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Conference Paper

Precipitation Processes in Concentrated Electrolytic Solutions and Temperature Effects on Silver Halide Sols *in statu nascendi**

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For the differentiation of physical, and chemical characteristics of various interactions playing part in interboundary layer (methorical layer) of solid/liquid systems the kinetics of precipitation under systematic variation of internal and external factors, and especially of concentration and temperature, is used.

The discontinuities in the formation of the precipitate as well as the differences in the morphology and behavior enables the definition of the formation of various substructures as a result of at least five subsystems from which the precipitating system is usually composed.

For illustration some ionic systems, mainly exemplified by silver halides, where the complexation, embryonation, nucleation, crystal growth, micellation (formation of primary particles), and aggregation (two-step crystallisation, coagulation, or flocculation) could be distinguished, are presented.

The solubility effects (in very great excess of one of the precipitating ion — the complex solubility, and the simple ionic solubility) and the changing pattern of the precipitation maxima between two extremes are correlated to the prevailing tendencies either of agglomeration (concentration maxima) or of ordering (crystallisation maxima). The concentration maximum, and especially the boundary towards the complex solubility limit is characterized by various approaches to equilibrium states by direct mixing of precipitation components at 20 °C, or by cooling the homogeneous, already mixed systems from 90 °C to 20 °C.

The chemistry and physics of the surface layer of the solid, the structure and specific concentrational condition (*e. g.*, the steady state in the stagnant layer) of the constituents in methorical layer, and the chemical and physical changes occurring owing to the difference in concentrations and entropy either in the methorical layer or in bulk solution, are taken as responsible for stability/instability conditions of the emerging colloidal particles.

For discussion of such effects the discontinuities in the kinetics ('critical time' and 'corresponding critical time') of precipitation of silver halides are related to various precipitation maxima (concentration, isoelectric, crystallization, transition), and to coagulation of simple counter ions at various temperature (in

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[**] in collaboration with E. Bonetta, D. Dimitrovski, I. Fišer, M. Kramberger, and N. Stubičar.

the range between 5° and 90 °C). It was found that the usual influence of the size and valency of counter ions in the whole range of temperature is preserved. In general, the behavior of the systems under small but definable step by step changes in concentration and temperature reveal many features which should be considered as essential in discussing crystallisation and precipitation phenomena.

There is an enormous number of facts about the influence of the concentrational environment and temperature effects on the formation and qualities of precipitates in analytical and synthetic chemistry. As we have devoted much attention to the model systems of silver halide precipitates, it seems appropriate to investigate, from a more general point of view, not only the behavior of such systems as sols *in statu nascendi,* but also those parts of the 'precipitation body' where the crystallization and the aggregation phenomena, as well as coagulation or flocculation, may have a prominent role. Those parts may especially be of interest where there are interferences of processes other than the situations with regular steady state flow of material accross the liquid/solid boundary. Namely, the regular growth, *e. g.* of seed crystalls can be accomplished only under quite special precautions, while in nature, laboratory, and technological applications, other cases prevail. To follow the approaches which started about forty years ago, it may be time to summarize the results.

For such a purpose direct or indirect observations of discontinuities in the formation of the crystalline precipitate from electrolytic solution in relationship to substantial composition, volume, pressure, temperature, mode of mixing, and effects of external fields (gravitational, magnetic, electric, ultrasonic, thermal, radiation, *etc.*), may be very indicative for special conditions, structures, and compositions characterizing all or some of the transition steps from homogeneous solution to real solids.

For the elucidation of the role of some of these factors it seems necessary to gather a great number of various experiences with one series of systems where substantial characteristics are either similar or differing only in one or very few properties. In this respect there are already very extensive studies of some of such series, reported *e. g.*, those of silver halides, or sparingly soluble sulfates. Leaving a broader discussion of the similarities and differences of the various series for an other occasion, we will try to present through some diagrams the characteristic features of silver halides. Of course, the limitations of our approach, also, have to be made clear. Namely, we have followed a simple and very frequently used technique of direct mixing of solutions containing the precipitating components. How much possibility such a method gives to draw conclusions about the state of the constituents, and their interactions with emerging subsystems, has to be left to experiments. The starting point for our considerations was to ascertain if and when some discontinuities appear in the process of the formation of the precipitate as a function of a small but definable variation of influencing factors. For the greater part, we used tyndallometry as probably the simplest and most direct method of observation. Dealing with predominantly white sols, it was possible by using the so called DQ_T-Method (tyndallometrical dispersion quotients for the scattering of blue and red light by particles) to obtain the approximate size of the particles.

Influence of Concentration

As to the influence of concentrations it is necessary to distinguish at least four groups, namely:

(1) of the main precipitating components, especially, when one is kept constant while the other undergoes systematic variation;

(2) of the various so called foreign electrolytes while the concentrations of the main precipitating components are kept constant;

(3) of the various solutes, especially of polyionic and macromolecular character; and

(4) of the mixed solvents (changing the dielectric constant, chemical interactions, *etc.*).

As to the influences of temperature the whole range from 5 to 90 °C may be of interest, because there are not only the changes of solubility but also essential processes of dynamic interplay of equilibrated and non-equilibrated situations responsible for stability/instability states, interfering with the aggregation of particles during their crystal growth.

Besides such influences it should not be forgotten the possible interventions of the 'age' of solution, or the purity and mode of their preparation, as well as the reproducibility of the manner of mixing of the precipitating solutions.

'Precipitation Bodies' and 'Precipitation Maxima'

The overall state of the systems about 10 minutes after mixing of silver nitrate and potassium chloride precipitating solutions may be represented by a 'precipitation body' as shown in Fig. 1. Similar 'bodies' may be found for

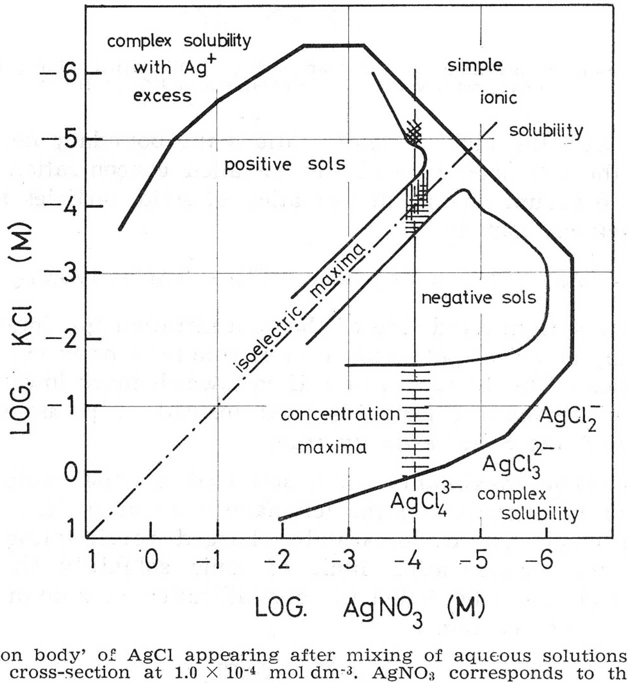


Fig. 1. 'Precipitation body' of AgCl appearing after mixing of aqueous solutions of $AgNO_3$ and KCl at 20 °C; the cross-section at 1.0×10^{-4} mol dm^{-3}. $AgNO_3$ corresponds to the tyndallogram presented in Fig. 2.

silver bromide and silver iodide[1]. The typical section representing the so-called concentration tyndallogram, where the concentrations of potassium chloride varied from 1.0 to 1×10^{-6} mol dm^{-3} while the concentration of silver nitrate was kept constant at 1.0×10^{-4} mol dm^{-3}, is given in Fig. 2. There are three maxima different in character[2].

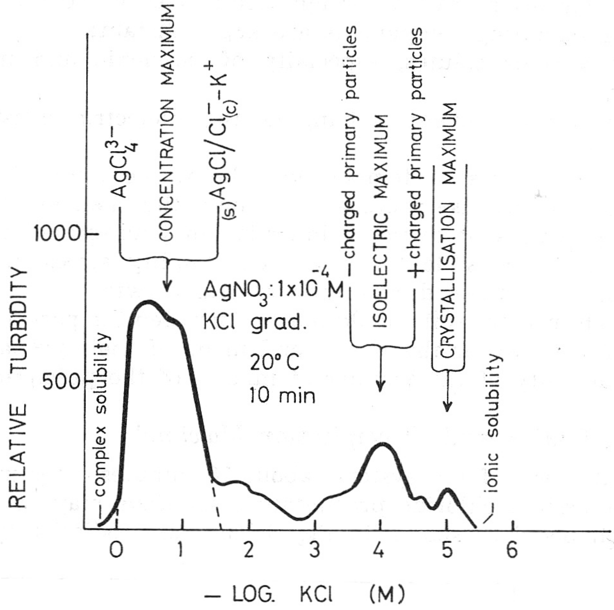


Fig. 2. Cross-section of 'precipitation body' appearing 10 min after mixing 1.0×10^{-4} mol dm^{-3}, $AgNO_3$ with varying concentrations of KCl at 20 °C.

Starting with the highest concentrations the boundary between the clear system and the left-hand side of the so-called concentration maximum demonstrates the abrupt change in formation of solid particles by at least two kinds of reactions, namely:

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)}, \text{ and } AgCl_4^{3-} + 3\,Ag^+ \rightarrow 4\,AgCl_{(s)}$$

The limit on the right-hand side of the concentration maximum is caused by the coagulating action of potassium ions as counter ions to negatively charged primary particles. This limit may be shifted towards much lower concentrations if barium or lathanum chloride is used instead of potassium chloride, in accordance with the Schulze-Hardy rule.

The isoelectric maximum is characterized by the rapid neutralization of predominantly negative (on the left-hand side) or positive (on right-hand side) primary particles by oppositely charged precipitating ions. Finally, approaching the concentration limit of ionic solubility there is a small maximum which could be called the crystallization maximum formed by the predominatly ionic reactions:

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)};$$

while the left-hand limits of the maximum have to be attributed to the stabilizing action of the excess of precipitating ions, the right-hand side is open to ionic solubility. This last limit may be very much dependent on the quantity of solid substance, as well as on time. By reducing the concentrations of silver nitrate the crystallization maximum[3] is shifted towards higher concentrations of the chloride component as it is shown in Fig. 3.

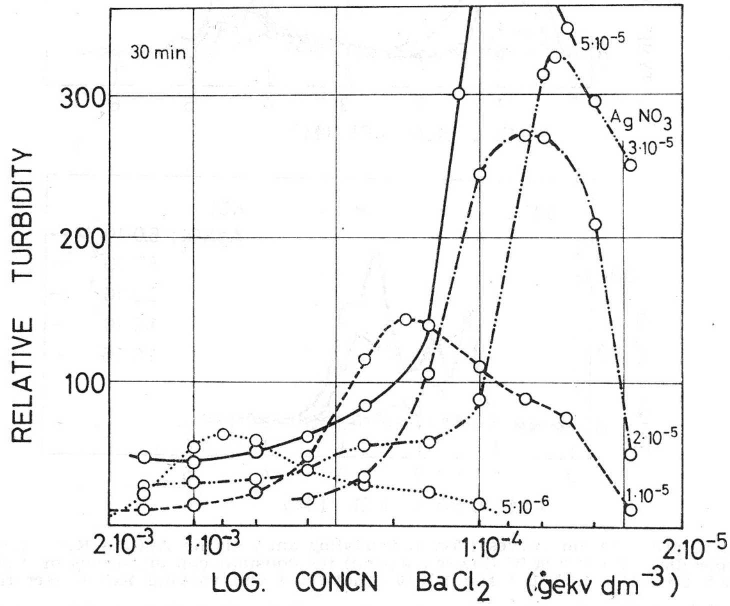


Fig. 3. Concentration tyndallogram of the series of systems 30 min after mixing of either 5×10^{-6}, or 1×10^{-5}, or 2×10^{-5}, or 3×10^{-5}, or 5×10^{-5} mol dm^{-3} solutions of $AgNO_3$ with varying concentrations of $BaCl_2$, at 20 °C.

Temperature Effects

By performing such series of precipitations at higher temperatures the phenomena are radically changed. Instead of two characteristic maxima at highest and lowest concentrations there is only one maximum in the middle, as it is exemplified in Fig. 4, a and b. The systems of silver bromide and silver iodide behave similarly, only in a wider range of concentrations; the differences are in much slower rise of the maximum or maxima in the transitional region of concentrations between two extremes.

While the crystallization maxima may be regarded as the nearest to the general conceptions about the formation of crystalline aggregates, special attention should be directed to more complex cases of precipitation at higher concentrations. In that region the limit between the non-precipitating and precipitating systems is certainly caused by the formation of complexes, either mononuclear or polynuclear. Their composition may be approximately identified[4] by the slopes in the diagrams in Fig. 5.

However, the effect of higher temperature is reflected also at the other boundary of our concentration maximum, as it is illustrated by composite diagrams in Fig. 6, where besides situations presented in Fig. 5, there are schematic presentations of what happens by raising the temperature in con-

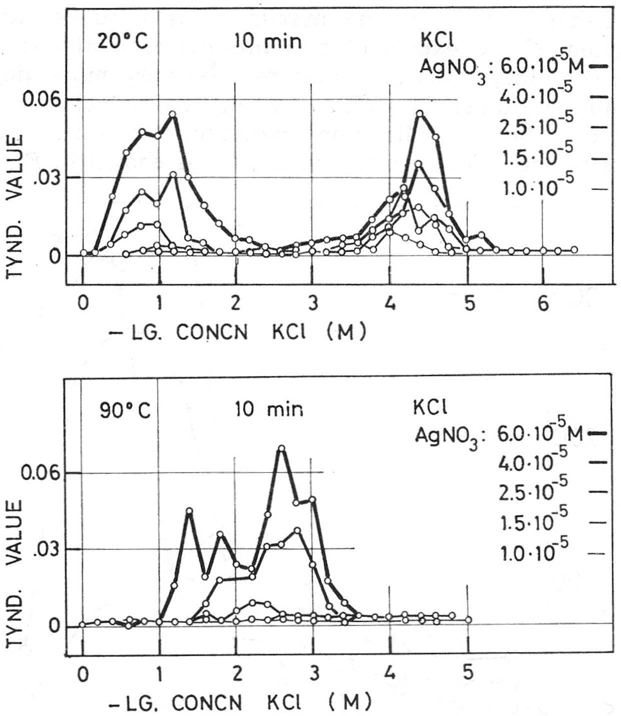


Fig. 4. Typical precipitation curves (10-min tyndallograms) of the $AgNO_3$—KCl aqueous systems at 20 °C (upper diagram) and 90 °C (lower diagram) for constant concentrations of $AgNO_3$ (6×10^{-5}, 4×10^{-5}, 2.5×10^{-5}, 1.5×10^{-5} and 1×10^{-5} mol dm^{-3}) and varying KCl concentrations.

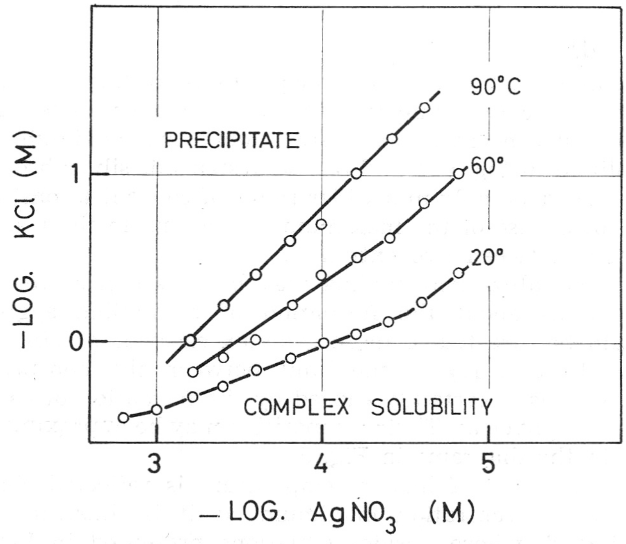


Fig. 5. Temperature effect 20, 60 and 90 °C) on the boundary between precipitating and non-precipitating systems of $AgNO_3$—KCl aqueous solutions (KCl excess).

centrational sections along variation of silver nitrate (potassium chloride: 4×10^{-1} mol dm^{-3}), or potassium chloride (silver nitrate: 1×10^{-4} mol dm^{-3}), concentrations, respectively. By encountering a multitude of factors influencing the chronology and morphology of precipitates it seems worthwhile to see many more features of this region.

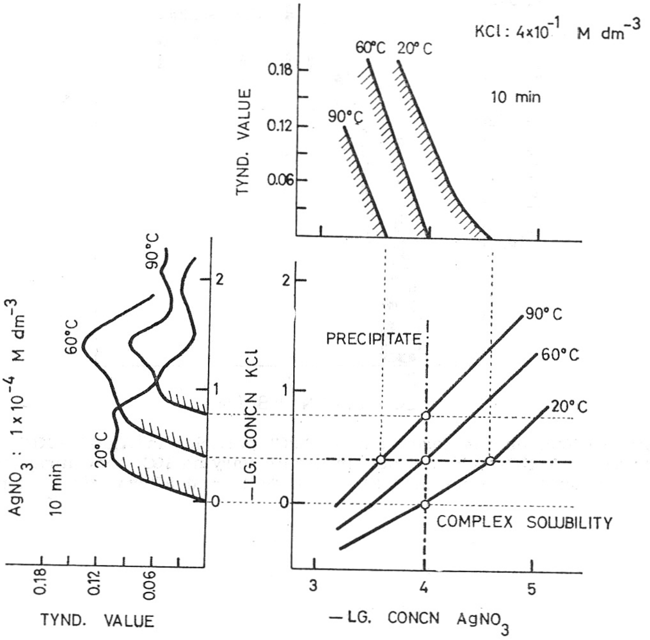


Fig. 6. Schematic presentation of the effect of temperature (20, 60 and 90 °C) on aqueous systems of KCl (4×10^{-1} mol dm^{-3}) and varying $AgNO_3$ concentrations (upper part), and of $AgNO_3$ (1×10^{-4} mol dm^{-3}) and varying KCl concentrations (left part), 10 min after mixing of precipitating components.

One of the first tasks should be to see how far the appearance and morphology, or at least the size of the grains, correspond to the changed temperature conditions. Two approaches may be illustrative for this purpose, one by the direct mixing of the component solution, and the other by cooling the system consisting of already mixed but clear solution owing to the complex solubility at higher temperature. Figs. 7 and 8 show the splitting of that part of the concentration maximum which is on the boundary toward complex solubility. Thus, there is a diference in the formation of the precipitate when we are preparing the systems by direct mixing at 20 °C or by cooling the mixture from 90 °C. In a new minimum, or in a region connecting the higher turbidity limit to the limit of complex solubility, there are larger particles, and if the cooling is performed in the presence of a neutral electrolyte, monodisperse sols may appear on the right-hand side of the new minimum of turbidity. Similar effects could be detected with silver bromide and silver

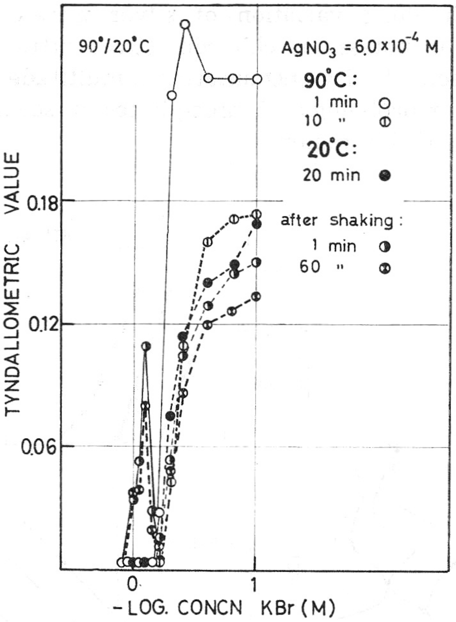


Fig. 7. Temperature effect on the formation of AgCl particles in AgNO$_3$—KCl aqueous systems cooled from 90 to 20 °C; AgNO$_3$ (6×10^{-4} mol dm^{-3}) with varying KCl concentrations; after cooling, the systems were standing 20 min at 20 °C, and afterwards shaken.

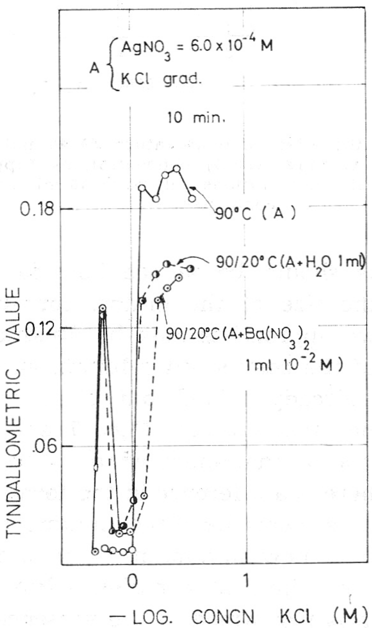


Fig. 8. Temperature effect on the formation of AgCl particles in AgNO$_3$—KCl aqueous systems cooled from 90 to 20 °C: A — to 9.0 cm^3 of AgNO$_3$—KCl systems at 20 °C, 1.0 cm^3 water was added; B — 1.0 cm^3 BaNO$_3$ (1×10^{-2} mol dm^{-3}) was added.

iodide systems. The composite effects of embryonation, nucleation, crystal growth, and coagulation, the kind of ions in the initial stages of mixing, or the gradual rise of temperature dependent supersaturations control the formation of precipitate in such cases. Some systems with lower concentrations of foreign ions (in the simplest case the accompanying ions of the precipitating electrolyte) may show how far the influences of each of these factors could be isolated. For this reason the attention should be paid to the right-hand limit of the concentration maximum. Therefore, some of the temperature effects are shown for silver bromide systems in Figs. 9, 10, 11, and 12. The

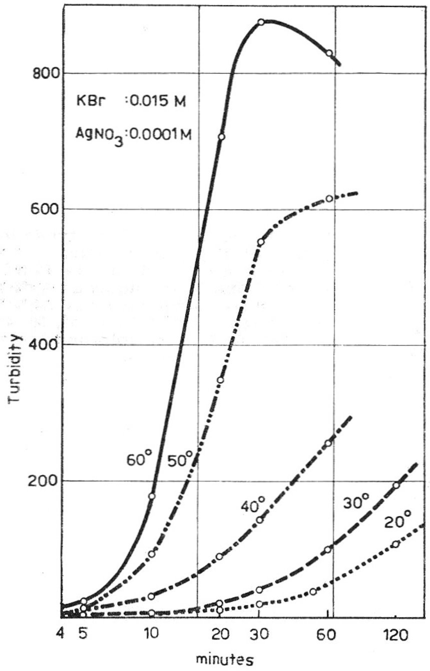


Fig. 9. Temperature effect on the relative turbidity of aqueous systems of $AgNO_3$ (1.0×10^{-4} mol dm^{-3}) and KBr (1.5×10^{-2} mol dm^{-3}) at 20, 30, 40, 50 and 60 °C.

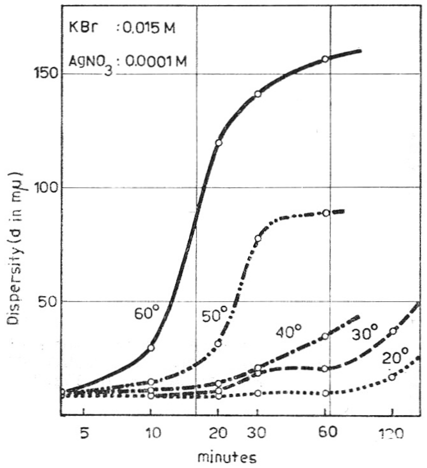


Fig. 10. Temperature effect on the dispersity of the systems presented in Fig. 9.

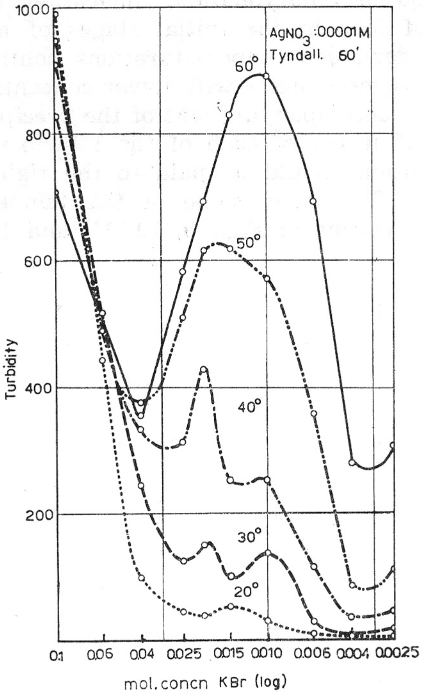


Fig. 11. Concentration tyndallograms of the concentration (1.0 × × 10^{-4} mol dm^{-3}) and varying 60 min after mixing of the aqueous $AgNO_4$ —KCl systems for constant $AgNO_3$ concentrations of KBr at 20, 30, 40 50 and 60 °C; precipitating components.

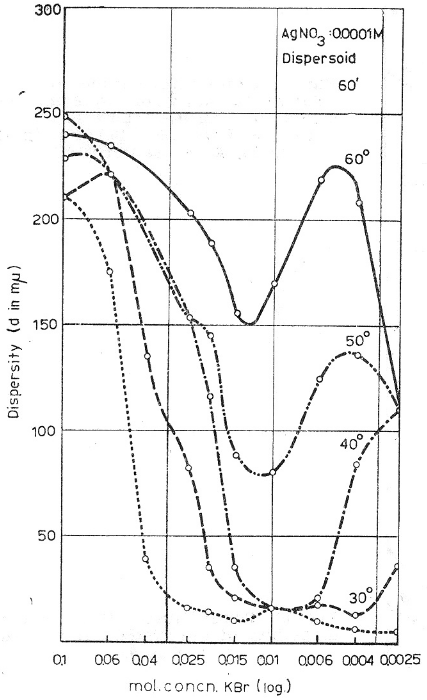


Fig. 12. Concentration dispersoidograms of the aqueous $AgNO_3$—KCl systems presented in Fig. 11.

deformation of the coagulation boundary and the rise of a new turbidity maximum consisting of the smallest particles are shown in these diagrams. For an analysis of the conditions which can enable the determination of coagulation characteristics under changed temperature conditions we shall present some figures describing the results with silver iodide systems.

'Critical Times' of Precipitation

Fig. 13 shows the various developing stages for silver iodide in the presence of various concentrations of calcium nitrate. The intersections of the lines which were drawn from the steepest part of the rising values of turbidity with the abscissa are taken as critical times[5].

Fig. 14 gives the basis for the determination of the characteristic critical times which represent discontinuities in a plot of the logarithm of critical times against the logarithm of corresponding concentrations.

Figs. 15 and 16 show what are the differences when the usual coagulating—non-coagulating limits for the determination of the critical coagulation concentration (coagulation value) are used either after 10 minutes or after corresponding critical times. There are some shifts of the limits with temperature towards lower concentrations in both cases; however, the corrections by using characteristic critical times seems to eliminate the errors due to accelerating growth of the primary particles with rising temperature.

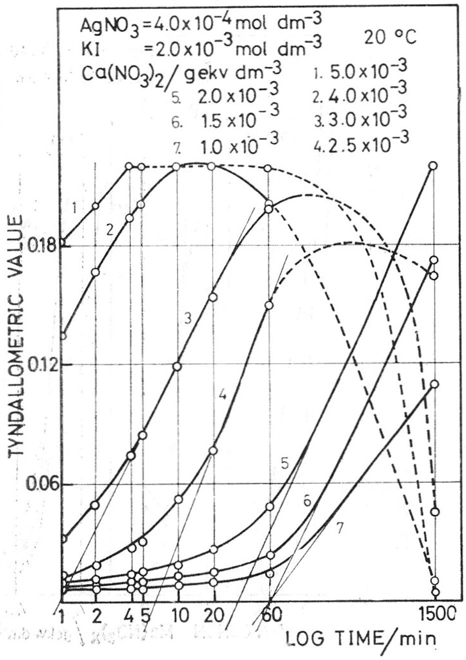


Fig. 13. Time (log) tyndallograms of the aqueous systems with constant concentration of $AgNO_3$ (4.0×10^{-4} mol dm^{-3}) and KI (2.0×10^{-3} mol dm^{-3}) and varying concentrations of $Ca(NO_3)_2$ at 20 °C; intersection points of the linear continuation of the steepest part of the rising tyndallometric values and the abscissa denote 'critical times' of coagulation.

The dependence of the logarithm of the critical coagulation concentration of various univalent and divalent counter ions on absolute temperature is given in Figs. 17 and 18, respectively. There are similar relationships for silver

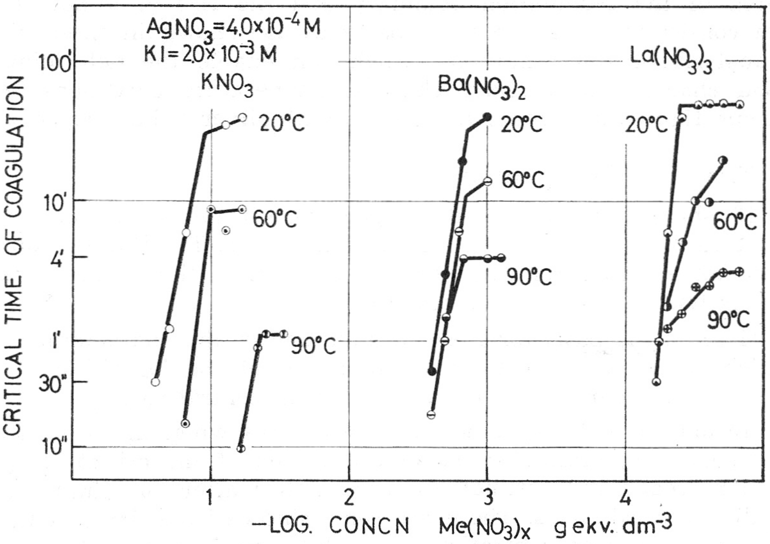
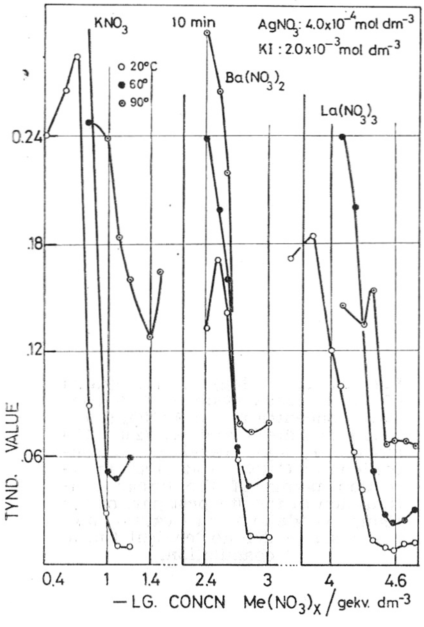


Fig. 14. Plot of critical times of the aqueous systems with constant concentration of AgNO$_3$ (4.0 × 10^{-4} mol dm^{-3}) and KI (2.0 × 10^{-3} mol dm^{-3}) against varying concentrations of KNO$_3$, Ba(NO$_3$)$_2$ and La(NO$_3$)$_3$ at 20, 60 and 90 °C showing the 'corresponding critical times' as the discontinuities in relationship between the critical times and concentration of counter ions.



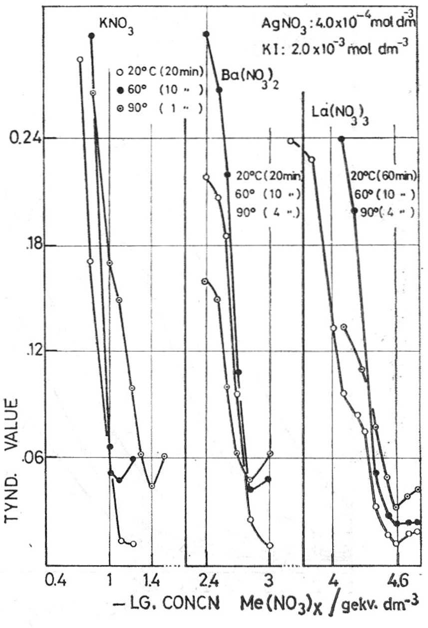


Fig. 15. Concentrations tyndallograms (10-min after mixing) for the aqueous systems of AgNO$_3$ at 4.0 × 10^{-4} and KI at 2.0 × 10^{-3} mol dm^{-3} and varying concentrations of KNO$_3$, Ba(NO$_3$)$_2$ and La(NO$_3$)$_3$ at 20, 60 and 90 °C.

Fig. 16. Concentration tyndallograms for the systems presented in Fig. 15 but instead of 10-min the corresponding critical times are used.

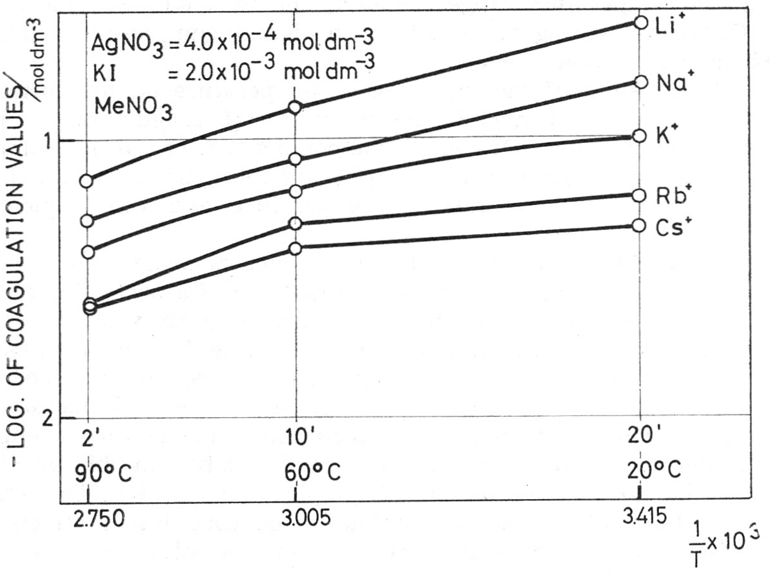


Fig. 17. Dependence of the coagulation values of univalent counter ions at correspondent critical times on the absolute temperature for aqueous system of $AgNO_3$ at 4.0×10^{-4} and KI at 2×10^{-3} mol dm^{-3}.

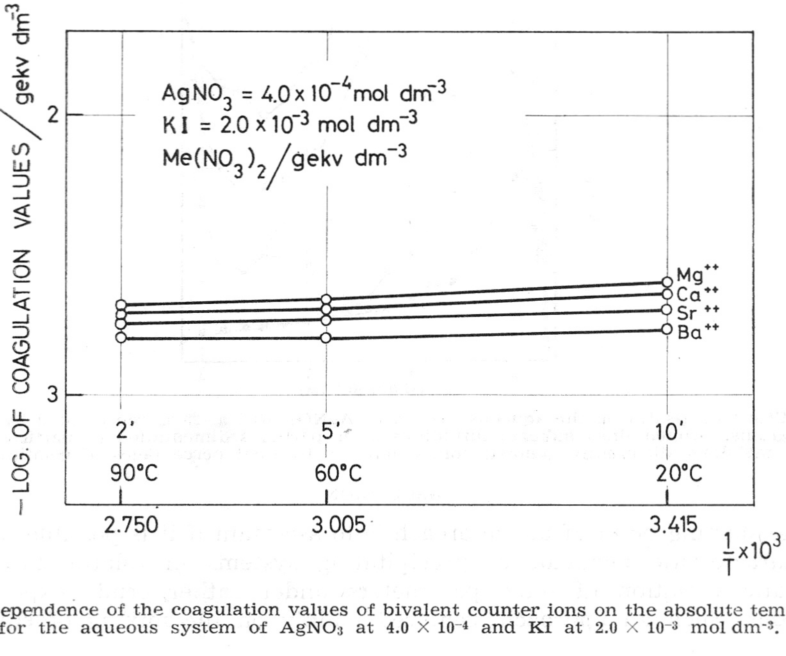


Fig. 18. Dependence of the coagulation values of bivalent counter ions on the absolute temperature for the aqueous system of $AgNO_3$ at 4.0×10^{-4} and KI at 2.0×10^{-3} mol dm^{-3}.

bromide in the temperature range 20—90 °C and for silver chloride from 5 to about 60 °C; the coarsening of particles at a higher temperature usually overshadowed the coagulation effects.

Generally, in spite of the influence of temperature on the formation of complexes, embryos, and nuclei, the processes of coagulation of primary particles could be revealed. Of course, the composition of various components, starting from the concentration of precipitating solutions, solvent and various solutes' characteristics, their mixing, temperature and time, among other factors, have to be respected.

Just such special conditions, and the presence of some substances in the system may help to eliminate or accentuate the role of a particular component or factor. In this respect it seems necessary to distinguish at least as stability/ /instability factors those which may be responsible for the aggregation of crystallites during their growth, coagulation, and flocculation. Especially the flocculation and stabilization effects of polyelectrolytes and macromolecules may intervene during the formation of precipitates causing very strong effects on their morphology. Gelatine, for instance, may sensitize, inhibit, or eliminate[6] all together the coagulating action of simple counter ions. The results in Fig. 19 show that 0.4% gelatine eliminates the coagulation effects on the right-hand side of the concentration maximum of silver chloride. Similar effects will be found also in systems where the concentration of the neutral electrolyte is quite high (*e. g.* 0.5 mol dm^{-3} $NaNO_3$).

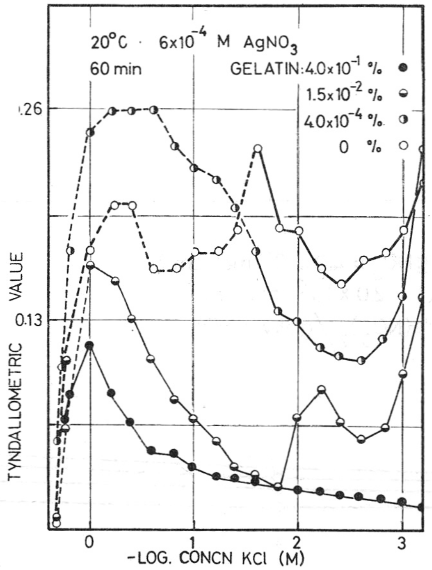


Fig. 19. Effect of gelatin on the aqueous system of $AgNO_3$—KCl at 20 °C represented by a 60-min tyndallograms. Broken lines indicate turbidities after partial sedimentation of particles; $AgNO_3$ 6.0 × 10^{-4} mol dm^{-3}; differently denoted points indicate different percentages of gelatine content.

DISCUSSION

The starting point of our approach is to ascertain if it is possible to reveal the characteristic behavior of precipitating systems in relationship to the systematic variation of some parameters under rather crude experimental conditions. Such an approach, centered mainly on the mixing of equivalent amounts of precipitating components giving precipitates of barium sulfate was a life-long occupancy of P. P. von Weimarn[7], S. Odén[8], and D. Balarew[9]. G. A. Hullet[10], Th. Richards[11], O. Hahn[12], I. M. Kolthoff[13], R. Willstätter[14], V. Kohlschütter[51], L. G. Sillén[16] may be mentioned among those who moved the frontier of our knowledge to a better appreciation of the most important factors playing part in the formation of precipitates. However, some missing roles and links of complex and dynamic assemblies put forward the need to take into account some basic characteristics of the precipitating systems more systematically. Among these there are some which were elaborated in sometimes quite separate fields of research, *e. g.*, nature of electrolytes, solubility of solids, origin and transfer of charges on the solid particles, phenomena of adsorption, nucleation and crystal growth, coagulation and flocculation, a number of time dependent processes of mixed characteristics giving various structures conditioned by interplay of various genotypical and phenotypical factors, and especially the characteristics of the 'new parts' or specific structures in the methorical layer, that is in the interboundary or interphasial layer between two or more bulk phases.

The series of figures which are presented in this paper may give cross--sections not only of one of our 'precipitation bodies' but also of some material which needs a much more experimentally and theoretically elaborated system approach. The experimental objects have to be chosen from substantial groups where the similarities on one side, and differences on the other side are pointed out. Silver halides, sparingly soluble sulfates, metal hydroxides, phosphates, silicates, among others, may represent substances for such a task of comprehensive and comparative study.

An approximation in this direction we have already attempted[1], and from this point of view we may restrict our discussion to only three aspects where concentrational and temperature effects are of definable control, namely: (*i*) the solubility effects; (*ii*) the interplay of nucleation, growth, and coagulation processes; and (*iii*) the role of size and valency of the coagulating counter ions. In order to facilitate the overview all experimental results are based on the series of silver halides obtained by only one technique, that is by tyndallometrical observations of the systems during a period of time between 1 minute and a few hours or days. In expressing turbidities we used relative turbidity or tyndallometric values based on Sauer's standard[17]; both expressions are indicative for quantity of precipitate. As it is interesting to know also the relationship between turbidity and dispersity of the light scattering particles this was done for transition systems just outside the limit of coagulating action of counter ions (Figs. 11 and 12).

Since the earlier investigators paid attention mainly to systems where the precipitating components were in equivalent amounts, our systems were usually composed of one precipitating component of constant concentration (constant precipitating component), while for the other precipitating component the concentration was systematically varied (varied precipitation component).

The Solubility Effects

In our cases the solubilities could be clearly differentiated in accordance with a large or small excess of one of the precipitating ions; on one side there were effects of complex solubility, and on the other of ionic solubility. On both sides of the extremes there are developed maxima in short periods of time; on the complex solubility side the so-called concentration maxima, and on the ionic solubility side so-called crystallization maxima.

Owing to the stabilizing effects of the excess of one of the precipitating ions on the primary particles there is distinctive formation of so-called isoelectric maxima. With a lower and lower concentration of the constant precipitating component, the isoelectric maximum is systematically shifted towards a lower concentration of the other precipitating component, following nearly the equivalency ratio, until the concentrations are reached where with lowering of the concentration of the constant precipitation component the trend is changed in the opposite directions; namely, by further lowering the concentration of the constant precipitating component the maximum is shifted towards higher concentration of the varied one. This change of direction means also the change of the isoelectric into the crystallization maximum.

Such features may be used for discussion of the distinction between velocities of agglomeration and velocities of ordering, or in F. Haber's formulation[18] of *Häufungsgeschwindigkeit* and *Ordnungsgeschwindigkeit.* Already, we have used expressions for the degree of precipitation supersaturation *(Grad der Fällungsübersättigung)*, $C_{X/P}$, and the degree of crystallization supersaturation *(Grad der Kristallisationsübersättigung)*, $C_{CrM/Cr'}$ for the characterization of the complexity of the resulting particles[19]. The actual concentration of the precipitating ions before and after the precipitation occurred were denoted by X and P, respectively, while analogous concentrations of crystallization maximum before and after crystallization were denoted by CrM and Cr. By using these expressions, the degrees of agglomeration, Agg, and ordering, Org, may be given by

$$\mathrm{Agg} = \frac{C_X}{C_{CrM}}\text{; and } \mathrm{Org} = \frac{C_{CrM}}{C_X}\text{, respectively.}$$

How far such relationships are reflected in the morphology of the precipitating particles has to be seen under defined conditions of precipitation. It is interesting that monodisperse sols may be obtained on both extremes of the concentration gradient: in the regions of concentration as well as of crystallization maxima.

The Interplay of Nucleation, Growth, and Coagulation Processes

Silver halides express in a very distinctive manner the characteristics which could be attributed to the complex solubility, the nucleation from concentrated solutions, the growth of nuclei, and the coagulation of primary particles, all in the form of concentration maxima with a quite clear stability/instability limit for concentrational influence of counter ions to charged primary particles. These qualities make it possible to easily prepare the sols with definite properties, and opened the way, now in frequent use, of an operational method and technique for the determination of coagulation and flocculation effects (experiments with sols *in statu nascendi*).

Certainly, the rise of maxima at both ends of the concentration gradient, or, generally, at the boundaries of our 'precipitation bodies' for silver halides seems to indicate that the embryonation stage is rapidly transformed into nucleation, and that into coagulation or crystalline aggregation subsystems. In usual theories of crystallization, there is only the old distinction between nucleation and crystal growth, or their velocities *(Keimbildungsgeschwindigkeit und Kristalisationsgeschwindigkeit)* but the aggregation (packing of minute crystals during their growth, coagulation, flocculation, or agglomeration in general) are more or less ignored phenomena. That the more immediate encounter of the ionic species which are contained in separate precipitating solutions although conditioned at definite temperature may give quite different crystalline particles than the same already mixed system after cooling, reminds us that the states of mononuclear and polynuclear complexes, as well as embryos, play a very prominent role in nucleation and aggregation processes which as specific subsystems follow the first two stages. Figs. 7 and 8 speak for themselves in this sense.

Special situations are those which could be found in the region just lower than the critical coagulation concentration. Figs. 11 and 12 show that by raising the temperature there is a tendency for the formation of a larger number of smaller particles giving one of the so-called transition maxima which appear between the concentration and isoelectric or crystallization maxima after longer periods of time. What the cause for the formation of such a maxima is is difficult to ascertain. One very simple explanation was given quite early taking into account the possibility of special structures in thicker and thicker methorical layers by dilution of the electrolyte medium[20]. Nowadays, it seems advisable to be more cautious owing to the need to include in the discussion the interplay of many subsystems. Nevertheles, as it was pointed out earlier, the separate features of these subsystems and, moreover, their interactions reflected in a full analysis of the dynamic morphology of the resulting sols or precipitates may present an interesting approach to the structures, or to the 'new parts' in the methorical layer between solid and liquid phases with similar but much more supporting data than previous suppositions.

The Role of Size and Valency of the Counter Ions

It may be a surprising fact that in spite of the complexity of the various subsystems of which the precipitation is composed, there are persistent regions where the simple relationships for the coagulating activity of counter ions could exist. At first it seems doubtful, owing to accelerating effects of the temperature on nucleation and crystallization processes, that it will be possible to follow the coagulation at a higher temperature. But, taking into account the characteristic discontinuity in kinetics of precipitation expressed in concentrational dependency of critical times, it is possible to determine coagulation values in nearly the whole range between 20 and 90 °C. This was the case not only for silver iodide, but also for silver bromide, and, partially (in the range from 5 to 60 °C) for silver chloride. By raising the temperature the general trend is towards lower critical coagulation concentrations, but not uniformly for all three valencies. Namely, by changing the concentration of the precipitating ion in excess (I-, Br- and Cl-ions) small differences in changes of critical times are observed within one valency group and between ions of various valencies.

However, the general relationships which were expressed earlier[21] could be taken as a first approximation approach. The ion pair formation between complexoid negative charges fixed on the surfaces of primary particles and the specific counter ions demonstrated again the influence of their size (Fig. 20) and valency (Figs. 21, 22 and 23).

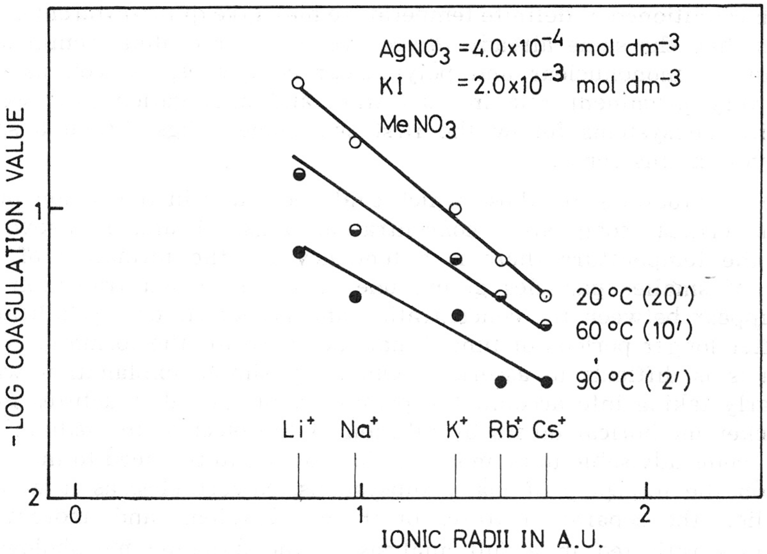


Fig. 20. Relationships between size of the univalent counter ions and their coagulation values at 20, 60 and 90 °C for the aqueous system of $AgNO_3$ at 4.0×10^{-4} and KI 2.0×10^{-3} mol dm^{-3} using corresponding critical times.

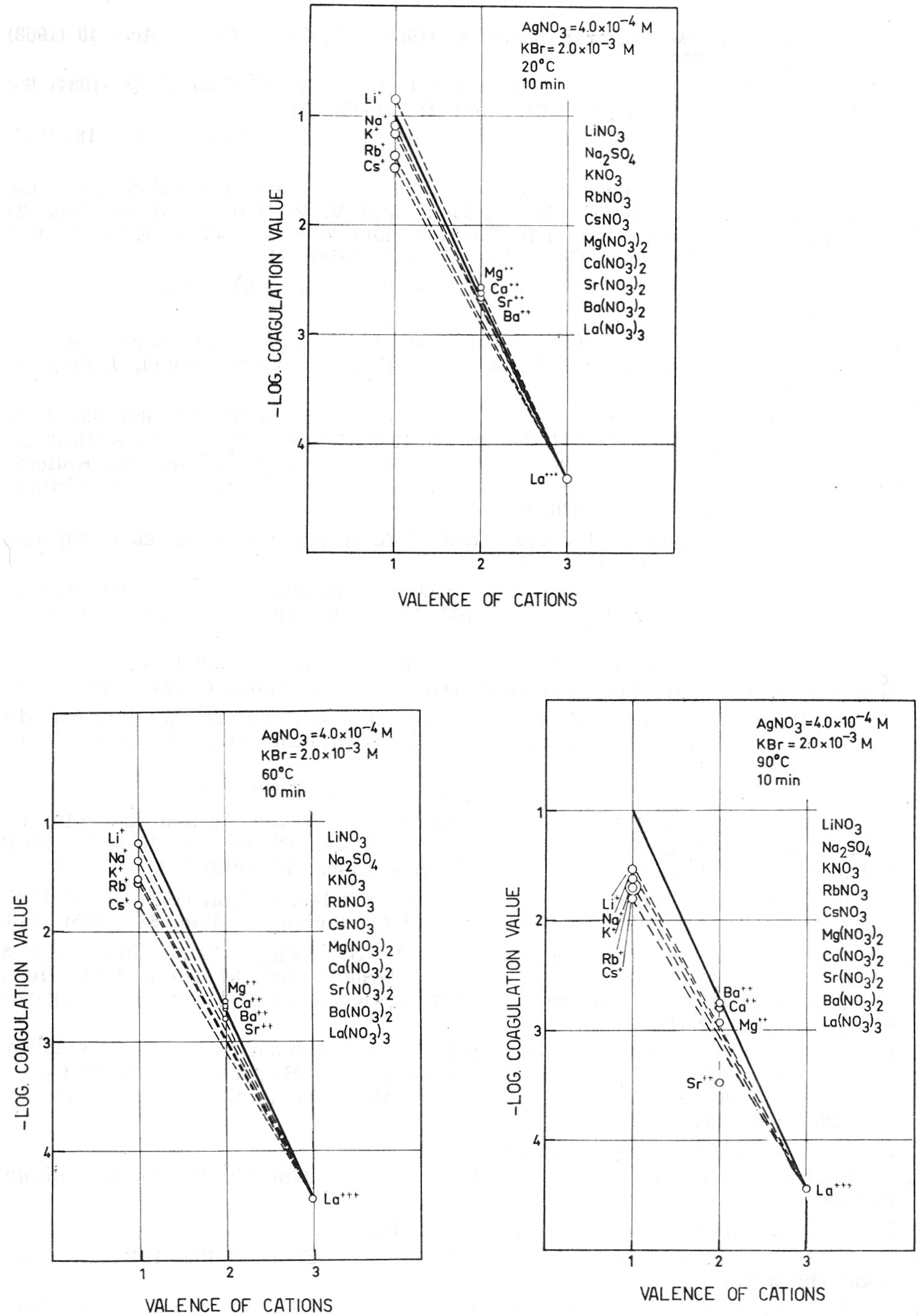
The expressions:

$$\log C_{(coag)} = -za + \log C_{i(fix)}, \text{ and}$$

the log $C_{i\,(coag)}$ as a linear function of coulombic interactions:

$$\delta_{crit} = \frac{ze^2}{2\,DkT},$$

seem to be very useful in elucidating the mechanism of coagulation. Taking into account the change of dielectric constant of water with temperature, the critical Bjerrum's distance is changed from 3,55 to 3.76 and 3.95 ångstroms, for 20, 60 and 90 °C, respectively. Comparable changes in critical coagulation values are detected, but further improvements, especially in experimental methods and techniques, are expected.



Figures 21, 22 and 23. Relationships between size and valency of the counter ions and their coagulation values at 20⁰ (Fig. 21), 60⁰ (Fig. 22 and 90 ⁰C (Fig. 23) for the aqueous systems of $AgNO_3$ at 4.0×10^{-4} and KBr at $2.0 \times {}^{-3}$ mol dm^{-3} 10 min after mixing.

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IZVOD

Precipitacioni procesi u koncentriranim elektrolitnim otopinama te temperaturni efekti na solovima argentum halogenida *in statu nascendi*

B. Težak i Đ. Težak

U cilju razlikovanja fizičkih i kemijskih karakteristika različitih interakcija, koje igraju ulogu u međusloju (metoričkom sloju) sistema kruto/tekuće ispitivana je kinetika precipitacije uz sistematsko variranje vanjskih i unutarnjih faktora (posebno koncentracije i temperature).

Diskontinuiteti u stvaranju precipitata te razlike u morfologiji i ponašanju omogućuju da se definira formiranje različitih substruktura kao rezultat najmanje pet subsistema od kojih je obično sastavljen precipitacioni sistem.

Radi ilustracije pokazani su neki realni sistemi, uglavnom argentum halogenidi, kod kojih se mogu razlikovati procesi kompleksacije, embrionacije, nukleacije, kristalnog rasta, micelacije (izlučivanja primarnih partikula) i agregacije (dvostepene kristalizacije, koagulacije i flokulacije). Pojave topljivosti (u vrlo velikom suvišku jednog od precipitacionih iona — kompleksna topljivost, i jednostavna ionska topljivost) i promjena tipa precipitacionih maksima između dvaju ekstrema koreliraju s prevladavajućim tendencijama ili aglomeracije (koncentracioni maksima), ili redanja (kristalizacioni maksima). Koncentracioni maksimum, a posebno područje prema granici kompleksne topljivosti karakterizirano je različitim pristupima ravnotežnom stanju, i to direktnim miješanjem precipitacionih komponenata kod 20 °C, ili hlađenjem homogenih već izmiješanih sistema od 90 do 20 °C.

Kemija i fizika površinskog sloja čvrste faze, struktura i specifični koncentracioni uvjeti (npr. ravnotežno stanje u stagnantnom sloju) konstituenata u metoričkom sloju, i kemijske i fizičke promjene uzrokovane razlikom u koncentraciji i entropiji ili u metoričkom sloju, ili u unutrašnjosti otopine, uzeti su kao odgovorni za stanja stabilnosti/nestabilnosti nastalih koloidnih čestica.

U svrhu diskusije tih efekata dovedeni su u vezu diskontinuiteti u kinetici precipitacije argentum halogenida (kritična vremena i korespondentna kritična vremena) s različitim precipitacionim maksimima (koncentracioni, izoelektrični, kristalizacioni, prijelazni) i koagulacijom jednostavnih protuiona na različitim temperaturama (između 5 i 90 °C). Nađeno je da je uobičajeni utjecaj veličine i valencije protuiona sačuvan u cijelom ispitanom temperaturnom području. Općenito ponašanje sistema pod malim, ali definiranim promjenama 'korak po korak' s obzirom na koncentraciju i temperaturu, otkriva mnoge pojedinosti za koje se može smatrati da su bitne u diskusiji o kristalizacionim i precipitacionim fenomenima.

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