Literature Cited

(1) Orr, F. M.; Yu, A. D.; Lien, C. L. *Soc. Pet. Eng. J.* **1981**, 480-92.
(2) Turek, E. A.; Metcalfe, R. S.; Yarborough, L.; Robinson, R. L., paper SPE 9231 presented at the SPE 1980 Technical Conference and Exhibition, Dallas, TX Sept 21-24, 1980.
(3) Im, V. K.; Kurata, F. *J. Chem. Eng. Data* **1971**, *16*, 412-5.
(4) Hottovy, J. D.; Luks, D. K.; Kohn, J. P. *J. Chem. Eng. Data* **1982**, *27*, 298-302.
(5) Schneider, G.; Alwani, Z.; Heim, W.; Horvath, E.; Franck, E. *Chem.-Ing.-Tech.* **1967**, *39*, 649-56.
(6) Schneider, G. *Chem. Eng. Prog. Symp. Ser.* **1968**, *64*, 9-15.
(7) Schneider, G. *Adv. Chem. Phys.* **1970**, *17*, 1-42.
(8) Kulkarni, A. A.; Zarah, B. Y.; Luks, K. D.; Kohn, J. P. *J. Chem. Eng. Data* **1974**, *19*, 92-4.
(9) Hottovy, J. D.; Luks, K. D.; Kohn, J. P. *J. Chem. Eng. Data* **1981**, *26*, 256-8.
(10) Fall, D. J.; Luks, K. D. *J. Chem. Eng. Data* **1984**, *29*, 413-7.
(11) Huie, N. C.; Luks, K. D.; Kohn, J. P. *J. Chem. Eng. Data* **1973**, *18*, 311-3.
(12) Van Konynenburg, P. H.; Scott, R. L. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *298*, 495-540.
(13) Luks, K. D.; Kohn, J. P. In "Proceedings of the 63rd Annual Convention, Gas Processors Association, New Orleans, LA, March 21, 1984"; Gas Processors Association: Tulsa, OK, 1984; pp 181-6.
(14) Fall, D. J.; Fall, J. L.; Luks, K. D. *J. Chem. Eng. Data* **1985**, *30*, 82-8.
(15) Vargaftik, N. B. "Tables on the Thermophysical Properties of Liquid and Gases", 2nd ed.; Wiley: New York, 1975; pp 167-8.

Received for review July 30, 1984. Accepted November 5, 1984. Support for this research was provided by the National Science Foundation (Grant No. CPE-8100450). The apparatus used is part of the *PVTx* laboratory at The University of Tulsa and was purchased with funds provided by several industries, The University of Tulsa, and a National Science Foundation specialized equipment grant (No. CPE-8014650).

Solubility of Octacalcium Phosphate at 25 and 45 °C in the System $Ca(OH)_2$–H_3PO_4–KNO_3–H_2O

J. C. Heughebaert[†] **and G. H. Nancollas***

Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214

The solubility product of octacalcium phosphate ($Ca_4H(PO_4)_3\cdot 2.25H_2O$) has been determined in the system $Ca(OH)_2$–H_3PO_4–KNO_3–H_2O at 25 and 45 °C by allowing both growth and dissolution experiments over a range of ionic strength to come to equilibrium. Values of pK_{so} = 49.6 ± 0.2 and 49.8 ± 0.3, respectively, were obtained by taking into account activity coefficient corrections and ion-pair formation.

Introduction

Octacalcium phosphate ($Ca_4H(PO_4)_3\cdot 2.5H_2O$, hereafter OCP) is one of the most important calcium phosphate phases since it has been implicated as a percursor to the formation of hydroxyapatite ($Ca_5(PO_4)_3OH$, hereafter HAP), in biological mineralization (1, 2). Although values of the solubility have been reported at 25 and 37 °C (*3*, *4*), it was discovered that OCP could be grown in a range of solution composition which, on the basis of these data, would be expected to be undersaturated (*5*). A redetermination of the solubility at 37 °C indicated a value smaller than that previously reported and it was possible to demonstrate the crystallization of pure OCP within the pH range 6-7 (*6*). The unusually large difference between the solubilities at 25 and 37 °C in the literature prompted us to redetermine the values at other temperatures and to ensure the stability of the OCP phase by allowing both growth and dissolution experiments to come to equilibrium.

Experimental Section

Deionized, triply distilled water purged with presaturated nitrogen gas to exclude carbon dioxide was used to prepare solutions. Potassium hydroxide was prepared from Dilutit reagents (J. T. Baker Co.) and was standardized against potassium hydrogen phthalate (J. T. Baker Co.) by using both potentiometric and colorimetric (thymolphthalein blue) titrations. Stock solutions of calcium nitrate (Ventron Co. Alfa Division) potassium dihydrogen phosphate (J. T. Baker Co.) and potassium nitrate (Ventron Co. Alfa Division) were prepared from the ultrapure-grade salts. Analyses for calcium and potassium ions in these stock solutions were made by passing aliquots through Dowex 50W-XB ion-exchanger columns in the hydrogen form and titrating the eluted acid against potassium hydroxide solution.

The OCP sample was prepared by using the constant-composition crystallization method at a pH of 6.0 (*6*). The solid phase was filtered through a 0.2-μm filter (Millipore, Beford, Ma) and X-ray powder diffraction (XRG 3000 Phillips diffractometer, Cu Kα radiation, Ni filter) gave no evidence of any phase other than OCP. Calcium and phosphate were analyzed by uisng absorption spectroscopy (Perkin-Elmer Model 503) for calcium and spectrophotometry (Varian Model Cary 210) for phosphate (*7*). Chemical analysis of the OCP preparation gave a molar calcium/phosphate ratio of $1.33_8 \pm 0.01$. The specific surface area of the crystals, 9.0 ± 0.2 m^2 g^{-1}, was determined by a single-point BET method (70/30, He/N_2 gas mixture, Quantasorb, Quantachrome, Greenvale, NY).

The solubility of OCP was determined by allowing OCP crystal growth and dissolution experiments to proceed to equilibrium in solutions initially supersaturated or undersaturated with respect to OCP. Approximately 30 mg of crystals was added to 100 mL of solutions containing calcium nitrate, potassium dihydrogen phosphate, and potassium nitrate at a pH of 6.2. The suspensions were sealed in Pyrex vessels and shaken in a thermostat at 25 or 45 °C. Equilibrations were allowed to proceed for 28 days at 25 °C and 12 days at 45 °C using different conditions of stirring, initial concentrations, and ionic strength. At the end of these time periods the pH was measured by using a glass electrode (Beckmann Instruments) and a silver/silver chloride reference electrode. The latter incorporated an intermediate liquid junction containing potassium chloride solution at the same ionic strength as the solution being studied. For the calcium and phosphate determinations, care was taken to use standard solutions of the same ionic composition as the test media. It was important to verify, by chemical analysis, X-ray diffraction, and infrared spectroscopy, the absence of solid phases other than OCP in the experiments.

Results and Discussion

The concentrations of ionic species in the equilibrated calcium phosphate solutions were calculated by using expressions

---

[†] Laboratoire de Physico-Chimie des Solides, ERA CNRS No. 263, 31400 Toulouse, France.

Table I. Equilibrium Data

	dissocn and assocn constants			
	25 °C	37 °C	45 °C	ref
$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$	7.11×10^{-3}	6.22×10^{-3}	5.63×10^{-3}	8
$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}$	6.30×10^{-8}	6.58×10^{-8}	6.61×10^{-8}	9
$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$	4.73×10^{-13}	6.61×10^{-13}	$(6.61 \times 10^{-13})^a$	10
$Ca^{2+} + H_2PO_4^- \rightleftarrows CaH_2PO_4^+$	25.6	31.9	36.5^b	11
$Ca^{2+} + HPO_4^{2-} \rightleftarrows CaHPO_4$	548	681	787^b	11
$Ca^{2+} + PO_4^{3-} \rightleftarrows CaPO_4^-$	2.9×10^6	3.46×10^6	$3.86 \times 10^{6\,b}$	11
$Ca^{2+} + OH^- \rightleftarrows CaOH^+$	13.8	21.3^c	28.4^b	12
$H^+ + OH^- \rightleftarrows H_2O$	1.004×10^{-14}	2.42×10^{-14}	4.09×10^{-14}	13

[a] Assumed to be the same as the value at 37 °C. [b] Extrapolated value. [c] Interpolated from data at 25 and 40 °C.

Table II. OCP Solubility Experiments at 25 °C

	initial conditions[a]				equilibrium		
expt no.[b]	10^3T_{Ca}, mol L^{-1}	10^3T_p, mol L^{-1}	$10^3(KNO_3)$, mol L^{-1}	$10^4(KOH)$, mol L^{-1}	10^3T_{Ca}, mol L^{-1}	10^3T_p, mol L^{-1}	pH
52G	1.500	1.125	0	1.883	1.486	1.13	6.05
52D	0.704	0.528	2.97	0.760	0.796	0.624	6.54
50G	3.00	2.25	0	4.54	2.80	2.09	5.68
50D	0.353	0.265	9.82	0.388	0.510	0.413	6.95
48G	4.00	3.00	5.12	6.54	3.63	2.78	5.62
48D	0.570	0.427	17.8	0.659	0.721	0.614	6.75
47G	4.00	3.00	24.9	6.58	3.74	2.80	5.73
47D	0.600	0.450	37.6	0.759	0.797	0.659	6.78
46G	4.00	3.00	44.7	6.68	3.73	2.85	5.77
46D	0.667	0.500	57.4	0.900	0.882	0.727	6.78
44G	4.00	3.00	84.5	6.88	3.82	2.89	5.87
44D	0.728	0.546	97.1	1.067	0.994	0.782	6.82

[a] T_{Ca} and T_p denote the total concentration of calcium and phosphate; initial pH 6.2; 30 mg of OCP seed (SSA = 9.1 $m^2\ g^{-1}$). [b] G and D represent growth experiments and dissolution experiments, respectively.

Table III. OCP Solubility Experiments at 45 °C

	initial conditions[a]				equilibrium		
expt no.[b]	10^3T_{Ca}, mol L^{-1}	10^3T_p, mol L^{-1}	$10^3(KNO_3)$, mol L^{-1}	$10^4(KOH)$, mol L^{-1}	10^3T_{Ca}, mol L^{-1}	10^3T_p, mol L^{-1}	pH
31G	2.00	1.50	0.0	2.71	1.912	1.42	5.75
31D	0.528	0.396	5.49	0.556	0.612	0.460	6.51
30G	3.00	2.25	0.0	4.54	2.86	2.13	5.74
30D	0.353	0.265	9.82	0.388	0.465	0.356	6.84
28G	4.00	3.00	5.12	6.54	3.82	2.80	5.56
28D	0.570	0.427	17.8	0.659	0.683	0.512	6.62
27G	4.00	3.00	24.9	6.58	3.77	2.88	5.68
27D	0.600	0.450	37.6	0.759	0.732	0.557	6.68
26G	4.00	3.00	44.7	6.67	3.80	2.83	5.73
26D	0.667	0.500	57.4	0.900	0.814	0.628	6.68
24G	4.00	3.00	84.5	6.876	3.76	2.80	5.88
24D	0.728	0.546	97.1	1.067	0.873	0.653	6.75

[a] T_{Ca} and T_p are the total concentrations of calcium and phosphate; initial pH 6.2; 30 mg of OCP seed (9.1 $m^2\ g^{-1}$). [b] G and D represent growth experiments and dissolution experiments, respectively.

for mass balance, electroneutrality, and the proton dissociation and ion-pair association constants listed in Table I (*5*). The calculations were made by successive approximations for the ionic strength, I, and the activity coefficients of z-valent species, y_z, were calculated from the extended form of the Debye-Hückel equation proposed by Davies (*14*).

$$-\log y_z = Az^2[I^{1/2}/(1 + I^{1/2}) - 0.3I] \quad (1)$$

In eq 1, A is the temperature-dependent Debye-Hückel constant. The thermodynamic solubility product of OCP, K_{so}, may be expressed in terms of the conditional value K'_{so} by eq 2, in

$$K_{so} = (Ca^{2+})^4(H^+)(PO_4^{3-})^3y_2^4y_3^3y_1 = K'_{so}y_2^4y_3^3y_1 \quad (2)$$

which the ionic species are expressed as molar concentrations. Introduction of activity coefficients results in eq 3. Typical

$$pK'_{so} = pK_{so} - 44A\,[I^{1/2}/(1 + I^{1/2}) - 0.3I] \quad (3)$$

experimental conditions are summarized in Table II, in which (KOH) represents the concentration of base required to bring

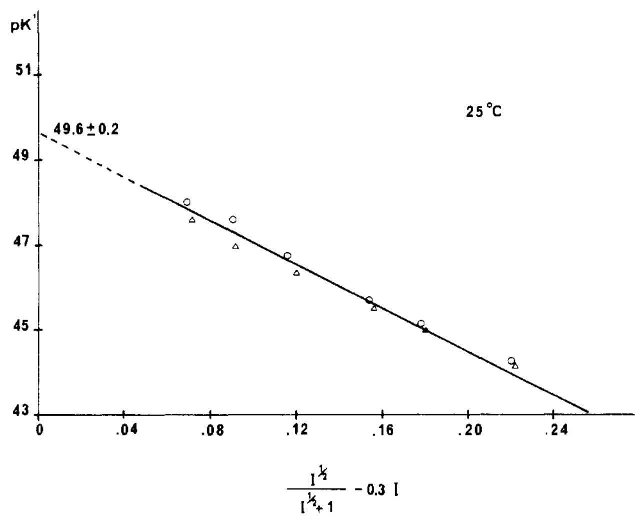

Figure 1. 25 °C plots of pK_{so} for OCP against $I^{1/2}/(1 + I^{1/2}) - 0.3I$: 28-day equilibration from growth (O) and dissolution (Δ) experiments.

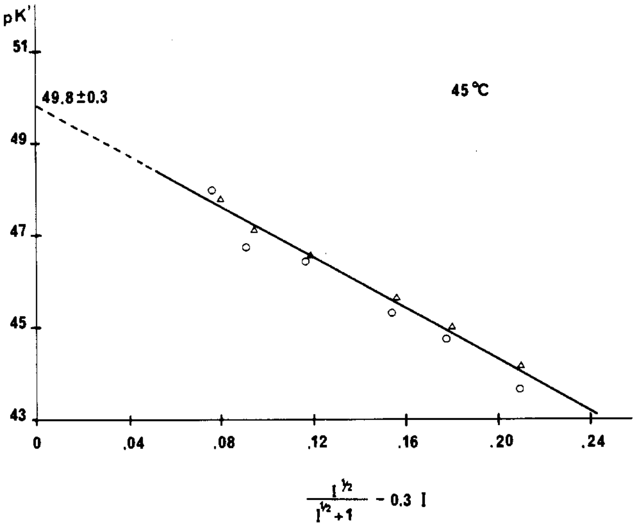

Figure 2. 45 °C plots of pK_{s0} for OCP against $I^{1/2}/(1 + I^{1/2}) - 0.3I$: 12-day equilibration from growth (○) and dissolution (△) experiments.

the calcium and phosphate solutions to the desired pH value of 6.2. This pH was chosen so that after equilibration, the final pH fell in the region 5.5-7.0, in which the exclusive growth of OCP has been demonstrated (*15*). Exploratory measurements made over a range of equilibration times at 25 and 45 °C confirmed that equilibrium at these temperatures required about 14 and 2 days, respectively. The equilibrium data in Table II were obtained after equilibration times of 28 days at 25 °C and 12 days at 45 °C.

The results of the solubility determinations are shown in Tables II and III, and pK'_{s0} values are plotted as a function of ionic strength (eq 3) in Figures 1 and 2. These figures include data obtained from both growth and dissolution experiments and the excellent agreement confirms the attainment of equilibrium. The corresponding values of pK_{s0} obtained by extrapolation to zero ionic strength, 49.6 ± 1.2 and 49.8 ± 0.3 at 25 and 45 °C, respectively, are close to that, 49.3 ± 0.2, obtained at 37 °C (*5*). They confirm the finding that the solubility product of OCP is considerably lower than the value expected from previously reported data (*3*). The mean molar calcium/phosphate ratios of the solid phases after equilibrium in these experiments were 1.30 ± 0.05 at 25 °C and 1.33 ± 0.02 at 45 °C, confirming the good stability of OCP in the aqueous media under these conditions of temperature and pH. In particular, hydrolysis of OCP into an HAP-like phase at 45 °C in the pH range 5.5-6.8 was never detected under the experimental conditions used (see Table III). The marked dependence of solubility of OCP upon ionic strength (see Figures 1 and 2) emphasizes the importance of taking into account activity coefficient corrections when calculating thermodynamic precipitation driving forces in the calcium phosphate systems.

Registry No. $Ca_4H(PO_4)_3$, 13767-12-9.

Literature Cited

(1) Brown, W. E. *Nature (London)* **1962**, *196*, 1048.
(2) Brown, W. E.; Smith, J. P.; Lehr, J. R.; Frazier, A. W. *Nature (London)* **1962**, *196*, 1050.
(3) Moreno, E. C.; Brown, W. E.; Osborn, G. *Soil Sci. Am. Proc.* **1960**, *24*, 99.
(4) Madsen, H. E. L. *Acta Chem. Scand.* **1970**, *24*, 1671.
(5) Shyu, L. J.; Perez, L.; Zawacki, S. J.; Heughebaert, J. C.; Nancollas, G. H. *J. Dent. Res.* **1983**, *62*, 398.
(6) Heughebaert, J. C.; Nancollas, G. H. *J. Phys. Chem.*, **1984**, *88*, 2478.
(7) Tomson, M. B.; Barone, J. P.; Nancollas, G. H. *At. Absorpt. Newsl.* **1977**, *16*, 117.
(8) Bates, R. G. *J. Res. Natl. Bur. Stand.* **1951**, *47*, 127.
(9) Bates, R. G.; Acree, S. F. *J. Res. Natl. Bur. Stand.* **1943**, *30*, 129.
(10) Bjerrum, N.; Unmack, A. *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **1929**, *9*, 98.
(11) Chughtai, A.; Marshall, R.; Nancollas, G. H. *J. Phys. Chem.* **1968**, *72*, 208.
(12) Bates, R. G.; Bower, V. E.; Canham, R. G.; Prue, J. E. **1959**, *55*, 2062.
(13) Ackermann, Th. *Z. Elektrochem.* **1958**, *62*, 411.
(14) Davies, C. W. "Ion Association"; Butterworth: London, 1960; p 41.
(15) de Rooij, J. F.; Heughebaert, J. C.; Nancollas, G. H. *J. Colloid Interface Sci.*, **1984**, *100*, 350.

Received for review August 2, 1984. Accepted October 29, 1984. This research was supported by the Stauffer Chemical Co. and by a grant from the National Institute of Dental Research (Grant No. DE03223).

Vapor-Liquid Phase Equilibria for the Binaries Isoprene-Dicyclopentadiene and *n*-Pentane-Dicyclopentadiene at 313 and 323 K

Colin S. Howat and George W. Swift*

Kurata Thermodynamics Laboratory, Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045

This article presents new total pressure data for the two binary systems, isoprene-dicyclopentadiene and *n*-pentane-dicyclopentadiene, at 313 and 323 K. New vapor pressure data for dicyclopentadiene spanning the temperature range of 313-359 K are also presented. The experimental errors of measurement described as standard deviation are 0.003 mole fraction, 0.03 K, and 0.08 kPa. The data are generally described within the experimental error using a full range vapor pressure equation and a solution model for the total pressures. These are the first data to appear in the literature for these binaries.

Introduction

Three components generally present in isoprene purification are isoprene, *n*-pentane, and dicyclopentadiene (DCPD). Although these C_5-C_{10} binaries are wide boiling and, therefore, easily separated by distillation, it is important to have accurate knowledge of the liquid nonideality for them when studying the ternary isoprene, *n*-pentane, and cyclopentadiene: cyclopentadiene readily dimerizes to DCPD (dicyclopentadiene) at industrially important temperatures. Consequently, any liquid mixture containing cyclopentadiene contains significant amounts of DCPD. Since the literature does not contain phase equilibria data for the isoprene-DCPD and *n*-pentane-DCPD binaries and

0021-9568/85/1730-0281$01.50/0