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Note

SOLUBILITY OF CADMIUM HYDROGEN PHOSPHATE IN AQUEOUS MEDIA

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A review of earlier work [1,2] on phosphates of cadmium indicated that studies on the solubility behaviour of cadmium hydrogen phosphate, $CdHPO_4$, in aqueous media has not been undertaken. Since cadmium, in cases of acute poisoning, is considered to be associated [3–5] with calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, the final crystalline product [6] formed during calcification, it was considered desirable to investigate the possible mode of association through the study of the solubility of $CdHPO_4$ between the temperatures 37 and 52°C. The related thermodynamic parameters ΔG^0, ΔH^0, ΔS^0, and ΔC_p^0 have been calculated and are presented here.

PROCEDURE

$CdHPO_4$ was prepared by saturating orthophosphoric acid with cadmium hydroxide at pH 4.5 maintained by the dropwise addition of 0.01 M NaOH. The sample was filtered, washed with carbon dioxide-free water, acetone, and ether and dried in vacuo for 48 h. Cadmium and phosphorus were determined complexometrically [7]. The analytical results (found: Cd 52.95 wt. %, P 14.32 wt. %, Cd/P g atom ratio = 0.99; calcd.: Cd, 53.90 wt. %, P 14.87 wt. %, Cd/P g atom ratio = 1.0) corresponded to anhydrous $CdHPO_4$.

The IR spectrum of the sample was obtained using a Perkin-Elmer grating infrared spectrophotometer in the range 600–4000 cm^{-1}. Peaks at 990, 1060, 1140, 1380, 1640 and 2240 cm^{-1}, corresponding to the absorptions [8] of $CaHPO_4$, were obtained.

Solubility studies at pH 5.0 in different ionic environments of $NaNO_3$ were made by the equilibration method between the temperatures 37 and 52°C. Attainment of saturation was established by kinetic studies. Cadmium and phosphorus were determined in saturated solutions [7].

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CALCULATION OF SOLUBILITY PRODUCT AND STANDARD THERMODYNAMIC DATA

The ionic strength, μ, is defined in these calculations by

$$\mu = P\left[Q + \frac{H^+}{2P} + \frac{R}{N}\right] + E_i \tag{1}$$

where P and H^+ represent the molar concentrations of phosphorus and hydrogen ion, respectively. The symbols in eqn. (1) are defined by

$$Q = \frac{2M}{P} \tag{2}$$

$$R = \frac{(H^+)}{2K_2 f'} + \frac{2}{f''} \tag{3}$$

$$N = \frac{(H^+)^2}{K_1 K_2} + \frac{(H^+)}{K_2 f'} + \frac{1}{f''} \tag{4}$$

and E_i in eqn. (1) refers to the molar concentrations of the other ionic species of the equilibration medium. In eqns. (2)–(4), (H^+) and M represent the hydrogen ion activity and molar concentrations of cadmium ion, respectively, K_1 and K_2 are the first and second dissociation constants for orthophosphoric acid, and f' and f'' are the molar activity coefficients for the species $H_2PO_4^-$ and HPO_4^{2-}, respectively. The values of K_1 [9] at different temperatures were obtained from

$$\log K_1 + 2.0304 = 5 \times 10^{-5}(t + 18)^2 \tag{5}$$

and that of K_2 by interpolation of the second dissociation constant values of Nims [10]. Equations (1)–(4) are consistent with the assumption that the only ionic phosphate species present in significant concentrations are HPO_4^{2-} and $H_2PO_4^-$. The contributions of hydroxyl ion to the ionic strength is considered negligible in comparison with that of the ionic species.

An approximate ionic strength was obtained by the use of the eqns. (1)–(4) assuming the values of f' and f'' to be 1. An improved ionic activity coefficient f'_i was then calculated by the use of the extension of the Debye–Huckle limiting law

$$-\log f'_i = \frac{AZ_i^2\sqrt{\mu}}{1 + \beta_{a_i}\sqrt{\mu}} \tag{6}$$

where the terms a_i, Z_i, β and A have their usual significance. The values of $a_i = 5 \times 10^{-8}$ for Cd^{2+} and $a_i = 4 \times 10^{-8}$ for HPO_4^{2-} and $H_2PO_4^-$ were used. With the activity coefficient obtained from eqn. (6), a new value for μ was calculated from eqns. (1)–(4); iteration was continued until convergence was attained. $\log f'_i$ is thus referred to as the apparent activity coefficient. The true activity coefficient, $\log f_i$, was obtained from the modified Hückle equation

$$\log f_i = \log f'_i + B\mu \tag{7}$$

where B is an adjustable parameter introduced to allow for variation of the dielectric constant with concentration. Using the values of $\log f_i$ in eqn. (4), the activity of HPO_4^{2-}, (HPO_4^{2-}), was calculated from

$$\left(HPO_4^{2-}\right) = \frac{P}{N} \tag{8}$$

The solubility product, K_{sp}, for $CdHPO_4$ was then obtained using

$$K_{sp} = Mf_{Cd} \times \left(HPO_4^{2-}\right) \tag{9}$$

The values of K_{sp} at various temperatures were fitted by the method of least squares to eqn. (10).

$$pK_{sp} = \frac{Am}{T} + Em + CmT \tag{10}$$

TABLE 1

Solubility product of cadmium hydrogen phosphate in systems containing different concentrations of $NaNO_3$ at 37–52°C

Temp. (°C)	Salt concn. ($M \times 10^3$)	Ionic strength ($\mu \times 10^4$)	Concentration (g ions l^{-1})		$K_{sp} \times 10^9$
			$Cd \times 10^3$	$P \times 10^3$	
37	4.5	253	1.52	1.465	2.4717
	34.5	557.7	1.52	1.586	2.6769
	105.0	1259.2	1.534	1.62	2.7584
	165.0	1861.3	1.646	1.58	2.8867
					Ave. 2.6985
42	4.5	251.7	1.43	1.52	2.4481
	34.5	553.0	1.49	1.57	2.6256
	105.0	1257.9	1.47	1.60	2.6481
	165.0	1860.5	1.62	1.52	2.7783
					Ave. 2.6250
47	4.5	252.6	1.52	1.38	2.3801
	34.5	553.6	1.54	1.51	2.6252
	105.0	1258.2	1.50	1.56	2.6417
	165.0	1860.1	1.60	1.52	2.7456
					Ave. 2.5981
52	4.5	253.5	1.53	1.36	2.3634
	34.5	552.2	1.47	1.50	2.4406
	105.0	1258.2	1.51	1.52	2.5405
	165.0	1859.5	1.57	1.52	2.6484
					Ave. 2.4982

TABLE 2

Solubility product and thermodynamic data for the dissolution of cadmium hydrogen phosphate

Temp. (°C)	(−) log K_{sp}		$\Delta G^0 \times 10^{-3}$ (J mole^{-1} deg^{-1})	(−)$\Delta H^0 \times 10^{-3}$ (J mole^{-1} deg^{-1})	(−)$\Delta S^0 \times 10^{-2}$ (J mole^{-1} deg^{-1})	(−)$\Delta Cp^0 \times 10^{-2}$ (J. mole^{-1} deg^{-1})
	Exptl.	Calcd.				
37	8.568	8.568	50.778	1.650	1.691	9.364
42	8.580	8.580	51.661	6.370	1.842	9.515
47	8.585	8.585	52.620	11.166	1.993	9.666
52	8.602	8.602	53.625	16.037	2.144	9.817

The values of the thermodynamic functions were calculated from eqn. (10) and the equations

$$\Delta G^0 = -RT \ln Km = -2.3026R(Am + BmT + CmT^2) \tag{11}$$

$$\Delta S^0 = -\frac{\mathrm{d}(\Delta G^0)}{\mathrm{d}t} = -2.3026R(Bm + 2CmT) \tag{12}$$

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 = 2.3026R(Am - CmT^2) \tag{13}$$

and

$$\Delta C_\mathrm{p}^0 = \frac{\mathrm{d}(\Delta H^0)}{\mathrm{d}T} = -2.3026R(2CmT) \tag{14}$$

where R is the gas constant. For $CdHPO_4$ ($m = 1$) the function refers to the dissolution of 1 mole of $CdHPO_{4(s)} \rightleftharpoons Cd^{2+}_{(aq)} + HPO_{4(aq)}$.

The dependence of solubility and solubility product on ionic environment at different temperatures is given in Table 1 and the related thermodynamic parameters of the process of dissolution in Table 2. The solubility and solubility product decreased with increase in temperature, indicating that the standard free energy of formation of $CdHPO_4$ must increase with temperature more rapidly than the sum of the free energies of formation of Cd^{2+} and HPO_4^{2-} ions.

In cases of acute cadmium poisoning in vivo, most of the cadmium ions are taken up by the metal binding sites of the metallothionein [11]. A very low level of cadmium is thus released into the blood serum. It is understood that calcification in vivo is due to the incipient deposition of dicalcium hydrogen phosphate dihydrate, $CaHPO_4 \cdot 2\ H_2O$, at the ossifying sites. Since cadmium hydrogen phosphate has a lower K_{sp} than dicalcium hydrogen phosphate dihydrate [12–14] at 37°C association of cadmium with the calcium apatite of bones is possible through the precipitation of $CdHPO_4$ along with $CaHPO_4 \cdot 2\ H_2O$ during calcification.

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