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Solubility of Urea Phosphate in Water + Phosphoric Acid from (277.00 to 354.50) K

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The solubility of urea phosphate in water + phosphoric acid from (277.00 to 354.50) K was measured by a synthetic method at atmospheric pressure, where laser monitoring observation equipment was used. The experimental data were correlated with the Apelblat equation, and the average relative deviation (ARD) between experimental data and calculated data was only 1.61 %. The result is a necessary complement to the data of urea phosphate solubility.

Introduction

Urea phosphate is an amino structural complex manufactured by the reaction between urea and phosphoric acid. Besides being used as chemicals, agricultural fertilizer, or livestock feed directly, urea phosphate can also be blended with nitrogenous fertilizer, phosphate fertilizer, and potassium fertilizer to adjust the proportions of various nutrient contents.[1,2] On the basis of the properties of urea phosphate, such as high-analysis nutrient content (total nutrient mass fraction is up to 60 %) for crops, good solubility of product in water, and its acidic solution, a water-soluble compound fertilizer manufacturing technology with processing urea phosphate plus potassium chloride was developed by Jian-wei Tang et al.[3] for the agricultural application of dripping/spraying irrigation. The solubility of urea phosphate in water + phosphoric acid is very important in studying the crystallization mechanisms during the synthesis reaction between urea and phosphoric acid. However, only the solubility of urea phosphate in water at 319.15 K (202 $g \cdot L^{-1}$) can be found in previous data.[4−6] The solubility of urea phosphate in water + phosphoric acid was measured systematically.

Experimental Section

Chemicals. Phosphoric acid, AR grade, mass fraction of 85.0 %, was produced by Tianjin Huadong Chemical Reagent Factory. Urea, AR grade, purity mass fraction of 99.0 %, was produced by Tianjin Huadong Chemical Reagent Factory. Urea phosphate was synthesized by the abovementioned phosphoric acid and urea and recrystallized three times for purity mass fraction of 99.0 %. Distilled water was self-made.

The solute and solvent were quantified by an electronic balance (type AR2140, within the measure range from (0 to 210) g and an uncertainty of ± 0.0001 g) and manufactured by Mettler-Toledo Corp.

Apparatus. The solubility of urea phosphate in water + phosphoric acid was determined by a synthetic method[7−11] with a laser monitoring observation system. Its main part was a jacketed glass vessel (100 mL), which was maintained at a desired temperature through circulating water provided by a constant temperature bath (type CH1015, with the water temperature controlled at an accuracy of ± 0.1 K), made by Shanghai Hengping Instrument & Apparatus Factory, China, with a magnetic stirrer (type 85-2), made by Shanghai Lengpu Instrument & Apparatus Factory, China. A laser monitoring observation system (made by Zhengzhou University, China, and consisting of a laser transmitter, a signal acceptor, and a digital reader) was used to judge the dissolving termination. The temperature of the system was determined by a thermometer inserted in the materials, with an uncertainty of ± 0.01 K.

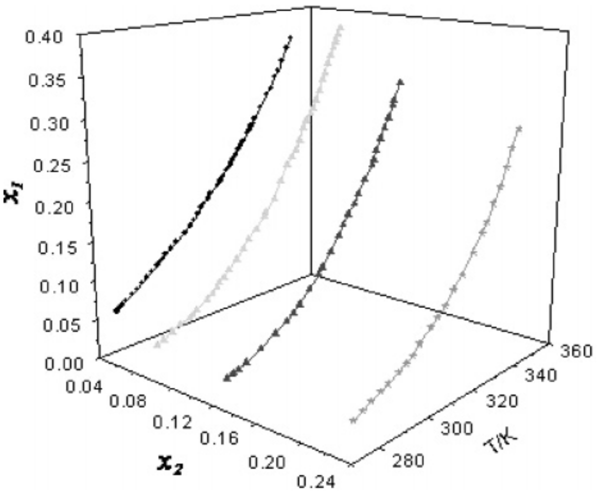

Figure 1. Experimental solubility mole fraction x_1 of urea phosphate (1) in water + phosphoric acid (2) with mole fraction x_2 from T = (277.00 to 354.50) K.

Procedure. Predetermined solute and solvent were placed into the jacketed vessel, and the magnetic stirrer was run to mingle with the two phases. Meanwhile, the laser monitoring observation system started to record the resolving status of the solid. The laser beam signal from the laser transmitter permeated the vessel and got into the signal acceptor, and the transformed electric signal was displayed on the digital reader. When the system was slowly heated with continuous stirring, the particles in the solvent disappeared thoroughly at some time, and the signal approached a maximum value. The solubility, x, of urea phosphate at the temperature can be recorded.[7−10]

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Table 1. Experimental Solubility as Mole Fraction x_1 and Calculated Value $x_{1,c}$ of Urea Phosphate (1) in Water + Phosphoric Acid (2) with Mole Fraction x_2 from T = (277.00 to 354.50) K

T/K	x_1/%	$x_{1,c}$/%	$\delta x_{1,c}$/%	RD/%	T/K	x_1/%	$x_{1,c}$/%	$\delta x_{1,c}$/%	RD/%	T/K	x_1/%	$x_{1,c}$/%	$\delta x_{1,c}$/%	RD/%
x_2 = 0.000														
277.00	5.21	5.48	0.28	−5.31	307.04	14.02	14.07	0.05	−0.41	327.09	22.57	22.75	0.18	−0.77
277.98	5.49	5.68	0.20	−3.58	308.55	14.67	14.64	−0.03	0.20	328.16	23.09	23.27	0.18	−0.78
278.95	5.79	5.89	0.10	−1.73	310.14	15.42	15.26	−0.16	1.02	330.18	24.03	24.28	0.25	−1.05
280.28	6.12	6.17	0.05	−0.80	311.07	15.81	15.63	−0.18	1.12	331.06	24.45	24.73	0.28	−1.12
282.57	6.73	6.69	−0.04	0.67	312.83	16.39	16.34	−0.05	0.30	331.99	24.90	25.20	0.30	−1.20
284.40	7.08	7.12	0.04	−0.55	314.04	16.99	16.84	−0.15	0.87	332.67	25.23	25.55	0.32	−1.27
286.56	7.74	7.65	−0.09	1.10	317.08	17.99	18.13	0.14	−0.78	333.30	25.75	25.88	0.13	−0.52
288.13	8.31	8.06	−0.25	3.05	318.20	18.36	18.62	0.26	−1.40	335.66	27.18	27.12	−0.06	0.23
290.21	8.87	8.62	−0.25	2.82	319.26	18.80	19.09	0.29	−1.51	339.05	28.82	28.95	0.13	−0.44
292.30	9.40	9.20	−0.20	2.07	320.78	19.58	19.77	0.19	−0.98	340.84	29.63	29.94	0.31	−1.04
293.18	9.73	9.46	−0.27	2.79	321.44	19.82	20.07	0.25	−1.26	342.56	31.01	30.90	−0.11	0.35
294.36	10.08	9.81	−0.27	2.67	322.00	20.02	20.33	0.31	−1.53	344.10	31.83	31.77	−0.06	0.18
295.54	10.51	10.16	−0.35	3.31	322.58	20.25	20.60	0.35	−1.71	345.94	33.20	32.83	−0.37	1.14
297.60	11.08	10.81	−0.27	2.51	323.10	20.54	20.84	0.30	−1.46	348.28	34.89	34.19	−0.70	2.03
299.83	11.74	11.53	−0.21	1.76	323.60	20.84	21.07	0.23	−1.13	350.08	36.08	35.24	−0.84	2.32
303.28	12.64	12.71	0.07	−0.50	324.86	21.40	21.67	0.27	−1.25	351.60	37.22	36.15	−1.07	2.89
305.40	13.36	13.47	0.11	−0.79	326.20	22.06	22.31	0.25	−1.16					
x_2 = 0.044														
276.92	2.65	2.71	0.06	−2.44	310.56	11.25	11.00	−0.25	2.26	340.41	27.00	27.11	0.11	−0.40
279.40	3.10	3.06	−0.04	1.17	313.15	12.24	12.03	−0.21	1.72	341.54	27.68	27.91	0.23	−0.85
282.62	3.69	3.56	−0.13	3.49	316.16	13.25	13.30	0.05	−0.41	343.15	28.75	29.08	0.33	−1.15
285.68	4.19	4.10	−0.09	2.20	319.52	14.73	14.84	0.11	−0.72	344.65	29.95	30.20	0.25	−0.83
288.91	4.66	4.72	0.06	−1.40	320.22	15.16	15.17	0.01	−0.10	346.28	31.26	31.44	0.18	−0.57
290.17	4.92	4.99	0.07	−1.34	324.28	16.69	17.21	0.52	−3.11	347.16	32.30	32.12	−0.18	0.56
291.75	5.31	5.34	0.03	−0.54	327.04	18.83	18.70	−0.13	0.69	348.44	33.39	33.13	−0.26	0.77
295.85	6.17	6.32	0.16	−2.54	329.93	20.76	20.35	−0.41	1.96	350.00	34.43	34.38	−0.05	0.15
297.90	6.71	6.86	0.16	−2.35	331.92	21.75	21.54	−0.21	0.97	351.13	35.38	35.31	−0.07	0.22
299.80	7.27	7.40	0.13	−1.77	333.81	22.54	22.71	0.17	−0.73	351.95	36.18	35.99	−0.19	0.52
300.65	7.76	7.64	−0.11	1.47	335.60	23.76	23.85	0.09	−0.41	352.54	36.57	36.48	−0.09	0.23
302.77	8.18	8.29	0.11	−1.38	337.25	25.25	24.94	−0.31	1.24	353.43	37.20	37.23	0.03	−0.08
304.69	9.13	8.91	−0.23	2.47	338.86	26.14	26.03	−0.11	0.40	354.50	37.89	38.15	0.26	−0.69
307.86	10.09	10.00	−0.09	0.97										
x_2 = 0.109														
279.47	1.22	1.34	0.12	−10.11	311.58	8.15	8.14	−0.01	0.07	339.48	21.81	22.31	0.50	−2.29
280.95	1.51	1.49	−0.02	1.48	315.80	9.70	9.76	0.06	−0.64	340.40	22.46	22.90	0.44	−1.97
281.77	1.61	1.57	−0.04	2.31	317.65	10.38	10.53	0.15	−1.40	341.53	23.49	23.64	0.15	−0.64
283.31	1.81	1.74	−0.07	3.67	320.98	11.96	12.01	0.05	−0.45	343.49	24.98	24.94	−0.04	0.16
286.58	2.16	2.15	0.00	0.10	324.58	13.72	13.74	0.02	−0.16	345.23	26.28	26.12	−0.16	0.60
291.90	3.08	2.98	−0.11	3.45	326.52	14.98	14.74	−0.24	1.62	347.27	27.48	27.52	0.04	−0.15
297.73	4.28	4.13	−0.15	3.48	328.82	16.20	15.96	−0.24	1.50	349.20	29.09	28.87	−0.22	0.74
302.29	5.29	5.24	−0.05	0.85	331.52	17.29	17.47	0.18	−1.06	349.76	29.65	29.27	−0.38	1.29
305.27	5.90	6.08	0.18	−2.96	333.23	18.51	18.46	−0.05	0.29	352.40	31.69	31.15	−0.54	1.71
307.68	6.74	6.82	0.08	−1.18	336.42	20.13	20.38	0.25	−1.25					
x_2 = 0.216														
281.68	1.48	1.64	0.17	−11.36	308.27	6.43	6.16	−0.27	4.20	336.23	16.55	17.11	0.56	−3.35
285.22	2.01	2.01	0.00	0.23	313.47	7.67	7.64	−0.04	0.50	338.25	17.72	18.20	0.48	−2.75
288.54	2.57	2.40	−0.17	6.53	316.05	8.50	8.46	−0.05	0.56	341.22	19.73	19.89	0.16	−0.82
292.37	3.11	2.93	−0.18	5.63	319.38	9.46	9.61	0.15	−1.54	344.20	21.53	21.68	0.15	−0.67
295.31	3.53	3.40	−0.13	3.77	323.36	11.09	11.12	0.03	−0.30	347.03	23.80	23.46	−0.34	1.42
299.93	4.18	4.24	0.06	−1.42	327.16	12.32	12.71	0.39	−3.22	349.50	25.96	25.08	−0.88	3.39
302.85	4.82	4.85	0.03	−0.69	332.16	14.62	15.03	0.41	−2.83	352.57	28.07	27.18	−0.89	3.18
305.46	5.34	5.45	0.11	−1.99										

Table 2. Parameters of Equation 1 for Urea Phosphate (1) + Water + Phosphoric Acid (2)

x_2	$10^{-2}A$	$10^{-2}B$	C	ARD/%
0.000	0.76	−57.07	−10.42	1.43
0.044	0.90	−71.08	−12.04	1.18
0.109	2.49	−152.74	−35.23	1.64
0.216	14.00	−99.94	−19.28	2.74

Results and Discussion

The experimental solubility of urea phosphate in water + phosphoric acid was presented in Table 1, where T/K is the absolute temperature. The mole fractions x_1 and $x_{1,c}$ are the experimental solubility and calculated value, respectively, of urea phosphate in water + phosphoric acid with mole fraction x_2. All the experimental solubility data were fitted with the following Apelblat equation[11] (eq 1), and the parameters A, B, and C were listed in Table 2.

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

The deviation ($\delta x_{1,c}$), relative deviation (RD), and average relative deviation (ARD) between the experimental value and the calculated value were defined as follows in eq 2 to eq 4, respectively

$$\delta x_{1,c} = x_{1,c} - x_1 \tag{2}$$

$$\mathrm{RD} = \frac{x_1 - x_{1,c}}{x_1} \tag{3}$$

$$\mathrm{ARD} = \frac{[\sum_{i=1}^{N} |(x - x_c)/x|]}{N} \tag{4}$$

where N is the number of experimental values. The ARD of urea phosphate in different solvents was presented in Table 2. The total ARD of 141 data points for the phosphate + water system at various contents of phosphoric acid in the mixed solvent was 1.61 %, which shows that the experimental data conform with the above-mentioned eq 1 very well.

Figure 1 shows that the solubility of urea phosphate in the water + phosphoric acid system is fairly large. When the concentration of solvent is fixed, the solubility of urea phosphate varies exponentially with temperature. At a fixed temperature, the solubility decreases with the increase of phosphoric acid concentration in the solvent, especially at a high temperature. It can be attributed to the common ion effect resulting from the ionization of urea phosphate and phosphoric acid. On the basis of the previous mentioned properties, the production and purification of urea phosphate can be implemented by a cooling crystallization process.

Conclusion

The solubility of urea phosphate in water + phosphoric acid was measured systematically, which may serve as the theoretical basis in related experimental research and industrial production. The experimental data were correlated with the Apelblat equation, $\ln x_c = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K})$, and the total ARD of 141 experimental points between the experimental value and the calculated value was only 1.61 %. The results show that the method is available and that the data determined are acceptable.

Literature Cited

(1) Song, X.-P.; Han, C.-R. *Fine Organic Chemical Product Practical Production Technology*; China Petrochemistry Press: Beijing, 2001.

(2) U.S.P. 5454850.

(3) Mu, R. Z.; Tang, J. W.; Zhang, B. L. Study on the process of full water-soluble high-analysis NPK compound fertilizer. *Ind. Miner. Process.* **2006**, *35* (1), 16−17, 42.

(4) Li, C. B.; Li, Y. Q.; Peng, Y. M. Mensuration for the Construction of Urea Phosphate and Its Physicochemical Properties. *Chem. Fert.Catal.* **1988**, *3*, 59−61, 47.

(5) Chen, J. F.; Tan, G. X. *Production and Application of the Phosphate*; Chengdu Scientific and Technological University Press: Chengdu, 1989.

(6) Ran, L. W. *Technology of Fined Phosphate Chemical*; Chemical Industry Press: Beijing, 2005.

(7) Ren, B.-z.; Chong, H.-g.; Li, W.-r.; Wang, F.-a. Solubility of Potassium *p*-Chlorophenoxyacetate in Ethanol + Water from (295.61 to 358.16) K. *J. Chem. Eng. Data* **2005**, *50*, 907−909.

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

(9) Wang, L. C.; Wang, F. A. Solubility of Niacin in 3-Picoline + Water from (287.65 to 359.15) K. *J. Chem. Eng. Data* **2004**, *49*, 155−156.

(10) Ma, P. S.; Chen, M. H.; Dong, Y. Solid−liquid Equilibria of Several Binary and Ternary Systems Containing Maleic Anhydride. *Chin. J. Chem. Eng. Data* **2002**, *10*, 323−327.

(11) Apelblat, A.; Manzurola, E. Solubilities of *o*-acetylsalicylic, 4-aminosalic, 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.

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