[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF OKLAHOMA]

Preparation and Properties of Calcium Monofluorophosphate Dihydrate

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Calcium monofluorophosphate dihydrate was prepared by a precipitation method involving solutions of stoichiometric amounts of sodium monofluorophosphate and reagent grade calcium chloride. Partial dehydration of the dihydrate to the hemihydrate was accomplished by heating samples in a vacuum desiccator over phosphorus pentoxide at 65°. Hydration studies indicated a monohydrate–hemihydrate equilibrium system was stable at room temperature below 3.5 mm. of water vapor. The solubility curve in water was determined over a limited temperature range but was not extended to higher temperatures due to probable hydrolysis at the higher temperatures. No organic solvent for the salt was found among those tested. The dihydrate crystals were classed as monoclinic and were observed to form twin crystals. The properties of calcium monofluorophosphate showed marked similarity to gypsum.

Fluorophosphate compounds have been considered for industrial application as catalysts, electrobrightening agents, fungicides, fluxes, insecticides against moths, dental-caries inhibitors and medicinals. It was hoped that basic research on calcium monofluorophosphate might be helpful in making commercial use of this and other FP (fluorophosphate) compounds. The calcium monofluorophosphate first reported by Lange[1] in 1929 was a slimy solid obtained by alcohol extraction from a mixture of calcium chloride and ammonium monofluorophosphate solutions. No description of the properties of the gelatinous substance was given; therefore the purpose of this work was the preparation of a pure crystalline solid phase and a study of its properties.

Experimental

Preparation.—Calcium monofluorophosphate dihydrate was prepared as a white crystalline solid by the precipitation method using calcium chloride and sodium monofluorophosphate solutions. The sodium monofluorophosphate had been prepared in a silver container by fusion of stoichiometric amounts of sodium fluoride and sodium metaphosphate.[2,3] The approximately 15% of phosphate impurities in the metaphosphate preparation was first removed by precipitation with a calculated amount of calcium chloride solution. Additional calcium chloride added dropwise to the clear filtrate precipitated white crystalline $CaPO_3F \cdot 2H_2O$. The precipitate was washed with distilled water to remove sodium and calcium chloride impurities and was dried in an evacuated desiccator over anhydrous calcium chloride. Yields of calcium monofluorophosphate exceeded 90%, based on both fluorine and calcium content; however, even higher yields could be obtained using alcohol extraction, but a relatively impure product resulted.

Analysis.—The prepared salt was analyzed for calcium, total fluorine, total phosphorus, chloride and fluorophosphate ion. Results showed an average purity of 95% (Table I) on preparations obtained by straight precipitation methods. Those obtained by alcohol extraction were approximately 75% pure.

The calcium determination presented no difficulties and employed the standard oxalate precipitation.[4] In addition, a volumetric method[5] was employed involving titration with a standard solution of disodium dihydrogen ethylenediaminetetraacetate (trade name: disodium dihydrogen Versenate) containing a trace of magnesium ions and using UniVer (Hach Chemical Company, Ames, Iowa) water hardness indicator. The titration method was successful with solutions of *p*H 10 and calcium concentrations of a few parts per million but was unsuccessful with higher concentrations.

Total fluorine was determined using the Willard–Winter[6] method of steam distillation with perchloric acid and subsequent titration of the distillate with thorium nitrate according to the procedure of Rowley and Churchill.[7] The method was tedious and gave reliable and reproducible results only after considerable familiarization with the technique.

TABLE I

ANALYSES OF $CaPO_3F \cdot 2H_2O$ PREPARATIONS

Preparation	Yield, %	F, %	Ca, %	Purity calcd. on % F	Purity calcd. on % Ca
$CaPO_3F \cdot 2H_2O$ (pure)		10.9	23.0	..	..
1	75.2	10.2	21.6	93.6	93.9
2	95.9	10.3	21.8	94.5	94.8
		10.4	22.1	95.4	96.1
3	92.3	10.5	22.6	96.3	98.3
		10.5	22.6	96.3	98.3
4	96.2	10.4	22.5	95.4	97.8

Total phosphorus was determined after heating the sample with nitric acid to hydrolyze all phosphorus containing ions to the orthophosphate ion. After adjustment to *p*H 7, an excess of standard silver nitrate was added to precipitate silver orthophosphate and the excess precipitant determined by the standard thiocyanate titration.

Volhard determinations[8] showed negligible chloride content in samples of the preparation which had been thoroughly washed with distilled water.

The analysis was further checked in several instances by determination of the fluorophosphate ion. The procedure[9] is better adapted to the more soluble monofluorophosphates than to slightly soluble fluorophosphate compounds. The fluorophosphate ion was determined by precipitating silver monofluorophosphate from an aqueous solution containing approximately 0.05 g. of $CaPO_3F$ by the addition of silver perchlorate solution. The solution containing the weighed sample of $CaPO_3F$ was adjusted with dilute sodium hydroxide or nitric acid until two drops of phenol red indicator gave an orange color. After addition of the precipitating agent a sufficient volume of ethanol was added to make the total suspension 80% in alcohol. The $AgPO_3F$ was separated by centrifugation after standing for 15 minutes between 0 and 5°. The precipitate was washed several times with cold 80% ethanol and after the final decantation the residue was transferred to the fluorine distillation apparatus and the procedure for fluorine determination was repeated.

Properties.—Numerous attempts to remove the water of hydration showed the dihydrate to be relatively stable. Benzene refluxing was unsuccessful and heating to 100 and 500° at atmospheric pressure for varying periods of time led

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[1] W. Lange, *Ber.*, **62**, 793 (1929).

[2] C. O. Anderson (to Ozark–Mahoning Co.), U. S. Patent 2,481,-807 (September 13, 1949). The product used in this investigation was obtained from the Ozark–Mahoning Co., Tulsa, Oklahoma.

[3] O. F. Hill and L. F. Audrieth, "Inorganic Syntheses," Vol. III, The Maple Press Co., New York, N. Y., 1950, pp. 106–108.

[4] H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1940, pp. 395–397.

[5] H. Diehl, C. A. Goetz and C. C. Hach, *J. Am. Water Works Ass.*, **42**, No. 1 (January, 1950).

[6] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

[7] R. B. Rowley and H V. Churchill, *ibid.*, **9**, 551 (1937).

[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, pp. 543–544.

[9] Wayne E. White, Ozark–Mahoning Co., Tulsa, Okla., private communication.

to decomposition. Heating at temperatures below 100° and at reduced pressures proved time consuming and inadequate. Above 80° prolonged heating always resulted in the loss of some fluorine due to hydrolysis.

Successful partial dehydration was accomplished in an evacuated desiccator over phosphorus pentoxide at 65° in approximately 50 hr. Loss of total sample weight and fluorine and phosphorus analyses indicated the hemihydrate formation. When held for 9 days at these conditions, there was no additional loss in weight and analytical data indicated pure hemihydrate.

There was no particular consistency in the rate of dehydration and influencing factors were sample size, exposed surface, condition of the phosphorus pentoxide and degree of evacuation of the desiccator.

The only evidence for the existence of a stable monohydrate was obtained by hydrating the hemihydrate. When placed at 20° in a constant relative humidity of 15% (approximately 3.5 mm. of water vapor) the hemihydrate gained sufficient weight to convert theoretically to the monohydrate.

There was no additional gain in weight with time, and there was no loss in weight when placed over anhydrous calcium chloride. The monohydrate gained in weight to the dihydrate value when placed in a 51% relative humidity atmosphere at 25°. However, this second water molecule could now be removed by drying over anhydrous calcium chloride at room temperature whereas the original dihydrate water could not be removed in this manner.

Elevated temperatures failed to yield the anhydrous salt. Decomposition with loss of fluorine resulted in every case. The theoretical composition of possible hydrates of calcium monofluorophosphate are given in Table II for comparison.

TABLE II

COMPOSITION OF POSSIBLE HYDRATES

Hydrate	Ca, %	F, %	P, %
$CaPO_3F \cdot 2H_2O$	23.0	10.9	17.8
$CaPO_3F \cdot H_2O$	25.6	12.2	19.9
$CaPO_3F \cdot {}^1/_2H_2O$	27.2	12.9	21.1
$CaPO_3F$	29.0	13.8	22.5

TABLE III

SOLUBILITY OF $CaPO_3F \cdot 2H_2O$ IN WATER

Temp., °C.	G. of $CaPO_3F$/100 ml. soln.
5	0.486 ± 0.006
17	.476 ± .006
27	.417 ± .006
37	.390 ± .006
48	.438 ± .006
58	.486 ± .006

The solubility of the salt in water (Table III) was determined by volumetric analysis of the saturated solution and all solubilities were less than 0.5 g. of $CaPO_3F$ per 100 ml. of saturated solution. Equilibrium was reached by constant stirring of a solution containing excess solid for 24 hr. with longer periods of stirring time showing no increase in solubility. After 2 months of solid–liquid contact, the salt was found to be negligibly soluble at room temperature in all organic solvents tested. These included: 95% ethanol, carbon tetrachloride, chloroform, 1,4-dioxane, tetrahydrofuran, ethyl acetate, furfural, pyridine, thiophene, ethylene glycol, ethylene glycol monoethyl ether and carbon disulfide.

Crystallographic studies were hampered by the difficulty of obtaining large perfect crystals. However, studies revealed the dihydrate crystals had an inclined extinction angle whose measurements varied between 33 and 37° and also a parallel extinction angle. These indicated the monoclinic crystal system for the dihydrate, which was also observed to form twin crystals. The hemihydrate crystals appeared light brown in color and had the same general shape as the dihydrate. However, it was suspected that they did not belong to the same crystal system but that a case of pseudomorphism had been observed.

It has been noted that the properties of monofluorophosphate compounds closely resemble those of the corresponding sulfates. This investigation shows a marked similarity between calcium monofluorophosphate and gypsum, $CaSO_4 \cdot 2H_2O$.

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The Surface Chemistry of Bone. IX. Carbonate: Phosphate Exchange[1]

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Under carefully controlled conditions, hydroxyapatite crystals were equilibrated with bicarbonate buffers. Bicarbonate was found to penetrate the hydration shells of the crystals and, in addition, displace phosphate ions from the surfaces of the crystals. These two physicochemical processes may account for the large amounts of CO_2 found in bone. The exchange reaction is quantitatively of the most physiological importance since the crystals of mature bone are poorly hydrated *in vivo*.

In 1881, Hoppe-Seyler[2] attempted to describe bone salt by a formulation which included carbonate ions as part of the "molecule." Today, it is generally recognized that bone salt cannot be represented as a "molecule" but rather is best described as microcrystalline material exhibiting the lattice structure of hydroxyapatite.[3] The exact nature of the ever-present carbonate of bone mineral is still uncertain, however, and there exists in the literature an array of suggestions and theories, none of which has been experimentally established beyond reasonable doubt.[3b]

None of these suggestions takes into account the recently-discovered fact that crystals of hydroxyapatite, in an aqueous medium, possess hydration shells.[4] Therefore, a series of investigations of a model system (aqueous buffer–hydroxyapatite crystals) was conducted to clarify the problem of carbonate fixation in bone.

Materials and Methods.—A well-characterized preparation of crystalline hydroxyapatite[5-8] was used for all equilibration studies. All other chemicals were commercially available, C.P. grade. The methods and apparatus used

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(1) This paper is based on work performed under contract with the United States Atomic Energy Commission at The University of Rochester Atomic Energy Project, Rochester, New York.

(2) F. Hoppe-Seyler, *Z. Physiol. Chem.*, Berlin (1881).

(3) (a) S. Eisenberger, A. Lehrman and W. D. Turner, *Chem. Revs.*, **26**, 257 (1940); (b) W. F. Neuman and M. W. Neuman, *ibid.*, **53**, 1 (1953).

(4) W. F. Neuman, T. Y. Toribara and B. J. Mulryan, THIS JOURNAL, **75**, 4239 (1953).

(5) W. F. Neuman, Atomic Energy Report UR-238 (1953).

(6) J. H. Weikel, Jr., W. F. Neuman and I. Feldman, THIS JOURNAL, **76**, 5202 (1954).

(7) G. J. Levinskas and W. F. Neuman, *J. Phys. Chem.*, **59**, 164 (1955).

(8) W. R. Stoll and W. F. Neuman, THIS JOURNAL, **78**, 1585 (1956).