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Effect of humic compounds and some organic acids added during dicalcium phosphate dihydrate crystal growth process

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Abstract

A constant composition method was used to investigate the influence of humic compounds and phytic, mellitic and citric acids on the crystal growth of dicalcium phosphate dihydrate (DCPD). The additives studied strongly inhibit the crystallization of DCPD. The inhibition effect can be attributed to an interaction between functional groups and calcium ions on the crystal surface.

1. Introduction

The present work was aimed at investigating the role of humic substances and three organic acids: phytic, mellitic and citric, on the crystal growth of dicalcium phosphate dihydrate (DCPD). The processes of crystallization and dissolution of calcium phosphate are very important because of the role these salts play in fertilizers, biological calcification and waste-water treatment processes. Dicalcium phosphate dihydrate $CaHPO_4 \cdot 2H_2O$ (DCPD) in particular is widely used as a phosphate fertilizer; it also occurs in the area of biological mineralization and especially as dental scale. The formation, evolution, dissolution and also inhibition of DCPD crystals are of considerable interest in these two different areas. Understanding the fate of DCPD and the mechanisms of its interaction with humic compounds is important for the efficient use of fertilizers; moreover, its interaction with organic groups is important in biological mineralization.

It is difficult to study the crystallization process and the effects on it of inhibitors using classical methods, owing both to the concentration changes during crystal growth and to the fact that adsorption and crystal growth take place simultaneously. These problems have been overcome by the constant solution composition method [1–3] which is well suited to the quantitative measurement of the effect of additives on the crystal growth process of sparingly soluble salts [4, 5]. With this method, two titrant solutions are added to keep the pH, the ionic strength and the ionic activities of all the species in solution constant. Crystal growth is initiated by the introduction of DCPD seeds.

We describe experimental results concerning the effect of humic compounds and also that of magnesium citrate, mellitic and phytic acids on the crystallization of DCPD, using the constant composition method.

2. Materials and methods

2.1. Preparation of DCPD seed crystals

DCPD seed crystals were prepared from a saturated monocalcium phosphate solution. A dilute ammonium hydroxide solution was added slowly until the pH of the solution reached 5.0, at which value DCPD crystals were formed. The precipitate was aged for one hour, and then was separated from the liquid by filtration and dried overnight at 50 °C. The crystals prepared were characterized from their powder X-ray diffraction pattern (CGR Theta 60), which showed the characteristic peaks for DCPD (ASTM file card 9-77), by infrared spectrometry (Perkin Elmer 430), by chemical analysis which yielded a molar ratio of total calcium:total phosphate equal to unity, by scanning electron microscopy (SEM, JEOL-JSM25) and from the Brunauer–Emmett–Teller (BET) specific surface area (Quantasorb II, Quantachrome, Greenvale, NY).

2.2. Preparation of humic compounds

A stabilized compost was used as the starting material (weight composition: hydrogen, 70.4%; nitrogen, 2.12%; ash, 15.5%). Avoiding the presence of metallic ions which would affect the crystallization process of DCPD, the compost was extracted with a pH 10.0 buffer solution made of concentrated ammonia (94% v/v of 1 M ammonia) and 0.5 M ammonium carbonate (4% v/v) at 50 °C under vacuum. The organic compound content of the solution was 0.99 g l^{-1} and its pH was 8.0. The solution was then stored at 6 °C.

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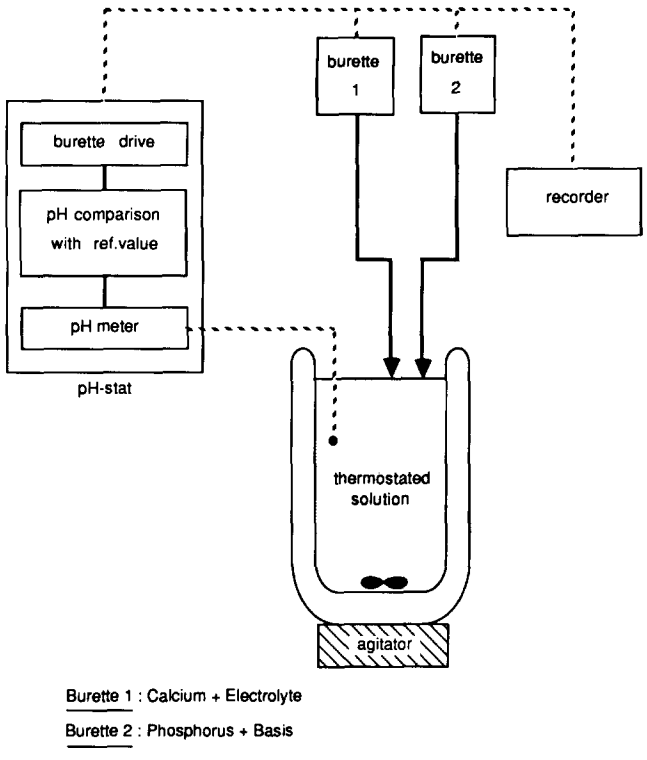

Fig. 1. Experimental apparatus. Burette 1, calcium plus electrolyte; burette 2, phosphate plus base.

2.3. Citric, mellitic and phytic acids

Phytic acid (myoinositol hexaphosphoric acid $C_6H_6(OPO(OH)_2)_6$) is found in plants; mellitic acid $C_6(COOH)_6$ is a calcium sequestrant, naturally occurring in peat, and magnesium citrate $(C_6H_5O_7)_2Mg_3$ is also a well-known calcium sequestrant. High grade compounds were used.

2.4. Crystallization experiments

A schematic representation of the experimental set-up is shown in Fig. 1. All experiments reported herein were done at constant temperature in a water-jacketed pyrex glass reactor thermostated within ± 0.1 °C. The supersaturated solutions, each with a volume totalling 0.2 l were prepared in the glass reactor by mixing equal volumes of calcium nitrate and potassium phosphate solutions of the appropriate concentrations. Next, the pH was adjusted by slowly adding small volumes of standard potassium hydroxide solution and the solution was allowed to equilibrate for a period of at least two hours. The crystallization process was initiated by the addition of well-characterized DCPD seed crystals. The crystal growth process started immediately without any appreciable induction period. A change in the pH of the solution as small as 0.005 pH units, concomitant with the precipitation of calcium phosphate, triggered the addition of titrant solutions from two electrically coupled burettes in an automatic titrator (impulsomat 614 Methrom). At the end of the experiment, the solid was filtered and dried: the formation of DCPD was confirmed by X-ray diffraction and infrared spectroscopy.

The composition of the titrant solutions was calculated such that the pH, calcium and phosphate concentrations and the ionic strength were kept constant.

The burettes were connected to a recorder, and from a plot of the volume of titrants added dv against time t, the rates of crystallization R_c could be accurately measured:

$$R_c = dvc/(tm_0SSA) \quad (1)$$

In eqn. (1), SSA is the specific surface area of the inoculated DCPD seed crystals, m_0 the initial mass and c the effective titrant concentration.

Considering the low concentrations of additives used, it is not necessary to take into account the variation in the calcium concentration caused by calcium sequestration.

3. Experimental results

3.1. Humic compounds

Supersaturation of the solution was computed by taking into account the equilibria summarized in Table 1, the mass balance equations for total calcium and total phosphate and the electroneutrality conditions by successive approximations for the ionic strength, using the Davies formulation for activity coefficients [8, 9]. The driving force for the crystallization of DCPD is the change in the Gibbs free energy ΔG in going from the supersaturated solution to equilibrium:

$$\Delta G_{DCPD} = -\frac{RT}{2}\frac{[Ca^{2+}][HPO_4^{2-}]}{K_{SO}} \quad (2)$$

In eqn. (2) R is the gas constant and T the absolute temperature; K_{SO} is the thermodynamic solubility product of DCPD and brackets denote the activities of the respective ions. All the experiments were performed

TABLE 1. Equilibrium data at 25 °C [6] and 37 °C [7]: dissociation constants (mol l^{-1}) and association constants (l mol^{-1})

Equilibrium	25 °C	37 °C
$H_3PO_4^0 \leftrightarrow H^+ + H_2PO_4^-$	7.11×10^{-3}	6.22×10^{-3}
$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$	6.30×10^{-8}	5.58×10^{-8}
$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$	4.73×10^{-13}	6.61×10^{-13}
$H^+ + OH^- \leftrightarrow H_2O$	1.004×10^{-14}	2.42×10^{-14}
$Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO_4^0$	398	681
$Ca^{2+} + H_2PO_4^- \leftrightarrow CaH_2PO_4^+$	27.54	31.9
$Ca^{2+} + PO_4^{3-} \leftrightarrow CaPO_4^-$	2.95×10^6	3.46×10^6
$Ca^{2+} + OH^- \leftrightarrow CaOH^+$	16.98	21.3

TABLE 2. Effect of the concentration of humic compounds C_H on the crystallization of DCPD on DCPD seed crystals in aqueous solutions[a]

	C_H (10^{-14} g l^{-1})				
	0	0.7	1.1	1.4	3.1
R/R_0 ($\times 100$)	100	37	28	24	11

[a]Total calcium equals total phosphate at 2.2×10^{-2} M; ionic strength, 0.12 M; pH, 5.0; temperature, 25 °C; R, growth rate of DCPD with additive; growth rate of pure DCPD without additive $R_0 = 7.1 \times 10^{-5}$ mol min^{-1} m^{-2}.

at 25 °C and a pH of 5.0 with calcium and phosphate concentrations equal to 2.2×10^{-2} M and an ionic strength of 0.12 M. These conditions correspond to $\Delta G = -1.06$ kJ mol^{-1}. Crystallization was induced with 100 mg of DCPD seed crystals (SSA, 1.1 m^2 g^{-1}). The humic compounds were introduced into the working solution during the crystal growth process. A large reduction in the DCPD growth rate was observed. The experimental results are reported in Table 2 and Fig. 2. The growth rate observed was only 10% of the initial rate R_0, with a humic concentration of 3×10^{-4} g l^{-1} (*i.e.* 1.4×10^{-4} acid group equivalents [10]). These results strongly suggest that humic compounds act at the crystal growth stage. The surface adsorption of the organic compounds is evidently responsible for the reduction in the rates of crystal growth: their reactivity is primarily due to the presence of carboxylic and enolic functional groups [11].

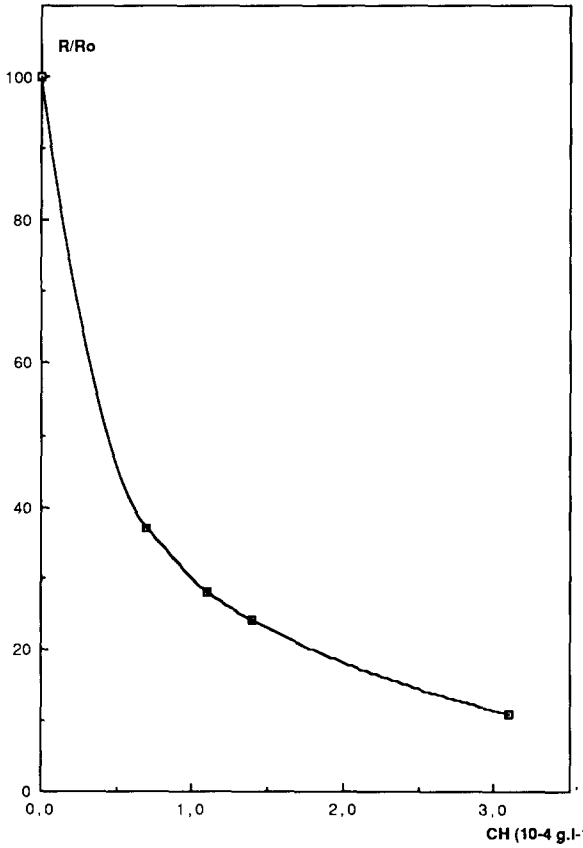

Fig. 2. Ratio R/R_0 as a function of concentration of humic compounds.

Humic compounds strongly inhibit the growth of DCPD crystals and, conversely, also their dissolution; consequently they act on the dissolution of DCPD in soil, limiting the uptake of phosphate fertilizers.

3.2. *Phytic, mellitic and citric acids*

All the experiments were performed at 37 °C and a pH of 5.0, with calcium and phosphate concentrations equal to 1.5×10^{-2} M. Under these conditions, the enthalpy of formation of DCPD is $\Delta G = -0.55$ kJ mol^{-1}. Seed crystals (25 mg; SSA, 0.5 m^2 g^{-1}) were introduced into the solution. During the crystal growth process (after about 10% growth), the inhibitor agent was introduced: an immediate decrease in the rate of crystallization was noticed. The experimental results are reported in Table 3. The variation of the ratio R/R_0 vs. inhibitor concentration in the working solution is plotted in Fig. 3.

In the case of citric or mellitic compounds, the ratio R/R_0 decreases down to a lower limit when the inhibitor concentration increases. For a concentration of 25×10^{-6} M, the limiting R/R_0 ratio is equal to 25% for mellitic acid and 50% for citrate: mellitate seems to have a better inhibitor effect than citrate. Nevertheless, the most efficient inhibitor is phytic acid: at very low concentrations (5×10^{-8} M) DCPD crystal growth is almost stopped.

TABLE 3. Effect of the concentration of phytic acid C_p, mellitic acid C_m and magnesium citrate C_c on the crystallization of DCPD on DCPD seed crystals in aqueous solutions[a]

	C_p (10^{-8} mol l^{-1})							
	0	1.2	2.4	3.0	3.6	4.1	4.8	6.0
R/R_0 ($\times 100$)	100	96	61	45	27	13	13	<10
	C_m (10^{-6} mol l^{-1})							
	0	1.2	2.4	4.9	7.3	9.8	12.2	24.7
R/R_0 ($\times 100$)	100	61	60	41	37	30	32	26
	C_c (10^{-5} mol l^{-1})							
	0	0.6	1.2	2.4	3.7	4.9		
R/R_0 ($\times 100$)	100	80	58	62	51	52		

[a]Total calcium equals total phosphate at 1.5×10^{-2} M; ionic strength, 0.12 M; pH, 5.0; temperature, 37 °C; R, growth rate of DCPD with additive; growth rate of DCPD without additive $R_0 = 4.5 \times 10^{-5}$ mol min^{-1} m^{-2}.

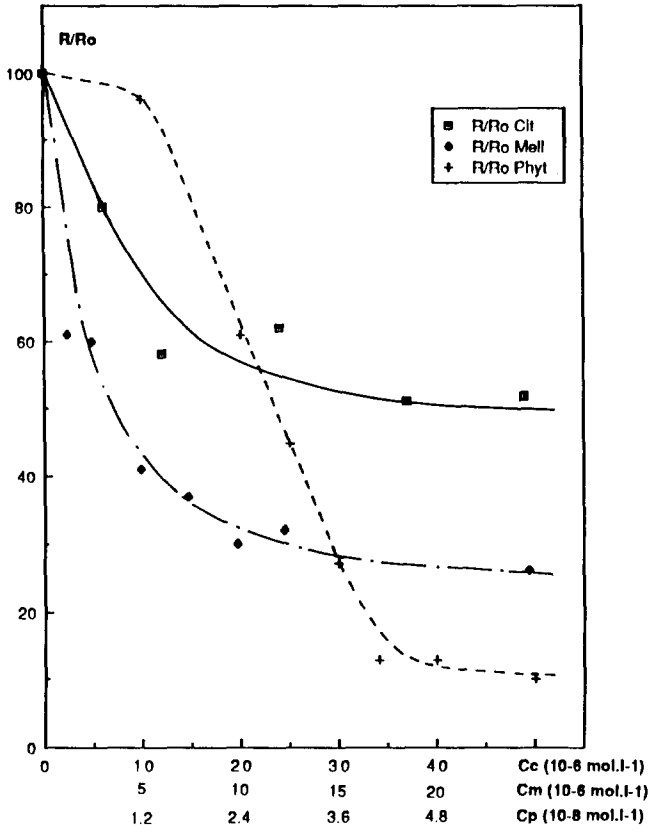

Fig. 3. Ratio R/R_0 as a function of concentration of magnesium citrate C_c, mellitic acid C_m and phytic acid C_p.

The inhibitor properties of these compounds can be explained by their adsorption on to the active growth sites on the crystal surface and the interaction of carboxylic or phosphate groups with the calcium ions on the surface.

The mellitic and citric molecules used each contain six carboxylic functional groups: the stronger inhibiting action of mellitic acid can be attributed to the steric effect of the aromatic structure. DCPD growth is never totally stopped in either case. However, the very strong efficiency of phytic acid which stops crystal growth almost completely is certainly due to the presence of phosphate groups which readily bind to calcium ions.

These three compounds inhibit DCPD crystal growth with varying efficiency; the most efficient is phytic acid and the least is magnesium citrate. They are used or can be used to limit the formation of dental tartar (dental tartar is largely composed of DCPD [12, 13]).

4. Conclusions

This work shows the usefulness of the constant composition method for the study of crystallization processes and inhibitor effects. In the case of DCPD, the influence has been shown of different organic compounds with different molecular weights, functional groups and steric behaviour. All the compounds studied in this work have adsorption properties which induce a substantial decrease in the DCPD crystal growth rate. The adsorption properties are due to the interaction of the functional groups (carboxylic, phosphate) with the calcium ions on the DCPD surface.

The changes in the crystallization rate — and conversely in the dissolution rate — suggest possible applications of these inhibitors in the domains of agriculture and dentistry.

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