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# Investigations of Complex Precipitation Systems

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A survey of methods available for investigations of complex precipitation systems under dynamic conditions and under conditions of stable and metastable equilibrium is represented. Examples given pertain to the calcium and magnesium phosphate and calcium oxalate precipitation systems. Solubility curves as well as precipitation curves and diagrams yield information on the influence of reactant concentrations (and/or concentrations of other solution constituents) on the properties of precipitates. Characteristic parts of precipitation diagrams are the precipitation boundary (boundary between metastable and unstable solutions) and the boundary between the concentration regions within which heterogeneous and homogeneous nucleation respectively prevail. At equilibrium the precipitation boundary enables calculations of solubility and complex stability constants, otherwise it yields information on the kinetics of mononuclear crystal growth. From the heterogeneous/homogeneous nucleation boundary the critical supersaturation for homogeneous nucleation and the interfacial energy and critical radius of the respective homogeneous nucleus may be determined.

Kinetic experiments give information on the rates and mechanisms of the rate determining precipitation processes involved. It has been shown that in the concentration region of heterogeneous nucleation crystal growth and subsequent (or simultaneous) aggregation are rate determinant, whereas in the homogeneous nucleation region aggregation of particles is dominant in all stages of precipitate formation and the formation of colloids (hydrophobic precipitates) and highly hydrated precursors (hydrophilic precipitates) may be expected. Examples of kinetic curves pertaining to the heterogeneous and homogeneous nucleation region respectively are presented.

Most precipitation systems encountered in biology, medicine, environmental sciences and industry are complex systems in which one or more cations and anions (including hydrogen or hydroxyl ions) react to give chemically and/or physically different precipitates. The reaction between strong acid(s) and strong base(s) will be largely independent of the pH. Examples are the formation of silver halides, alkaline earth sulphates, etc. However, much larger is the group of systems in which salts are formed by interaction of weak acids with strong bases and vice versa, or of weak acids with weak bases. In such systems the distribution of ionic species in solution largely depends on the solution pH and consequently so do the actual supersaturation and the properties of the resulting precipitates. Examples are metal oxides[1], alkaline earth carbonates[1], phosphates[2], oxalates, magnesium ammonium phosphate[3] and complex systems such as the human urine producing crystalluria or multicomponent systems encountered in technology, such as the systems uranyl nitrate — alkaline earth — sodium carbonate[4,5]. Usually the investigator is interested to predict the properties of precipitates which will form under certain experimental conditions. The purpose of this paper is to suggest a logical approach and describe some of the methods available for such studies.

## PRECIPITATION PROCESSES

Regardless of the system involved, precipitates are formed by a succession of precipitation processes[6]. The birth of a precipitate is called nucleation and it is possible to differentiate between nucleation upon specific or nonspecific heteronuclei (heterogeneous nucleation) and homogeneous nucleation, which occurs beyond a critical supersaturation. Successive processes are growth, agglomeration and finally ageing, i. e. physical transformation in the sense of Ostwald ripening and chemical transformation of metastable phases into thermodynamically stable ones. The properties of precipitates depend on the rates and mechanisms of the prevalent precipitation processes, but how and when one or the other process will become rate controlling, depends on the experimental conditions, such as reactant concentrations (supersaturation and reactant concentration ratio), pH, ionic strength, additives, temperature, etc.[7,8]. With so many variables involved, only a very systematic approach is likely to give the expected result, i. e. a reasonably good description of a precipitation system.

## EXPERIMENTAL APPROACH

The obvious first step in the investigation of an unknown precipitation system is a precise definition of the experimental conditions of interest. Here we shall be guided by the need to compromise between the practical and theoretical purpose. For instance, in an industrial or biological precipitation system the recurrent reactant concentrations might be quite limited, but in order to get valuable explanations, a much broader concentration range will have to be investigated. A compromise is then made to get the best possible results with the highest possible efficiency.

The next logical step is the construction of appropriate solubility diagrams[1] using literature values of solubility and complex stability constants[9]. Such diagrams show, which of the solid phases are stable within a given range of pH and reactant concentrations and may also indicate potential metastable precursors. Thus from the solubility diagram of magnesium orthophosphate «Figure 1, ref. 10) it is possible to deduce the range of stability of $MgHPO_4 \cdot 3H_2O$ and $Mg_3(PO_4)_2 \cdot 8H_2O$. The structure $Mg_3(PO_4)_2 \cdot 22H_2O$ is unstable in the whole pH range, but according to previous experience it might be expected to appear as a metastable precursor at high initial reactant concentrations[11].

Further investigations are based on systematic variations of the experimental conditions and observation of the system at a predetermined time long enough to allow the establishment of metastable or stable equilibrium. The information thus obtained is used for the construction of precipitation curves and diagrams[7,8,11,12]. Precipitation diagrams show the dependence of precipitate

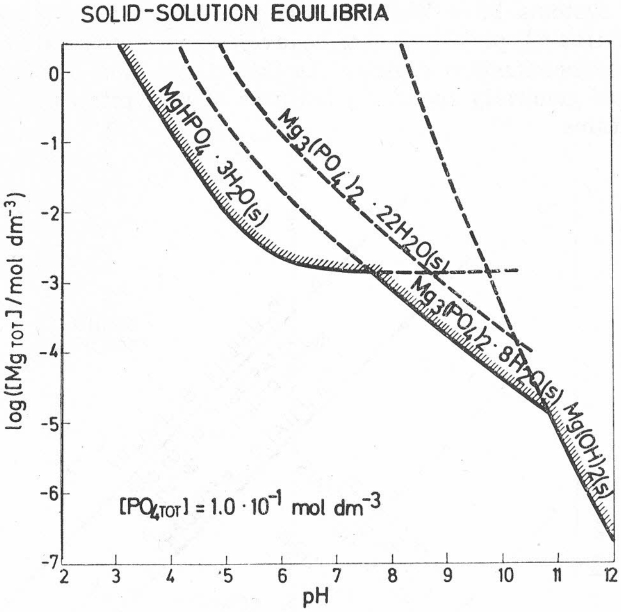

Figure 1. Solubility curves of magnesium orthophosphate at 25 °C (after ref. 10).

characteristics on reactant concentrations and/or other solution constituents, providing thus an overall picture of the precipitation system. Such diagrams also give information on heterogeneous equilibria[7,8,12] and on changes of the nucleation mechanism due to concentration changes[11].

Finally, kinetic experiments will be performed, to obtain information on the rate and mechanism of the precipitation processes which are rate determining at a given time under given experimental conditions.

## PRECIPITATION CURVES AND DIAGRAMS

As early as 1935 Težak[13] suggested the examination of precipitates by precipitation curves in which experimental data, reflecting some characteristic feature of the precipitate (turbidity, or other) are represented as a function of the concentration of one of the components (A) at constant concentration of the other (B). A series of such curves with different constant concentrations of (B) may be arranged in a three-dimensional plot, a »precipitation body«[7,12]. For simplicity it is preferable to present the results in the form of precipitation diagrams, i. e. as a projection of the »precipitation body« in a plane with contours showing equal values of the chosen experimental parameter. These may be replaced by boundaries, showing concentration regions within which precipitates with similar characteristic properties (for instance morphology) appear. Obviously, dicomponent systems may be fully characterized by one precipitation diagram, while two or more diagrams are needed for multicomponent systems[4,8]. One of the first experimental systems, to be represented in this form was the dicomponent system $AgNO_3$ — KBr, which was presented by Težak and collaborators in 1954[14]. Later over the years, many different precipitation systems have been thus characterized and it has been shown that many confusing problems can be avoided by systematically »scanning« large enough concentration regions. At this stage, then, it seems appropriate to discuss some generally recurring features of precipitates in terms of precipitation diagrams.

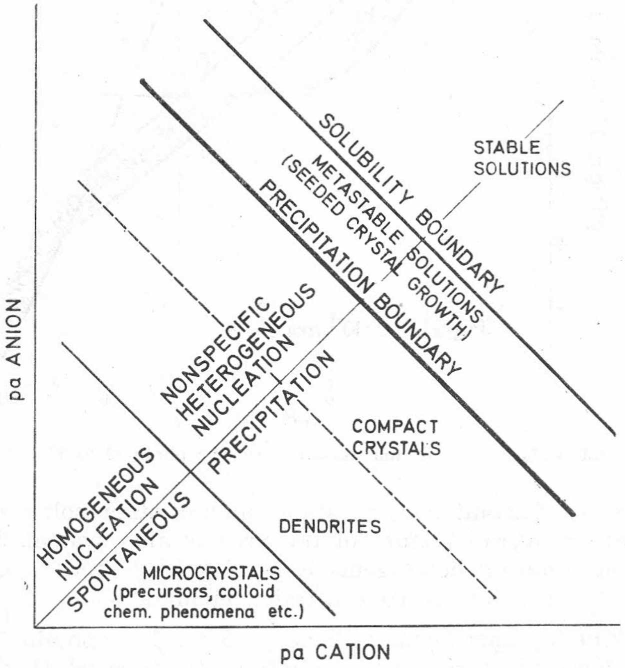

Figure 2. Schematic presentation of a precipitation diagram of a two-component system constructed on the assumption that complex formation is negligible and that the chemical composition of the precipitate is independent on the reactant concentration ratio. The coordinates are negative logarithms of initial ionic activities of the constituent ions. The mechanisms of precipitate formation and the corresponding morphology of the precipitate are indicated within the proper range of reactant concentrations.

Figure 2 is a schematic presentation of a precipitation diagram (log/log scale) of a two-component system. For simplicity reasons it was assumed that complex formation in this system is negligible and chemical composition of the precipitate is independent on the reactant concentration ratio. In order to avoid deviations due to changes in ionic strength, initial reactant concentrations have been replaced by ionic activities. It can be easily shown[8] that in such a diagram the solubility boundary is a straight line perpendicular to the line showing equimolar ratios of the reactants.

On the assumption that in this system the rate and mechanism of nucleation and growth depend mainly on the supersaturation (an oversimplification which will be corrected later) the precipitation boundary (boundary between clear solutions and first detectable precipitates) and the boundaries of the different precipitation regions have been plotted parallel to the solubility limit.

The position of the precipitation boundary in the diagram depends on experimental factors, such as the method of detection, time of observation, etc. At equilibrium it may coincide with the solubility limit and may be used to obtain information on the prevailing heterogeneous equilibria and to determine solubility and complex stability constants as was first demonstrated by Kratohvil, Težak and Vouk[15]. This approach has been described in detail[7,8,12] and will not be reiterated here.

At metastable equilibrium the precipitation boundary is shifted towards higher supersaturations, dividing thus the region of metastable solutions (where precipitation can be induced by specific seed crystals) from the region of spontaneous precipitation. In terms of nucleation and growth kinetics it corresponds to a constant induction time, which is the time of observation. In other words, the precipitation boundaries are »isochrones« showing the dependence of the induction period on solution composition[16]. Figure 3 shows a set of precipitation boundaries of calcium hydrogen phosphate dihydrate obtained at different times of observation (10 min — 3 months). Apparently, over a wide range of reactant concentrations the induction periods are not a sole function of the supersaturation, but depend on the reactant concentration ratio as well. If, after Nielsen[17], such »long« induction periods are related to mononuclear crystal growth one observes, that growth is slowest in the isoelectric region and increases in excess of calcium and phosphate ions. This has been explained by a contribution of electrostatic interaction forces at the solid/liquid interface[16].

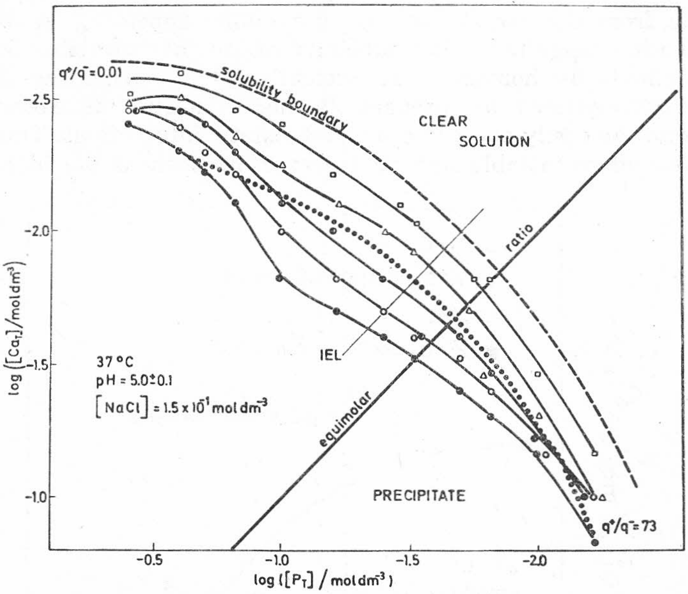

Figure 3. Precipitation boundaries of the system calcium chloride — sodium phosphate — 0.15 mol dm$^{-3}$ sodium chloride, obtained at constant pH (pH = 5.0). The position of the boundaries was determined 10 min (●), 60 min (○), 3 h (lhs filled circle), 24 h (△) and 1 month (□) after sample preparation. Broken line: calculated solubility limit of calcium hydrogen phosphate dihydrate ,dotted curve: constant supersaturation, $S = (Ca^{2+})(HPO_4^{2-})/(Ca^{2+})_s(HPO_4^{2-})_s = 2.54$. IEL: calculated isoelectric line; $q^+/q^-$ : calculated ratio of positive and negative charges in solution. After ref. 16.

In the region of spontaneous precipitation solid phase formation is initiated either by heterogeneous nucleation upon nonspecific impurities, or by prevalently homogeneous nucleation. In the former case the number of heteronuclei and particles is constant and relatively small ($10^6 — 10^7$). The morphology of the precipitates formed is determined by crystal growth and subsequent aggregation. The relationship between supersaturation, growth mechanism and particle morphology has been explained by Nielsen[6,17]. Some morphological forms are indicated in Fig. 2 within the proper concentration range.

At high supersaturations, where precipitation is initiated by prevalently homogeneous nucleation many more particles are formed simultaneously ($> 10^{12}$) and the supersaturation is practically exhausted in the process. Therefore aggregation becomes the dominant process in precipitate formation as has been demonstrated on the silver halide[7,12], calcium phosphate[2,11,18] and strontium sulphate[11] precipitation systems. In the silver halide system the difference between the two types of precipitates reflects in a marked difference in turbidity from the »crystallization maximum« appearing in the heterogeneous nucleation range to the low turbidity region characterizing the formation of stable colloids by homogeneous nucleation[7,11,12]. During the formation of hydrophilic precipitates by prevalently homogeneous nucleation hydration forces may not be easily overcome by electrostatic interactions. Thus we expect the formation of metastable hydrated precursors such as the higher hydrates

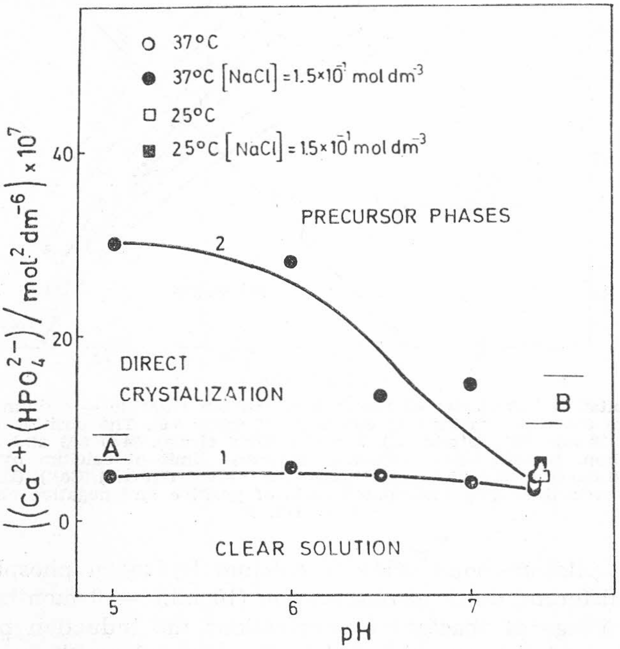

Figure 4. Precipitation diagram of the system calcium chloride — sodium phosphate — pH represented in terms of the initial mean ionic activity products of constituent ions and the initial pH (after ref. 2). Curve 1 — precipitation boundary, curve 2 — boundary between the regions of heterogeneous and homogeneous nucleation (»direct crystallization« and »precursor phases« respectively). The data were recalculated from the respective precipitation diagrams obtained at different constant initial pH values[19,36]. A — concentration region within which crystal growth of calcium hydrogen phosphate dihydrate could be followed by the pH-stat technique[2,23]; B — concentration region within which experiments pertaining to the formation, growth and transformation of amorphous calcium phosphate were carried out[2,18,29,35] (Figure 6).

of calcium oxalate[20] or the highly hydrated, X-ray amorphous calcium phosphate[2,21]. Even though in many cases metastable precursors may only be detected by fast kinetic measurements, the properties of precipitates formed by their recrystallization usually significantly differ from those which were formed by direct crystal growth in the heterogeneous nucleation range.

Thus, in any case in a precipitation diagram the boundary between the regions of heterogeneous and prevalently homogeneous nucleation appears as a discontinuity which may be recognized by turbidimetry, morphological observations or other means[11]. As an example, a precipitation diagram of the calcium phosphate system, showing the concentration regions of direct crystal growth upon heteronuclei and the formation of percursor phases by homogeneous nucleation respectively, is represented in Figure 4. It has been shown[11], that the boundary between the regions of heterogeneous and prevalently homogeneous nucleation may be conveniently used to determine the critical supersaturation for homogeneous nucleation as an average value over a wide concentration range. Using classical nucleation theory[22] the essential parameters of the homogeneous nucleus, the interfacial energy and critical radius, may thus be determined.

## KINETIC STUDIES OF SPONTANEOUS PRECIPITATION

In principle, kinetic studies provide information on the rate and mechanism of precipitation processes. Some of the methods most commonly used for this purpose are listed and commented in Table I (see also refs. 23—27). Usually it is essential to combine two or more methods to obtain complete and reliable information.

Typical progress curves may be obtained by following changes of the amount of solid phase formed as a function of time, which is possible either by continuous solution analysis or by using Coulter counter data[26-28]. In the region of nonspecific heterogeneous nucleation such curves are continuous and sigmoidal, indicating that precipitation is autocatalytic. An example, showing the kinetics of precipitation of calcium oxalate[28] is given in Figure 5 (upper diagram). The corresponding rate vs. supersaturation curve (lower diagram in Figure 5) shows an initial rapid surge up to a maximum (A) which is due to rapid initial growth upon heteronuclei. The subsequent linear part (B) indicates that crystal growth prevails during that period and may be used to determine the rate and mechanism of this process. In the given example the following deviation from linearity (C) is due to the onset of aggregation as indicated by a steady decrease in the number of particles in that region.

It must be kept in mind, that in most systems the range of supersaturations in which growth may be separated from aggregation is quite narrow compared to the complete region of heterogeneous nucleation (see for example region A in Figure 4).

At somewhat higher supersaturations both crystal growth and aggregation appear to be parallel processes and there is no detectable linear part in the rate vs. supersaturation curve.

In the homogeneous nucleation region progress curves may be discontinuous indicating the formation and transformation of metastable precursors. An example is shown in Figure 6 where the formation of amorphous calcium phosphate and subsequent precipitation of crystalline octacalcium phosphate

TABLE I

*A Comparison of Commonly Used Experimental Methods for Studies of Precipitation Kinetics*

| Determination of | Methods | Advantages | Restrictions | |
|---|---|---|---|---|
| Solution concentrations | Chemical analysis | wide application | discontinuous, previous separation of precipitate neccessary | Information restricted to crystal growth kinetics, as opposed to aggregation of particles |
| | Conductometry | sensitive, fast, continuous | restricted to low ionic strength | |
| | ion selective electrodes | selective, continuous, usage possible at any ionic strength | Restrictions depend on the kind of electrode used. Electrodes used for divalent ions have restricted sensitivity and relatively slow response. | |
| Concentrations of ions needed to keep constant hydrogen ion activity or solution concentration | pH-stat (23, 24) | Direct quantitative relationship between the amount of precipitate formed and the amount of $OH^-$ or $H^+$ ions used to keep constant pH. Changes in the system due to pH changes (dissolution, recrystallization) are avoided | Restricted to systems in which the pH changes as a consequence of precipitation. | |
| Solution concentrations | constant composition (25) | constant chemical potential of all constituent ions, i. e. constant »driving force«, particularly useful in seeded crystal growth experiments | experimental difficulties in studies of spontaneous precipitation | |
| Precipitate properties | turbidimetry | fast, simple, continuous, optimal range of particle sizes 5—200 nm | quantitative interpretation difficult | |
| | Particle number and size analysis (Coulter Counter) (26,27) | fast, sensitive yields direct information on crystal growth and aggregation, particularly useful in media of high ionic strength | Ionic strength $> 0.05$, detects only particles of volume diameter $> 0.5$ µm, discontinuous | |
| | light and electron microscopy, scanning electron microscopy | qualitative observation, facilitates interpretation of quantitative data | Preparation of samples for electron microscopy may produce artifacts | |

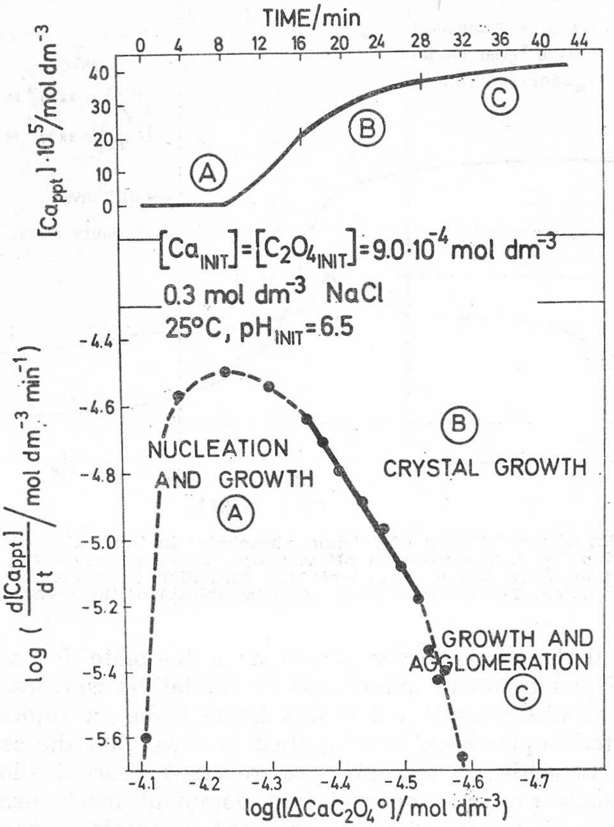

Figure 5. Kinetics of precipitation of calcium oxalate in the region of spontaneous heterogeneous nucleation[28]. Upper diagram: the amount of precipitated calcium as a function of time. Lower diagram: the rate of the reaction as a function of the supersaturation, expressed in terms of the soluble neutral complex, $CaC_2O_4^0$. Regions A, B and C are corresponding in time. The prevalent precipitation processes are indicated.

are followed by simultaneously recording changes in pH and turbidity[29]. This type of experiment gives information on the lifetime of the precursor and the onset of secondary precipitation. Since the system itself has been of particular interest as a model in biological mineralization[30] thorough qualitative and quantitative investigations carried out in our and other laboratories[2,18,28-35] resulted in a fairly good description of the precursor and the processes involved in its formation and transformation. Some of these results will be summarized to present an example of the resolution of an extremly complex precipitation system by combining different experimental techniques.

Amorphous calcium phosphate is formed by homogeneous nucleation and subsequent agglomeration of primary particles into spherical, approx. monodispersed structures, as shown by a combination of quantitative solution analysis and electron microscopy[2,18]. It is a highly hydrated material[31] and its chemical composition depends on the composition of the liquid phase from which it is formed[29,32]. Morphological and other observations suggest that the crystalline phase is formed in intimate contact with the amorphous pre-

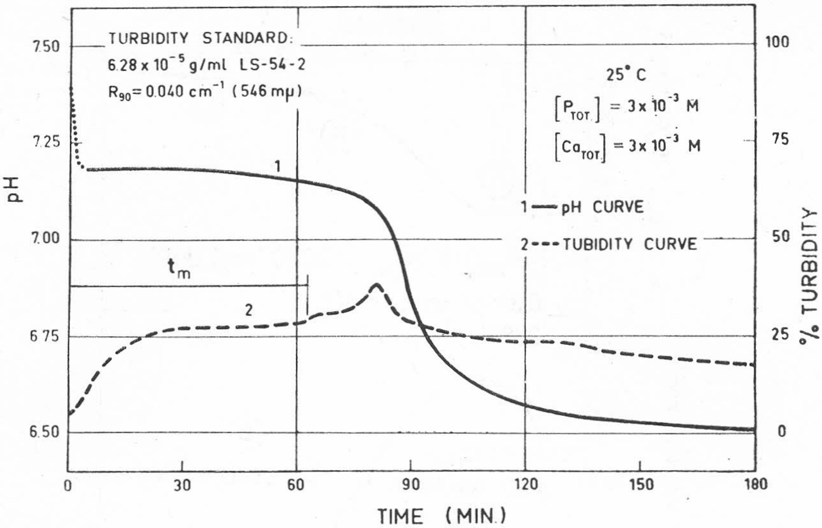

Figure 6. Kinetics of precipitation of calcium phosphates in the region of prevalently homogeneous nucleation[2,18,29,35]. The two-step pH v. s. time curve (curve 1) and the corresponding turbidity v. s. time curve (curve 2) indicate the formation of a precursor and subsequent secondary precipitation. The life-time (time of metastability) of the precusor is indicated ($t_m$).

cipitate, i. e. that the precursor serves as a template for secondary precipitation[29,33]. The kinetics of amorphous to crystalline conversion was investigated by X-ray techniques[34] and it was found to be an autocatalytic process. Radiometric techniques have been applied to show that the course of further equilibration depends on the pH and reactant concentrations, established during secondary precipitation and that dominant mechanisms are solution mediated recrystallization with concomittant composition changes[35].

## CONCLUSIONS

An approach to investigations of complex precipitation systems is described, which concentrates on the influence of concentrations of solution constituents (reactants and other) and the reaction time on the properties of the precipitates.

The dependence of precipitate characteristics on the supersaturation and the reactant concentration ratio (as well as on the concentration of other solution constituents) is shown by precipitation curves and diagrams. These are obtained by studying the precipitates at a predetermined time, after the establishment of stable or metastable equilibrium in the system. Within a precipitation diagram the precipitation boundary divides the region of metastable solutions (where crystal growth can be initiated by seeding) from the region of spontaneous precipitation. In an equilibrium situation this boundary reflects on solid/solution equilibria, otherwise it yields information on mononuclear crystal growth kinetics. In the heterogeneous nucleation range crystal growth and subsequent aggregation determine the morphology of particles while in the region of prevalently homogeneous nucleation aggregation is dominant in all stages of precipitate formation. In the latter region hydrophobic precipitates form colloid dispersions while in hydrophylic precipitates the formation of hydrated metastable precursors may be expected. The boundary between the two concentration regions is easily recognizable in many systems and may be used for the determination of the critical supersaturation for homogeneous nucleation as an average value over a wide concentration range. Kinetic studies confirm the above conclusions and give information about the rate and mechanism of the processes, which are rate determinant at any given time.

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## SAŽETAK

### Ispitivanja kompleksnih taložnih sistema

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Opisane su metode za ispitivanje kompleksnih taložnih sistema u dinamičnim uvjetima, kao i u uvjetima stabilne i metastabilne ravnoteže. Kao primjeri prikazani su rezultati dobiveni prilikom izučavanja kalcij- i magnezij-fosfata, te kalcij-oksalata. Krivulje topljivosti te taložne krivulje i dijagrami daju informacije o utjecaju koncentracija reaktanata (i drugih sastojaka otopine) na svojstva nastalih taloga u uvjetima ravnoteže, odn. u unaprijed određenom vremenu. Za taložne dijagrame karakteristične su granice taloženja (granica između metastabilnih i nestabilnih otopina) i granica između koncentracijskih područja gdje prevladava heterogena, odn. homogena nukleacija. U ravnotežnim uvjetima iz granice taloženja mogu se izračunati konstante topljivosti i konstante stabilnosti kompleksa u ravnoteži s talogom, dok odgovarajuće granice dobivene u uvjetima metastabilne ravnoteže daju informacije o mononuklearnom rastu kristala. Granica između područja heterogene i homogene nukleacije omogućuje određivanje presićenosti koja je kritična za homogenu nukleaciju, odn. međupovršinske energije i kritičnog radiusa homogenog nukleusa.

Rezultati kinetičkih eksperimenata služe za određivanje brzine i mehanizma taložnih procesa koji kontroliraju brzinu reakcije u odgovarajućim eksperimentalnim uvjetima. Pokazano je da u području heterogene nukleacije prevladava kristalni rast i naknadna ili simultana agregacija čestica, dok u području homogene nukleacije agregacija dominira u svim fazama nastajanja taloga. U tom području hidrofobni se talozi pojavljuju u obliku koloida, dok hidrofilni talozi često tvore vrlo hidratizirane, metastabilne prekursore. Prikazani su primjeri kinetičkih krivulja karakterističnih za područje heterogene odn. homogene nukleacije.

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