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Methorics of Precipitation from Electrolytic Solutions as Revealed through Relationship between Concentrational Factors and Kinetics of Solid Phase Formation

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For an explanation of the pecularities of precipitating systems they are treated as composed of five subsystems: *(i)* formation of complex species (simple and monomers, as well as polynuclears and polymers); *(ii)* embryonation (aggregates without core formation); *(iii)* nucleation and direct growth (the growing core); *(iv)* micellation (formation of primary particles with colloid individuality); and *(v)* secondary structures of micro and macro particles. It is assumed that the transition from ideal liquidus structures (ILS) to ideal solidus structures (ISS) usually proceeds through stages characterized by the development of methorical structures and textures (MS & T).

Applying the method of continuous variation of concentration of precipitating components the characteristic four types of precipitation bodies (PB, as a plot of logarithm of concentration of the cationic component against anionic one) are used for description and discussion of experimental results.

For illustration some contours of PBs are given (silver bromide; silver salts of fluoresceine group; uranyl phosphates; iron-III hydroxides, thorium hydroxides, hydroxides of lanthanides, all in aqueous solutions).

In discussing the morphology of the precipitates obtained by »solution aging« or under the conditions of »homogeneous« precipitation, it was pointed out that the phenomena may be explained by taking into account the role of subsystems and the discontinuities caused by aggregation of submicrons into larger units.

It seems that the simple approach to the structure and properties of precipitates through the kinetics of their formation and dissolution in functional relationship with concentrational factors is far from being exhausted. In this respect the first useful generalizations in preparation of colloid systems were those of von Weimarn. His classical system of barium sulfate has found many investigators up to our days. However, more elaborate experimental and theoretical approaches for an application of a balanced physical and chemical mechanism are needed. *E. g.*, the influence of concentration and composition of the electrolytic solution on supersaturation, embryonation, nucleation, direct and indirect crystalline growth, the structures of such agglomerates or orderly packed blocks, the polydispersity and monodispersity, the purity of precipitates, as well as the dependence of all these phenomena on internal and/or external factors such as volume, pressure, temperature, or gravitational, electrical, and some other field, have to be considered. Although recent experimental and theoretical advances may give more emphasis on quantitative approach, the majority of data cannot reveal fundamental features without very careful systematic, diachronic, and qualitative analysis and synthesis.

The Subsystems of Transition

The chain of events in precipitating systems include at least five critical stages (or subsystems) starting from physical and chemical interactions in solution: *(i)* the solution, although homogeneous, is in a saturated or supersaturated state, and is very sensitive to concentration and temperature variations because of the formation of complex ions, polynuclear and polymer species; *(ii)* the embryos, as stable or unstable aggregates of precipitating species but without the distinctive core of a stable crystal lattice; *(iii)* the

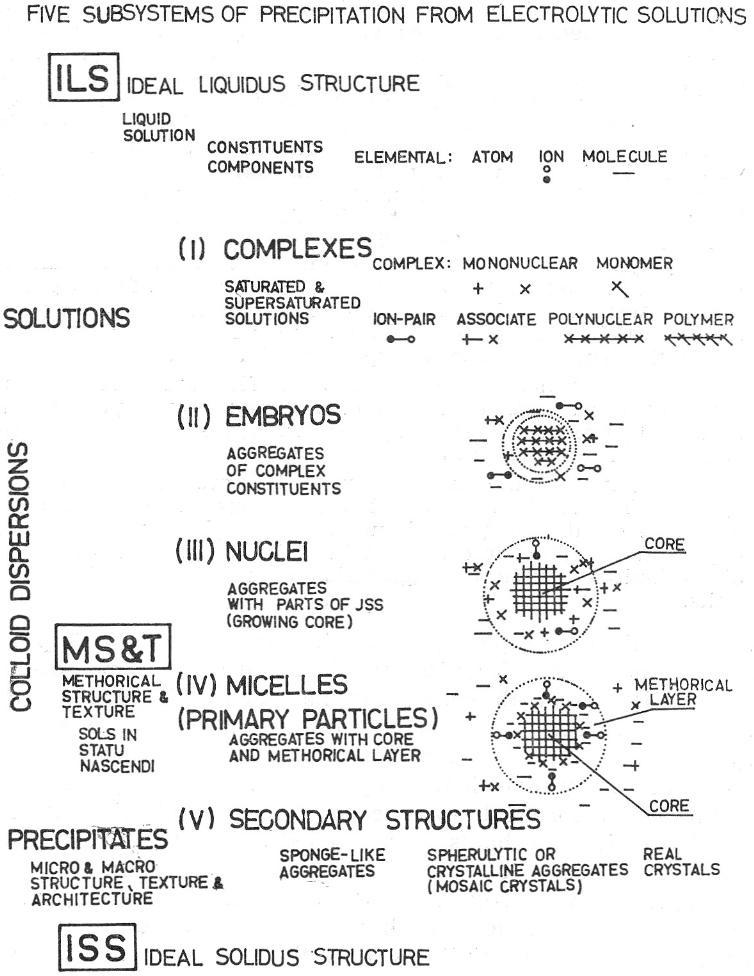


Fig. 1. Transition stages from homogeneous electrolytic solution to heterogeneous precipitating systems.

nuclei, as growing units with a core having a crystal lattice; *(iv)* the primary particles, as units with relatively well expressed colloid individuality owing to the development of the methorical layer with peculiar composition and structure which is different from that of the solid and of the solution phase; and *(v)* the secondary structures, which may be represented either by loosely aggregated primary particles, or by oriented growing blocks of crystalline units (mosaic crystals). Fig. 1 shows the composite scheme[1] of these five subsystems or transition stages from ideal liquidus structures (ILS) to ideal solidus structures (ISS) with intermediate stages, mainly colloid units characterized by methorical structures and textures (MS & T).

Assuming ideal bulk phases, each of the subsystems has to be experimentally and theoretically investigated using different approaches: (1) the system under equilibrium condition; (2) the behaviour of the subsystems under action of an external field (gravitational, electrical, *etc.*); (3) the subsystems under stability and instability conditions; (4) the subsystems under conditions of electron transfer; and (5) the subsystems under conditions of transfer of ions, molecules or other units through the methorical layer.

The Types of Precipitation Bodies, PB

Owing to the complexity of the factors and phenomena involved it is very important to use for presentation and interpretation a frame which may enable one to put into coherent relationship all discontinuities as effects of continuous variations of concentrations either of the main precipitating components or of various ingredients in solutions.

For this purpose we are using the so-called precipitation bodies (PB) which are diagrammatical presentations[1,2] of multidimensional systems in a basic plot of logarithm of the normal or molar concentration of the main cationic component as abscissae against that of anionic ones ordinates, while as origin of the system of coordinates high concentrations of the reacting components (usually 1.0 normal or molar) are chosen. Such diagrams show primarily the boundaries between precipitating and non-precipitating regions, as well as the discontinuities in the rate of precipitation in general. In reality, PBs present by projection reduction the four-dimensional topological systems of five elements (usually two precipitating electrolytes, solvent, emerging precipitate, and time factor), and may be used as synoptical maps illustrating an immense number of deliberately chosen conditions of internal and external environment for the systems under observation. As to the methods and techniques used for detecting and measuring the effects, they are limited mainly by the sensitivity and the denaturalisating conditions of the applied procedure. In principle, the same limitations are valid for dissolution processes as for precipitation or crystallisation systems: the radical interactions of analytical processes and operations have to be judged by their relation to the synthetical constructions of the natural behaviour of the undisturbed subsystems.

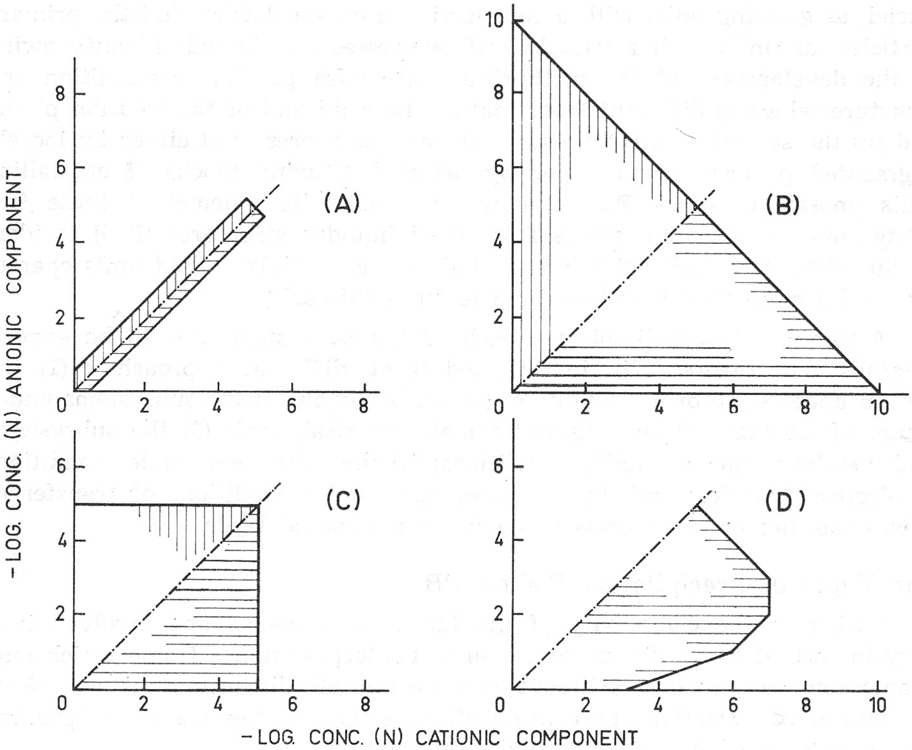


Fig. 2. The types of precipitation bodies (PB) in general precipitation diagram: (A) the neutralization, (B) the ionic solubility, (C) the formation of ion-pairs and associates, and (D) the unsymetrical ionic reactivity.

Pointing the relationship to the dominant processes of transition of solute species to solid phase, the four types of PB are named: (A) neutralization; (B) ionic solubility; (C) formation of ion pairs and associates; and (D) unsymmetrical ionic activity. In Fig. 2 are represented all four types of PB.

The precipitation bodies are very rarely coincidental with those which are expected from constant ionic solubility product, and the type (B) representing the constancy of ionic solubility product is rather an exception. Therefore our precipitation bodies should be considered from the point of view: *(a)* of the formation of complex species which are dominant in specific areas in the diagrams; *(b)* of the stability-instability of subcolloidal, somewhat like polymeric structures in the preeembryonal stage of the system; *(c)* of the genotypical factors controling the appearence of the solid phase and tending to give the system the most stable equilibrium state of ideal solidus structure; and *(d)* of the phenotypical factors which reflect the environmental conditions, especially morphological fixation of the succession of events through which the role of subsystems in the final state of the system could be structurally ascertained.

The Experimental PBs

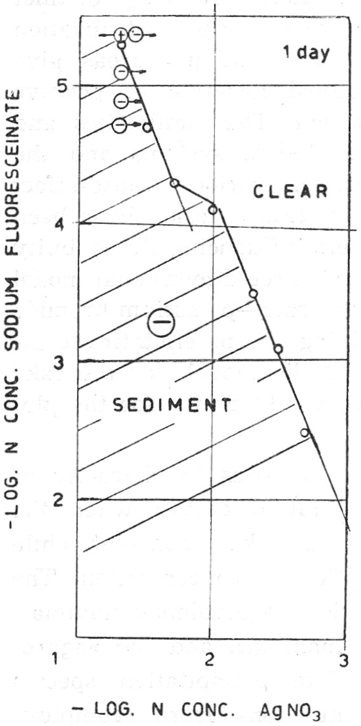
The diagrams of experimental precipitation bodies are in most cases combinations of two, or sometimes of all four types, and, for their understanding all four viewpoints have to be discussed and put in right perspective. Also, instead of initial concentrations of precipitating components, the analytically determined equilibrium or quasi-equilibrium concentrations can be plotted. Such a procedure could be useful for complex where ionic equilibria with the solvent are involved. With water such cases are frequent (hydrolysis of metal ions, polybasicity of acids), and therefore both kinds of diagrams, with the initial concentrations of the reacting components, as well as those with resulting concentrations might be necessary for a correct interpretation.

One of the first experimental systems was presented as a three-dimensional model of precipitation body[3] for silver nitrate—potassium bromide in aqueous solution at the *General Discussion of the Faraday Society* (Coagulation and Flocculation) in 1954. Looking back it seems that the precipitating systems of silver halides are very convenient models because they represent the combination of all four types of precipitation bodies, namely, in addition to the outer precipitating—non precipitating limits, there are very distinct internal countours within the precipitation body delineating the neutralization of isoelectric maxima while the neighbouring concentrational areas give nearly symmetrical and experimentally well defined negative or positive colloidal systems of so-called sols *in statu nascendi*. The similarities and differences between silver chloride, bromide and iodide systems and the possibility to differentiate experimentally between various cause-effect relationships, have been the reason that such sols *in statu nascendi* have been very extensively used in investigations of parameters influencing the stability of colloidal systems. Figs. 3 and 4 represent the first three-dimensional model of the precipitation phenomena in the system silver nitrate—potassium bromide in aqueous solution at 20^0 C, 10 minutes after mixing the precipitating components. It should be noted that the orientation of the model, for the sake of better perspective, is different from the one we would prefer for the plot of cationic component against anionic component.

We have, also, pointed very early[4] to the differences in character of various precipitation maxima reflected in precipitation curves when the concentration of one of the precipitation components is kept constant while the other component undergoes continuous variation of concentration. The most characteristic maxima are called the »isoelectric or equivalency maxima«, the »concentration maxima«, the »crystallization maxima«, and the »aggregation maxima«. They characterize something like precipitation spectra appearing under continuous variation of concentrations from »complex« solubility to the precipitating—ion precipitating limit of ionic solubility. Such maxima are very well expressed with silver halide systems, but with many others they may be obscured by simultaneously occurring processes of direct growth and aggregations on many levels of developing subsystems. All these are expressed in the kinetics of the formation and dissolution of precipitates within the precipitation body.

The precipitation bodies for various substances are quite different in shape in spite of similar solubilities. We have mentioned the differences in precipitating processes encoutered with silver chloride and barium sulfate, as well as the quite different stabilizing properties of silver ion as compared with the ones of silver halides, thiocyanate and cyanide[4]. The ionic solubility products estimated from precipitation experiments may differ from the solubility product obtained from solubility data determined using conventional methods, or — they are not constants at all for a given salt but are functions of the concentration of precipitating substance as it was demonstrated[6] for cases of sparingly soluble metal fluorides (magnesium, calcium, lanthanum and thorium).

An interesting series, where instead of usual equivalency maxima of precipitation the equivalency minima are developed, is found by silver salts of fluoresceine group[7]. Figs. 5, 6 and 7 represent precipitation bodies of silver fluoresceine, eosine and erythrosine in aqueous medium.



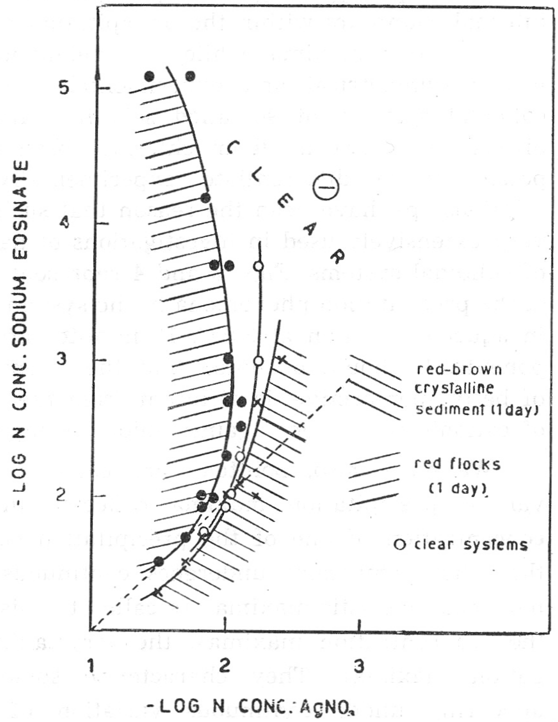
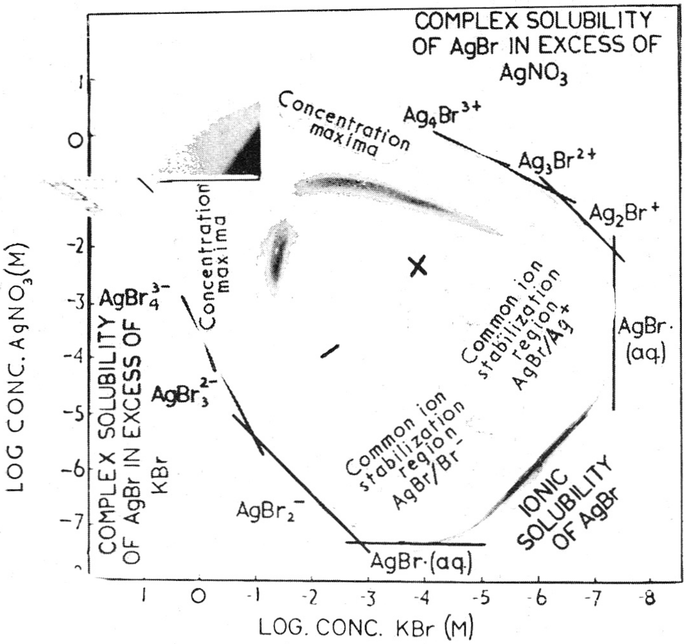
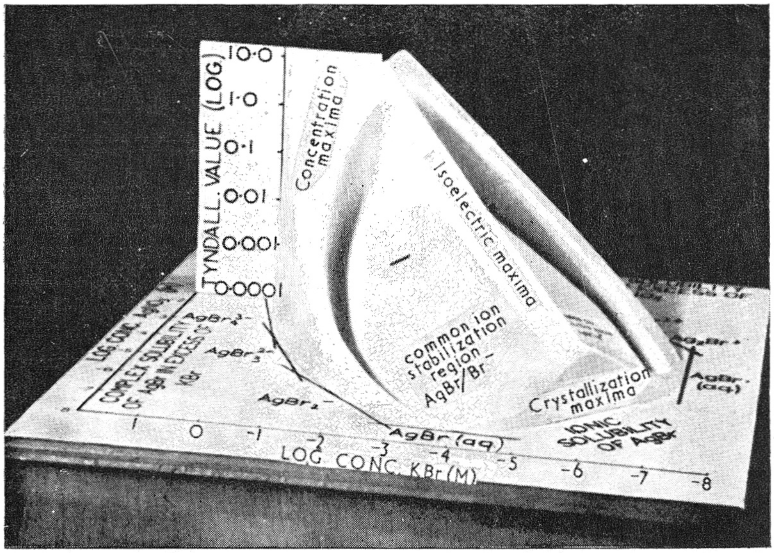


Fig. 5. Contour of the precipitation body of silver nitrate and sodium fluoresceinate in aqueous solution, after 24 hours.

Fig. 6. Contour of the precipitation body of silver nitrate and sodium eosinate in aqueous solution, after 24 hours.





Figs. 3 and 4. Three-dimensional model of the precipitaion phenomena in the system: silver nitrate and potassium bromide in aqueous solution at 20°, 10 minutes after mixing components.

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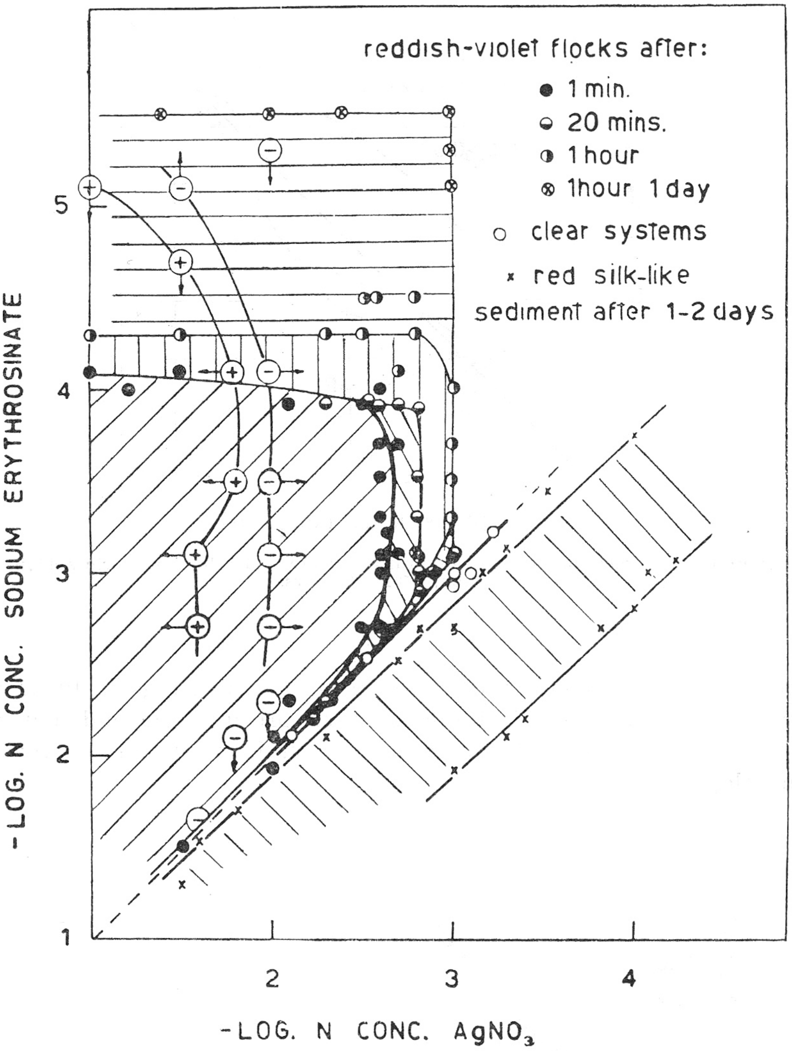


Fig. 7. Contour of the precipitation body of silver nitrate and sodium erythrosinate in aqueous solution, after 1, 20 and 60 minutes, and 24 hours.

That in certain areas within the precipitation body various substances may be found is demonstrated in Fig. 8 by the case of the system uranyl nitrate—orthophosphoric acid[8]. In this system, it is easy to detect by means of fluorescence effects, the regions of neutral uranyl orthophosphate (non fluorescent) and monohydrogen uranyl phosphate (fluorescent); the middle portion of the precipitation body shows a mixture of both species, which is changing with time; our diagram corresponds to a situation 24 hours after mixing.

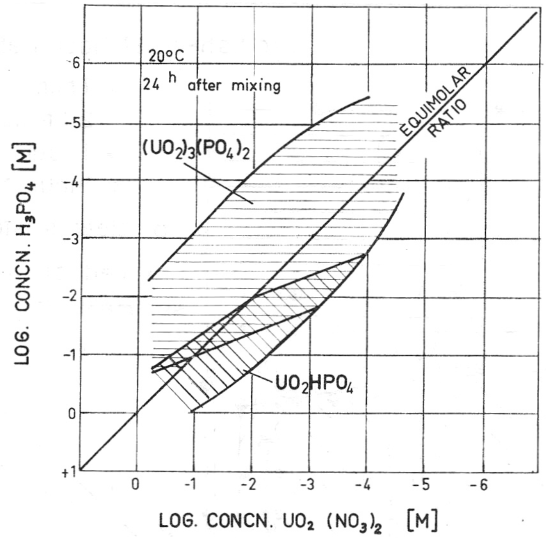
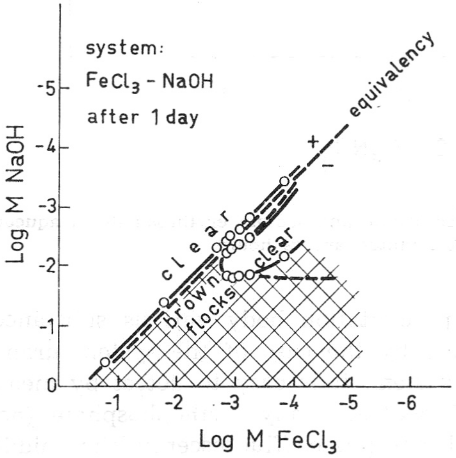


Fig. 8. Contour of the precipitation body of uranyl nitrate and othophosphoric acid in aqueous solution, after 24 hours.

Some examples of metal hydroxides[9-11] are given in Figs. 9, 10, 11 and 12, where there are characteristic limits between precipitating and non precipitating regions indicating the presence of various hydrolytic species by changing slopes.



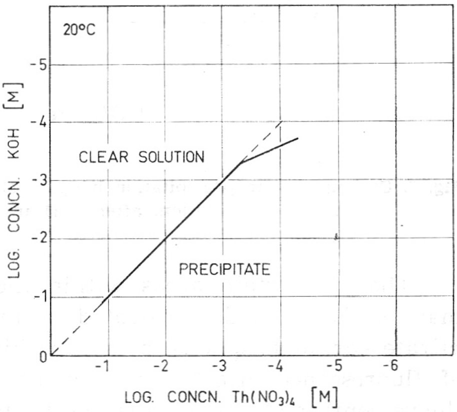
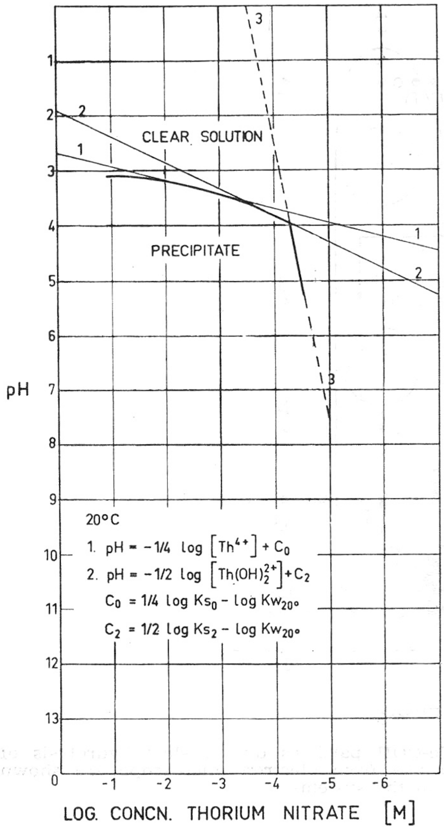


Fig. 9. Contour of the precipitation body of iron-III chloride and sodium **hydroxide** in aqueous solution, after 24 hours.

Fig. 10. Counter of the precipitation body of thorium nitrate and sodium hydroxide in aqueous solution, after 10 minutes.



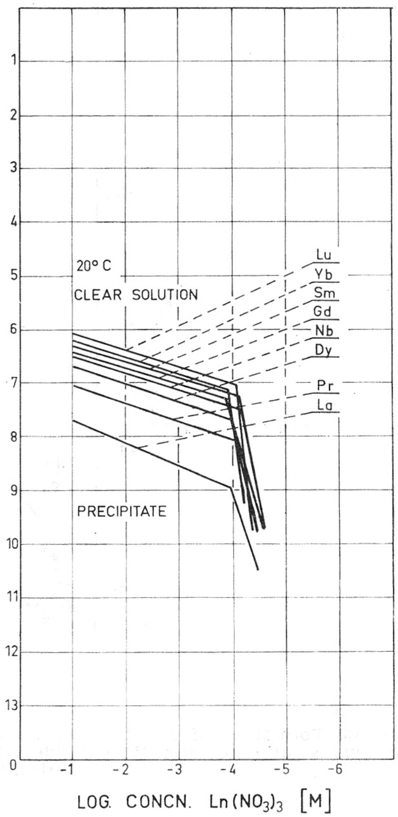


Fig. 11. Plot of logarithm of concentrations of thorium nitrate against *p*H, after 24 hours.
Fig. 12. Plot of logarithm of concentrations of lanthanide nitrates against *p*H, after 24 hours.

Precipitates from aged *or* homogeneous *Solutions*

In the theory and praxis of precipitation it is usually assumed that the method of so-called precipitation from homogeneous solutions[12] can assure the undisturbed direct growth from nuclei to the size of micro and macro crystals. That we are dealing here also with discontinuous aggregation of smaller units of our subsystems is clearly demonstrated in the formation of iron oxides and hydroxides[13], and especially in development of β-FeOOH structures. Fig. 13 shows the developing stages[14] of such structures by »solution aging« of iron trichloride solutions, while the possible composition of the resulting somatoides is schematically presented[13] by packing of subcrystals represented by hollow rods (Fig. 14).

The same discontinuous mechanism of formation of primary particles and their more or less regular aggregation may be found in all precipitates whether they have been obtained by precipitation from so-called homogeneous solutions or by procedures used for production of monodisperse grains[15].

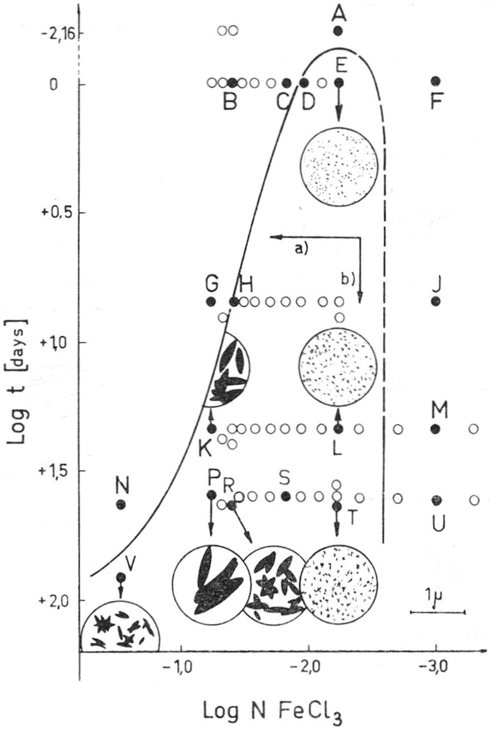


Fig. 13. **Formation** of spindle-shaped colloidal **β-Fe-OOH particles** during slow **hydrolysis of** aqueous **solution** of iron-III chloride; the photographs from electron microscope are shown schematically for some of the systems.

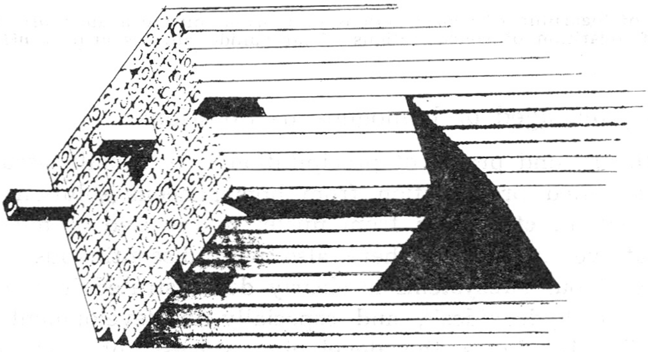


Fig. 14. Drawing to illustrate a possible structure for the β-FeOOH crystals wherein the subcrystals are hollow rods.

In Fig. 15 there is the electron-microscopic picture of monodisperse[18] barium sulfate particles obtained by application of Takiyama[17] method of precipitation from homoneneous solution. The particles are monodisperse and of ellipsoidal shape. In Fig. 16 there are pictures of ultrathin sections[16] of similar grains (the arithmetic main lengths of the long and short axes

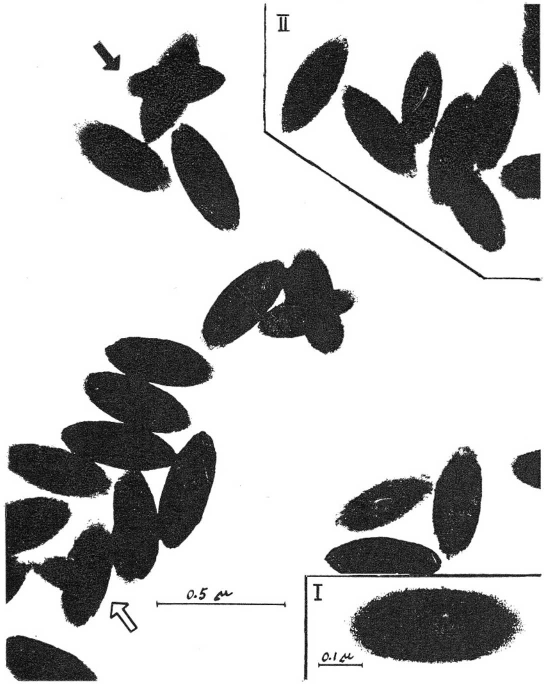


Fig. 15. Electron micrograph of barium sulfate precipitated by Takiyama method.
Fig. 16. Electron micrograph of typical sections of barium sulfate particles at manification 200.000 : 1.

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are 200 and 97 mμ respectively) which clearly show that the smaller units of about 30 to 40 Å are aggregated in sponge-like structures; the pores are nearly of the same size. The sections illustrate the internal particle structure with no indication of some preferential orientation of primary units.

From these and other results of experimental findings it may be assumed that in the majority of cases the mechanism of aggregation is a very important intermediate step functionally connected with either crystallinic growth, or coagulation, or flocculation of primary particles. As it was pointed out in interpretation of typical coagulation phenomena, microcomponents (the ions and molecules of solutes) in the methorical layer play a decisive role.

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IZVOD

Metorika precipitacije iz elektrolitnih otopina kako se otkriva iz kinetike stvaranja krute faze u relaciji prema koncentracionim faktorima

B. Težak

Radi tumačenja raznih pojava kod precipitacije smatra se da su precipitacioni sistemi obično sastavljeni od pet podsistema: (i) stvaranja kompleksnih mononuklearnih i polinuklearnih vrsta; (ii) embrionacije; (iii) nukleacije i direktnog rasta; (iv) micelacije (stvaranje koloidnih čestica); te (v) stvaranja sekundarnih struktura (mikro i makro čestica). Prelaz od idealnih likvidus-struktura (ILS) u idealne solidus-strukture (ISS) obično prolazi kroz stanja koja karakteriziraju metoričke strukture i teksture (MS & T).

Primjenom metode kontinuelnih varijacija za koncentracije precipitacionih komponenata dobivaju se četiri karakteristična tipa precipitacionih tijela (PB kao obrisi u diagramu gdje su logaritmi koncentracija kationske komponente apscise a anionske komponente ordinate, dok je ishodište predstavljeno visokim koncentracijama, obično 1 M ili 1 N).

Za ilustraciju su prikazani obrisi PB nekih realnih sistema, a u diskusiji je naglašeno da skoro općenito moramo računati s agregacijom submikrona u veće čestice kao s redovitom pojavom stvaranja krute faze. To vrijedi također i za precipitate koji su dobiveni iz »homogenih« otopina ili »starenjem otopina«.

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