J. Chem. Eng. Data **2008,** *53,* 564–565

Short Articles

Influence of Solubility of Ammonium Sulfate Caused by Decreasing pH or Adding Fe^{3+} from (288.15 to 359.15) K

Zhenxing Zhu,*,[†] Zhengang Zhu,[‡] and Ping Yin[†]

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China, and First Teaching Hospital of Tianjin University of Traditional Chinese Medicine, Tianjin 300193, People's Republic of China

Using a laser monitoring observation technique, the solubility of ammonium sulfate in pure water, sulfuric acid solution (pH = 2.5), and ferric sulfate solution from (278.98 to 338.35) K was experimentally measured by a synthetic method. The results were correlated with a semiempirical equation and provided an indication of the solution nonidealities on the solubility of the solute, which can be used as a useful model in the production of ammonium sulfate.

Introduction

Ammonium sulfate (CAS No.: [7783-20-2]) is a white orthorhombic crystal,[1] which is precipitated from COG (coke oven gas) of steelworks and the outgrowth of producing caprolactam. Ammonium sulfate is an important material in fertilizer, the pharmacy industry as the source of nitrogen for fermentation, a dyeing additive, used in beer brewing, and so on.[2] It is necessary therefore to measure the solubility of ammonium sulfate in sulfuric acid solution (pH = 2.5) and ferric sulfate solution (the concentration of Fe^{3+} is 0.0017 $mol\cdot L^{-1}$) because it is usually produced by absorption of NH_3 in COG with sulfuric acid. Furthermore, Fe^{3+} is a basic component in the production of absorption of COG and accounts for the quality of final production to a certain degree. However, no experimental solubility data are available in the literature until now. In this work, the solubility of ammonium sulfate in pure water, sulfuric acid solution (pH = 2.5), and ferric sulfate solution was experimentally determined using a laser monitoring observation technique.[3,4]

Experimental Section

A white crystal of ammonium sulfate with a melting point of (786.15 ± 2) K and a decomposing point of (553.15 ± 1) K was used, and its purity is higher than 99.5 mass %. The materials used to prepare the solvents including sulfuric acid, iron trioxide, and deionized water (purchased from the Tianjin Kewei Co. of China) were of analytical reagent grade, and their purity was higher than 99.8 mass %. The solubility of ammonium sulfate in different solvents was measured by a synthetic method which is described in the literature.[5–8] All the experiments were conducted three times, and the mean values were used to calculate the mole fraction solubility x_1. The uncertainty of the experimental solubility values is within 0.02.[9–11] The uncertainty in the solubility values is due to uncertainties in the temperature measurements, weighing procedure, and instabilities of the water bath.

Table 1. Mole Fraction Solubility Data of Ammonium Sulfate in Different Solvents

T/K	$10^2\cdot x_1^{exptl}$	RD %	T/K	$10^2\cdot x_1^{exptl}$	RD %
		Pure Water			
288.15	8.763	−0.090	327.15	10.23	−0.034
297.15	9.108	0.206	336.15	10.58	−0.167
308.15	9.474	−0.216	344.15	10.94	0.115
317.15	9.856	0.191			
		Sulfuric Acid Solution (pH = 2.5)			
292.15	8.616	0.112	335.15	10.43	0.211
304.15	9.144	−0.106	346.15	10.83	0.250
316.15	9.661	−0.067	353.15	11.05	0.151
326.15	10.04	−0.245	359.15	11.19	−0.310
		Ferric Sulfate Solution (the Concentration of Fe^{3+} is 0.0017 $mol\cdot L^{-1}$)			
292.15	9.009	0.1159	335.15	10.52	−0.033
304.15	9.392	−0.2315	347.15	10.97	0.0701
316.15	9.836	−0.004	354.15	11.22	−0.080
325.15	10.18	0.164			

Results and Discussion

The solubilities of ammonium sulfate in pure water, sulfuric acid solution, and ferric sulfate solution at different temperatures are listed in Table 1. x_1^{exptl} expresses the experimental value of the solubility, and RD is defined as follows

$$RD = \frac{x_1^{exptl} - x_1^{calcd}}{x_1^{exptl}} \tag{1}$$

where x_1^{calcd} expresses the calculated value of solubility. This variable can be computed by the Apelblat equation[12] as follows

$$\ln x = A + \frac{B}{T} + C\cdot \ln T \tag{2}$$

The experimental solubility values were correlated with eq 2 using the least-squares method, and the difference between experimental and calculated results is presented in Table 1. The values of the three parameters, A, B, and C, together with

---

* Corresponding author. Phone: +86 (0)22 27405754. Fax: +86 (0)22 27400287. E-mail: michaelzhu@tju.edu.cn.

[†] Tianjin University.

[‡] First Teaching Hospital of Tianjin University of Traditional Chinese Medicine.

10.1021/je7004243 CCC: $40.75

Table 2. Parameters of the Apelblat Equation for Ammonium Sulfate in Different Solvents

solvent	*A*	*B*	*C*	$10^3 \cdot$rmsd
pure water	−16.44	325.57	2.27	0.154
sulfuric acid solution	10.03	−943.18	−1.63	0.210
ferric sulfate solution	−11.34	114.60	1.50	0.120

the root-mean-square deviations (rmsd), are listed in Table 2. The rmsd is defined as the following

$$\text{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}(x_i^{\text{calcd}} - x_i^{\text{exptl}})^2\right]^{1/2} \tag{3}$$

where *N* is the number of experimental points.[10–13]

Conclusions

From Tables 1 and 2 and Figure 1, we can draw the following conclusions: (1) The solubility of ammonium sulfate in pure water, sulfuric acid solution, and ferric sulfate solution is a function of temperature, and it increases slowly with an increase in temperature. (2) The solubility of ammonium sulfate decreases with the reduction of solution pH value. (3) The solubility of ammonium sulfate decreases slightly with the addition of impurity Fe^{3+}, when the operating temperature is higher than 330 K, and the trend becomes more and more obvious with increasing the operating temperature continuously. (4) The calculated solubility of ammonium sulfate sets a good coherence with the experimental values, and the experimental solubility and correlation equations in this work can be used as essential data and models in the evaporative cooling crystallization process of ammonium sulfate.

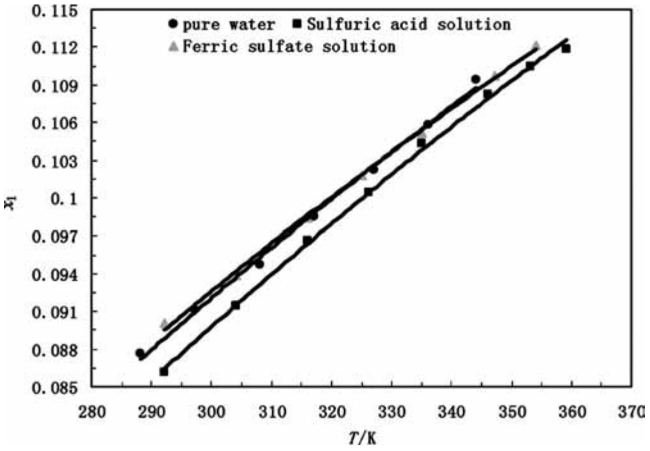

Figure 1. Solubility of ammonium sulfate in different solvents.

Literature Cited

(1) Mullin, J. W. *Crystallization*, 4th ed.; Butterworths: London, U.K., 2001.

(2) Zhang, S. Q. *Handbook of Chemical Engineering*; Shandong Science & Technology Press: Jinan, China, 1986.

(3) Brandani, S.; Brandani, V. Isothermal Vapor-Liquid Equilibria and Solubility in the System Methanol + 1,3,5-Trioxane. *J. Chem. Eng. Data* **1994**, *39*, 203.

(4) Nyvlt, J. *Solid-Liquid Equilibria*; Czechoslovak Academia of Sciences: Praha, Czechoslovakia, 1997.

(5) Roberts, 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.

(6) Hao, H. X.; Wang, J. K.; Wang, Y. L. Solubility of dexamethasone sodium phosphate in different solvents. *J. Chem. Eng. Data* **2004**, *49*, 1697–1698.

(7) Nie, Q.; Wang, J. K.; Wang, Y. L.; Wang, S. Solubility of 11α-hydroxy-16α,17α-epoxyprogesterone in different solvents between 283 and 323 K. *J. Chem. Eng. Data* **2005**, *50*, 989–992.

(8) Ren, G. B.; Wang, J. K.; Yin, Q. X.; Zhang, M. J. Solubilities of Proxetine Hydrochloride Hemihydrate between 286 and 363 K. *J. Chem. Eng. Data* **2004**, *49*, 1671–1674.

(9) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall Inc.: Upper Saddle River, 1999.

(10) Kondepudi, D. K.; Prigogine, I. *Modern Thermodynamics*; John Wiley & Sons Ltd.: Chichester, England, 2002.

(11) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1963.

(12) Apelblata, A.; Manzurola, E. Solubilities of o-aeetylsalicylic, 4-aminosalicylic, 3,5-dinitrosalicylic, and P-toluic acid and magnesium-DL-aspartate in water from *T* = (278 to 348)K. *J. Chem. Thermodyn.* **1999**, *31*, 85–91.

(13) Wang, S.; Wang, J. K.; Yin, Q. X. Measurement and correlation of solubility of 7-aminocephalosporanic acid in aqueous acetone mixtures. *Ind. Eng. Chem. Res.* **2005**, *44*, 3783–3787.

Received for review July 26, 2007. Accepted December 24, 2007.

JE7004243