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Repartition of various soluble and insoluble species in supersaturated solutions

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Abstract: The hydrated ion-pair model for uncharged soluble species in equilibrium with many solid polymorphs is applied to examples from various fields of interest. The role of such precursors and their changes on ageing can explain the often observed evolution of a hydrated precipitate to successively more dehydrated solid forms. The cases studied concern the precipitation of calcium carbonates, oxalates and phosphates.

INTRODUCTION

It is now well known that the precipitation / dissolution processes involve the intermediate formation of an uncharged soluble species (ion-pair) whose evolution through hydrated and solid phase modifications is of major importance. Thus, any thermodynamic model for systems dealing with weakly soluble ionic compounds has to take into account the formation constant of these species (ref. 1).

Usually, for a series of equilibria in water such as:

$$MX_s \Longleftrightarrow MX^o_{aq} \Longleftrightarrow M^+_{aq} + X^-_{aq}$$

we only know the solubility product

$$K_s = |M^+_{aq}| \times |X^-_{aq}|$$

but in order to study the system more precisely we have to consider the thermodynamic formation constant for the uncharged soluble species

$$ß = |MX^o_{aq}| / |M^+_{aq}| \times |X^-_{aq}|$$

and, when the limiting solubility s is obtained (*i.e.* at the beginning of precipitation):

$$|MX^o_{aq}| = s \qquad \text{therefore} \qquad ß = s / K_s$$

Even if s and K_s are both very small, ß might be high.

The importance of this concept is illustrated here with some examples of applications to various fields of interest.

SCALE FORMATION

In the case of scale formation, metastable solutions supersaturated in calcium carbonate are frequently observed. Our model takes into account hydrated $CaCO_3^o$ species in solution, in equilibrium with many solid polymorphs (ref. 2). Thus a hydrated solid precipitates at first and subsequently evolves through dehydration of the soluble species (see the Scheme) towards the thermodynamically stable solid, *i.e.* anhydrous calcite (ref. 2, 3).

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Scheme

$CaCO_3{}^{o}h_{(\alpha)}$ <=>	$CaCO_3{}^{o}h_{(\beta)}$ <=>	$CaCO_3{}^{o}h_{(\gamma)}$ <=>	$CaCO_3{}^{o}h_{(\delta)}$ <=>	$CaCO_3{}^{o}h_{(\varepsilon)}$ <=>	$CaCO_3{}^{o}h_{(\zeta)}$
⇑⇓	⇑⇓	⇑⇓	⇑⇓	⇑⇓	⇑⇓
$CaCO_{3(s)}$	$CaCO_{3(s)}$	$CaCO_{3(s)}$	$CaCO_{3(s)}$	$CaCO_{3(s)}$	$CaCO_{3(s)}$
(amorphous)	(ikaite)	(monohydrate)	(vaterite)	(aragonite)	(calcite)

These equilibria were studied by pH titrations of $CaCl_2$ + $NaHCO_3$ mixed solutions at constant NaOH addition rate and by experimental determination of the so-called 'critical pH' (ref. 2, 4).

The role of precursors

We have considered scaling phenomena taking into account formation equilibria for all $CaCO_3{}^{o}$ hydrated forms in solution. In saturated solutions, when near to the formation equilibria for metastable solid polymorphs (*i.e.*, monohydrate; ikaite = hexahydrate; amorphous), calculations showed that the soluble form occurs in high concentrations (ref. 2), thus playing the role of a precursor.

When the ion activity product (IAP) is such that we are near supersaturation for the calcite form, the $CaCO_3{}^{o}$ concentration in solution is only *ca.* 10^{-5} M. There are too few of these precursors for significant encounters to occur for formation of a calcite precipitate. If there is precipitation of the amorphous solid polymorph there is a constant concentration of the soluble species in the vicinity of the solid due to its redissolution process (Fig. 1). We can thus observe an evolution towards the anhydrous solid polymorphs whose solubility products are succesively reached.

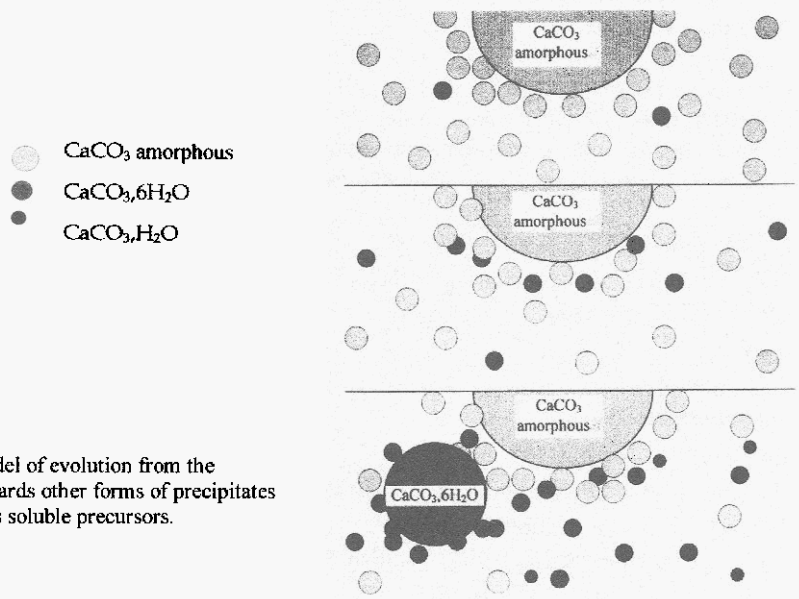

Fig. 1 The model of evolution from the amorphous towards other forms of precipitates through various soluble precursors.

The action of inhibitors

In order to reduce the scaling events in industrial plants, various precipitation inhibitors are sometimes added. We present here our results with ATMP, a phosphonate compound. Its influence on the calco-carbonic equilibria is twofold. *(i)* the development of the metastable state is delayed by slowing down the germination step; an effect related to the ratio between the amount of precursors and the inhibitor concentration. *(ii)* the growing rate of crystals is also slowed down by the inhibitor (ref. 4).

ATMP moreover stabilizes the calcocarbonic metastable state for a given solid polymorph. This depends on the actual value of the IAP, and the nature of the precipitate depends on the inhibitor concentration. In the presence of 0.75 ppm ATMP ikaite is preferentially formed, and at 0.50 ppm the monohydrate .

Speciation diagrams corresponding to changes during 'critical pH' titrations can be drawn for such systems, thanks to previous determinations of stability constants in the $H^+/Ca^{2+}/ATMP/CO_3^{2-}$ system (ref. 5). We observe that the presence of ATMP does not modify the titration curves, as inhibitor forms complexes with only a small fraction of total calcium. Moreover, whatever the degree of titration, ATMP (or H_6L) is almost totally in the form of complexes with calcium, the most abundant species being $CaHL^{3-}$ at lower pH and at the end of titration both CaL^{4-} and Ca_2L^{2-}. Data also show that at the metastable state's breaking point, i.e. when IAP $\approx K_s$ for ikaite, the most abundant inhibitor species is Ca_2L^{2-}.

In a study of the cooling towers of a nuclear power generator plant we observed that the river water can have an intrinsic inhibitory capacity probably arising from humic substances (ref. 4). In order to take better account of this parameter when treating river water, we recommend the determination of this inhibitory capacity, *e.g.* by anodic stripping voltammetry with copper as a titrating ion (ref. 6) or by use of a 'scaling index' (ref. 4).

The ageing of precursors

We observed that, although the first precipitate is an amorphous hydrated $CaCO_3$, the crystals obtained at the end of our experiments are mainly of the vaterite form. So the evolution of precipitates goes through successive polymorphs with decreasing solubilities, with calcite as the ultimate solid if sufficient time is allowed. This is in good agreement with the results of Sawada (ref. 3) indicating an ageing of the precipitate first obtained, giving place to successive steps in the variation of IAP with time. As explained here, during the precipitation of a given form, the solubility s and the solubility product K_s of this form are respected in solution and there is an equilibrium between various states of precursors. But when the limiting solubility of a more soluble form is attained, there is another precipitate formed with simultaneous dissolution of the preceding form. The successive steps in the IAP *vs.* time curves are due to the more soluble forms present although a less soluble solid is actually precipitating.

Due to such an ageing process it is very important not to retain prepared solutions too long. The double decomposition process, as used by Sawada in the case of calcium carbonates (ref. 3), is certainly the most useful as there is an immediate precipitation process without artefacts. In contrast the CO_2 stripping process, which is sometimes used, gives different results depending on the CO_2 partial pressure in the stripping gas.

UROLITHIASIS

Urolith formation and development cannot be directly observed *in vivo* , and only results of *in vitro* experiments are available. The mechanism of growth of renal stones consisting of calcium oxalate is therefore a subject of wide interest to both biologists and chemists.

In such a system three hydrated CaOx solid polymorphs (mono-, di- and tri-hydrate,. COM, COD and COT respectively) have been characterized. In stirred supersaturated solutions with constant composition, COT precipitates first (ref. 7) although it is the thermodynamically less stable species. In unstirred solutions however there is formation of both COM and COT while there is agglomeration of precursors and ion diffusion towards solid forms. The kinetics of crystallization (ref. 8) and dissolution (ref. 9) have confirmed that solutions saturated in COT or COD are supersaturated in COM, the crystallites of which can be formed in the presence of suitable nucleation sites. Stirring facilitates the encounter of $CaOx^o_{aq}$ precursors to form COT solid, but in the absence of stirring there is an ageing (kinetically controlled) transformation to give

less hydrated COD or COM. This has led to an interest in the best procedures to specifically obtain either COM, COD or COT (ref. 10).

PRECIPITATION OF CALCIUM PHOSPHATES

Calcium phosphates constitute a more complex case where the various solid species have different stoicheiometries; nevertheless, we can now gain a new insight into previous results concerning the behaviour of a *high rate pond* (ref. 11), *i.e.* a natural waste-water treatment plant reducing pollution fluxes by algal and phytoplankton productions.

Here the calcium concentration in water and the high pH obtained in this natural reactor results in the precipitation of calcium phosphate minerals. Although the pH variations (± 1 pH unit during the diurnal period) are clearly correlated with the algal photosynthetic activity (ref. 12), the observed correlations between total phosphate concentration and calcium concentration or pH cannot be explained by either the formation of apatite $Ca_5(PO_4)_3OH$ or brushite $CaHPO_4$, the thermodynamically more favoured forms. The agreement between experimental and calculated data is only obtained by taking into account the amorphous tricalcium phosphate $Ca_3(PO_4)_2$ phase (ref. 11). Such a result seems somewhat astonishing as, although sediment analyses indicate the presence of apatite only, all natural aquatic media are supersaturated with respect to apatite. In the present case however, in spite of the great number of ionic species to be taken into account and the presence of H^+ or OH^- ions, an evolution model through precursors can been applied but kinetic factors have to be included in the model. Thus, although brushite is preferentially obtained at pH < 7, in the conditions of the high rate pond ($8 \leq pH \leq 10$) it is the amorphous form which subsequently evolves into apatite within several days.

The successive evolution of the amorphous precipitate to various forms of calcium phosphate minerals has been previously studied by Christoffersen *et al.* (ref. 13). It appears from recent unpublished experiments (ref. 14) that precursors of many crystalline forms can be present simultaneously, even near precipitates which have already formed. Thus a mixture at pH ≈ 7-8 of both freshly precipitated amorphous and brushite forms will give place to a solid of apatite structure. We have shown that this pH range is the optimum range as estimated by modelling with log ß = 20.5 for amorphous tricalcium phosphate at 25°C.

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