Solid−Liquid Phase Diagram of the Ternary System of *p*-Nitroaniline + *o*-Nitroaniline + Ethanol

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The mutual solubility for the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system was measured at (273.15 to 323.15) K. Three isothermal phase diagrams of the system were constructed on the basis of the measured solubilities. The phase diagrams of the ternary system were similar at all temperatures investigated. Two solid phases were formed and confirmed by the Schreinemaker's wet residue method; one was *p*-nitroaniline, and the other was *o*-nitroaniline. The crystallization regions of *p*-nitroaniline and *o*-nitroaniline increase as the temperature decreases. At the same temperature, the crystallization region of *p*-nitroaniline is larger than that of *o*-nitroaniline.

Introduction

p-Nitroaniline is utilized as a manufacturing intermediate for dyes, agricultural chemicals, pharmaceuticals, and so forth, and *p*-phenylenediamine obtained by reduction of *p*-nitroaniline is useful as a manufacturing intermediate for polyamides, rubber compounding agents, synthetic resin additives, dyes, pharmaceuticals, and agricultural chemicals.[1–4] Hence, an increased demand for *p*-nitroaniline as an industrial material is expected. Several methods have been proposed for preparing *p*-nitroaniline.[5–10] The common synthesis of *p*-nitroaniline takes several steps: reduction of nitrobenzene to aniline, acetylation of aniline to form acetanilide, nitration of acetanilide to form *p*- and *o*-nitroacetanilide, and hydrolysis of the nitroacetanilides to liberate *p*- and *o*-nitroanilines. In the process for preparing *p*-nitroaniline that is thus far customary, the crude product contains both *o*- and *p*-nitroaniline, and the major isomer is *p*-nitroaniline (the amount of dinitroaniline present is negligible). A separation must be performed to remove *o*-nitroaniline, which is also formed in a small amount during the reaction. Generally, separation of the *p*-nitroaniline is accomplished by crystallization in ethanol.[10–12] The major product, *p*-nitroaniline, is almost insoluble in ethanol. In contrast, *o*-nitroaniline is soluble in ethanol. Thus, the crude mixture of solid *p*- and *o*-nitroaniline is taken up in ethanol, and the *p*-isomer is insoluble and can be filtered out while the *o*-isomer is soluble and is present in the filtrate. Since *p*-nitroaniline is soluble to some extent in ethanol, the filtrate still contains a mixture of *p*- and *o*-nitroaniline.

It is well-known that solid−liquid phase equilibrium data is very important in crystallization processes. It is recognized that the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system is relevant to the separation process by crystallization in ethanol. It is very important to study the system and construct the phase diagram of the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system. Some studies have been done on the solubilities for the isomers of nitroaniline. Collett and John,[13] Sysoeva et al.,[14] and Stephen and Stephen[15] reported the solubility of *p*-nitroaniline or *o*-nitroaniline in different solvents. Lepree et al.[16] and Huyskens et al.[17] investigated the solubility of *p*-nitroaniline in binary solvent mixture. Besides, the solid−liquid phase equilibrium of *o*-, *m*-, and *p*-nitroaniline systems was studied by differential scanning calorimeter.[18] To the best of our present knowledge, no further investigations on the solubility or phase diagram for the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system were made so far. The objectives of this research are to generate and analyze the phase diagram of the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system at (273.15, 298.15, and 323.15) K and to compare the ternary phase diagrams at the three different temperatures.

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 Schreinemaker's method of wet residues[19] 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 composition, 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, the Schreinemaker's wet residue method was employed to study the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system.

Experimental Section

Materials. The *p*-nitroaniline was purchased from Shandong Liangzou Mineral Industry Group, China, with a mass fraction of 0.991. The *p*-nitroaniline was crystallized several times from water, yielded, on solution in hot ethanol, a reddish residue; so, it was recrystallized from ethanol and subsequently from water. The final product consisted of light yellow needles. The content of the crystalline *p*-nitroaniline was determined in our laboratory by high-performance liquid chromatography (HPLC), which had a mass fraction purity of 0.999.

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Analytically pure grade *o*-nitroaniline was provided by Zhejiang Fusheng Holding Group Co. Ltd., China, with a mass fraction of 0.990. It was crystallized from 0.95 ethanol and then repeatedly from hot water, from which it came out in fine orange-colored needles. The content of the crystalline *o*-nitroaniline were also determined in our laboratory by HPLC, which had a mass fraction purity 0.998.

The analytical grade ethanol, with a mass fraction purity of 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 $< 5\ \mu\mathrm{S}\cdot\mathrm{cm}^{-1}$).

Procedure. The Schreinemaker's wet residue method was used during experiments. The experimental saturated solutions were prepared by adding an excess solute, *p*-nitroaniline and/or *o*-nitroaniline, 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 actual temperature in the water bath was monitored by a Pt resistance thermometer (model: TES1300; uncertainty: ± 0.01 K). A condenser was connected to the flask to prevent the solvent from evaporating. Attainment of equilibrium was verified by both repetitive measurement of *p*-nitroaniline and *o*-nitroaniline after a minimum of 3 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 22.6 h to reach equilibrium. After equilibrium was achieved, the liquid phase and the solid phases with a little saturated liquid were taken out and then quantitatively analyzed. This procedure was repeated by varying the ratio of *p*-nitroaniline and *o*-nitroaniline to obtain different compositions of the solid and liquid phases.

Analysis. The moist solid samples and the equilibrium liquid phase were dissolved in ethanol and analyzed by a Shimadzu-6A high-performance liquid-phase chromatograph with the Eurospher 100-5 Si (120 mm × 4 mm) chromatographic column. The elution solution consisted of 55/45 (v/v) methanol−water.[20] Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis. The uncertainty of the experimental solubility values is about 1.3 %. The uncertainty in the solubility can be due to uncertainties in the HPLC measurements and weighing procedure.

Results and Discussion

The measured solubilities for the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system at (273.15, 298.15, and 323.15) K are shown in Tables 1 to 3, respectively. The ternary phase diagrams are given in Figures 1 to 3.

In Figures 1 to 3, along the solubility curve S_1C_1, S_2C_2, or S_3C_3, 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 *o*-nitroaniline on a wet basis. Along the solubility curve S'_1C_1, S'_2C_2, or S'_3C_3, 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 *p*-nitroaniline. The results indicate that two solids are present in the system: one is *o*-nitroaniline, and the other is *p*-nitroaniline. 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 1. Mass Fraction Solubilities of the Ternary *p*-Nitroaniline (w_1) + *o*-Nitroaniline (w_2) + Ethanol ($1 - w_1 - w_2$) System at 273.15 K

equilibrium liquid phase		moist solid phase		equilibrium solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	14.05	0	83.22	*o*-nitroaniline
0.43	13.89	0.071	85.17	*o*-nitroaniline
0.85	13.56	0.15	84.33	*o*-nitroaniline
1.26	13.38	0.19	86.65	*o*-nitroaniline
1.78	13.07	0.31	85.12	*o*-nitroaniline
2.01	12.88	0.41	81.86	*o*-nitroaniline
2.12	12.86	43.01	39.54	*o*-nitroaniline + *p*-nitroaniline
2.16	11.75	80.53	2.3	*p*-nitroaniline
2.25	10.04	81.78	1.84	*p*-nitroaniline
2.4	7.93	81.32	1.46	*p*-nitroaniline
2.54	5.97	83.37	0.95	*p*-nitroaniline
2.69	4.64	81.61	0.83	*p*-nitroaniline
2.82	3.39	82.87	0.57	*p*-nitroaniline
2.97	2.07	82.11	0.36	*p*-nitroaniline
3.13	1.01	84.74	0.11	*p*-nitroaniline
3.27	0	83.68	0	*p*-nitroaniline

Table 2. Mass Fraction Solubilities of the Ternary *p*-Nitroaniline (w_1) + *o*-Nitroaniline (w_2) + Ethanol ($1 - w_1 - w_2$) System at 298.15 K

equilibrium liquid phase		moist solid phase		equilibrium solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	21.81	0	84.06	*o*-nitroaniline
0.56	21.63	0.13	82.63	*o*-nitroaniline
1.04	21.36	0.2	83.66	*o*-nitroaniline
1.53	21.17	0.33	82.19	*o*-nitroaniline
2.11	21.05	0.43	84.31	*o*-nitroaniline
2.64	20.87	0.52	84.47	*o*-nitroaniline
3.17	20.74	42.37	36.25	*o*-nitroaniline + *p*-nitroaniline
3.21	19.36	83.49	3.3	*p*-nitroaniline
3.39	17.21	82.74	3.04	*p*-nitroaniline
3.61	14.28	84.45	2.26	*p*-nitroaniline
3.89	11.29	82.23	2.08	*p*-nitroaniline
4.25	8.13	84.62	1.35	*p*-nitroaniline
4.59	6.21	81.78	1.13	*p*-nitroaniline
4.98	3.84	83.49	0.66	*p*-nitroaniline
5.33	1.92	82.11	0.41	*p*-nitroaniline
5.77	0	83.46	0	*p*-nitroaniline

Table 3. Mass Fraction Solubilities of the Ternary *p*-Nitroaniline (w_1) + *o*-Nitroaniline (w_2) + Ethanol ($1 - w_1 - w_2$) System at 323.15 K

equilibrium liquid phase		moist solid phase		equilibrium solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	66.96	0	84.65	*o*-nitroaniline
1.03	66.54	0.47	84.73	*o*-nitroaniline
2.4	66.27	1.06	85.18	*o*-nitroaniline
3.37	65.95	1.61	84.11	*o*-nitroaniline
4.54	65.79	2.05	84.5	*o*-nitroaniline
5.04	65.73	24.94	69.19	*o*-nitroaniline + *p*-nitroaniline
5.18	63.16	79.62	13.61	*p*-nitroaniline
5.35	59.45	80.93	11.88	*p*-nitroaniline
5.63	54.44	82.22	10.23	*p*-nitroaniline
6.01	47.66	79.63	10.21	*p*-nitroaniline
6.64	38.23	81.15	7.9	*p*-nitroaniline
7.23	30.81	80.69	6.44	*p*-nitroaniline
8.09	21.5	82.01	4.05	*p*-nitroaniline
8.71	15.88	82.39	3.01	*p*-nitroaniline
9.42	10.14	84.54	1.73	*p*-nitroaniline
10.31	4.23	83.07	0.89	*p*-nitroaniline
10.86	0	83.66	0	*p*-nitroaniline

As shown in all figures, there are three crystallization fields in the phase diagrams: unsaturated region ($C_1S_1ES'_1$ in Figure 1, $C_2S_2ES'_2$ in Figure 2, and $C_3S_3ES'_3$ in Figure 3), *o*-nitroaniline (OS_1C_1 in Figure 1, OS_2C_2 in Figure 2, and OS_3C_3 in Figure 3),

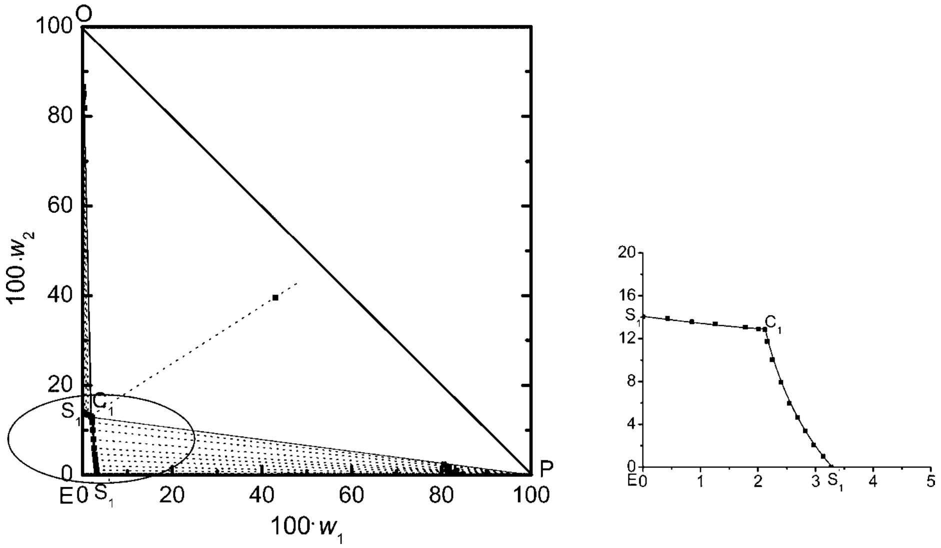

Figure 1. Phase diagram of the ternary *p*-nitroaniline (1) + *o*-nitroaniline (2) + ethanol (3) system at 273.15 K: ■, experimental data point; O, *o*-nitroaniline; P, *p*-nitroaniline; E, ethanol; S_1, S'_1, solubility of *o*-nitroaniline and *p*-nitroaniline in ethanol, respectively; C_1, cosaturated point; $C_1S_1ES'_1$, unsaturated region; OS_1C_1, crystalline region of solid *o*-nitroaniline; PS'_1C_1, crystalline region of solid *p*-nitroaniline; OC_1P, crystalline region of solids *o*-nitroaniline and *p*-nitroaniline; *w*, mass fraction.

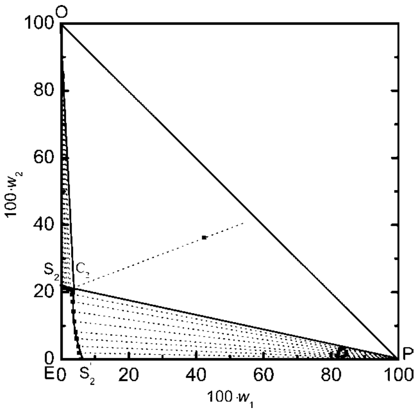

Figure 2. Phase diagram of the ternary *p*-nitroaniline (1) + *o*-nitroaniline (2) + ethanol (3) system at 298.15 K: S_2, S'_2, solubility of *o*-nitroaniline and *p*-nitroaniline in ethanol, respectively; C_2, cosaturated point; $C_2S_2ES'_2$, unsaturated region; OS_2C_2, crystalline region of solid *o*-nitroaniline; PS'_2C_2, crystalline region of solid *p*-nitroaniline; OC_2P, crystalline region of solids *o*-nitroaniline and *p*-nitroaniline; ■, O, P, E, and *w* have the same meaning as described in Figure 1.

p-nitroaniline (PS'_1C_1 in Figure 1, PS'_2C_2 in Figure 2, and PS'_3C_3 in Figure 3), and the mixture of *o*-nitroaniline and *p*-nitroaniline (OC_1P in Figure 1, OC_2P in Figure 2, and OC_3P in Figure 3). The phase diagrams have two invariant curves. S_1C_1, S_2C_2, and S_3C_3 are saturation curves corresponding to the solid-phase *o*-nitroaniline at (273.15, 298.15, and 323.15) K, respectively; S'_1C_1, S'_2C_2, and S'_3C_3 are saturation curves corresponding to the solid-phase *p*-nitroaniline. C_1, C_2, and C_3 are invariant points at different temperatures, which represent the equilibrium of the two solid phases *o*-nitroaniline and *p*-nitroaniline.

The phase diagrams presented in all figures also illustrate the influence of temperature on the solubilities of the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system. When the temperature increases from (273.15 to 323.15) K, the solubility of *o*-nitroaniline and *p*-nitroaniline increases, and the cosaturated point moves upward. The crystalline regions of *o*-nitroaniline and *p*-nitroaniline increase as the temperature decreases. No adduct is formed in the system at studied temperatures. At each temperature, the crystalline region of *p*-nitroaniline is larger than that of *o*-nitroaniline.

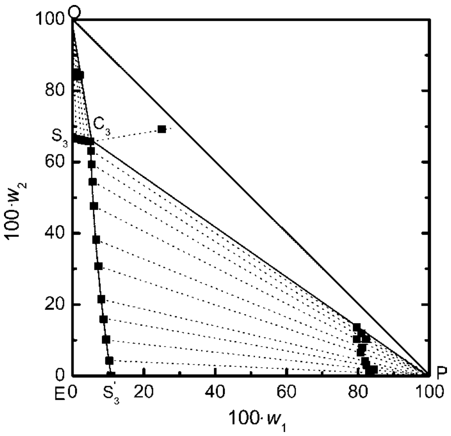

Figure 3. Phase diagram of the ternary *p*-nitroaniline (1) + *o*-nitroaniline (2) + ethanol (3) system at 323.15 K: S_3, S'_3, solubility of *o*-nitroaniline and *p*-nitroaniline in ethanol, respectively; C_3, cosaturated point; $C_3S_3ES'_3$, unsaturated region; OS_3C_3, crystalline region of solid *o*-nitroaniline; PS'_3C_3, crystalline region of solid *p*-nitroaniline; OC_3P, crystalline region of solids of *o*-nitroaniline and *p*-nitroaniline. ■, O, P, E and *w* have the same meaning as described in Figure 1.

Conclusion

The solubilities of the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system at (273.15, 298.15, and 323.15) K were determined experimentally, and the respective ternary phase diagrams were constructed. The solid phases were confirmed by Schreinemaker's wet residue method. At the studied temperatures, two solid phases were formed in the ternary *p*-nitroaniline + *o*-nitroaniline + ethanol system corresponding to *o*-nitroaniline and *p*-nitroaniline. The phase diagrams had three crystallization fields (*o*-nitroaniline, *p*-nitroaniline, and a mixture of *o*-nitroaniline and *p*-nitroaniline), two invariant curves, and one invariant point at each temperature. The solubility of *o*-nitroaniline and *p*-nitroaniline increases with increasing temperature. The phase diagrams of the ternary system were similar at different temperatures. At each temperature, the crystalline region of *p*-nitroaniline was larger than that of *o*-nitroaniline. 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 nitroanilines.

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