

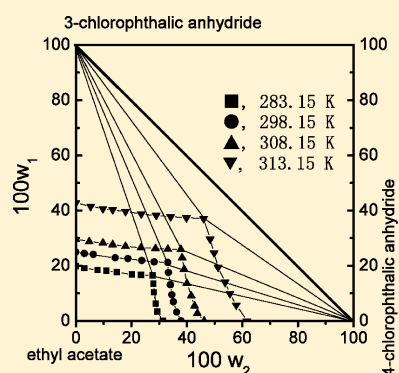
Solid–Liquid Equilibrium and Phase Diagram for the Ternary 4-Chlorophthalic Anhydride + 3-Chlorophthalic Anhydride + Ethyl Acetate System

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ABSTRACT: In this paper, the mutual solubility for ternary system of 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate was measured experimentally at different temperatures. Four isothermal phase diagrams of the system were constructed based on the measured solubility. At each temperature, there existed two pure solid phases, pure 4-chlorophthalic anhydride and pure 3-chlorophthalic anhydride, which were identified by the Schreinemakers' wet residue method. When temperature decreases, the crystallization regions of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride increase. At a certain temperature, the crystallization region of 4-chlorophthalic anhydride is smaller than that of 3-chlorophthalic anhydride.



INTRODUCTION

Monochlorophthalic anhydride includes two isomers, 3-chlorophthalic anhydride (CAS Registry No. 117-21-5) and 4-chlorophthalic anhydride (CAS Registry No. 118-45-6). They are all used extensively in the synthesis of polyurethane, dyes, medicines, agrochemicals, and so on.^{1–5} There are two methods to prepare monochlorophthalic anhydride. One way is chlorination of phthalic anhydride in the liquid or vapor phase.^{6–12} The other method is chlorination of nitrophthalic acid or nitrophthalimide.^{13–16} However the product of these two methods is a mixture of 3-chlorophthalic anhydride, 4-chlorophthalic anhydride, and dichlorophthalic anhydride with various proportions. To obtain 3-chlorophthalic anhydride and 4-chlorophthalic anhydride with high purity, some methods are employed to separate the isomeric mixtures. Ding and some other co-workers proposed a distillation method to separate 3- or 4-chlorophthalic anhydride from the isomeric mixtures.¹⁷ Since the difference of boiling point of the two isomers is small, this method has a high cost. Crystallization is another alternative but common method to separate monochlorophthalic anhydride from its isomeric mixtures. During the separation process via crystallization, the solubilities of 3-chlorophthalic anhydride or/and 4-chlorophthalic anhydride in different solvents are put into consideration for optimizing process conditions. Recently the solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in ethyl acetate, acetone, 1,4-dioxane, and water are all reported.¹⁸ However, the solubility of ternary system of 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + solvent are unknown.

Solid–liquid phase equilibrium data are of importance in crystallization processes design. During the separation process

of monochlorophthalic anhydride from its isomeric mixtures via crystallization, it is necessary to know the mutual solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in solvent. Ethyl acetate is a suitable solvent for the crystallization process. The separation process is carried out on the basis of the phase diagram of the ternary system of 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate. It is very important to determine the mutual solubility of the 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate system. Nevertheless, the research on the mutual solubility of the ternary 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate system has not been discussed in previous documents. The aim of this investigation is to study the phase diagrams of the ternary 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate system at different temperatures by Schreinemakers' method of wet residues^{19–21} and analyze the temperature dependence of the ternary phase diagram.

When a ternary solid–liquid system arrives at equilibrium, at least one solid and one liquid phase exist. The composition of the solid phase is usually not determined directly, because it is difficult to remove the adhering mother liquor from them and obtain the pure crystals. Schreinemakers' method of wet residues was employed to get the composition of the solid phase. This method is based on the application of the straight line rule: points characterizing the liquid phase, wet solid phase, and the pure equilibrium solid phase must lie on a single

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straight line. If we construct straight lines connecting points that represent the liquid phase and the wet residue for several different initial systems and the identical equilibrium solid phases are formed in the systems, the straight lines intersect at the point corresponding to the equilibrium solid phase. In this work the Schreinemakers' method of wet residues was used to construct phase diagrams of the ternary system of 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate at different temperatures.

EXPERIMENTAL SECTION

Materials. 3-Chlorophthalic anhydride and 4-chlorophthalic anhydride are all purchased from ZiBo XinPeng Chemical Promoter Factory. The mass fraction of 4-chlorophthalic anhydride was 0.9981, which was used without further purification. The 3-chlorophthalic anhydride, with a mass fraction of 0.982, was recrystallized from acetone; nearly colorless needles were formed with a mass purity of 0.9934. The ethyl acetate, with a mass fraction purity of 0.999, was provided from Nanjing Chemical Reagent Co. Ltd., China. It was used without further purification in the work. The water used in the experiment was deionized (conductivity < 5 $\mu\text{S}\cdot\text{cm}^{-1}$).

Procedure. The solubility was measured by the isothermal solution saturation method. The pure solid phase was confirmed by the method of Schreinemakers' wet residue.¹⁹ The saturated solutions were obtained by adding an excess 4-chlorophthalic anhydride and/or 3-chlorophthalic anhydride to ethyl acetate. The composition of the saturated solution fell in the desired portion of the solubility curve when the components were taken in proportions. The system was placed in a water jacketed vessel with motor stirring in a constant temperature water bath for 3 days to ensure equilibrium. The isothermal water bath (Neslab, model RTE-101) was recirculated through a copper coil. The actual temperature in the water bath was controlled via a resistance thermometer (type, TES1300; accuracy, ± 0.1 K). A condenser is attached to the flask to prevent ethyl acetate from evaporating. A method was employed to verify the equilibrium by both measuring repetitively the content of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride after 3 additional days and approaching equilibrium from supersaturation at a higher temperature. Equilibration had been attained when the composition of the liquid phase became constant. Results showed that the equilibrium could be reached in 13 h. After equilibrium was achieved, the solid phase adhering a little of saturated liquid, and the equilibrium liquid phase were taken out respectively and analyzed quantitatively by HPLC. To get different compositions of the solid and liquid phase, the same experimental procedure was carried out by altering the ratio of 3-chlorophthalic anhydride to 4-chlorophthalic anhydride.

Analysis. The saturated solutions of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride and the moist solid were transferred into a volumetric flask. 3-Chlorophthalic anhydride and 4-chlorophthalic anhydride in solutions are hydrolyzed totally to 3- and 4-chlorophthalic acid in excessive hot water at (353 to 373) K before use. The content of 3- or 4-chlorophthalic acid is measured by a Shimadzu-6A high-performance liquid-phase chromatograph (HPLC). The chromatographic column used in this study is a unimicro Kromasil C18, 5 μm (250 mm \times 4.6 mm) which was set to 308.1 K. The wavelength of the UV single spectrophotometric detector was set to 254 nm. The mobile phase included

60(mL)/40(mL)/3.3(mL)/2.65(g) methanol/water/ H_3PO_4 / Na_2SO_4 , and the flow rate in the analysis is 1.2 $\text{mL}\cdot\text{min}^{-1}$. The concentration ranges from (0 to 1) $\text{mg}\cdot\text{mL}^{-1}$ of solutes were employed for construction of calibration curves. Each analysis is repeated three times, and the average value is considered as the final value of the analysis.

The uncertainty of the measured solubility values is approximately 2.0 %. The uncertainty is caused by uncertainties in the temperature measurements and sampling procedure.

RESULTS AND DISCUSSION

The mutual solubilities for the ternary system of 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate at different temperatures are given in Tables 1, 2, 3, and 4, respectively. The corresponding phase diagrams of the ternary system are shown in Figures 1, 2, 3, and 4.

Table 1. Mass Fraction Solubility of the Ternary 4-Chlorophthalic Anhydride (1) + 3-Chlorophthalic Anhydride (2) + Ethyl Acetate (3) System at 283.15 K^a

liquid phase		wet solid phase		solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	19.84			N
3.02	19.12	1.04	76.15	N
7.76	18.43	2.54	73.05	N
10.92	18.18	3.19	77.36	N
14.79	17.67	4.77	73.19	N
20.2	16.85	6.48	73.03	N
23.45	16.62	6.38	77.14	N
27.64	16.51	33.19	50.82	M + N
27.91	13.43	76.94	4.46	M
28.73	6.29	79.68	2.85	M
28.1	10.36	76.46	2.23	M
29.34	3.41	72.99	1.13	M
31.30	0			M

^a w , mass fraction; M, 4-chlorophthalic anhydride; N, 3-chlorophthalic anhydride. The relative standard uncertainty of the mass fraction solubility is $u_r(w) = 0.02$ and for the measured temperature, $u(T) = 0.02$ K.

Points M, N, and A in Figures 1 to 4 stand for the pure solids of 4-chlorophthalic anhydride, 3-chlorophthalic anhydride, and ethyl acetate, respectively. Points S_1 , S_2 , S_3 , and S_4 represent the equilibrium solubility of 4-chlorophthalic anhydride in ethyl acetate at 283.15 K, 298.15 K, 308.15 K, and 323.15 K, respectively, and S_1' , S_2' , S_3' , and S_4' stand for the equilibrium solubility of 3-chlorophthalic anhydride at different temperatures. S_1C_1 , S_2C_2 , S_3C_3 , or S_4C_4 are solubility curves, which indicate the compositions of saturated solution that are in equilibrium with pure solid of 4-chlorophthalic anhydride at 283.15 K, 298.15 K, 308.15 K, and 323.15 K, respectively. Solubility curves $S_1'C_1$, $S_2'C_2$, $S_3'C_3$, or $S_4'C_4$ indicate the compositions of saturated solutions which are in equilibrium with the pure solid 3-chlorophthalic anhydride. Points C_1 , C_2 , C_3 , and C_4 are cosaturation points, which show a solution saturated with the two solids 3-chlorophthalic anhydride and 4-chlorophthalic anhydride. The compositions of the cosaturation points are shown in Tables 1 to 4.

It can be seen from Figures 1, 2, 3, and 4 that a solid solution is not formed in the ternary system of 3-chlorophthalic anhydride + 4-chlorophthalic anhydride + ethyl acetate at different temperatures. The phase diagram was divided into

Table 2. Mass Fraction Solubility of the Ternary 4-Chlorophthalic Anhydride (1) + 3-Chlorophthalic Anhydride (2) + Ethyl Acetate (3) System at 298.15 K^a

liquid phase		wet solid phase		solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	24.90			N
6.26	24.08	1.04	75.78	N
3.02	24.44	1.78	81.72	N
14.16	22.86	4.26	77.03	N
18.82	22.50	6.49	73.31	N
23.76	21.87	6.97	77.14	N
28.19	21.39	6.86	81.94	N
33.13	21.14	38.45	45.38	M + N
33.38	17.52	81.40	4.85	M
34.11	13.09	78.07	3.98	M
34.59	9.41	75.22	3.61	M
35.10	6.94	77.19	2.37	M
36.31	3.24	74.96	1.38	M
37.90	0			M

^aThe relative standard uncertainty of the mass fraction solubility is $u_r(w) = 0.02$ and for the measured temperature, $u(T) = 0.02$ K.

Table 3. Mass Fraction Solubility of the Ternary 4-Chlorophthalic Anhydride (1) + 3-Chlorophthalic Anhydride (2) + Ethyl Acetate (3) System at 308.15 K^a

liquid phase		wet solid phase		solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	29.62			N
4.79	28.76	1.55	76.77	N
9.73	28.28	3.02	80.10	N
13.18	27.66	4.26	77.51	N
17.86	27.04	4.88	81.57	N
23.50	26.56	7.23	77.62	N
28.69	26.31	9.20	77.36	N
33.13	26.02	11.43	74.75	N
37.81	25.91	55.21	33.25	M + N
38.29	22.94	78.18	8.29	M
39.02	18.76	80.16	5.84	M
40.01	13.60	81.65	3.87	M
41.51	9.17	77.45	3.61	M
42.72	5.47	74.34	2.85	M
43.76	2.77	77.19	1.13	M
46.19	0			M

^aThe relative standard uncertainty of the mass fraction solubility is $u_r(w) = 0.02$ and for the measured temperature, $u(T) = 0.02$ K.

three crystallization fields: 4-chlorophthalic anhydride crystallization fields (II), 3-chlorophthalic anhydride crystallization fields (III), and mixture solids of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride crystallization fields (IV). The phase diagram includes two invariant curves and one cosaturation point at each temperature as shown in Figures 1 to 4.

Along solubility curves S_1C_1 , S_2C_2 , S_3C_3 , or S_4C_4 , and in the crystallization region of 4-chlorophthalic anhydride(II), the points representing the liquid phase, wet solid phase, and the pure 4-chlorophthalic anhydride must lie on a single straight line. So connecting the component points of saturated liquid phase and corresponding wet residue and extrapolating, the point of intersection of these tie-lines is approximately the pure solid-phase component for 4-chlorophthalic anhydride. Along

Table 4. Mass Fraction Solubility of the Ternary 4-Chlorophthalic Anhydride (1) + 3-Chlorophthalic Anhydride (2) + Ethyl Acetate (3) System at 323.15 K^a

liquid phase		wet solid phase		solid phase
100 w_1	100 w_2	100 w_1	100 w_2	
0	42.76			N
5.28	41.46	1.78	82.19	N
9.73	40.70	3.42	78.75	N
13.18	40.22	4.01	82.44	N
17.86	39.66	6.49	78.48	N
23.51	38.70	7.48	80.95	N
28.92	38.24	9.71	79.73	N
34.11	37.74	11.94	78.24	N
39.76	37.34	12.67	80.21	N
46.03	37.06	47.53	47.36	M + N
48.39	29.61	85.86	8.04	M
49.76	24.61	80.92	9.29	M
51.23	19.42	82.89	6.83	M
53.71	14.00	84.50	4.61	M
55.48	9.91	79.79	4.60	M
57.76	5.69	83.12	2.37	M
61.62	0			M

^aThe relative standard uncertainty of the mass fraction solubility is $u_r(w) = 0.02$ and for the measured temperature, $u(T) = 0.02$ K.

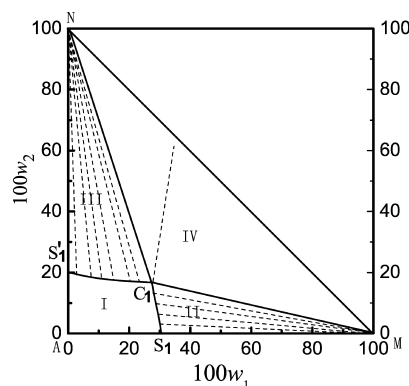


Figure 1. Phase diagram for the ternary 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate system at 283.15 K; A, ethyl acetate; M, 4-chlorophthalic anhydride; N, 3-chlorophthalic anhydride; C_1 , cosaturation point of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride; S_1 , solubility of 4-chlorophthalic anhydride in ethyl acetate; S_1' , solubility of 3-chlorophthalic anhydride in ethyl acetate.

solubility curves $S_1'C_1$, $S_2'C_2$, $S_3'C_3$, or $S_4'C_4$, and in the crystallization region of 3-chlorophthalic anhydride (III), connecting the component points of saturated liquid phase and corresponding wet residue and extrapolating, the point of intersection of these tie-lines is approximately the pure solid-phase component for 3-chlorophthalic anhydride. The region IV is the crystallization field of the mixture solids of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride. In this region, the composition of cosaturation point is constant, but the composition representing the solid phase may vary in the range from 0 to 1, which depends on the original mass ratio of the two isomers.

Figures 1 to 4 further illustrate the influence of the temperature on the phase diagram for the ternary system of 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate. The solubility of 3-chlorophthalic anhydride and

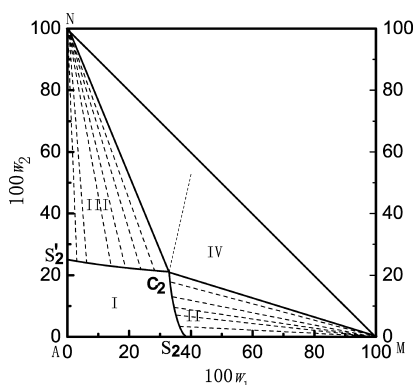


Figure 2. Phase diagram for the ternary 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate system at 298.15 K; C_2 , cosaturation point of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride; S_2' , solubility of 4-chlorophthalic anhydride in ethyl acetate; S_2 , solubility of 3-chlorophthalic anhydride in ethyl acetate; A, M, and N have the same meanings as described in Figure 1.

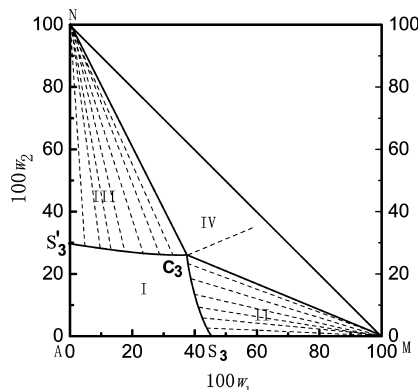


Figure 3. Phase diagram for the ternary 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate system at 308.15 K; C_3 , cosaturation point of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride; S_3' , solubility of 4-chlorophthalic anhydride in ethyl acetate; S_3 , solubility of 3-chlorophthalic anhydride in ethyl acetate; A, M, and N have the same meaning as described in Figure 1.

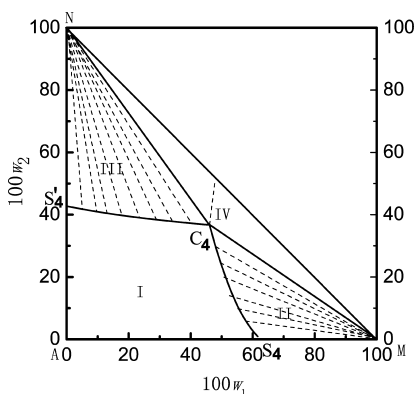


Figure 4. Phase diagram for the ternary 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate system at 323.15 K; C_4 , cosaturation point of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride; S_4' , solubility of 4-chlorophthalic anhydride in ethyl acetate; S_4 , solubility of 3-chlorophthalic anhydride in ethyl acetate; A, M, and N have the same meaning as described in Figure 1.

4-chlorophthalic anhydride increases with the increases in temperature from (283.15 to 323.15) K, and the cosaturation

point moves upward. The crystalline regions of two pure solids (II and III) increase as the temperature decreases. The crystallization region of 3-chlorophthalic anhydride (III) is larger than that of 4-chlorophthalic anhydride (II) at the same temperature.

CONCLUSION

The mutual solubility of the ternary system of 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate at 283.15 K, 298.15 K, 308.15 K, and 323.15 K were measured experimentally, and the corresponding phase diagrams were constructed based on the measured solubility. At each temperature, there are two solid phases formed in the ternary 4-chlorophthalic anhydride + 3-chlorophthalic anhydride + ethyl acetate system, which correspond to 4-chlorophthalic anhydride and 3-chlorophthalic anhydride. The phase diagram includes three crystallization fields (4-chlorophthalic anhydride, 3-chlorophthalic anhydride, and a mixture of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride), two invariant curves, and one cosaturation point. The solubility of 4-chlorophthalic anhydride and 3-chlorophthalic anhydride increases with an increase in temperature. The crystallization region of 3-chlorophthalic anhydride is larger than that of 4-chlorophthalic anhydride at the same temperature. The mutual solubility data and the phase diagram of the ternary system can provide the basis for the separation process of monochlorophthalic anhydride isomers.

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Notes

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