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Interpretation of Coagulation Kinetics Observed by Light Scattering

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The coagulation process interpreted as a second order reaction and it is assumed that the intensity of scattered light on the colloidal particles follows the Raileygh eq. At each collision of two aggregates the smaller aggregate loses a given number of primary particles while the bigger aggregate increases by the same number of primary particles. The »critical time« (t_{crit}) is determined by the intersection of the tangent through the inflection of the plot »I vs. $\lg t$« with the $\lg t$ axis (I = intensity of scattered light, t = time from the start of coagulation). The coagulation halflife ($t_{1/2}$) can be calculated because the following eq. is derived

$$t_{1/2} = t_{\text{crit}}\, e^{2}$$

The intercept of the tangent on the steepest part of the plot »I vs. $\lg c$« with the $\lg c$ axis (c = variable coagulator concentration), measured at a suitable time t, is the »critical coagulation concentration«, c.c.c. = $c_{\text{coag, t}}$. It proves the validity of eq.

$$c_{1/2,\,\text{t}} = e^{2/\text{A}}\, e_{\text{coag, t}}$$

Exponent A is explained as the number of coagulator ions which react with a single primary particle in a fast ionic reaction which induces coagulation. This means that in the calculated concentration $c_{1/2,\,\text{t}}$ the suitable time equals the coagulation hilflife, i. e. $t = t_{1/2}$. It is also suggested that the theoretical linear plot »$1/I$ vs. $1/t$« could be used for the determination of $t_{1/2}$. The intersection of the plot with the $1/I$ ordinate for $1/t = 0$ is $1/I_{\infty}$. The value $2/I_{\infty}$ determines the reciprocal of the time which equals the reciprocal of the halflife, i. e. at $2/I_{\infty}$ is $1/t = 1/t_{1/2}$. It is also proved that the linear plots »$\lg c_{\text{coag, t}}$ vs. $\lg c$« and the plot »$\lg t_{\text{crit}}$ vs. $\lg c$« are equivalent to the »$\lg W$ vs $\lg c$« plot. Here, W is the »stability factor« defined as $W = k_{\max}/k = t_{1/2}/t_{1/2,\min}$. Each coagulator has a concentration in which the rate constant $k = 1/t_{1/2}$ has its maximal value $k_{\max} = 1/t_{1/2,\,\min}$. The same concentration is occasionally called coagulation concentration, c_{coag}. Arguments are given suggesting that t_{crit} and $c_{\text{coag, t}}$ can be measured with the highest possible precision. In short times after the start of coagulation the measured I is the sum of I_{s} scattered on single primary particles and of I_{a} scattered by the aggregates, i. e. $I = I_s + I_a$, therefore, the tangent on the plot »I vs. t« for $t \to 0$ determines neither the halflife of the disappearance of single primary particles nor the halflife of the increase of the aggregates.

INTRODUCTION

In the course of many years, various precipitation processes (nucleation crystal growth, coagulation or flocculation, recrystallization, peptization, solubilities . . .) were studied ⟨by Težak's[1] (or Yugoslav) school of colloid chemistry⟩ ⟨1⟩, ⟨mainly by the technique of measuring the intensity of scattered light⟩. The results were published in over 200 papers and approximately 40 different systems were investigated, ⟨2⟩. The results were mainly presented graphically, in the form of »time tyndallograms« and »concentration tyndallograms«, from which the values of »critical« time, »critical« coagulation concentration (or value) and other characteristic quantities were derived. Occasionally, the results were also presented in two or three dimensions and the shapes thus obtained were called »precipitation bodies«. The same results were used for empirical description of some processes; theoretical explanations of some observations were also given. However, many observations were not interpreted in terms of current theories of light scattering and theories of kinetics of physico-chemical processes.

Light scattering technique is one of the most direct methods for observing precipitation processes. In European literature, this technique is also known as »tyndallometric« technique or »tyndallometry«. The main advantage of this technique lies in the fact that the measurement does not affect the process under observation (except in the case of photochemically activated systems). Its disadvantage is that the intensity of scattered light depends on many factors. Interpretation of the observations can in many cases be simplified because many of them (e. g. the index of refraction of the medium and of dispersed particles, wavelength of incident light, angle and distance of the scattering system from the light surce) are kept constant. However, the main problem still remains: how to interpret the data taken for a process in which the quantity of the solid phase in formation, or size of the formed particles, or the arrangement of the smaller »primary« particles in the aggregates are changeable during the measurement.

The use of the term »primary particle« in the aggregate does not mean that the observed smaller particles forming the aggregates are formed in their original size and shape prior to coagulation. It simply means that, at the time of observation, the aggregate is thought of as being composed of smaller particles and these are called »primary« particles, the space between the primary particles being filled up with the intermicellar liquid. It is difficult to interpret the results because of a broad statistical scatter of the sizes of primary particles and of the number of primary particles in the aggregates. Despite all the complicating factors mentioned, it is worthwhile to analyze the theoretically possible influences on the intensity of scattered light on the basis of conventional theories of light scattering and kinetics of physico-chemical processes.

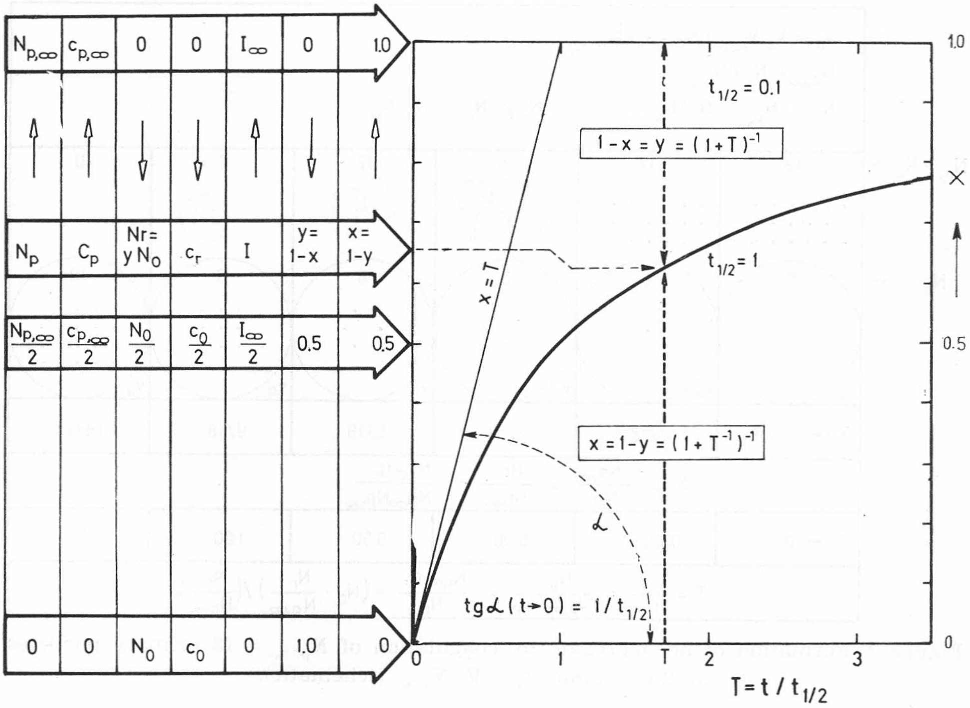

Figure 1. Intensity of scattered light against time plot. Ordinate: $x = I/I_\infty$, abscissa: $T = t/t_{1/2}$. Plot for $t_{1/2} = 1$. Tangent for $t_{1/2} = 1$ when $T \to 0$.

The present analysis is an effort to apply the light-scattering theory, i. e. the Rayleigh-equation, to interpretation of the coagulation process. The Rayleigh law is usually given in the form

$$I = I_o (9\pi^2 V^2 n^4/\lambda^4 x^2) [(n_1^2 - n^2 /(n_1^2 + 2n^2)]^2 \sin^2 \alpha \tag{1}$$

where I_o denotes the intensity of incident beam (of wavelength λ), I is the intensity of the beam scattered in the direction of angle α at distance x, n and n_1 are refraction indices of the medium and the particle, respectively, and V is the volume of scattering particles. Interpretation of the coagulation will be based on the assumption of the exact validity of the Rayleigh equation.

For the case when the aggregates are formed from »primary« particles and the intermicellar liquid, the following, somewhat modified, equation should be used

$$I = I_o [9\pi^2 [v f N_o M/N_A \varrho (1 - \varphi)]^2/\lambda^4 x V_s] [(n_1^2 - n^2)/(n_1^2 + 2n^2)]^2 \sin^2 \alpha \tag{2}$$

Here N_A denotes the Avogadro constant, v the volume of the micelle or of the aggregate (i. e. of the coagulated particle), V_s the volume of the scattering system, N_o the total number of macromolecules or primary particles in volume V_s; M is the relative molecular mass of macromolecules or primary particles, φ the ratio »intermicellar volume/total volume of the scattering particles«,

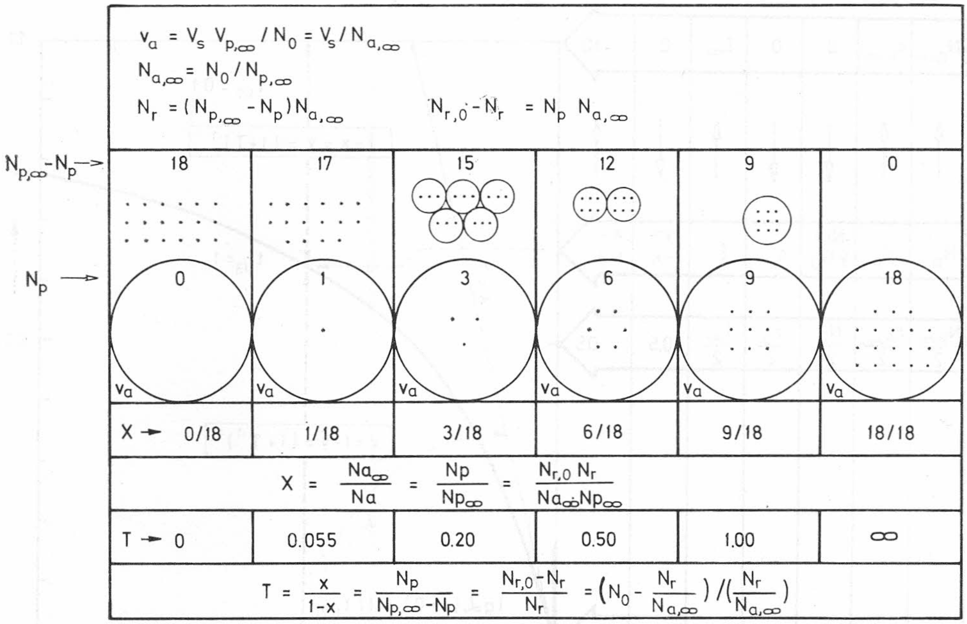

Figure 2. Formation of an aggregate by coagulation of $N_{p,\infty} = 18$ primary particles in the volume $v_a = V_s/N_{a\infty}$ (schematic).

f the correction factor for polydispersity, and ρ the density of primary particles.[1,2]

COAGULATION

We shall assume that coagulation sets in only after the processes of nucleation and crystal growth have come to their end, so that a constant number, N_o, of primary particles is present in the system. During the coagulation process, the average aggregate size, N_p, is steadily increasing, i. e. the distribution of aggregate sizes is being steadily shifted towards higher values.

For the purposes of our theoretical analysis we shall further assume that coagulation is a second-order process consisting of collisions of a) two primary particles, or b) a primary particle and an aggregate, or c) two aggregates. This process can generally be written as

$$P_m + P_n = P_{m\pm i} + P_{n\pm i}, \tag{3}$$

where P stands for the primary particle while m and n denote the numbers of primary particles in the two colliding aggregates ($m, n = 1, 2, \ldots$), and i is the number of primary particles exchanged in a collision. Stoichiometric indices m, n, i are subject to the following mass-balance constraints

$$m + n \leqq N_o,$$

$$1 \leqq i \leqq \min(m, n).$$

A collision is considered to be »efficient« »whenever $i = \min(m, n)$, i. e. whenever two particles form only one new aggregate. A collision with a

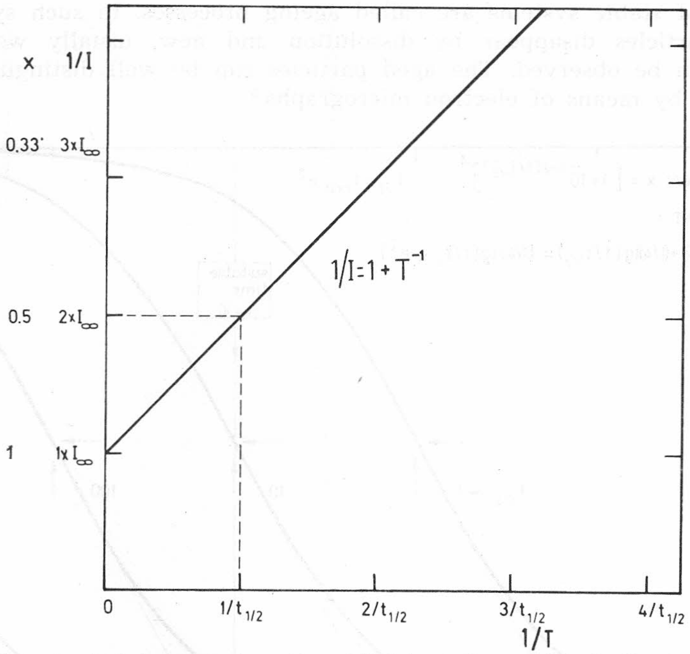

Figure 3. Linearized »intensity of scattered light vs. time« plot. Ordinate: $1/x = I_{\infty}/I$, abscissa: $1/T = t_{1/2}/t$.

primary particle ($m = 1$, or $n = 1$) will be termed »unit collision« and the uniting of an aggregate with a primary particle »efficient unit collision«.

The consequence of repeated efficient collisions is the formation of ever greater aggregates and the disappearance of the smallest ones. In most systems, after the aggregates become big enough they start to sediment. As a consequence, in the early phases of the process coagulation can follow a given kinetics, e. g. the kinetics of the second-order reaction. When sedimentation becomes remarkable, one should assume that coagulation cannot follow the assumed kinetics or that coagulation has finished.

COAGULATORS

Many substances cause coagulation when present in sufficiently high concentrations. Such substances are called coagulators. They are usually ions of the sign opposite to that of the colloid particle charge or charged or uncharged macromolecules, which are called tensides or surface active substances. As a rule, there is a limiting concentration of a coagulator (c_{coag}). Up to the limiting concentration increased concentration causes an increase of coagulation rate, while above the limiting concentration the coagulation rate remains constant, i. e. the rate constant or the reaction halflife remains constant. At low concentrations when $c < c_{coag}$, $t_{1/2}$ decreases and when $c > c_{coag}$, $t_{1/2}$ remains constant. »Light scattering vs. logarithm time« plots or »time tyndallograms« are shifted to the left side (Figure 4.). Systems with low coagulator concentration, where coagulation cannot be established even after a prolonged time of observation, are called colloidally stable systems. The processes of stable systems are called ageing processes. In such systems, the present particles disappear by dissolution and new, usually well formed, crystals can be observed. The aged particles can be well distinguished from aggregates by means of electron micrographs.[3]

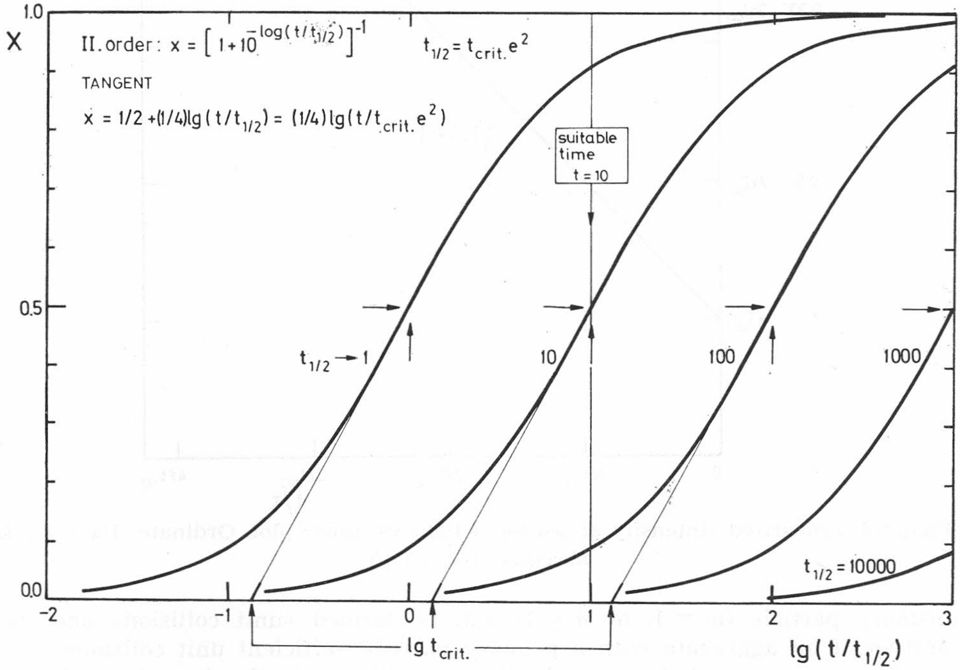

Figure 4. »Intensity of scattered light vs. logarithm of time« plot. Ordinate: $x = I/I_{\infty}$, abscisa: $\lg T = \lg(t/t_{1/2})$. Plots for $t_{1/2} = 1$, 10, 100, 1000, 10000. Intersection of the tangent through $x = 1/2$ with the abscissa is $\lg t_{crit}$.

In the ageing processes, the »I vs. t« plots (I intensity of scattered light, time tyndallograms) usually have an induction period, i. e. in the early phases of observation the increase of I cannot be observed. The values t_{crit} and $t_{1/2}$ are higher than in the coagulating systems and the slopes of the plots are lower.

In the literature, »fast« coagulations are occasionally distinguished from the »slow« ones, while the ageing processes are not mentioned. It is, therefore, hardly possible to see whether a »slow coagulation should be understood as an ageing process or as a coagulation with an increasing rate while under fast coagulation a coagulation in the range $c > c_{coag}$ with a constant and maximum rate should be understood. In the majority of various systems the rate of coagulation is of the same order of magnitude, while the ageing rate depends, to a much greater extent, upon the system observed. The rate of coagulation depends primarily on the concentration and on the type of coagulator.

Many surface active substances or tensides at their highest concentrations prevent coagulation, they »stabilize« the sols. In such substances, in addition to the range of stability, range of the increasing coagulation rate and the range of constant coagulation rate, a fourth range can be observed, the range of »stabilization«. Here also the increase of I is caused by an ageing process and not by coagulation. During the induction period virtually no changes can be observed.

Poorly soluble binary precipitates are colloidally stable due to the adsorbed »potential determining« ions. Adsorbed anions cause a negative, and adsorbed cations a positive charge. When precipitates are formed with a systematically varying excess of ions of either sign, then there is a region of their activities in which the special case of »isoelectric« coagulation can be observed.[4,5] For instance, in the AgI sols in the range $\text{pAg} > 6.2$ the sols have a negative charge and are colloidally stable. In the range $\text{pAg} < 4.5$ they have a positive charge. A consequence are negative and positive electrophoretic mobilities of the stable sol particles.[6] By direct measurement of the adsorbed constituent ions it can be proved that particles with negative mobility have adsorbed anions and those with positive mobility have adsorbed cations. Both the limiting values, $\text{pAg} = 6{,}2$ and 4.5, can be called the negative and positive limits of stability. In the region between these values, a coagulation can be observed as well as the change of anion-adsorbing state into the cation--adsorbing state, with an pAg intermediate where adsorption is zero. In the same range one also observes a change of the sign of electrophoretic mobility. The point of zero adsorption, or zero electrophoretic mobility, depends on the conditions of preparing the system. Since the logarithm solubility product of AgI is $\text{p}K_{\text{AgI}} = 16$, the isoelectric activity in solution is $\text{pAg} = \text{pI} = 8$, it follows that the negative charge can be observed up to $6.2 < \text{pAg} > 4.5$, i. e. for an excess of Ag^+ far higher than its isoelectric concentration ($\text{pI} = \text{pAg} = 8$).[7]

The electrokinetic mobility of coagulated sols can be observed by electro-osmotic techniques. Precipitates coagulated with counterions retain the sign of their mobility. Precipitates coagulated with cations remain negative, and those precipitated with anions remain positive. In the »isoelectric region«, the precipitates change their sign, or the sign may depend on the time of measurement and on other factors. Obviously, »isoelectric« coagulation is a consequence of the adsorption instability of constituent ions. A negative charge can easily be transformed into a positive charge and vice versa.[8]

After coagulation and sedimentation, many precipitates (e. g. Ag halides, sulfides, BaSO_4, TlI and others) exchange their constituent ions, built-in into their structure during precipitation and sedimentation, with the same ions in the solution. Occasionally, during this exchange, the crystallographic form of the precipitate also changes. The exchange can be proved by the radioactive tracer method and was named heterogeneous exchange. For example, the cubic orange TlI transforms into the yellow rhombic form while the not radioactive Tl^+ isotope incorporated in the precipitate leaves it and the radioactive $^{204}\text{Tl}^+$ ion enters it. After a sufficiently long ageing (240 hours) this exchange can no more be observed.[9]

The reaction of coagulator ions K with, say, A primary particles (P), assumed to be present in the sol before the start of coagulation, can be written as

$$\text{P} + \text{A}\,\text{K} \rightarrow \text{P}\,\text{K}_\text{A} \tag{4}$$

The equilibrium constant, K_c, can be defined by

$$\frac{[\mathrm{P}]\,[\mathrm{K}]^{\mathrm{A}}}{[\mathrm{P\,K_A}]} = K_c \tag{5}$$

This reaction, being ionic (adsorbed constituent ion + its ion cloud reacts with coagulator), can be assumed to be very fast, as compared to the subsequent process of coagulation.

For the purpose of theoretical analysis it will be assumed that primary particles are formed prior to the start of coagulation, which is induced by the addition of a coagulator of a given concentration to the system. Occasionally, in fresh sols, the inducing step includes transformation of stable sol particles into the form which, during coagulation, we call primary particles. Obviously, the cause of coagulation is due to thermodynamic reasons. An aggregate of a given number of primary particles and a given ratio of intermicellar liquid represents the aggregate in equilibrium with the mother liquor. In most systems, the primary particles are polydisperse, i. e. their sizes are statistically scattered around a mean value; the aggregates are also polydisperse, i. e. the numbers of primary particles they contain are also scattered around a mean value. For theoretical purposes one can assume that a real system with a given mean primary particle size and a given mean aggregate size behaves, as far as the coagulation process is concerned, analogously to a hypothetical monodisperse system with equal characteristics.

Two different phases of coagulation should be distinguished: the early phase of coagulation, where free primary particles are still present and the aggregate contains a relatively small number of primary particles (order of magnitude ~10), and the second, advanced phase where no primary particles

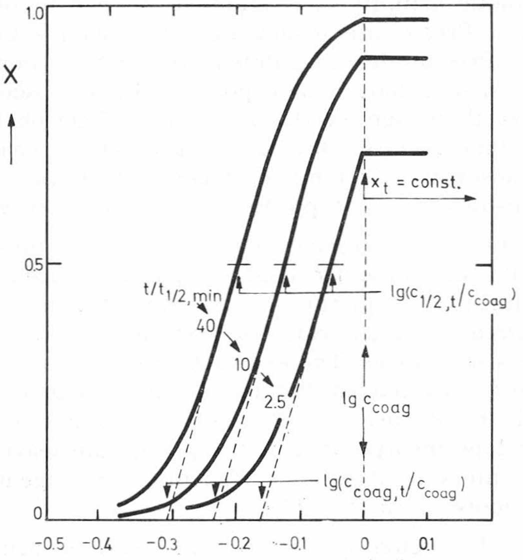

Figure 5. »Intensity of scattered light against lg c« plot. Ordinate: $x = I/I_\infty$, abscissa: $\lg(c/c_{coag})$. $\lg(c_{coag}/c_{1/2,\max}) = 0$. Plots for $t/t_{1/2,\min} = 2.5$, 10, 40.

are present any more. The early phase with single primary particles is analyzed in Figure 6 while Figures 1 to 5 describe the case when no single primary particles are present in the coagulating system. Electron micrographs in Ref. 3 (Figs. 5—7) can be considered convincing evidence that this is true, at least in AgI sols.

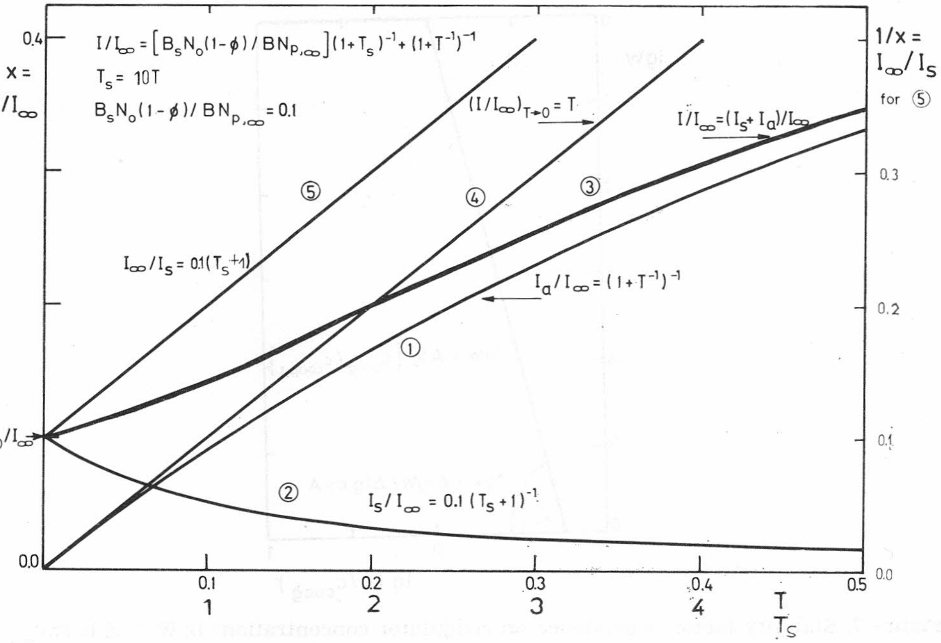

Figure 6. Coagulation of primary particles. Ordinate: $x = I/I_{\infty}$, abscissa: $T = t/t_{1/2}$. »Intensity of scattered light vs. time« plots for: (1) I_a/I_{∞} of aggregates, (2) I_s/I_{∞} of stable particles, (3) $(I_s + I_a)/I_{\infty}$ of their sum, (4) tangent on (1) for $t \to 0$, (5) linearized plot of (2) when $I_0/I_{\infty} = 0.1$, abscissa: T_s; ordinate: I_{∞}/I_s.

If we assume that the reaction of the coagulator ion with the primary particle (eqs. 4 and 5) is fast in comparison with coagulation process (eq. 3)

TABLE I

Comparison of Coagulation Values of Silver Halides (Reproduced From ref. 15 and Obtained on the Basis of ref. 12 Figure 6)

	log (coagulation concentration)/mol dm^{-3}			Schulze-Hardy rule constant B		
	K^+	Ba^{++}	La^{+++}	K-Ba	Ba-La	Mean
AgI	—0.83	—2.74	—4.51	1.91	1.77	1.84
AgBr	—1.24	—2.68	—4.3	1.44	1.62	1.53
AgCl	—1.80	—2.68	—3.86	0.88	1.18	1.03

and that equilibrium is shifted towards the side of the reaction product, PK_A, then prior to the start of coagulation, all primary particles are in the state ready for coagulation. This means that the starting concentration (activity) is defined by $[PK_A] = N_o/V_s = c_o$ where N_o is (constant) total number of primary particles present and V_s is the volume of the system. At constant concentration of the sol $c_o = [PK_A] = \text{const.}$ and the equilibrium constant can be defined as $k = 1/c_o\, t_{1/2}$ where $t_{1/2}$ depends on the coagulator and its concentration $c = |K|$.

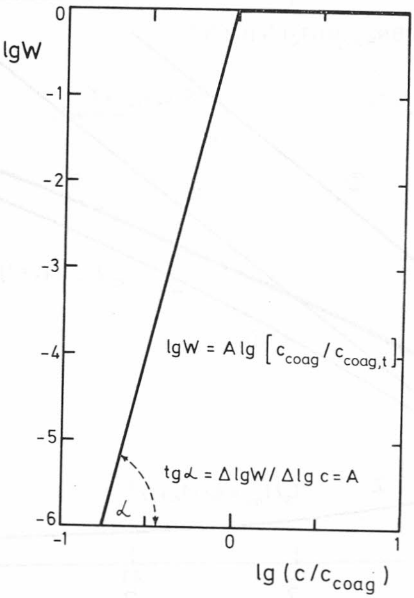

Figure 7. Stability factor dependence on coagulator concentration: $\lg W = A \lg (c/c_{\text{coag}})$. Ordinate: $\lg W$, abscissa: $\lg (c/c_{\text{coag}})$.

THEORETICAL AND DISCUSSION

LIGHT SCATTERING OF COAGULATING SYSTEMS

Wavelength of light, the scattering volume, angle and distance of observation, refraction indices, primary particle size and their number and intermicellar volume fraction in the aggregates are usually constant in light scattering experiments. Also, the average number of primary particles in aggregates at a given time can replace their number size distribution. The average size and the assumed constant particle number would cause the same intensity of scattered light. All these assumptions permit the use of the Rayleigh equation in its simpler form (eq. 6). The use of the simpler form of Rayleigh equation enables at least qualitative conclusions on the size, number and arrangement of primary particles in the aggregates. A sound estimate of theoretical predictions of the deviation of conclusions made can be arrived at only on the basis of a comparison of a sufficiently large number of experimental data. Semiquantitative or even quantitative conclusions can give a deeper insight into the character of the observed processes.

The simplified Rayleigh equation can be written in the form

$$I = B' \,[M/N_A\, \varrho\, (1 - \varphi)]^{-2}\, v^2\, N_a/V_s = B\, N_a\, v^2/V_s \tag{6}$$

B' and B are constants determined by the intensity of unpolarized incident light, I_o, refraction indexes of the particles and medium, wavelength, angle and distance of observation, M is the relative mass, ρ density of primary particles, $\varphi = (v - N_p v_p)/v$ the fraction of the intermicellar liquid in the aggregate volume, v the volume of each aggregate, N_a the number of aggregates in the system of volume V_s. If v_p is the volume of primary particles and N_p the average number of primary particles in the aggregates, then the total (constant) number of primary particles, N_o, in the volume V_s is

$$N_o = N_a N_p \tag{7}$$

Consequently, volume v of each aggregate is proportional to the number of particles in the aggregate. Volume v_p of primary particles is defined by

$$v_p = M/\varrho N_A \tag{8}$$

and the volume, v, of aggregates by

$$v = N_p v_p/(1 - \varphi) = N_p M/\varrho N_A (1 - \varphi) \tag{9}$$

where N_A is the Avogadro constant. Combining eqs. (6), (8) and (9) one obtains

$$I = B N_p^2 N_a \tag{10}$$

We can define the sol number concentration by $c_o = N_o/V_s$ which is constant during coagulation. Analogously, we can define the concentration of primary particles as $c_p = N_p/V_s$ and the concentration of aggregates as $c_a = N_a/V_s$. This is the number of aggregates N_a of size N_p in volume V_s.

By inserting eq. (7) into (10), one obtains:

$$I = B' N_o^2/V_s N_a = B'' c_o^2/c_a \tag{11}$$

and by eliminating N_a in eq (11) one obtains:

$$I = B' N_o N_p/V_s = B'' c_o c_p \tag{12}$$

B, B' and B'' are constants which can be derived from eqs. 6—10. It follows that, analogously to $N_o = N_p N_a = \text{const.}$, the following relation also holds:

$$c_o = c_p c_a = \text{const.} \tag{13}$$

Based on the experience and analogy with chemical reactions, we assume that during coagulation the number of primary particles assympotically approaches a maximum value $N_{p,\infty}$ and, consequently, the ideal intensity approaches the value I_∞ and we can define

$$I_\infty = B'' N_o N_{p,\infty} = B''' c_o c_{p,\infty} \tag{14}$$

and

$$I_\infty - I = B'' N_o (N_{p,\infty} - N) = B''' c_o (c_{p,\infty} - c_p) \tag{15}$$

and

$$I/(I_\infty - I) = N_p/(N_{p,\infty} - N_p) = c_p/(c_{p,\infty} - c_p) \tag{16}$$

The value of I_∞ can hardly ever be directly measured in a real system.

CHARACTERIZATION OF COAGULATORS

(1) Derjaguin-Landau-Verwey-Overbeek theory (DLVO) of coagulation and colloid stability[22,23] uses, for the purpose of characterization of coagulators, the stability factor and its dependence on the logarithm of coagulator concentration (Figure 7).

To characterize various coagulators Težak proposed:

(2) Dependence of the critical time on the logarithm of coagulator concentration, i. e. the plots »t_{crit} vs. log c«.

(3) Critical coagulation value (c.c.c.) measured at time t suitable for a given coagulator, $c_{\text{coag, t}}$, with the aid of concentration tyndallograms.

(4) Dependence of the maximal slope of the »scattered light against time plot«, i. e. »I vs. t« when $t \rightarrow 0$, i. e. the slope $(\Delta I/\Delta t)_{t\rightarrow 0}$.

DEPENDENCE OF SCATTERED LIGHT INTENSITY ON COAGULATION TIME

In the following discussion, coagulation will be assumed to be a second order reaction, i. e. it will be assumed that the aggregates, at the beginning the primary particles, collide. Smaller aggregates become smaller and smallest disappear, while bigger aggregates grow. It follows that the average number of primary particles in the aggregates $N_p = c_p \cdot V_s$ increases. A suitable form equation of the second order reaction kinetics can be written in the form:

$$c_p/(c_{p,\infty} - c_p) = t/t_{1/2} = t\,k/c_o \qquad (17)$$

Here, c_p is the (increasing) concentration of the reaction product. In the present analysis the same symbol is used for the increasing concentration of primary particles defined by $c_p = N_p/V_s$. The maximum, equilibrium concentration of the reacting component is given by $c_{p,\infty} - c_p = (N_{p,\infty} - N_p)/V_s$. The time since the beginning of coagulation, usually since the time of addition of coagulator to the sol, is denoted by t, while $t_{1/2}$ is the halflife, i. e. the time in which half of the reaction product is formed, i. e. $t = t_{1/2}$ when $c_p = c_{p,\infty}/2$ or when $N_p = N_{p,\infty}/2$. Since the starting concentration of the reactant is $c_o = N_o/V_s$

$$t_{1/2} = 1/c_o\,k = V_s/N_o\,k \qquad (18)$$

Here, k is a second order rate constant. Using eqs. (16) and (17) we obtain the »scattered light intensity — time« relation in the form

$$I/(I_\infty - I) = t/t_{1/2} \qquad (19)$$

For practical reasons we can define the fraction of the maximum amount of reaction product in the following way:

$$x = c_p/c_{p,\infty} = N_p/N_{p,\infty} = I/I_\infty \qquad (20)$$

The fraction of the reactant can be defined analogously:

$$1 - x = (c_{p,\infty} - c_p)/c_{p,\infty} = (N_{p,\infty} - N_p)/N_{p,\infty} = (I_\infty - I)/I_\infty \qquad (21)$$

In a coagulation process, x is the fraction of primary particles which at a given time form the aggregates and $1 - x$ is the fraction of nonaggregated particles. The ratio $t/t_{1/2} = T$ can be called the relative coagulation time.

INTENSITY OF SCATTERED LIGHT AGAINST TIME PLOT

Equations (19) and (20) can be recast into the form

$$x = I/I_{\infty} = (1 + T^{-1})^{-1} \tag{22}$$

which represents the »I against t« plot (time tyndallogram) and is shown in Figure 1. It can be given also in the form

$$x/(1 - x) = I/(I_{\infty} - I) = T \tag{23}$$

If the symbol for the number fraction of non-aggregated particles is $y = 1 - x = (N_{p,\infty} - N_p)/N_{p,\infty}$, then the fraction of particles forming the aggregate at time T is $1 - y = x = N_p/N_{p,\infty}$ and eq. (23) can be written in the form

$$(1 - y)/y = I/(I_{\infty} - I) = T \tag{24}$$

The meaning of both eqs. is the same:

$$\frac{\text{[reaction product]}}{\text{[reactant]}} = \frac{\text{number of primary particles in aggregates}}{\text{number of non-aggregated primary particles}} = \text{relative time} \tag{25}$$

The following alternative forms of the second order rate equation are also used:

$$(c_o - c_r)/c_o = N_p/N_{p,\infty} \tag{26}$$

and

$$c_r/c_o = (N_{p,\infty} - N_p)/N_{p,\infty} \tag{27}$$

where c_r is the reactant concentration. Inserted in eq. (25) both relations give

$$y = 1 - x = (1 + T)^{-1} \tag{28}$$

and

$$(1 - y)/y = x/(1 - x) = T \tag{29}$$

The conclusion based on eqs. (22) and (28) is that whether we derive the reaction kinetics eqs. from increasing product concentrations or decreasing reactant concentrations, we obtain identical equations.

The use of fractions x and y for the progress of reaction certainly offers the simplest way of writing the reaction kinetics equations and of graphical presentation of the corresponding plots.

Values N_o, $N_{p,\infty}$, $N_{a,\infty}$, V_s, v_p, C_o, $c_{p,\infty}$, I_{∞} and $t_{1/2}$ are the parameters of each experiment. Theoretical plots can be obtained after inserting concrete values of the parameters in the equations. In Figure 1. the course of a theoretical coagulation is given which is valid for any set of chosen or given parameters. For an example of an experimental plot see e. g. Ref. 10.

A simplified, hypothetical example of a coagulation is described in Figure 2. with the purpose to explain the formation of an aggregate of the average value $N_{p,\infty} = 18$ primary particles by a second order kinetics. The volume of electrolyte in which such an aggregate is formed is $V_a = V_s N_{p,\infty}/N_o = V_s/N_{a,\infty}$. Coagulation of a single aggregate is described from the time $t = 0$ when no primary particles are aggregated to the infinite time when 18 primary particles enter a single aggregate. There are three constant parameters, V_s, $N_{p,\infty}$, and N_o, and two interdependent parameters, N_p or N_a and T.

All the remaining parameters can be derived from these. The steps of formation are given when the aggregates are formed by 0, 1, 3, 6, 9, and 18 primary particles in relative times $T = 0$, 0.55, 0.2, 0.5, 1, and ∞. In real systems the final $N_{p,\infty}$ is many orders of magnitude greater[11]: ($N_{a,\infty} = N_o/N_{p,\infty}$ is $10^{16} - 10^{19}$). The plot of the intensity of scattered light against time (eq. (22)), is presented in Figure 1. The value of x approaches assymtotically 1, i. e. $x = I/I_{\infty} \rightarrow 1$.

The first derivative of eq. (22) reads

$$\mathrm{d}x/\mathrm{d}t = (1 - x)^2/t_{1/2} = t_{1/2}/(t_{1/2} + t)^2 = 1/t_{1/2}\,(1 + T)^2 \tag{30}$$

It represents the dependence of the plot slope on time. For $T \rightarrow 0$ also $x \rightarrow 0$, $I \rightarrow 0$, and $N_p \rightarrow 0$. The slope for $t \rightarrow 0$ reads therefore

$$1/t_{1/2} = c_o\, k = N_o\, k/V_s \tag{31}$$

Thus, in principle the slope of the tangent through the origin of the coordinate system can serve for the determination of the reaction rate constant or of reaction halflife $t_{1/2}$. The equation of the tangent through the origin reads

$$x = I/I_{\infty} = N_p/N_{p,\infty} = T \tag{32}$$

The tangent for $t_{1/2} = 1$ is shown in Figure 1.

In real systems it is usually impossible to measure exact values for I after longer periods. When aggregates become too big, the Rayleigh equation is not valid any more. One of the reasons is that the aggregates are too big and the other is the inner absorption of the scattered light. The scattered light is partly absorbed by the optically too dense system. In addition, when aggregates are too big, they start to sediment so that only smaller aggregates remain in the scattered beam.

These complicating factors are the reason why the slope of the tangent through the origin cannot be determined with sufficient accuracy. In addition, when a stable sol, prior to the start of coagulation, scatters the light due to the scatter of primary particles, the plot does not go through the origin and this case is analyzed in Figure 6.

LINEARIZATION OF THE PLOT: INTENSITY OF SCATTERED LIGHT AGAINST TIME

Equation (32) can also be written in the form

$$1/x = I_{\infty}/I = 1 + T^{-1} \tag{32a}$$

and plotted in the system »$1/x$ vs. $1/T$« or »$1/I$ vs. $1/T$« (Figure 3). In this case the plot is a straight line. The intercept of the line on the ordinate axis corresponds to $1/T = t_{1/2}/\infty = 0$, and $1/I = 1/I_{\infty}$ or $I = I_{\infty}$. The value of $1/x = 2$ or $1/I = 2/I_{\infty}$ on the plot determines the value for $1/T = t_{1/2}/t = 1$ or $t = t_{1/2}$. According to eq. (18) $t_{1/2}$ is inversely proportional to k and c_o. The linear plot of Figure 3 illustrates the possibility of determining k and $t_{1/2}$. For this purpose it should be possible to measure a sufficient number of reliable points near the origin so as to enable a reliable extrapolation to $T = 0$. However, this method was not used by Težak and his associates.

INTENSITY OF SCATTERED LIGHT AGAINST LOGARITHM OF TIME PLOT

It was the generally accepted practice of Težak's school to present coagulation experiments as »intensity of scattered light against logarithm of time« plots. Obviously, the main reason for such a choice was the need for displaying the coagulation data collected in prolonged periods of time; no theoretical reason was ever given. However, these plots can be advantageously used for estimating $t_{1/2}$ or k. The theoretical plot »x vs. $\log t$« (Figure 4) is S-shaped, with an inflection in its steepest part (see e. g. Ref. 12). The tangent through the steepest part can be extrapolated to $x = 0$ and the intercept of the tangent on the abscissa is the logarithm of what is called »critical coagulation time«, which is a characteristic property for a given sol concentration and a given coagulator concentration. Težak realized the importance of critical coagulation time, but he did not give a theoretical explanation for it in terms of common formalism of reaction kinetics.

In the following text the interrelation of the critical coagulation time and the coagulation of halflife (i. e. the second order reaction constant k) will be derived.

CRITICAL COAGULATION TIME

The logarithmic and exponentional forms of eq. (23) read

$$\ln\{x/(1-x)\} = \ln T, \quad x = (1 + e^{-\ln T})^{-1} \tag{33}$$

The »x vs. $\log T$« plots are shown in Figure 4. for $t_{1/2} = 1$, 10, 100, 1000. Each increase of $t_{1/2}$ for a factor of 10 shifts the plots parallelly for $\log T = 1$. In the same way increase also the values t_{crit}. In a sol of $c_o = \text{const.}$, increasing concentrations of coagulator cause a parallel shift of the plots to the left. The t_{crit} and $t_{1/2}$ values are shifted in the same way. The theoretical interrelation between t_{crit} and $t_{1/2}$ will be derived as follows. The derivative of eq. (33) reads

$$dx/d\,(\ln t) = x\,(1-x) \tag{34}$$

and the second derivative

$$d^2x/d^2\,(\ln T) = 1 - 2\,x \tag{35}$$

For $x = 1/2$, the value of the second derivatives is 0. This is a proof that, at $x = 1/2$, the plot has an inflection point. The slope in the inflection points is

$$\operatorname{tg}\alpha = 1/4 \tag{36}$$

The equation of the tangent through the inflection reads

$$x = (1/4)\ln\,(t/t_{\text{crit}}) \tag{37}$$

where t_{crit} is the intercept of the tangent on $\ln t$ (abscissa) axis. For $x = 1/2$ and $t = t_{1/2}$ one obtains

$$\ln\,(t_{1/2}/t_{\text{crit}}) = 2 \tag{38}$$

and the equation of the tangent is

$$x = I/I_\infty = (1/4)\ln\,(t/t_{1/2}) + 1/2 \tag{39}$$

Since $x = I/I_\infty$ and since it is impossible to determine I_∞ experimentally (because of inner adsorption of the scattered light, invalidity of the Rayleigh equation and partial sedimentation), it is also impossible to apply eq. (39) to determining $t_{1/2}$. However, it is possible to derive t_{crit} because the lower plot part with its steepest slope is determined with the highest precision possible. Deviation of the lower part of the experimental plot from the theoretical prediction is very small. The following is therefore valid ((38) + (39))

$$t_{1/2} = t_{\mathrm{crit}}\, e^2 = 7.389\, t_{\mathrm{crit}} \quad \text{and} \quad t_{1/2,\,\mathrm{min}} = t_{\mathrm{crit,\,min}}\, e^2 \tag{40}$$

and

$$k = 1/c_{\mathrm{o}}\, t_{1/2} = 1/c_{\mathrm{o}}\, 7.389\, t_{\mathrm{crit}}$$

and

$$k_{\mathrm{max}} = 1/c_{\mathrm{o}}\, t_{1/2,\,\mathrm{min}} \tag{41}$$

It follows that t_{crit} obtained from the »intensity of scattered light against log t« plot can serve for the determination of $t_{1/2}$ and of the reaction rate constant k.

»INTENSITY OF SCATTERED LIGHT AGAINST LOG COAGULATOR CONCENTRATION« PLOT

For different applied concentrations (c) of the coagulator (this is not the sol concentration c_{o} which is constant (!)) different values of $t_{1/2}$, t_{crit}, and k are observed. The influence of c upon the same parameters is considerable and can be described (at c_{o} = const., from eq. (41)) by:

$$t_{1/2}/t_{1/2,\,\mathrm{min}} = (c_{1/2,\,\mathrm{max}}/c)^{A} \tag{42}$$

The higher the exponent A, the higher is the influence of concentration upon $t_{1/2}$ and the narrower the region of varying rates of coagulation between the maximal and minimal ones, which cannot be observed. Value $t_{1/2}$ calculated from (42) and inserted into (22) gives for t = const., (when $x = x_{\mathrm{t}}$):

$$x_{\mathrm{t}} = \{1 + (c_{1/2,\,\mathrm{max}}/c)^{A}\, (t_{1/2,\,\mathrm{min}}/t)\}^{-1} \tag{43}$$

The latter equation represents the »x_{t} vs. lg c« plot, i. e. the »concentration tyndallogram« of Težak (Figure 5). For an experimental example see e. g. Ref. 13.

CRITICAL COAGULATION CONCENTRATION

If a »suitable« t is chosen, the steepest part of the plot can be measured with sufficient precision. This means that, for each plot, $x_{\mathrm{t}} \leq 0.6$—0.7. Then, it is possible to draw the tangent through the steepest part of (43), Figure 5, i. e. through the inflection. The intercept of the tangent on the log c axis (abscissa) determines $c_{\mathrm{coag,t}}$. Težak used $c_{\mathrm{coag,t}}$ for the characterization of coagulators and called the same quantity »critical coagulation concentration (c.c.c.)« or »critical coagulation value«. The theoretical meaning of $c_{\mathrm{coag,t}}$ can be derived as follows. The first derivative of eq. (43), i. e. the slope of function x_{t} in eq. (43), reads

$$\mathrm{d}x_{\mathrm{t}}/\mathrm{d}\,[\ln (c/c_{1/2,\,\mathrm{max}})] = A\, x_{\mathrm{t}}\, (1 - x_{\mathrm{t}}) \tag{44}$$

The equation of the tangent is thus:

$$x_{\mathrm{t}} = (\mathrm{d}x/\mathrm{d}t)\, \ln (c/c_{\mathrm{coag,\,t}}) \tag{45}$$

This means that for each chosen t there is another value $c_{\text{coag,t}}$, which can be determined experimentally if the choosen t is suitable. Then, for $x_t = 1/2$, $c = c_{1/2,t}$ and $dx/dt = A/4$ (from (44)):

$$1/2 = (A/4) \ln (c_{1/2,\,t}/c_{\text{coag},\,t}) \tag{46}$$

and

$$c_{1/2,\,t} = e^{2/A}\, c_{\text{coag},\,t} \quad \text{and} \quad c_{1/2,\,\max} = c_{\text{coag}} \tag{47}$$

At concentration $c_{1/2,t}$ the value t is in fact $t_{1/2}$, i. e. $t_{1/2} = t$, $x_t = 1/2$ and from (41) and (43) one obtains

$$c_o\, c^A_{1/2,\,\max}/k_{\max}\, e^2 = t_{1/2,\,\min}\, c^A_{\text{coag}}/e^2 = c^A_{\text{coag},\,t}\, t \tag{48}$$

If exponent A can be anticipated or determined experimentally (see the chapter on the stability factor, W) the experimentally determined product $c^A_{\text{coag,t}}\, t$ represents a value which is proportional to $t_{1/2,\min}$ or inversely proportional to $k_{\max}$ and it could, therefore, serve as a relative parameter characterizing various coagulators.

Coagulation values determined for a given sol at a constant sol concentration, i. e. when $c_o = \text{const.}$ and $t = \text{const.}$, characterize the coagulating property or power of any coagulator because then

$$\text{c.c.c.} = c_{\text{coag},\,t} = (t_{1/2,\,\min}/\,t\, e^2)^{1/A}\, c_{\text{coag}} \tag{49}$$

It follows that the equality $c_{\text{coag,t}} = \text{c.c.c.}$ can well serve for comparison of various coagulators if determined at $c_o = \text{const.}$, and $t = \text{const.}$ Each coagulator has its characteristic values $k_{\max}$ and $c_{1/2,\max}$.

Težak proposed his coagulation values, i. e. $c_{\text{coag,t}} = \text{c.c.c.}$ for the characterization of various coagulators. The present analysis is intended to furnish a theoretical proof that parameter c.c.c. can serve for the characterization of various coagulators equally well as $k_{\max}$ or $t_{1/2,\min}$ if parameter $A = \text{const.}$; the time, t, should also be constant and suitably chosen.

In many investigations performed by Težak and his associates the »linear« Schulze-Hardy rule was established with certainty. It can be formulated in the form

$$\log c_z = \log c_{z=0} - z\, B \tag{50}$$

Here, $c_z = c_{\text{coag,t}}$ is the coagulation value of counterions of charge number z. In some experimental examples[14,15] the suitable time t was obtained by experience, i. e. for the AgI sols it vas $t \leqq 10$ min, for AgBr $\leqq 5$ min, and for AgCNS $t \leqq 1$ min. The same rule was many times reproduced in other investigations. A review proving its validity in many colloidal systems has also appeared.[16] Ref. 24 suggests also the same rule using stability factor w. B is an empirical constant which can be derived by thermodynamic methods.[17] In fact, it is determined by the electrochemical potential of the ions adsorbed on the sol particles, or the contribution of the electrostatic free energy of unit elementary charge of the counterion. According to this rule, the plot »log c_z vs. z« is a straight line (therefore »linear« rule!). The extrapolation of line to $z = 0$ gives the intercept $\log c_{z=0}$ which represents the chemical free energy which is the same for various counterions.

The influence of the counterion radius r upon $c_{\text{coag,t}}$ for ions of the same charge number z was also established.[18] By extrapolating the line $c_{z,r}$ to $r = 0$

for each category of ions of $z = 1, 2, 3$, a value $c_{z,r=0}$ could be obtained for which the same rule is valid with great precision.[19]

In another work it was also shown that $c_{\mathrm{coag},t} = \mathrm{const.}$ in a broad range of $1 < \mathrm{p}I < 8$—10 of excess concentration of the constitutive ion c_{I^-} — defined by $\mathrm{p}I = - \log c_{\mathrm{I}^-}$.[20,21] In the same investigation it was also shown that the coagulation concentration of the constitutive Ag^+ ion was the same in the AgCl, AgBr and AgI systems.

THE PLOT »$(\Delta I/\Delta t)_{\max}$ AGAINST t«

The value of $(\Delta I/\Delta t)_{\max} = (\Delta I/\Delta t)_{t\to 0}$ is the slope of the steepest, starting part of the »I vs. t« — plot (Figure 1). At high coagulator concentrations, when $c > c_{\mathrm{coag}}$, this slope is practically constant. In an intermediate range it decreases and at low concentrations it is not measurable or equal zero. Theoretically, this slope is the experimentally measured value of the first derivative of the »I vs. t« plot. For its determination only some of the first measured points can be used. Therefore, the statistical error of the determined value is always very high. A systematic error is also inevitable because the value obtained will be the slope of a secant through the origin and, therefore, it will be too low. If I_0 of the stable sol is appreciable, compared with I_∞, then the cases described in Figure 6. should be considered. For these reasons the value k or $t_{1/2}$ obtained from $(\Delta I/\Delta t)_{t\to 0}$ is very unreliable. However, in principle it is valid

$$(\Delta I/\Delta t)_{t\to 0} = 1/t_{1/2} = k\, c_0 \tag{51}$$

Perhaps, it could be possible to compare the rates of various coagulators by determining $(\Delta I/\Delta t)_{t\to 0}$.

COAGULATION IN THE PRESENCE OF STABLE PRIMARY PARTICLES

Immediately after the beginning of coagulation, i. e. immediately after the addition of coagulator to the sol, or, when experimenting with the technique called »in statu nascendi«, i. e. immediately after the preparation of the sol with coagulator added to one of the precipitating components, it should be anticipated that in the coagulating sol single primary particles are present (which are ready for coagulation) along with aggregates with a relatively small number of primary particles of the order of 10 or less. Since the number of primary particles is great ($N_0 = 10^{15} - 10^{18}/\mathrm{dm}^3$)[22], the light is scattered by stable particles and by aggregates. Therefore, in the early stage of coagulation the following analysis should be considered.

The aggregates contain a certain amount of intermicellar liquid. As a consequence, for aggregates and single primary particles two equations of the form (6) are valid. For single primary particles the following holds (see eq. (28)):

$$I_s = B_s N_0 (1 + T_s)^{-1} \tag{52}$$

and for aggregates (from (22))

$$I_a = B N_{p,\infty} (1 + T^{-1})^{-1} \tag{53}$$

Here, I_s, B_s, T_s and I_a, B, T are the intensity of scattered light, proportionality constant, relative coagulation time for single primary particles and for aggregates, respectively. The sum of both intensities

$$I = I_s + I_a = B_s N_o (1 + T_s)^{-1} + B N_{p,\infty} + (1 + T^{-1})^{-1} \qquad (54)$$

and it is measured in short times of coagulation.
When $T_s \to \infty$, $T \to \infty$, $I \to I_\infty = B N_{p,\infty}$, also, when $T_s = 0$ then $I_a = 0$. $I = I_o = B_s N_o$ and one obtains

$$x = I/I_\infty = (I_o/I_\infty)(1 + T_s)^{-1} + (1 + T^{-1})^{-1} \qquad (55)$$

Prior to the start of coagulation, when the primary particles are small, I_o is small compared with I_∞, i. e. $I_o/I_\infty \ll 1$. Also in many sols, like AgI, the primary single particles dissapear very quickly. This means that $T_s \ll T$, i. e. $t_{1/2,s} > t_{1/2}$. For illustration, in Figure 6. values $I_o/I_\infty = 0.1$ and $t_{1/2,s}/t_{1/2} = 0.1$ are used which approximately correspond to the values of AgI sols obtained by direct mixing of the precipitating components and coagulator. It follows from Figure 6 that the plot »I vs. T« cannot be distinguished from the tangent through $T = 0$. One can easily see that tangent 3 (through point $t = 0$, $I = I_o$) cannot be used for the characterization of either line 5 (eq. (33)), which is valid for single particles, or tangent 4 which is valid for the aggregates.

STABILITY FACTOR

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of coagulation (Ref. 22, 23, 24; see also discussion in Ref. 17, p. 198—200) uses for the characterization of a coagulator the stability factor W, which is the ratio of the maximal reaction kinetics constant k_{max} and its varying values k in lower (medium) concentrations, i. e.

$$W = k_{max}/k$$

The dependence of W on c can be represented as the plot »$\log W$ vs. $\log c$« (Figure 7). In the medium range of concentrations, the plot is a line with slope A. In high concentrations, when $c \geqq c_{coag}$ $W = 1$. The intersection of the line with slope A with the horizontal line $\log W = 0$ is then the coagulation concentration c_{coag} (not $c_{coag,t}$ of Figure 5!).

Considering eqs. (40), (41), (47) and (55) one obtains from (43) for $x_t = 1/2$, $t = t_{1/2}$, $c = c_{1/2,t}$

$$(c_{1/2,\max}/c_{1/2,t})^A = (c_{coag}/c_{coag,t})^A = t_{1/2}/t_{1/2,\min} = t_{crit}/t_{crit,\min} = k_{max}/k = W \qquad (57)$$

It was already shown that the values of $c_{coag,t}$ (for $t =$ const.) and t_{crit} can be measured with the highest precision. Substituting into them eq. (57) and taking the logarithm one obtains:

$$\log W = \log (t_{crit}/t_{crit,\min}) = A \log(c_{coag}/c_{coag,t}) \qquad (58)$$

Plot »$\log c_{coag,t}$ vs. $\log c$« will, therefore, be in the medium range of concentration a straight line with slope A. In the range $c \geqq c_{coag}$ it should be constant. The same plot is equivalent to the plot »$\log W$ vs. $\log c$«. The intercept of the line with the abscissa gives $\log c_{coag}$ value. Slope A can be explained by eqs. (4) and (5) as the number A of coagulator ions K which react with a single primary particle P. The concentration of coagulator ion is $[K] = c = c_{coag,t}$, the concentration of primary particles ready for coagulation is $[PK_A] = c_o$ and both are constant because the concentration [P] of unreacted primary particles which are in equilibrium with the coagulator is negligible.

The same is valid for the plot »log c_{crit} vs. log c«. In principle, it is therefore possible to determine from both experimental plots the coagulation concentrations c_{coag} and parameter A of eqs. (4) and (5).

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SAŽETAK

Tumačenje procesa koagulacije

M. Mirnik

Proces koagulacije tumači se kao reakcija drugog reda, uz pretpostavku da intenzitet raspršenog svjetla slijedi Rayleigh-jevu jednadžbu. Pri sudaru dvaju agregata manji se agregat smanji za određeni broj primarnih čestica, a veći se za taj isti broj poveća. »Kritično vrijeme« (t_{crit}) određeno je odsječkom tangente kroz infleksiju na krivulji »I *vs.* lg t« na osi lg t (I = intenzitet raspršenog svjetla, t = = vrijeme od početka koagulacije). Vrijeme polukoagulacije ($t_{1/2}$) može se izračunati po jednadžbi izvedenoj u radu:

$$t_{1/2} = t_{crit}\, e^2$$

Odsječak tangente na najstrmiji dio krivulje »I *vs.* lg c« na osi lg c (c = promjenljiva koncentracija koagulatora), izmjerene u prikladno vrijeme t, jest »kritična koagulacijska koncentracija«, c.c.c. = $c_{coag,\,t}$. Dokazana je valjanost jednadžbe

$$\text{c.c.c.} = c_{1/2,\,t} = e^{2/A}\, c_{coag,\,t}$$

Eksponent A protumačen je kao broj iona koagulatora koji reagiraju s pojedinom primarnom česticom u brzoj ionskoj reakciji koja prethodi reakciji koagulacije. To znači da je u proračunanoj koncentraciji $c_{1/2,\,t}$ prikladno vrijeme t jednako $t_{1/2}$ za tu koncentraciju, tj. $t = t_{1/2}$. Dokazano je da teorijski pravac »1/I *vs.* 1/t« može poslužiti za određivanje $t_{1/2}$. Odsječak toga pravca na ordinati 1/I određuje vrijednost $1/I_{\infty}$, tj. $1/t = 1/\infty = 0$ vrijednost $1/I = 1/I_{\infty}$. Vrijednost na pravcu $2/I_{\infty}$ određuje vrijeme polukoagulacije, tj. za $1/I = 2/I_{\infty}$, $1/t = 1/t_{1/2}$. Dokazano je također da su linearne funkcije »lg $c_{coag,\,t}$ *vs.* lg c« i »lg t_{crit} *vs.* lg c« ekvivalentne linearnoj funkciji »lg W *vs.* lg c«. Ovdje je W »faktor stabilnosti« definiran kao $W = k_{max}/k = t_{1/2}/t_{1/2,\,min}$. Svaki koagulator pokazuje, naime, određenu koncentraciju u kojoj konstanta brzine koagulacije k poprima maksimalnu vrijednost k_{max}, a vrijeme polukoagulacije minimalnu vrijednost $t_{1/2,\,min}$. Ta se koncentracija katkad naziva koagulacijska koncentracija, c_{coag}, koja je karakteristična za svaki koagulator. Objašnjeno je zašto se mogu t_{crit} i $c_{coag,\,t}$ mjeriti s najvećom mogućom preciznošću. U kratka vremena nakon početka koagulacije mjereni I je zbroj intenziteta svjetla raspršenog na pojedinim primarnim česticama, I_s, i svjetla raspršenog na agregatima, tj. $I = I_s + I_a$. Tangenta na funkciju »I *vs.* t« za $t \to 0$ u tom slučaju ne određuje niti vrijeme polukoagulacije nestajanja primarnih čestica niti rasta agregata.