J. Chem. Thermodynamics 105 (2017) 21–29

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Determination and modeling of binary and ternary solid-liquid phase equilibrium for the systems formed by 3,5-dinitrobenzoic acid, *m*-nitrobenzoic acid and acetone

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ARTICLE INFO

Article history:
Received 23 August 2016
Received in revised form 25 September 2016
Accepted 1 October 2016
Available online 4 October 2016

Keywords:
m-Nitrobenzoic acid
3,5-Dinitrobenzoic acid
Acetone
Solubility
Solid-liquid phase equilibrium
Phase diagram

ABSTRACT

The solubility of 3,5-dinitrobenzoic acid in acetone at the temperatures ranging from (283.15 to 318.15) K and the mutual solubility of the ternary *m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid + acetone system at (283.15, 298.15 and 313.15) K were determined experimentally by using the isothermal saturation method under atmosphere pressure (101.2 kPa). Three isothermal ternary phase diagrams were constructed according to the measured mutual solubility data. In each ternary phase diagram, there was one co-saturated point, two boundary curves, and three crystalline regions. The modified Apelblat equation, λh equation, NRTL model and Wilson model were used to correlate the solubility of 3,5-dinitrobenzoic acid in acetone; and the NRTL and Wilson models, the mutual solubility for the ternary *m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid + acetone system. The value of root-mean-square deviation (*RMSD*) was 8.53×10^{-4} for the binary system of 3,5-dinitrobenzoic acid + acetone; and the largest value of *RMSD* was 81.08×10^{-4} for the ternary system.

1. Introduction

3,5-Dinitrobenzoic acid (CAS No. 99-34-3) and *m*-nitrobenzoic acid (CAS No. 121-92-6) are all important pharmaceutical intermediates and have been widely used in many fields. 3,5-Dinitrobenzoic acid is applied to synthesize several kinds of drug molecules in pharmaceutical industry, such as sulfa chrysoidine and ampicillin [1–2]. *m*-Nitrobenzoic acid is used for production of agricultural chemicals and dyes, in particular for the synthesis of procaine hydrochloride, procaine ammonium salts and amino-nitro benzoic acid [3–6]. It reports that benzoic acid reacts with a three mole ratio of the $BF_3{\cdot}N_2O_5$ complex in carbon tetrachloride in 36 h at 70 °C to form 3,5-dinitrobenzoic acid (70% yield) and *m*-nitrobenzoic acid (9.3% yield) [7]. At present, 3,5-dinitrobenzoic acid is mainly prepared through nitration of benzoic acid by mixed nitric acid and sulphuric acid [8–11]. During the production process of 3,5-dinitrobenzoic acid, however, the *m*-nitrobenzoic acid is also generated as by-product. The mixture of 3,5-dinitrobenzoic acid and *m*-nitrobenzoic acid should be separated before further reaction and preparation of single pure compound. Thus, it is a necessary step to separate the mixture of 3,5-dinitrobenzoic acid and *m*-nitrobenzoic acid in industry.

Solvent crystallization is commonly employed as an essential separation and purification step. The solubility of solid compound in solvents plays a significant role for understanding the (solid + liquid) equilibrium (SLE) in the development of a crystallization process. Solvent crystallization is effective for nitrobenzoic acid purification. Pure *m*-nitrobenzoic acid or 3,5-dinitrobenzoic acid can be separated from the crude product by repeated recrystallization from solvents, such as water, alcohol, a mixture of alcohol and water, acetone and so on [6,12]. During the process of our study, we notice that acetone is a suitable solvent in separating the two products. It is well known that the separation process of *m*-nitrobenzoic acid and 3,5-dinitrobenzoic acid mixture via solvent crystallization is based on the solid-liquid phase equilibrium and the phase diagram for the ternary system of *m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid + acetone. In previous works, the solubility of *m*-nitrobenzoic acid in acetone is reported [13]. However, the solubility of 3,5-dinitrobenzoic acid in acetone and the mutual solubility for the ternary systems cannot be found in the literatures. In order to enrich the solubility data and provide the detailed fundamental data for engineering fields, the objectives of this investigation are to (1) determine the solubility of 3,5-dinitrobenzoic acid in acetone at elevated temperatures;

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http://dx.doi.org/10.1016/j.jct.2016.10.004
0021-9614/

(2) determine the solid-liquid phase equilibrium and construct the phase diagram for the ternary system of *m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid + acetone at different temperatures; and (3) correlate the binary and ternary solid-liquid phase equilibrium with different thermodynamic models.

2. Experimental section

2.1. Materials and apparatus

3,5-Dinitrobenzoic acid and *m*-nitrobenzoic acid with mass fraction of 0.985 and 0.981 were purchased from Beijing Ouhe Chemical Technology Co., Ltd. They were crystallized three times in acetone, respectively. The final purities of 3,5-dinitrobenzoic acid and *m*-nitrobenzoic acid used for solubility determination were 0.993 and 0.995 in mass fraction, which were further confirmed by a high performance liquid chromatography (HPLC, Agilent-1260). Analytical grade acetone provided by Sinopharm Chemical Reagent Co., Ltd., China was used directly in solubility determination without further purification. The detailed information of the materials employed in this work was collected and tabulated in Table 1.

The experimental apparatus for determination of solid-liquid phase equilibrium used in this work was shown graphically in Fig. 1. It contained a 100 ml jacketed glass vessel, a magnetic stirrer and a circulating water system employed to control the system temperature. The temperature of circulating water was controlled by a smart thermostatic water bath (Neslab, model RTE-101) with a standard uncertainty of 0.02 K. A condenser was connected to the jacketed glass vessel to prevent the solvent from volatizing. Before experiment, the reliability of experimental apparatus was verified by determining the solubility of benzoic acid in toluene [14,15]. The mass of solvent, solute, equilibrium liquid phase and equilibrium wet solid phase was determined by an analytical balance (model CPA225D), which had a standard uncertainty of 0.0001 g and was provided by Satorius Scientific Instrument (Beijing, China).

2.2. Experimental procedure

In the present work, the solid-liquid phase equilibrium were established by using the isothermal saturation method [14–17], and the solubility of 3,5-dinitrobenzoic acid and/or *m*-nitrobenzoic acid in acetone were analyzed by a high-performance liquid chromatography (Agilent-1260). Excess 3,5-dinitrobenzoic acid or (*m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid) mixture was introduced into the jacketed glass vessel filled with about 60 ml acetone. For the ternary system of *m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid + acetone, initial solutions were prepared with the relevant amounts being chosen to vary the mass ratio of *m*-nitrobenzoic acid/3,5-dinitrobenzoic acid from 0 to 1. The solution was agitated

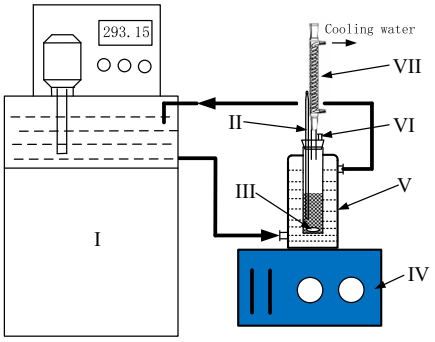

Fig. 1. Schematic diagram of experimental apparatus: I, smart thermostatic water bath; II, mercury-in-glass thermometer; III, magnetic stirrer; IV, stirrer controller; V, jacketed glass vessel; VI, sampling port; VII, condenser.

continuously using the magnetic stirrer at a speed of 120 rpm. In order to obtain equilibrium time of the investigated system, the liquid phase was taken out at an interval of 1 h by using a 5 ml syringe connected with a 0.2 μm pore filter, and analyzed with the high-performance liquid chromatography (HPLC). The solution was assumed to be in equilibrium if the composition of the liquid phase became constant. Analytical results showed that it took about 15 h to arrive at equilibrium for the investigated system. Once the studied system reached equilibrium, the magnetic stirring was stopped to allow any solid(s) to precipitate from the solution. Then 3 ml of the equilibrium liquid phase were got out with the 5 ml syringe attached with a preheated or precooled filter (PTFE 0.2 μm). The sample and corresponding solid phase adhering a little amount of saturated liquid phase were transferred into a 25 ml volumetric flask, diluted to 25 ml with acetone, and then analyzed with the high performance liquid chromatography (HPLC). Each analysis was carried out three times to check the repeatability and three samples were taken for each equilibrium solution at a certain temperature. All the final solubility data were the average value of three measurements. During the experiment, the atmosphere pressure was about 101.2 kPa.

In this work, the Schreinemakers' method of wet residue [18–20] was used to investigate the ternary systems of *m*-nitrobenzoic acid + 3,5-dinitrobenzoic acid + acetone. Here this method is described in briefly. In ternary solid-liquid phase equilibrium, the composition of the solid phase is often determined indirectly, or the adhering mother liquid must be removed completely from the solids, which is very difficult to achieve. In terms of the Schreinmakers' method of wet residue [18–20], once a solid-liquid system reaches equilibrium, tie-line connecting the saturated liquid phase and solid phase represents the intermediate composition of varies amounts of liquid and solid phases. Thus connecting a pair of points representing saturated liquid and wet residue, composition point of the pure solid is on the extended line. Repeat the work for several times, we can obtain such pairs of

Table 1
Source and purity of the materials used in this work.

Chemicals	Molar mass $g \cdot mol^{-1}$	Melting point K	Melting enthalpy $kJ \cdot mol^{-1}$	Density $kg \cdot m^{-3}$	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
3,5-dinitrobenzoic acid	167	414.3[a]	19.33[a]	1498[c]	Beijing Ouhe Chemical	0.985	Crystallization	0.993	HPLC[f]
m-nitrobenzoic acid	212.12	480.4[b]	22.8[b]	1688[d]	Technology Co., Ltd.	0.981		0.995	HPLC
acetone	58.08			789.9[e]	Sinopharm Chemical Reagent Co., Ltd., China	0.995	None	0.995	GC[g]

[a,b,c,e] *m*-NBA, *m*-nitrobenzoic acid.
[d] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2016 ACD/Labs).
[f] high performance liquid chromatography.
[g] Gas chromatography.