Solubilities of Isonicotinic Acid in (Methanol, Ethanol, 1-Propanol, 2-Propanol, and 1,2-Propanediol, Respectively) from (289.65 to 358.75) K

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The solubilities of isonicotinic acid in (methanol, ethanol, 1-propanol, 2-propanol, and 1,2-propanediol, respectively) have been determined experimentally from (289.65 to 358.75) K by a dynamic method. The experimental data were correlated with the modified Apelblat equation.

Introduction

Isonicotinic acid is an important intermediate in the synthesis of anti-TB drugs and can also be used as an anticorrosion reagent, as plating additives, and as a photosensitive resin stabilizer.[1] It is manufactured through several chemical methods including potassium permanganate oxidation, air oxidation, and ozone oxidation.[2] An alternative method is the electrolytic method using 4-methylpyridine as the raw material and aqueous sulfuric acid solution as the supporting electrolytes. The reaction conditions are mild, giving high product purity, reducing waste, and nonpolluting.[3] In the synthesis and purification process of isonicotinic acid, it is necessary to know the solubility data of isonicotinic acid in some organic solvents (such as methanol, ethanol, 1-propanol, etc.), but only the solubility data of isonicotinic acid in water have been reported.[4] In this study, the solubilities of isonicotinic acid in (methanol, ethanol, 1-propanol, 2-propanol, and 1,2-propanediol, respectively) have been measured experimentally from (289.65 to 358.75) K at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation.[5−7]

Experimental Section

Materials. Analytical grade isonicotinic acid obtained from the Shanghai Huixing Biochemical Reagents Co. Ltd. was further purified by recrystallization, and its purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co. Ltd.) to be 0.990 in mass fraction. Methanol, ethanol, 1-propanol, 2-propanol, and 1,2-propanediol were of AR grade, were obtained from Shanghai Chemical Reagent Co., and had the purities 0.995, 0.997, 0.995, 0.997, and 0.990 in mass fraction, respectively.

Apparatus and Procedure. The solubilities were measured by a dynamic method[8−10] at atmospheric pressure. The laser monitoring observation technique[11−14] was used to determine the dissolution temperature of a solid−liquid mixture of known composition. The laser monitoring system consists of a laser generator, a photoelectric transformer, and a recorder. The experiments were carried out in a magnetically stirred, jacketed glass vessel (60 cm^3). A constant temperature (± 0.01 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 upright 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 ± 0.01 K.

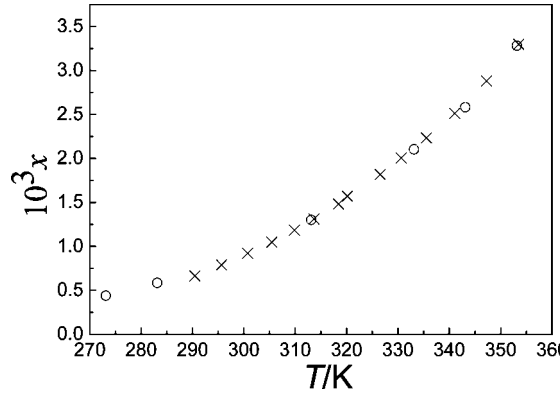

Figure 1. Solubility of isonicotinic acid in water: ○, literature data;[4] ×, experimental data.

Solvents for the solubility measurement were weighed on an electronic balance (type AW120, Shimadzu Co.) with an uncertainty of ± 0.0001 g and transferred into the vessel. Before the solubility measurement, through the condenser, high-purity nitrogen (99.9995 % by mass, 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 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

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10.1021/je800824h CCC: $40.75
Published on Web 01/16/2009

Table 1. Solubilities of Isonicotinic Acid in (Methanol, Ethanol, 1-Propanol, 2-Propanol, and 1,2-Propanediol, Respectively)

T/K	10^2x	rel dev (%)	T/K	10^2x	rel dev (%)
		Methanol			
303.85	0.07383	0.078	325.65	0.1555	−0.35
312.05	0.09721	0.23	329.05	0.1778	0.89
317.45	0.1158	0.33	332.95	0.2030	−0.0046
321.55	0.1352	−0.86	336.65	0.2318	−0.29
		Ethanol			
301.05	0.06148	−1.1	332.25	0.2194	−0.16
304.75	0.08146	0.52	336.45	0.2527	−0.38
312.25	0.1102	0.37	340.05	0.2922	0.81
318.15	0.1337	0.12	344.75	0.3455	0.82
323.75	0.1613	−0.38	350.25	0.4054	0.14
327.15	0.1881	0.75			
		1-Propanol			
289.65	0.05314	−1.8	331.15	0.2790	1.1
299.05	0.08213	1.8	336.15	0.3243	−1.4
306.85	0.1130	2.1	340.25	0.3735	0.56
313.25	0.1418	−0.34	344.65	0.4325	−1.6
318.85	0.1734	0.36	348.55	0.5113	2.3
322.95	0.2047	−0.18	354.85	0.6169	−1.4
326.95	0.2382	−1.5			
		2-Propanol			
299.35	0.05631	−0.70	335.35	0.2668	−0.75
306.75	0.08286	1.0	340.35	0.3238	−0.055
313.35	0.1184	−0.95	346.05	0.3970	0.034
322.45	0.1556	−3.9	350.05	0.4637	1.7
326.65	0.1894	−1.3	354.95	0.5369	−0.18
330.95	0.2251	0.40	358.75	0.609	0.070
		1,2-Propanediol			
301.55	0.0692	−0.80	339.55	0.2914	−1.4
309.15	0.1040	1.4	343.05	0.3362	0.60
318.35	0.1481	0.30	347.25	0.3847	−0.28
325.55	0.1807	−1.3	350.55	0.4255	−0.87
330.45	0.2152	−0.40	353.45	0.4738	0.65
335.35	0.2527	−0.40	356.85	0.5374	0.070

Table 2. Parameters of Equation 1 and the Absolute Average Deviation (AAD) for Isonicotinic Acid + (Methanol, Ethanol, 1-Propanol, 2-Propanol, and 1,2-Propanediol, Respectively) Systems

solvent	A	B	C	10^4rmsd	10^2AAD
methanol	−235.839	7773.71	35.5186	0.075	0.38
ethanol	52.5839	−6137.79	−6.92583	0.41	2.41
1-propanol	−34.3093	−1937.79	5.90569	0.45	1.26
2-propanol	23.8424	−5077.56	−2.5141	0.10	0.39
1,2-propanediol	−23.6778	−2435.66	4.29640	0.59	2.3

two or three times to check the reproducibility. The reproducibility of the measurements was 0.1 K, which corresponds to a relative deviation in composition smaller than 1.0 %.

Results and Discussion

To verify the reliability of the measurement, the solubilities of isonicotinic acid in water were measured, and the experiment results and the literature data are both shown in Figure 1. 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 methanol, ethanol, 1-propanol, 2-propanol, and 1,2-propanediol, respectively, at different temperatures are presented in Table 1, and the experimental data were correlated with the modified Apelblat equation[5−7]

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

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. The rmsd is defined as

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

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 calculated value are also listed in Table 1. Relative deviations are calculated according to

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

The absolute average deviations (AAD) are also listed in Table 2. The AAD is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_{i}^{N}\left|\frac{x_i - x_{ci}}{x_i}\right| \quad (4)$$

From Tables 1 and 2, it can be found that the calculated solubilities show good agreement with the experimental data, and the overall rmsd of 56 data points for the alcohol system is $1.6\cdot10^{-4}$. The relative deviations among all these values do not exceed 1.7 %, which indicates that the modified Apelblat equation is fit to correlate the solubility data of isonicotinic acid in five pure solvent systems.

The graphical presentation of solubilities of isonicotinic acid in alcohols is shown in Table 1. It can be observed from Table 1 that the solubilities of isonicotinic acid in (methanol, ethanol, and 1-propanol, respectively) increase as the C content of the alcohol increases, the solubilities of isonicotinic acid in (2-propanol and 1,2-propanediol, respectively) decrease as HO content of alcohol increases, and the solubilities of isonicotinic acid in 2-propanol are higher than that in 1-propanol.

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Received for review November 5, 2008. Accepted December 19, 2008.

JE800824H