Solubility of *N*-(Phosphonomethyl)iminodiacetic Acid in Different Binary Mixtures

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The solubilities of *N*-(phosphonomethyl)iminodiacetic acid in water, ethanol + water, propan-1-ol + water, and propan-2-ol + water were measured in the temperature range from (293 to 333) K at atmospheric pressure. A laser monitoring observation technique was used to determine the dissolution process. A semiempirical equation was found to provide an accurate mathematical representation of the experimental data.

1. Introduction

N-(Phosphonomethyl)iminodiacetic acid (PMIDA, CAS Registry No. 5994-61-6, MW 227.11; see Figure 1) is a kind of white or almost white crystalline powder. The glyphosate is a widely used pesticide, and the PMIDA is the main raw material of glyphosate synthesis.[1] In industrial manufacturing, PMIDA is usually purified by antisolvent addition crystallization. To design an optimized crystallization process, it is essential to know its solubility in different solvent mixtures.

In this paper, the solubilities of PMIDA in water, ethanol + water, propan-1-ol + water, and propan-2-ol + water have been experimentally determined in the temperature range from (293 to 333) K by a laser monitoring observation technique under atmospheric pressure. By using this method, solubility data can be obtained much faster and more readily than with an analytical method.[2,3] The experimental data were well-correlated with a modified semiempirical equation.

2. Experimental Section

Materials. A crystal of PMIDA ($C_5H_{10}NO_7P$), with a decomposition point of 483.15 K, was prepared by recrystallization from aqueous solution two times. Its mass fraction purity is higher than 99.8 %. It was dried in a vacuum at 343.15 K for 24 h and stored in an airproof bag. Ethanol, propan-1-ol, and propan-2-ol were of analytical reagent grade from Beijing Chemical Works, China, and distilled water was used.

Apparatus and Procedures. A laser monitoring observation technique was used to determine the dissolution process. The solubility apparatus set was similar to that described in previous literature.[4−10] The apparatus consisted of a jacketed glass vessel (500 mL, chosen according to solubility) maintained at a desired temperature by water circulated from a water bath with a thermoelectric controller (fluctuates within 0.05 K). A calibrated mercury-in-glass thermometer (uncertainty of ± 0.05 K) was inserted into the inner chamber of the vessel for the temperature measurement.

This method is based on sequentially adding known masses of a solid to a stirred solution kept at a predetermined temperature. The masses of PMIDA and excess amounts of solvents were determined using an analytical balance (Sartorius CP224S, Germany, uncertainty of 0.1 mg) and placed in the inner chamber of the vessel. The contents of the vessel were magnetically stirred continuously at an invariable and required temperature, and the PMIDA was added to the vessel simultaneously. During the experiments, the fluid in the glass vessel was monitored by a laser beam. Along with the dissolution of the particles of the PMIDA, the intensity of the laser beam increased gradually. When the last portion of PMIDA just disappeared, the laser intensity reached the maximum. Then additional PMIDA of a known mass of about (0.5 to 2) mg was introduced into the vessel. This procedure was repeated until the PMIDA could not dissolve completely; then the laser beam was scattered by the undissolved PMIDA particles in the solution, and the penetrating laser intensity was below the maximum. The interval of the addition was at least 90 min. Then, the addition of PMIDA was stopped, and the amount of the PMIDA used in the experiment was recorded. The same experiment was conducted three times, and the mean values were used to calculate the mole fraction solubility (x_0) based on eq 1. The composition (mole fraction) of the solvent mixture (x_2^0, x_3^0, x_4^0) was defined by eqs 2, 3, and 4:

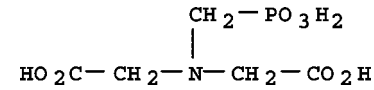

Figure 1. Chemical structure of *N*-(phosphonomethyl)iminodiacetic acid (PMIDA).

$$x_0 = \frac{m_0/M_0}{\sum_{i=0}^{4}(m_i/M_i)} \quad (1)$$

$$x_2^0 = \frac{m_2/M_2}{m_1/M_1 + m_2/M_2} \quad (2)$$

Table 1. Experimental Mole Fraction Solubility (x_0) of PMIDA (0) in Water (1) from (293 to 333) K

water (1)					
T/K	$10^4\,x_0$	$10^2(x_0 - x_0^{cal})/x_0$	*T*/K	$10^4\,x_0$	$10^2(x_0 - x_0^{cal})/x_0$
292.96	5.004	0.30	318.07	9.559	0.73
298.60	5.785	−0.03	322.65	10.62	0.00
305.06	6.796	−0.63	328.55	12.18	−0.57
308.25	7.424	0.07	334.00	13.99	0.29
313.15	8.421	0.31			

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$$x_3^0 = \frac{m_3/M_3}{m_1/M_1 + m_3/M_3} \quad (3)$$

$$x_4^0 = \frac{m_4/M_4}{m_1/M_1 + m_4/M_4} \quad (4)$$

where m_0 and M_0 represent the mass of PMIDA used in the experiment and its molecular weight. m_1, m_2, m_3, and m_4 and M_1, M_2, M_3, and M_4 represent the mass of distilled water, ethanol, propan-1-ol, and propan-2-ol used in the experiment and their molecular weights, respectively. For the case of ethanol + water, $m_3 = 0$ and $m_4 = 0$ in eq 1, and for the case of propan-1-ol + water, $m_2 = 0$ and $m_4 = 0$, while for the case of propan-2-ol + water, $m_2 = 0$ and $m_3 = 0$.

3. Results and Discussion

The mole fraction solubilities of PMIDA in water, ethanol + water, propan-1-ol + water, and propan-2-ol + water are listed in Tables 1, 2, 3, and 4, respectively. The variation of solubility with temperature in water and ethanol + water is shown in Figure 2. The relationship between temperature and solubility of the PMIDA is correlated with a modified semiempirical equation:[11,12]

$$\ln x_0 = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \quad (5)$$

where T is the absolute temperature and A, B, and C are empirical constants. The difference between experimental and calculated results is also presented in Tables 1 to 4. The values of the three parameters A, B, and C together with the root-mean-square deviations (rmsd's) are listed in Table 5. The rmsd is defined as follows:

$$\mathrm{rmsd} = \left[\sum_{i=1}^{n} \frac{(x_0 - x_0^{\mathrm{cal}})^2}{N}\right]^{1/2} \quad (6)$$

where N is the number of experimental points, x_0^{cal} is the solubility calculated from eq 5, and x_0 is the experimental value of solubility.

From Tables 1 to 4 and Figure 2, we could draw the following conclusions: (1) The solubility of PMIDA increases with an increase in the temperature in water and the binary solvent mixtures. (2) The solubility of PMIDA in pure water is the maximum; the organic solvent has an obvious effect on the solubility of PMIDA. With concentrations of organic solvent increasing, the solubility of PMIDA decreases clearly. (3) From the solubility data of

Table 2. Experimental Mole Fraction Solubility (x_0) of PMIDA (0) in Ethanol (2) + Water (1) with Various Concentrations of Organic Solvent (x_2^0) from (293 to 333) K

ethanol (2) + water (1)					
T/K	$10^4\,x_0$	$10^2(x_0 - x_0^{\mathrm{cal}})/x_0$	T/K	$10^4\,x_0$	$10^2(x_0 - x_0^{\mathrm{cal}})/x_0$
		$x_2^0 = 0.0417$			
293.35	3.283	−0.40	318.80	6.964	−0.29
298.47	3.849	0.00	323.67	7.983	−0.44
305.07	4.691	0.11	328.85	9.209	−0.67
308.35	5.180	0.35	334.15	10.79	0.46
313.53	5.995	−0.12			
		$x_2^0 = 0.0888$			
294.05	2.320	−0.60	318.77	5.244	−0.38
298.95	2.772	0.54	322.85	5.977	−0.12
303.66	3.236	0.25	328.53	7.093	−0.56
308.85	3.852	0.60	333.43	8.332	0.62
313.60	4.448	−0.38			
		$x_2^0 = 0.1443$			
293.67	1.731	0.00	318.35	4.083	0.54
299.05	2.115	0.43	322.80	4.670	−0.21
303.85	2.476	−0.85	328.67	5.577	−0.66
308.80	2.973	0.40	333.60	6.543	0.46
313.45	3.466	0.14			
		$x_2^0 = 0.2074$			
292.70	1.308	0.00	317.65	3.109	−0.16
299.15	1.648	0.00	322.68	3.689	0.33
305.15	2.018	−0.84	328.60	4.364	−2.13
309.10	2.340	0.34	332.80	5.163	1.28
312.65	2.659	0.98			
		$x_2^0 = 0.2801$			
293.43	1.067	−0.84	317.52	2.395	0.63
299.04	1.287	−0.54	323.13	2.846	−0.60
304.07	1.519	−0.59	329.13	3.411	−2.23
309.13	1.792	−0.73	333.87	4.080	0.17
313.20	2.033	−1.57			
		$x_2^0 = 0.3684$			
292.75	0.796	−1.39	318.40	1.777	−1.13
298.97	0.984	0.61	323.14	2.107	0.85
305.14	1.177	−0.68	328.97	2.420	−3.88
309.15	1.341	−0.15	333.40	2.937	1.46
314.65	1.583	−0.88			
		$x_2^0 = 0.4774$			
292.97	0.594	−1.56	318.13	1.150	−1.65
298.38	0.683	−0.12	323.35	1.353	−1.48
303.65	0.800	2.61	328.65	1.576	−3.24
309.05	0.905	0.51	333.95	2.002	3.05
315.15	1.081	1.02			
		$x_2^0 = 0.6095$			
292.85	0.479	−2.26	318.77	0.766	−3.39
300.20	0.552	2.21	323.77	0.897	−0.67
303.37	0.580	1.78	328.83	1.026	−1.66
308.90	0.644	1.82	334.15	1.263	2.85
315.65	0.737	0.43			

Table 3. Experimental Mole Fraction Solubility (x_0) of PMIDA (0) in Propan-1-ol (3) + Water (1) with Various Concentrations of Organic Solvent (x_3^0) from (293 to 333) K

propan-1-ol (3) + water (1)					
T/K	$10^4\,x_0$	$10^2(x_0 - x_0^{\mathrm{cal}})/x_0$	T/K	$10^4\,x_0$	$10^2(x_0 - x_0^{\mathrm{cal}})/x_0$
		$x_3^0 = 0.0334$			
293.13	3.227	−0.59	317.25	6.962	−0.13
297.85	3.855	0.86	322.35	8.011	−0.20
303.05	4.534	−0.09	328.15	9.257	−1.03
307.90	5.272	−0.30	333.25	10.72	0.84
312.35	6.099	0.82			
		$x_3^0 = 0.0693$			
293.35	2.417	−2.03	317.30	5.649	−2.09
297.95	3.022	1.39	322.25	6.558	−1.72
303.15	3.616	0.08	327.60	7.586	−1.95
308.00	4.197	−1.98	332.70	8.876	0.54
312.35	4.967	0.52			
		$x_3^0 = 0.1144$			
293.35	2.012	−1.94	318.16	4.720	−0.49
298.20	2.498	1.84	322.15	5.294	−0.85
302.85	2.921	1.03	327.80	6.224	−0.72
307.39	3.388	0.47	332.80	7.270	1.25
312.80	3.990	−0.73			
		$x_3^0 = 0.1675$			
293.28	1.671	−1.62	317.70	3.802	0.68
298.35	2.079	2.36	322.00	4.278	−0.12
302.97	2.383	0.34	328.05	5.039	−0.77
307.27	2.727	−0.26	333.14	5.867	0.67
312.50	3.178	−1.48			
		$x_3^0 = 0.2308$			
293.25	1.424	0.63	317.90	2.947	−1.02
298.55	1.662	−0.42	323.05	3.505	1.11
303.15	1.912	−0.21	327.85	3.975	−0.40
307.80	2.230	1.21	332.65	4.594	0.04
312.75	2.542	−0.47			
		$x_3^0 = 0.3105$			
293.45	1.164	1.55	316.95	2.060	0.24
298.56	1.273	−0.31	322.25	2.504	3.83
303.15	1.391	−2.16	327.45	2.818	−0.64
308.15	1.589	−1.45	332.15	3.258	−1.60
312.20	1.805	0.44			

Table 4. Experimental Mole Fraction Solubility (x_0) of PMIDA (0) in Propan-2-ol (4) + Water (1) with Various Concentrations of Organic Solvent (x_4^0) from (293 to 333) K

propan-2-ol (4) + water (1)					
T/K	$10^4\ x_0$	$10^2(x_0 - x_0^{cal})/x_0$	T/K	$10^4\ x_0$	$10^2(x_0 - x_0^{cal})/x_0$
		$x_4^0 = 0.0337$			
293.53	3.087	0.68	317.90	6.472	−0.29
298.45	3.541	−1.24	322.54	7.445	0.08
303.15	4.149	−0.07	328.25	8.722	−0.61
308.30	4.914	1.02	332.85	10.05	0.50
312.85	5.602	0.34			
		$x_4^0 = 0.0722$			
293.70	2.107	0.66	317.07	4.844	−0.08
298.35	2.478	−1.33	321.77	5.604	−0.32
302.73	2.968	0.30	327.66	6.688	−0.34
307.85	3.576	0.56	332.50	7.738	0.38
312.20	4.149	0.46			
		$x_4^0 = 0.1160$			
293.26	1.627	0.86	317.75	3.766	−1.73
298.95	1.952	−2.25	322.42	4.463	0.18
303.45	2.343	−0.30	327.80	5.289	0.30
307.97	2.846	3.20	332.80	6.142	0.05
313.15	3.275	−0.43			
		$x_4^0 = 0.1703$			
293.36	1.293	−0.23	317.27	2.8836	−0.69
298.96	1.598	1.19	322.20	3.4407	1.43
303.55	1.832	−0.93	328.66	4.0547	−2.05
307.85	2.112	−1.14	333.25	4.7964	0.98
312.70	2.550	1.73			
		$x_4^0 = 0.2323$			
293.21	0.997	0.21	317.75	2.205	−1.13
298.40	1.186	−0.34	322.15	2.563	0.43
302.85	1.361	−1.54	327.75	2.982	−1.24
307.85	1.683	3.21	333.15	3.572	0.98
313.03	1.918	−0.26			
		$x_4^0 = 0.3099$			
293.35	0.765	0.71	316.93	1.524	−0.20
299.45	0.906	−0.64	321.80	1.746	−0.74
303.05	1.018	0.29	327.55	2.069	−0.43
307.70	1.190	2.19	332.75	2.454	1.67
312.65	1.372	1.82			

PMIDA, the ethanol, propan-1-ol, and propan-2-ol can be used as an effective antisolvent in the crystallization process. PMIDA dissolved a little more in propan-1-ol + water than in other binary mixtures, and the solubility in propan-2-ol + water is the lowest. Thereby, propan-2-ol should be the best antisolvent in the crystallization process. (4) All of the experimental data can be regressed by eq 5 and show good agreement with it. The experimental solubility and correlation equation in this work can be used as an essential model and data in the manufacturing and separating processes of PMIDA.

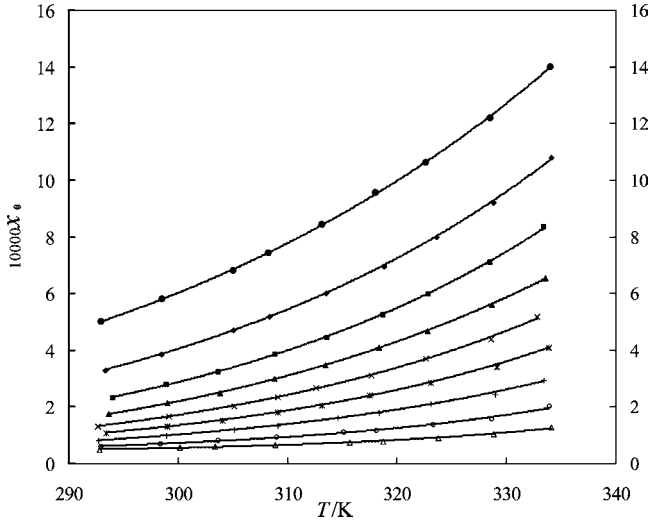

Figure 2. Experimental mole fraction solubility (10 000 x_0) of PMIDA (0) in water (1) and the ethanol (2) + water (1) solvent mixture with various concentrations of organic solvent (x_2^0): ●, water; ◆, $x_2^0 = 0.0417$; ■, $x_2^0 = 0.0888$; ▲, $x_2^0 = 0.1443$; ×, $x_2^0 = 0.2074$; ∗, $x_2^0 = 0.2801$; +, $x_2^0 = 0.3684$; ○, $x_2^0 = 0.4774$; △, $x_2^0 = 0.6095$. Solid line, calculated from eq 5.

Table 5. Parameters of Equation 5 for PMIDA (0) in Water (1), Ethanol (2) + Water (1), Propan-1-ol (3) + Water (1), and Propan-2-ol (4) + Water (1) with Various Concentrations of Organic Solvent (x_2^0, x_3^0, x_4^0) Mixtures

	A	B	C	10^6 rmsd
		Water (1)		
	−59.574	343.71	8.9432	3.970
		Ethanol (2) + Water (1)		
$x_2^0 = 0.0417$	−72.444	598.29	10.981	3.080
$x_2^0 = 0.0888$	−65.244	−17.238	10.108	2.594
$x_2^0 = 0.1443$	−17.133	−2345.3	2.8962	1.984
$x_2^0 = 0.2074$	−65.450	−169.45	10.052	3.973
$x_2^0 = 0.2801$	−133.92	3068.3	20.122	2.933
$x_2^0 = 0.3684$	−150.73	3958.2	22.500	3.626
$x_2^0 = 0.4774$	−310.62	11593	46.009	2.934
$x_2^0 = 0.6095$	−422.66	17290	62.274	1.769
		Propan-1-ol (3) + Water (1)		
$x_3^0 = 0.0334$	55.065	−5353.3	−7.8927	4.909
$x_3^0 = 0.0693$	121.03	−8634.9	−17.595	8.343
$x_3^0 = 0.1144$	55.205	−5560.7	−7.8751	4.533
$x_3^0 = 0.1675$	26.600	−4178.9	−3.7019	3.200
$x_3^0 = 0.2308$	−105.10	2007.5	15.735	2.028
$x_3^0 = 0.3105$	−340.65	13087	50.509	3.958
		Propan-2-ol (4) + Water (1)		
$x_4^0 = 0.0337$	−62.412	40.552	9.5361	3.489
$x_4^0 = 0.0722$	63.785	−6109.1	−9.0551	2.341
$x_4^0 = 0.1160$	−4.9169	−2954.6	1.1019	4.111
$x_4^0 = 0.1703$	−36.152	−1420.5	5.6400	4.092
$x_4^0 = 0.2323$	−34.521	−1440.1	5.3191	2.737
$x_4^0 = 0.3099$	−101.64	1855.6	15.109	1.919

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