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Methorics of the Precipitation from Electrolytic Solutions

The Precipitation Bodies, PB, and Their Meaning for Determination of Characteristics of the Dispersed Phase, the Dispersing Medium, and the Methorical Layer

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Using the method of continuous variation of concentration of the main precipitating components, as well as of the composition of the solution medium from which the precipitate emerges (genetic approach), the essential data for a precipitating system and the internal environment of the precipitating sub-systems may be obtained. The results are best presented in the form of the typical precipitation bodies (PB), which are given as a plot of the logarithm of the concentration of the cationic component against the logarithm of the concentration of the anionic components; such plots show boundaries between precipitating and non-precipitating regions, as well as the discontinuities in the rate of precipitation in general.

The main types of PB are named according to the dominant processes leading to transition of the solute species into the solid phase: (A) neutralization; (B) ionic solubility; (C) formation of ion-pairs and associates and (D) unsymmetrical ionic reactivity. The discontinuities in the precipitation rate manifested by internal contours of PB are explained by looking at the precipitation process as composed usually from five sub-systems: (i) formation of various complexes (mononuclear and polynuclear); (ii) embryonation; (iii) nucleation; (iv) micellation (formation of primary particles) and (v) secondary aggregation (crystalline aggregation, coagulation, floculation, formation of secondary structures, mosaic crystals).

If the determinations of the shape of PB are limited to the main precipitating components, the pattern of the contours of the discontinuities in the precipitation rate may be used as the »internal environment indicating homo heterogeneous systems«, that is the systems showing the state of the main solute species in transition to the solid phase. Such a system, or a convenient part of it, can be used as a sensitive indicator for various interacting foreign species. These may influence some stages but not essentially change the characteristics of the main precipitating system. In the investigation of such processes we deal with »internal environment indicating hetero heterogeneous systems«.

Such a systematic and mainly genetic approach in observing the rate of precipitation, and plotting the shapes of the precipitation bodies, may be used as a powerful method in the study of chemistry and physics of electrolytic solutions and transition phases.

Although precipitations play a very prominent role in nature, in the laboratory, and in technology, the theory and the experimental material on precipitation phenomena, processes and systems are far from being satisfactorily understood. On the one hand, many simplifications are usually made which give wrong pictures of the facts, and on the other hand, there is an enormous number of experimental findings which, without a coherent frame, are nearly lost.

Probably, there should be an intermediate path between the unsurpassed classical deductions of J. Willard Gibbs' *Equilibrium of Heterogeneous Substances,* and the inductive method and techniques which would enable us to grasp the essential elements of analytical and synthetic approaches completely.

Our approach is mainly from a genetic point of view, taking into account the topochemical and diachronic phenomena of precipitation, and using the experimental and diagrammatical simplexes for the presentation of a series of very complex systems or sub-systems.

The first step in this direction should be to define the coordinates of our models. If we are working with multicomponent systems of *n* components, than we need (*n*-1) dimensional spaces for their presentation. However, in order to avoid, at least for the start, the complexities when a greater number of components and external parameters are involved, we are restricting ourselves mainly to four-component, isobaric, isothermal systems. In these, the volume-composition and changes of phases, with special emphasis on coexistent and critical phases, are presented in two or three dimensional diagrams. Hence, taking into account the time factor, we shall try to confine ourselves to a four-dimensional space.

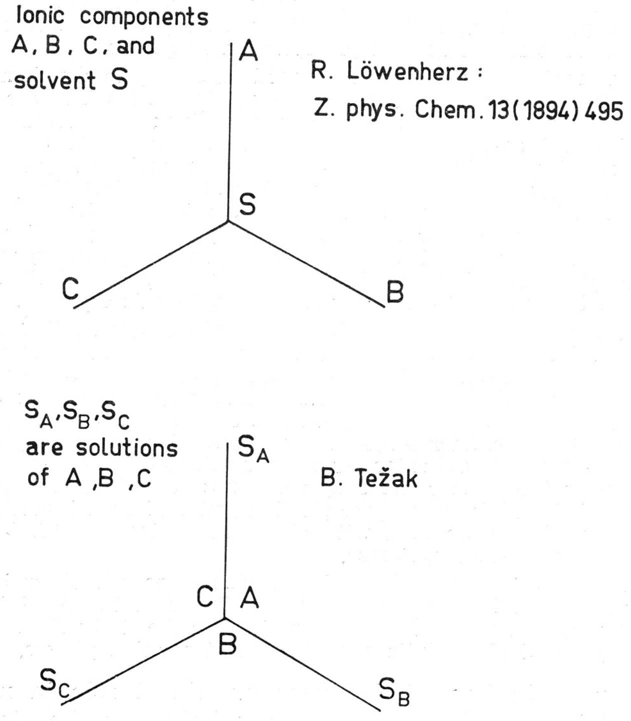


Fig. 1. The method of presentation of phase diagrams composed from electrolytic components: (1) according to R. Löwenherz, and (2) according to B. Težak.

As the origin of our coordinates systems of high concentration (usually 1.0 molar or normal) of the two main reacting components and of the resulting precipitate are chosen, while the corresponding dilution (expanding volume) of the system is represented by the logarithm of the molar or normal concentration on three mutually perpendicular axes.

Fig. 1 shows the characteristics of our presentation in comparison with that of Löwenherz[1] which was frequently used to show phase diagrams composed from electrolytic components. Fig. 2 illustrates the effect of volume changes on concentration axes of the main precipitating components and of the emerging precipitate solubility; actually, it represents something similar to an expanding cube obtained by dilution of the precipitating system with the solvent component. Using this procedure it is easy to construct the so-called precipitation body (PB), which by its points, lines and surfaces, shows the boundary values between the precipitating and non-precipitating regions, or discontinuities in the rate of precipitation as a function of the external parameters. Simultaneously, it also gives the changes of the internal environment of the precipitating units. Naturally, the parameters, in addition to the initial volume and composition (concentration) of the precipitating components, should either be kept constant (pressure and temperature), or left to the spontaneous adjustment (energy, entropy). The latter could be followed in some way by

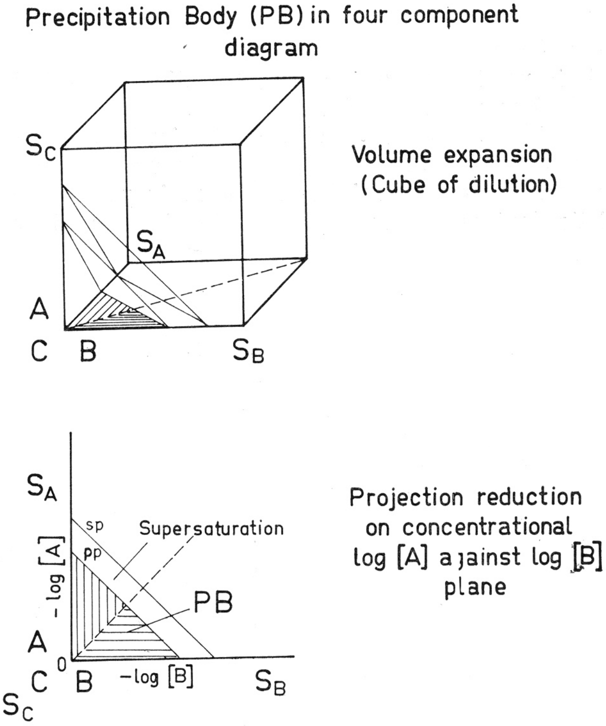


Fig. 2. Precipitation body (PB) in four component diagram showing ideal solubility plane (sp) and precipitation plane (pp), in a three dimensional cube of dilution, and two dimensional plot of logarithm of concentrations of two main precipitating components.

changeable characteristics of the systems (kinetics of the appearance of a new phase as well as other changes of the composition and the form of the precipitate under changing conditions). Using such an approach we have attempted to determine the changes from a homogeneous (or quasi-homogeneous) mixture of solutions containing precipitating components through all stages of precipitation, and — sometimes — the recrystallization or the restructuring processes. Thus, the formation of the precipitate was followed genetically from "birth to death" (from the appearance of a new phase to the most stabile equilibrium state).

In such a process, the most important morphological region is the boundary between disperse phase and dispersing medium. As the phases which meet at the critical interboundary region may strictly be defined in the bulk only, we have used for their transition structures the name: methorical layer[2].

Precipitation Bodies (PB)

Nowadays it is possible to utilize a systematic approach to various types of precipitation bodies encountered in practice. Using visual observation or instrumental detection one can determine the limits between precipitating and non-precipitating systems from electrolytic solutions with satisfactory precision at shorter or longer times after mixing of the main precipitating components. The characteristic features of such boundaries in our diagrammatical pre-

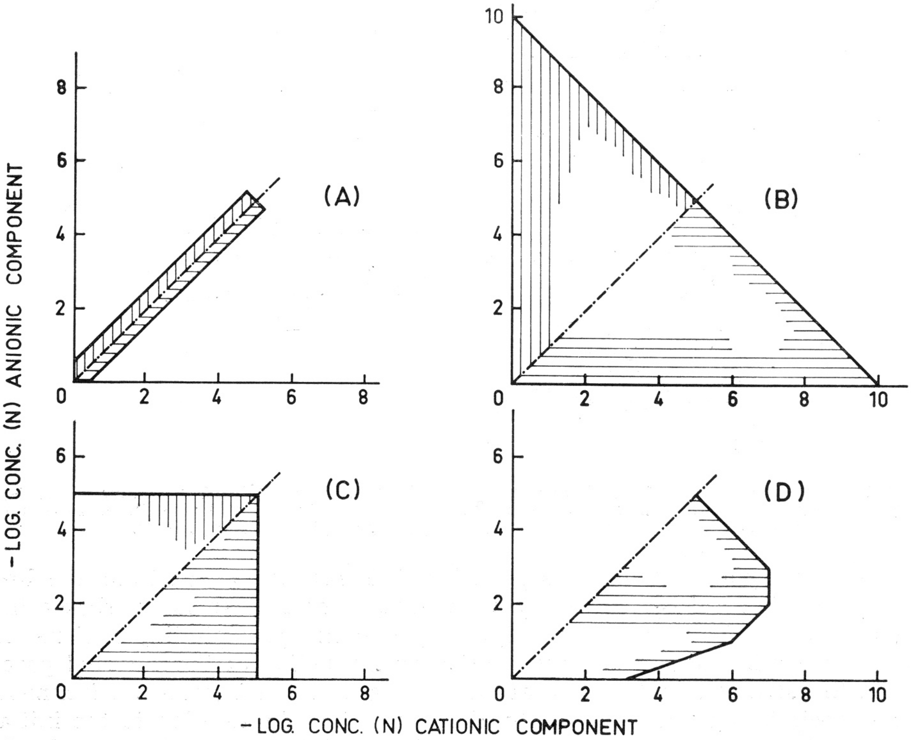


Fig. 3. Four main types of precipitation bodies, PB, in a general precipitation diagram: *(A)* neutralization, *(B)* ionic solubility, *(C)* formation of ionic-pairs and associates and *(D)* unsymetrical ionic reactivity.

sentations may be summarized by four main types of precipitating systems (precipitation bodies, PB). They may be named according to the dominant processes of transition of solute species to the solid phase: (*A*) neutralization; (*B*) ionic solubility; (*C*) formation of ion-pairs and associates; and (*D*) unsymmetrical ionic reactivity[3].

In Fig. 3 all four types of precipitation bodies are represented. Scheme (*A*) shows the precipitation as a neutralization phenomenon where the boundaries along the equivalency line are the results of the high solubility of the complexes formed by precipitating ions in excess, or of the high colloidal stability of the charged micelles. *e. g.*, fluorescein-rhodamin B. Scheme (*B*) is the ideal picture of a system dominated by constant ionic solubility product, *e. g.*, strontium sulfate, barium chromate (except in regions of high excess of one of the precipitating components). Scheme (*C*) gives the boudaries resulting from the formation of ion-pairs or other associates between precipitating components or constituents, *e. g.*, nickel dimethyglyoxime. Scheme (*D*) shows unsymmetrical precipitation when ionic excess produces formation of complexes which may cause the disappearance of the precipitate in larger parts (either with cationic or anionic excess) of the precipitation body, *e. g.*, iron(III)-chloride — sodium hydroxide, or silver cyanide. The diagrams of the experimental systems are in most cases combination of two, or sometimes of all four types.

One of the first experimental systems was presented at the *General Discussion of the Faraday Society*[4] in 1954, and it is schematically reproduced in Fig. 4; for comparison the precipitation body of barium sulfate is also shown.

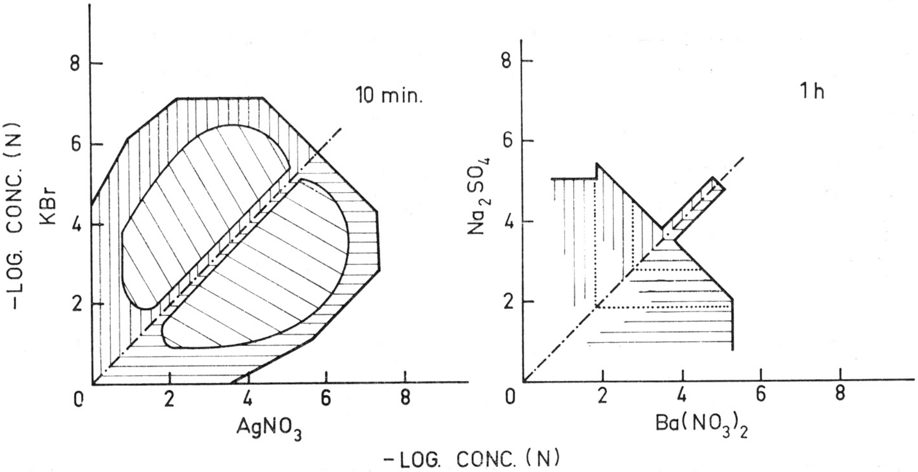


Fig. 4. Precipitation bodies of silver bromide (plot of log. norm. conc. of silver nitrate against potassium bromide), and of barium sulfate (plot, of log. norm. conc. of barium nitrate against sodium sulfate), in aqueous solution, 20° C.

Curiously enough, it seems that precipitating systems of silver halides present one of the most complex cases. It appears that the combination of all our four types of precipitation produces, in addition to the outer limits, very distinct internal contours within the precipitation body. In spite of their complex nature, the experimentally well defined precipitating systems of silver halides, especially of silver bromide and iodide, as so-called sols *in statu nascendi*[5], have been very extensively used in investigations of many parameters influencing the stability of colloid systems[6].

Some other systems were also investigated with more or less deliberate additions of various substances which may affect the precipitating processes. As examples we will mention the hydrolysis of metal salts (solution aging), or interaction of various simple or complex species (aluminum salts[7]), iron(III)-hydroxyde[8], thorium phthalate and hydroxyde[9], uranyl-barium-carbonate systems[10], uranyl phosphates[11], thorium, zirconium, and uranium salts in hydroxide and carbonate media[12], silver salts of fluoresceine series[13], as well as some more common systems: silver and barium chromate, strontium and barium sulfate[14], silver, lead, and lanthanum iodate[15], lead oxalate[16] and sulfate, and others). For an illustration, some experimental representations of our four types of PB are given in Fig. 5.

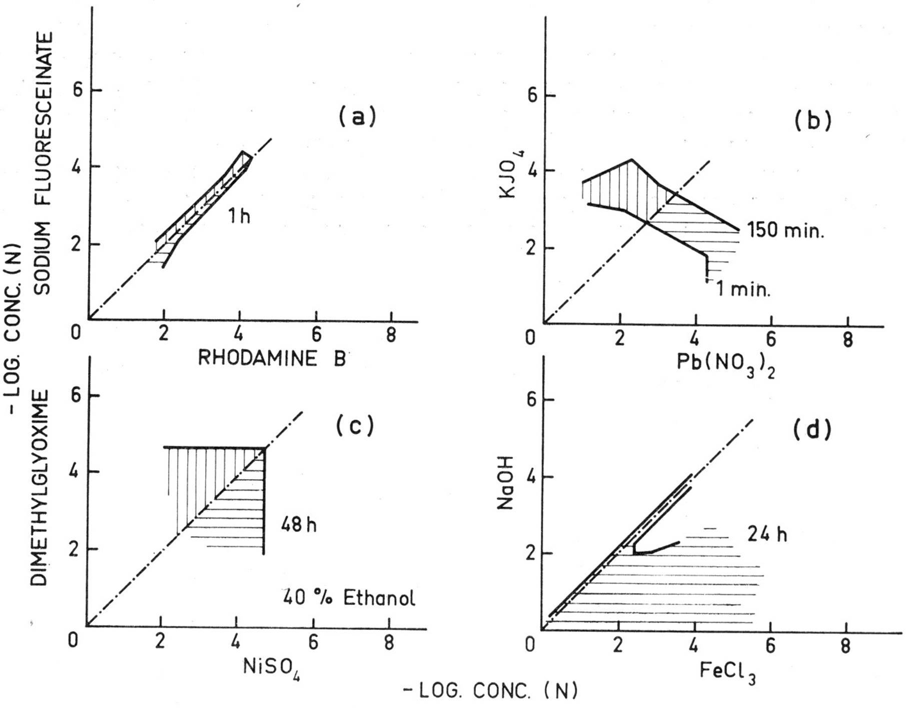


Fig. 5. Illustrations of main types of precipitation bodies: *(a)* silver fluoresceinate—rhodamine B; *(b)* lead nitrate—potassium iodate; *(c)* nickel sulfate—dimethyl glyoxime (40% ethanol); *(d)* iron(III) chloride—sodium hydroxide. All in aqueous solution, 20° C. Times after mixing of reacting components are given in the diagrams.

It should be pointed out that for full exploitation of our precipitation bodies it is necessary to analyze also the inside contours or structural features which may be controlled by factors of second or lower order in comparison to strong chemical and physical forces playing the main role in shaping the outer contours. In this respect, to comply with a large number of important results in crystallography and mineralogy[17], it seems appropriate to call the factors expressing the usual chemical and physical forces in compounds and crystal lattices as genotypical and those which reflect the environmental circumstances as phenotypical. Genotypical factors tend to give the system the most stable equilibrium state in general, while the phenotypical ones are influential in the habit formation for ultramicro, micro and macro units of a precipitating system or its sub-systems.

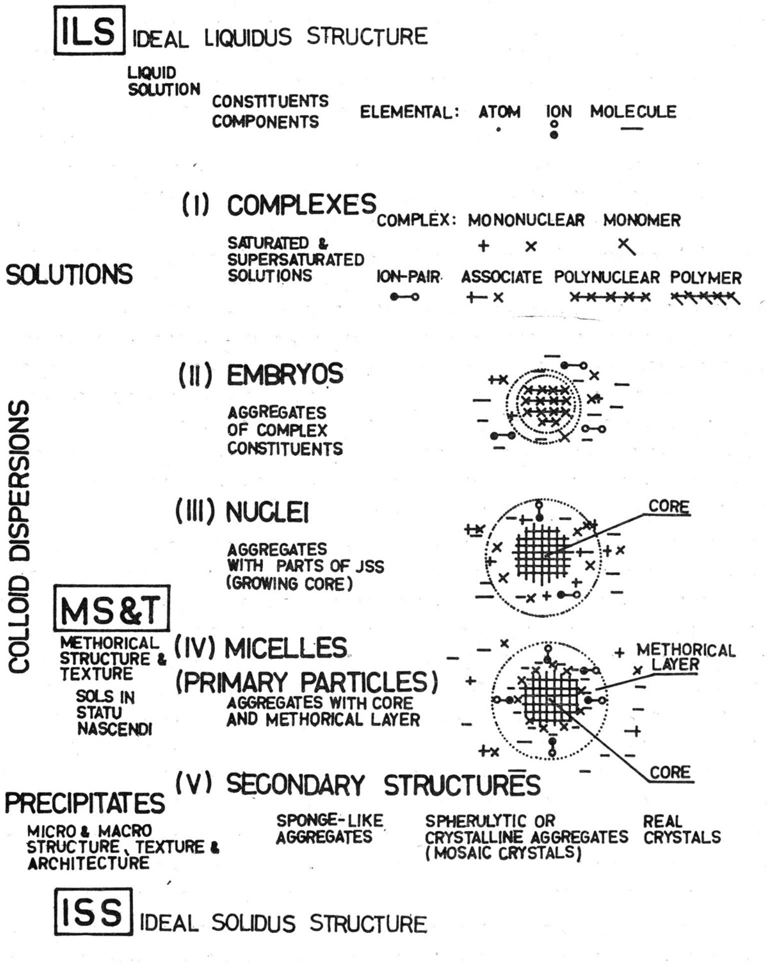
Sub-systems of Precipitation

By analogy to the crystallization process from melts, it is also customary in precipitation processes from solutions to distinguish between the nucleation and the growth of nuclei. However, the multitude of factors mentioned above indicates that it is necessary to differentiate at least five stages or subsystems[18]: (i) the solution, although homogeneous, is in a saturated or supersaturated state and is thus very sensitive to concentration and temperature variations because of the resulting changes in the complex ions, and especially in the 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 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). Table I shows the composite scheme of these five sub-systems or transition stages from ideal liquidus structures (ILS) to ideal solidus structures ISS) with intermediate stages, manly colloid units characterized by methorical structures and textures (MS&T).

It should be noted that it is incorrect to consider homogeneous, isotropic solutions as containing only simple molecules and ions. The results of Niels and Jannik Bjerrum's, as well as of Sillén's schools[19], among others, show that by varying the concentration of a solute, the probability of finding a variety of species starting from individual complexes and monomers, to formation of polynuclear complexes and polymers, has to be considered. The change in the concentration of a component or a constituent may cause a change in the species in a continuous or a discontinuous manner. In saturated, especially in supersaturated solutions, the specific situations should be expected that may give a number of transition structures very near to embryos.

Embryos may be represented by either dynamic and unstable, or by stable, more static units which are composed from aggregates of polynuclear or small polymer species where the crystalline growth is not a dominant process.

In the sub-system of nuclei, it is necessary to distinguish the process of direct crystal growth from the indirect process of aggregation of growing crystalline blocks and some subsequent recrystallization effects (Tammann's and Ostwald's ripening). The aggregation of growing crystallites is a very frequent phenomenon and sometimes it is difficult to distinguish the aggregation of growing nuclei and crystalline particles from formation of the grains by coagulation or flocculation. The outer regular appearance of crystallites may also be the reason why the real crystals are not usually treated as specific aggregates. If and when the growth of nuclei is slowed down or completely stopped either by exhaustion of the precipitated mass in formation of too large numbers of nuclei, or by some other competing equilibria controlled by the appearance and distribution of specific surface species (complexoides), it is likely that the precipitating system will be represented mainly by a sub-system of more or less stable primary particles of colloid dimensions. Usually, such systems are called sols *in statu nascendi.*



FIVE SUBSYSTEMS OF PRECIPITATION FROM ELECTROLYTIC SOLUTIONS

The formation of either crystalline aggregates, real crystals, or secondary structures formed through coagulation or flocculation can be considered as the next stage. The names of the primary particles and secondary structures were introduced by S. Odén[20] who was the first to demonstrate that the usual crystalline barium sulfate grains could be peptized and coagulated by changing the composition and concentration of the electrolytic medium.

Of course, the manifestation of these sub-systems and their characteristic morphology will be the result of the dynamic interplay of a number of genotypical and phenotypical factors. By changing the chemical and concentrational composition, it should be possible to change the characteristic features of the systems, in some casses to a limited and in some cases to a quite substantial extent. If the main components and the external parameters of the precipitating system are limited to the most essential elements only, the PB features may reflect with their outer and inner contours the existence of main solute species and some critical states of sub-systems. The whole pattern of PB is in reality an »internal environment indicating homo heterogeneous system«.

However, if only a typical part of the precipitation body is used, namely, if one with a dominant and more defined mechanism (in well expressed characteristics of one of the subsystems, *e. g.*, primary particles formation) is taken as a test system, and the various other environmental conditions are changed in a more or less systemmatic way, using a 'step-by-step' and a 'step-and-repeat' approach, the specific sub-systems have the role of a very sensitive indicator for the state of change of the species which are sometimes very difficult to detect. Therefore, a precipitating system, the essential parameters of which are kept constant, may be used, despite its complexity, as an experimental simplex, which, in reality, represents: »internal environment indicating hetero heterogeneous system«. The frequently used simplex of such a kind is one used for drawing concentration diagrams representing the critical concentrations for coagulation (c. c. c.), flocculation (c. f. c.), stabilization (c. s. c.) or protection (c. p. c.) of various ions and molecules when either preformed sols or sols *in statu nascendi* are taken as the precipitating systems.

Genetic Approach and Phenotypical Factors

As we have seen, precipitation is a very composite process, where we have formation of something like sub-embryos, then embryos, nuclei, and micelles (primary particles) and finally the appearance of microscopic and macroscopic, crystalline or so-called amorphous grains (secondary structures). Also, there is always a dynamic competition between the processes of direct growth on the one hand, and the aggregation (coagulation, flocculation, agglomeration) on the other. How and when one or the other process will prevail depends on a large number of factors, and all of them will be reflected in the morphology of the precipitate. The importance of this complexity of the precipitation processes in elucidating the structure and behavior of solid bodies was very strongly emphasized by Volkmar Kohlschütter[21] in his genetic approach to the inorganic »Somatoides«, and our aim is to follow his experience in a more systematic way by constructing our precipitation bodies.

Owing to the relative simplicity in the experimental definition of the phases in bulk, the thermodynamic and structural data for genotypical phenomena are much more easily acquired than those for phenotypical processes and structures. While the determination of bulk phases belong usually to chemistry and physics, the characterization of phenotypical phenomena is a very difficult task for which an elaborate strategy and tactics have to be applied in using almost simultaneously various physical, chemical, physico-chemical, and sometimes biological methods and techniques.

Although our precipitation bodies (PB) are the results of a variety of mechanisms and sub-systems, they can be utilized for an overall strategic approach. The next step in strategy may be to outline the demarkation line between genotypical and phenotypical groups of factors, structures, and processes. In general, the functions expressing the chemical and physical data of ideal liquidus and solidus structures (ILS and ISS) of the initial homogeneous solution and the final heterogeneous system, have to be taken to represent genotypical states and processes.

The phenotypical factors are mainly expressed by discontinuities in processes of embryonation, nucleation, growth and aggregation, and by stable or unstable critical, coexistent and transition phases.

As representative of such systems may be considered the cumulative functions:

$$\Delta G_{\text{cum}} = \Delta H_{\text{cum}} - T\Delta S_{\text{cum}} \tag{1}$$

expressing the dependence between the Gibbs free energy changes, and the changes in enthalpy and entropy for the case where the initial state is a relatively stable colloid solution (taken cumulatively for all kinds of colloid particles), and the final state a system with macroscopically separated phases.

In such a system the stability is dependent upon the structural and concentration differences between the methorical layer and the bulk solution. Fig. 6 (a) gives the general scheme. The change in concentration of the microcomponents with translational degrees of freedom in the methorical layer may be taken as one of the most important steps in determining the stability-instability relationship.

Consequently, all processes which may lead to higher concentrations of the microcomponents in the methorical layer (concentration gaining processes) in comparison with the concentration in bulk will be stabilizing; on the other hand, all concentration losing processes are those which induce or enhance the aggregation of the dispersed particles.

As colloid particles (macrocomponents) exist with either charged or uncharged surfaces, and since the interacting microcomponents are represented by species which are either charged (ions, polyions) or uncharged (molecules, macromolecules), a scheme which offers a possibility of following interaction effects in all possible cases is certainly preferred. Such a scheme is given in Fig. 6 (b), where the interactions between an ion of the solution and a constituent or complex group (complexoid) of the boundary structure of the solid phase, as well as interactions between molecules and the wall, are represented. The total potential of an interacting ion or molecule may be divided into separate component parts:

$$\mu_{\text{total}} = \mu_{\text{chem}} + \mu_{\text{stereo}} + \mu_{\text{coul}} + \mu_{\text{collig}} \tag{2}$$

giving the chemical, μ_{chem}, specific adsorbability, μ_{stereo}, coulombic, μ_{coul}, and translational, μ_{collig}, terms. According to the individual species, some terms may be so dominating that the other can be neglected.

In the case of ions interacting with discrete charges of the surface[22], the critical situation is reached when, according to the fixed distribution of surface charges, the probability for formation of ion-pairs in the methorical layer is greater than in the bulk of the solution.

For the interactions between one discrete charge (ionogenic group, complexoid) fixed at the wall and an ion in the vicinity, it is possible to divide the ionic potential, μ_i, into two parts: one which reflects the interactions of the uncharged species according to the concentrational pattern of the distribution of discrete charges at the wall, $\mu_{i(\mathrm{fix})}$, and the other as a function of coulombic interactions, $\mu_{i(\mathrm{coul})}$:

$$\mu_i = \mu_{i(\mathrm{fix})} + \mu_{i(\mathrm{coul})}. \tag{3}$$

Taking $\mu_i = \mu^0 + kT \ln c_i$, and $\mu_{i(\mathrm{fix})} = \mu^0 + kT \ln c_{i(\mathrm{fix})}$, (4)

we obtain $\mu_{i(\mathrm{coul})} = kT \ln a_i/a_{i(\mathrm{fix})}$. (5)

Introducing the critical coulombic interactions (1—1 valent ions) for the compensating thermal energy of agitation, $2kT = e^2/D\delta$, where D is macro-

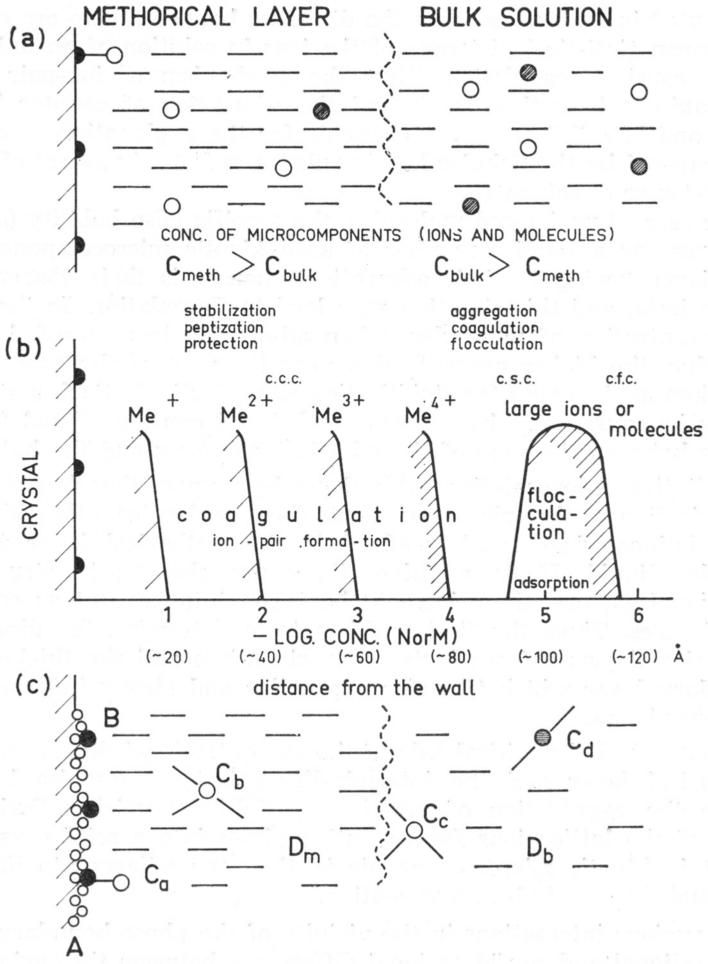


Fig. 6. General scheme of the boundary region (methorical layer) between crystal and solution, emphasizing the distribution of charges on the wall and of microcomponents (ions and molecules) between methorical layer and the bulk solution: *(a)* concentrational relationships responsible for stability-instability conditions of dispersed particles; *(b)* interacting mechanism for counter ions in critical concentration for coagulation (ion pair formation), and for large ions and molecules in critical concentrations for flocculation and protection and *(c)* schematic presentation of points of physical and chemical change for changed substantial or concentrational conditions of the colloid system (*e. g.* the change in *p*H).

dielectric constant and δ the length which may be called the critical distance for ion-pair formation, as well as from Debye-Hückel theory: $\mu_{i(\mathrm{coul})} = kT \ln f$, and $\ln f = -(e^2/2\,DkT)\,\varkappa$, there is a simple relationship between critical distances δ and activities: $\delta = -1/\varkappa\,(\ln c_i/c_{i(\mathrm{fix})})$ or for counter ions of z valency, there is the general formulation of Schulze-Hardy rule:

$$-z\,a = \log\,(c_i/c_{i(\mathrm{fix})})_{\mathrm{coag}} \tag{6}$$

where a is a constant reflecting the ratio of critical distance to the $1/\varkappa$ length of Debye-Hückel, and including the conversion factor for logarithms.

For our model it is essential to look upon the charged surface of the solid phase as a pattern (texture) of separate discrete charges (complexoids) which are distributed in such a way that the distances between them are comparable with the mean statistical distances of the ions in solution of an uni-univalent electrolyte causing coagulation. Thus the mechanism of ion-pair formation proposed quite a long time ago[23], and the adsorption of counter ions found by Herak and Mirnik[24] represent elements for the explanation of coagulation effects expressed by the Schulze-Hardy rule, as well as the effect of a mixture of electrolytes or of solvents[25].

In the case of uncharged molecules, the specific adsorbability (μ_{stereo}) may be the cause for a smaller number of such kinetic microcomponents in the methoric layer (owing to their adsorption) than it is their concentration in solution in bulk, and this situation may lead to flocculation. In the case of a higher concentration of molecules, when adsorption has exceeded some maximum value, the higher concentration near the wall of the colloid particles may be taken as the cause for stabilization or protection[26]. Such a stabilization effect may be caused also by concentrational and configurational (entropical) differences between the zone of the adsorbed polymers and the bulk solution.

Quantitative interpretations are dependent upon the determination of the concentration of the microcomponents (ions, molecules, other kinetic units with translational degrees of freedom) in the methorical layer and in the intermicellar liquid. If, in addition, there are changes in structural and configurational factors, these have to be taken into account as contributing entropy changes. Thus, the first problem is to determine the dimensions of the methorical layer: the products of quasi-surface and the thickness of the interboundary layer which is under a peculiar and strong influence of both the adjacent phases.

Our concept of the critical role of the concentrational differences between the methorical layer and the intermicellar solution may also have to be applied to the aggregation of growing crystalline particles. Owing to the transition of the lattice ions from solution phase into a solid crystal lattice, the deficit in kinetic microcomponents in the zone adjacent to the growing particle boudary may induce aggregation.

Thus, various interactions in the vicinity of the phase boundary, resulting in concentrational and configurational differences between the region adjacent to the solid phase (methorical layer) and the solution in bulk, are responsible not only for coagulation-peptization and flocculation-stabilization, but also for sensitization, protection, coacervation and other colloid phenomena, as well as for aggregation of crystallites during their growth. For a theoretical interpretation of all these situations, Langmuir's approach[27] has to be followed.

Open Questions

In our genetic approach, by systematic mapping of discontinuities in the rate of precipitation, it is found that many steps are represented by processes which are either too fast or too slow to be measured. Also, the way of mixing of precipitating components may be the cause of some doubtful results, as well the impurities which may act as heterogeneous nuclei. However, in general at least, for orientational purposes, the rather crude and simple analysis of the data presented by boundaries of the precipitation bodies may correct many wide-spread erroneous conclusions about the continuity of particle growth or general applicability of the solubility product constant. By improving the experimental methods and techniques and by proper combinations of »Internal environment indicating homo« and »hetero heterogeneous systems« an open field for synoptical gathering of many essential data about physical. chemical, mineralogical, biological, either scientific or practical structures, states and aspects may be obtained.

It is well known that many important properties of solid bodies are structure sensitive. Therefore, it is an obvious task to find the relationship between various sub-systems and qualities of precipitates. Still, the dimensions, the structure and the role of the methorical layer is not yet understood.

The change in concentration, and even more in the chemical composition (sometimes in tracer amounts), may be reflected in continuous or discontinuous phenomena where by the presence of various sub-systems may promote or retard the resulting effect. The points of attack are many, and they are schematically presented in Fig. 6 (c). For instance, the change in *p*H may influence the state of the constituents of the solid, A, the ionogenic potential determining groups, B, the counter ion in respect of ion-pairing, C_a, specific adsorbability or other characteristics, C_b and C_c, or the general behavior of the solvent molecules in the methorical layer, D_m, or in bulk solution, D_b. Therefore, precautions should be taken not to cross the energetic barrier where phenotypical factors, instead of genotypical factors, may be encountered.

Certainly, some of the strategic paths of the 'grand design' approach lead to extensive use of »homo and hetero heterogeneous systems« by mapping patterns of formation and deformation of precipitation bodies using 'step-by-step' (that is systematic concentrational variations), and 'step-and-repeat' (that is systematic environment changes) procedures. For this purpose, nearly all of the macroanalytical and microanalytical methods and techniques may and should be applied. In using many methods, it is necessary to limit the range of investigation, or to change the natural environment of the system. Such 'denaturated' conditions may be the cause of essential changes in the systems investigated. To avoid this, it is preferred to use the methods by which the observed system could remain *in situ* or with as little disturbance as possible.

The other very important path is to try to find the more direct ways and means for the determination of the dimension, the composition and the structure of the methorical layer between various bulk phases. Apparently, in order to reach the first quantitative physical elements of the methorical layer, it is necessary to prepare colloid systems with very definite properties in respect to the size and quality of the surface, and to find the relationships between various surface determinations and the general colloid behavior.

Some methods reflect the thickness of the methorical layer; of more recent methods may be mentioned intrinsic viscosity measurements[28], ellipsometrical[29] and attenuated total reflection[30] determinations. The data about the chemical and physical composition and structure of surfaces are usually obtained with dry samples under high vacuum. How many of the results thus obtained apply to wet surfaces is a special question. Some answers may be found in specificities of biological or catalytic reactions, but generally our insight into the region between the ionic or molecular dense matrix and solution (especially electrolytic) is neither experimentally nor theoretically satisfactory. Only by a proper combination of various results may we arrive at the possition where we are able to translate and correlate many current concepts, models and theories into a balanced and much more qualitative and quantitative picture than is possible nowadays.

As a contribution to this end, it may be appropriate to have at our disposal a larger and better collection of precipitation bodies of electrolytic systems belonging to a wider spectrum of chemical and physical characteristics.

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IZVOD

Metorika precipitacije iz elektrolitnih otopina
Precipitaciona tijela, PB, te njihovo značenje za određivanje karakteristika disperzne faze, dispergirajućeg medija, i metoričkog sloja

B. Težak

Upotrebljavajući metodu kontinuelne varijacije za koncentracije glavnih precipitacionih komponenata, kao i sastava medija otopine iz koje se pojavljuje precipitat (genetski pristup), mogu se dobiti bitni podaci za precipitacioni sistem te tzv. unutarnju okolinu precipitacionih sub-sistema. Rezultati se najbolje mogu prikazati u obliku tipičnih precipitacionih tijela (PB — Precipitation Body), koja su dana u diagramu gdje su na apcisnu os naneseni logaritmi koncentracija kationske komponente, a na ordinatnu os logaritmi koncentracija anionske komponente. Takvi diagrami pokazuju granice između područja gdje nastaje i gdje ne nastaje precipitat, a također i diskontinuitete u brzini stvaranja precipitata.

Glavni tipovi PB nazvani su prema dominantnim procesima za prijelaz otopljenih ionskih i drugih vrsta u krutu fazu: (A) neutralizacije; (B) ionske topljivosti; (C) formacije ionskih parova i asocijata, te (D) nesimetričnog ionskog reaktiviteta. Diskontinuiteti u brzini precipitacije, koji se pojavljuju kao obrisi unutar PB, bili su protumačeni promatrajući precipitacioni proces kao sastavljen od pet sub-sistema: (i) stvaranje raznih kompleksa (mononuklearnih i polinuklearnih); (ii) embrionacije; (iii) nukleacije; (iv) micelacije (stvaranje primarnih partikula), te (v) sekundarne agregacije (agregacije kristalita, koagulacije, flokulacije, stvaranje sekundarnih struktura, mozaik-kristali).

Ako je određivanje oblika PB ograničeno na glavne precipitacione komponente, uzorak kojeg nam daju diskontinuiteti u brzini precipitacije mogu se upotrijebiti kao za »unutarnju okolinu indicirajući homo-heterogeni sistemi«, što znači da su to sistemi koji pokazuju stanje glavnih vrsta u otopini kod prelaza u krutu fazu. Takvi sistemi, ili pogodni njihovi dijelovi, mogu se upotrebiti kao osjetljivi indikatori za različite strane vrste konstituenata, koje mogu utjecati na neke prelazne oblike ali ne mogu bitno promijeniti karakteristike glavnog precipitacionog sistema. Kod toga imamo za »internu okolinu indicirajuće hetero-heterogene sisteme«.

Ovakav sistematski i uglavnom genetski pristup u promatranju brzine precipitacije, uz utvrđivanje oblika precipitacionih tijela, PB, može se smatrati snažnom metodom u studiju kemije i fizike jednako elektrolitnih otopina kao i prelaznih faza.

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