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Solid−Liquid Phase Equilibrium for the Ternary System 3-Chlorophthalic Acid + 4-Chlorophthalic Acid + Water at (283.15 and 313.15) K

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The solid−liquid phase equilibrium and mutual solubility for the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system were determined at (283.15 and 313.15) K. The phase diagrams of the system were constructed on the basis of the measured solubility. The solid phases formed in the studied system were confirmed by Schreinemaker's method of wet residues. At (283.15 and 313.15) K, both 3-chlorophthalic acid and 4-chlorophthalic acid were formed in the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system. Besides, an adductive compound with the formula (3-$C_6H_3Cl(COOH)_2 \cdot$4-$C_6H_3Cl(COOH)_2$) existed. The crystallization field of 3-chlorophthalic acid was larger than that of the adduct or 4-chlorophthalic acid at each studied temperature. The solubility data and the ternary phase diagram for the system of 3-chlorophthalic acid + 4-chlorophthalic acid + water at (283.15 and 313.15) K can provide the fundamental basis for the preparation of 3-chlorophthalic anhydride from 3-chlorophthalic anhydride and 4-chlorophthalic anhydride mixtures.

Introduction

3-Chlorophthalic anhydride and 4-chlorophthalic anhydride are commercial intermediates in the synthesis of a number of valuable compounds.[1] The isomeric mixtures of these compounds are formed by several synthetic methods, in various proportions of 3- and 4-chlorophthalic anhydrides.[2−6] In particular, the commercial product of 3-chlorophthalic anhydride is, at present, obtained via reduced pressure distillation from the isomeric mixture of 3- and 4-chlorophthalic anhydrides.[7,8] However, the energy consumption of the distillation process is very high. Thus, crystallization is proposed as a separation method due to its low energy consumption and the possibility of obtaining products with higher purity than that achieved by other conventional separation operations. Hence, it is possible to separate 3-chlorophthalic acid and 4-chlorophthalic acid mixtures via crystallization using water as a solvent, since the solubility of 3-chlorophthalic acid in water was much less than that of 4-chlorophthalic acid.[9] During the crystallization separation process, the optimization of process conditions is closely related to the solubility of 3-chlorophthalic acid and 4-chlorophthalic acid in water. Therefore, it is important to study the system and construct the phase diagram of the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system for improving the separation process.

It is well-known that solid−liquid phase equilibrium data are important in crystallization processes. Although the solubility of the binary systems of 3-chlorophthalic acid + water and 4-chlorophthalic acid + water has been determined and the corresponding binary phase diagrams constructed,[9] to the best of our knowledge, no investigations on the solubility or phase diagram for the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system have been made. The objective of this research is to investigate and generate the phase diagrams of the ternary system at (283.15 and 313.15) K by Schreinemaker's method of wet residues which demonstrates the temperature dependence of the ternary phase diagram.[10−13]

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 separation crystals and the complete removal of the adhering mother liquor from them. Extrapolation is made by Schreinemaker's method of wet residues, based on the following: The tie line joining the composition of the pure solid and 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 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.

Experimental Section

Materials. 3- and 4-Chlorophthalic acids are provided from XinPeng Chemical Promoter Factory, China, with a mass fraction of 0.995 and 0.999, and used without further purification. The water used to prepare solutions is twice-distilled (conductivity < 5 $\mu S \cdot cm^{-1}$).

Apparatus and Procedure. An external thermostat was used in this experiment, with a device for rotating several bottles at a time. A known mass of 3-chlorophthalic acid and 4-chlorophthalic acid was dissolved in 25 mL of water. The saturated solution was transferred to a conical flask. The conical flask was covered with rubber cap and placed in a device rotating the flasks at (283.15 ± 0.01) K or (313.15 ± 0.01) K in a constant-temperature bath. The water temperature was controlled by a constant-temperature water bath (Neslab, model RTE-101) recirculating flow water through a copper coil in the water bath.

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Table 1. Mass Fraction Solubility of the Ternary 3-Chlorophthalic Acid + 4-Chlorophthalic Acid + Water System 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	2.20	0	91.45	N
1.82	1.98	1.01	66.48	N
4.9	3.07	2.39	50.36	N
10.91	5.02	4.03	64.19	N
13.57	6.26	9.31	34.71	N
17.52	6.23	7.31	61.54	N
20.99	7.75	12.33	45.51	N
23.62	7.59	8.27	65.91	N
28.49	8.3	11.19	63.74	N
31.38	9.29	16.01	54.28	N
34.79	9.23	28.22	30.58	N + A
36.63	9.58	30.67	34.54	A
38.81	9.56	30.96	38.03	A
41.38	9.14	47.32	27.93	M + A
43.14	5.19	68.19	2.57	M
46.45	2.79	63.98	2.09	M
49.29	0	89.97	0	M

[a] w_1, mass fraction of 4-chlorophthalic acid; w_2, mass fraction of 3-chlorophthalic acid; M, 4-chlorophthalic acid; N, 3-chlorophthalic acid; A, adduct of 3-chlorophthalic acid and 4-chlorophthalic acid with the mole ratio of 4:1.

The actual temperature in the water bath was monitored by a resistance thermometer (type, TES1300; uncertainty, ± 0.01 K). The water was stirred using a Teflon-coated magnetic stirring bar. To ensure that sampling was performed at equilibrium conditions, a preliminary test was carried out in which the liquid composition was measured as a function of time. Two types of experiments were carried out, one starting from a supersaturated solution in which the solid phase precipitates to reach equilibrium and the other starting from a nonsaturated solution in which solid dissolves to reach equilibrium. In our experiments, sampling was performed at least for 4 h. The results show that in both cases about 48 h was sufficient to reach equilibrium. After equilibrium was achieved, the liquid phase and the solid phase with a little of saturated liquid were taken out and then quantitatively analyzed. This procedure was repeated by varying the ratio of 3-chlorophthalic acid and 4-chlorophthalic acid to obtain different compositions of the solid and liquid phases.

Analysis. Aliquots of saturated 3- and 4-chlorophthalic acid solutions are transferred into a tarred volumetric flask. The composition of 3- and 4-chlorophthalic acids in water is determined using a Bisep-1100 high-performance liquid phase chromatograph (HPLC). The Diamonsil C18 (250 mm × 4.6 mm) chromatographic column is used. The mobile phase consists of four eluents which are water, methanol, aqueous sodium sulfate, and aqueous phosphoric acid. The uncertainty of the measurement was less than 0.001 g of 3- or 4-chlorophthalic acid per 100 g of water. Each analysis was repeated three times, and the average value of the three measurements was considered as the final value of the analysis.

Results and Discussion

The measured solubility of the equilibrium liquid phase for the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system at (283.15 and 313.15) K is shown in Tables 1 and 2, respectively. The ternary phase diagrams are given in Figures 1 and 2, respectively.

In the phase diagrams as shown in Figures 1 and 2, N, M, and W represent 3-chlorophthalic acid, 4-chlorophthalic acid, and water, respectively. E_1 and E_2 represent the solubility of 3-chlorophthalic acid in water at (283.15 and 313.15) K; F_1 and F_2 represent the solubility of 4-chlorophthalic acid in water at (283.15 and 313.15) K. In Figures 1 and 2, along E_1C_1 or E_2C_2, 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 the compound 3-chlorophthalic acid on a wet basis. Similarly, along the solubility curve F_1D_1 or F_2D_2, linking the component points of the liquid phase and wet solid phase and an extension thereof, the point of intersection of these tie-lines is the approximate solid-phase component for 4-chlorophthalic acid. Along the solubility curve C_1D_1 or C_2D_2, linking the component points of the liquid phase and wet solid phase and an extension thereof, the point of intersection of these tie-lines is the approximate solid-phase component for adduct of 3-chlorophthalic acid with 4-chlorophthalic acid, in which the mole ratio of the two compositions is 4:1, named as adduct A in the present work.

E_1C_1 and E_2C_2 are saturation curves corresponding to the solid-phase 3-chlorophthalic acid at (283.15 and 313.15) K,

Table 2. Mass Fraction Solubility of the Ternary 3-Chlorophthalic Acid + 4-Chlorophthalic Acid + Water System at 313.15 K[a]

liquid phase		moist solid phase		
100 w_1	100 w_2	100 w_1	100 w_2	equilibrium solid phase
0	4.04	0	93.24	N
5.53	6.48	3.38	47.97	N
12.34	9.18	3.23	76.34	N
17.67	11.18	8.76	56.73	N
25.96	13.13	12.29	58.99	N
31.14	13.73	14.08	66.6	N + A
31.18	13.70	18.43	67.59	N + A
36.62	14.56	32.01	32.18	A
43.37	14.98	28.05	57.09	A
49.46	14.1	31.34	54.29	A
53.85	13.93	43.11	34.39	A
57.92	12.83	51.9	32.49	M + A
62.06	9.08	80.19	4.52	M
66.21	4.7	84.95	2.11	M
70.05	1.78	82.49	1.46	M
73.53	0	90.21	0	M

[a] w_1, w_2, M, N, and A have the same meaning as described in Table 1.

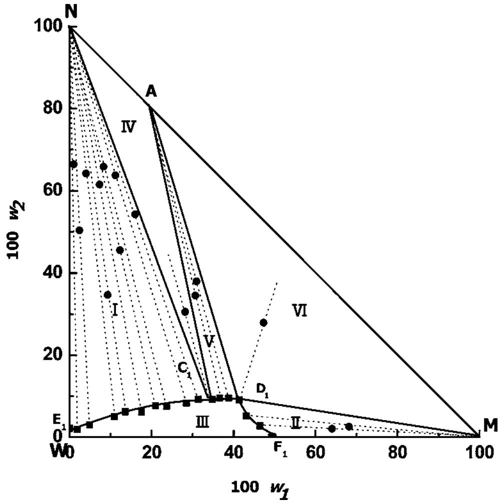

Figure 1. Phase diagram for the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system at 283.15 K. W, H_2O; M, 4-chlorophthalic acid; N, 3-chlorophthalic acid; A, adduct of 3-chlorophthalic acid and 4-chlorophthalic acid, with the mole ratio of 4:1; C_1, cosaturated point of 3-chlorophthalic acid and adduct A; D_1, cosaturated point of 4-chlorophthalic acid and adduct A; E_1, solubility of 3-chlorophthalic acid in water; F_1, solubility of 4-chlorophthalic acid in water; ■, liquid phase composition; ●, moist solid phase composition.

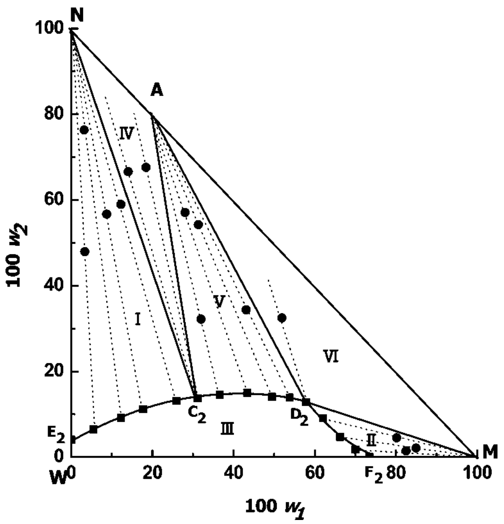

Figure 2. Phase diagram for the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system at 313.15 K. W, M, N, A, ■, and ● have the same meaning as described in Figure 1. C_2, cosaturated point of 3-chlorophthalic acid and adduct A; D_2, cosaturated point of 4-chlorophthalic acid and adduct A; E_2, solubility of 3-chlorophthalic acid in water; F_2, solubility of 4-chlorophthalic acid in water.

respectively; F_1D_1 and F_2D_2 are saturation curves corresponding to the solid-phase 4-chlorophthalic acid, and C_1D_1 and C_2D_2 are saturation curves corresponding to the solid phase of adduct A. C_1 (C_2) is an invariant point at 283.15 K (313.15 K), which represents the cosaturated solution of the solid phases 3-chlorophthalic acid and adduct A, and D_1 (D_2) represents the cosaturated solution of the solid phases 4-chlorophthalic acid and adduct A at 283.15 K (313.15 K).

Each figure is divided into six regions by three solubility curves, respectively. The regions in the two-phase diagrams are denoted as follows: I (E_1NC_1 or E_2NC_2), crystalline region of pure solid 3-chlorophthalic acid; II (F_1MD_1 or F_2MD_2), crystalline region of pure solid 4-chlorophthalic acid; III ($C_1E_1WF_1D_1$ or $C_2E_2WF_2D_2$), unsaturated region; IV (ANC_1 or ANC_2), crystalline region of solid 3-chlorophthalic acid and adduct A; V (C_1AD_1 or C_2AD_2), crystalline region of pure solid adduct A; VI (D_1AM or D_2AM), crystalline region of solid 4-chlorophthalic acid and adduct A. Figures 1 and 2 also show that adduct A is an unsymmetric double salt.

Figures 1 and 2 further illustrate the temperature dependence of the phase diagram for the ternary 3-chlorophthalic acid + 4-chlorophthalic acid + water system. When the temperature increases from (283.15 to 313.15) K, the solubility of 4-chlorophthalic acid and the adduct of 3-chlorophthalic acid with 4-chlorophthalic acid in water increase significantly, whereas the solubility of 3-chlorophthalic acid varies a little with respect to a rise in temperature. As a result the crystallization field of 3-chlorophthalic acid was larger than that of the adduct or 4-chlorophthalic acid at each studied temperature. Moreover, the invariant point moves upward, and the crystalline region of the solid adduct enlarges apparently.

Conclusion

The solid−liquid phase equilibrium and the solubility data for the ternary system 3-chlorophthalic acid + 4-chlorophthalic acid + water at (283.15 and 313.15) K were determined experimentally. The solid−liquid phase diagrams were constructed. The solid phase was confirmed by Schreinemaker's method of wet residues. Three solid phases were formed in the ternary system 3-chlorophthalic acid + 4-chlorophthalic acid + water at each studied temperature, which corresponded to 3-chlorophthalic acid, 4-chlorophthalic acid, and adduct A ($3\text{-}C_6H_3Cl(COOH)_2 \cdot 4\text{-}C_6H_3Cl(COOH)_2$)). Each phase diagram has three crystallization fields, three univariant curves, and two invariant points. With an increase in temperature, the crystalline region of solid adduct A is enlarged. 3-Chlorophthalic acid has a bigger crystallization field than the adduct A or 4-chlorophthalic acid.

The solubility data and the ternary phase diagram for the 3-chlorophthalic acid + 4-chlorophthalic acid + water system at (283.15 and 313.15) K can provide the fundamental basis for the preparation of 3-chlorophthalic anhydride from 3-chlorophthalic anhydride and 4-chlorophthalic anhydride mixtures.

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