0225	0.9479	0.7355	0.0068	0.2577	*p*-$C_7H_5NO_4$
0.0284	0.0367	0.9349	0.6672	0.0141	0.3187	*p*-$C_7H_5NO_4$
0.0238	0.0490	0.9272	0.8146	0.0122	0.1732	*p*-$C_7H_5NO_4$
0.0269	0.0649	0.9082	0.6913	0.0230	0.2857	*p*-$C_7H_5NO_4$
0.0227	0.1019	0.8754	0.6342	0.0418	0.3240	*p*-$C_7H_5NO_4$
0.0208	0.1124	0.8668	0.7429	0.0305	0.2266	*p*-$C_7H_5NO_4$
0.0173	0.1289	0.8538	0.7004	0.0416	0.2580	*p*-$C_7H_5NO_4$
0.0225	0.1678	0.8097	0.7318	0.0471	0.2211	*p*-$C_7H_5NO_4$
0.0220	0.2214	0.7566	0.7611	0.0544	0.1845	*p*-$C_7H_5NO_4$
0.0214	0.2371	0.7415	0.6396	0.0876	0.2728	*p*-$C_7H_5NO_4$
0.0202	0.2843	0.6955	0.7226	0.0803	0.1971	*p*-$C_7H_5NO_4$
0.0187	0.2991	0.6822	0.6303	0.1118	0.2579	*p*-$C_7H_5NO_4$
0.0197	0.3026	0.6777	0.4589	0.3364	0.2047	*p*-$C_7H_5NO_4$ + *m*-$C_7H_5NO_4$
0.0185	0.3052	0.6763	0.0072	0.7674	0.2254	*m*-$C_7H_5NO_4$
0.0116	0.3096	0.6788	0.0055	0.7787	0.2158	*m*-$C_7H_5NO_4$
0.0054	0.3158	0.6788	0.0019	0.8211	0.177	*m*-$C_7H_5NO_4$
0	0.3166	0.6834	0	0.8321	0.1679	*m*-$C_7H_5NO_4$

[a] w_1: mass fraction of *p*-nitrobenzoic acid; w_2: mass fraction of *m*-nitrobenzoic acid; w_3: mass fraction of ethanol.

Results and Discussion

The equilibrium solubility data for the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at 273.1 K, 283.1 K, and 313.1 K are shown in Tables 1, 2, and 3, respectively. The corresponding ternary phase diagrams are plotted in Figures 1, 2, and 3.

In Figures 1, 2, and 3, points P, M, and E represent the solids *p*-nitrobenzoic acid, *m*-nitrobenzoic acid, and ethanol, respectively. Points S_1, S_2, and S_3 show the solubilities of *m*-nitrobenzoic acid at 273.1 K, 283.1 K, and 313.1 K, respectively, and points and S_1', S_2', and S_3' show the solubilities of *p*-nitrobenzoic acid at 273.1 K, 283.1 K, and 313.1 K. Along the solubility curve S_1C_1, S_2C_2, or S_3C_3, linking the component points of liquid phase and wet residue and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for *p*-nitrobenzoic acid on a wet basis. Along the solubility curve $S_1'C_1$, $S_2'C_2$, or $S_3'C_3$, linking the component 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 *m*-nitrobenzoic acid.

Curves S_1C_1, S_2C_2, and S_3C_3 indicate the compositions of saturated ternary solutions that are in equilibrium with the solid *m*-nitrobenzoic acid at 273.1 K, 283.1 K, and 313.1 K, respectively. Curves $S_1'C_1$, $S_2'C_2$, and $S_3'C_3$ indicate the compositions of saturated ternary solutions that are in equilibrium with the solid *p*-nitrobenzoic acid. C_1, C_2, and C_3 are invariant points, which indicate a solution saturated with the coexisting solids *m*-nitrobenzoic acid and *p*-nitrobenzoic acid whose compositions are shown in Tables 1, 2, and 3. As seen in Figures 1, 2, and 3, it is clear that the ternary system does not form a solid solution. In the phase diagrams as shown in Figures 1, 2, and 3, there are three crystallization fields: *m*-nitrobenzoic acid (MC_1S_1 in Figure 1, MC_2S_2 in Figure 2, and MC_3S_3), corresponding to the coexistence of solid *m*-nitrobenzoic acid and the saturated solution; *p*-nitrobenzoic acid (PC_1S_1' in Figure 1, PC_2S_2' in Figure 2, and PC_3S_3' in Figure 3), region corresponding to the coexistence of solid *p*-nitrobenzoic acid and the saturated solution; mixture of *m*-nitrobenzoic acid and *p*-nitrobenzoic acid

Table 3. Mass Fraction Solubilities of the Ternary System *p*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 313.1 K[a]

liquid phase			wet residue			
w_1	w_2	w_3	w_1	w_2	w_3	equilibrium solid phase
0.0504	0	0.9496	0.8232	0	0.1768	*p*-$C_7H_5NO_4$
0.0489	0.0505	0.9006	0.7595	0.0121	0.2284	*p*-$C_7H_5NO_4$
0.0484	0.0779	0.8737	0.7023	0.0268	0.2709	*p*-$C_7H_5NO_4$
0.0465	0.1123	0.8412	0.7518	0.0324	0.2158	*p*-$C_7H_5NO_4$
0.0459	0.1434	0.8107	0.7319	0.0415	0.2266	*p*-$C_7H_5NO_4$
0.0462	0.1742	0.7796	0.8102	0.0361	0.1537	*p*-$C_7H_5NO_4$
0.0436	0.2018	0.7546	0.741	0.0564	0.2026	*p*-$C_7H_5NO_4$
0.0428	0.2449	0.7123	0.7908	0.0527	0.1565	*p*-$C_7H_5NO_4$
0.0421	0.2864	0.6715	0.7465	0.0768	0.1767	*p*-$C_7H_5NO_4$
0.0403	0.3273	0.6324	0.7576	0.0841	0.1583	*p*-$C_7H_5NO_4$
0.0394	0.3725	0.5881	0.7704	0.0878	0.1418	*p*-$C_7H_5NO_4$
0.0386	0.4101	0.5513	0.7296	0.1154	0.1550	*p*-$C_7H_5NO_4$
0.0355	0.4428	0.5217	0.3429	0.5485	0.1086	*p*-$C_7H_5NO_4$ + *m*-$C_7H_5NO_4$
0.0341	0.4453	0.5206	0.0110	0.8117	0.1773	*m*-$C_7H_5NO_4$
0.0271	0.4544	0.5185	0.0093	0.7934	0.1973	*m*-$C_7H_5NO_4$
0.0184	0.4625	0.5191	0.0037	0.834	0.1623	*m*-$C_7H_5NO_4$
0.0082	0.4753	0.5165	0.0019	0.8283	0.1698	*m*-$C_7H_5NO_4$
0	0.4874	0.5126	0	0.8235	0.1765	*m*-$C_7H_5NO_4$

[a] w_1: mass fraction of *p*-nitrobenzoic acid; w_2: mass fraction of *m*-nitrobenzoic acid; w_3: mass fraction of ethanol.

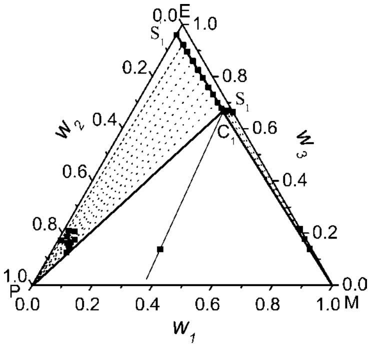

Figure 1. Phase diagram of the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at 273.1 K: P, *p*-nitrobenzoic acid; M, *m*-nitrobenzoic acid; E, ethanol; S'_1, S_1, solubility of *p*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol, respectively; C_1, cosaturated point indicating a solution saturated with *p*-nitrobenzoic acid and *m*-nitrobenzoic acid; $ES_1C_1S'_1$, unsaturated region; PS'_1C_1, region corresponding to the coexistence of solid *p*-nitrobenzoic acid and the saturated solution; MS_1C_1, region corresponding to the coexistence of solid *m*-nitrobenzoic acid and the saturated solution; PMC_1, region corresponding to the coexistence of solids *p*-nitrobenzoic acid and *m*-nitrobenzoic acid and the saturated solution with composition C_1; *w*, mass fraction.

(PC_1M in Figure 1, PC_2M in Figure 2, and PC_3M in Figure 3), region corresponding to the coexistence of solids *p*-nitrobenzoic acid and *m*-nitrobenzoic acid and the saturated solution. The phase diagram has two invariant curves at each temperature.

Figures 1, 2, and 3 further illustrate the temperature dependence of the phase diagram for the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system. When the temperature increases from (273.1 to 313.1) K, the solubility of *m*-nitrobenzoic acid and *p*-nitrobenzoic acid increases, and the cosaturated point moves upward. The crystalline regions of *m*-nitrobenzoic acid and *p*-nitrobenzoic acid increase as the temperature decreases. At each temperature, the crystallization field of *p*-nitrobenzoic acid is larger than that of *m*-nitrobenzoic acid.

The solubility and phase diagram of the systems *o*-nitrobenzoic acid + *p*-nitrobenzoic acid + acetone, *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol, and *m*-nitrobenzoic acid + *o*-nitrobenzoic acid + acetone have been previously studied.[15−17] The phase diagram of the system *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol was similar to the systems *o*-nitrobenzoic acid + *p*-nitrobenzoic acid + acetone at each temperature. The crystallization field of *p*-nitrobenzoic acid is larger than that of *m*-nitrobenzoic acid or *o*-nitrobenzoic acid at the same temperature. Therefore, *p*-nitrobenzoic acid is very easily separated out from these systems.

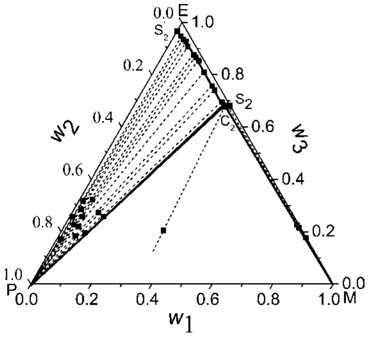

Figure 2. Phase diagram of the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at 283.1 K: P, *p*-nitrobenzoic acid; M, *m*-nitrobenzoic acid; E, ethanol; S'_2, S_2, solubility of *p*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol, respectively; C_2, cosaturated point indicating a solution saturated with *p*-nitrobenzoic acid and *m*-nitrobenzoic acid; $ES_2C_2S'_2$, unsaturated region; PS'_2C_2, region corresponding to the coexistence of solid *p*-nitrobenzoic acid and the saturated solution; MS_2C_2, region corresponding to the coexistence of solid *m*-nitrobenzoic acid and the saturated solution; PMC_2, region corresponding to the coexistence of solids *p*-nitrobenzoic acid and *m*-nitrobenzoic acid and the saturated solution with composition C_2; *w*, mass fraction.

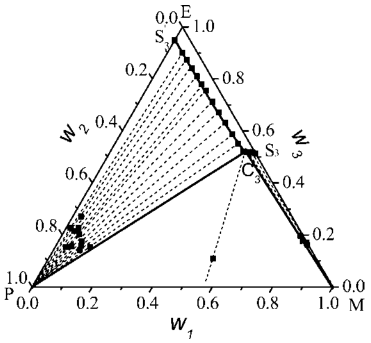

Figure 3. Phase diagram of the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at 313.1 K: P, *p*-nitrobenzoic acid in ethanol; M, *m*-nitrobenzoic acid in ethanol; E, ethanol; S'_3, S_3, solubility of *p*-nitrobenzoic acid and *m*-nitrobenzoic acid in ethanol, respectively; C_3, cosaturated point indicating a solution saturated with *p*-nitrobenzoic acid and *m*-nitrobenzoic acid; $ES_3C_3S'_3$, unsaturated region; PS'_3C_3, region corresponding to the coexistence of solid *p*-nitrobenzoic acid and the saturated solution; MS_3C_3, region corresponding to the coexistence of solid *m*-nitrobenzoic acid and the saturated solution; PMC_3, region corresponding to the coexistence of solids *p*-nitrobenzoic acid and *m*-nitrobenzoic acid and the saturated solution with composition C_3; *w*, mass fraction.

Conclusion

The solubilities of the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system at 273.1 K, 283.1 K, and 313.1 K were determined experimentally, and the respective ternary phase diagrams were constructed. At the studied temperatures, two solid phases were formed in the ternary *p*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system corresponding to *m*-nitrobenzoic acid and *p*-nitrobenzoic acid. The phase diagrams had three crystallization fields (*m*-nitrobenzoic acid, *p*-nitrobenzoic acid, and a mixture of *m*-nitrobenzoic acid and *p*-nitrobenzoic acid), two invariant curves, and one invariant point at each temperature. The solubility of *m*-nitrobenzoic acid and *p*-nitrobenzoic acid increases with increasing temperature. The crystalline region of *p*-nitrobenzoic acid was larger than that of *m*-nitrobenzoic acid at each temperature. The solubility data and the phase diagram of the ternary system can provide the basis and serve as a guide for the separation process for the mixture of isomeric nitrobenzoic acids.

Literature Cited

(1) Nakaoka, K.; Sonoyama, H.; Suematsu, M. Preparation of m-nitrobenzoic acid. JP Patent 59,051,242, March 24, 1984.
(2) Torigata, H.; Nakaoka, K. Preparation of m-nitrobenzoic acid. JP Patent 57,181,040, November 8, 1982.
(3) Torigata, H.; Nakaoka, K. Preparation of m-nitrobenzoic acid. JP Patent 58,021,650, January 8, 1983.
(4) Manfred, D. R. Process for the production of m-ntrobenzoic acid. DE Patent 3,113,821, January 7, 1982.
(5) Dolmatov, V.; Zubarev, P.; Zyuzko, V.; Lebedev, B.; Pyaterikov, V.; Shutov, D. Preparation of m-nitrobenzoic acid via oxidation of m-nitrotoluene with diluted nitric-acid under pressure. *Khim.-Farm. Zh.* **1990**, *24*, 67–69.
(6) Evald, N. B. Preparing meta-nitrobenzoic acid. DE Patent 2,540,899, April 15, 1976.
(7) Natanael, B. N. E. Preparing meta-nitrobenzoic acid. GB Patent 1,519,602, August 2, 1978.
(8) Lin, C. Y.; Stuber, F. A.; Uorich, H. Process for nitrating aromatic hydrocarbons. U.S. Patent 4,123,466, October 31, 1978.
(9) Harm, B.; Doesburg, J. T. S. D. V.; Deumens, J. J. M.; Delahaye, H. J. Process for nitrating aromatic compounds in liquid sulfur dioxide. U.S. Patent 3,415,876, December 10, 1968.
(10) Cooper, K. E.; Ingold, C. K. CXXI.-The nature of the alternating effect in carbon chains. Part XVI. The directive action of some groups of the form COR in aromatic substitution. *J. Chem. Soc.* **1927**, 836–841.
(11) Rosner, M. D. Process for the production of m-nitrobenzoic acid. GB Patent 2,073,753, October 21, 1981.
(12) John, H. B.; Kendall, P. N. Process for recovering 3-nitrobenzoic acid. U.S. Patent 4,288,615, September 08, 1981.
(13) Stephen H.; Stephen T. *Solubility of Inorganic and Organic Compounds*; Pergamon: Oxford, 1979.
(14) Collett, A. R.; Lazell, C. L. Solubility relations of isomeric nitro benzoic acids. *J. Phys. Chem.* **1930**, *34*, 1338–1447.
(15) Zhao, H. K.; Zhang, Q. H.; Li, R. R. Solid-liquid phase equilibrium and phase diagram for ternary o-nitrobenzoic acid + m-nitrobenzoic acid + ethanol system. *J. Chem. Eng. Data* **2008**, *53*, 1367–1370.
(16) Zhao, H. K.; Zhang, Q. H.; Li, R. R.; Meng, X. C. Solid-liquid phase equilibrium and phase diagram for ternary o-nitrobenzoic acid - p-nitrobenzoic acid - acetone system at 283.1 and 313.1 K. *Fluid Phase Equilib.* **2008**, *266*, 101–104.
(17) Zhao, H. K.; Zhang, Q. H.; Li, R. R.; Zhang, D. S.; Qu, Q. S. Equilibrium phase diagram of the tenary 2-nitrobenzoic acid - 3-nitrobenzoic acid - acetone system at 283.1 and 313.1 K. *J. Phase Equilib. Diff.* **2008**, *29*, 333–336.
(18) Schott, H. A mathematical extrapolation for the method of wet residues. *J. Chem. Eng. Data* **1961**, *6*, 324.
(19) Shu, Y. G.; Lu, B. L.; Wang, X. R. *Phase Diagram Analyses in Inorganic Chemical Production: Basic Theory*; Chemical Industrial press: Beijing, 1985 (in Chinese).
(20) Chen, P. R.; Zhang, M. J. Separation of positional isomers of nitrobenzoic acid by Reversed-phase liquid chromatography with 2-propanol-water-acetic acid as eluent. *J. Chromatogr. A* **1997**, *773*, 365–367.
(21) Su, T. T.; Cheng, Y. C. Analysis of nitrobenzoic acid isomers by high-performance liquid chromatography. *J. Chromatogr. A* **1982**, *241*, 416–418.

Received for review April 20, 2009. Accepted June 27, 2009.

JE900364Y