Solubilities of *p*-Aminophenol in Sulfuric Acid + Water from (286.15 to 362.80) K

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Using a laser monitoring observation technique, the solubilities of *p*-aminophenol in sulfuric acid + water have been determined experimentally from 286.15 K to 362.80 K. The experimental data were correlated with the modified Apelblat equation. The calculated results showed good agreement with the experimental data.

Introduction

p-Aminophenol (PAP), also known as 4-aminophenol or 4-hydroxyaniline, which is an aromatic amphoteric compound with unique physical, chemical, and biological properties, is an important fine chemical intermediate.[1−3] It is manufactured through several chemical methods.[4] An alternative method is the electrolytic method[5−7] using nitrobenzene as the raw material and aqueous sulfuric acid solution as the supporting electrolytes. The reaction conditions are mild, giving high product purity and reduced waste. In the synthesis and purification process of *p*-aminophenol, it is necessary to know the solubility data of *p*-aminophenol in sulfuric acid + water, but the solubility data which have been reported[8−10] are only in water or some organic solvents. In this study, the solubilities of *p*-aminophenol in sulfuric acid + water have been measured from 286.15 K to 362.80 K at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation.[11,12]

Experimental Section

Materials. High-grade sulfuric acid from Louyan Chemical Reagent Co. was used directly without further purification, and its purity was greater than 99% by mass. Analytical-grade *p*-aminophenol from Peking Biotech. Co. Ltd. was further purified by recrystallizations from solutions of water. After filtration, the sample was first vacuum-dried to constant mass and then was further vacuum-dried over anhydrous NaOH to remove any existing traces of water. Its purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co. Ltd.) to be 99.7% by mass. The water used in the experiments was double distilled water.

Apparatus and Procedure. The solubilities were measured by a dynamic method.[13,14] The laser monitoring observation technique[15−18] 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.

Solvents for the solubility measurement were prepared by mass using 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 (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 *p*-aminophenol were weighed 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 *p*-aminophenol dissolved. When the last portion of *p*-aminophenol disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded as the liquidus temperature.[15] 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. The reproducibility of the measurements was 0.1 K, which corresponds to a relative error in composition smaller than 1%. To verify the reliability of the measurement, the solubilities of *p*-aminophenol in water were measured, and the results are shown in Figure 1 together with the measurements of Dunn.[8] In Figure 1, T is the absolute temperature and x is the experimental solubility in mole fraction. It is clear from Figure 1 that our experimental results show good agreement with the literature data. Compared with the literature data, the deviations of the solubility are less than 2%. In this work, the uncertainty for solubility measurement is estimated on the basis of the principle of the error propagation to be ±1% at the 95% confidence level.

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10.1021/je049552d CCC: $30.25
Published on Web 03/29/2005

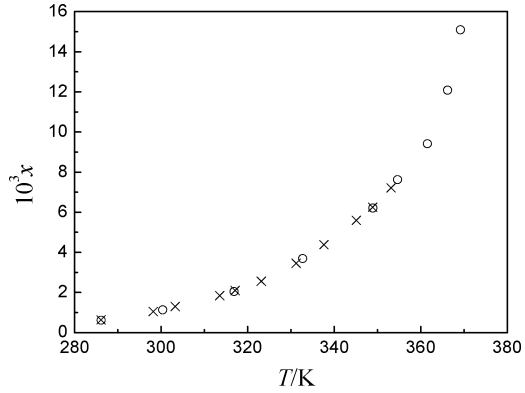

Figure 1. Solubility of *p*-aminophenol in water: ×, this work; ○, Dunn.[8]

Results and Discussion

The measured mole fraction solubilities (x) of *p*-aminophenol in sulfuric acid + water at different temperatures (T) are presented in Table 1. The mass fraction (w) of sulfuric acid in the solvents is 0, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30, respectively. The temperature dependence of *p*-aminophenol solubility at fixed solvent composition is described by the modified Apelblat equation[11,12]

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

where x is the mole fraction solubility of *p*-aminophenol, 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's) are listed in Table 2. The rmsd is defined as

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

where N is the number of experimental points and x_c is the solubility calculated by eq 1. The calculated solubilities (x_c) of *p*-aminophenol using eq 1 are also listed in Table 1. From Tables 1 and 2, 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 *p*-aminophenol in sulfuric acid + water. The overall rmsd of 85 data points for the sulfuric acid + water system at various contents of sulfuric acid in the mixed solvent is 2.1×10^{-4}. The experimental solubility and correlation equation in this work can be used as essential data and models to serve the synthesis and purification process of *p*-aminophenol.

By using the data shown in Table 1, the $T-x$ curves for the *p*-aminophenol + sulfuric acid + water system were given in Figure 2. It described the temperature dependence of the solubility at various compositions of the mixed solvent. Besides, Figure 3 was given as well based on the results calculated from eq 1. It showed the relations between the solubility and the composition of the mixed solvent at fixed temperatures. From the results shown in Table 1 and Figures 2 and 3, it can be seen that the solubility of *p*-aminophenol in sulfuric acid + water is higher than that in water, and with the increase of the amount of sulfuric acid in the mixed solvent, the solubility of *p*-aminophenol increases at constant temperature. The probable reason is that *p*-aminophenol is an aromatic amphoteric compound containing both a hydroxyl group and an amino group in its molecule; when it dissolves in sulfuric acid + water, the interaction between the alkaline amino group in its molecule and the H^+ in the mixed solvent makes the solubility of *p*-aminophenol in the mixed

Table 1. Mole Fraction Solubilities (x) of *p*-Aminophenol in (w) Sulfuric Acid + (1 − w) Water, Where w is the Mass Fraction

T/K	10^2x	10^2x_c[a]	T/K	10^2x	10^2x_c
		$w = 0.00$			
286.15	0.0639	0.0648	331.25	0.3463	0.3488
298.20	0.1048	0.1044	337.65	0.4387	0.4338
303.25	0.1303	0.1267	345.10	0.5593	0.5562
313.55	0.1844	0.1860	348.90	0.6254	0.6299
317.10	0.2099	0.2117	353.15	0.7215	0.7227
323.15	0.2563	0.2628			
		$w = 0.05$			
289.10	1.073	1.081	317.75	1.621	1.628
292.65	1.166	1.153	323.05	1.712	1.715
296.55	1.249	1.231	328.95	1.804	1.803
307.05	1.459	1.443	336.65	1.924	1.906
		$w = 0.10$			
288.25	1.231	1.247	324.83	2.331	2.340
291.95	1.356	1.355	332.25	2.516	2.539
297.25	1.531	1.515	338.65	2.686	2.697
304.65	1.756	1.741	344.11	2.795	2.820
311.55	1.961	1.952	350.18	2.943	2.942
318.35	2.162	2.154	355.86	3.079	3.042
		$w = 0.15$			
286.65	1.252	1.260	316.05	2.607	2.598
289.35	1.359	1.372	321.75	2.844	2.856
291.95	1.483	1.482	334.65	3.336	3.383
294.63	1.595	1.601	344.65	3.671	3.712
304.75	2.075	2.067	357.45	3.995	4.005
306.35	2.152	2.143	362.35	4.110	4.076
311.55	2.393	2.388			
		$w = 0.20$			
292.35	1.585	1.604	326.85	3.690	3.676
297.36	1.869	1.885	335.80	4.107	4.158
302.50	2.199	2.188	342.45	4.423	4.467
309.05	2.609	2.590	344.25	4.534	4.542
315.35	3.005	2.983	351.75	4.797	4.811
322.25	3.413	3.405	358.57	5.044	4.991
		$w = 0.25$			
290.15	1.492	1.475	321.10	3.721	3.688
293.30	1.656	1.664	326.90	4.176	4.131
298.75	2.030	2.018	333.05	4.589	4.581
302.75	2.302	2.296	340.45	5.033	5.078
304.96	2.448	2.456	344.90	5.373	5.345
307.05	2.587	2.610	353.35	5.789	5.775
310.85	2.912	2.896	362.80	6.141	6.117
316.05	3.321	3.297			
		$w = 0.30$			
289.05	1.389	1.375	315.20	3.590	3.577
293.75	1.673	1.691	319.05	4.002	3.970
298.95	2.053	2.085	323.65	4.422	4.450
302.85	2.401	2.411	328.95	4.968	5.006
304.25	2.538	2.534	329.65	5.048	5.079
306.95	2.775	2.771	334.10	5.559	5.539
311.35	3.193	3.195	339.35	6.039	6.065

[a] The solubility values calculated from eq 1.

Table 2. Parameters of eq 1 for the *p*-Aminophenol + Sulfuric Acid + Water System at Various Contents of Sulfuric Acid (w) in the Mixed Solvent

w	A	B	C	10^4(rmsd)
0.00	−64.292	−370.57	10.297	0.34
0.05	117.68	−6621.1	−17.524	1.2
0.10	126.57	−7312.8	−18.642	1.7
0.15	204.09	−11231	−29.918	2.3
0.20	239.76	−13124	−35.048	2.8
0.25	256.34	−14153	−37.348	2.4
0.30	270.81	−15182	−39.278	2.3

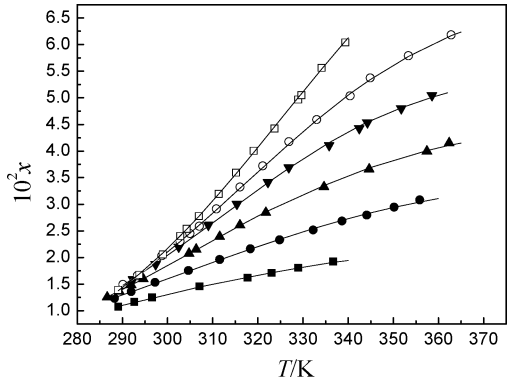

Figure 2. Solubilities of *p*-aminophenol in (*w*) sulfuric acid + (1 − *w*) water, where *w* is the mass fraction: ■, *w* = 0.05; ●, *w* = 0.10; ▲, *w* = 0.15; ▼, *w* = 0.20; ○, *w* = 0.25; □, *w* = 0.30; —, calculated from eq 1.

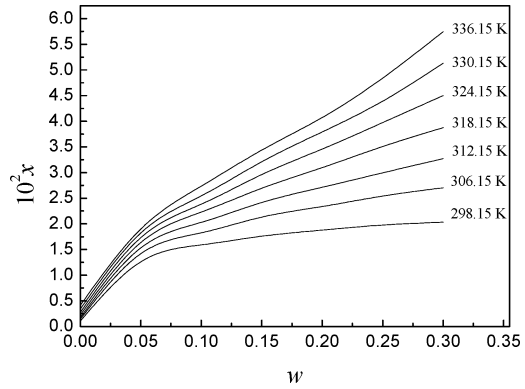

Figure 3. Dependence of the solubilities (*x*) calculated from eq 1 and values of *A*, *B*, and *C* at (298.15 to 336.15) K on the mass fraction (*w*) of sulfuric acid in solvent for *p*-aminophenol + sulfuric acid + water systems.

solvent higher than that in water, and with the increase of the amount of sulfuric acid in the mixed solvent, the interaction becomes stronger, which leads to the increase of the solubility of *p*-aminophenol at constant temperature.

The values of parameters *A*, *B*, and *C* are dependent on the composition of sulfuric acid in the mixed solvent. The higher the content of sulfuric acid, the greater the value of parameter *A* would be and the smaller the values of parameters *B* and *C* would be; that is, with an increase of the sulfuric acid amount in the mixed solvents, the value of parameter *A* increases but the values of parameters *B* and *C* decrease.

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Received for review December 17, 2004. Accepted March 5, 2005.

JE049552D