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Coagulation as a Second Order Process — a Basis for Computer Simulation

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Coagulation is interpreted as a second-order process caused by efficient collisions either between free primary particles (FPPs), FPPs and aggregates (AGGs) or between AGGs themselves. The following relations and definitions are derived theoretically: size distribution of AGGs: $P_1(I) = (T-1)P_o + I \leqq P_a = TP_o < P_r(I) = (T+1)P_o - I + 1$ for $1 \leqq I \leqq P_o$; total number of PPs present in AGGs defined by the distribution parameter T: $S_p(T) = 2V(T)P_o$ $\sum_{I=1}^{P_o} 2^I = 4V(T)P_o(2^{P_o}-1)$; relative volume in which AGGs defined by a given T are present: $V(T) = (T+1)V(T=1)/2$; number of AGGs of size $P_1(I)$ and $P_r(I)$: $A_I(I) = N_p(I)/P_1$ and $A_r(I) = N_p(I)/P_r$; number of PPs in AGGs of size $P_1(I)$ and $P_r(I)$: $N_p(I) = V(T)P_o 2^I$; coagulation time of FPPs: $T_f = T_{fab}/T_{f2} = S_p(P_o)/[S_p - S_p(P_o)]$ where $S_p = S_p(P_{o,max})$; coagulation time of AGGs: $T_c = T_{cab}/T_{c2} = 1/(A_a - 1)$; number of AGGs of average size P_a; $A_a(T) = S_p(T)/P_a = V(T)T_o/T$ where $T_o = S_p/P_o$, $1 \leqq T \leqq T_o$ and $0 < T_c \leqq \infty$. It is demonstrated that A_a is the reciprocal ratio of reactant concentration, P_a is the relative reaction product concentration for the coagulation of AGGs. The reaction product concentration for the coagulation of FPPs is $S_p(P_o)/V(T=1)$ and $[S_p(P_{o,max}) - S_p(P_o)]/V(T=1)$ is the reactant concentration. The relative coagulation times of FPPs and of AGGs resp. are defined as the ratio [reaction product]/[reactant] of second order reactions. The formation of AGGs defined by $P_o = 6$ from FPPs and the growth of AGGs defined by $T = 1$ into those defined by $T = 2$ in steps of $\Delta T = 1/P_o$ is also demonstrated numerically as an example. Simple programs can be set up to demonstrate graphically the shift of the histograms "A_1, A_r vs, P_1, P_r" and "N_p vs. P_1, P_r" with increasing T_c and to calculate the values A_a for any value of P_o the computer can process. One of the aims of the experiments should be to evaluate the values of S_p (exp). Then, as rule, a P_o value can be established for which $S_p(P_o) < S_p(\text{exp}) < S_p(P_o + 1)$ is valid and a correction factor F for which $F = S_p(\text{exp})/S_p(P_o)$ is valid. Then is F the number of AGGs of maximal size. When only T-*th* AGG size is present in the coagulating sol, then the smallest AGG size is $P_1(I=1) = T$ and the width of the histogram is defined by $P_o' = TP_o$ instead of P_o.

Notation: P_o = parameter defining the width of the AGG size (= number of PPs) histogram; $P_{o,max}$ = the same when all FPPs

have reacted and transformed into AGGs; T = parameter defining the sizes P_l, P_a, P_r of the AGGs; P_l, P_a, P_r left hand, average and right hand size of the AGG size histogram; T_{fab} = time and T_{f2} half-life of coagulation of FPPs; T_{cab} = time and T_{c2} = half-life of coagulation of AGGs; $V(T = 1)$ volume in which S_p of PPs are present; $D(T) = \sqrt[3]{V(T)}$ = side length of the cube of volume $V(T)$, $V_m(T)$ = volume in which one AGG of maximal size $P_r(I = 1, T)$ is present.

INTRODUCTION[1]

The purpose of the present theoretical investigation is to interpret coagulation as a second order process which is a consequence of collisions of single free primary particles (FPPs) and of aggregates (AGGs) due to Brownian motion. As PPs those particles are understood which form during coagulation the AGGs. The space between the PPs in AGGs is filled up with intermicellar liquid. As a rule in experimental systems, PPs are polydisperse with an average size and form. A theoretical sol with monodisperse average PPs is supposed to coagulate in the same manner as the polydisperse real sol. Prior to the start of coagulation, induced by addition of a coagulator, it is supposed that all PPs are dispersed as FPPs.

Suppose that a sol, prior to the addition of a coagulator, consists of a given number concentration of FPPs. Due to the absence of the coagulator the sol is stable, i.e. the rate of coagulation is infinitesimally small. Due to Brownian motion, FPPs collide but their surface prevents the colliding FPPs to adhere to each other, i.e. to form AGGs.

After addition of the coagulator, all, or a given fraction of collisions, are efficient. This means that AGGs of 2, 3, ... PPs are formed. We call the number of PPs in an AGG the (number) size, P, of the AGG. After a sufficiently long time, all FPPs will disappear from the sol and the coagulation will proceed due to collisions of the AGGs only. A fundamental assumption here is that only those collisions can be efficient which, at a given time of coagulation, produce AGGs of sizes, P, and PPs numbers, N_p, between a minimal and a maximal value which fit into the histogram.

At the absolute time T_{ab} an average number of AGGs, A_a, of the average number size, P_a and of a constant number of PPs in all AGGs, S_p, in a relative volume $V(T = 1) = 1$ would form theoretical sol.

The aim of the present paper is to propose an AGG size and number distribution, a histogram, as function of the coagulation time, while coagulation is supposed to be a second order process, i.e. a reaction caused by efficient collisions between two FPPs, a FPP and an AGG or two AGGs, respectively. There are no whatsoever speculations on the actual form of the AGGs because they are evidently no dense regular spheres. They are loose flocks of PPs filled with intermicellar liquid between them and can be of a very irregular form and size indeed.

Useful theories on coagulation should be able to predict or to explain the absolute value of the halflife of coagulation (T_{fab}, T_{cab}), or at least, the influence of sol concentration, coagulator concentration and charge, electric chagers or potentials on PPs and AGGs, diffusion coefficients, viscosity, temperature, and others.

THEORETICAL

Collisions of free primary particles

After addition of a coagulator, as long as FPPs are present in the coagulating sol, the AGG size due to unit efficient collisions can be calculated using the equation:

$$P + 1 = (P + 1) \tag{1}$$

The size of FPPs is $P = 1$, the size of the colliding AGGs is $1 \leqq P$, that of the newly formed AGG is $(P + 1)$. A sequence of efficient collisions can produce AGGs of any size $P \leqq S_p + TP_o$.

Sizes of AGGs can be defined in the following way:

$$P_l \leqq (T - 1)\, P_o + I \leqq P_a = T\, P_o < P_r = (T + 1)\, P_o - I + 1 \tag{2}$$

for $1 \leqq T \leqq T_o$, $1 \leqq I \leqq P_o$ (all are integers, for T_o see eq. 19). This means that the dependence of PP number and AGG number is represented by a histogram. The left hand side of the histogram form AGGs of size P_l and the right hand side those of P_r. The average size is $P_a = TP_o$.

As long as FPPs are present in the sol $T = 1$ and characteristic stages are obtained when P_o stepwise increases by one. The smallest AGG has the size $P_l = 1$. The average size is $P_a = P_o$ and the biggest AGG has the size $P_r = 2P_o$. The number of PPs in an AGG of size P is $N(P)$.

The number of AGGs of any size P can be designated by $A(P)$ and defined by (for $T = 1$):

$$A(P) = N(P)/P \tag{3}$$

and it must be valid:

$$A(P_r - 1) > A(P_r) \geqq A(2P_o) \tag{4}$$

Since $A(2P_o) = 1$ must be minimum and consequently $N(2P_o) = A(2P_o) = 2P_o$ the following is also valid:

$$A(2P_o - 1) > 1 \tag{5}$$

The smallest integer factor greater than one is 2 and

$$N(2P_o - 1) > N(2P_o) \tag{6}$$

and as a consequence:

$$N(2P_o - 1) = 2 \cdot P_o \tag{7}$$

and, for any P_r:

$$N(P_r) = N(2P_o - I + 1) = 2^I P_o,\ 1 \leqq I \leqq P_o \tag{8}$$

The rate of efficient collisions of the smallest AGGs is the highest, because the smallest AGGs can collide efficiently with any AGG of size P_l according to eq. (1). Consequently, the following is valid:

$$A(P_l) < A(P_l + 1) \tag{9}$$

and also

$$N(P_l) < N(P_l + 1) \tag{10}$$

The number of PPs disappearing in all P_l is equal to the number of PPs for which P_r increase. Consequently, the histogram will be symetric

and we shall assume that $N(P = 1) = N(2P_o) = 2P_o(I = 1)$ and $N(P_a) = N(P_a + 1)$ and again the smallest rational integer factor greater than one is 2 and the following must be valid:

$$N(P = 2) = 2N(P = 1) = 2 \cdot 2P_o \tag{11}$$

and for any $P_l = (T - 1)P_o + I$:

$$N(P_l) = 2^l P_o, \quad 1 \leqq I \leqq P_o \tag{12}$$

An additional argument for basis 2 in equations 8, 12 is the fact that the PP number of the left hand side of the histogram must be even so that all PPs can react and dissappear in collisions of two AGGs. Analogously, the right hand side PP number must be even since it is always formed from the left hand side PPs.

The AGGs increase from 1 to the size $P_r = 2P_o$ which will be reached when the last FPP will disappear. We shall assume formally that a part of PPs of size $P_l = 1$ are AGGs of size $P_l = 1$. The formation of AGGs of the maximal size $P_{o,max}$ can be described by the stepwise increase of $P_o = 1$ to $P_{o,max}$, i.e. when $1 \leqq P_o \leqq P_{o,max}$. In Ttable I, the formation of AGGs defined by $P_{o,max} = 6$ and $S_p = 1512$ is illustrated as an example.

TABLE I

Formation of aggregates of maximal size $P_r = 2P_o = 12$ *when* P_o *stepwise increases from* $P_o = 1$ *to 6. The number of primary particles is* $N(P_l) = N(P_r) = P_o 2^l$. *The number of all primary particles in all agregates for a given* P_o *is* $S_p(P_o)$ *and for* $P_o = 6$, $S_p = S_p(6) = 1512$. *The relative coagulation time of free primary particles is* T_f *for* $1 \leqq P_o \leqq P_{o\,max}$.

$P \rightarrow$	1	2	3	4	5	6	7	8	9	10	11	12	$S_P(P_o)$	T_F
1	1.2^1	1.2^1	←										4	.0027
2	2.2^1	2.2^2	2.2^2	2.2^1	←								24	.0161
3	3.2^1	3.2^2	3.2^3	3.2^3	3.2^2	3.2^1	←		← $N(P) = P_o \cdot 2^l$				84	0588
4	4.2^1	4.2^2	4.2^3	4.2^4	4.2^4	4.2^3	4.2^2	4.2^1	←				240	.1887
5	5.2^1	5.2^2	5.2^3	5.2^4	5.2^5	5.2^5	5.2^4	5.2^3	5.2^2	5.2^1	←		620	.6951
6	6.2^1	6.2^2	6.2^3	6.2^4	6.2^5	6.2^6	6.2^6	6.2^5	6.2^4	6.2^3	6.2^2	6.2^1	1512	∞
$P_o \uparrow$	1	$\leqslant P_L \leqslant$				P_o	$< P_R = 2P_o - I + 1 \leqslant$					$2P_o$		
	1	$\leqslant I \leqslant$				P_o	P_o		$\geqslant I$		$\geqslant$	1		

Coagulation time of free primary particles

The total number of PPs in the AGGs will be designated by $S_p(P_o)$ and can be calculated as the sum of all PPs in all AGGs using the summation:

$$S_p(P_o) = \sum_{p=1}^{2P_o} N(P) = P_o \sum_{I=1}^{P_o} 2^I + P_o \sum_{I=P_o}^{1} 2^I = 2P_o \sum_{I=1}^{P_o} 2^I \tag{13}$$

for $1 \leqq I \leqq P_o$.

It can be proved (see *Remark) that the same sum can be calculated using the following very simple equation:

$$S_p(P_o) = 4P_o(2^{P_o} - 1) \tag{14}$$

The sum $S_p(P_o)$ can also be calculated in the following way. For $T = 1$ $P_a = P_o$, the maximal A_{ao} and E_o can be calculated when inserted in eq. (3) by the following equation:

$$A_{ao} = S_p(P_o)/P_o = 2^{E_o} (= T_o) \tag{15}$$

where A_{ao} is the number of AGGs of average size $P_a = T_oP_o$. We define the exponent E_o by the following equation:

$$2^{E_o} = 4(2^{P_o} - 1) \tag{16}$$

The logarithm of the same equation after rearrangement gives:

$$E_o = 1g\,[4(2^{P_o} - 1)] \,/\, 1g2 \tag{17}$$

The sum $S_p(P_o)$ can therefore be obtained also from the following very simple equation:

$$S_p(P_o) = P_o 2^{E_o} \tag{18}$$

The sum for $P_o = P_{o\,max}$ will from now on be designated by $S_p = S_p(P_{o,max})$ and the parameter T_o defined as:

$$T_o = S_p/P_o \tag{19}$$

The number of FPPs, in the relative volume $V(T = 1) = 1$, equals their concentration and it can be calculated by the equation:

$$N(\text{FPP}) = S_p - S_p(P_o) \tag{20}$$

According to the theory of second order reaction kinetics, the relative reaction time is defined by[2,3].

$$\text{relative reaction time} = [\text{reaction product}] \,/\, [\text{reactant}] \tag{21}$$

The reaction product concentration or activity of FPPs will be assumed to be equal to $S_p(P_o)/V(T = 1)$ and the reactant activity to $N(\text{FPP})/V(T = 1)$. The coagulation time of FPPs is T_{fab} and the halflife of FPPs is T_{f2}, and the relative coagulation time of FPP, T_f, is then defined by:

$$T_f = T_{fab}/T_{f2} \tag{22}$$

and it can be calculated as the ratio:

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* Remark:

$$2\sum_{I=1}^{P_o} 2^I = \sum_{I=2}^{P_o} 2^I + 2^{P_o+1}\ ; \qquad 2^{P_o+1} = 2\sum_{I=1}^{P_o} 2^I - \sum_{I=2}^{P_o} 2^I;$$

$$2^{P_o+1} - 2 = 2\sum_{I=1}^{P_o} 2^I - (\sum_{I=2}^{P_o} 2^I + 2); \qquad 2(2^{P_o} - 1) = 2\sum_{I=1}^{P_o} 2^I - \sum_{I=1}^{P_o} 2^I;$$

$$2(2^{P_o} - 1) = \sum_{I=1}^{P_o} 2^I; \qquad 4P_o(2^{P_o} - 1) = 2P_o \sum_{I=1}^{P_o} 2^I \text{ (see eqs. 13, 14)}$$

$$T_f = S_p(P_o) \;/\; [S_p - S_p(P_o)], \qquad 1 \leqq P_o \leqq P_{o,max} \tag{23}$$

For illustration, the values of $N(P)$, $S_p(P_o)$ and T_f for $1 \leqq P_o \leqq P_{o,max} = 6$, $S_p = 1512$ are listed in Table I.

Coagulation time of aggregates

The size of all AGGs defined by a given T can be replaced in calculations by their average size, P_a, and defined by:

$$P_a = TP_o \tag{24}$$

Then, the average number, A_a, of AGGs of average size P_a, can be obtained using the equation:

$$A_a = S_p/P_a = T_o/T \tag{25}$$

Now, the supposition is made that a monodisperse sol with AGGs of size, P_a, and their number, A_a, in the relative volume $1 \leqq V(T)$ would coagulate at the same rate as the polydisperse sol.

The reaction product concentration in eq. (21) is proportional to $P_a/V(T)$, and the reactant concentration to $(S_p - P_a)/V(T)$. The absolute coagulation time is T_{cab} the halflife of coagulation of AGGs is T_{c2}, the relative coagulation time is T_c and the following is valid:

$$T_c = T_{cab}/T_{c2} \tag{26}$$

The same entities inserted in eq. (21) give the definition of the relative AGG coagulation time, T_c, which reads:

$$T_c = P_a/(S_p - P_a) = T/(T_o - T) \tag{27}$$

The latter equation combined with eq. (25) reads

$$T_c = (A_a - 1)^{-1} = (T_o/T - 1)^{-1} \quad (\text{or } (1 + T_c)^{-1} = 1 - A_a^{-1}) \tag{28}$$

or

$$A_a = 1 + T_c^{-1} \tag{29}$$

For illustrative calculations, as independent preset parameters, integers of $A_a \geq 2$ or powers $A_a = 2^E$ for $E_o > E$ (integers) $\geqq 1$ in eq. (28) or integers of $T \geqq 1$ in eq. (29) can be used (Tables III a and III b). The preset values of $V(T)$, $V_m(T)$, T, or P_a can also be rationally chosen. In this way, an evenly distributed sufficient number of calculated values can be obtained for illustration. In Tables III a and III b, the preset parameters are marked with an asterisk*.

The progress of coagulation is a consequence of efficient collisions of AGGs of size $1 \leqq P_1, P_1' \leqq P_a = TP_o$ which are already present when $T_c < \infty$ and $1 \leqq T \leqq T_o$. The general equation for the calculation of the AGG sizes can be written in the form

$$P_1 + P'_1 = (P_1 - J) + (P_1' + J) \tag{30}$$

where $1 \leqq P_1 \leqq P'_1$ and $1 \leqq J \leqq P_1$. Each of the AGGs of any size can collide with any other AGG. If $(P_1' + J)$ and $N(P_1' + J)$ are equal to the values of the right hand side of the histogram for the last T, the collision can be efficient. The newly formed AGG of size $P_{1,new} = (P_1 - J)$ will collide effi-

ciently again and produce $(P_1' + J)$ if it fits in the right hand side of the histogram and the collisions of $P_{1,new}$ will be repeated as many times as necessary that the last $P_{1,new}$ to disapper. The halflife of $P_{1,new} < P_1$ are extremely small as compared with those fitting in the histogram.

When $T = T_o$, $c_o = N_o/V_s$, one single maximal AGG of size $P_r = (T_o + 1) P_o$ will be formed in an absolute volume V_o' defined by

$$V_o' = (T_o + 1) S_p/c_o \tag{31}$$

Here c_o is the concentration and N_o the number of PPs in an absolute volume of the system V_s. When $1 \leqq T \leqq T_o$ then:

$$V'(T) = (T + 1) S_p/c_o \tag{32}$$

and for $T = 1$

$$V'(T = 1) = 2S_p/c_o \tag{33}$$

The volume, $V'(T)$, in which one maximal AGG is formed for a given T, can therefore be defined by:

$$V'(T) = V'(1) (T + 1)/2 \tag{34}$$

The volumes V_o', $V'(T)$, $V'(1)$ are absolute volumes. We can define a relative reduced volume

$$V(T = 1) = V'(T = 1) c_o/2S_p = 1 \tag{35}$$

a relative volume

$$V(T) = (T + 1)/2 \tag{36}$$

and a relative volume

$$V(T_o) = (T_o + 1)/2 \tag{37}$$

The length of the sides, $D(T)$, of the corresponding cubes are defined by:

$$D(T) = \sqrt[3]{V(T)} \tag{38}$$

TABLE II

Size of aggregates P_I *and* P_r *in which the number of primary particles is* $N(I) = P_o 2^I$ *for* $1 \leqq I \leqq P_o = 6$ *and* $1 \leqq T \leqq 2$. *The relative coagulation time is* T_c *and the relative volume in which one aggregate of maximal size* $(T + 1) P_o$ *is formed is* $V(T)$. *If assumed to be a cube, its side lenght is* $D(T) = \sqrt[3]{V(T)}$, $V_m(T) = 1/A_c(T, I = 1)$ *is the volume in which one aggregate of maximal size* $A_r(T, I = 1)$ *is present.*

$\vec{I}$	1	2	3	4	5	6	6	5	4	3	2	1	$T_c \cdot 10^3$	$V(T)$	$V_m(T)$
$\vec{N(I)}$	6.2^1	6.2^2	6.2^3	6.2^4	6.2^5	6.2^6	6.2^6	6.2^5	6.2^4	6.2^3	6.2^2	6.2^1			
1+0/6	1	2	3	4	5	6	7	8	9	10	11	12	3.9841	1	1
1+1/6	2	3	4	5	6	7	8	9	10	11	12	13	4.6512	1.083	1.1527
1+2/6	3	4	5	6	7	8	9	10	11	12	13	14	5.3191	1.16	1.305
1+3/6	4	5	6	7	8	9	10	11	12	13	14	15	5.938	1.25	1.483
1+4/6	5	6	7	8	9	10	11	12	13	14	15	16	6.6578	1.3	1.61
1+5/6	6	7	8	9	10	11	12	13	14	15	16	17	7.3234	1.416	1.7638
1+6/6	7	8	9	10	11	12	13	14	15	16	17	18	8	1.5	1.916

$$T \uparrow \quad (T-1)P_o+1 \leqslant P_L \leqslant TP_o \qquad \frac{TP_o}{+1} \leqslant P_R \leqslant (T+1)P_o$$

All this means that one single AGG of maximal size $(T + 1)P_o$ is present in the relative volume $V(T)$. A rational increase of T is $1/P_o$ which represents the increase of P_a by one. Then, the new $T_{new} = T + 1/P_o$ and the new $P_{new} = P + 1$ and also $P_{a,new} = P_a + 1$. If however $I_{new} = I - 1$, then is $P_{l,new}$ for $2 \leqq I \leqq P_o$ and $1 \leqq I_{new} \leqq P_o - 1$ and the new sizes are defined by:

$$P_{l,new} = (T_{new} - 1)\,P_o + I - 1 \leqq T_{new}P_o < P_{r,new} = (T_{new} + 1)\,P_o - I + 1 \tag{39}$$

In Table II, the values of P_l, P_r, are listed for $P_o = 6$. Each foregoing line gives the values without index and each next line those with index »new«. The following conclusions can be drawn for an increase of T to $T + 1/P_o$:

(A) All AGGs of size $P_l(I = 1) = (T - 1)P_o + 1$ dissappear and the same number of PPs appears in one AGG of size $P_{r,new}$ because:

$$N\,[(T - 1)\,P_o + 1] = N(T + 1)P_o = N_l(I = 1) = N_r(I = 1) = P_o 2^1 \tag{40}$$

and also:

$$V_{new} = (T_{new} + 1)/2 \tag{41}$$

(B) AGGs of size $P_r(I = P_o) = TP_o + 1$ remain AGGs of equal size and number of PPs, however designated by $P_{l,new} = TP_o$ while their number of PPs remains unchanged, i. e.

$$N_r(TP_o + 1) = N_l(T_{new}P_o) \tag{42}$$

(C) The number of PPs in AGGs of size $(T - 1)P_o + 2 \leqq P_l \leqq TP_o$ reduces to one half, and the number of PPs of AGGs of size $TP_o + 2 \leqq P_{l,new} < (T + 1)P_o$ increases by a factor of two. Then the following is valid, namely (for $1 \leqq I \leqq P_o$):

$$N_l(I + 1)/2 = N_l(I) \tag{43}$$

$$N_l(I + 1)/2 + N_r(I) = N_r(I + 1) \tag{44}$$

$$N_r(I + 1) = 2N_r(I) \tag{45}$$

The values of $N_l(I)$ are equal to those on $N_r(I)$ for any $1 \leqq T = \text{const} \leqq T_c$. The increase of T for $1/P_o$ takes place in halflives of $P_l(I = 2) \leqq P_l \leqq P_l(I = P_o)$. The halflife of AGGs of $P_l(I = 1)$ is extremely small and the halflife of AGGs of $P_r(I = P_o)$ is long as compared with those of $2 \leqq I \leqq P_o$.

In principle, using convenient experimental techni.ques, T_a, T_{c2}, P_a, A_a, S_p can be measured. As a rule, S_p (exp), determined experimentally, will be different for any $S_p(P_o)$ determined with any $1 < P_o$, i. e. $S_p(P_o) < S_p$ (exp) $< S_p(P_o + 1)$. In such a case a factor F should be introduced to fit the equation:

$$FS_p(P_o) = S_p \text{ (exp)} \tag{46}$$

Factor F can be explained as a relative volume from which, at $T_c \to \infty$, F AGGs of maximal size $V_o(S_p + P_o)$ or F AGGs of average size $P_a = V_oS_p$ $(A_a = 1)$ would be the result.

It is evident that the interdependent variables T_c, A_a, T/T_o are valid for any second order experimental or theoretical process characterized by concrete values of P_o, T_o, S_p, F. A useful theory of coagulation should be able, therefore, to predict the values of T_{f2} and T_{c2}, F, P_o for a given sol,

that is the influences upon the parameters T_{f2}, T_{c2} like: sol and coagulator concentration, type and charge of the coagulator, dielectric permittivity of the solvent or the solvent composition, viscosity, diffusion coefficients of FPPs and AGGs, temperature and others, supposing that the model used is correct.

TABLE III a

Coagulation kinetics of aggregates defined by $P_c = 6$, $S_p = 1512$, $T_o = 252$ *for* $1 \leqq T \leqq T_o/2 = 126$. *If each* $P_I = IT$ *and* $P_r = (2P_o - I)\,T + 1$, *only* $1 \leqq I \leqq P_o$ *is present in the histogram, then is the size of the smallest aggregates* $P_I(I = 1) = T$. *Values valid for any second order process are* E, A_a, T_c, T/T_o. *Values valid for* $P_o = 6$ *only are* T, P_a, V(T), $V_m(T)$.

Valid for any second order reaction				Valid for $P_o = 6$, $T_o = 252$, $S_p = 1512$			
E	$A_a = 2^E$	$T_c = (A_a - 1)^{-1}$	$T/T_o = A_a^{-1}$	$T = T_o/A_a$	P_a	V(T)	$V_m(T)$
$E_0 = 7.9773$	$T_0 = 252$	$3.9841\ 10^{-3}$	$3.968254\ 10^{-3}$	*1	*6 = P_o	*1	1
*7	*128	$2.8740\ 10^{-3}$	$7.8215\ 10^{-3}$	1.9688	11.8125	1.484	1.8880
6.9773	126	$8\ 10^{-3}$	$7.9365\ 10^{-3}$	*2	*12	1.5	1.416
*6	64	$1.5873\ 10^{-2}$	$1.5625\ 10^{-2}$	3.9375	23.625	2.4688	3.6927
*5	*32	$3.2258\ 10^{-2}$	$3.125\ 10^{-2}$	7.875	47.25	4.4375	7.302
	16,8	$6.3291\ 10^{-2}$	$5.9524\ 10^{-2}$	15	90	8	13.83
*4	*16	$6.6'\ 10^{-2}$	$6.25\ 10^{-2}$	15.75	94.5	8.375	14.5208
*3	*8	$1.4286\ 10^{-1}$	.125	31.5	189	16.25	28.958
	4.7547	$2.6633\ 10^{-1}$	.210	53	318	27	48.6'
*2	*4	$3.3'\ 10^{-1}$	.25	63	378	32	57.83'
	*3	$5\ 10^{-1}$	.3'	84	504	42.5	77.083'
*1	*2	*1	.5	126	756	63.5	115.583'

TABLE III b

The same as in Table IIIa for $T_o/2 = 126 \leqq T \leqq 252$.

Valid for any second order reaction			Valid for $P_o = 6$, $T_o = 252$, $S_p = 1512$			
$A_a = 1 + T_c^{-1}$	$T_c = (A_a - 1)^{-1}$	$T/T_o = A_a^{-1}$	$T = T_o/A_a$	P_a	V(T)	$V_m(T)$
2.0	*1	.5	126	756	63.5	115.583'
1.9843	1.016	.50397	127	762	**64**	**116.5**
1.5	*2	.6'	168	1008	84.5	154.083'
1.3'	*3	.75	189	1134	95	173.3'
1.25	*4	*.8	201.6	1209.6	101.3	184.883'
1.2	*5	.83'	210	1260	105.5	192.583'
1.16'	*6	.8571	216	1296	108.5	198.083'
1.1429	*7	.875	220.5	1323	110.75	202.208
1.125	*8	.8'	224	1344	112.5	205.416'
1.1'	*9	.9	226.8	1360.8	113.9	207.983'
1.1	*10	.909	229.09	1374.545	115.05	210.083'
1.09'	*11	.916'	231	1386	116	211.83'
1.083'	*12	.9231	232.61	1395.69	116.81	213.314
1.0416'	*24	.96	241.92	1451.52	121.46	221.843'
1.02083'	*48	.9796	246.86	1481.14	123.93'	226.368
1.01205	*83	.9881	249	1494	125	228.3'
1.010416'	*96	.9897	249.40	1496.412	125.20	228.702
1.00066	1510.999	.9993	251.83'	*1511	126.416'	230.930
1	∞	1	252	1512	126.5	231.083

In chemical reactions

$$A_a = [\text{reactant at time } T_c]/[\text{reactant at time } T_c = 0] =$$

$$= [\text{reaction product at time } T_c = \infty]/[\text{reaction product at } T_c] \quad (47)$$

is a relative dimensionless concentration ratio.

In Tables II, III a, III b, the coagulation is illustrated for $1 \leqq P_o \leqq P_{o,max} = 6$, $2 \leqq A_a \leqq 2^{Eo}$, $E_o > E(\text{integers}) \geqq 1$ or $1 \leqq T_c(\text{integers}) \leqq \infty$, in which way a sufficiently illustrative and acceptable number of values was obtained. The preset values of either E, A_a, T_c $V(T)$ or $V_m(T)$ are marked with*.

Broadening of histogram

Experiments suggest that the polydispersity of the coagulating sols is much greater than the acceptable P_o values permit. Broader histograms (increased polydispersity) can be obtained if each 2-, 3-,... N-th AGG size is assumed to be present in the sol. Then, the sizes of present AGGs can be defined by:

$$P_l = TP_o - N(P_o - I) \quad (48a)$$

$$P_r = TP_o + N(P_o - I) + 1, \; 1 \leqq I \leqq P_o \quad (48b)$$

The maximal possible $N = T$ and from it the broadest possible histogram is obtained. In this case:

$$P_l = IT \quad (49a)$$

$$P_r = (2P_o - I)\,T + 1, \; 1 \leqq I \leqq P_o \quad (49b)$$

while S_p remains constant. Then, the smallest AGG sizes are $P_l(I = 1) = T$, the average sizes are $P_l(I = P_o) = TP_o$, and the biggest sizes are $P_r(I = 1) = T(2P_o - 1) + 1$. The width of the histogram is defined by $P'_o = TP_o$. In Tables, *II*, *IIIa*, *IIIb*, the T integer values are at the same time also the values of $P_l(I = 1)$ if each *T-th* AGG size is present in the sol, i.e. $P_l(I = 1) = T$. The volume, $V_m(T)$, in which one AGG of maximal size is present is:

$$V_m(T) = 1/A_r(I = 1) = [(2P_o - 1)\,T + 1]/2P_o \quad (50)$$

The $V_m(T)$ values for $P_o = 6$ are presented in Tables II, IIIa, IIIb.

DISCUSSION

Von Smoluchowski's Theory of Fast Coagulation

One of the probably most cited theoretical papers on Brownian coagulation kinetics is that of von Smoluchowski.[3] Its eq. (24) reads:

$$\nu_k = \nu_o(a\nu_o t)^{k-1}/(1 + a\nu_o t)^{k+1} \quad (51)$$

where in our notation, $T_{ca} = t$, $T_{c2} = 1/a\nu_o$, $T_c = t\,a\nu_o$ (in fact $T_f = t\,a\nu_o$, because FPP of $k = 1$, never disappear) while k (= P in our notation) is the AGG size ("$k = 1, 2, 3, \ldots$ für die ein-, zwei-, drei-fachen Teilchen"). The total number concentration of PPs is ν_o (»Teilchenzahl pro Volumeninhalt«) and $\nu_k (= \nu_p)$ is the corresponding number concentration of AGGs of size k. The same equation can therefore be written (in our notation):

$$\nu_p/\nu_o = T_c^{p-1}/(1 + T_c)^{p+1} \tag{52}$$

Eq. (52) can be transformed (after division with T_c^{p+1} of the denominator and numerator) into:

$$\nu_p/\nu_o = T_c^{-2}/(1 + T_c^{-1})^{p+1} \tag{53}$$

and the corresponding sum reads:

$$(1/\nu_o)\,\Sigma\nu = \sum_{p=1}^{\infty} T_c^{-2}/(1 + T_c^{-1})^{p+1} \tag{54}$$

Eq. (23) of ref. 3 can be written in the form:

$$(1/\nu_o)\,\Sigma\nu = (1 + T_c)^{-1} \tag{55}$$

Combining eqs. (54) and (55) one obtains:

$$1/(1 + T_c) = \sum_{p=1}^{\infty} T_c^{-2}/(1 + T_c^{-1})^{p+1} \tag{56}$$

The same equation multiplied by T_c after rearrangement reads:

$$T_c = \sum_{p=1}^{\infty} (1 + T_c^{-1})^{-p} \tag{57}$$

Considering eq. (29), the same equation (57) can also written in the form:

$$T_c = \sum_{p=1}^{\infty} A_a^{-p} \tag{58}$$

By computation it can be proved that the T_c values calculated with the A_a values (eq. 28) and those calculated using equation (57) are equal. By computation, is also possible to prove the validity of

$$(1/\nu_o)\,\Sigma\nu = (1 + T_c)^{-1} \text{ (Smoluchowski}^3\text{, eq. 23, eq. 55)} =$$

$$= 1 - A_a^{-1} \text{ (eq. 28)} \tag{59}$$

This means that Smoluchowski's kinetics (ref. 3, eq. 24) follows the second order kinetics of the present article (Tables IIIa, IIIb).

Smoluchowski's $\Sigma\nu$ is the total AGG number concentration, i.e. the sum of the number of AGGs irrespectibily of their size, $P(= k)$, per unit volume. Its definition reads (obtained from eq. 52):

$$(1/\nu_o)\,\Sigma\nu = (1/\nu_o) \sum_{p=1}^{\infty} \nu_p = \sum_{p=1}^{\infty} T_c^{p-1}/(1 + T_c)^{p+1} \tag{60}$$

The number of PPs in unit volume in AGGs of size P is $\nu_p p\ (= \nu_k k)$ and for any T_c the following is valid:

$$(1/\nu_o) \sum_{p=1}^{\infty} P\nu_p = \sum_{p=1}^{\infty} PT_c^{-1}/(1 + T_c)^{p+1} = 1 \tag{61}$$

The numerical computation of equation (61) depends on the capacity of the computer or on the desired precision of the result. In any case, the term $(1 + T_c)^{p+1}$ cannot be bigger than the maximum number the computer can process.

If the summation of equation (61) is performed according to:

$$\sum_{P=1}^{P_a} P\,[T_c(P_a)]^{P-1} / [(1 + T_c(P_a)]^{P+1} = .5 \qquad (62)$$

then P_a is the average size of AGGs in the characteristic coagulation time $T_c(P_a)$. *Since* $1 \leqq P_a$ are integers, then the following $T_c(P_a)$ values are obtained:

P_a	1	2	3	4	6	8	9	11
$T_c(P_a)$	.4142	.5	1.5925	2.1866	3.3766	4.5673	5.1628	6.354
P_a	13	14	16	18	19	21	23	
$T_c(P_a)$	7.5454	8.1411	9.3325	10.524	11.1198	12.3113	13.5029	
P_a	24	26	28	.....				
$T_c(P_a)$	14.0987	15.2902	16.4818	.....				

However, equation (24) of Smoluchowski[3] is not applicable to experimental systems. Some of the reasons are:

(1) It is impossible that $P_a < 1$ in coagulation times $T_c < \sqrt{2} - 1 = .4142$ as it follows from equation (62). At any T_c, only PPs of size $P = 1$ can be the smallest and for any $\sqrt{2} - 1 \geqslant T_c(P_a = 1)\, P_a \geqq 1$ can only be valid.

(2) In experimental systems, PPs of size $P = 1$ dissappear very soon[4] (Tables I, II).

(3) The average size of AGGs in observable coagulation times of approximatelly $.01 \leqq T_c \leqq 7$, the average size P_a is of the order of 10^3 to 10^4 and not $P_a \leqq 11$ as it follows from equation (24) of ref. (3) or eq. (62).

(4) Hardly any argument can be cited why should not be valid in coagulation the laws of chemical kinetics (eq. 21) but the law of the »radius of dense spheric AGGs« used by Smoluchowski for the calculation of the collision probability, α.

(5) AGGs are not dense sphere, they are spongy irregular structures filled with electrolyte between the PPs (see e.g. ref. 4). Collision probabilities calculated from the radius of dense spheres cannot, therefore, be correct.

(6) It is quite impossible that in coagulation times $1 < T_c$ AGGs of sizes $P \to \infty$ would be present even in negligibly small concentrations as it follows from equations (23) and (24) of reference (3).

Valioulis, I. A. and List, E. J.[5] extended Smoluchowski's Brownian collision rate theory taking into account hydrodynamic, van der Waals and double layer forces between approaching particles. Since the Brownian collision probability, α, is also here the basis of calculations, all what was said above for the Smoluchowski's theory is valid also for the latter extensions. The same can be said for the work of Valioulis, I. A.[6]

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SAŽETAK

Koagulacija kao proces drugog reda — temelj kompjutorskoj simulaciji

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Koagulacija je zamišljena kao reakcija II. reda prouzrokovana efikasnim sudarima između slobodnih primarnih čestica (FPP), između FPP i agregata (AGG) ili između samih AGG. Na podlogi teorijskih pretpostavki izvedene su slijedeće definicije: veličina AGG: $P_l(I) = (T-1)P_o + I \leqq P_a = TP_o < P_r(I) = (T+1)P_o - I + 1$ za $1 \leqq I \leqq P_o$; ukupan broj PP koje su prisutne u svim AGG definiranima parametrom $T : S_p(T) = 2V(T)P_o \sum_{I=1}^{P_o} 2^I = 4V(T)P_o\,(2^{P_o} - 1)$; relativni volumen u kome su prisutni AGG definirani s $T : V(T) = (T+1)V(T=1)/2$; broj PP u AGG-ima veličine $P_l(I)$ i $P_r(I) : N_p(I) = V(T)P_o\,2^I$; broj AGG: $A_l(I) = N_p(I)/P$; $A_r(I) = N_p(I)/P_r$; vrijeme koagulacije FPP: $T_f = T_{fab}/T_{f2} = S_p(P_o)/[S_p - S_p(P_o)]$ a $S_p = S_p(P_{o\,max})$; vrijeme koagulacije AGG: $T_c \doteq T_{cab}/T_{c2} = 1/(A_a - 1)$, broj AGG prosječne veličine $P_a : A_a(T) = S_p/P_a = V(T)T_o/T$, gdje je $T_o = S_p/P_o$, $1 \leqq T \leqq T_o$ i $0 < T_c \leqq \infty$. Pokazano je da je A_a recipročni omjer koncentracije reaktanta, a P_a relativna koncentracija produkta, oboje za koagulaciju AGG. Koncentracija produkta koagulacije FPP je $S_p(P_o)/V(T=1)$, a $[S_p(P_{o\,max}) - S_p(P_o)]/V(T=1)$ je koncentracija reaktanta koagulacije FPP. Relativno vrijeme koagulacije FPP i AGG je omjer [produkt]/[reaktant] reakcije II. reda. Nastanak AGG definiranih sa $P_o = 6$ od FPP i rast AGG koji su definirani s $T \doteq 1$ u agregate koji su definirani sa $T = 2$ u koracima $\Delta T = 1/P_o$ također je prikazan numerički. Jednostavnim programima može se pokazati pomicanje histograma sa rastućim T odnosno T_c i računati A_a, T, P_a, $V(T)$, $V_m(T)$ za svaku vrijednost P_o koju dopušta kapacitet računala. Jedna od svrha eksperimentiranja jest utvrđivanje $S_p(\text{exp})$. U pravilu mora postojati vrijednost P_o za koju vrijedi: $S_p(P_o) < S_p(\text{exp}) < S_p(P_o + 1)$, a faktor korekcije $F = S_p(\text{exp})/S_p(P_o)$ jednak je broju AGG maksimalne veličine kada je $T = 1$. Ako je samo svaki AGG veličine IT prisutan u koagulirajućem solu onda je najmanji AGG $P_l(I=1) = T$, a širina histograma je definirana sa $P'_o = TP_o$.

Simboli: P_o = parametar koji definira širinu histograma; $P_{o\,max}$ = isto kada su nestale sve FPP; T = parametar koji definira P_l, P_a, P_r = veličine lijevih, prosječnih, desnih AGGa u histogramu; T_{fab} = vrijeme, T_{f2} = vrijeme polukoagulacije FPPa; T_{cab} = vrijeme, T_{c2} = vrijeme polukoagulacije AGG; $V(T=1)$ = volumen u kome se nalazi S_p FPP; $D(T) = \sqrt[3]{V(T)}$ = stranica kocke volumena $V(T)$, $V_m(T)$ = volumen u kojem je prisutan jedan AGG maksimalne veličine $A_r(T, I=1)$.