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The growth morphology of gypsum crystals: an experimental study

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Gypsum (calcium sulfate dihydrate, $CaSO_4.2H_2O$) is the most abundant sulfate mineral throughout natural earth systems and is also present in a wide range of industrial processes (e.g. construction material, fertilizer) where the morphology and size of the crystals determines the final characteristics of the product. But despites its importance in natural and artificial processes neither the growth nor equilibrium morphology of gypsum crystals are properly understood [1]. A series of crystallization experiments were conducted to identify the key parameters that control the growth morphology of gypsum crystals.

When gypsum precipitates from a supersaturated $CaSO_4$ solution, single crystals, twins and spherulites are formed. All of them present the same trend in growth morphology as a function of temperature and supersaturation. At low temperatures (≈4ºC) mainly plate like crystals are formed and morphology varies little with supersaturation. At higher temperatures (≥20ºC) crystals with needle habits are dominant, becoming more elongated as supersaturation increases. When supersaturation surpasses a critical value crystal size starts to decrease. The influence of temperature and supersaturation on the growth morphology can be, roughly, explained in terms of changing growth kinetics with varying temperature [2] and increased nucleation at higher supersaturation. Although it should be mentioned that crystals grown under the same experimental conditions always present a large variation in growth morphology (except at 4ºC). Transmission Electron Microscopy was used to observe the growth morphology of crystals at the early stages of crystallization and this large variation in morphology was also observed (Figure 1). These results indicate that the nucleation stage and/or the early stages of growth have a large influence on the growth morphology of gypsum.

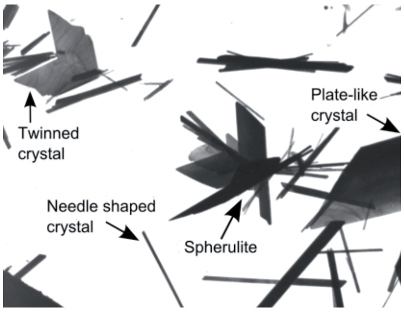

Figure 1. TEM image of gypsum crystals grown at room temperature (Saturation Index $_{gypsum}$= 0.73). Chemical reaction stopped after 4 minutes since reagents are in contact.

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Crystallization of acetaminophen on a polymer surface

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Polymorphic control has long been desired. One of the ways to achieve this control is by heterogeneous nucleation. Recently the use of polymers as heteronuclei has been investigated and the results suggest that the polymers to some extent are able to facilitate selective growth of polymorphs [1]. Furthermore heterogeneous nucleation can be a way to obtain polymorphs, which have not been produced before because of a large kinetic barrier in the aggregation step.

In this study the mechanisms behind heterogeneous nucleation on a noncrystalline polymer surface are investigated. An important factor in the initial aggregation of molecules on a surface could be the roughness of the surface. In addition to the roughness the polarity of the surface is too suspected to contribute to the selective growth.

The roughness of spin-coated polymer surfaces is determined by AFM, and the polymorphic form and orientation of acetaminophen crystallized on the surface is determined by powder X-ray diffraction.

In addition to the experimental work a theoretical approach is also taken. Because of the substantial size of acetaminophen interaction with the surface, it is not feasible to treat the whole system quantum mechanically. The system is therefore treated with quantum mechanics/molecular mechanics. This implies that the system is divided into a smaller part treated by quantum mechanics and a part treated by molecular mechanics.

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In situ study of temperature effects on protein crystallization

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Despite the number of protein structures solved by X-ray diffraction increases exponentially, the quality of the single crystal samples obtained from standard crystallization procedures still limit structural studies and results obtained. The classical theory for crystallization some nuclei may become crystals when they exceed the free energy barrier and the critical size. Physical-chemical parameters such as temperature, pH and concentration alter the height of the free energy barrier and consequently the critical nuclei size and the growth rate. Indeed the physical-chemical changes in the protein solutions during the crystallization process are complex and far from well understood [1].

According to Marseille Protein Crystallization Database crystallization essays have been performed in two preferential temperatures: 277K or 293K [2]. Results presented in the literature