Solubility of 1-Hydroxyethane-1,1-diphosphonic Acid Monohydrate in Aqueous Acetic Acid Mixtures

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The solubility of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) monohydrate (A) in binary acetic acid (B) + water (C) solvent mixtures was measured by using the isothermal method from (293.15 to 328.15) K. A laser monitoring observation technique was employed to determine the dissolution of the solid phase in a solid + liquid mixture. The solubility data were correlated by the combined nearly ideal binary solvent (CNIBS)/Redlich−Kister equation.

Introduction

The HEDP with the chemical name 1-hydroxyethane-1,1-diphosphonic acid or (hydroxyethylidene) diphosphonic acid (Figure 1) is an organophosphoric acid corrosion inhibitor. It can chelate with Fe, Cu, and Zn ions to form stable chelating compounds and dissolve the oxidized materials on the surfaces of these metals. It shows excellent scale and corrosion inhibition effects under a temperature of 250 °C. The solid state of HEDP is crystal powder, suitable for usage in winter and freezing districts. Because of its high purity, it can be used as a cleaning agent in electronic fields and as additives in daily chemicals.[1–4]

Pure HEDP is an almost white powdered crystal which can be solved in water. In industrial manufacturing, HEDP is crystallized from solution in the purification step. To design an optimized crystallizer, it is necessary to know its solubility. The published works relating to HEDP are mainly concerned with synthesis and chelation. Investigations of solubility are relatively rare. Since acetic acid and water are two components for the preparation of HEDP in most manufacture processes, it is important to know the solubility of HEDP in the solvent mixtures. In this paper, its solubility in binary acetic acid + water solvent mixtures in the temperature range from (293.15 to 328.15) K at atmospheric pressure was measured using an isothermal method. In addition, the solvent composition (x_C^0) range is from 0.0 to 1.0 in this paper. A laser monitoring observation technique was used to determine the solubility.

Experimental Section

Materials. A crystalline powder of 1-hydroxyethane-1,1-diphosphonic acid monohydrate (relative molar mass is 224.03) was obtained from Jiangsu Jianghai Chemical Co., Ltd., China. It had a mass fraction purity of 99.38 % which was determined by an automatic titrator. It was dried in vacuo at 50 °C for 24 h and stored in a brown desiccator. The melting point is (196 ∼ 198.5) °C. No polymorphic transition was found in the treatment of material. The acetic acid is an analytical research grade reagent from Tianjin Chemical Reagent Co., China, and distilled water was used.

Method and Apparatus. The solubility of 1-hydroxyethane-1,1-diphosphonic acid monohydrate was measured by an isothermal method.[5,6] The apparatus set was similar to that described in the previous literature.[7–9] We have used the laser monitoring technique to measure solubility of HEDP in the binary solvent mixture at a constant temperature. The laser system consists of a laser generator, a photoelectric transformer, and a light intensity display.

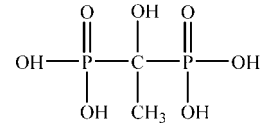

Figure 1. Chemical structure of 1-hydroxyethane-1,1-diphosphonic acid.

The solubility apparatus consisted of a jacketed glass vessel with water circulated from a water bath with a thermoelectric controller (type 501A, China). The jacket temperature was controlled to be constant (fluctuating ± 0.05 K). A submersible magnetic stirrer was used to stir the solution. A condenser was connected with the vessel to prevent the solvents from evaporating. A mercury-in-glass thermometer with an uncertainty of 0.05 K was inserted into the inner chamber of the vessel for the measurement of the temperature. An analytical electronic balance (Mettler Toledo AB204-N, Switzerland) was used to weigh the sample to an accuracy of ± 0.0001 g.

This method is based on sequentially adding known masses of solute to a stirred solution kept at a fixed temperature. Predetermined amounts of solute and solvent were transferred into the jacketed vessel. The amount of solvent was a small excess. After being stirred at a fixed temperature for 1 h, an additional solute of known mass (about 10 mg) was introduced into the vessel with continuous stirring. This procedure was repeated until the last addition of solute could not dissolve completely within the interval of addition of 30 min. Then, the total amount of the solute added (including the last addition) was used to calculate the solubility. The dissolution of the solute was monitored by a laser beam. When the solute dissolved completely, the solution was clear, and the laser intensity penetrating through the solution attained its maximum. When the laser intensity did not exceed 90 % of the maximum, the solute was believed not to be dissolved completely. The amount of solute leading to the laser intensity decrease of 10 % from the maximum is less than 1.0 mg. The uncertainty in the solubility values is estimated to be 1.0 %. All determinations

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Table 1. Experimental Solubility (x_A) of HEDP in Binary Acetic Acid (B) + Water (C) Solvent Mixtures in the Temperature Range from (293.15 to 328.15) K

x_c	x_A^{exptl}	x_A^{calcd}	x_c	x_A^{exptl}	x_A^{calcd}	x_c	x_A^{exptl}	x_A^{calcd}
	(T/K) = 293.15			(T/K) = 298.15			(T/K) = 303.15	
0.00000	0.00181	0.00066	0.00000	0.00190	0.00121	0.00000	0.00196	0.00137
0.10163	0.00231	0.00173	0.10163	0.00253	0.00251	0.10163	0.00253	0.00299
0.20020	0.00448	0.00455	0.20020	0.00521	0.00780	0.20020	0.00615	0.00696
0.30086	0.01324	0.01159	0.30086	0.01485	0.01363	0.30086	0.01720	0.01636
0.40114	0.02354	0.02628	0.40114	0.02761	0.02986	0.40114	0.03272	0.03506
0.50030	0.05156	0.05093	0.50030	0.05705	0.05690	0.50030	0.06609	0.06497
0.60030	0.08509	0.08408	0.60030	0.09444	0.09272	0.60030	0.10395	0.10287
0.69991	0.11783	0.11780	0.69991	0.12765	0.12788	0.69991	0.13829	0.13835
0.80027	0.14260	0.14406	0.80027	0.15141	0.15338	0.80027	0.16050	0.16280
0.90017	0.16166	0.16051	0.90017	0.16980	0.16802	0.90017	0.17852	0.17632
1.00000	0.17408	0.17444	1.00000	0.18167	0.18214	1.00000	0.18981	0.19038
	(T/K) = 308.15			(T/K) = 313.15			(T/K) = 318.15	
0.00000	0.00200	0.00092	0.00000	0.00200	0.00093	0.00000	0.00214	0.00078
0.10163	0.00301	0.00281	0.10163	0.00328	0.00323	0.10163	0.00359	0.00345
0.20020	0.00756	0.00780	0.20020	0.00903	0.00947	0.20020	0.01102	0.01127
0.30086	0.01995	0.01971	0.30086	0.02362	0.03014	0.30086	0.02874	0.02942
0.40114	0.03963	0.04250	0.40114	0.04858	0.05060	0.40114	0.05975	0.06078
0.50030	0.07772	0.07653	0.50030	0.08938	0.08805	0.50030	0.10164	0.10181
0.60030	0.11855	0.11632	0.60030	0.13092	0.12942	0.60030	0.14650	0.14404
0.69991	0.14980	0.15078	0.69991	0.16288	0.16352	0.69991	0.17615	0.17710
0.80027	0.17044	0.17304	0.80027	0.18220	0.18469	0.80027	0.19485	0.19714
0.90017	0.18795	0.18509	0.90017	0.19847	0.19576	0.90017	0.20960	0.20718
1.00000	0.19770	0.19845	1.00000	0.20693	0.20767	1.00000	0.21518	0.21586
	(T/K) = 323.15			(T/K) = 328.15				
0.00000	0.00225	0.00114	0.00000	0.00224	0.00144			
0.10163	0.00391	0.00483	0.10163	0.00425	0.00644			
0.20020	0.01372	0.01500	0.20020	0.01757	0.01995			
0.30086	0.03605	0.03712	0.30086	0.04708	0.04769			
0.40114	0.07384	0.07306	0.40114	0.09053	0.08934			
0.50030	0.11658	0.11755	0.50030	0.13590	0.13684			
0.60030	0.16285	0.16112	0.60030	0.18073	0.18000			
0.69991	0.19323	0.19358	0.69991	0.21120	0.21023			
0.80027	0.20995	0.21190	0.80027	0.22350	0.22642			
0.90017	0.22157	0.21963	0.90017	0.23489	0.23252			
1.00000	0.22458	0.22512	1.00000	0.23475	0.23540			

were repeated two more times, and the mean values were used to calculate the mole fraction solubility.

Together with the mass of the solute, the solubility would be obtained. The saturated mole fraction solubility of the solute (x_A) in binary acetic acid + water solvent mixtures can be obtained as follows

$$x_A = \frac{m_A/M_A}{m_A/M_A + m_B/M_B + m_C/M_C} \quad (1)$$

where m_A, m_B, and m_C represent the mass of the solute, acetic acid, and water, respectively, and M_A, M_B, and $M_C$are the molecular weight of the solute, acetic acid, and water, respectively. The same solubility experiment was conducted two more times. The uncertainty of the experimental solubility values is about 0.5 %. The uncertainty in the solubility values is due to uncertainties in the temperature measurements, weighing procedure, and instabilities of the water bath.

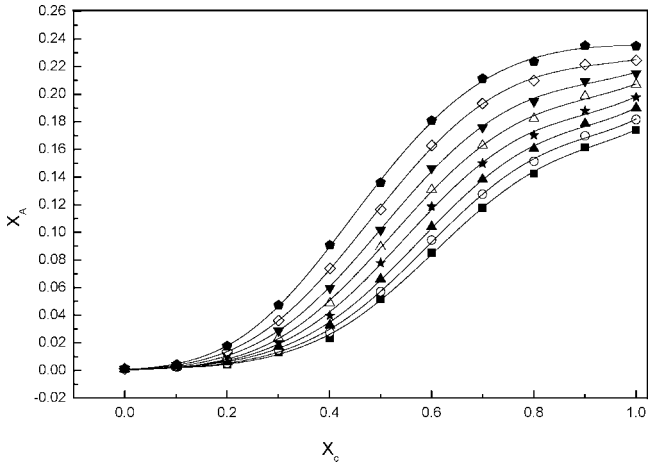

Figure 2. Solubility of HEDP in binary acetic acid (B) + water (C) solvent mixtures: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ★, 308.15 K; △, 313.15 K; ▼, 318.15 K; □, 323.15 K; ●, 328.15 K.

Results and Discussion

The solubility data of 1-hydroxyethane-1,1-diphosphonic acid monohydrate in binary acetic acid + water solvent mixtures at the temperature range from (293.15 to 328.15) K are presented in Table 1. The solubility data in binary acetic acid + water are correlated by the combined nearly ideal binary solvent (CNIBS)/ Redlich−Kister model (eq 2), which was suggested by Acree and his co-workers[10–12]

Table 2. Curve-Fitting Parameters of HEDP in Binary Acetic Acid (B) + Water (C) Solvent Mixtures in the Temperature Range from (293.15 to 328.15) K

T/K	B_0	B_1	B_2	B_3	B_4	10^3 rsmd
293.15	−7.32264	9.0224	6.51083	−18.7683	8.81152	1.237
298.15	−7.18312	9.02531	6.62262	−19.4032	9.23487	1.3827
303.15	−7.02585	9.54211	4.71941	−17.5918	8.6968	1.2898
308.15	−7.4241	13.74931	−5.40367	−8.12856	5.58943	1.6496
313.15	−7.72578	17.60758	−15.6738	2.46105	1.75808	1.4809
318.15	−7.47172	17.9714	−18.0657	5.47732	0.55544	1.3533
323.15	−7.26567	18.80612	−21.7993	10.04496	−1.278	1.0929
328.15	−7.12605	20.40852	−27.7433	16.97511	−3.9621	1.3496

$$\ln x_A = x_B^0 \ln(x_A)_B + x_C^0 \ln(x_A)_C + x_B^0 x_C^0 \sum_{i=1}^{N} S_i (x_B^0 - x_C^0)^i \quad (2)$$

The model has been shown as a possible mathematical representation for describing how the experimental isothermal solubility of a crystalline solute dissolved in a binary solvent mixture varies with binary solvent composition, in which S_i is the model constant and N can be equal to 0, 1, 2, and 3, respectively. Depending on the values of N, four equations can be obtained from eq 2. ${x_B}^0$ and ${x_C}^0$ refer to the initial mole fraction composition of the binary solvent calculated as if the solute (A) was not present. $(x_A)_i$ is the saturated mole fraction solubility of the solute in pure solvent i. Substitution of $(1 - {x_C}^0)$ for ${x_B}^0$ in eq 1 with $N = 2$ and subsequent rearrangements result in

$$\ln x_A = \ln(x_A)_B + [\ln(x_A)_C - \ln(x_A)_B + S_0 + S_1 + S_2]x_C^0 + [-S_0 + 3S_1 + 5S_2]x_C^{02} + [-2S_1 - 8S_2]\, x_C^{03} + [-4S_2]x_C^{04} \quad (3)$$

which can be written as

$$\ln x_A = B_0 + B_1 x_C^0 + B_2 x_C^{02} + B_3 x_C^{03} + B_4 x_C^{04} \quad (4)$$

The experimental solubility data (${x_A}^{\mathrm{exptl}}$) and the calculated solubility (${x_A}^{\mathrm{calcd}}$) correlated with eq 4 are listed in Table 1. For comparison with each of the experimental points, the values of the solubility of HEDP in binary acetic acid (B) + water (C) solvent mixtures in the temperature range from (293.15 to 328.15) K are presented in Figure 2. The values of the five parameters B_0, B_1, B_2, B_3, and B_4 are listed in Table 2 together with the root-mean-square deviations (rmsd). The rmsd is defined as

$$\mathrm{rmsd} = \left[\frac{1}{n}\sum_{i=1}^{N} (x_i^{\mathrm{calcd}} - x_i^{\mathrm{exptl}})^2\right]^{1/2} \quad (5)$$

where n is the number of experimental points; x_i^{calcd} represents the solubility calculated from eq 4; and x_i^{exptl} represents the experimental solubility values. From Tables 1 and 2 and Figure 2, we can draw the following conclusions:

(1) The solubility of HEDP monohydrate in binary acetic acid + water solvent mixtures is a function of temperature, and solubility increases with the rise in temperature.

(2) The solubility decreases with an increase of concentration of acetic acid in the solvent mixture.

(3) The calculated solubility of HEDP monohydrate shows good agreement with the experimental values, and the experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of HEDP.

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