Solubilities of Isonicotinic Acid in Sulfuric Acid + Water and 4-Methylpyridine + Sulfuric Acid + Water from (293.55 to 361.45) K

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The solubilities of isonicotinic acid in sulfuric acid + water and 4-methylpyridine + sulfuric acid + water have been determined experimentally from (293.55 to 361.45) K by a dynamic method. The experimental data were correlated with the modified Apelblat equation.

Introduction

Isonicotinic acid, also named as 4-pyridinecarboxylic acid, is an important intermediate in the synthesis of antituberculosis drugs; it also can be used as anticorrosion reagent, plating additive, and photosensitive resin stabilizer.[1] The traditional synthetic methods include potassium permanganate oxidation, air oxidation, ozone oxidation, and electro-oxidation.[2] The authors have developed a new technique for electrochemical synthesis of isonicotinic acid using 4-methylpyridine as the raw material and a sulfuric acid aqueous solution as supporting electrolytes. The electrochemical oxidation method involves many advantages such as low cost and being nonpolluting.[3] In the synthesis and purification process of isonicotinic acid, it is necessary to know the solubility data of isonicotinic acid in the related solvents, but only the solubility data of isonicotinic acid in water have been reported.[4] In this study, the solubilities of isonicotinic acid in sulfuric acid + water and 4-methylpyridine + sulfuric acid + water have been measured from (293.55 to 361.45) K at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation.[5−9]

Experimental Section

Materials. High-grade sulfuric acid from Louyan Chemical Reagent Co. was used directly without further purification, and its purity was greater than 0.990 in mass fraction. 4-Methylpyridine obtained from Shanghai Chemical Reagent Co. was of analytical reagent grade and was further purified by distillation; the purity was determined by UV spectrometry (type UV-2401PC, Shimadzu Co.) to be 0.997 in mass fraction. Analytical grade isonicotinic acid obtained from Peking Biotech. Co., Ltd. was further purified by recrystallization from aqueous solutions. After filtration and drying, its purity was determined by titration to be 0.996 in mass fraction. Water used in experiments was double-distilled water.

Apparatus and Procedure. The solubility was measured by a dynamic method.[10−12] A laser monitoring observation technique[13−15] was used to determine the dissolution temperature of a solid−liquid mixture of known composition. The laser monitoring system consists of a laser, a photoelectric transformer, and a recorder. The experiments were carried out in a magnetically stirred, jacketed glass vessel (60 cm^3). A constant temperature (± 0.02 K) was maintained by circulating water through the outer jacket from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) at the required temperature. A condenser was connected with the vessels to prevent the solvents from evaporating. A mercury-in-glass thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature. The uncertainty of temperature was ± 0.05 K.

Solvents for the solubility measurement were weighed on an electronic balance (type AW120, Shimadzu Co.) The balance has a range of measurement up to 120 g, with an uncertainty of ± 0.0001 g. Before the solubility measurement, through the condenser, high-purity nitrogen (0.999995 in mass fraction, 50 $mL \cdot min^{-1}$) was fed into the solvent for 1 h to remove the dissolved oxygen. Predetermined amounts of isonicotinic acid were weighed on an electronic balance (type AW120, Shimadzu Co.) and transferred into the vessel. The contents of the vessel were heated very slowly at rates less than 2 $K \cdot h^{-1}$ with continuous stirring, and the increasing rate of temperature was controlled by a temperature-programmed (TP) technique (temperature controller type AI-708P, Xiamen Electronic Technology Co., Ltd.). In the early stage of the experiment, the laser beam was blocked by the turbidity of the solution, so the intensity of the laser beam penetrating the vessel was diminished. The intensity increased gradually along with the increase of the amount of isonicotinic acid dissolved. When the last portion of isonicotinic acid disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded as the liquidus temperature.[11] In the processes of solubility measurement, the high-purity nitrogen flowing at 1.5 $mL \cdot min^{-1}$ was maintained to prevent air from entering the vessel. Some of the solubility experiments were conducted two or three times to check the reproducibility. In this work, the uncertainty for solubility measurement is estimated to be 2.0 % at the 95 % confidence level.

Results and Discussion

To verify the reliability of the measurement, the solubilities of isonicotinic acid in water were measured, and the experimental results and the literature data are both shown in Figure 1.[16] In Figure 1, T is the absolute temperature, and x is the experimental solubility in mole fraction. It is clear from Figure 1 that the experimental results show good agreement with literature data,[4] and the deviations of the measured solubility from the literature values are less than 2.0 %.

The measured solubilities of isonicotinic acid in sulfuric acid + water at different temperatures are presented in Table 1 and

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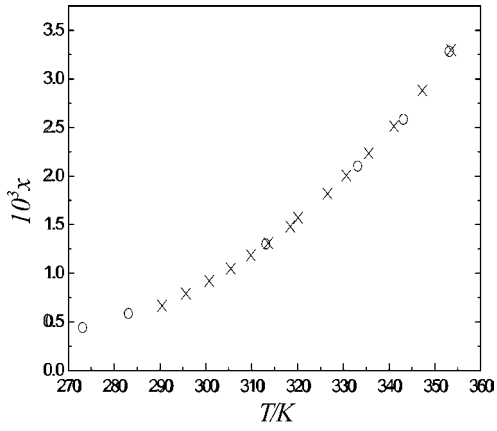

Figure 1. Mole fractions of solubility x of isonicotinic acid in water: ×, experimental data; ○, literature data.[4]

Table 1. Solubilities of Isonicotinic Acid (1) in Sulfuric Acid (2) + Water (3); x, Experimental Solubility

T/K	$10^2\,x$	$(x - x_c)/x \cdot 100$	T/K	$10^2\,x$	$(x - x_c)/x \cdot 100$
		$w_2 = 0.20$			
298.15	5.035	−0.08	340.55	5.523	−0.09
315.25	5.234	0.11	345.75	5.59	−0.04
321.95	5.311	0.11	351.45	5.659	−0.07
328.65	5.383	−0.02	356.35	5.729	0.05
334.85	5.456	−0.06	361.05	5.79	0.07
		$w_2 = 0.25$			
290.55	5.964	−0.32	332.25	6.581	−0.23
297.45	6.072	−0.36	337.45	6.649	−0.21
301.45	6.21	0.87	342.25	6.716	−0.12
312.15	6.337	0.32	347.35	6.782	−0.06
320.85	6.438	−0.05	352.35	6.852	0.09
326.85	6.514	−0.15	357.25	6.921	0.26
		$w_2 = 0.30$			
294.55	6.438	−0.22	336.15	8.265	−0.01
299.45	7.265	0.03	340.65	8.325	0.04
320.95	8.101	−0.04	346.95	8.392	0.02
326.25	8.157	0.04	351.15	8.459	0.05
331.35	8.213	0.00	355.45	8.522	−0.04

in 4-methylpyridine + sulfuric acid + water at different temperatures in Table 3, and the experimental data were correlated with the modified Apelblat equation[5−9]

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

where x is the mole fraction solubility of isonicotinic acid, T is the absolute temperature, and A, B, and C are the parameters in eq 1. The values of these parameters together with the root-mean-square deviations (rmsd values) are listed in Table 2 and Table 4. The rmsd is defined as

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

where N is the number of experimental points and x_c is the solubility calculated by eq 1. The relative deviations between the experimental value and the calculated value are also listed in Table 1. Relative deviations are calculated according to

$$\text{relative deviations} = \left(\frac{x - x_c}{x}\right) \cdot 100 \qquad (3)$$

From Tables 1 to 4, it can be found that the calculated solubilities show good agreement with the experimental data, which indicate that the modified Apelblat equation can be used to correlate the solubility data of isonicotinic acid in sulfuric acid + water and 4-methylpyridine + sulfuric acid + water systems. The overall rmsd of 32 data points for the sulfuric acid + water system at various contents of sulfuric acid in the mixed solvent is $1.1 \cdot 10^{-4}$. The overall rmsd of 31 data points for the 4-methylpyridine + sulfuric acid + water system at various contents of 4-methylpyridine in the mixed solvent is $1.3 \cdot 10^{-4}$. The experimental solubility and correlation equation in these works can be used as essential data and models to serve the synthesis and purification process of isonicotinic acid.

Table 2. Parameters of Equation 1 for Isonicotinic Acid (1) + Sulfuric Acid (2) + Water (3) System at Various Contents of Sulfuric Acid (w_2) in the Mixed Solvent

solvent	A	B	C	10^4 rmsd
$w_2 = 0.20$	−13.057	286.99	1.5982	0.402
$w_2 = 0.25$	−0.17046	−311.69	−0.27734	2.05
$w_2 = 0.30$	108.63	−5638.4	−16.215	0.892

Table 3. Solubilities of Isonicotinic Acid (1) in 4-Methylpyridine (2) + ($w_3 = 0.25$) Sulfuric Acid (3) + Water (4); x, Experimental Solubility

T/K	$10^2\,x$	$(x - x_c)/x \cdot 100$	T/K	$10^2\,x$	$(x - x_c)/x \cdot 100$
		$w_2 = 0.10$			
302.35	83.21	−0.01	336.45	83.51	0.00
312.25	83.3	0.00	342.55	83.57	0.00
319.15	83.36	0.01	347.75	83.63	0.00
325.35	83.41	0.00	355.05	83.7	0.00
330.85	83.46	0.00	359.25	83.75	0.00
		$w_2 = 0.20$			
297.65	2.578	−0.35	339.05	2.907	−0.28
309.45	2.671	0.34	344.25	2.959	−0.30
315.75	2.72	0.40	349.05	3.015	−0.13
322.15	2.762	0.07	354.05	3.077	0.07
329.05	2.821	0.04	359.15	3.146	0.38
334.35	2.863	−0.21			
		$w_2 = 0.30$			
288.25	0.5126	−0.10	339.25	0.9615	−0.04
293.55	0.6542	−0.05	344.55	1.014	−0.10
320.15	0.8124	0.07	350.25	1.082	0.00
327.55	0.8638	3.44	355.95	1.149	0.26
334.75	0.9097	−0.04	361.45	1.23	0.16

Table 4. Parameters of Equation 1 for Isonicotinic Acid (1) + 4-Methylpyridine (2) + ($w_3 = 0.25$) Sulfuric Acid (3) + Water (4) System at Various Contents of 4-Methylpyridine (w) in the Mixed Solvent

solvent	A	B	C	10^4 rmsd
$w_2 = 0.10$	−1.1576	36.989	0.1491	0.364
$w_2 = 0.20$	−34.815	1218	4.7522	0.726
$w_2 = 0.30$	−17.089	−353.09	2.3169	2.71

The graphic presentation of solubilities of isonicotinic acid in the sulfuric acid + water system is shown in Table 1 and solubilities of isonicotinic acid in the 4-methylpyridine + sulfuric acid + water system in Table 3. It can be observed from Tables 1 and 3 that the solubilities of isonicotinic acid in the sulfuric acid + water system increase as the content of the sulfuric acid increases at constant temperature and the solubilities of isonicotinic acid in 4-methylpyridine + sulfuric acid + water system decrease as the content of 4-methylpyridine increases.

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