Solubility of *N*-(Phosphonomethyl) Iminodiacetic Acid in Aqueous Sodium Chloride Solutions from (292 to 353) K

Hui Li, Yixin Qu, and Shui Wang*

Beijing Key Laboratory of Bioprocess, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

The solubility of *N*-(phosphonomethyl) iminodiacetic acid in aqueous sodium chloride solutions were measured using a laser technique with a temperature range from (292 to 353) K. The results of these measurements were correlated with a semiempirical equation.

Introduction

Glyphosate is now widely used as a weedicide for its efficiency, low harmful effects, and low remainder.[1] *N*-(Phosphonomethyl) iminodiacetic acid (PMIDA) is the main raw material of glyphosate synthesis, and its industrial production is becoming particularly important. In the production process of PMIDA, how to deal with wastewater and effectively reclaim PMIDA from wastewater has already been an important research topic. Most wastewater contains sodium chloride close to saturation (18 to 22) %,[2]and so it is essential to know the solubility of PMIDA in the different molalities of sodium chloride solution. In this paper, the solubility of PMIDA was measured in the temperature range from (292 to 353) K in seven various molalities of aqueous sodium chloride solution using a laser monitoring observation technique.

Experimental Section

Materials. A white crystalline powder of PMIDA ($C_5H_{10}NO_7P$, with a molar mass 227.11 $g \cdot mol^{-1}$, CAS registry no. 5994-61-6), purchased from Anhui Huaxing Chemical Industry Co., Ltd., was purified by twice recrystallizing from water. Its mass fraction purity was higher than 99.2 %. Other reagents are analytical research grade reagents from Beijing Chemical Reagent Co. All of the solvents used in the experiments have a minimum purity of 99.5 %.

Apparatus and Procedures. The solubility of PMIDA was measured by using an apparatus similar to that described in literature,[3,4] and we do not describe the procedure here.

In the experiment, the concentration of aqueous sodium chloride solutions $x^\circ(\mathrm{mol \cdot kg^{-1}})$ were based on the following equation:

$$x^\circ = \frac{m_S/M_S}{(m_W + m_S)/1000} \tag{1}$$

where m_w and m_s represent the masses of the water and sodium chloride, respectively, and M_S is the molecular weight of the sodium chloride.

The uncertainty of the experimental solubility values is about 2.0 %. The uncertainty in the solubility can be due to uncertainties in the temperature measurements and weighing procedure.

* To whom correspondence should be addressed. E-mail: wangshui2000@yahoo.cn. Fax: +0086-10-64444785.

Table 1. Mole Fraction Solubility (x_1) of PMIDA in an Aqueous Sodium Chloride Solution of Different Molalities between (292 and 353) K

T/K	$10^4\ x_1$	$10^2\ (x_1 - x_1^{calc})/x_1$	T/K	$10^4\ x_1$	$10^2\ (x_1 - x_1^{calc})/x_1$
		$x^\circ = 0.0000$			
294.25	5.763	1.37	333.55	14.08	−0.75
303.75	7.100	0.62	338.45	15.60	−3.23
313.05	8.632	−0.08	343.77	18.52	−0.17
323.15	11.03	0.81	353.57	24.43	0.78
		$x^\circ = 0.8558$			
292.50	6.034	−1.30	333.35	15.02	−1.38
305.10	8.067	0.98	338.25	16.78	−1.96
313.25	9.815	2.52	343.55	19.29	−0.71
323.55	12.10	−0.05	353.67	25.35	2.02
		$x^\circ = 1.711$			
292.75	5.540	−1.20	333.20	13.02	−2.04
304.15	7.153	2.53	337.97	14.53	−2.90
313.10	8.573	2.28	342.75	16.87	0.04
323.20	10.54	0.50	353.07	22.64	2.51
		$x^\circ = 2.567$			
292.87	4.983	−2.87	333.05	11.78	−2.95
304.25	6.640	3.66	337.70	13.13	−3.29
312.95	7.942	3.31	342.55	15.21	−0.43
322.85	9.590	0.25	352.60	20.36	3.56
		$x^\circ = 3.422$			
292.57	4.592	0.94	333.50	11.10	0.77
303.25	5.501	−1.28	339.05	12.76	0.80
313.80	7.033	1.12	343.65	14.28	0.36
323.25	8.559	−0.63	353.45	18.35	−0.34
		$x^\circ = 4.277$			
292.80	4.206	1.19	332.55	9.960	1.45
303.15	5.019	−0.82	337.65	11.26	0.97
313.25	6.217	−0.63	342.85	12.86	0.97
322.70	7.727	−0.27	353.18	16.55	−0.10
		$x^\circ = 5.134$			
292.95	3.899	0.82	332.35	9.136	2.12
302.84	4.560	−0.99	337.30	10.17	0.02
313.05	5.555	−2.05	342.35	11.68	0.44
322.27	6.929	−0.77	353.00	15.40	−1.59

Results and Discussion

The solubilities of PMIDA in a series of concentrations of aqueous sodium chloride solutions are listed in Table 1. The relationship between temperature and solubility of the PMIDA is correlated with a semiempirical equation:[5]

10.1021/je9005745
Published on Web 09/28/2009

$$\ln(x_1) = a + \frac{b}{T/\mathrm{K}} + c\ln(T/\mathrm{K}) \qquad (2)$$

where T is the absolute temperature and a, b, and c are model constants. The difference between experimental and calculated results is also presented in Table 1. The values of the three parameters a, b, and c together with the root-mean-square deviations (rmsd) are listed in Table 2. The rmsd is defined as follows:

$$\mathrm{rmsd} = \left[\frac{\sum_{j=1}^{N}(x_{1,j} - x_{1,j}^{\mathrm{calc}})^2}{N-1}\right]^{1/2} \qquad (3)$$

where N is the number of experimental points, $x_{1,j}^{\mathrm{calc}}$ is the solubility calculated from eq 2, and $x_{1,j}$ is the experimental value of solubility.

Table 2. Parameters of Equation 2 for PMIDA in an Aqueous Sodium Chloride Solution of Different Molalities

x°	a	b	c	10^4 rmsd
0.0000	−209.63	7513.8	31.076	0.5645
0.8558	−142.94	4436.6	21.198	0.7104
1.711	−206.92	7492.0	30.611	0.8101
2.567	−177.09	6082.2	26.189	0.1994
3.422	−200.86	7163.4	29.704	0.4166
4.277	−202.68	7237.9	29.963	0.2852
5.134	−244.24	9184.3	36.097	0.3453

From Tables 1 and 2, we could elicit the following conclusions: (1) The solubility of PMIDA in aqueous sodium chloride solutions increases with temperature, but the increase with temperature varies according to different molalities of sodium chloride solution. (2) The effect of sodium chloride on the solubility of PMIDA can be divided into two stages: a salting-in effect when the molality of aqueous sodium chloride solution is low and a salting-out effect when it is high. (3) The experimental data can be regressed by eq 2 for these seven groups. The experimental solubility and correlation equation in this work can be useful in the manufacturing and separating processes of PMIDA in industry.

Literature Cited

(1) Mao, Q. W. *Productive Technology Summarize and It's Developing Trend of Glyphosate*; Anhui Chemical Industry: Anhui, China, 2008; pp 5−7.
(2) Cheng, D. Study on the Technology for Treating Glyphosate Wastewater. *Agrochem. Today* **2009**, *4*, 26–28.
(3) Li, D. Q.; Liu, D. Z.; Wang, F. A. Solubility of 4-methylbenzoic acid between 288 and 370 K. *J. Chem. Eng. Data* **2001**, *46*, 234–236.
(4) 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.
(5) Grand, D. J. W.; Mehdizadeh, M.; Chow, A. H. L.; Fairbrother, J. E. Non-linear van't Hoff solubility-temperature plots and their pharmaceutical interpretation. *Int. J. Pharm.* **1984**, *18* (1−2), 25–38.

Received for review July 8, 2009. Accepted September 15, 2009.

JE9005745