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X-Ray Identification of 1-Hydroxyethane-1,1-diphosphonic Acid

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Abstract — The single-phase nature of 1-hydroxyethane-1,1-diphosphonic acid monohydrate samples was proved by powder X-ray diffraction. The X-ray patters of the anhydrous substance is presented.

1-Hydroxyethane-1,1-diphosphonic acid $CH_3C(OH)(PO_3H_2)_2$ (H_4L) has been described by Baeyer and Hoffman in 1897 [1]. Nowadays it is industrially produced in many countries and applied in drug and oil production, heat and power engineering, agriculture, and scientific research much more wider than any other alkanediphosphonic acid [2].

Crystals of 1-hydroxyethane-1,1-diphosphonic acid monohydrate $H_2L \cdot H_2O$ can be obtained by slowly evaporating its aqueous soluions [3–6]. However, this method is hardly practical for purification of this compound because of the very high solubility of $H_4L \cdot H_2O$ in water [7, 8] and high viscosity of its saturated solution. 1-Hydroxyethane-1,1-diphosphonic acid is moderately soluble in glacial acetic acid [7, 8] and readily crystallizes from aqueous solutions with high contents of CH_3COOH [7, 9–11]. On cooling saturated solutions, well-formed crystals precipitate at room temperature.

1-Hydroxyethane-1,1-diphosphonic acid has been identified by elemental analysis and melting point measurements {$H_4L \cdot H_2O$: 103–105°C [12], 104–105°C [7], 105°C [13]; H_4L: 203°C [14], 198–199°C [7], 197–198°C [15]}, paper [3, 16, 17] and thin-layer chromatography [18], potentiometric pH titration with alkali solutions [10, 19], ^1H, ^{13}C, and ^{31}P NMR spectroscopy in aqueous solutions [3, 18, 230-23] and in solid phase [24]. 1-Hydroxyethane-1,1-diphosphonic acid exists in two crystalline forms, $H_4L \cdot H_2O$ and H_4L, which are difficult to distinguish by chromatographic and spectral methods. The monohydrate loses water of crystallization when heated above 60–70°C to form H_4L [10]; the latter undergoes intramolecular dehydration in a vacuum at 170–180°C [17], and at higher temperatures it decomposes with C–P bond fission [10]. For this reason, melting points are not sufficiently quite reliable characteristics of these compounds.

In many cases powder X-ray diffraction gives more information as to the purity and phase composition of preparations containing 1-hydroxyethane-1,1-diphosphonic acid.

The experimental powder X-ray diffraction patterns of three $H_4L \cdot H_2O$ samples obtained from aqueous and ethanol solutions, as well as 80% acetic acid at room temperature are similar to each other and to that calculated from the single-crystal X-ray pattern [4] (Table 1). This result provides evidence for the phase

Table 1. Powder X-ray diffraction data for 1-hydroxyethane-1,1-diphosphonic acid[a]

d, Å		*I*, %[b]		*h*	*k*	*l*	*d*, Å		*I*, %[b]		*h*	*k*	*l*
experiment	calculation	experiment	calculation				experiment	calculation	experiment	calculation			
8.82	8.807	4	0.7	0	2	0	2.481	2.483	3	1.5	$\bar{1}$	5	2
6.68	6.646	4	0.1	1	0	0	2.422	2.428	11	4	2	3	1
6.32	6.320	52	100	0	1	1		2.417		1	2	5	0
6.25	6.218	100	79	1	1	0	2.355	2.359	5	4	$\bar{1}$	1	3
5.47	5.462	2	7	$\bar{1}$	1	1	2.315	2.317	6	6	$\bar{3}$	1	1

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Table 1. (Contd.)

d, Å		*I*, %[b]		*h*	*k*	*l*	*d*, Å		*I*, %[b]		*h*	*k*	*l*
experiment	calculation	experiment	calculation				experiment	calculation	experiment	calculation			
5.38	5.368	32	34	0	2	1	2.257	2.259	2	3	$\bar{3}$	2	1
	5.305		8	1	2	0	2.235	2.239	6	3	0	1	3
	4.812		1.5	$\bar{1}$	2	1	2.226	2.226	2	3	$\bar{2}$	5	2
4.493		3					2.199	2.198	12	0.8	3	1	0
	4.436		2	0	3	1	2.184	2.186	11	4	0	2	3
	4.403		25	0	4	0		2.186		15	$\bar{3}$	1	2
4.402	4.400	92	51	1	3	0		2.149		1.6	1	7	1
4.107	4.106	5	7	$\bar{1}$	3	1	2.136	2.138	8	2	1	5	2
4.022	4.022	8	19	1	1	1	2.126	2.126	6	3	2	5	1
3.745	3.740	14	10	1	2	1	2.102	2.107	4	4	0	3	3
3.695	3.691	2	1	0	4	1	2.092	2.094	5	2	$\bar{1}$	4	3
3.498	3.501	29	25	$\bar{1}$	0	2		2.094		1	0	8	1
3.382	3.386	8	1.6	0	0	2	2.074	2.073	2	1	3	3	0
	3.378		2	1	3	1		2.062		2	$\bar{3}$	3	2
3.324	3.325	4	1.6	0	1	2	2.053	2.056	5	5	$\bar{1}$	8	1
	3.323		0.2	2	0	0		2.053		1.3	$\bar{2}$	6	2
	3.265		1	2	1	0		2.011		1.7	2	2	2
3.253	3.254	7	10	$\bar{1}$	2	2	2.009	2.009	5	3	0	4	3
3.209	3.212	24	23	$\bar{2}$	2	1		1.979		0.9	3	4	0
3.160	3.158	8	15	0	2	2	1.972	1.974	3	1.3	2	6	1
	3.125		1.7	0	5	1	1.948	1.948	4	4	2	3	2
3.110	3.112	16	10	1	5	0	1.944	1.944	5	1	1	1	3
	3.109		1	2	2	0	1.899	1.900	4	1.8	0	5	3
3.010	3.013	16	10	1	4	1	1.863		4				
	3.007		8	$\bar{1}$	3	2	1.846	1.846	1	1.4	0	8	2
	3.003		5	$\bar{1}$	5	1	1.834	1.835	2	0.7	2	8	0
2.975	2.974	3	1	$\bar{2}$	3	1		1.835		0.8	3	3	1
2.931	2.933	19	33	0	3	2	1.766	1.769	2	1	3	4	1
2.890	2.892	5	8	2	3	0	1.760	1.762	3	1.6	$\bar{3}$	6	2
2.868	2.873	10	16	$\bar{2}$	0	2	1.713	1.715	2	2	$\bar{4}$	2	1
2.738	2.740	9	6	$\bar{1}$	4	2	1.701	1.703	3	1.7	1	10	0
	2.731		1.7	$\bar{2}$	2	2	1.685	1.686	3	2	2	9	0
	2.715		2	$\bar{2}$	4	1	1.609	1.609	2	1.4	$\bar{3}$	1	4
2.683	2.685	14	17	1	6	0	1.594	1.599	3	1.4	4	3	0
2.649	2.652	7	1.4	2	4	0		1.596		1.1	2	7	2
2.638	2.636	9	3	2	1	1	1.587	1.590	1	2	$\bar{3}$	2	4
2.579	2.580	2	1.5	$\bar{2}$	3	2	1.582	1.583	3	3	1	9	2
2.572	2.573	4	1.5	1	2	2	1.555	1.555	5	0.6	4	4	0

[a] Given are the interplanar spacings (*d*) corresponding to reflections with I_{exp} or I_{calc} > 1%.
[b] Integral intensities of reflections.

Table 2. Interplanar spacings (*d*) and relative intensities (*I*) in the power X-ray diffraction pattern of anhydrous 1-hydroxyethane-1,1-diphosphonic acid[a]

d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
7.99	31	3.525	15	2.532	25	1.918	4
5.40	52	3.435	24	2.458	5	1.869	11
5.27	35	3.373	16	2.389	10	1.806	11
5.15	75	3.267	5	2.312	23	1.784	14
4.78	60	3.168	23	2.284	55	1.736	10
4.65	28	3.027	12	2.253	14	1.708	5
4.46	35	2.930	100	2.218	7	1.603	6
4.10	88	2.879	40	2.178	7	1.591	5
3.994	10	2.755	6	2.101	8	1.525	7
3.911	12	2.701	38	2.045	19	1.510	5
3.757	12	2.668	22	1.985	7	1.482	7
3.687	11	2.607	17	1.934	6	1.469	11
						1.424	5

[a] Given are the *d* values corresponding to reflections with $I > 4\%$.

individuality of the samples. The X-ray pattern of H_4L (Table 2) obtained by drying $H_4L \cdot H_2O$ at 80°C to constant weight shows no reflections of the starting monohydrate.

EXPERIMENTAL

1-Hydroxyethane-1,1-diphosphonic acid monohydrate and the anhydrous acid were identified as described in [10, 25]. The powder X-ray patterns were obtained on an HZG-4A diffractometer (CuK_α radiation, graphite monochromator, 2θ 7–80°).

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