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Solubility Product of the Cadmium Phosphate $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ at 37 °C

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The solubility product of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ at 37 °C has been determined by mixing dilute solutions of cadmium nitrate and ammonium phosphate and measuring cadmium and phosphate concentrations as well as the pH values of the saturated solutions. Using the definition $K_{sp} = a(Cd^{2+})^5 a(HPO_4^{2-})^4/a(H^+)^2$, the value $pK_{sp} = (30.9 \pm 0.3)$ was found. Necessary values of stability constants of cadmium phosphate complexes in solution were estimated from literature values determined at high ionic strength with the aid of mean ion activity coefficients from independent sources.

Introduction

In a study of crystallization of different pure and mixed heavy metal phosphates,[1] we needed the solubility product of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ in order to be able to calculate supersaturations in mixed solutions of cadmium nitrate and ammonium phosphate. The only value which could be found in the literature was that of Hietanen, Sillén, and Högfeldt,[2] which is valid at 25 °C and an ionic strength of 3.0 M. It equals

$$K_{csp} = \frac{[Cd^{2+}]^5[HPO_4^{\,2-}]^4}{[H^+]^2} = 10^{-25.4}\ M^7 \qquad (1)$$

We are interested only in ionic strengths up to a little above 0.1 M, and most of our experiments have been carried out at 37 °C. We believe that our results could be of interest to others investigating the inorganic and crystal chemistry of toxic heavy metals or developing measures of environmental protection in connection with the production of phosphorus compounds, including fertilizers, from cadmium-containing rock phosphate. The work also demonstrates how to estimate products of ion activity coefficients at high ionic strengths from independent sources.

Experimental Section

Apparatus. pH was measured with a Radiometer PHM 240 pH-meter, using a Metrohm Solitrode combination electrode. For calibration we used three ISO standard buffers: potassium hydrogen phthalate, 0.05 m, pH = 4.028; potassium dihydrogen phosphate and sodium hydrogen phosphate, both 0.025 m, pH = 6.841; and Borax, 0.01 m, pH = 9.088, all values at 37 °C.

Cadmium was determined by atomic absorption spectrometry using a Perkin-Elmer model 3300 atomic absorption spectrophotometer. Phosphate was determined by spectrophotometry using a Zeiss DMR 21 spectrophotometer.

To check the identity of precipitates, they were examined by optical microscopy either in situ, through the bottoms of the flasks, with a Zeiss Axiovert 25 inverted microscope, or ex situ with a Zeiss Jenapol polarization microscope.

Reagents and Solutions. All reagents and solutions were prepared from Merck analytical grade chemicals with a stated purity of at least 99%. The water used for precipitation experiments was demineralized water further purified by passing through a filter with activated carbon and a second mixed-bed ion-exchange column. The conductivity of the water never exceeded 0.1 μS/cm.

Phosphate Determination. Phosphate was determined with the molybdenum blue method, using ascorbic acid as reducing agent and potassium antimonyl tartrate as catalyst. Potassium dihydrogen phosphate was used as standard. Absorbances of samples were measured at 890 nm.

Precipitations. Different volumes of (0.100 ± 0.001) M $Cd(NO_3)_2$ solution were mixed with different volumes of (0.100 ± 0.001) M $NH_4H_2PO_4$ solution, (0.100 ± 0.001) M $(NH_4)_2HPO_4$ solution, or mixtures of both in different ratios, in 100 mL conical flasks. The flasks were filled up to (50.0 ± 0.1) mL with water and kept at (37.0 ± 0.1) °C. When no further evolution of the precipitate in a flask could be detected by inspection with the inverted microscope, usually after 6−10 days, it was assumed that equilibrium had been attained. pH was then measured (±0.001 pH) and samples were withdrawn for analysis. They were centrifuged, before cadmium (±1%) and phosphate (±0.5%) were determined in the supernatant. The identity of the solid phase was established by petrographic microscopy, as stated above, X-ray powder diffraction, and IR spectroscopy.

Results and Calculations

Forty-nine experiments were carried out. The results of three were discarded, because the values of pH and cadmium and phosphate concentrations turned out to be mutually inconsistent. Figure 1 shows the distribution of calcium and phosphate concentrations. Many of the points represent more than one experiment, because the ratio of the concentrations of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ was varied between the extremes 1:0 and 0:1. The final pH was found to lie between 1.0 and 6.7.

The conventional way of writing the solubility product of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ is

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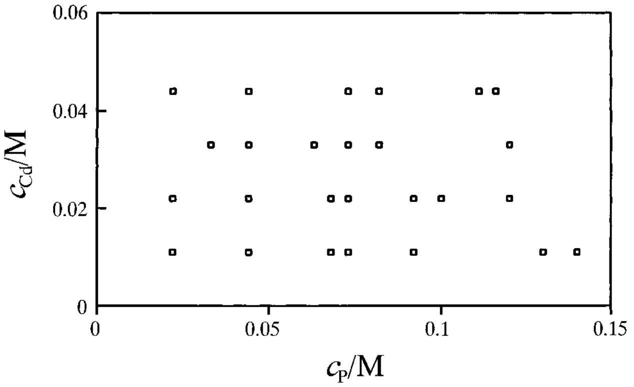

Figure 1. Corresponding initial cadmium and phosphate concentrations in individual experiments. One point may indicate two or more experiments with varying initial pH.

$$K_{sp} = a(Cd^{2+})^5 a(H^+)^2 a(PO_4{}^{3-})^4 \qquad (2)$$

We prefer, however, to use the expression

$$K_{sp} = \frac{a(Cd^{2+})^5 a(HPO_4{}^{2-})^4}{a(H^+)^2} \qquad (3)$$

corresponding to the reaction

$$Cd_5H_2(PO_4)_4{\cdot}4H_2O + 2H^+ \rightleftarrows 5Cd^{2+} + 4HPO_4{}^{2-} + 4H_2O$$

because this is independent of the third dissociation constant of phosphoric acid, which, due to its low value, is not known with the same precision as the two others. A similar convention was adopted for the calcium phosphates by Bjerrum[3] and later used for other systems.[2]

To obtain the activities of Cd^{2+} and $HPO_4{}^{2-}$, the following equations have to be solved with respect to $[Cd^{2+}]$, $[HPO_4{}^{2-}]$, $[NH_3]$, and $[H^+]$:

(1) Mass balance:

$$[Cd^{2+}] + \sum_{n=1}^{4}[Cd(NH_3)_n{}^{2+}] + [CdHPO_4] + [CdH_2PO_4{}^+] = C_{Cd} \qquad (4)$$

$$[H_3PO_4] + [H_2PO_4{}^-] + [HPO_4{}^{2-}] + [PO_4{}^{3-}] + [CdHPO_4] + [CdH_2PO_4{}^+] = C_p \qquad (5)$$

$$[NH_3] + [NH_4{}^+] + \sum_{n=1}^{4} n[Cd(NH_3)_n{}^{2+}] = C_N \qquad (6)$$

$$[H^+] + [NH_4{}^+] + [H_2PO_4{}^-] + 2[H_3PO_4] - [PO_4{}^{3-}] + [CdH_2PO_4{}^+] = C_H \qquad (7)$$

(2) Equilibrium:

$$K_{a1} = \frac{a(H^+)a(H_2PO_4{}^-)}{a(H_3PO_4)} \qquad (8)$$

$$K_{a2} = \frac{a(H^+)a(HPO_4{}^{2-})}{a(H_2PO_4{}^-)} \qquad (9)$$

$$K_{a3} = \frac{a(H^+)a(PO_4{}^{3-})}{a(HPO_4{}^{2-})} \qquad (10)$$

$$K_N = \frac{a(H^+)a(NH_3)}{a(NH_4^+)} \qquad (11)$$

$$\beta_n = \frac{a(Cd(NH_3)_n{}^{2+})}{a(Cd^{2+})a(NH_3)^n} \qquad n = 1 ,..., 4 \qquad (12)$$

$$K_{MHL} = \frac{a(CdHPO_4)}{a(Cd^{2+})a(HPO_4{}^{2-})} \qquad (13)$$

$$K_{MH2L} = \frac{a(CdH_2PO_4{}^+)}{a(Cd^{2+})a(H_2PO_4{}^-)} \qquad (14)$$

Activity coefficients have been calculated with the Debye–Hückel equation

$$\log \gamma_i = -\frac{Az_i{}^2\sqrt{I}}{1 + Ba_i\sqrt{I}} \qquad (15)$$

where the ion radius parameter a_i for ion species i is obtained from Kielland's table.[4] The cadmium complexes are not found there, so we have used the same value as for the hydrated cadmium ion.

The values of the stability constants may be found in Vol. 4 of *Critical Stability Constants*[5] with the exception of those of the cadmium phosphate complexes, K_{MHL} and K_{MH2L}. The former has been determined by Ramamoorthy and Manning[6,7] for $I = 0.1$ M; they found

$$K_{cMHL} = \frac{[CdHPO_4]}{[Cd^{2+}][HPO_4{}^{2-}]} = 10^{2.91}\ M^{-1}$$

The relatively low value of I means that we may calculate the thermodynamic value by using (15); the result is

$$K_{MHL} = 10^{3.81}$$

The authors ignore the existence of $CdH_2PO_4{}^+$. Hietanen et al.[2] have determined both values at $I = 3.0$ M; they fund

$$K_{cMHL} = 10^{2.68}\ M^{-1}$$

$$K_{cMH2L} = \frac{[CdH_2PO_4{}^+]}{[Cd^{2+}][H_2PO_4{}^-]} = 10^{0.78}\ M^{-1}$$

With such a high ionic strength the Debye–Hückel equation is no longer valid. We may, however, estimate the thermodynamic value as follows:

We assume, as usual, that electrically neutral species behave ideally. Therefore, we have

$$K_{MHL} = \frac{K_{cMHL}}{\gamma(Cd^{2+})\gamma(HPO_4{}^{2-})} \qquad (16)$$

We further assume that there is no specific interaction

Table 1. Values of Dissociation Constants of Phosphoric Acid at Two Ionic Strengths, 25 °C

eq	pK_a ($I = 0$ M)	pK_c ($I = 3.0$ M)
8	2.148	1.86
9	7.199	6.26

between Cd^{2+} and NO_3^-, between H^+ and phosphate species, and between H^+ and NO_3^- in solutions with $I = 3.0$ M. If this assumption is valid, we may calculate the denominator in (16) from known mean ion activity coefficients of 1 M cadmium nitrate solution and 3 M nitric acid as well as dissociation constants of phosphoric acid at $I = 0$ and 3.0 M. The values at 25 °C given by Robinson and Stokes are[8,9]

$$Cd(NO_3)_2 \qquad 1.0\ \text{m:} \quad \gamma_\pm = 0.433$$

$$HNO_3 \qquad 3.0\ \text{m:} \quad \gamma_\pm = 0.909$$

We thus have

$$\gamma(Cd^{2+})\gamma(NO_3^{\;-})^2 = \gamma_\pm^{\;3} = 0.0812$$

$$\gamma(H^+)\gamma(NO_3^{\;-}) = \gamma_\pm^{\;2} = 0.826$$

The first and second dissociation constants at 25 °C of phosphoric acid are as shown in Table 1.[5] From these we obtain

$$K_{a1}K_{a2} = K_{c1}K_{c2}\gamma(H^+)^2\gamma(HPO_4^{\;2-}) \tag{17}$$

whence

$$\gamma(H^+)^2\gamma(HPO_4^{\;2-}) = 0.0593$$

Elimination of $\gamma(H^+)$ and $\gamma(NO_3^-)$ now yields

$$\gamma(Cd^{2+})\gamma(HPO_4^{\;2-}) = 0.0071$$

When this is inserted in (16), we finally obtain

$$K_{MHL} = 10^{4.83}$$

at 25 °C. It should be noted that in using the data of Robinson and Stokes we have neglected the difference between molality and molarity.

The thermodynamic value of K_{MH2L} cannot be found in this way, because we have no independent information about $\gamma(CdH_2PO_4^+)$ at $I = 3.0$ M. On the basis of a comparison with phosphate complexes of other divalent metals,[5] we make the estimate

$$K_{MH2L} = 10^{1.8}$$

Table 2 gives a summary of the values of equilibrium constants and other parameters used in the calculations of K_{sp}. With the exception of the stability constants of the phosphate complexes, which are known only at 25 °C, all values refer to 37 °C.

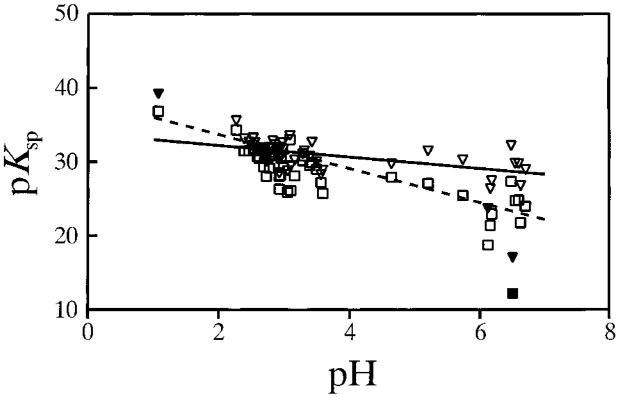

Figure 2. Solubility product values from individual experiments plotted against final pH with two different values of stability constant of neutral cadmium phosphate complex. □ and - - -: log $K_{MLH} = 3.81$. ▽ and —: log $K_{MLH} = 4.83$. ■ and ▼: Not included in mean values.

Table 2. Equilibrium Constants and Parameters Used in Calculation of the Solubility Product

constant	T/°C	value	eq	ref
pK_{a1}	37	2.206	8	14
pK_{a2}	37	7.182	9	14
pK_{a3}	37	12.180	10	15
pK_N	37	8.890	11	16
log β_1	37	2.50	12	5
log β_2	37	4.45	12	5
log β_3	37	5.74	12	5
log β_4	37	6.52	12	5
log K_{MHL}	25	3.81	13	6, 7
		4.83		2
log K_{MH2L}	25	1.8	14	2
Debye−Hückel a_i/Å				
Cd^{2+}, $Cd(NH_3)_n^{2+}$, $CdH_2PO_4^+$		5	15	4
$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}		4	15	4
NH_4^+		2.5	15	4
H^+		9	15	4

Table 3. Selected Results To Illustrate the Importance of Cadmium Phosphate Complexes

Measured Values					
$c_{Cd}/10^{-3}$ M	7.43	5.75	6.51	8.86	0.0204
$c_P/10^{-3}$ M	33.4	24.5	55.2	26.0	25.5
pH	2.267	2.977	3.161	3.560	6.477
Calculated Concentrations (10^{-3} M) with log $K_{MHL} = 4.83$ and log $K_{MH2L} = 1.8$					
$[Cd^{2+}]$	4.33	4.12	2.44	6.14	0.000 244
$[HPO_4^{2-}]$	0.000 685	0.002 01	0.0152	0.007 65	9.12
$[CdHPO_4]$	0.0306	0.0786	0.286	0.440	0.0200
$[CdH_2PO_4^+]$	3.07	1.55	3.79	2.28	0.000 126
pK_{sp}	35.605	32.579	30.245	28.250	32.193
Calculated Concentrations (10^{-3} M) with log $K_{MHL} = 3.81$					
$[Cd^{2+}]$	7.42	5.74	6.44	8.79	0.002 29
$[HPO_4^{2-}]$	0.000 781	0.002 26	0.0165	0.009 36	9.12
$[CdHPO_4]$	0.005 42	0.0115	0.0741	0.0704	0.0179
pK_{sp}	34.305	31.708	28.098	27.207	27.333

The calculations were carried out for both selections of stability constants of cadmium phosphate complexes, using a previously described general computer program.[10,11] Table 3 shows a few of the results for illustration, and all the results of pK_{sp} are plotted in Figure 2 with pH as the abscissa. In the calculation of mean values, one result was excluded in the case of log $K_{MHL} = 3.81$ and three results were excluded in the case of log $K_{MHL} = 4.83$ and log $K_{MH2L} = 1.8$, both on the basis of a statistical analysis of extreme deviations.[12] These results are marked with filled symbols in Figure 2. The remaining results yield, with standard deviations of the means

$$\log K_{MHL} = 3.81: \qquad pK_{sp} = 28.6 \pm 0.5$$

$$\log K_{MHL} = 4.83, \quad \log K_{MH2L} = 1.8: \qquad pK_{sp} = 30.9 \pm 0.3$$

Discussion

From the regression lines in Figure 2 it is evident that the calculated value of pK_{sp} shows a significant dependence on pH if it is assumed that there is only one cadmium phosphate complex with the stability constant given by Ramamoorthy and Manning,[6] whereas we can hardly attach any significance to the variation found using the two stability constants determined by Hietanen et al.[2] We therefore consider the values of stability constants of the latter the most reliable ones. A still better agreement could be found by adjustment of the two stability constants, but such a procedure does not seem entirely justified, since we have not designed the present investigation with the aim of determining more precise values of these constants. However, we regard our results as a confirmation of the suitability of the method we have used for indirect estimation of activity coefficients at high ionic strengths.

Table 3 demonstrates the importance of knowledge of stability constants for a precise determination of a solubility product. At low pH more than half of the dissolved Cd may be bound as $CdH_2PO_4^+$, and at high pH as much as 98% is bound as $CdHPO_4$. The influence of these complexes on the concentration of HPO_4^{2-} is less pronounced. A species such as $CdPO_4^-$ may play a role as well, especially at high pH. Calculations show, however, that even a value for the stability constant of this complex as high as 10^{10}, which is very unlikely, would change individual values of pK_{sp} by less than the standard deviation.

The scatter of experimental results around the mean value is relatively high, but this is not unusual for an equilibrium constant, in which the sum of powers of individual ion activities equals a value as high as 11. The probable error of pK_{sp} was estimated as follows:

For a representative selection of results, we changed one concentration at a time (cadmium, nitrate, ammonium, or phosphate) by 1% and recalculated pK_{sp}. pH was changed by 0.005. The squares of deviations of pK_{sp} thus calculated for one experiment were added, and the square root of the result was taken as the probable error. We found the average value ± 0.14, that is, half the standard deviation actually found. However, we may have underestimated pH uncertainty. A pH deviation of 0.005 corresponds to a potential difference of only 0.3 mV, and variations of liquid-junction potentials at the reference electrode, usually neglected or assumed to be eliminated in conventional pH measurements, may easily be much larger than this value.

Inspection of Figure 2 shows that use of better values of stability constants reduces not only the correlation between pK_{sp} and pH but also the scatter. Exclusion of the value corresponding to the lowest pH in the calculation of the mean value is justified not only by statistics but by the fact, too, that at pH ≈ 1 an ordinary glass and reference electrode chain is no longer quite reliable.[13] The two excluded values at high pH are subject to experimental errors arising from the low solubility under these circumstances.

It is, of course, somehow problematic that not all the values for equilibrium constants used are valid at 37 °C. However, most phosphate complexes have been studied only at 25 °C. On the other hand, those stability constants which are known also at higher temperature show very little dependence on temperature. For this reason, we believe that our values are reasonably reliable at 37 °C.

In conclusion, we have found the value $K_{sp} = 10^{-30.9}$ at 37 °C.

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