2004 China
dl 5/16/2020

Solubility of Niacin in 3-Picoline + Water from (287.65 to 359.15) K

weight fraction w = gm/100 gm

Liu-Cheng Wang* and Fu-An Wang

College of Chemical Engineering, Zhengzhou University, Zhengzhou, Henan 450002, People's Republic of China

The solubilities of niacin in 3-picoline + water have been determined experimentally by a laser monitoring observation technique at temperatures from 287.65 K to 359.15 K. There is a satisfactory agreement between our solubility data at 298.15 K and the literature values. The experimental data were correlated with the modified Apelblat equation.

Introduction

Niacin, also known as nicotinic acid or vitamin B_5, is an important drug, feed additive, and intermediate with wide uses and optimum application prospects.[1] The preparative methods for obtaining niacin include ammoxidation,[2] air oxidation,[3] and electrooxidation of alkylpyridines.[4−6] In the electrochemical synthesis of niacin, electrons are used as oxidizing agents to oxidize 3-picoline to form niacin in niacin aqueous solution[4] or another medium.[5,6] Accordingly, the oxidizing agents can be obtained inexpensively and cleanly; the reaction conditions are mild, and products are of high purity. In the synthesis and purification process of niacin, it is necessary to know the solubilities data of niacin in 3-picoline + water, but the solubilities data which have been reported[4] are only at 298.15 K. In this study, the solubilities of niacin in 3-picoline + water have been measured from 287.65 K to 359.15 K at atmospheric pressure. The experimental data were correlated with the solubility equation of Apelblat modified by the author.[7]

Experimental Section

Materials. Analytical grade niacin from Peking Biotech. Co. Ltd. was further purified by recrystallizations in solutions of water. After filtration and drying, its purity was determined by titration to be 99.8% by mass. The sample was analyzed with elementary analysis, mass spectrometric detection, infrared spectrometer detection, and NMR spectrometer detection; the results are consistent with theory. Analytical grade 3-picoline from Shanghai Chemical Reagent Co. was further purified by distillation; the purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co.) to be 99.7% by mass. Water used in experiments was double distilled water.

Apparatus and Procedure. The solubilities were measured by a dynamic method.[8,9] The laser monitoring observation technique[10−12] 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 (±0.02 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.

* To whom correspondence should be addressed. E-mail: Wanglc@zzu.edu.cn. Fax: 0086-371-3887327.

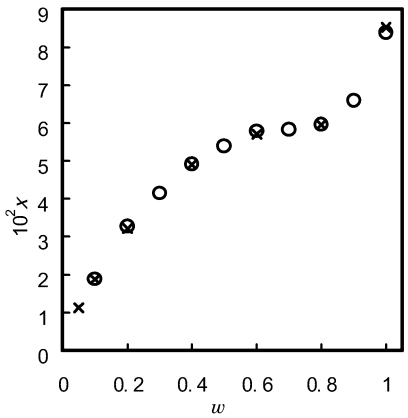

Figure 1. Mole fraction solubility x of niacin in (w)3-picoline + (1 − w)water at 298.15 K: × , this work; ○, data of Toomey.[4]

Solvents for the solubility measurement were prepared by mass using an electronic balance (type AW120, Shimadzu Co.). The balance has an accuracy of ±0.0001 g. Predetermined amounts of niacin was weighed and transferred into the vessel. The contents of the vessel were heated very slowly at rates less than 2 K·h^{-1} with continuous stirring. To improve the accuracy of the experimental results, 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 unsolved particles of niacin in the solution, so the intensity of the laser beam penetrating the vessel was lower. The intensity increased gradually along with the increase of the amount of niacin dissolved. When the last portion of niacin just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded as the liquidus temperature.[10] The partial results are compared with the literature data in Figure 1; the deviations of the solubility are less than 2%.

Results and Discussion

The measured mole fraction solubilities (x) of niacin in 3-picoline + water at different temperatures are presented in Table 1. The mass fraction (w) of 3-picoline in the

10.1021/je034165+ CCC: $27.50
Published on Web 12/02/2003

Table 1. Mole Fraction Solubilities x of Niacin in (w)3-Picoline + (1 − w)Water with w = Mass Fraction

T/K	10^2x	10^2x_c [a]	T/K	10^2x	10^2x_c
		$w = 0$			
297.15	0.2426	0.2441	331.45	0.5850	0.5817
304.45	0.2980	0.2961	335.65	0.6468	0.6428
311.15	0.3520	0.3521	340.45	0.7166	0.7194
318.15	0.4218	0.4202	345.05	0.7960	0.8002
325.95	0.5129	0.5093			
		$w = 0.05$			
287.65	1.048	1.051	325.55	1.461	1.445
291.85	1.077	1.081	333.35	1.558	1.566
297.85	1.130	1.129	339.05	1.665	1.665
305.65	1.201	1.202	346.65	1.797	1.811
312.85	1.282	1.280	353.15	1.944	1.952
320.35	1.369	1.373	359.15	2.104	2.094
		$w = 0.1$			
291.15	1.818	1.819	330.85	2.360	2.356
298.15	1.875	1.879	338.35	2.517	2.515
304.65	1.939	1.948	346.15	2.690	2.703
309.15	2.021	2.003	353.65	2.888	2.908
318.15	2.127	2.131	359.15	3.095	3.075
324.15	2.237	2.231			
		$w = 0.4$			
292.95	4.770	4.825	333.15	6.211	6.264
297.95	4.901	4.922	338.75	6.530	6.595
305.95	5.119	5.125	344.15	6.899	6.949
313.15	5.360	5.357	350.95	7.401	7.448
320.05	5.615	5.625	356.75	7.917	7.924
326.55	5.900	5.920			
		$w = 0.8$			
295.75	5.656	5.683	335.75	10.75	10.74
298.35	5.952	5.943	341.65	11.71	11.70
307.15	6.948	6.891	347.25	12.72	12.67
316.35	7.974	7.996	352.95	13.66	13.71
323.65	8.950	8.960	358.15	14.74	14.71
329.65	9.817	9.815			
		$w = 1$			
293.65	7.918	7.918	327.55	13.55	13.56
298.45	8.522	8.609	332.05	14.33	14.44
304.05	9.546	9.460	335.35	15.13	15.10
308.85	10.26	10.23	340.25	16.11	16.12
313.15	10.92	10.94	343.75	16.88	16.87
317.65	11.70	11.73	350.65	18.43	18.41
321.75	12.56	12.47			

[a] The solubility values calculated from eq 1.

solvents is 0, 0.05, 0.1, 0.4, 0.8, and 1, respectively. The temperature dependence of niacin solubility at fixed solvent composition is described by the modified Apelblat equation[7]

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

where x is the mole fraction solubility of niacin. T is the absolute temperature, and A, B, and C are the parameters in eq 1. The values of the parameters A, B, and C are presented in Table 2. The calculated solubilities x_c of niacin using eq 1 are given in Table 1. The calculated results show satisfactory agreement with the experimental data. The root-mean-square deviations (rmsd's) are presented in Table 2. The rmsd is defined as

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

where N is the number of experimental points and x_{ci} and x_i refer to the solubility values calculated from eq 1 and to the experimental solubility. The result shows that the modified Apelblat equation can be used to correlate the solubility data of niacin in 3-picoline + water. The overall rmsd of 67 data points for the niacin + water system at various contents of 3-picoline in the mixed solvent is 3.2×10^{-4}. The experimental solubility and correlation equation in this work can be used as essential data and models regarding the synthetic process of niacin.

Table 2. Parameters of Eq 1 for the Niacin + 3-Picoline + Water System at Various Contents of 3-Picoline (w) in the Mixed Solvent

w	A	B	C	10^4(rmsd)
0	−49.611	−77.307	7.7018	0.29
0.05	−95.865	3489.1	13.985	0.78
0.1	−97.687	3782.7	14.221	1.2
0.4	−114.95	4645.7	16.912	3.8
0.8	−19.898	−537.66	3.3128	3.1
1	3.5269	−1565.3	−0.12889	5.5

From the experimental data in Table 1, it can be seen that the solubility of niacin in 3-picoline is the highest and that solubility decreases with the increase of the content of water in the mixed solvent at constant temperature. The solubility of niacin in water is the lowest. The changing regularity needs to be further studied.

Literature Cited

(1) Guiot, P. M.; Ryan, A.; Scriven, E. F. V. Preparations and Applications of Nicotinic Acid and Nicotinamide. *Chim. Oggi* **1996**, *14*, 55−57.

(2) Narayana, K. V.; Masthan, K. S.; Rao, V. V.; Raju, B. D.; Rao, P. K. Influence of V_2O_5 Content on Ammoxidation of 3-Picoline Over V_2O_5/AlF_3 Catalysts. *Catal. Commun.* **2002**, *3*, 173−178.

(3) Shishido, T.; Song, Z. X.; Kadowaki, E.; Wang, Y.; Takehira, K. Vapor-phase Oxidation of 3-Picoline to Nicotinic Acid over $Cr_{1-x}Al_xVO_4$ Catalysts. *Appl. Catal., A: General* **2003**, *239*, 287−296.

(4) Toomey, Jr. Electrochemical Synthesis of Niacin and other N-Heterocyclic Compounds. US Patent 5002641, 1991.

(5) Iniesta, J.; Michaud, P. A.; Panizza, M.; Comninellis, Ch. Electrochemical Oxidation of 3-Methylpyridine at a Boron-doped Diamond Electrode: Application to Electroorganic Synthesis and Wastewater Treatment. *Electrochem. Commun.* **2001**, *3*, 346−351.

(6) Zhang, Y. M.; Zhang, H. B.; Cao, X. J.; Wang, X.; Ji, C. Z. Studies on Electrooxidation of 3-Picoline to Nicotinic Acid. *Chem. J. Chin. Univ.* **2003**, *24*, 509−512.

(7) Ren, B. Z.; Li, C.; Yuan, X. L.; Wang, F. A. Determination and Correlation of Melamine Solubility. *J. Chem. Ind. Eng. (China)* **2003**, *54*, 1001−1003.

(8) Robert, K. L.; Rousseau, R. W.; Teja, A. S. Solubility of Long-Chain *n*-Alkanes in Heptane between 280 and 350 K. *J. Chem. Eng. Data* **1994**, *39*, 793−795.

(9) Domanska, U.; Kozlowska, M. K. Solubility of Imidazoles in Ethers. *J. Chem. Eng. Data* **2003**, *48*, 557−563.

(10) Li, D. Q.; Liu, D. Z.; Wang, F. A. Solubilities of Terephthalaldehydic, p-Toluic, Benzoic, Terephthalic, and Isophthalic Acids in *N*-Methyl-2-pyrrolidone from 295.65 K to 371.35 K. *J. Chem. Eng. Data* **2001**, *46*, 172−173.

(11) Li, D. Q.; Liu, D. Z.; Wang, F. A. Solubilities of 4-Methylbenzoic Acid between 288 K and 370 K. *J. Chem. Eng. Data* **2001**, *46*, 234−236.

(12) Li, D. Q.; Liu, J. C.; Liu, D. Z.; Wang, F. A. Solubilities of Terephthalaldehydic, p-Toluic, Benzoic, Terephthalic, and Isophthalic Acids in *N*,*N*-Dimethylformamide from 294.75 K to 370.75 K. *Fluid Phase Equilib.* **2002**, *200*, 69−74.

Received for review August 28, 2003. Accepted November 2, 2003.

JE034165+