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Solid/Liquid Interfaces

General Introduction

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An introductory paper to the material of a scientific conference has many purposes. In few words it should give an orientation about the circumstances, origin and goals of such an organized attempt to concentrate attention on one specially chosen scientific topic; further, it is expected that something of the general historical background should be mentioned; moreover, it is meant to give a frame for the presentation and discussion of relevant and pertinent material and for drawing conclusions.

In this order we shall try to give more or less satisfactory presentation of the material of the international summer school and conference: *The chemistry of solid/liquid interfaces* (Dubrovnik-Cavtat, 1969).

Although there are elements of widest interest in physical, chemical, biological, geological, technological, and other aspects of the composition, structure, and kinetics of the region between the solid and the liquid phase (where the solid is represented by various substances, and the liquid is an electrolytic solution) few systematic treatments are available. Nearest to the subject matter of our approach is the material published in the *General Discussions of the Faraday Society:* on the Electrical Double Layer (1939), on Coagulation and Flocculation (1954), and on Colloid Stability in Aqueous and Non-Aqueous Media (1966). Our aim is to establish an international, open, and more frequent forum which would focus attention to this field. The first steps have been encouraging and the present publication is the first result.

In discussing the subject matter of the Summer School and Conference on *Solid/Liquid Interfaces* helt at Dubrovnik-Cavtat 1969, it has been realized that the best way would be to publish the proceedings in a scientific periodical as original or semi-original papers together with the abstracts, extended abstracts, glossaries, and pertinent bibliography.

The invited lecturers have proposed that the authors themselves should decide whether to prepare for publication the original lecture, extended papers of more or less original character, or to publish only the material in the form in which it already appeared at the Conference.

Some Historical and General Remarks

One hundred years ago, in June 1869, Joshua Willard Gibbs (1839—1903) returned to his Alma Mater, Yale College, after three years sojourn in Paris, Berlin and Heidelberg, where as a young student he studied physics and mathematics with Magnus, Kirchhoff and Helmholtz. Although the scientific writings of the Professor of Mathematical Physics at Yale College were unknown and neglected for a number of years, nowadays it is impossible to treat any subject connected with chemical thermodynamics without referring to Gibbs' fundamental work. Much more so in the case of this Summer school, which is a cummulative name for a conference, an open forum, a workshop seminar, and a series of lectures.

It is interesting to note that in the same year (1873) when Gibbs developed his graphical method in the thermodynamics of fluids, and a method of geometrical representation of the thermodynamic properties of substances by means of surfaces, van der Waals tried to solve the problems of the liquid state of matter by introducing the '*quasi* gaseous' analogy. Then, as now, the liquid state of mater presented one of the most involved problems to solve.

While the 'ordered' nature of crystals, as a contrast to 'disordered' or amorphous states of matter was widely treated, and the thermodynamics of phase changes made a remarkable progress, the true nature of structural elements in the boundary region was generally ignored.

In Gibbs' work *On the Equilibrium of Heterogeneous Substances* (1878) the heterogeneous masses in contact are considered to be separated by mathematical surfaces, »each mass being unaffected by the vicinity of the others, so that it might be homogeneous quite up to the separating surfaces both with respect to the density of each of the various components, and also with respect to the densities of energy and entropy«. Such a dividing plane is called the »Gibbs surface«.

Now after a magnificent accumulation of precise data about the structure and properties of solids it seems appropriate to try to integrate the points of view of physicists, chemists, crystallographers, metallurgists, geologists, biologists, and to look at the interface region between solid and liquid with much more attention paid to the physical and chemical characteristics of structural bearers, of ordering-disordering atoms, molecules, ions, and other discrete building units.

We are aware that in the variety of cases starting from mono-component to very complex poly-component solid/liquid, equilibrated and nonequlibrated, systems, there is always a region where the ordering of solid in close vicinity of the liquid is distorted, and the 'statistical mathematics' and 'geometry' of liquid units is not yet restored, in comparison with the bulk phases. The dimensional and structural characteristics of such a region may be interpreted only if the peculiarities of the transitional state of matter are respected. On one side, there are ordered close packed atoms, molecules and ions with more or less fixed and discrete sites open to the other phase, and on the other side, the dynamic — but certainly very far from chaotic — distribution of atoms, molecules, ions and 'holes' of a '*quasi* crystalline' liquid medium.

Such a region, which may have the thickness of a few millimicrons up to several microns, we have called the »methorical layer«, following the suggestion of Wo. Ostwald. To be precise, we are able to characterize directly the encountering bulk phases only, while the immediate structure, the physics and chemistry of the region lying outside the limits of the composition and structure of the bulk phases may be usually traced indirectly through the behavior and the properties of the complex system, either in part or as a whole.

However, in spite of the complexity of the solid/liquid systems, there is some hope that experiences with assemblies where constituents of the dynamic liquid phase are much more under control in the vicinity of the solid, may give precious information on the attractive and repulsive forces as well as on the ordering and randomization processes of the physics and chemistry of this critical region simultaneously influenced by both adjacent phases. As is usual in science, the first steps are in collecting as much experimental evidence as feasible.

Following this line of reasoning we have tried to organize the contributions of our lecturers under four sections according to the complexities of the elements involved.

In Section I the starting point is the experimental and theoretical treatment of the boundary region in equilibrated state incorporating concepts and properties of the main components from which the solid/liquid interphase is composed. Interactions in solutions, phenomena of adsorption, techniques for probing into interfaces, electrical and other characteristics, application of old and new direct methods to the study of interfaces, theoretical descriptions, are encountered here.

In Section II are treated: behaviour of systems where there are some changes in the interfaces, or the interactions between the units, characterized by specific properties of boundary layers, as well as the stability of dispersions and changes caused by coagulation and flocculation.

In Section III are approaches to the interface characterized by kinetics of electron transfer through the boundary of various electrodes under the influence of adsorption layers.

Section IV is concerned with transition from the solution to the precipitate, taking into account various stages such as the formation of embrios, nuclei, primary particles and secondary structures, all under discussion from experimental and theoretical aspects of nucleation and crystal growth.

Thus, starting with explanations and interpretations of simpler, more statical models, we have to proceed to the dynamical behavior of the systems with built-in characteristics of the region between adjacent solid and liquid phases where the influences from outside are limited to the interface itself; afterwards we have to see the traditional field of electrochemistry reflecting the state of things at the electrode-solution boundary influencing the transfer of charges; finally, the various steps in formation of solids from melts, and above all from electrolytic solutions are to be dealt with.

As the basis for a more specifically pointed discussion, without the danger of losing the common ground for the whole field of our conference topic, we can offer as an introduction three approaches: a terminological one; a general outline of the paths available for the investigation of the inter-boundary layer between solid and liquid phases; and an attempt to give a collection of experimental facts, and a semi-quantitative picture of the structural elements of the solid/liquid interfaces consisting of the model of an ionic crystal in contact with an electrolytic solution.

Terminology

First of all a few words about the terminology. As mentioned above, we should like to give preference to the words »methoric«, »methorical«, and »methorics« when referring to the experimentally and theoretically defined region between two phases. In *Chemical Abstracts Index* the word »methorical region« is treated as identical in meaning with »interfacial layer« or »interface«. We have tried to introduce the word »methorics« as the name for the physics and chemistry of the interboundary region quite a long time ago[1]. At a recent *Symposium on Interfacial Phenomena at Colloid and Electrode Interfaces,* held in Atlantic City in September 1968, Conway and Gordon deliberately distinguish the usages »interfacial« and »interphasial«; the former refers to the two-dimensional »electronic« surface of the metal in contact with the solution and the latter to the thin, but three-dimensional, region which accommodates the local changes of concentration and other properties arising on account of adsorption.

It seems that the term »methorical layer« embracing all interfaces between two bulk phases has some advantages as compared with any other one-word description of the critical transition region. As specific interfaces in this three-dimensional boundary layer we may distinguish: *(1)* the interface between regular lattice and distorted lattice of the crystalline condensed phase; *(2)* the interface between the distorted lattice and the constituents distributed in a two-dimensional pattern subject to the influences of the solutions; *(3)* the interface between specifically distributed carriers of electrical charge or chemical activity (ionogenic groups, complexoids) exposing the crystalline substrate to the solute and solvent constituents and including the counter-ion layer; *(4)* the co-ion layer; *(5)* the slipping plane or the breaking interface manifested in kinetic and electrokinetic phenomena; and *(6)* the region of the concentrational differences between the layer near the solid phase and the bulk of the solution.

Fig. 1 is a schematic picture of all these interfaces.

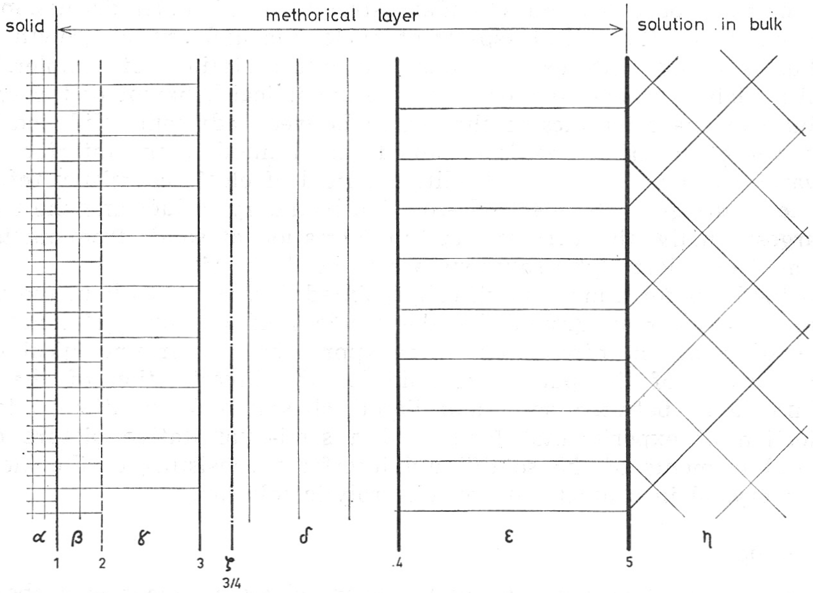


Fig. 1. Interfacial layers in methorical region (space between undistorted crystal phase and electrolytic solution of bulk properties); α undistorted crystal phase; β distorted lattice ions; γ potential determining complexes (complexoides),δ counter ions; ε co-ions; η solution in bulk; ζ electrokinetical plane of shear.

Dimensions and structures of these and other possible interfacial layers may vary not only from system to system but also in one system of the same composition at various stages of development where the characteristic time limits may be quite different and very far from the moment characterized by the conditions of equilibrium. Especially, such cases are very frequent in the formation of solid aggregates as a results of instability of isolated particles.

The common nomenclature and terminology are reflected in following quotation[3]:

»A boundary between two phases is called a surface or interface; interface is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly. The region of space comprising and adjoining the phase boundary within which the properties of matter are perceptively different from the equilibrium values in the homogeneous bulk phases, is called surface layer or interfacial layer (Fig. 2). In addition it may be expedient to be more explicit and to define a surface (or interfacial) layer of finite and constant thickness (τ, δ) bounded by two appropriately chosen surfaces parallel to the phase boundary, one in each of the adjacent homogeneous bulk phases; a layer of this kind is sometimes called a »Guggenheim layer«.

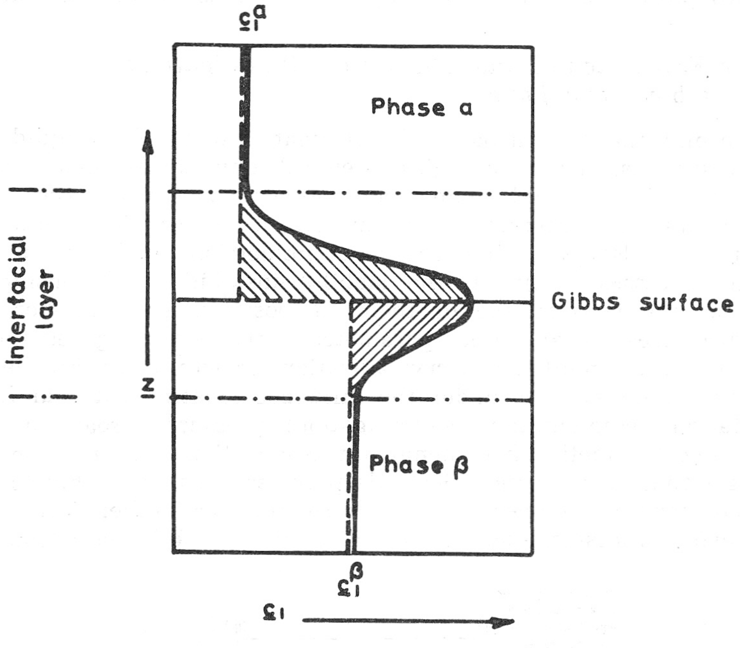


Fig. 2. Concentration profile (c_1) as a function of distance (z) normal to the phase boundary; (a) full line — in the real system; (b) broken line — in the reference system; (c) chain dotted lines — boundaries of the interfacial layer.

»Adsorption of one or more of the components, at one or more of the phase boundaries, of a multicomponent, multiphase system, is said to occur if the concentrations in the interfacial layer are different from those in the adjoining bulk phases, so that the overall stoichiometry of the system deviates from that corresponding to a system of homogeneous bulk phases whose volumes and/or amounts are defined by chosen dividing surfaces«.

»Gibbs dividing surface (or Gibbs surface) is a geometrical surface chosen parallel to the phase boundary and used to define the volumes of the bulk phases applying the foregoing definition to the calculation of the extent of adsorption, and of other surface excess properties. It is usual to choose the Gibbs surface within the inhomogeneous boundary region. Excess thermodynamic quantities referred to the Gibbs surface are denoted by superscript σ to distinguish them from quantities relating to the interfacial layer, for which superscript s is employed«.

»The surface excess amount or Gibbs adsorption of i, n_i, which may be positive or negative is defined as the excess of the amount of this component actually present in the system over that present in a reference system of the same volume as the real system and in which the bulk concentrations in the two phases remain uniform up to the Gibbs dividing surface«.

Paths for Experimental and Theoretical Investigations of the Interboundary Layer

Concerning the general paths of investigation of the solid/liquid boundary we may distinguish: *(i)* the energies (chemical, physical, biological, direct and indirect) of solid and liquid, composition and structures or adsorbent/adsorbate or similar mutually interacting systems (work of adhesion, contact angles, free energy of adsorption, free energy of immersion, topochemical reactions, biological processes, *etc.*); *(ii)* the stability-instability relationships of the particles as the consequence of their composition, size, number, medium, temperature, pressure and other parameters (processes of aggregation, coagulation, flocculation, multistaged crystallization, growth, *etc.*); *(iii)* the behavior of the solid/liquid systems under the influence of some external fields such as gravitation (sedimentation, centrifugation), pressure (streaming, viscosity), electrical (electrokinetic phenomena), ultrasonic, thermal, radiation, *etc.; (iv)* the charge transfer processes (electrode processes in relationship to potential, charge, composition, temperature, pressure, time and other factors); *(v)* the mass transfer processes, such as formation of the solid phase (embrionation,

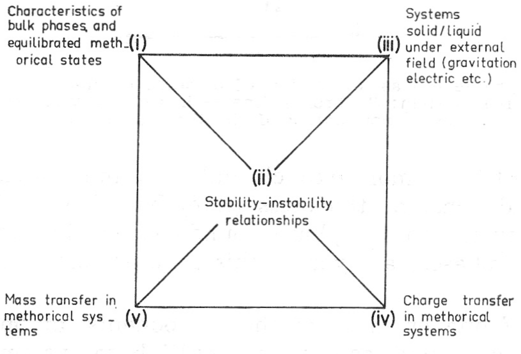


Fig. 3. Scheme of the five different but complementary approaches to the study of methorical layer (interfaces).

nucleation, micellization, direct or indirect particle growth, crystallization, precipitation, coagulation, flocculation, aggregation, recrystallization, diffusion, aging, exchange, restructuring *etc.*).

The first three points are connected with characterization of systems which are equilibrated or pass through reversible stages. In systems involving charge and mass transfer complex mechanisms are encountered. Fig. 3 summarizes schematically the five different approaches to the study of interfaces.

The program of the Conference reflects this subdivision, except for point *(iii)*, where specific presentation is lacking.

Experimental Facts

Experimentally and theoretically it is important to find the common ground for a great number of phenomena which may be put into some interconnected groups. For our purpose, probably, one of the easiest ways is to observe stability-instability relationships of the dispersed particles under various conditions. The changes in stability, and especially the abrupt changes may be taken as internal signals of the changes in the methorical layer. In this respect the following groups of phenomena may be considered: *(a)* the influence of the substance of the core of the particles; *(b)* the physical and chemical characteristics of the species in solution interacting with the particles; *(c)* the effect of valency and size of counter ions; *(d)* the adsorption of counter ions; *(e)* the crystallization effects; *(f)* the effect of mixture of simple electrolytes; *(g)* the negative adsorption of co-ions; *(h)* the effect of large ions and molecules; *(i)* the phenomena of reversal of charge; *(j)* the electrokinetic phenomena; *(k)* the influence of the dielectric constant of the medium; *(l)* the influence of the sol concentration; *(m)* the phenomena of peptization; and other related experimental findings.

In order to give the frame for conceptual and theoretical approaches we shall follow some facts according to points *(a)* to *(m)*.

(a) The influence of the substance of the solid core

Besides lyophilic and lyophobic characteristics there are many others controlling the chemical and physical behaviour of the disperse particles.

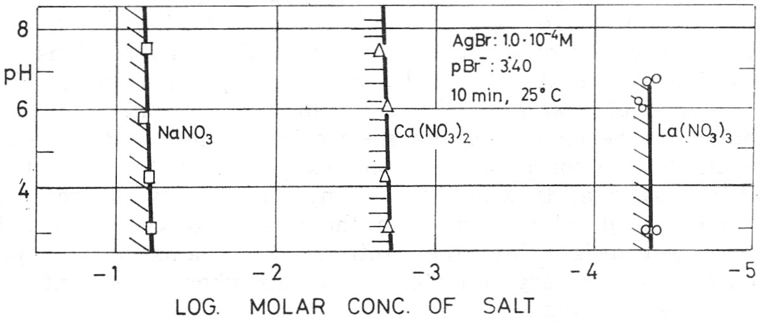


Fig. 4. **Logarithm** of critical **coagulation** concentrations of sodium, calcium and lanthanum ions as a function of *p*H for a negative silver bromide sol *in statu nascendi*, 10 minutes after mixing reacting **components** (coagulation on hatched side).

E. g., striking differences have been found in the precipitating or coagulating action of univalent, divalent and trivalent cations for a negatively charged silver bromide sol and silica sol when the concentration of hydrogen ions in aqueous solution is changed. In Figs. 4 and 5 critical coagulation resp. precipitation concentrations for both sols over a wide *p*H range are shown[4].

Generally, it may be said that such great differences are rather exceptions. Typical hydrophobic sols behave like that represented in Fig. 4.

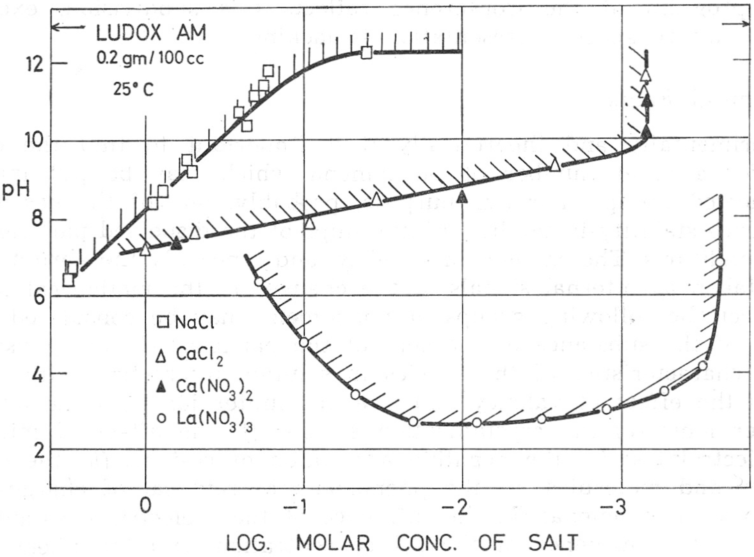


Fig. 5. Logarithm of critical precipitation concentrations of sodium, calcium and lanthanum ions as a function of *p*H for a Ludox AM silica sol, 1 hour after mixing components (precipitation on hatched side).

(b) The chemistry of interacting ions

If the ionic species interacting with particles undergoes chemical changes, it may produce significant differences in critical coagulation concentration. Such changes may be rapid or slow and concentration (*p*H) dependent. Sometimes it is appropriate to speak about solution aging. The best known examples are solutions of ferric, aluminum, and thorium salts, which may give a whole spectrum of coagulation values[5]. Also, as these ions are highly charged and/or represented by hydrolytic species, the changed adsorptivity and the reversal of charge should be taken into account. Some effects can be attributed to the change of the species in solution, and some to special situations in the methorical layer. Complex phenomena may be found with anions of polybasic acids where the change in valency is accompanied by changes in chemical interactions with the core of dispersed particles[5]. The best way to get insight into the controlling mechanisms is to perform a systematic survey of a large number of systems where important parameters are changed step-by-step.

A good example of complex behaviour are systems with aluminum species[6] represented in Fig. 6.

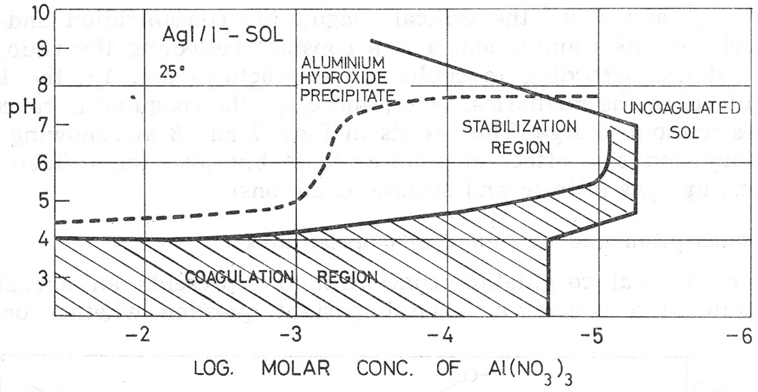
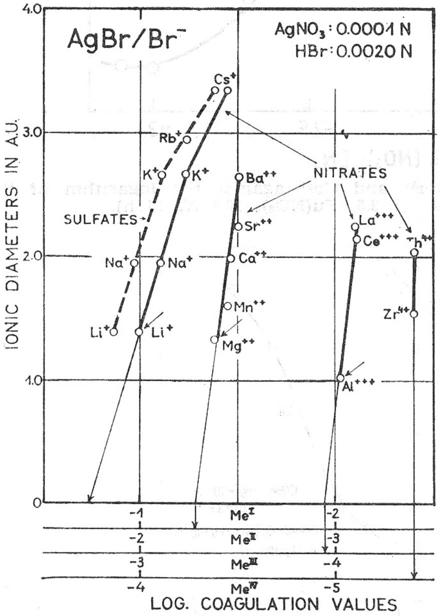


Fig. 6. **Logarithm of aluminum nitrate — *p*H contours for negative silver iodide sol *in statu nascendi*, 10 minutes after mixing reacting components; hatched area indicates coagulation region.**

(c) The Schulze-Hardy rule

Probably the most typical example of the behaviour of hydrophobic sols is the Schulze-Hardy rule: the higher the valency of the counter ions the more powerful is their coagulating action. This rule was expressed by the author[7] in the quantitative relationship:

$$\log c_{i\,(coag)} = -za + \log c_{i\,(fix)}$$



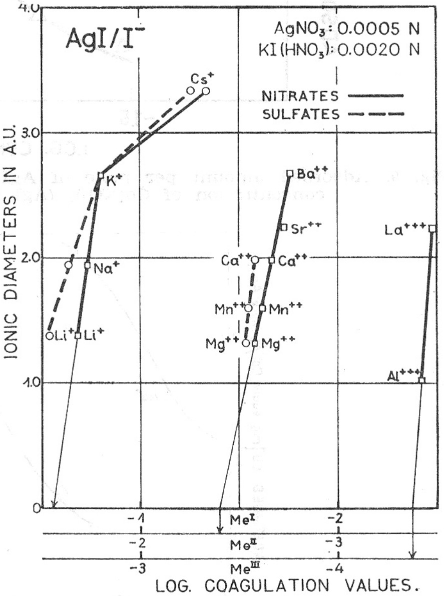


Fig. 7. **The relationship between the crystallographic radii of the coagulating cations and their coagulation values for negative silver bromide sol *in statu nascendi*.**

Fig. 8. **The same relationship as in Fg. 7 for silver iodide sol.**

where $c_{i\,(coag)}$ and z are the critical coagulation concentration and valency, respectively, of the counter ion, a is a constant reflecting the ratio between critical distance according to coulombic interactions and $1/\varkappa$ the length of Debye-Hückel in the methorical layer, and $c_{i\,(fix)}$ the coagulating concentration of species without charge. The results in Figs. 7 and 8 are showing not only the valency and size effect of counter ions[8] but also the influence of the accompanying ions (nitrate and sulfate as co-ions).

(d) The adsorption and exchange of counter ions

As the critical coagulation concentration represents an abrupt change of the state of a system, it is an important question whether or not the

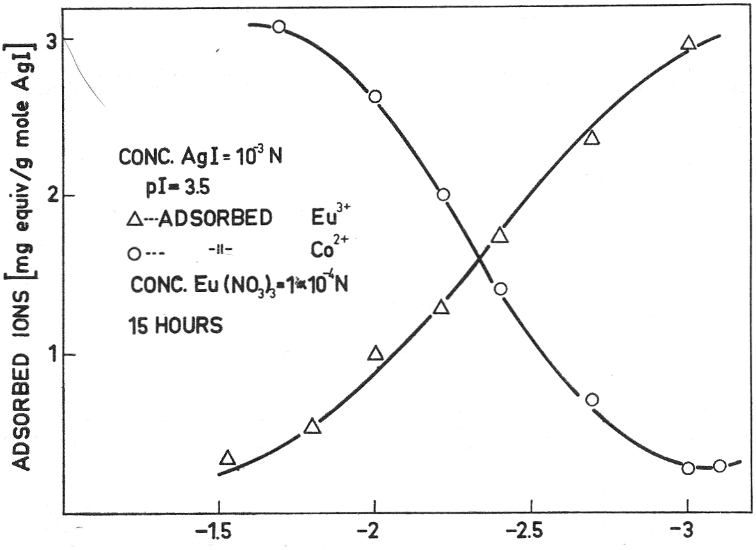


Fig. 9. Adsorbed amount per mole of AgI of Eu^{3+} and Co^{2+} against the logarithm of the concentration of $Co(NO_3)_2$ (AgI 10^{-3} *M*, *p*I 3.5, $Eu(NO_3)_3$ 10^{-4} *N*, 15 h).

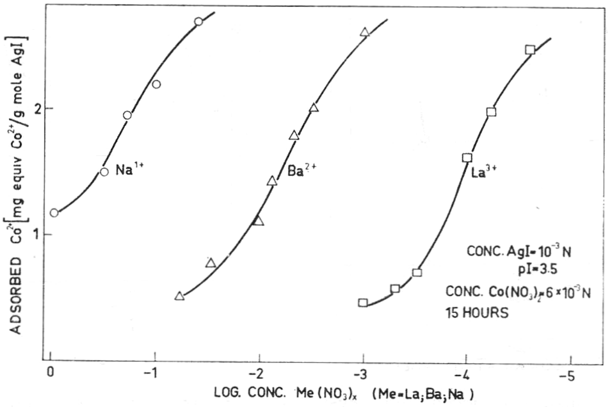


Fig. 10. Adsorbed amount per mole of AgI against the logarithm of the concentration of La^{3+}-, Ba^{2+}- and Na^{+}-nitrates (AgI 10^{-3} *M*. *p*I 3.5, $Co(NO_3)_2$ 6 × 10^{-3} *N*, 15 h).

counter ions are bound in a definite manner. The ionic exchange experiments[9] represented in Figs. 9 and 10 show that above the coagulation value the counter ions are adsorbed in equivalent amounts and that adsorption-desorption processes are accompanying the critical coagulation concentration of the respective ions.

(e) The crystallization effect

Quite opposite to the usual valency effect of counter ions are some cases where the same order appears but instead of precipitation at the side of higher concentrations there are relatively more stable systems. Fig. 11 shows such critical concentrations for the precipitation of barium sulfate[10]. It seems highly probable that such retardation effects could be explained by the inhibiting action of the ion-pair formation on the direct crystal growth.

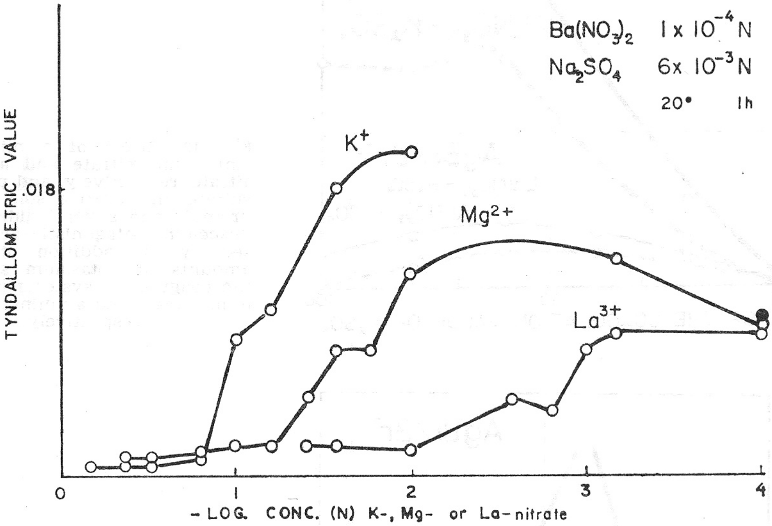


Fig. 11. Plot of turbidities against concentration of potassium, magnesium and **lanthanum nitrate** (logarithmic scale) for the precipitating system of barium nitrate (1×10^{-4} *N*) and sodium sulfate (6×10^{-3} *N*; 1 hour after mixing of reacting components.

(f) The effect of the mixture of electrolytes

Various effects ranging from superadditivity, additivity and antagonism have been exemplified by a great number of hydrophobic sols. The main characteristics of all such systems is the difference of valency between ions which may act as counter-ion and co-ions against charged particles for a given pair of electrolytes. Figs. 12, 13 and 14 represent typical antagonistic and superadditivity effects[11]. They demonstrate also the influence of the higher charge density on the wall of the dispersed particles. By performing the experiments in water-ethanol media (Fig. 14) an increase of superadditivity as well as of antagonism was observed.

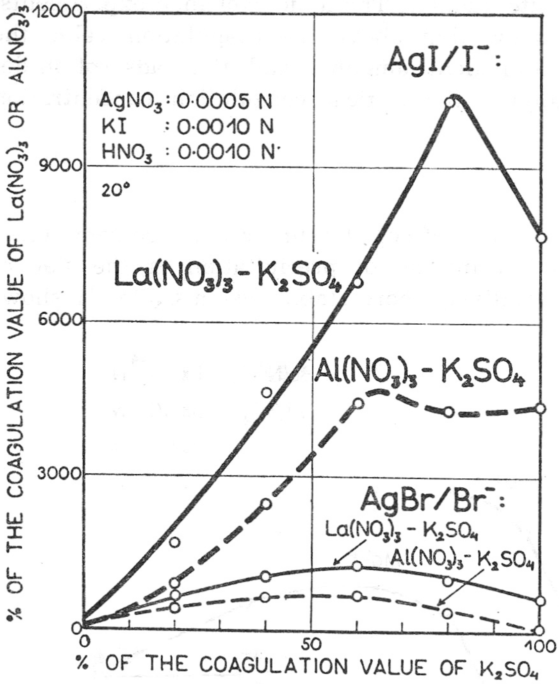


Fig. 12. Effect of a mixture of lanthanum nitrate and aluminum nitrate, respectively, and potassium sulfate on negative sols of silver bromide and silver iodide *in statu nascendi*. Antagonistic action caused by the addition of various amounts of potassium sulfate to the coagulating systems of lanthanum nitrate and aluminum nitrate, respectively.

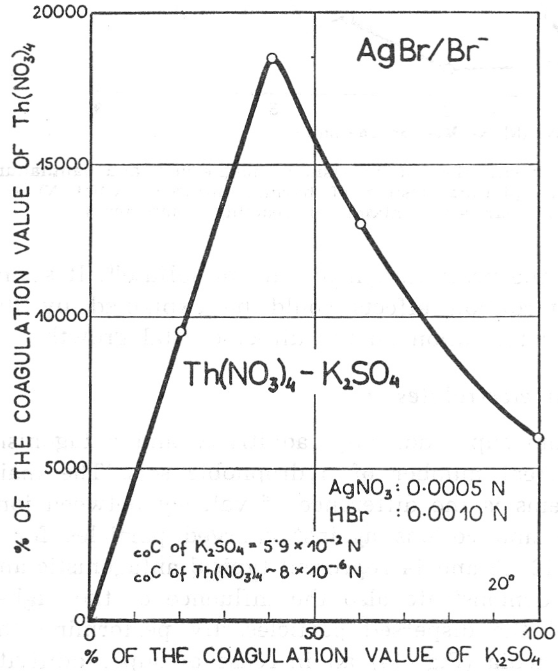


Fig. 13. Effect of mixture of thorium nitrate and potassium sulfate on a negative silver bromide sol *in statu nascendi*. Antagonistic action caused by the addition of various amounts of potassium sulfate to the coagulating system of thorium nitrate (coagulation values: $K_2SO_4 : 5.9 \times 10^{-2}$ *N*; $Th(NO_3)_4 : 8 \times 10^{-6}$ *N*).

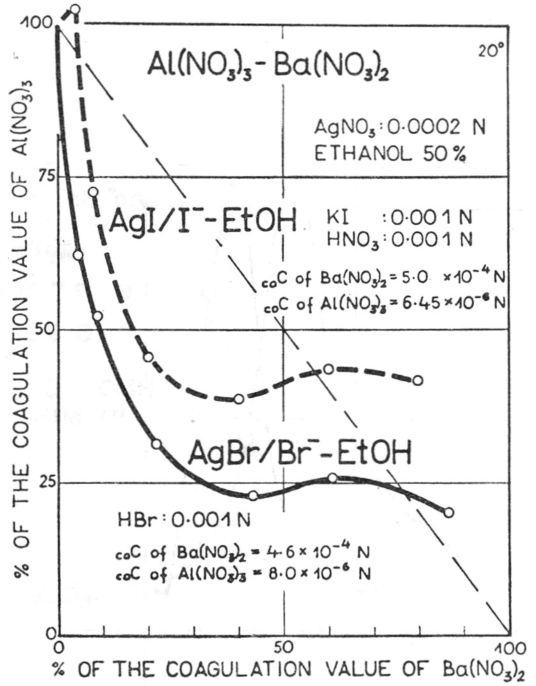


Fig. 14. Efect of a mixture of aluminum nitrate and barium nitrate on negative sols of silver bromide and silver iodide *in statu nascendi* in water-ethanol medium (50 per cent ethanol by wt). Sensitizing action caused by the addition of various amounts of barium nitrate to the coagulating system of aluminum nitrate.

(g) The negative adsorption of co-ions

It is quite natural to expect that besides the layer of counter ions which are attracted by the charges localized at the particles there is a layer from which the ions of the like charge are repelled. That such effects are measurable and may lead to the determination of the surface area adjacent to the volume of excluded ions, was shown by Shofield[12].

Edwards, Posner, and Quirk have given new evidence for discretness of charge on clay surfaces by measuring the area from which co-ions were excluded. It is interesting to note that on homo-ionic Fithian illites (non-expanding mica-like material) with approximately one charge per 60 Å^2 it was found the reduction of measured surface from 80 m^2/g in case of Li-illites to 70, 35, 10, and 0 m^2/g in case of Na-, K-, Rb- and Cs-illites, respectively. Thus the number of charged sites will vary both with the concentration of electrolyte and the nature of the cation.

(h) The flocculation effect

If there are greater possibilities of adsorption of ions and molecules, the effects may be named sensitization, flocculation, and protection, and the whole picture is usually characterized by the appearence of a maximum when the concentration is systematically changed.

Figs. 15 and 16 summarize some results[13,14]. In Fig. 17 are again illustrated some typical relationships[15].

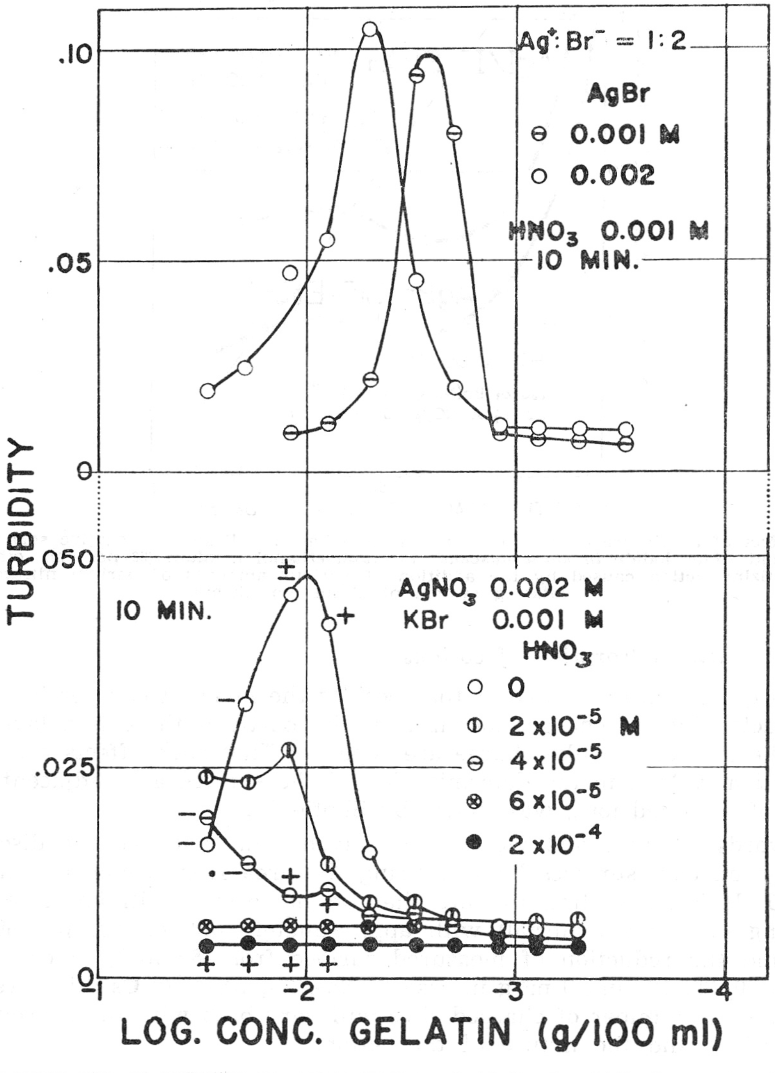


Fig. 15. Lower: plot of turbidity *vs.* concentration of gelatin for AgBr in excess of Ag^+ ion and with varying amounts of nitric acid. The plus and minus signs along the curves represent the sign of the particle charge (from electrophoresis). Upper: plot of turbidity *vs.* concentration of gelatin (positively charged owing to the presence of 0.001 *M* HNO_3) for AgBr in excess of Br^- ions.

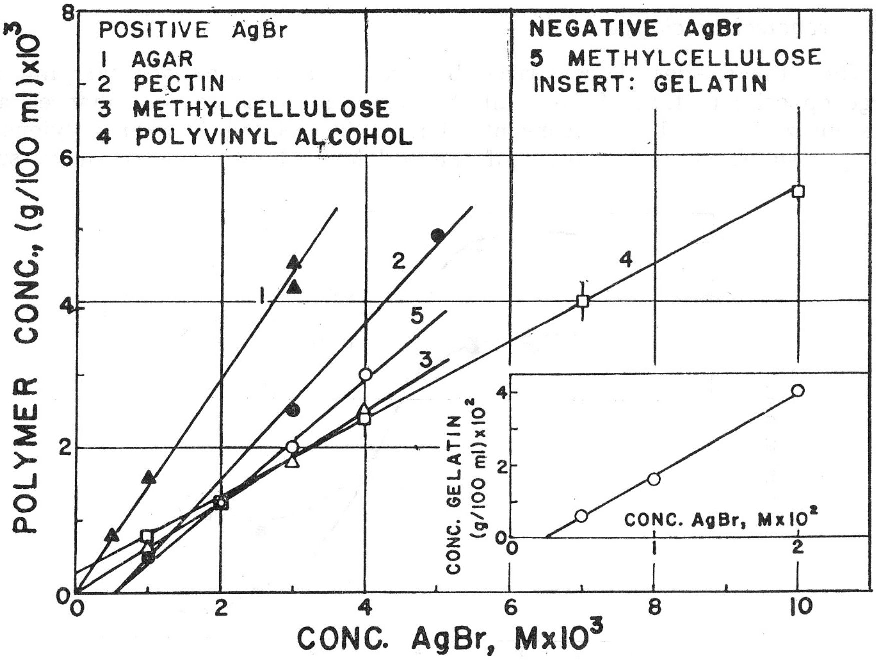


Fig. 16. Plot of the polymer concentration at the turbidity maximum *vs.* concentration of AgBr for agar (curve 1; 1 minute after mixing), pectin (2; 10 minutes), methylcellulose (3; 10 minutes), polyvinyl alcohol (4; 60 minutes) (all for positive AgBr), and methylcellulose (5; 10 minutes) and gelatin (insert; 24 hours) for negative AgBr.

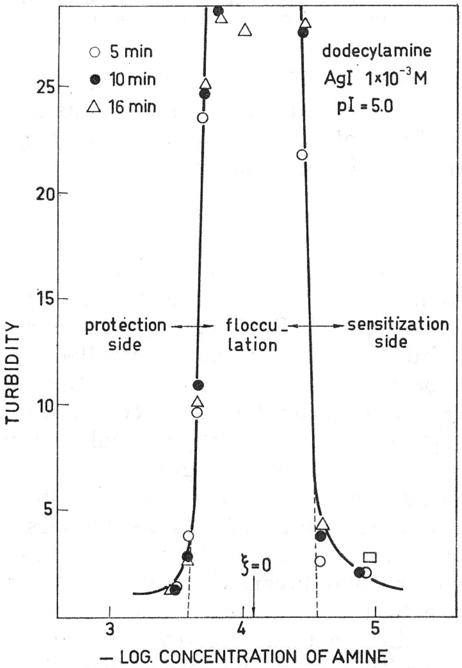


Fig. 17. Sensitization side, flocculation zone, and protection side of a negative silver iodide sol *in statu nascendi* as the function of the concentration of dodecylamine nitrate.

(i) The reversal of charge

When the species characterized by greater adsorption are carrying the charge opposite to that of the wall the flocculation is greatly enhanced and the stabilization at higher concentration of interacting ions or polyions is accompanied by charge reversal of the colloid particles. Fig. 18 shows such effects for the systems represented in Fig. 17. Also, there are very expressed influences of the valency of the cations on the sensitization (negative) side, and of the anions on the protection (reversed, positive) side in a plot zeta-potential-log. concentration of dodecylamine.

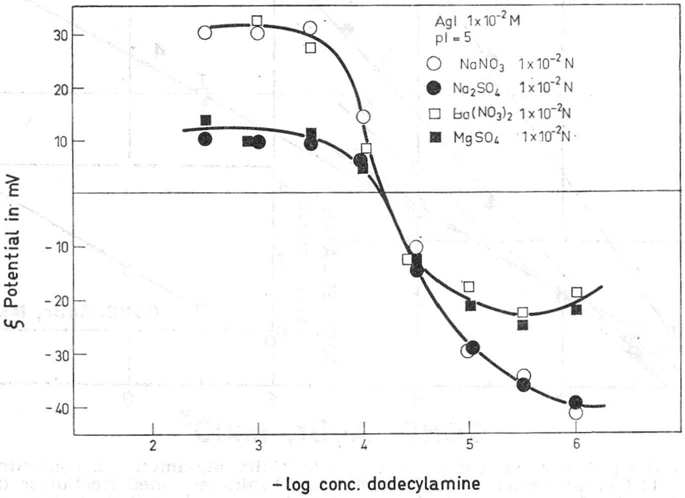


Fig. 18. The magnitude and the sign of the zeta-potential of a negative AgI precipitate as the function of the charge of the counter ion and the concentration of dodecylamine.

(j) The zeta-potential

A large number of interactions between charged and uncharged colloid particles and ions and molecules of the solution are accompanied by characteristic changes of zeta-potential. Such changes have created the impression that the stability-instability conditions are controlled by repulsion-attraction relationships for the particles as integral units. However, there are many cases where the aggregation (coagulation, flocculation) is not caused either by neutralization or by reduction of zeta potential of the particles; moreover some systems represent aggregation of highly charged particles of the same sign. Therefore, it seems reasonable to distinguish the zeta potentials with respect to the origin and character of charge carriers. At least it is a big difference in chemical, stereochemical and coulombic energies in changing the configuration in the methorical layer. Further, there are uncertainties about the position and the actual role of the plane of shear for the interacting particles. That the so-called neutral electrolytes have marked influence on the isoelectric points resulting from the interaction of precipitating (potential determining) ions is shown in Fig. 19. In connection with these results an

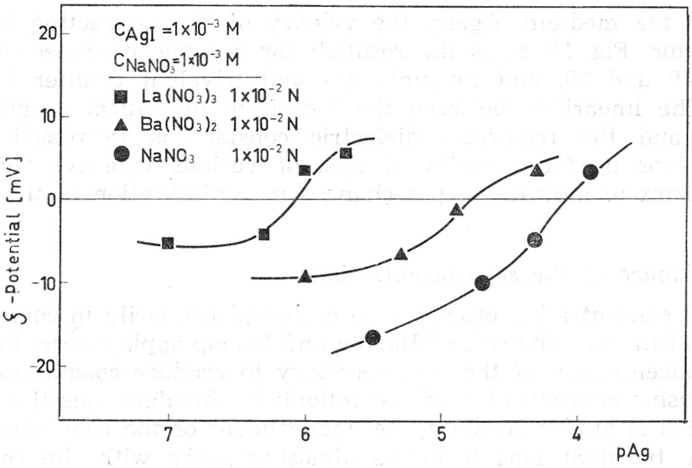


Fig. 19. The zeta-potential of AgI precipitates *in statu nascendi* in presence of sodium, barium and lanthanum nitrate (1×10^{-2} *N*) as the function of *p*Ag of the solution.

interesting problem is the influence of the bulk dielectric constant of the system upon the zeta potential. Curiously enough, for the AgI system the dependence of the magnitude of the zeta potential on the counter ion valence is manifested in many cases, while the change in concentration of the potential determining ion over a very wide range is without effect[16], an exception constitutes a relatively narrow isoelectric region.

(k) The effect of the medium

A very frequent phenomenon is the regularity of the relationship between critical coagulation concentration of the counter ions and the bulk dielectric

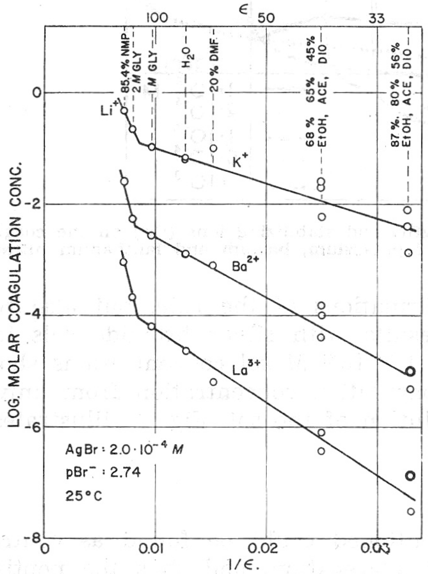


Fig. 20. Plot of the critical coagulation concentration (ccc) for a negative silver bromide sol *in statu nascendi* vs. $1/\varepsilon$ for K^+, Ba^{2+}, and La^{3+}, for various solvent mixtures as indicated at top of the figure. Concentrations: AgBr, 2.0×10^{-4} *M*; excess concentration of Br^-, 6×10^{-4} *M* (GLY = glycine, DIO = dioxane, ACE = acetone, EtOH = ethanol).

constant of the medium. Again, the valency of the interacting ions is controlling factor. Fig. 20 gives the results[17] for a range of dielectric constants between 140 and 30, and for uni-, di- and trivalent counter ions (K, Ba and La). The linearity[18] between the logarithm of critical coagulation concentration and the reciprocal dielectric constant is expressed either for individual ions or for a series of ions of various valency. The break in linearity seems to indicate deeper changes in configuration of the methorical layer.

(l) The influence of the sol concentration

The sol concentration effects were discussed primarily in connection with the purity of the sol. The rule of Burton and Bishop applies here: for univalent ions the concentration of the ions necessary to produce coagulation increases with decreasing concentration of the colloid; for bivalent ions the coagulation concentration is almost constant, *i. e.* independent of the concentration of the colloid; for trivalent ions it varies almost directly with the concentration of the colloid. There are many confirmations of the rule, but also results which show opposite effects. Our results with silver bromide sols in the concentration range from 1×10^{-5} to 1×10^{-3} *M* sol concentrations show an increasing lowering of the critical coagulation concentration from univalent to trivalent counter ions with the dilution of the sol. Fig. 21 illustrates this behaviour.

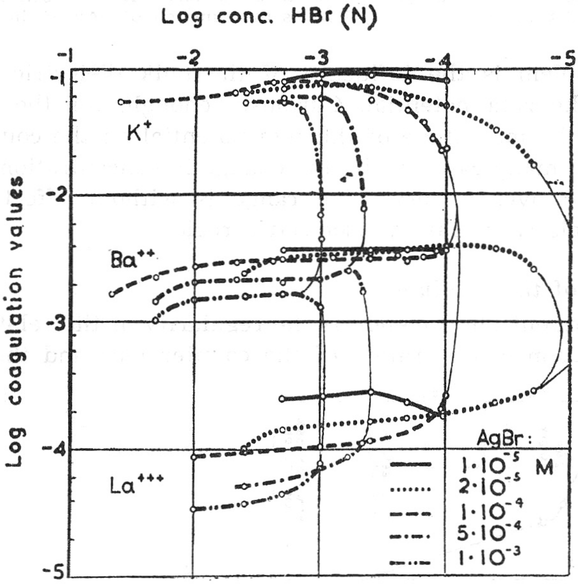


Fig. 21. Effect of the concentration of sols (AgBr) and stabilizing ions (Br^-) on the coagulation values (critical coagulation concentration) of potassium, barium and lanthanum nitrates.

(m) The peptization effects

Many of the factors already mentioned could be found as controlling the reversibility or irreversibility of aggregation, and thus the peptization and deflocculation phenomena have to be put in relationship with points *(a)* to *(l)*. Illustrative examples were presented by Odén[20] and author[21] for barium sulfate precipitates.

(n) Other effects

There is a great number of other effects or systems, either of simple or of very complex nature, which should be taken into consideration for the elucidation of the controlling mechanisms of the methorical layer. After a relatively long period of observations of preformed sols, we have tried to see in how far the kinetics of the precipitation could be compared with the experiences of classical colloid chemistry.

Generally, the so-called sols *in statu nascendi* have shown striking similarity to or even identity of behavior with classical, preformed sols. Moreover, it seems that the sols *in statu nascendi* have many advantages because of the direct and simple mode of preparation, and the enormous possibilities in variation of all important factors. Besides, they are closely connected with the vast field of naturally occuring solid/liquid systems.

Mechanisms, Concepts, Models, Theories

For the explanation of the experimental results we have developed some concepts which seem to be quite helpful in building the common ground for a large number of phenomena encountered. Some of the mechanisms, concepts, models and theories are classified under following subheadings.

(o) The coagulation (flocculation, aggregation) — peptization scheme

The state of the methorical layer is reflecting both the composition of the core of the disperse system and that of the solution. The most simple

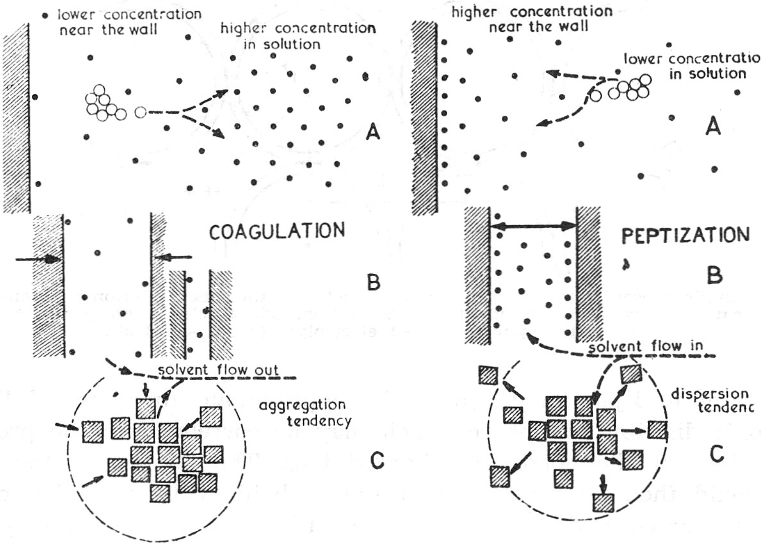


Fig. 22. Schematic representation of the situation near the surface of the colloid particle (macrocomponent) when the concentration of the microcomponent near the surface is *(i)* lower than in the bulk solution; as a result of the differences in osmotic pressures there is the tendency to coagulation (left); *(ii)* larger than in the solution in bulk; as a result of the differences in osmotic pressures there is the tendency to peptization (right).

and the most far-reaching assumed mechanism has to take into account the concentration differences between microcomponents (ions, molecules, colligative units) in the methorical layer and in the bulk of solution: the higher the concentration of such individually active microcomponents in the methorical layer in comparison to that in the bulk of the solution the greater is the stability of the sol. The presentation[22] of the state of things is given by the rough schemes of Fig. 22; the figure is selfexplanatory.

(p) The structural elements of ionic solution

The transition layer may be considered as bridging the gap between the static, fixed matrix, and the dynamic 'lattices' or 'holes' of quasi ordered components and constituents of solution. For this purpose it seems convenient to use the concept of distribution spheres[23] as something like structural elements of the electrolytic solution. Assuming the ideal distribution of ions each ion may be statistically found in a sphere whose radius is obtained by dividing the volume of the solution by the total number of ions present. Such spheres may be considered distribution elements of the statistical structure of the system. The ions attract or repel each other by coulombic interaction of their charges, the potential function being e^2/Dd, where e is the charge in electrostatic units, D the dielectric constant of the solvent and d the distance between the ions.

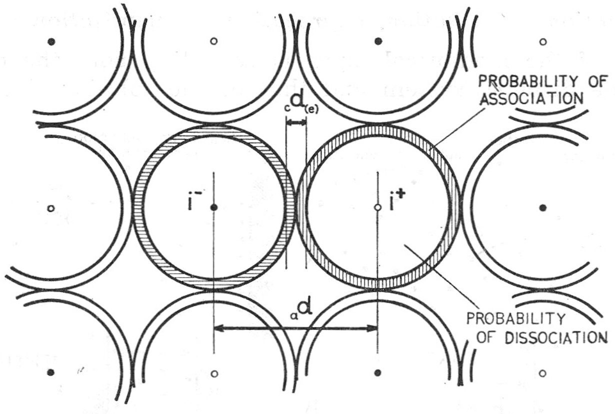


Fig. 23. Schematic presentation of the relationship between the mean interionic distance, $_ad$, and the Bjerrum distance of electrostatic interaction, $_cd$. Circles correspond to the ionic distribution spheres of 1—1 electrolyte (conc. ~ 0.06 *M*).

Acording to Bjerrum, 1/2 $_cd$ is the approximate thickness of the shell of the ionic distribution sphere which may be correlated to the probability of association of the oppositely charged ions. The volume of the internal sphere would then be a function of the probability that the ion exists in a free, dissociated state. Thus, a given ratio between the volume of the inner and outer sphere corresponds to a given activity coefficient of the electrolytic solution. These relations are given in Fig. 23 for a 1—1 electrolyte of approximately 6×10^{-2} *N*.

(q) *The configuration of the distribution spheres in the methorical layer*

At the boundary of the solid there is a special distribution of the sites which may be expressed as two-dimensional discrete charge density of concentration in dynamical equilibrium with the three-dimensional distribution of ionic or other microcomponents in solution. The coverage of localized fixed charges is usually small, about 1% or less of the area exposed, and thus the sites are 20 or 40 Å apart enabling us to treat the interactions of stabilizing ions and counter ions as separate elementary processes.

(r) *The sites of discrete charges*

In the case of ionic crystals the two-dimensional concentration of the fixed sites of charges have to be taken, primarily, as the result of chemical equilibria where the potential determining groups appear as specific chemical species (complexoides). Such a concept enables us to explain the constancy of the zeta-potential, of the critical coagulation concentration, and of the adsorption of counter ions, in spite of the change of excess of one of the precipitating ions. Fig. 24 shows a schematic representation of such a surface where only 1/200 of the possible sites are occupied by one species of complexoides (one charge on ca 1600 Å^2). If there is approximately one charge on 400—1000 Å^2, the density corresponds to the concentration of ions in electrolytic solution of about 0.1 to 0.01 *N*.

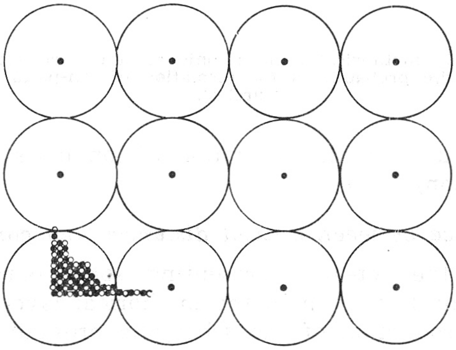


Fig. 24. Schematic presentation of the distribution of potential determining ions on the surface of the ionic crystal (density is about 1 ion on 1,600 A^2).

(s) *The methorical sublayers*

The section through the methorical layer given in Fig. 25, shows specific regions α, β, γ, δ, ε, η, and ξ, and the distribution spheres and shells. This Figure corresponds to the scheme in Fig. 1, but gives the structural elements of sublayers.

In the circumstances for aggregation or desaggregation according to scheme in Fig. 22, the concentration of microcomponents (ions or molecules) in the methorical layer is changed in respect to the concentration conditions of the solution in bulk. According to experimental findings the nearest

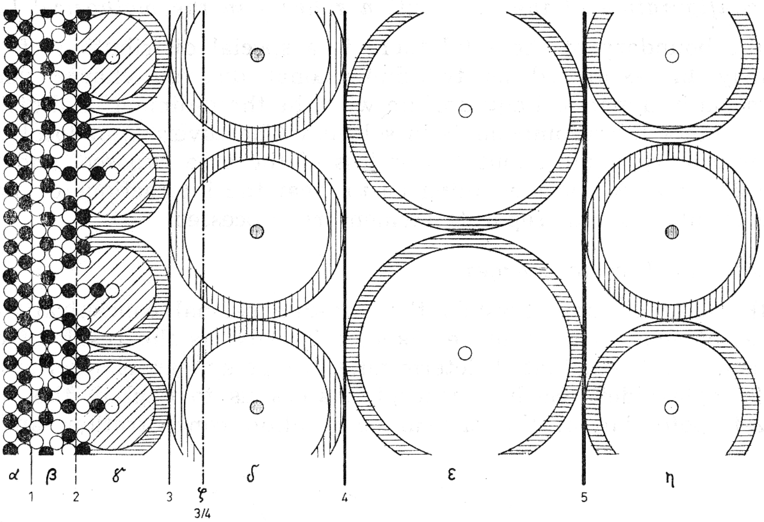


Fig. 25. Interfacial layer in methorical region: ionic crystal electrolytic solution, showing the distribution spheres and the probabilities for formation of ion-pairs (hatched portions of the circles).

answer should be sought in the formation of ion pairs (coagulation) and in adsorption (flocculation).

(t) The correspondence between critical distances and concentrations

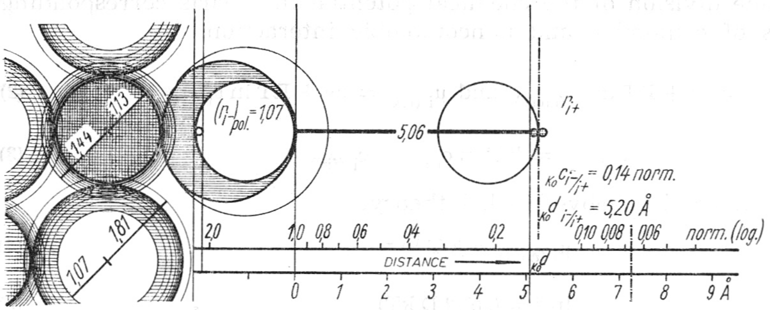
Fig. 26 shows the set-up representing some parameters for critical conditions for ion-pair formation in the methorical layer.

Fig. 26 is a reproduction of the schematic presentation published in Z. *physikal. Chem.* in 1942. The emphasis has been put on the relationship between the critical distances of potential determining ions and counter ions and the critical coagulation concentrations. For the $AgCl/Cl^-$ system and the interacting counter ion it happens that the point of origin (the point of nearest approach to the potential determining ion) coincides with the concentration of 1.0 normality. It should be borne in mind that all these relationships represent the mechanisms which are reflections of dynamical interactions in a methorical region of much greater thickness and in reality they are cumulative statistical results of the processes in γ, δ, ε and η-layers of our scheme in Fig. 25. The critical situation is reached when the probability for formation of ion pairs in the methorical layer becomes greater than the one in the bulk solution. Therefore attention has to be paid to circumstances where we may expect the corresponding states, such as critical coagulation concentration, to be in direct connection with the size and/or valency of counter ions.

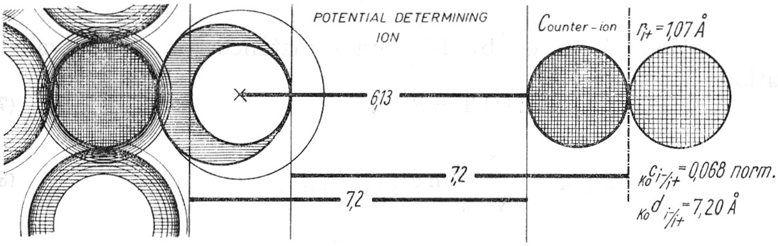
(u) The quantitative expression for the Schulze-Hardy rule

The starting expression is the chemical potential of the counter ion interacting with the fixed univalent potential determining ion of the solid surface[7]:

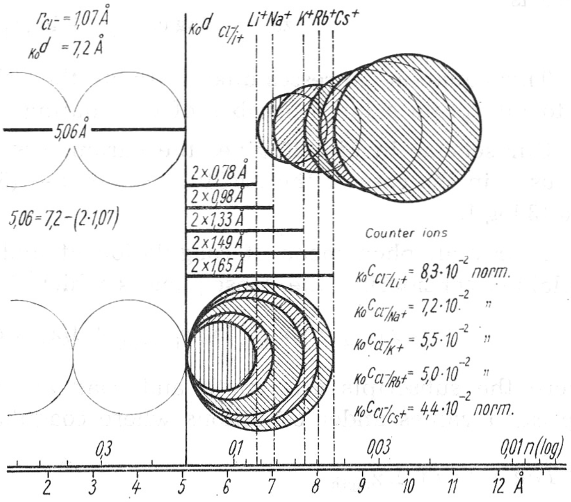
$$\mu_{i\,(coag)} = \mu_{i\,(fix)} + \mu_{i\,(coul)}\,; \qquad (1)$$



Scheme A



Scheme B



Scheme C

Fig. 26. Schematic presentation of the relationship between critical distance ($_{Ko}$d) and logarithm of critical coagulation concentration for AgCl/Cl$^-$-system and positive charge point (scheme A), **counter ion of $r_{l^+} = 1.07$ Å (scheme B), or Li-, Na-, K-, Rb- and Cs-counter ions (scheme C); schemes** show **critical distances and concentrations** just **inside** resp. **outside the range for formation of ion-pairs between** stabilizing ion and counter ion (adapted **Figs.** 9 and 10. **from** *Z. physikal Chem.* **A 191** (1942) 270).

In this we assume division of the chemical potential into parts corresponding to contributions of coulombic and noncoulombic interaction.
According to

$$\mu_{i\,(coag)} = \mu^o + RT \ln c_{i\,(coag)} \text{ and } \mu_{i\,(fix)} = \mu^o + RT \ln c_{i\,(fix)} \tag{2}$$

we obtain

$$\mu_{i\,(coul)} = k\,T \ln c_{i\,(coag)}/c_{i\,(fix)} \tag{3}$$

Introducing from the Debye-Hückel theory:

$$\mu_{i\,(coul)} = k\,T \ln f \tag{4}$$

and

$$\ln f = (ze^2/2\,D\,kT) \tag{5}$$

we obtain a simple relationship

$$-(ze^2/2\,D\,kT) = \frac{1}{\varkappa} \ln c_{i\,(coag)}/c_{i\,(fix)} \tag{6}$$

The critical condition is given by Bjerrum's distance for uni-univalent ion pair formation

$$e^2/2\,D\,kT = \delta_{crit.}, \tag{7}$$

thus giving

$$-z\,\delta_{crit} = \frac{1}{\varkappa_{meth}} \ln c_{i\,(coag)}/c_{i\,(fix)} \tag{8}$$

or expressing

$$\frac{\delta_{crit} \cdot \varkappa_{meth}}{0.4343} = a$$

there is

$$za = -\log c_{i\,(coag)} + \log c_{i\,(fix)} \tag{9}$$

This equation expresses quantitatively the Schulze-Hardy rule and enables us to interprete a large number of coagulating systems.

Our scheme in Fig. 26 gives the parameters for univalent counter ions of radius r_i in the case of the AgCl/Cl$^-$ system: $-(5.06 + 2\,r_i) = 6.13 \log c_{i(coag)} - 6.13 \log 1$.

Nearly all phenomena of coagulation of hydrophobic sols could be easily explained considering the consequences which follow from

$$-z\,\delta_{crit} = 1/\varkappa_{meth} \log c_{i\,(coag)} + 1/\varkappa_{meth}\, c_{i\,(fix)} \tag{10}$$

where the subscripts crit, meth and coag are pointing to the symbolically expressed values under conditions where coagulation takes place.

(v) The role of $1/\varkappa_{meth}$

It should be expresely stated that $1/\varkappa_{meth}$ is a critical thickness of the ionic atmosphere in the methorical layer and not that of the solution in bulk. Our scheme[7] in Fig. 26 gives this characteristic length in angstrom units (6.13 Å) corresponding to 1 logarithmic unit of the concentration of counter ions in normalities. While δ_{crit} is always approximately constant, or could be easily quantitatively expressed, $1/\varkappa_{meth}$ is a function of a large number of factors (presence of other ions and molecules in solution) and therefore the linear relationship such as in Figs. 27, 28 between the logarithm of critical coagulation concentration and Bjerrum's distance[24] may be the best

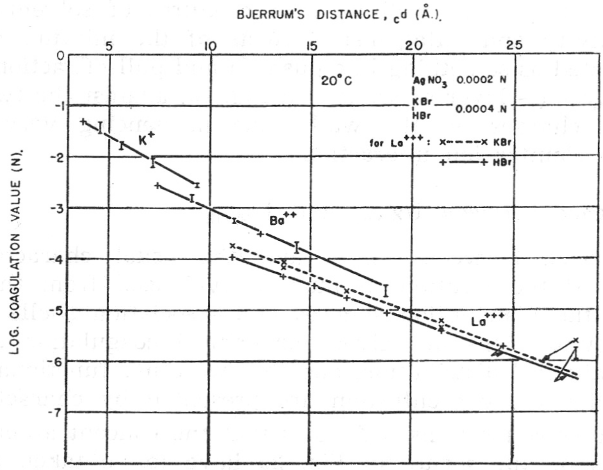


Fig. 27. Critical coagulation concentrations *vs.* Bjerrum's distance for various values of the dielectric constant. The data for various isodielectric mixtures fall within short vertical lines.

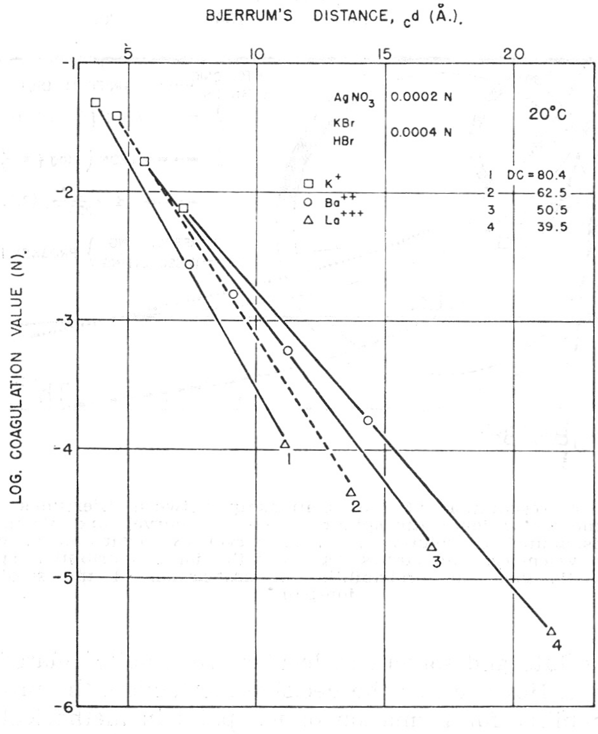


Fig. 28. Critical coagulation concentrations *vs.* Bjerrum's distance as they change with the valency of counterions for several dielectric constants. The points denote the mean values of coagulation concentrations for various isodielectric mixtures.

guide for the investigation of various systems in respect to their correspondence of state.

With such concepts it is easy to explain the effects connected with mixtures of electrolytes as well as with mixtures of solvents or solutions. The superadditivity and antagonistic effects of the mixture of electrolytes may be interpreted as something like push-on and pull-off action, respectively, of the co-ion layer (ε- layer of scheme in Fig. 25) against the two-dimensional distribution of charges on the wall, thus influencing very strongly the stabilizing ion—counter ion interactions.

(x) *The difference between* $1/\varkappa_{\mathrm{meth}}$ *and* $1/\varkappa_{\mathrm{bulk}}$

The difference between $1/\varkappa_{\mathrm{meth}}$ and the usual characteristic Debye-Hückel length of the solution in bulk is evidenced from the scheme[25] in Fig. 29 where the distribution spheres and association shells for potassium and barium counter ions are given for critical coagulation concentrations; the uniform statistical distribution, and the two other functional relationships of $1/\varkappa$-value with the concentration are presented by characteristic curves.

From these considerations it follows that the concentrational and dimensional elements of our set-up in Fig. 26 have to be taken as statistically representative interactions where such factors as atmosphere of co-ions, and other ions, solute and solvent molecules are usually related to the macro dielectric constant. However, as the decisive mechanism the process expressed by greater probability for formation of ion pairs in methorical layer, should always be taken and the consequent lowering of the microcomponent concentration, in comparison with the situation in the bulk solution.

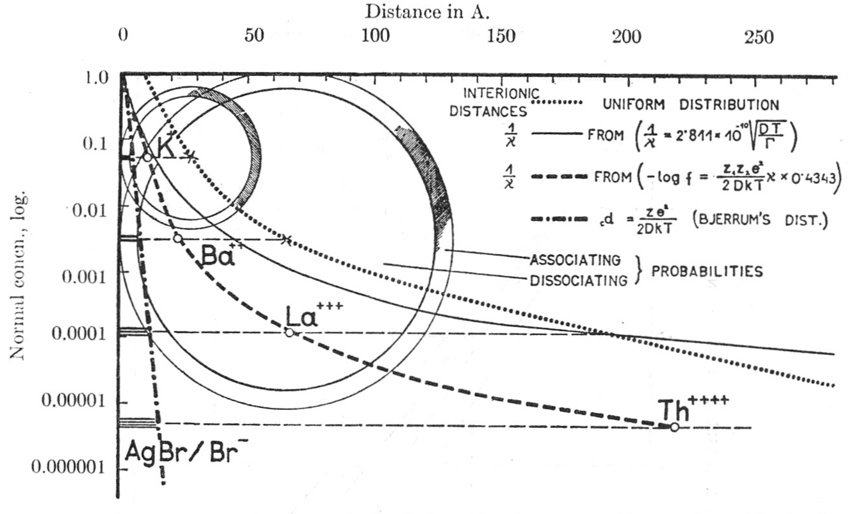


Fig. 29. Schematic representation of the relationship between Bjerrum's critical distances (–·–·– line), thicknesses of ionic atmosphere (———— curve), and distances between ions when uniformly distributed in solution (....... curve) *vs.* logarithm of coagulation value for ions of various valencies. The circles represent the ionic distribution spheres, while the partially shaded shells give the probabilities of association of the stabilizing-coagulating ion-pairs.

(y) The $c_{meth} - c_{bulk}$ *relationships*

Such differences in concentrations in the methorical layer, c_{meth}, and in bulk solution, c_{bulk}, have to be made responsible also for the characteristic sensitization, flocculation and protection phenomena caused by species which show greater adsorptivity towards the solid. The usual relationship between the stability of the colloid system and the concentration of such species is represented by flocculation maxima; on the side of smaller concentrations there are sensitization effects caused by changed conditions in respect to charged sites on the wall; then there is a flocculation maximum expressing the condition of greatest deficit of microcomponents in the methorical layer owing to formation of a complete adsorption layer; and afterwards, at still greater concentration there the behavior is determined by the presence of protecting film. In accordance with our scheme in Fig. 22 the general formulation for stabilization, peptization and protection is $c_{meth} > c_{bulk}$, or for aggregation, coagulation and flocculation, $c_{bulk} > c_{meth}$. Fig. 30 summarizes the whole concept[26]. This is a figure of partly hypothetic and partly experimental character which may have its reflections in the concepts of dynamical structure of γ, δ, ε, and η-layers, as well as in the electrokinetical and dynamical plane of shear (ξ-layer).

In reality there are critical concentrations and phenomena that indicate that in spite of the differences in neutral electrolyte effects (coagulation) and adsorption effects (flocculation) a common cause of the instability of colloidal particles is the concentrational deficiency of microcomponents in the methorical layer as compared with the concentration in the bulk solution.

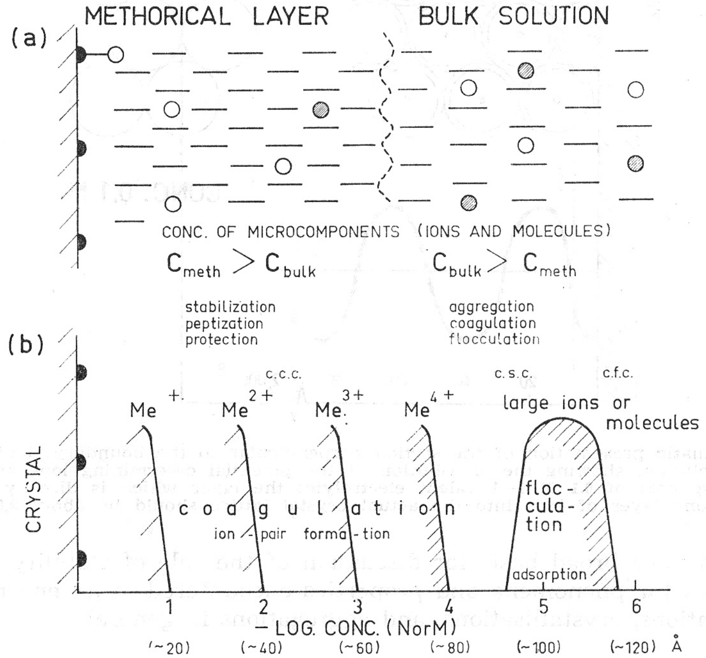


Fig. 30. Schematical presentation of corresponding states of interacting species (ions or molecules) of solution with constituents of solid phase boundary, controlling either coagulation (ion-pair formation), or flocculation and protecting stabilization (specific adsorption).

(z) The application to formation of real crystals

Such a concept gives, probably, a correct and simple explanation also to very common phenomena that real crystals are nearly always composed of small crystallinic units or submicrons. If the mass of the ions in the adjoining liquid layer of a growing crystal which are necessary for building only one complete layer of the crystal lattice is taken into account, there should be a significant deficiency of microcomponent concentration at the boundary when such condensation is taking place. Thus, again, owing to $c_{bulk} > c_{meth}$ a strong tendency for aggregation should be the result. Such circumstances are schematically presented[27] in Fig. 31, and the consequences may give a very broad basis for discussion of the role of stability-instability relationships for phenomena and properties encountered in an enormous field of precipitations, crystallisations, and aggregations in general.

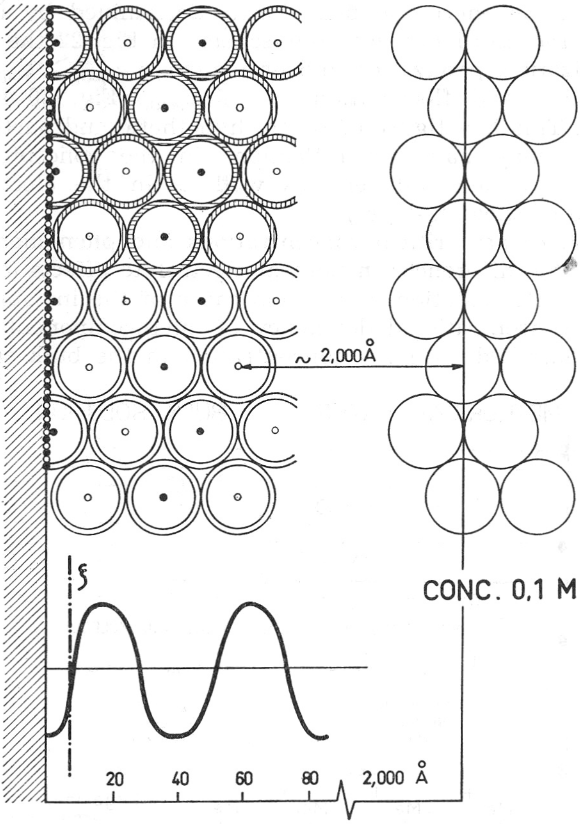


Fig. 31. Schematic presentation of the section perpendicular to the boundary: ionic crystal — electrolytic solution, showing the distribution of the potential determining ions and the ionic distribution spheres of 0.1 *M* 1—1 valent electrolyte; the layer which is directly engaged in building up one layer of ions into the actual crystal lattice should be about 2,000 Å thick.

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IZVOD

Međupovršine između faza kruto/tekuće

Opći uvod

B. Težak

Kao uvod u radove Internacionalne ljetne škole i konferencije: *Kemija međupovršina između faza kruto/tekuće (International Summer School and Conference The Chemistry of Solid/liquid Interfaces,* Dubrovnik Cavtat, 1969) dane su napomene prema poglavljima: (I) Historijski i opći osvrti; (II) Terminologija; (III) Putevi eksperimentalnih i teoretskih istraživanja međugraničnog sloja; (IV) Neke eksperimentalne činjenice; te (V) Neki mehanizmi, koncepti i modeli za pojave kod kojih je međugranični sloj (metorički sloj) bitni faktor.

Koloidni sistemi u »statu nascendi« su uglavnom upotrebljavani za opisivanje karakterističnih pojava te za tumačenja s pomoću predloženih mehanizama. Stvaranje ionskih parova između iona koji određuju potencijal koloidnih čestica (kompleksoida) i protuiona uzeto je kao uzrok za smanjenje koncentracije mikrokomponenata u metoričkom sloju u uporeðenju s koncentracijom u unutrašnjosti otopine, $C_{meth} < C_{bulk}$, te prema tome predstavlja kritičnu koagulacionu koncentraciju. Pojave flokulacije su slično protumačene promjenom koncentracije iona i molekula u metoričkom sloju uslijed adsorpcije (kod manjih koncentracija skoro potpuno odstranjenje mikrokomponenata iz metoričkog sloja uzrokujući senzitizaciju i maksimum flokulacije, dok kod viših koncentracija, nakon maksimalnog adsorpcionog prekrivanja koloidnih čestica, omogućava se viša koncentracija mikrokomponenata u metoričkom sloju što se izražava stabilizacijom i protekcijom). S ovim pristupom mogu se tumačiti skoro sve pojave stabilnosti i nestabilnosti koloidnih čestica u elektrolitnim medijima.

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