Solid−Liquid Equilibria for Benzoic Acid + *p*-Toluic Acid + Chloroform, Benzoic Acid + *p*-Toluic Acid + Acetic Acid, and Terephthalic Acid + Isophthalic Acid + *N,N*-Dimethylformamide

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Using a laser monitoring observation technique, solid−liquid equilibria in the systems benzoic acid + *p*-toluic acid + chloroform at 303.15 K, benzoic acid + *p*-toluic acid + acetic acid at 343.15 K, and terephthalic acid + isophthalic acid + *N,N*-dimethylformamide at 343.15 K have been investigated. The solid−liquid equilibrium phase diagrams for the three systems are plotted on the basis of the experimental data obtained.

Introduction

With the development of the polyester industry, large amounts of oxidation residues have been created during the manufacture of purified terephthalic acid (PTA). Benzoic, *p*-toluic, terephthalic, and isophthalic acids are major components in the residues. For the sake of environmental protection and efficient utilization of natural resources, it is necessary to pay attention to the separation and recovery of these oxidation residues. In preliminary experiments, we found that benzoic acid and *p*-toluic acid can be easily dissolved in chloroform or acetic acid, whereas terephthalic acid and isophthalic acid are almost insoluble in the above two solvents but have relatively high solubility in *N,N*-dimethylformamide. Therefore, we devised a process in which benzoic acid and *p*-toluic acid were first extracted and separated by chloroform or acetic acid and terephthalic acid and isophthalic acid were subsequently separated using *N,N*-dimethylformamide as the working solvent. To separate and recover the useful components in the residue effectively, some new solid−liquid equilibrium data for the above ternary systems are required. In this work, we report such data for the systems benzoic acid + *p*-toluic acid + chloroform at 303.15 K, benzoic acid + *p*-toluic acid + acetic acid at 343.15 K, and terephthalic + isophthalic acids + *N,N*-dimethylformamide at 343.15 K and also construct the phase diagrams for the three systems.

Experimental Section

Chemicals. Reagent-grade benzoic acid, terephthalic acid (benzene-1,4-dicarboxylic acid), isophthalic acid (benzene-1,3-dicarboxylic acid), chloroform (trichloromethane), acetic acid (ethanoic acid), and *N,N*-dimethylformamide were obtained from Shanghai Reagent Co. and had stated purities of 0.995, 0.995, 0.995, 0.990, 0.995, and 0.990 mass fraction, respectively. *p*-Toluic acid (4-methylbenzoic acid) with a mass fraction of 0.997 was obtained through purifying an industrial product that had a stated mass fraction of 0.985. *p*-Toluic acid was first extracted by chloroform at room temperature so that terephthalic acid, isophthalic acid, and phthalic acid were removed to give a purer sample of *p*-toluic acid, and then recrystallizations were carried out in acetic acid and distilled water. The purity of *p*-toluic acid was determined using a high-performance liquid chromatograph (LC-10A, Shimadzu). Melting points of all solutes used are reported in Table 1 and compared with the literature data.[1,2] The melting point of the terephthalic acid used in this work is 0.9 K higher than that in the literature, indicating that it is of high purity.

Table 1. Melting Points of the Solutes Used for Measurements

	T_m/K	
solute	expt	lit
terephthalic acid	703.1	702.2[a]
isophthalic acid	621.2	621.2[b]
p-toluic acid	555.1	555.2[b]
benzoic acid	395.5	395.6[b]

[a] Reference 1. [b] Reference 2.

Apparatus and Procedure. Solubilities were measured using a previously published method.[3,4] The solubility apparatus consisted of a jacketed glass vessel maintained at the desired temperature by water circulated from a water bath with a thermoelectric controller (type 501, China). The jacket temperature could be maintained within ±0.02 K of the required temperature. Continuous stirring was achieved with a magnetic stir bar. A condenser was connected to the vessel to prevent loss of solvents by evaporation. A mercury-in-glass thermometer that had an uncertainty of ±0.05 K was inserted into the inner chamber of the vessel for the temperature measurement. Two solutes and a portion of solvent, weighed by an analytical balance (type TG332A, China) with an accuracy of ±0.00001 g, were placed in the glass vessel and heated at the desired temperature with continuous stirring. During the process, additional accurately known masses of solvent were injected into the vessel very slowly. A laser beam was used to monitor the dissolution process. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light-intensity display. When the last portion of the solute dissolved and solid−liquid equilibrium was achieved, the intensity of the laser beam transmitted by the vessel reached a maximum, and the final composi-

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Table 2. Solid−Liquid Equilibrium Composition of Ternary Systems

x_1	x_2	x_3
Chloroform (1) + Benzoic Acid (2) + *p*-Toluic Acid (3) at 303.15 K		
0.8609	0.1391	0.0000
0.9740	0.0000	0.0260
0.9498	0.0173	0.0329
0.8875	0.0625	0.0500
0.8250	0.1164	0.0586
0.8472	0.0961	0.0567
0.8676	0.0788	0.0536
0.9159	0.0400	0.0441
0.8464	0.0965	0.0571
0.8035	0.1595	0.0370
0.8153	0.1237	0.0610
0.7891	0.1471	0.0638
0.7717	0.1688	0.0595
0.7729	0.1604	0.0657
0.7679	0.1688	0.0633
0.7862	0.1633	0.0505
0.8044	0.1567	0.0389
0.8417	0.1464	0.0119
0.8251	0.1524	0.0225
Acetic Acid (1) + Benzoic Acid (2) + *p*-Toluic Acid (3) at 343.15 K		
0.5861	0.4139	0.0000
0.8874	0.0000	0.1126
0.5452	0.4219	0.0329
0.4686	0.3752	0.1562
0.5024	0.4267	0.0709
0.4633	0.4283	0.1084
0.4216	0.4344	0.1440
0.4121	0.4352	0.1527
0.5147	0.3290	0.1563
0.5661	0.2827	0.1512
0.5791	0.2684	0.1525
0.6303	0.2221	0.1476
0.6871	0.1732	0.1397
0.7291	0.1351	0.1358
0.7640	0.1050	0.1310
0.7790	0.0922	0.1288
0.8164	0.0604	0.1232
0.8464	0.0358	0.1178
N,N-Dimethylformamide (1) + Terephthalic Acid (2) + Isophthalic Acid (3) at 343.15 K		
0.9603	0.0397	0.0000
0.8377	0.0000	0.1623
0.9119	0.0250	0.0631
0.8845	0.0191	0.0964
0.8621	0.0150	0.1229
0.8498	0.0128	0.1374
0.8430	0.0118	0.1452
0.8371	0.0105	0.1524
0.8554	0.0115	0.1331
0.8487	0.0100	0.1413
0.8345	0.0098	0.1557
0.8348	0.0096	0.1556
0.8372	0.0086	0.1542
0.8378	0.0104	0.1518
0.9443	0.0370	0.0187
0.9304	0.0314	0.0382
0.8963	0.0217	0.0820
0.8713	0.0173	0.1114
0.8363	0.0054	0.1583

tion was recorded as the solid−liquid equilibrium composition. Each experimental point took about 4 h, and some of the experiments were conducted two or three times to check the reproducibility. If repeated experiments were carried out, then the final solid−liquid equilibrium value obtained was the average of the closest experimental points. To verify the accuracy of the experiments, we performed one other experiment in which the solubility of benzoic acid in water was determined. The experimental value differed from the literature value[5] by less than 1%. In this work, the solid−liquid equilibrium data had an uncertainty of 0.0005 mole fraction.

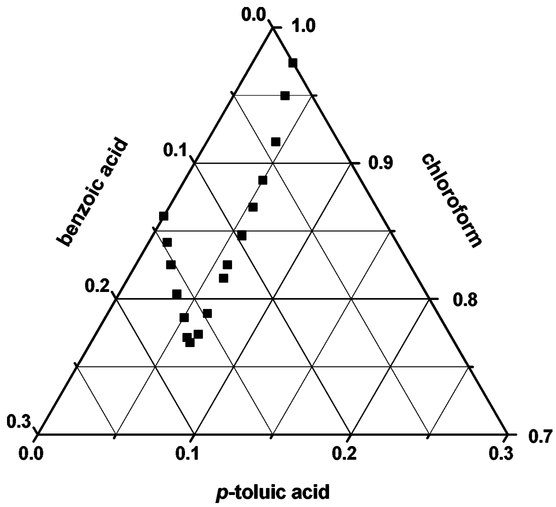

Figure 1. Ternary phase diagram for the system chloroform + benzoic acid + *p*-toluic acid at 303.15 K.

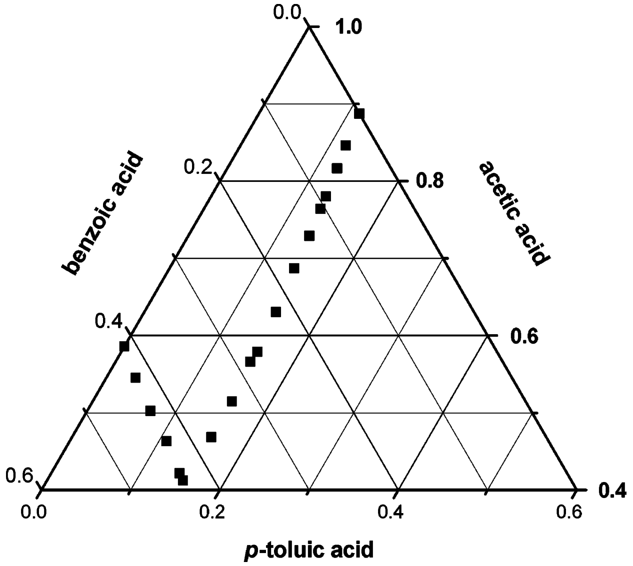

Figure 2. Ternary phase diagram for the system acetic acid + benzoic acid + *p*-toluic acid at 343.15 K.

Results and Discussion

Measured solid−liquid equilibrium data for the systems benzoic acid + *p*-toluic acid + chloroform at a temperature of 303.15 K, benzoic acid + *p*-toluic acid + acetic acid at 343.15 K, and terephthalic acid + isophthalic acid + *N,N*-dimethylformamide at 343.15 K are listed in Table 2. Figures 1 to 3 show the phase diagrams for the three systems in terms of the data in Table 2. The binary solubilities of *p*-toluic acid in chloroform and in acetic acid and terephthalic acid and isophthalic acid in *N,N*-dimethylformamide are in close agreement with the values in our previous paper.[3,4] In the benzoic acid + *p*-toluic acid + chloroform system, the three-phase point ($f = 0$) is very close to an experimental point, with contents of benzoic acid, *p*-toluic acid, and chloroform in the equilibrium solution of 0.7679, 0.1688, and 0.0633, respectively. On the left-hand side of the three-phase point, benzoic acid can be separated from the mixture of benzoic acid + *p*-toluic acid using chloroform as a separating solvent at relatively low temperatures, whereas on the right-hand side, *p*-toluic acid is obtained. Compared with the system benzoic acid + *p*-toluic acid + chloroform, the contents of benzoic acid and *p*-toluic acid in the system benzoic acid + *p*-toluic acid

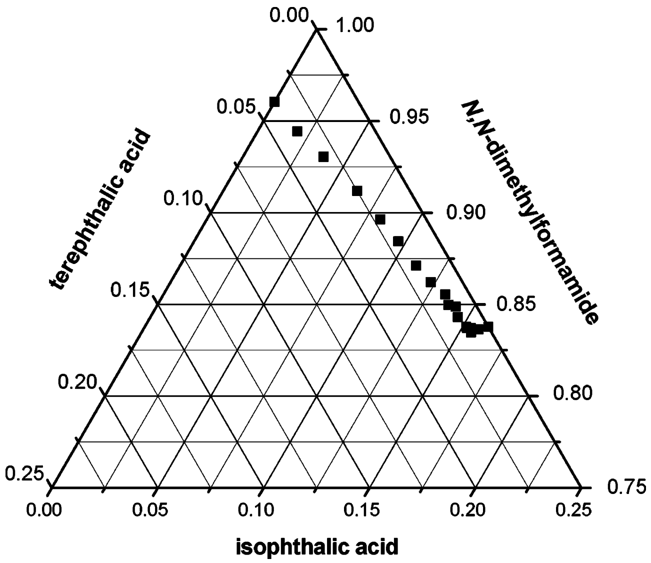

Figure 3. Ternary phase diagram for the system *N,N*-dimethylformamide + terephthalic acid + isophthalic acid at 343.15 K.

+ acetic acid at 343.15 K are much higher, indicating that acetic acid is a better separating solvent. The three-phase point ($f = 0$) for the system benzoic acid + *p*-toluic acid + acetic acid is very close to an experimental point with contents of benzoic acid, *p*-toluic acid, and acetic acid of 0.4352, 0.1527, and 0.4121, respectively. By means of concentration, pure benzoic acid or *p*-toluic acid can be obtained on the left-hand or right-hand side of the three-phase point, respectively. It is clear from Figure 3 that the content of terephthalic acid is always low in all experiments and that the three-phase point moves closer to the right-hand side, which indicates that separation from the ternary mixture containing terephthalic acid, isophthalic acid, and *N,N*-dimethylformamide is easy for isophthalic acid but difficult for terephthalic acid. For the system terephthalic acid + isophthalic acid + *N,N*-dimethylformamide at 343.15 K, the composition of the three-phase point is close to 0.8345, 0.0098, and 0.1557 for *N,N*-dimethylformamide, terephthalic acid, and isophthalic acid, respectively.

On the basis of the ternary phase diagrams discussed above, it can be concluded that pure benzoic acid, *p*-toluic acid, and isophthalic acid can be recovered from oxidation residues.

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