Equilibrium Solubility of 3- and 4-Nitrophthalic Acids in Water

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The equilibrium solubility of 3- and 4-nitrophthalic acids in water was measured experimentally using Schreinemaker's wet residue method at temperatures ranging from (285.15 to 348.15) K at atmospheric pressure. The solubility of 3- and 4-nitrophthalic acids in water increased with the increase of temperature. The experimental solubility is correlated by an empirical equation. The calculated values via the empirical equation agreed well with experimental results for 3- and 4-nitrophthalic acids.

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.[1,2] They are in general produced by nitration of phthalic anhydride with concentrated sulfuric acid.[3,4] The isomeric mixtures are formed in various proportions of 3- and 4-nitrophthalic acids with this method. In recent years, many studies have been made to purify 3- or 4-nitrophthalic acids and to separate them from the isomeric mixtures.[5,6] During the separation process, it is necessary to know the solubility of 3- and 4-nitrophthalic acids in water. The optimization of process conditions is closely related to the solubility of 3- and 4-nitrophthalic acids in water. Although the solubility of 3- and 4-nitrophthalic acids in water is very important for their separation process, previous solubility data reported are sparse.[7] Recently, S. Wang and co-workers measured the solubility of 3-nitrophthalic acid in different solvents using a synthetic method.[8]

The solubility of 4-nitrophthalic acid in water has not been reported in the literature. In this work, the equilibrium solubilities of the systems of 3-nitrophthalic acid + water and 4-nitrophthalic acid + water are systematically determined using Schreinemaker's wet residue method[9] in the temperature range from (283.15 to 348.15) K at atmospheric pressure and correlated using the empirical equation.

Experimental Section

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 $< 5\ \mu S \cdot cm^{-1}$).

Apparatus and Procedure. A 125 mL Erlenmeyer flask is filled with 50 mL of deionized water and placed into a constant-temperature bath. The water temperature is controlled by a constant-temperature water bath (Neslab, model RTE-101) recirculated through a copper coil in the water bath with an uncertainty of 0.01 K. A condenser is connected to the flask to prevent the water from evaporating. The water is stirred using a Teflon-coated magnetic stirring bar. Excess solute is placed in the flask and allowed to equilibrate in a constant-temperature water bath at a given temperature for at least 3 days. Ten minutes prior to sampling, stirring is ceased to allow any solid phase to settle. Attainment of equilibrium is verified both by repetitive measurements after a minimum of 3 additional days and by approaching equilibrium from supersaturation by preequilibrating the solutions at a higher temperature.

Analysis. Aliquots of saturated 3- or 4-nitrophthalic acid solutions are transferred through a coarse filter into a tarred volumetric flask. The concentration of 3- or 4-nitrophthalic acid 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 consisted 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. Each analysis is repeated three times, and the average value of the three measurements is considered as the final value of the analysis.

Results and Discussion

Measured solubilities of 3- and 4-nitrophthalic acids in water are presented in Table 1. The phase diagrams for the systems 3-nitrophthalic acid + water and 4-nitrophthalic acid + water are shown in Figures 1 and 2, respectively. It can be seen from Figures 1 and 2 that the solubility of 3-nitrophthalic acid is small at studied temperatures. However, when the nitro is in the para position of the phenyl ring (4-nitrophthalic acid), the nitro is responsible for some extent of the steric effect and the conjugate effect in the molecule, which make the electrons in 4-nitrophthalic acid more disperse than in 3-nitrophthalic acid.[10] As a result, the solubility of 4-nitrophthalic acid in water is larger than that of 3-nitrophthalic acid at the same temperature.

The measured solubility of 3-nitrophthalic acid in this work is smaller than that reported in the literature (see Figure 1).[8] In order to illustrate the difference between the two sets of solubility data, we determine again the solubility of 3-nitrophthalic acid in water by a synthetic method described in ref 8. The solubility of 3-nitrophthalic acid in water at 298.21 K is $1.789 \cdot 10^{-3}$ (mole fraction) and at 348.16 K is $17.19 \cdot 10^{-3}$ (mole fraction). The experimental solubility shows good agreement with the results reported in ref 8. However, when the saturated solutions are placed in a thermostat at 298.21 K or 348.16 K,

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10.1021/je7002594 CCC: $37.00
Published on Web 08/11/2007

Table 1. Mole Fraction Solubility of 3- and 4-Nitrophthalic Acids (x) in Water[a]

	3-nitrophthalic acid			4-nitrophthalic acid		
	liquid phase		solid phase	liquid phase		solid phase
T/K	$x_e \cdot 10^3$	$x_c \cdot 10^3$		x_e	x_c	
285.15	0.7741 ± 0.0002	0.6701	3-nitrophthalic acid	0.08696 ± 0.00005	0.08702	4-nitrophthalic acid
292.15	0.9836 ± 0.0004	0.9842	3-nitrophthalic acid	0.1031 ± 0.0004	0.1032	4-nitrophthalic acid
298.15	1.412 ± 0.005	1.331	3-nitrophthalic acid	0.1175 ± 0.0006	0.1177	4-nitrophthalic acid
306.15	1.889 ± 0.003	1.963	3-nitrophthalic acid	0.1372 ± 0.0007	0.1372	4-nitrophthalic acid
313.15	2.604 ± 0.007	2.674	3-nitrophthalic acid	0.1532 ± 0.0002	0.1542	4-nitrophthalic acid
320.15	3.525 ± 0.002	3.570	3-nitrophthalic acid	0.1715 ± 0.0008	0.1707	4-nitrophthalic acid
327.15	4.674 ± 0.006	4.675	3-nitrophthalic acid	0.1877 ± 0.0004	0.1863	4-nitrophthalic acid
333.15	5.809 ± 0.005	5.807	3-nitrophthalic acid	0.1996 ± 0.0008	0.1987	4-nitrophthalic acid
339.15	7.130 ± 0.004	7.123	3-nitrophthalic acid	0.2111 ± 0.0007	0.2100	4-nitrophthalic acid
344.15	8.473 ± 0.006	8.369	3-nitrophthalic acid	0.2180 ± 0.0003	0.2185	4-nitrophthalic acid
348.15	9.555 ± 0.008	9.468	3-nitrophthalic acid	0.2223 ± 0.0005	0.2247	4-nitrophthalic acid

[a] x_e, experimental values; x_c, calculated values.

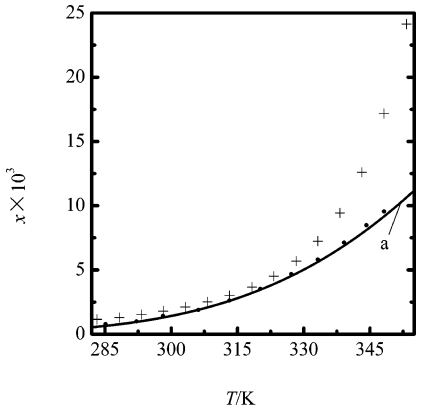

Figure 1. Solubility, x, of 3-nitrophthalic acid in water at different temperatures: ●, experimental data; —, calculated values; +, ref 8.

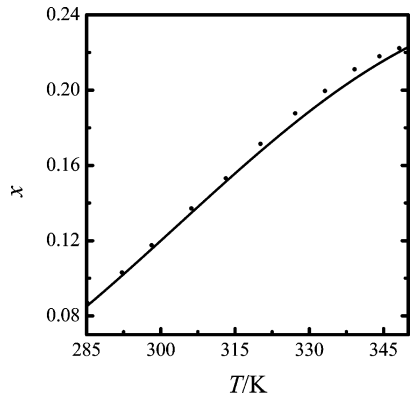

Figure 2. Solubility of 4-nitrophthalic acid in water: ●, experimental data; —, calculated values.

4 h later, white crystals appear in the system. The 3-nitrophthalic acid contents are $1.422 \cdot 10^{-3}$ (mole fraction) and $9.560 \cdot 10^{-3}$ (mole fraction), respectively, which agree well with those of the present work. It can be seen that a supersaturated solution is formed during Wang's experiments by the synthetic method.

The experimental values are correlated by an empirical equation[11]

$$\ln(x) = A + \frac{B}{(T/\mathrm{K})} + C \ln(T/\mathrm{K}) \qquad (1)$$

where A, B, and C are parameters; T is the absolute temperature; and x represents the solubility of the solute 3- or 4-nitrophthalic acids in water in mole fraction. The regressed values of A, B, and C together with the root-mean-square deviations (rmsd's) are given in Table 2. The rmsd is defined as

Table 2. Parameters of Equation 1 for 3- and 4-Nitrophthalic Acids in Water

solute	A	B	C	σ_x
3-nitrophthalic acid	109.51	$-8.93 \cdot 10^3$	−15.13	$6.52 \cdot 10^{-5}$
4-nitrophthalic acid	144.25	$-8.08 \cdot 10^3$	−20.94	$1.04 \cdot 10^{-3}$

$$\sigma_x = \left[\frac{1}{N}\sum_{i=1}^{N}(x_{ci} - x_i)^2\right]^{1/2} \qquad (2)$$

The calculated solubilities of 3- and 4-nitrophthalic acids are listed in Table 1 and plotted in Figures 1 and 2. The results indicate that the calculated values via an empirical equation agree well with experimental results for both 3-nitrophthalic acid and 4-nitrophthalic acid.

Acknowledgment

We appreciate the editors and the anonymous reviewers for their constructive suggestions.

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Received for review May 9, 2007. Accepted June 25, 2007. We thank the High Education Natural Science Foundation of Jiangsu Province (Grant No. HK051087), the Jiangsu Provincial Natural Science Foundation (BM2006549), and the Open Project Program of the Key Laboratory of Physical Chemistry, Yangzhou University, China, for their support.

JE7002594