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Where Are We in Explanations of Ionic Solubility, Precipitation, Coagulation, and Flocculation Phenomena? (Processes of Aggregation as Spatial-temporal Indicators of Dynamical Structures in the Electrolytic Solution, the Emerging Solid Phase, and the Methoric Layer between the Solid-liquid Bulk Phases)

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A confusion concerning the explanations, concepts and theories in the major sectors of the physics and chemistry of our environment exemplified in the case of real systems of aqueous solutions is pointed out. The much more general, coherent and integrating approaches have failed as it is evidenced by the treatment of phenomena of precipitation, ion-ion and ion-solvent interactions, and colloid stability.

To support such standpoints some remarks of R. H. Stokes[1], V. K. La Mer[2] and J. N. Mukherjee are mentioned. In this sense the application of van der Waals cumulative attraction and electrical double layer repulsion for colloid stability/instability (the so-called DLVO-theory) is taken to be a serious hindrance to the progress in this field. The same case is with the indiscriminate use of the solubility product constants.

In summarizing statements about the earlier material published in the proceedings of the International Schools, Conferences and Symposia on Solid/Liquid Interfaces held in Yugoslavia in 1969, 1972 and 1975, the influence of substantial composition as well as of concentrational conditions of the systems on the discontinuities in the formation of precipitates, including the embryonation, nucleation, crystal growth, and stability/instability states of primary particles (sols in statu nascendi) are emphasized.

The explanation of the discontinuities in the kinetics of aggregation is given by relationships between the concentration in bulk solution, the structure of emerging solid, and the concentration in the methoric layer between the solid-solution bulk phases. Higher concentration of osmotically active species in methoric layer than in the bulk solution is taken to be the cause for stability, and the lower one for instability of colloid particles.

For presentation of experimental results on precipitation the rational scheme in three-dimensional diagrams showing the time-dependent formation of solid phase in the basic plot of the logarithms of concentrations of the two precipitating components, thus representing the so-called 'precipitation bodies' (PBs) are given. The relevance of the expression given in Schulze-Hardy-Težak formulation:

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* It is a sad coincidence that this paper was received in the Editorial office on the same day when Professor Težak died.

$\log c_{i\,(coag)} = \log c_{i\,(fix)} - z\,a$, where $c_{i\,(coag)}$ is the critical coagulation concentration, $c_{i\,(fix)}$ the concentration of surface charges, z the valency of counterions and a the constant related to Bjerrum's critical distance: $d_c = \dfrac{z\,z\,e^2}{D\,2\,kT}$, is pointed out.

As new supporting collections of experimental data three groups of diagrammatical presentations are given:
(1) The 16 basic precipitability-solubility (PS) contours of Precipitation Bodies (PBs) for fluorescein (FLN), eosin (EOS), erythrosin (ERT) and rose bengal B (RBB) as anionic components against cationic components of silver, barium, lanthanum and thorium salts.
(2) The flocculation effects for thionine (Thi), methylene blue B (MBB), pyronine G (PyG), and rhodamine B (RhB) cationic dyes on negative silver iodide sols in statu nascendi; especially the systems of methylene blue are completed with data concerning the reactions where anionic components of chloride, bromide and iodide were involved.
(3) The discontinuities in linear portions of light scattering during the processes of precipitation-coagulation (of potassium, barium or lanthanum nitrate), and precipitation-flocculation (of nonionic triton T-X-305) in cases of negative silver bromide, and positive silver iodide sols, respectively, are observed, and the most expressive linear parts are taken for fundamental relationship between logarithms of critical time and critical coagulation or flocculation concentration.
The discussion emphasizes that the existence of various chemical species, such as simple aquo-complexes, associates of coulombic ion-pairs' type, and the variety of composite complexes are responsible for the colloid stability/instability conditions, as well as for the precipitability-nonprecipitability boundaries which are quite different from those expected according to the solubility product constant.
The conclusion reproduces the remarks which on author's request Prof. Lyklema read at Faraday Discussions on Colloid Stability in 1978.

It seems paradoxical that in the quite long history of about 150 years of physical chemistry there is a great confusion in some fundamental approaches to the phenomena which represent the major sectors of physics and chemistry of our environment. This is especially true for the real systems of aqueous solutions which are the predominant components of the dynamic layer of our planet, as well as nearly of all the bodies of living nature. Some kind of proof for such a rough statement may be also the ten years of experience in our international schools, conferences and symposia on solid/liquid interfaces, and the proceedings outside our circle, such as, e. g., the recent Faraday Discussions of the Chemical Society.

Although there exists quite representative scientific material illustrating special subjects of this field, the much more general, coherent, substantially balanced and integrating approaches have failed, and the many textbook[1] presentations remain untouched in spreading something which may be rightly called as scientific folklore.

Probably, exact natural sciences suffer also from what is called the »5 C-syndrome« attributed usually to soft sciences, namely, a lack of consistency, comprehensiveness, coherence, compatibility and conclusiveness. The causes certainly belong to the psychology and sociology of contemporary researchers and the scientific community at large, and therefore, in order to find the way out from the stalemate we will try to keep in touch with the subjects and

objects of our four foregoing gatherings. For a further broader frame as points of reference we will take the recent Faraday Discussions: Precipitation 1976[2]; Ion-Ion and Ion-Solvent Interactions 1977[3]; and Colloid Stability 1978[4].

The central problem is closely connected with electrolytic solubility for which seems to be still relevant F. Kohlrausch's statement[5] from the early years of this century: »Man muss schliessen, das von den Bedingungen der Löslichkeit ein wesentlicher Teil uns noch ganz unbekannt ist«. Adequate critical words may be found in Concluding Remarks of R. H. Stokes of the cited Faraday Discussion[6] in Oxford on Ion-Ion and Ion-Solvent Interactions. It is appropriate to quote some of this sentences:

> »About 35 years ago after I had been measuring the activity coefficients of a number of 2 : 1 electrolytes I was struck by the rapid rise of the activity coefficient at higher concentrations (compared with the much slower rise or continued fall with 1 : 1 salts) and came to the conclusion that it was due to the greater hydration of the divalent cations. I sent a paper incorporating this idea to the *Transactions of the Faraday Society* (as it was then) and in due course received a polite rejection note with a referee's comment that hydration of ions was a 19th-century idea, no longer needed now that we had Debye-Hückel theory! The emphasis on specific ion-solvent interactions in the present Discussion makes it clear that we have now advanced a great deal—into the 19th century, in fact.«

> »The art of disputation has been fostered in this city for about 800 years, and the tradition has been well maintained at this meeting. We have all heard of mediaeval debates (real or imaginary) about the number of angels that could stand on the point of a pin, and this fancy crossed my mind during some of the discussions about the number of water molecules in the hydration shell of an ion.«

> »The »structure of water« has been almost an obsession among physical chemists for about the last 30 years, and there seem to be as many disagreements about it now as ever.«

> »In conductance theory, there has been some discussion of the merits of alternative treatments of the concentration-dependence of the conductance at high dilutions. I believe that the minor differences between these treatments no longer justify the amount of effort being put into their resolution. The resulting values for the limiting conductance differ only sligthly, and it is time now to turn to a serious attack on a much more important problem: how to calculate the limiting mobilities of ions from known properties of the ions and the solvent molecules. Statistical mechanics has made great progress with simpler cases of this problem such as the calculation of the self-diffusion coefficient of liquid argon, but for ions in solution we have still nothing much better than the Stokes-Einstein relation, which has a sound theoretical basis in the limit of very large ions.«

No doubt, the relevance of the common ground in ion-ion and ion-solvent interactions for solubility and precipitability including colloid stability, cannot

be denied, but the narrow professional approach of a specialist-researcher is frequently counteractive the very spirit of science. Another danger lies in spreading beliefs in interpretations of some school of thought without doubting, asking and critically examining the thorough contents of underlying concepts. A concrete example of the case in point is the position of Kallmann-Willstät-ter-Derjaguin-Landau-Verwey-Overbeek or so-called DLVO-theory[7] of colloid stability which has its adherents in Dutch, Russian, English, American, Belgian, Australian and other scientific groups. After nearly 50 years of existence the DLVO-theory is unable to explain adequately some essential phenomena of colloid aggregation and disaggregation, but it is widely used although many are declining the usefulness of the theory and the former prominent adherent Victor K. La Mer[8] in a very critical moment in 1966 said: »It is quite a rubbish«. The oldest researcher in this field J. N. Mukherjee[9] has taken a similar standpoint in his comprehensive treatise. All these viewpoints are mentioned in an attempt to find a framework for the evaluation of some simple facts.

SUMARIZING STATEMENTS

In order to escape the repetition of the earlier material published in our proceedings of International Schools, Conferences and Symposia held in Yugoslavia in 1969, 1970, 1973 and 1975[10-12], the content of abstract to this 5th International Summer Conference: Chemistry of Solid/Liquid Interfaces; and International Symposium: Interfacial Phenomena in Colloid Systems, is reproduced here.

(0) Starting from the definition of substantial composition and concentrational step-by-step changes of the nearly equilibrated mixtures of the precipitating and other substances, and mixtures far from equilibrium, the discontinuities in formation of precipitates in such systems were observed; such procedures reveal some essential characteristics concerning the embryonation, nucleation, crystal growth, and stability/instability states of primary particles (sols in statu nascendi).

(1) Developing the most probable concepts for explanation of the discontinuities in the kinetics of the processes involved, the emphasis was laid on the relationships between the concentration in bulk solution, the structure of the emerging solid, and the concentration in the methoric layer between the solid and solution phases, enabling the differentiation between aggregation processes caused by ionic association (embryonation, coagulation), adsorption (flocculation), and various kinds of crystal growth.

(2) By coupling the data on distance, surface, and volume as concentrational-spatial factors with those of half-lives of the ionic, molecular, and other aggregational structures as temporal ones (critical times, simultaneity, succession, duration) in the process of formation of new phase from electrolytic solution, the fundamental relationships for precipitation phenomena was pointed out.

(3) Although 100 years have elapsed since the publication of »On the Equilibrium of Heterogeneous Substances« by Gibbs, the critical differences between the solubility as equilibrated, and the precipitability as mainly non-equilibrated states have not been put into right perspective; this especially becomes evident when the variety of precipitation stages are examined with respect to simple ionic solubility product constants.

(4) Reviewing the observations gathered through the century of studies on the precipitation phenomena it was stated that the large number of observable facts with reference to critical volume and surface concentrations and distances as well as to critical times, simultaneity, succession and duration, have not found relevant appreciation, and therefore much more systematic approaches to the presentation of experimental data are required.

(5) Pointing to the significance of observations and experimentation with systematical changes of the substantial, concentrational and other conditions (mode of mixing, temperature, etc.) determining the stability/instability of dispersed systems (mainly hydrosols *in statu nascendi*) from solutions, the rational scheme for the presentation of results was given in three-dimensional diagrams showing the time-dependent formation of solid phase in the basic plot of the logarithms of concentrations of the two precipitating components — thus representing the so-called 'precipitation bodies' (PBs); also, the distinction should be made for the processes representing the outer contours, and those inside the 'precipitation bodies' (systems far from equilibrium states); to support such an approach about 100 systems have already been elaborated.

(6) Trying to find the most obvious relationships of the spatial-temporal effects of the short-range and long-range interactions of the elementary constituents-components of the systems, the mechanisms of the elementary processes, which could be directly reflected as a first approximation of macroscopical effects, expressed in Schulze-Hardy-Težak[13] formulation

$$\log c_{(coag)} = \log c_{(fix)} - z\,a$$

was put forward, and directly related to the simple Bjerrum's relationship:

$$d_c = \frac{z_1\,z_2\,e^2}{D\,2\,kT}\;;$$

in this way it is possible to find a simple interpretation for experimental findings reflecting the Schulze-Hardy rule (as 'regular' and as 'reversed'[14] effects) besides the identity of the mechanisms observed with sols in *statu nascendi* and those with preformed sols.

(7) Explaining the discontinuities of the trends in kinetics of the appearence of the new phase by the concentrational differences in methorical layer and the bulk solution ($c_{meth} > c_{bulk}$ for stability, $c_{meth} < c_{bulk}$ for instability)[15] it was possible to apply the same principle for two-step crystallization, coagulation, flocculation and other types of aggregational processes including also flotation phenomena; by such interpretation the electrokinetic phenomena reflect the distribution of charge-bearers in the transition layer between methoric and bulk solution structures under the influence of outside electrical field, and therefore the data about electrical double layer as such cannot be taken as reflecting immediate cause of critical interactions between dispersed particles.

(8) Comparing other widespread interpretations of the stability/instability phenomena in colloid systems, especially the application of van der Waals cumulative attraction and electrical double layer repulsion (the so-called DLVO-theory), and the indiscriminate general use of the ionic solubility product constant, it was pointed out that such 'theories' represent serious hindrance to the progress in this field.

(9) Reflecting various discussions on relevant subjects held in these last 100 years particularly in the last 10 years since the first summer school and conference on solid/liquid interfaces in Yugoslavia — the dispersion into specific aspects and failure to concentrate on fundamentals, as well as the lack of appreciation for simple experimental facts, were noted to be a characteristic reaction among the participants. However, the retrospective remarks have to express the hope that the observations of events representing formation of new phase from aqueous« electrolytic solutions with all cosequences for theory and reality will be explored in future without the pressure of the futile and inadequate theoretical excursions, and in full accord with the following citations. »The only justification for our concepts and system of concepts is that they serve to represent the complex of our experiences; beyond this they have no legitimacy«[16].

»Again, it is agreed that there is a certain order observable in the progress of all exacter forms of knowledge. The study of every department of physical science begins with observation, it advances by the collation of facts, to a presumptive acquaintance with their connecting law, the validity of such presumption it tests by new experiments so devised as to augment, if the presumption is well founded, its probability indefinitely; and finally, the law of the phenomenon having been with sufficient confidence determined, the investigation of causes, conducted by the due mixture of hypothesis and deduction crowns the inquiry«[17].

We have to be aware that such advancing order of knowledge in many instances is nowadays reversed. Therefore, we should give precedence not only to doubting and questioning, but also to systematic gathering and direct recording of observable facts in most obvious manner. Definition of systems, processes, operations, and concepts used in an investigation should be provided. In view of their role in inorganic and organic world, the formation of new phase, and the systems of sols *in statu nascendi* in particular, certainly deserve full application of such procedures.

SUPPORTING COLLECTIONS OF NEW EXPERIMENTAL DATA

A number of diagrammatical presentations of experimental results are given here as a preliminary anouncement about the work going on in our laboratory. To emphasize our main approaches the results are divided into three groups.

(1) The proof that by changing the concentration of reacting components in solution there are characteristic changes of chemical species which control the formation of solid phase.

(2) The action of foreign ions or molecules as flocculants for sols *in statu nascendi*.

(3) The discontinuities in transition from homogeneous to heterogeneous electrolytic systems.

The first group is represented in Figure 1 by 16 basic precipitation-solution (PS) contours (logarithmic concentrational cationic-anionic plots) of so-called »precipitation bodies« (PBs): fluorescein (FLN), eosin (EOS, erythrosin (ERT), and rose bengal B (RBB) as anionic components against cationic components of silver, barium, lanthanum and thorium salts.
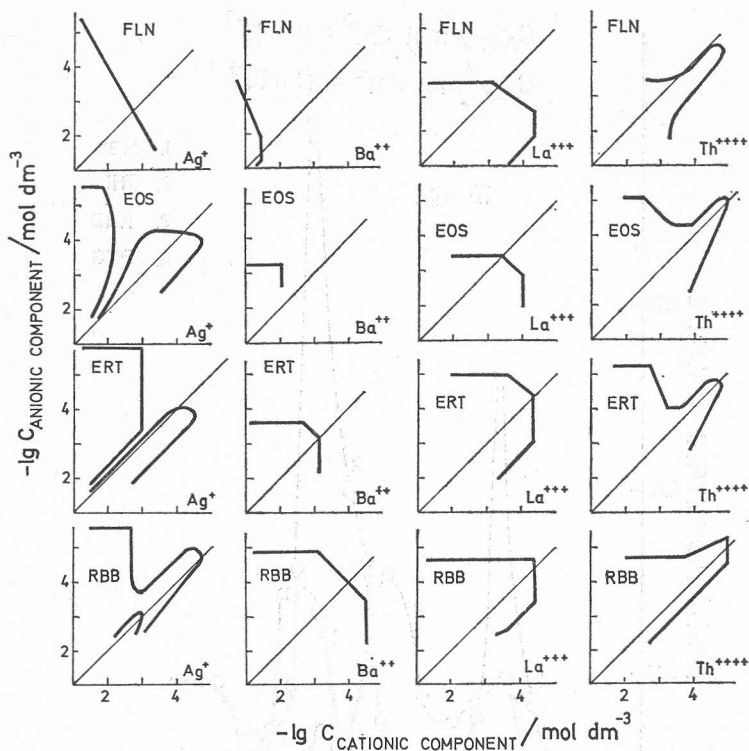
Figure 1. Precipitability-Solubility (PS) contours for fluorescein (FLN), eosin (EOS), erythrosine (ERT) and rose bengal B (RBB) in aqueous solutions of silver, barium, lanthanum and thorium nitrate at 293 K 10 minutes after mixing of precipitation components.

The second group in Figure 2 presents flocculation effects for a number of cationic dyes on negative silver iodide sols *in statu nascendi*. Especially the systems of methylene blue were completed by data concerning the reactions where anionic components of chloride, bromide and iodide as silver salts for flocculation, and as anionic components in PBs are involved.

The third group presents in Figures 5, 6, 7, and 8 observed discontinuities of linear portions of light scattering during the processes of precipitation-coagulation, and precipitation-flocculation for systems of silver halide sols, as well as diagrammatical relationships between logarithms of critical time and coagulant/flocculant concentration. As critical times were taken the intersections of the lines of steepest trend of light scattering curves on ordinates versus logarithm of time on abscissae.

DISCUSSION

In trying to define our systems in terms of either an operational or a conceptual definition it is necesary to keep in mind the classical relationships in physical chemistry expressed in thermodynamics, kinetics and mechanisms of elementary processes. The majority of our results in the first group reflect, by the contours of the PBs, nearly equilibrated states emphasizing the existence of various chemical species, such as simple ionic aquo complexes, asso-
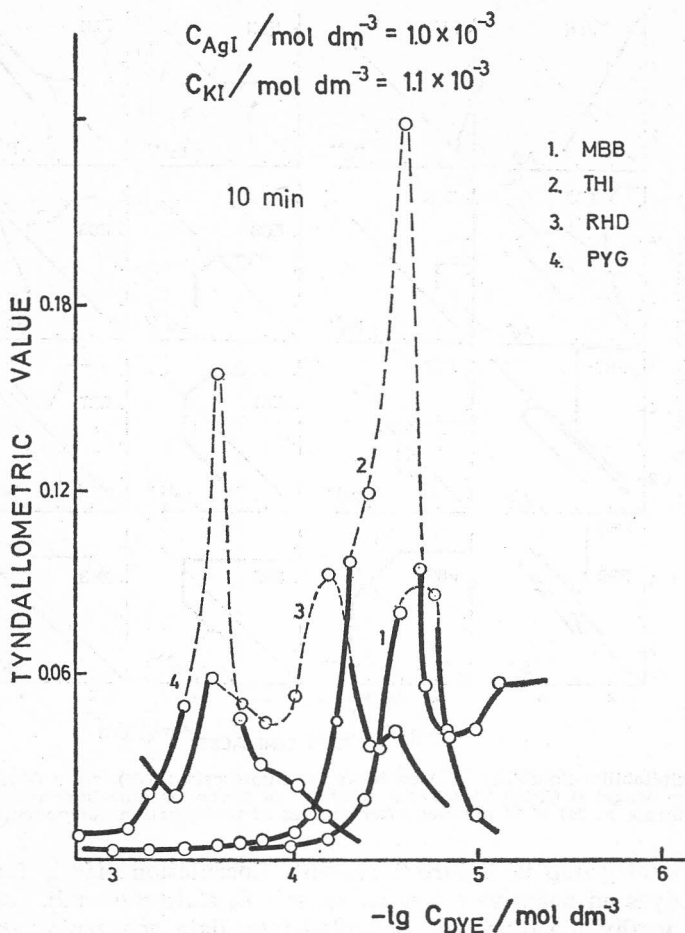
Figure 2. Flocculation effects of thionine (THI), methylene blue B (MBB), pyronine G (PYG) and rhodamine B (RHD) on silver iodide sols in statu nascendi; aqueous media at 293 K, 10 minutes after mixing of components.

ciates of coulombic ion-pair type, and a variety of composite complexes. Linear portions of the PBs contours give strong indications about the chemistry of dynamic structures as a result of concentrational changes of simple ionic precipitating components. The slopes of linear portions of the precipitating-non-precipitating (precipitation-solution) contours are direct evidence about the composition of the interacting solute species which are entering into solid or semi-solid structures; processes according to the simple solubility product constant are only one among others. Of course, the precipitating-nonprecipitating boundaries represent the prevailing mechanisms, and the non-linear portions of some of PBs are indicative of the mixtures of the reacting species. Especially, such examples are manifested with systems where the cationic components are either silver or thorium ions. However, the large number of characteristic contours of PBs elaborated up till now provide sufficient proof

for the role of the specific species resulting from various short and long range interactions of the ionic and molecular constituents of the system in question. Therefore the c h e m i c a l aspects have to be taken as the basic ones for interpretation of the processes and structures encountered in equilibrated, and much more so in nonequilibrated systems in precipitation, crystallization, coagulation, flocculation, as well as in other kindred phenomena.

Besides processes and structures near the equilibrated states of heterogeneous systems there are possibilities for a large number of transitional short, medium and long lived systems when the precipitation is performed by mixing much more concentrated precipitating components than there are present in the cases near the precipitating-nonprecipitating borderline contours

$C_{AgNO_3} = 4.0 \times 10^{-4}$ mol dm^{-3}

$C_{KI,KBr,KCl} = 5.0 \times 10^{-4}$ mol dm^{-3}

10 min

AgI o
AgBr ◐
AgCl ●

TYNDALLOMETRIC VALUE

0.18
0.12
0.06
0

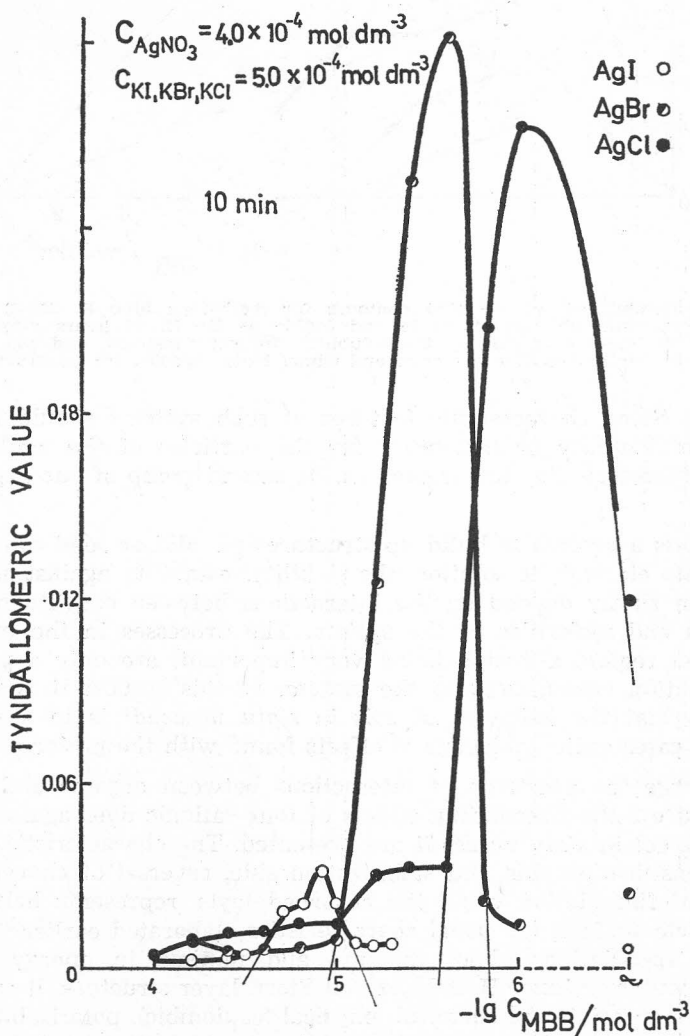4   5   6

$-\lg C_{MBB}$/mol dm^{-3}

Figure 3. Flocculation effects of methylene blue (MBB) on silver chloride, bromide and iodide sols in statu nascendi; aqueous media at 293 K, 10 minutes after mixing of components.
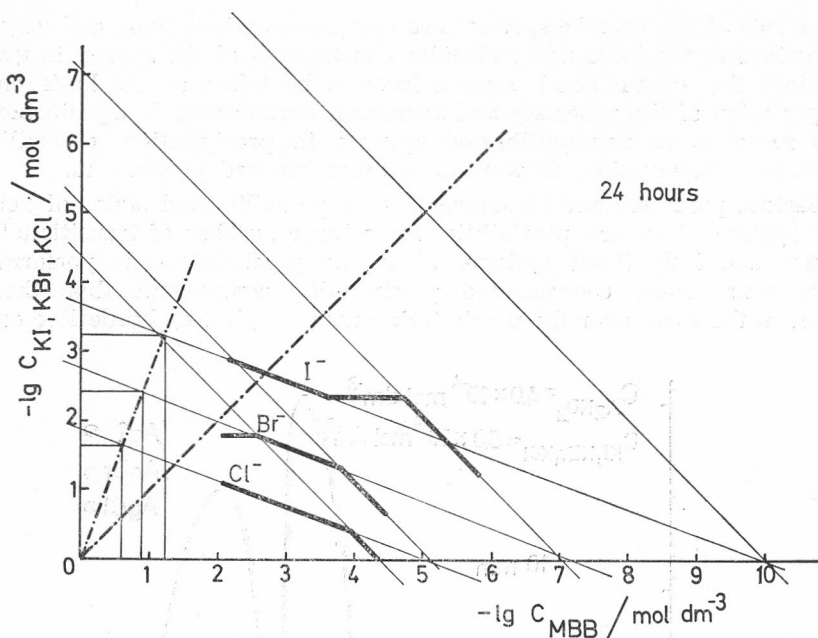
Fgiure 4. Precipitability-Solubility (PS) contours for methylene blue B (MBB) in aqueous solutions of potassium chloride, bromide and iodide at 293 K, 24 hours after mixing of components. The linear according to the solubility product constants, and the equivalency lines for methylene blue monomer and trimer halide species are constructed.

of our PBs. Some characteristic features of such systems should reveal the conditions of stability or instability for the particles of the emerging new phase, and therefore they are treated as the second group of our experimental results.

If there is a process to build up structures of solid or semi-solid particles dispersed into electrolytic solution, the stability/instability against aggregation should again firstly depend on the interactions between constituent or component ions and molecules of the system. The processes in the interphasial solid/solution region, although being very important, are only a part of the overall situation encountered in the system. In this respect it is interesting to find out that the behavior of sols *in statu nascendi* is in a very large majority of cases quite analogous to effects found with the preformed sols.

To enlarge the spectrum of interactions between organic and inorganic ions, in Figure 2 the flocculating effects of four cationic dyes against negative silver iodide sol *in statu nascendi* are presented. The characteristic maximum with the sensitization side and stabilization side, reversal of charge, and the maximum of flocculation when the adsorbed layer represents half coverage of the particle surface, are usual characteristics elaborated earlier[18-20]. Instead of various speculations about maxima and minima in energy functions, positions in outer or inner Helmholtz and Stern layer structure, it seems there is a need to appreciate the chemical, physical (coulombic), polarisability or van der Waals interactions between ionic or molecular constituents of the substrate and solute-solvent which are changing the concentration of the osmotically
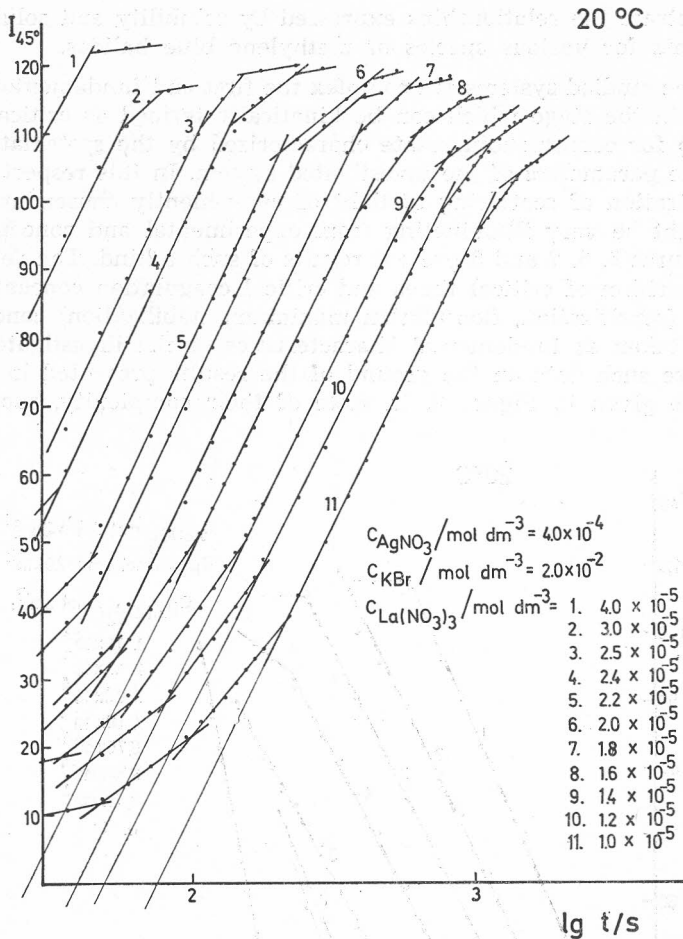
Figure 5. Plots of scattering of light against logarithm of time for systems: silver nitrate (4.0 × 10⁻⁴ mol dm⁻³) — potassium bromide (2.0 × 10⁻² mol dm⁻³) and potassium nitrate (gradient) in aqueous media at 293 K; sections of the steepest lines with log t abscissae are taken as critical times.

active species in the methoric layer as compared to the situation in bulk solution. In such circumstances the relationship between the half lives of all such interactions in the methoric layer and in the bulk of solution in comparison to the time and space of particle encounters is of decisive influence. In analysing various steps in such processes it might be helpful to know much more about chemical and physical properties of similar composite systems. To that purpose in Figure 3 the flocculating effects of methylene blue against silver chloride, bromide or iodide sols *in statu nascendi,* and in Figure 4 the interactions of methylene blue with chloride, bromide or iodide ions as PBs contours are presented. The influence of dispersity as well as the density of surface charges of the colloid particles is clearly manifested in the results given in Figure 3. The precipitation-solution contours in Figure 4 could be

used to illustrate the relationships expressed by solubility and solubility pro-
duct constants for various species of methylene blue halides.

When the studied systems are complex the first and fundamental approach
is to ascertain the stage which can be kinetically termed as critical (starting
or finishing) for corresponding state characterized by the systematic changes
of one of the parameters of the investigated system. In this respect the conti-
nuous registration of scattering of light of conveniently chosen precipitating
systems might be very illuminating from experimental and conceptual point
of view. Figures 5, 6, 7 and 8 present results of such a kind. The relationships
between logarithm of critical times and critical coagulation concentrations or
flocculation (sensitization, flocculation maximum, stabilization) concentrations
have to be taken as fundamental characteristics of the investigated systems
and therefore such data on the ground of the results presented in Figures 5,
6 and 7, are given in Figure 9. In spite of their complexity, such systems,
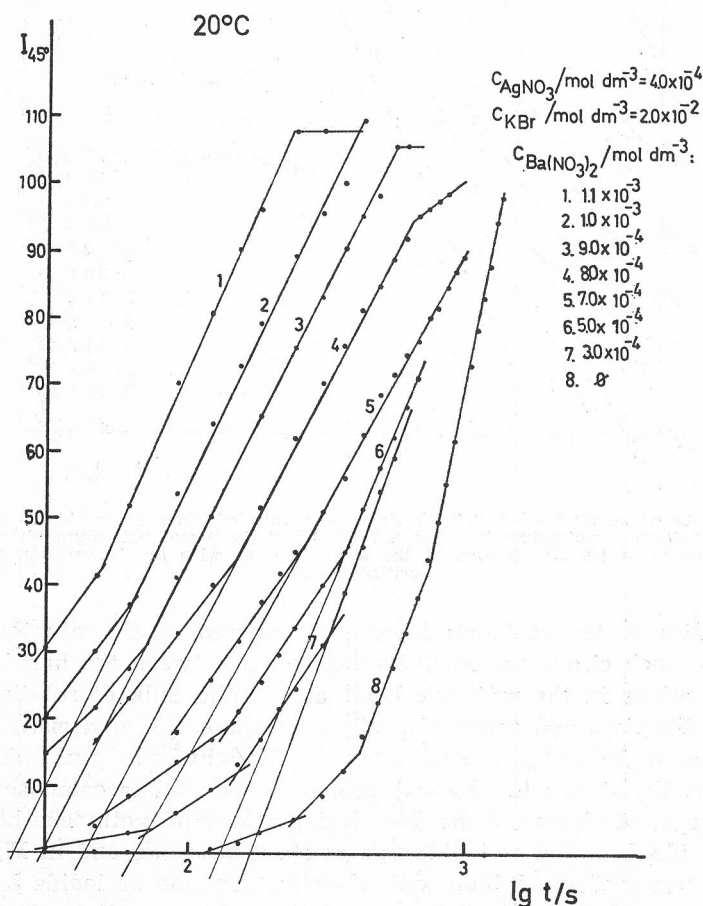

Figure 6. Plots of scattering of light against logarithm of time for systems: silver nitrate
(4.0 × 10⁻⁴ mol dm⁻³) — potassium bromide (2.0 × 10⁻² mol dm⁻³) and barium nitrate (gradient)
in aqueous media at 293 K; sections of the steepest lines with log t abscissae are taken as
critical times.

Figure 7. Plots of scattering of light against logarithm of time for systems: silver nitrate (4.0 × 10⁻⁴ mol dm⁻³) — potassium bromide (2.0 × 10⁻² mol dm⁻³) and lanthanum nitrate (gradient) in aqueous media at 293 K; sections of the steepest lines with log t abscissae are taken as critical times.

due to their sensitive response against changing parameters, represent a very convenient tool for exploring precipitation, ion-ion and ion-solvent interactions, as well as colloid stability phenomena. To emphasize such a standpoint at Faraday Discussions on Colloid Stability 1978[11] on the author's request Prof. Lyklema read the following remarks which are reproduced here.

SOME REMARK ON THE GENERAL DISCUSSION ON COLLOID STABILITY — 1978

It seems that the material presented for this General Discussion on Colloid Stability (the fourth one if we take that the first was in 1939, second in 1954. and third in 1966) is far from pointing towards the right type of the general conceptual framework. Insufficient attention has been paid not only to the uncertainties in the quantitative aspects of the theoretical elaboration but also to the conceptualization of the experimental resuls, and to the systematic
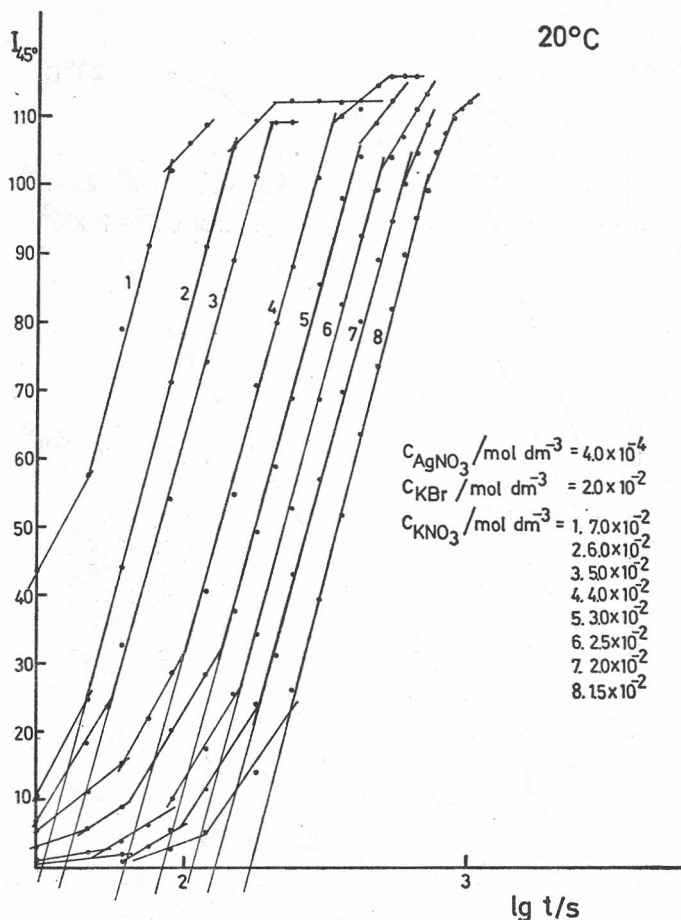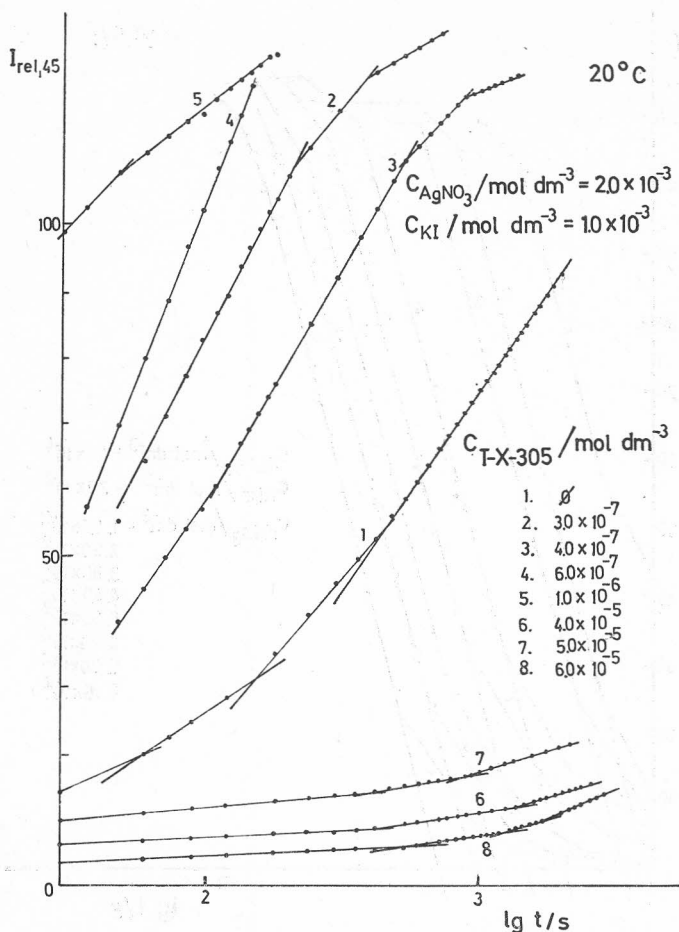
Figure 8. Plots of scattering of light against logarithm of time for systems: silver nitrate $(2.0 \times 10^{-3}$ mol dm^{-3}) — potassium iodide $(1.0 \times 10^{-3}$ mol dm^{-3}) and triton T-X-305 (gradient) in aqueous media at 293 K.

gathering of the facts. Certainly, a much more impartial approach has to take into account that we are dealing with a very complex phenomenon where separate treatment of some parts of it cannot give the true answer for the states of equilibrated colloidal systems, and much less so for the dynamical processes characterising the nonequilibrated ones.

In the DLVO theory which follows the conceptual scheme of Kallmann and Willstätter[21] the role of van der Waals attraction and double layer repulsion has been grossly overestimated without paying proper attention to the large number of other factors which should be included in the interpretation of experimental facts. For instance, one of the most important of the open question is the position of the effective borderline between boundary regions of the interacting particles. Undoubtly, such a dividing region is a result of many parameters where the physics and chemistry of all constituents and components are reflecting simultaneously the role of both bulk phases
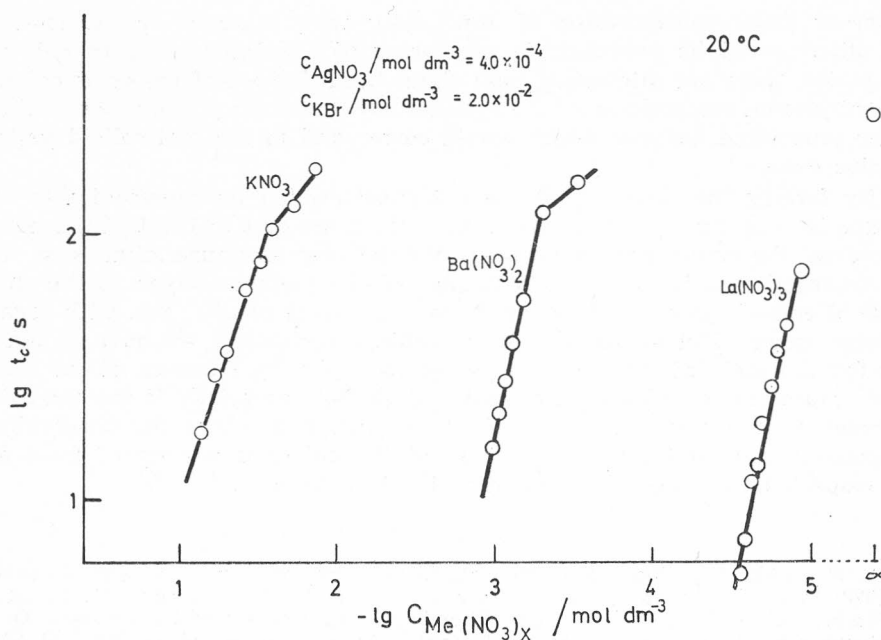
Figure 9. Plots of logarithm of critical times corresponding coagulation concentrations of potassium, barium and lanthanum nitrate (resulting plot of data presented in Figures 5, 6, and 7).

and the structure of the space between them (methoric layer). We have to admit that there is a threedimensional region simultaneously controlled by composition and concentration of both solid and solution bulk phases, and that the dynamic structure of such an transition layer is acting as some kind of feed-back controlling mechanism on the behaviour of the system as a whole. Earlier[22] was emphasized that the simplest and quite obvious conceptual approach to the stability/instability relationships of colloidal systems is the difference in the osmotic pressure (concentration, energy and entropy) of the constituents in a methoric layer against that of the more dynamically structured bulk phase. The higher osmotic pressure in the methoric layer results in stability and the lower in instability[23-25].

However, we have to be aware that the unknown position of the borderline region, something like effective surface of concentrational discontinuity of the layer adhering the solid (or other dispersed phase) against the continuous phase is crucial. In spite of many attempts to find the real structure and thickness of the methoric layer we have nowadays only the results of the critical behaviour of the total systems or some data about their isolated and distorted parts.

In this sense all results of the electrokinetic measurements as well as the force-distance determinations are of such a character. In electrokinetic measurements by imposing the system to the outside field (electrical or mechanical) the experimental results reveal the presence or absence of charges but not their true, natural environmental conditions. Namely, the higher zeta-potential or the neutrality of the »surface« means only that in the methoric layer the

higher or lower concentration of osmotically active charged species (co-ions and other) could be expected. In measuring of disjoining pressure between two plates, there are interesting data about the influence of the chemical and concentrational composition of the systems but the question about the position of the separating distance which would correspond to the real colloid system remains open.

By forcing the theory which is not substantiated by representative sets of experimental facts, it is the same as putting the cart in front of the horse. Of course, the contemporary probing into the true structure, dimension, and the synergetic spatial-temporal dynamics of the methoric layer as the third phase of colloid systems, has given many interesting results. Yet, with regard to some essential elements of the controlling mechanism we have to admit that for the state of the art it is proper to apply the meaning of the Latin word *ignoramus*. In addition, as a word of caution, especially if the one-sided approach to the complex systems is prevailing, and where the observation, experimentation, and conceptualization of the coherent variety of facts are not respected, we may easily come to the *ignorabimus*.

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SAŽETAK

Gdje smo u objašnjenjima ionske topljivosti, taloženja, koagulacijskih i flokulacijskih pojava?

B. Težak

Naglašena je zbrka u objašnjenjima, postavkama i teorijama u nekim područjima fizike i kemije vodenih otopina realnih sistema, posebno kod pojava taloženja, međudjelovanja ion-ion, ion-otapalo i koloidne stabilnosti. Posebno je smetnja na tom području tzv. DLVO teorija, koja tumači koloidnu stabilnost van der Waalsovskim privlačenjem i odbijanjem električnih dvosloja, kao i upotreba indiskriminatorne konstante produkta topljivosti za precipitabilitet.

U sumarizirajućim postavkama u vezi prijašnjih materijala publiciranih u radovima internacionalnih škola, konferencija i simpozija o međupovršinama čvrsto/tekuće održanih u Jugoslaviji 1969, 1972 i 1975 godine, naročito je naglašena važnost sastava supstance, te koncentracijskih uslova u metoričkom sloju i unutrašnjosti otopine, što se odražava na diskontinuitetima u stvaranju precipitata, uključujući i embrionaciju, nukleaciju i sekundarne agregacije kod kristalnog rasta kao i u stupnjevima stabilnosti/nestabilnosti primarnih čestica (stabilnost/nestabilnost solova *in statu nascendi*).

Prikazan je skup eksperimentalnih podataka u tri grupe dijagramatskih prikaza:
(1) 16 osnovnih obrisa taložljivosti-topljivosti za fluorescein, eozin, eritrozin i rose bengal B kao anionske komponente prema kationskim komponentama argentum, barium, lantanum i torium soli.
(2) flokulacijski efekti tionina, metilen plavog B, pironina G i rodamina B, kationskih boja na negativno nabijenim argentum jodid solovima *in statu nascendi*.
(3) Diskontinuiteti u linearnim dijelovima krivulja raspršenja svjetla i vremena tokom procesa precipitacije argentum halogenida u prisustvu elektrolita ili neionskog tritona T-X-305.

Diskutirano je stvaranje različitih kemijskih vrsta kao jednostavnih akvo-kompleksa, asocijata, različitost sastava složenih kompleksa, koji su odgovorni za uvjete stabilnosti/nestabilnosti, kao i granice taložljivosti/topljivosti, koje su sasvim različite od onih očekivanih prema konstanti produkta topljivosti.

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