Solid–liquid phase equilibrium and phase diagram for ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 283.15 K and 333.15 K

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Abstract

In this investigation, the solid–liquid phase equilibrium and the mutual solubility for ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system were determined at 283.15 K and 333.15 K. The phase diagrams of the system were constructed based on the measured solubility. The solid phases formed in the studied system were confirmed by Schreinemakers' method of wet residues. In addition, the density of equilibrium liquid phase was obtained. At 283.15 K and 333.15 K, both 3-nitrophthalic acid and 4-nitrophthalic acid were formed in the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system. Adductive compounds existed: 3:1:1 adduct $3\text{-}C_6H_3NO_2(COOH)_2 \cdot 4\text{-}C_6H_3NO_2(COOH)_2 \cdot H_2O$ at 283.15 K and 1:1 adduct $3\text{-}C_6H_3NO_2(COOH)_2 \cdot 4\text{-}C_6H_3NO_2(COOH)_2$ at 333.15 K. The adduct had a bigger crystallization field than 3-nitrophthalic acid or 4-nitrophthalic acid at each studied temperature. The solubility data and the ternary phase diagram for the system 3-nitrophthalic acid–4-nitrophthalic acid–water at 283.15 K and 333.15 K can provide the fundamental basis for preparation of 3-nitrophthalic acid from 3-nitrophthalic acid and 4-nitrophthalic acid mixtures.

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1. Introduction

3-Nitrophthalic acid (CAS Registry No. 603-11-2) and 4-nitrophthalic acid (CAS Registry No. 610-27-5) are commercially valuable intermediates for producing the widest variety of derivatives, such as pigments, dyes and plasticizers, particularly for PVC, polyesters, polyamides, peptides, agricultural active substances, and so forth [1–5]. They are in general produced by nitration of phthalic anhydride with concentrated sulfuric acid [6–12]. The isomeric mixtures are formed in various proportions of 3- and 4-nitrophthalic acids with this method. The commercial product of 3-nitrophthalic acid is obtained via crystallization from the isomeric mixture of 3- and 4-nitrophthalic acids in water at present. During the separation process, the mutual solubility of 3-nitrophthalic acid and 4-nitrophthalic acid in water are needed. The optimization of process conditions is closely related to the solubility of 3-nitrophthalic acid and 4-nitrophthalic acid in water. It is important to study the system

and construct the phase diagram of the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system for improving the separation process.

It is well known that solid–liquid phase equilibrium data is important in crystallization processes. Although the solubility of the binary systems 3-nitrophthalic acid–water and 4-nitrophthalic acid–water were determined and the corresponding binary phase diagrams were constructed [13,14], no studies have been reported on the phase diagram of the ternary system [15]. The objective of this research is to investigate and generate the phase diagrams of the ternary system at 293.15 K and 333.15 K by Schreinemakers' method of wet residues [16,17] and demonstrates the temperature dependence of the ternary phase diagram.

In ternary system involving at least one solid and one liquid phase, the composition of the solid phase is often determined indirectly, in order to avoid separating the crystals and completely removing the adhering mother liquor from them. Extrapolation is made by Schreinemakers' method of wet residues, 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 correspond-

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ing to varying amounts of solid and liquid phase. 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 from direct analysis obtained by crystallization after drying of the compound.

2. Experimental

2.1. Materials

3- and 4-Nitrophthalic acids are provided from KangDa Chemical Co. Ltd., with a mass fraction of 99.92%, and used without further purification. The water used to prepare solutions is twice distilled water (conductivity < 5 μS/cm).

2.2. Apparatus and procedure

Schreinmaker's wet residue method is used in this experiment. An external thermostat is used in this experiment, with a device for rotating several bottles at a time. A known mass of 3-nitrophthalic acid and 4-nitrophthalic acid is dissolved in 25 mL of water. The saturated solution is transferred to a conical flask. The conical flask is covered with rubber cap and placed in a device rotating the flasks at (283.15 ± 0.01 K) or (333.15 ± 0.01 K). To ensure that sampling is performed at equilibrium conditions, a preliminary test is carried out in which the liquid concentration and the density are measured as a function of time. Two types of experiments are 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 is performed at least for 4 h. The results show that in both cases about 21 h is sufficient to reach equilibrium. After the equilibrium is achieved, the solid phase and the liquid phase are separated by filtration and then both phases are analyzed. The composition of the solid phase is determined by Schreinemaker's wet residue method [11].

2.3. Analysis

Aliquots of saturated 3- or/and 4-nitrophthalic acid solutions are transferred through a coarse filter into a tarred volumetric flask. The concentration of 3- or/and 4-nitrophthalic acids in water is determined using a Shimadzu-6A high-performance liquid phase chromatograph (HPLC). The Diamonsil C18 (150 mm × 4.6 mm) chromatographic column is used. The mobile phase consists of four eluents which are water, methanol, Na_2SO_4 and H_3PO_4. The uncertainty of the measurement is less than 0.001 g of 3- or 4-nitrophthalic acid per 100 g of water. The densities (ρ) of the equilibrium liquid phase are measured using a pycnometer (11-FY) with an uncertainty of 0.0002 g cm^{-3}.
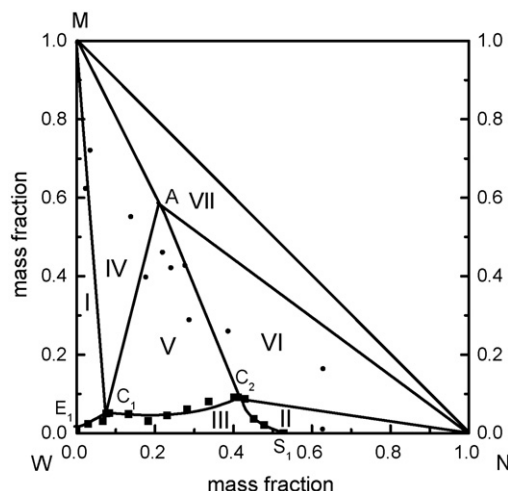

Fig. 1. Phase diagram for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 283.15 K; W, H_2O; M, 3-nitrophthalic acid; N, 4-nitrophthalic acid; A, adduct of 3-nitrophthalic acid, 4-nitrophthalic acid with water, in which the mole ratio of the three compositions is 3:1:1; C_1, cosaturated point of 3-nitrophthalic acid and *adduct A*; C_2, cosaturated point of 4-nitrophthalic acid and *adduct A*; E_1, solubility of 3-nitrophthalic acid in water; S_1, solubility of 4-nitrophthalic acid in water.
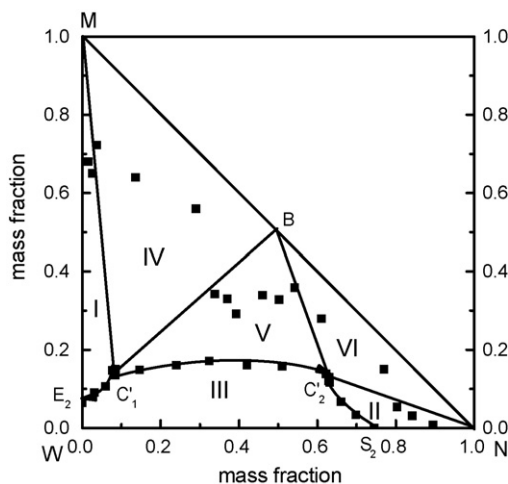

Fig. 2. Phase diagram for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 333.15 K; B, adduct of 3-nitrophthalic acid with 4-nitrophthalic acid, in which the mole ratio of the two compositions is 1:1; C_1', cosaturated point of 3-nitrophthalic acid and *adduct B*; C_2', cosaturated point of 4-nitrophthalic acid and *adduct B*; E_2, solubility of 3-nitrophthalic acid in water; S_2, solubility of 4-nitrophthalic acid in water; W, N and M have the same meaning as described in Fig. 1.

Each analysis is repeated three times, and the average value of the three measurements is considered as the final value of the analysis.

3. Results and discussion

The measured solubility and the density of the liquid phase for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 283.15 K and 333.15 K are shown in Tables 1 and 2, respectively. The ternary phase diagrams are given in Figs. 1 and 2.

Table 1
Mass fraction solubility of the ternary 4-nitrophthalic acid (1)–3-nitrophthalic acid (2)–water (3) system at 283.15 K[a]

Liquid phase		Moist solid phase		Density of liquid phase (g mL^{-1})	Solid phase
100 w_1	100 w_2	100 w_1	100 w_2		
0	0.90	0	90.45	0.9511	M
2.91	2.33	2.23	62.37	0.9988	M
6.65	3.03	3.45	72.11	1.0253	M
7.56	4.97	13.80	55.20	1.0351	M + A
8.35	5.08	17.60	39.80	1.0366	A
13.24	4.83	20.76	44.08	1.0357	A
18.23	3.08	21.89	46.08	1.0372	A
23.07	4.51	22.17	43.76	1.0518	A
28.16	6.08	24.06	42.16	1.0735	A
33.71	8.02	28.66	28.92	1.1007	A
40.10	9.14	27.60	42.80	1.1270	A
41.11	9.18	62.80	16.40	1.1427	A
42.88	8.73	38.59	25.99	1.1620	N + A
45.20	3.67	74.04	1.92	1.1419	N
47.88	2.08	62.69	1.03	1.1290	N
52.75	0	76.63	0	1.1422	N

[a] w, mass fraction; M, 3-nitrophthalic acid; N, 4-nitrophthalic acid; A, adduct of 3-nitrophthalic acid, 4-nitrophthalic acid with water, in which the mole ratio of the three compositions is 3:1:1.

In the phase diagrams as shown in Figs. 1 and 2, W, M, and N represent water, 3-nitrophthalic acid and 4-nitrophthalic acid, respectively. E_1 and E_2 represent the solubility of 3-nitrophthalic acid in water at 283.15 K and 333.15 K; S_1 and S_2 represent the solubility of 4-nitrophthalic acid in water at 283.15 K and 333.15 K. It can be seen from Figs. 1 and 2 that along the solubility curve E_1C_1 or E_2C_1', linking the component points of the liquid phase and wet solid phase and extended, the point of intersection of these tie-lines is the approximate solid-phase component for the compound 3-nitrophthalic acid on a wet basis. Similarly, along the solubility curve S_1C_2 or S_2C_2', linking the component points of the liquid phase and wet solid phase

and extended, the point of intersection of these tie-lines is the approximate solid-phase component for 4-nitrophthalic acid. At 283.15 K, along the solubility curve C_1C_2, linking the component points of the liquid phase and wet solid phase and extended, the point of intersection of these tie-lines is the approximate solid-phase component for adduct of 3-nitrophthalic acid, 4-nitrophthalic acid with water, in which the mole ratio of the three compositions is 3:1:1, named as *adduct A* in the present work. However, at 333.15 K, along the solubility curve $C_1'C_2'$, linking the component points of the liquid phase and wet solid phase and extended, the point of intersection of these tie-lines is the approximate solid-phase component for adduct of 3-nitrophthalic acid

Table 2
Mass fraction solubility of the ternary 4-nitrophthalic acid (1)–3-nitrophthalic acid (2)–water (3) system at 333.15 K[a]

Liquid phase		Moist solid phase		Density of liquid phase (g mL^{-1})	Solid phase
100 w_1	100 w_2	100 w_1	100 w_2		
0	6.41	0	82.37	0.9991	M
3.12	9.08	1.56	68.45	1.0134	M
5.90	10.60	2.65	65.55	1.0143	M
7.69	14.75	13.60	64.15	1.0152	M
8.43	13.55	3.69	72.24	1.0156	M + B
8.54	15.00	29.65	56.22	1.0350	B
14.62	14.86	33.82	34.26	1.0636	B
24.00	16.00	37.00	33.00	1.1125	B
32.37	17.15	39.27	29.19	1.1637	B
42.30	16.55	46.45	34.84	1.2023	B
51.02	15.80	50.25	32.86	1.2171	B
62.21	13.85	54.17	35.91	1.2041	N + B
62.83	12.00	61.00	27.99	1.1847	N
63.00	13.35	77.12	15.33	1.1710	N
63.13	11.67	80.33	5.33	1.1665	N
66.00	6.70	84.22	3.11	1.1567	N
69.82	3.36	89.50	0.73	1.2600	N
74.51	0	92.76	0	1.2737	N

[a] w, mass fraction; M, 3-nitrophthalic acid; N, 4-nitrophthalic acid; B, adduct of 3-nitrophthalic acid with 4-nitrophthalic acid, in which the mole ratio of the two compositions is 1:1.

with 4-nitrophthalic acid, in which the mole ratio of the two compositions is 1:1, named as *adduct B*.

E_1C_1 and E_2C_1' are saturation curves corresponding to the solid-phase 3-nitrophthalic acid at 283.15 K and 333.15 K, respectively; S_1C_2 and S_2C_2' are saturation curves corresponding to the solid-phase 4-nitrophthalic acid; C_1C_2 and $C_1'C_2'$ are saturation curves corresponding to the solid phase of *adduct A* and *adduct B*. C_1 is invariant point at 283.15 K, which represent the cosaturated solution of the solid phases 3-nitrophthalic acid and *adduct A*, and C_2, the cosaturated solution of the solid phases 4-nitrophthalic acid and *adduct A*. C_1' is invariant point at 333.15 K, which represent the cosaturated solution of the solid phases 3-nitrophthalic acid and *adduct B*; and C_2', the cosaturated solution of the solid phases 4-nitrophthalic acid and *adduct B*.

Fig. 1 is divided into seven regions by three solubility curves. The regions in the phase diagram are denoted as follows: I (E_1MC_1), crystalline region of solid 3-nitrophthalic acid; II (S_1NC_2), crystalline region of solid 4-nitrophthalic acid; III ($E_1WS_1C_2C_1$), unsaturated region; IV (AMC_1), crystalline region of solid 3-nitrophthalic acid and *adduct A*; V (C_1AC_2), crystalline region of solid *adduct A*; VI (C_2AN), crystalline region of solid 4-nitrophthalic acid and *adduct A*; VII (MNA), coexistent region of three solid phases 3-nitrophthalic acid, 4-nitrophthalic acid and *adduct A*. The phase diagram of the ternary system 3-nitrophthalic acid–4-nitrophthalic acid–water at 333.15 K is divided into six regions by three solubility curves. The regions in the phase diagram are denoted as follows: I (E_2MC_1'), crystalline region of solid 3-nitrophthalic acid; II (S_2NC_2'), crystalline region of solid 4-nitrophthalic acid; III ($WE_2C_1'C_2'S_2$), unsaturated region; IV (BMC_1'), crystalline region of solid 3-nitrophthalic acid and *adduct B*; V ($C_1'C_2'B$), crystalline region of solid *adduct B*; VI (NBC_2'), crystalline region of solid 4-nitrophthalic acid and *adduct B*. Figs. 1 and 2 also show that *adduct A* is an asymmetric double salt, whereas *adduct B* is a symmetric double salt.

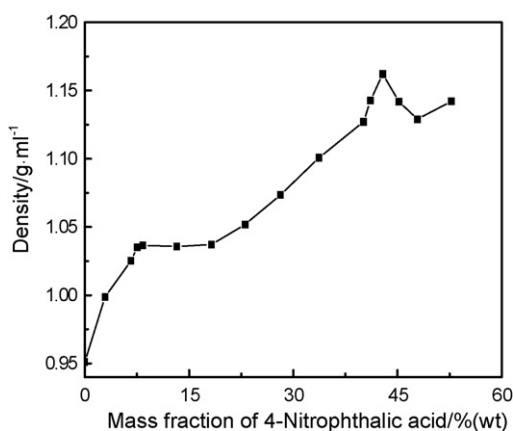Figs. 1 and 2 further illustrate the temperature dependence of the phase diagram for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system. When the temperature increases from 283.15 K to 333.15 K, the solubility of 3-nitrophthalic acid and 4-nitrophthalic acid in water increase significantly, and the invariant point moves upward. However, the phase diagrams of the ternary system are different at various temperatures. With an increase in temperature, the adduct formed in the ternary system changes from *adduct A* to *adduct B*.

On the basis of data collected in Tables 1 and 2, relationship between the density of the equilibrium liquid phase and the 4-nitrophthalic acid concentration values expressed in mass concentrations (Figs. 3 and 4) are found. The density of equilibrium liquid phase depends on total content of 3-nitrophthalic acid and 4-nitrophthalic acid. The minimum point corresponds to the lowest total content of 3-nitrophthalic acid and 4-nitrophthalic acid, and vice versa. The inflection points in Figs. 3 and 4 correspond to the cosaturated points in Figs. 1 and 2. It can be seen from Figs. 3 and 4 that two adducts are formed in the ternary system at 283.15 K and 333.15 K, respectively.

The solubility data and the ternary phase diagram for the system 3-nitrophthalic acid–4-nitrophthalic acid–water at 283.15 K and 333.15 K can provide the fundamental basis for preparation of 3-nitrophthalic acid from 3-nitrophthalic acid and 4-nitrophthalic acid mixtures. The mass ratio of 3-nitrophthalic acid and 4-nitrophthalic acid is not less than 3:7, and the 3-nitrophthalic acid and 4-nitrophthalic acid mixture must be added into much water in order to obtain pure 3-nitrophthalic acid.

4. Conclusion

The solid–liquid phase equilibrium and the solubility data for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 283.15 K and 333.15 K were determined experimentally. The solid–liquid phase diagrams were constructed. In addition, the densities of equilibrium liquid phase were obtained. The solid phase was confirmed by Schreinemakers' method of wet residues. Three solid phases were formed in the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water
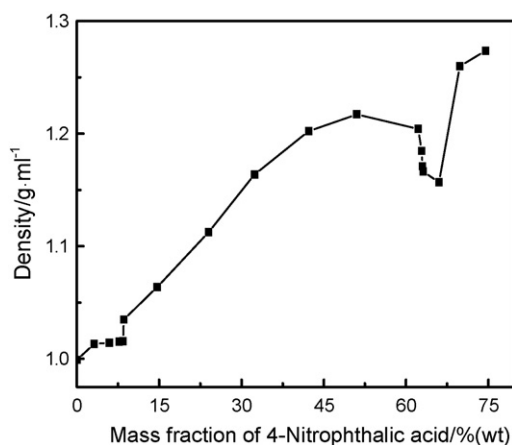

Fig. 4. Density value–composition relationship diagram for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 333.15 K: (■), experimental data point; (—), experimental relationship diagram.

Fig. 3. Density value–composition relationship diagram for the ternary 3-nitrophthalic acid–4-nitrophthalic acid–water system at 283.15 K: (■), experimental data point; (—), experimental relationship diagram.

system at 283.15 K, which corresponded to 3-nitrophthalic acid, 4-nitrophthalic acid and *adduct A*; while at 333.15 K, the three solids were 3-nitrophthalic acid, 4-nitrophthalic acid and *adduct B*. At each studied temperature, the phase diagram has three crystallization fields, three univariant curves and two invariant point. With an increase in temperature, the adduct formed in the ternary system changes from *adduct A* to *adduct B*. The *adduct A* or *adduct B* has a bigger crystallization field than 3-nitrophthalic acid and 4-nitrophthalic acid.

Acknowledgments

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