Solubility of 3-Nitrophthalic Acid in Different Solvents between 278 K and 353 K

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The solubility of 3-nitrophthalic acid in water, methyl acetate, ethyl acetate, butyl acetate, ethyl formate, tetrahydrofuran, acetone, and 1,4-dioxane between 278 K and 353 K were measured using a laser monitoring observation technique. Results of these measurements were correlated with a semi-empirical equation. For the eight solvents studied, the data are well fitted with a semi-empirical equation.

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Introduction

3-Nitrophthalic acid (CAS Registry No. 603-11-2) is a white or almost white crystalline powder and a useful chemical for an intermediate for the synthesis of corrosion inhibitors, medicines, and agrochemicals. To determine the proper solvent and to design an optimized crystallization process, it is necessary to know its solubility in different solvents. In this paper, the solubility of 3-nitrophthalic acid in water, methyl acetate, ethyl acetate, butyl acetate, ethyl formate, tetrahydrofuran, acetone, and 1,4-dioxane between 278 K and 353 K was measured using a laser monitoring observation technique at atmospheric pressure. The method employed in this work was classed as a synthetic method, which was much faster and more reliable than the analytical method.[1]

Experimental Section[1]

Materials. 3-Nitrophthalic acid used during the solubility measurements had a mass purity of 0.994 and was purchased from Zhe Jiang Lianhe Chemical Technology Co., Ltd. Other reagents are analytical research grade reagents from Shanghai Chemical Reagent Co.

Apparatus and Procedure. The solubility of 3-nitrophthalic acid was measured using an apparatus similar to that described in the literature[2−6] and described briefly here. A 200 mL jacketed vessel was used to determine the solubility. The temperature in the vessel was maintained at the desired value by continuous forced water circulation from a thermostat (temperature uncertainty of ± 0.05 K). A mercury-in-glass thermometer (uncertainty of ± 0.05 K) was used for the measurement of the temperature in the vessel. The dissolution of the solute was examined by the laser beam penetrating the vessel. To prevent the evaporation of the solvent, a condenser vessel was introduced. The masses of the samples and solvents were determined using an analytical balance (Sartorius CP124S, Germany) with an uncertainty of ± 0.1 mg.

Predetermined excess amounts of solvent and 3-nitrophthalic acid of known mass were placed in the inner chamber of the vessel. The contents of the vessel were stirred continuously at the required temperature. In the early stage of the experiment, the laser beam was decreased by the undissolved particles of 3-nitrophthalic acid in the solution. As the particles of the solute dissolved, the intensity of the laser beam increased gradually. When the solute dissolved completely, the solution was clear, and the laser intensity reached maximum. Then additional solute of known mass {about (1 to 3) mg} was introduced into the vessel. This procedure was repeated until the penetrated laser intensity could not return a maximum, or in other words, the last addition of solute could not dissolve completely. The interval of addition was 90 min. The total amount of the solute consumed was recorded. The same solubility experiment was conducted three times, and the mean values were used to calculate the mole fraction solubility x_1 based on

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m_1 and m_2 represent the mass of the solute and solvent, respectively, and M_1 and M_2 are the molecular weight of the solute and solvent, respectively.

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Results and Discussion

The solubility data of 3-nitrophthalic acid in water, methyl acetate, ethyl acetate, butyl acetate, ethyl formate, tetrahydrofuran, acetone, and 1,4-dioxane between 278 K and 353 K are presented in Table 1. The temperature dependence of 3-nitrophthalic acid solubility in pure solvents is described by the modified Apelblat equation, which is a semi-empirical equation:[7−9]

$$\ln x_1 = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \tag{2}$$

where x_1 is the mole fraction solubility of 3-nitrophthalic acid; T is the absolute temperature; and A, B, and C are the dimensionless parameters. The calculated solubility values of 3-nitrophthalic acid are also given in Table 1. The values of parameters A, B, and C and the root mean square deviations (rmsd) are listed in Table 2. The rmsd is defined as

$$\mathrm{rmsd} = \left[\frac{\sum_{j=1}^{N} (x_{1,j} - x_{1,j}^{\mathrm{calc}})^2}{N-1}\right]^{1/2} \tag{3}$$

where N is the number of experimental points, $x_{1,j}^{\mathrm{calc}}$ represents the solubility calculated from eq 2, and $x_{1,j}$ represents the experimental solubility values.

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Table 1. Mole Fraction Solubility of 3-Nitrophthalic Acid in Pure Solvents

T/K	100 x_1	100($x_1 - x_1^{calc}$)	T/K	100 x_1	100($x_1 - x_1^{calc}$)
		Water			
283.18	0.1152	−0.0041	323.18	0.4508	−0.0082
288.26	0.1295	−0.0029	328.31	0.5691	−0.0176
293.27	0.1521	0.0022	333.22	0.7242	−0.0269
298.21	0.1790	0.0061	338.18	0.9433	−0.0315
303.19	0.2110	0.0077	343.17	1.2592	−0.0213
308.22	0.2505	0.0067	348.16	1.7191	0.0201
313.19	0.3002	0.0037	353.28	2.4142	0.1215
318.29	0.3668	−0.0012			
		Methyl Acetate			
278.17	3.344	0.012	303.16	3.922	0.008
283.26	3.431	−0.003	308.22	4.071	0.013
288.27	3.535	−0.008	313.28	4.224	0.014
293.21	3.652	−0.006	318.17	4.373	0.006
298.24	3.783	0.000	323.19	4.525	−0.012
		Ethyl Acetate			
283.20	0.7926	−0.0043	313.16	1.160	−0.003
288.26	0.8467	0.0022	318.22	1.244	−0.005
293.28	0.9015	0.0046	323.16	1.337	−0.003
298.19	0.9577	0.0042	328.23	1.443	0.000
303.21	1.019	0.002	333.17	1.561	0.008
308.30	1.088	0.000			
		Butyl Acetate			
283.18	0.2433	−0.0074	323.22	0.7236	−0.0105
288.16	0.2970	−0.0007	328.24	0.7917	−0.0132
293.21	0.3532	0.0031	333.19	0.8605	−0.0143
298.19	0.4103	0.0044	338.28	0.9330	−0.0130
303.22	0.4698	0.0035	343.25	1.006	−0.008
308.26	0.5312	0.0010	348.24	1.080	0.000
313.27	0.5939	−0.0026	353.26	1.157	0.013
318.18	0.6570	−0.0067			
		Ethyl Formate			
283.17	0.2679	0.0010	308.19	0.3959	0.0013
288.18	0.2866	0.0000	313.27	0.4329	0.0016
293.21	0.3088	−0.0002	318.25	0.4729	0.0012
298.26	0.3346	0.0001	323.29	0.5173	−0.0004
303.16	0.3631	0.0007			
		Tetrahydrofuran			
278.28	20.34	−0.01	308.19	20.76	0.00
283.17	20.38	0.00	313.23	20.88	0.00
288.16	20.43	0.00	318.24	21.00	−0.01
293.21	20.50	0.01	323.16	21.14	0.00
298.29	20.57	0.00	328.19	21.29	0.00
303.28	20.66	0.00	333.17	21.45	0.00
		Acetone			
278.16	5.249	0.001	303.19	6.290	0.001
283.18	5.414	−0.002	308.32	6.570	0.002
288.27	5.604	−0.003	313.16	6.855	0.000
293.33	5.815	−0.002	318.20	7.173	−0.004
298.24	6.041	−0.001			
		1,4-Dioxane			
288.17	7.583	−0.105	323.29	13.93	−0.06
293.28	8.682	0.026	328.19	14.59	−0.09
298.31	9.705	0.088	333.18	15.21	−0.10
303.29	10.66	0.10	338.22	15.78	−0.08
308.26	11.56	0.08	343.16	16.27	−0.04
313.20	12.40	0.04	348.23	16.73	0.05
318.21	13.19	−0.01	353.32	17.12	0.17

From data listed in Tables 1 and 2, we can draw the following conclusions: (i) The solubility of 3-nitrophthalic acid increases with temperature in the eight solvents (see Figure 1). The solubility of 3-nitrophthalic acid in water is the lowest, and the solubility is largest in tetrahydrofuran. (ii) Water may be used for dilution in order to increase the yield of the product in crystallization process of 3-nitrophthalic acid. (iii) The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of 3-nitrophthalic acid. The calculated solubility shows good agreement with the experimental values.

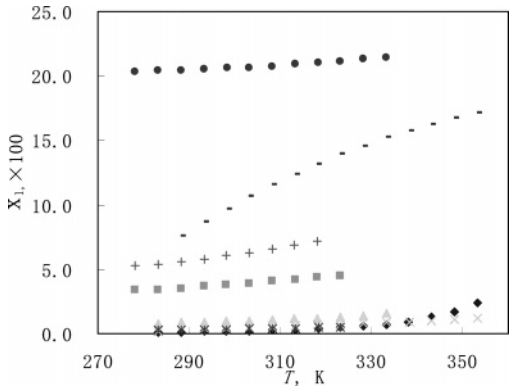


Figure 1. Mole fraction solubility of 3-nitrophthalic acid (x_1) in different solvents: ●, tetrahydrofuran (THF); −, 1,4-dioxane; +, acetone; ■, methyl acetate; ▲, ethyl acetate; ×, butyl acetate; ◆, water; ∗, ethyl formate.

Table 2. Parameters of Equation 2 for Solubility of 3-Nitrophthalic Acid in Pure Solvents

solvent	A	B	C	10^4 rmsd
water	−566.7	22621	85.03	3.58
methyl acetate	−54.07	1746	7.8873	0.97
ethyl acetate	−103.18	3427.5	15.275	0.42
butyl acetate	148.35	−9015.2	−21.697	0.87
ethyl formate	−141.71	4843.3	21.02	0.10
tetrahydrofuran	−19.492	735.44	2.7106	0.42
acetone	−79.296	2807.6	11.772	0.21
1,4-dioxane	178.46	−9552.9	−26.11	8.71

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