

# The effect of citrate on calcium phosphate deposition from simulated milk ultrafiltrate (SMUF) solution

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## Abstract

As has been widely reported, different calcium phosphate phases can be formed in solution depending on several physical-chemical aspects like the concentration of free calcium and phosphate ions, pH of the solution, temperature and the presence of interfering ions. The present work aims at studying the effect of pH and of citrates on the precipitation of calcium phosphate in a solution that simulates the mineral composition of milk (SMUF), as well as the subsequent effect on the deposition on stainless steel surfaces. The different calcium phosphate species formed during heating at different pH values and in the presence or absence of citrate were characterized by scanning electron microscopy, X-ray microanalysis and X-ray diffraction. Their fouling behaviour was characterized according to the amount of deposit formed on stainless steel surfaces and to the deposit's resistance to removal by hydrodynamic shear forces. The absence of citrate was responsible for the decrease in the solution pH and for the formation of a crystalline dicalcium phosphate dihydrate structure with a deposited mass which was almost twice the one obtained in the presence of citrate.

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## 1. Introduction

Fouling in milk processing is a complex process because it involves several simultaneous phenomena associated with protein aggregation and subsequent deposition and mineral salts deposition, the latter mainly caused by calcium phosphate (Jeurnink, Walstra, & deKruif, 1996). It has not yet been clarified whether calcium phosphate fouling is due to deposition of particles which have been formed in the bulk, or due to direct crystallization/precipitation on the surface (Andritsos, Yiantsios, & Karabelas, 2002). Therefore, the fouling process must be analysed not only in terms of deposit

adhesion and growth but also according to what is happening in the bulk solution.

The most widely used test solution in milk mineral deposition studies is called simulated milk ultrafiltrate (SMUF) which was first described by Jenness and Koops (1962). It is a simplified milk system which constitutes, so far, the best way to evaluate the role of the different milk mineral components on the overall milk fouling behaviour. Due to the use of this simplified system more is now known about the mechanisms of fouling of the different milk components but there are still remaining some key scientific problems related to the poor understanding of the role of some interfering ions such as citrate (also present in SMUF) on the precipitation behaviour of calcium phosphate under different pH values.

Calcium phosphate formation by precipitation from solution is determined by two mechanisms which only

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occur under supersaturated solutions: (i) nucleation and (ii) crystal growth. The latter is composed of several steps, starting with transport of ions from the bulk solution to the nuclei surface, followed by adsorption on energetically favourable sites.

The formation of calcium phosphate nuclei and, afterwards, the precipitation phenomenon are only observed after a defined concentration of the correspondent ions in solution is reached. That concentration, the solubility, varies with the overall solution conditions. In solutions containing calcium and phosphate, a number of calcium phosphate phases may be formed (Fig. 1), depending mainly on the pH and calcium concentration. As a result of that, calcium phosphate precipitation will depend on the phase closest to saturation at the prevailing solution conditions. However, in environments which mimic milk, urine or other natural biological solutions, the interactions caused by other ions are significant and the solubility isotherms can only be used as a starting point for prediction of the forming phase. The goal of this work is to obtain advances on the interactions between citrate ions and calcium phosphate in simulated milk solutions, in order to better understand the formation of unwanted deposits on surfaces and to design appropriate cleaning strategies.

There are a wide range of calcium phosphate phases that may precipitate, most likely as precursors to hydroxyapatite (HAP), as defended by several authors (House, 1999; Liu, Sethuraman, Wu, Nancollas, & Grynpas, 1997; Milev, Kannangara, & Ben-Nissan, 2003; van Kemenade & de Bruyn, 1987; Visser & Jeurnink, 1997), namely dicalcium phosphate dihydrate or brushite (DCPD), octacalcium phosphate (OCP), tricalcium phosphate (TCP) or amorphous calcium phosphate (ACP). It is well established that kinetic factors may be of great importance in determining the characteristics of the phases formed during the precipitation process together with equilibrium considerations. In other words, what is thermodynamically the most stable phase may not be the one which precipitates first because its precipitation kinetics is slower. The formation of the different calcium phosphates species can consequently be explained by kinetic, thermodynamic or solubility effects, or on the other hand be the result of the interactions with other substances present in solution. Little is currently known about the conditions or levels of supersaturation necessary to produce precipitation in the last case, more precisely to overcome the effect of organic ligands, because not much is yet known about the interactions between those organic molecules and the calcium phosphate compounds formed in solution.

A number of kinetic studies have attempted to establish the specific conditions for the formation of each precursor phase, most of them having been carried out under the constant composition method (Koutsoukos, Amjad, Tomson, & Nancollas, 1980). Ions such as magnesium have also been reported as important inhibitors for the precipitation of certain phases, by forming chemical complexes with the newly formed surfaces, blocking further precipitation (Abbona & Franchiniangela, 1990). Some studies do exist assessing the effect of organic ligands like citrate and acetate on the precipitation of dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP) and hydroxyapatite (HAP). In seeded solutions, they all reported inhibition of hydroxyapatite precipitation by adsorption of the organic molecules on active growth sites of the seeding material, resulting in the formation of phospho-citrate complexes (van der Houwen & Valsami-Jones, 2001). This inhibition effect of citrate on calcium phosphate kinetics was first presented in an earlier study, at the time concerned with the inhibition effect on the transformation of OCP into any other more stable crystalline form (Sharma, Johnson, Sallis, & Nancollas, 1992). Some work concerning the role of citrate on calcium phosphate precipitation from a SMUF solution was also presented in a recent publication by Andritsos et al. (2002) at pH values and temperatures different from those tested in the present paper and whose conclusions will be discussed later.

Although considerable work has been done on calcium phosphate precipitation and on the preferential precipitation phases, the majority of those studies was carried out in low ionic strength solutions, mainly composed of calcium and phosphorous. In the present work, the study of the different calcium phosphate phases formed under heating treatment and in the presence of citrate was evaluated for a solution which simulates the mineral composition of milk. The final goal is to contribute to the understanding of the fouling process in milk pasteurization processes.

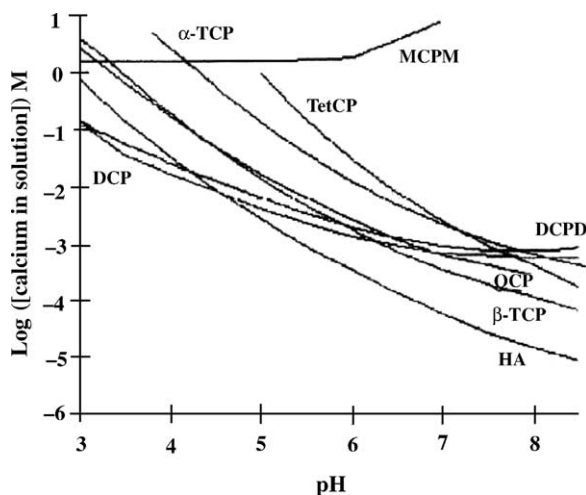


Fig. 1. Calcium phosphate solubility isotherms (Vereecke and Lemaitre, 1990).

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