

ISSN 0011-1643
UDC 541.1
CCA-2060

Original Scientific Paper

Coagulation Theory of Small Aggregates

Mirko Mirnik

*Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb,
41001 Zagreb, P.O.B. 163, Croatia*

Received November 23, 1991

The thermodynamic theory of coagulation kinetics¹ was extended in the present paper in order to explain the time evolution of doublets, triplets, ..., etc. from singlets. The experiments of reference [2] on the coagulation of singlets of hard polystyrene and soft polyvinyl acetate latexes, interpreted in terms of the same theory, confirm the theory in several ways: (a) the theoretical plots of time evolution of singlets, doublets and triplets fit the experimental points, (b) the maximum on the doublet plot is at the predicted value of 1.2 halflives, (c) the doublet plot becomes equal to the singlet plot at halflife 3, (d) the plot »reciprocal singlet fraction vs. reciprocal time« is linear, (e) von Smoluchowski's theoretical plot cannot be fitted to the experimental points, (f) the halflife values obtained by the application of Smoluchowski's theory in reference [2] are unacceptable because the singlet fraction, y_1 , is not reduced to 0.5, but to 0.2-0.3.

INTRODUCTION

The Thermodynamics Theory of Coagulation Kinetics

In reference¹ the thermodynamic principles were applied in coagulation kinetics. The number concentration of all primary particles in aggregates smaller than their average number size in a defined volume was proposed as that of the reactant concentration. The sum of all primary particles in aggregates bigger than the average size in the same volume was proposed as that of the product concentration. The thermodynamic theory of reaction kinetics is not concerned with the form and state of the product. In the case of coagulation of singlets, as long as the singlet number concentration is not smaller than that in the aggregates of maximal size, it represents the reactant concentration. The sum of singlets in all aggregates, *i.e.* in doublets, triplets, etc., is the product concentration. In the present paper, the thermodynamic principles will be applied to the problem of formation of aggregates of size $2 \leq p$, while in reference¹ they were applied to the problem of formation of aggregates of size $6 \leq p$.

Two cases, namely, can be distinguished:

(A) Prior to the addition of the coagulator, the sol particles are in the stable state characterized by their small size of less than *e.g.* 5 nm. After the addition of the coagulator, the stable particles coalesce and form bigger particles which can coagulate. The AgI system represents this case and it was described in Ref. [1]. The reactions of coalescence and coagulation are consecutive. As long as primary particles are present in the stable form, transformation of the stable particles into the coagulating singlets is rate determining.

(B) Immediately after the addition of the coagulator, the already present singlets react with the coagulator by a very fast, momentary reaction which enables them to coagulate. In short observable periods, the aggregates consist of a few singlets only. Such a case was described in reference [2] for the polystyrene, hard, and polyvinyl acetate, soft, singlets of primary particles.

In both cases, the coagulation rate is determined by the second order reaction rate equation which can be formulated in the following three ways:

$$t_r = [\text{product}]/[\text{reactant}] = n_{pr}/n_{re} \quad (1.1)$$

$$t_r = [n_{re}(t_r=0) - n_{re}(t_r)]/[n_{re}(t_r)] \quad (1.2)$$

$$t_r = [n_{pr}(t_r \rightarrow \infty)]/[n_{pr}(t_r \rightarrow \infty) - n_{pr}(t_r)] \quad (1.3)$$

For coagulation, the same equation can be modified into one of the following forms:

$$t_r = n_1/(p_0 - n_1), \quad p_0 = 6, \quad 0 \leq n_1 < p_0 \quad (2.1)$$

$$t_r = S_p/(S_0 - S_p); \quad S_0 = \sum n_p, \quad \text{for } p_{\min} \leq p \leq p_{\text{av}} \quad (2.2)$$

$$t_r = (z_0 - z_1)/z_1 \quad (2.3)$$

$$t_r = (1 - y_1)/y_1 \quad (2.4)$$

$$t_r = t_v/[t_r - (t_r - 1)], \quad \text{for } 1 \leq t_r \quad (2.5)$$

Here $t_r = t_a/t_{1/2}$ is the relative, t_a the absolute time and $t_{1/2}$ the halflife of coagulation, *i.e.* the absolute time which has elapsed from the moment of addition of the coagulator up to the time when half of the reactant is transformed into the product. S_0 is the constant sum of the numbers of singlets in all aggregates at any time.

The number concentrations z_p , of aggregates of sizes, p can be obtained by counting the numbers of aggregates of various sizes, p , in defined volumes. The same was done in reference [2]*.

One can define, y_1 , the decreasing fraction of singlets by:

$$y_1 = z_1/z_0, \quad (1 \leq y_1 \leq 0, \quad z_0 = z_1 \text{ at } t_r = 0, \quad 0 < t_r < \infty) \quad (3.1)$$

* Remark: In Ref. [2] $z_i = n_p/V(t)$; $i = p$. In Ref. [4] $k = p$!

and the increasing sum of fractions of doublets, triplets, ... p_{\max} i.e. of S_2 , by:

$$1 - y_1 = (z_0 - z_1)/z_1 = S_2; \quad z_0 = z_1 \quad \text{at} \quad t_r = 0 \quad (3.2)$$

Here S_2 represents the following sum:

$$S_2 = y_2 + y_3 + \dots y_p \dots + y_{p_{\max}} \quad (3.3)$$

Consequently, one can define the time function of the increasing product fraction by [See (2.4)]:

$$1 - y_1 = 1/(1 + 1/t_r) \quad (4.1)$$

and that of the decreasing reactant fraction by:

$$y_1 = 1/(1 + t_r) \quad (4.2)$$

Up to the time $t_r = p_0 - 1 = 5$, when it becomes $y_1 = y_2 = y_3 = \dots y_{p_{\max}} = 1/p_{\max} = 1/6 = 0.167$, aggregates of sizes up to the maximal size, $p_{\max} = p_0$ are present in sols. [See Table II (A)]. The terms: $z_1 = y_1 \times z_0$, $z_2 = y_2 \times z_0/2$, $z_3 = y_3 \times z_0/3$, ..., $z_{p_{\max}} = y_{p_{\max}} \times z_0/p_{\max}$ represent the primary particle fractions in aggregates of sizes p . The aggregates of sizes p , number concentrations, z_p , can be estimated by counting the aggregates in a defined volume. This was done in reference [2]. It follows that at any time $S_2 + y_1 = z_0$ and at $t = 0$, $z_1/z_0 = y_1 = 1$.

Time Evolution Doublets, Triplets, etc.

The increasing aggregate fractions, y_p , at short times, $0 \leq t_r \leq p \leq 2 p_0 - 1 = 11$, can be calculated using the equations:

$$y_2 = 1/(1 + t_{r2}) / (1 + 1/t_{r1}); \quad [\text{For } y_1 \text{ see (4.2)!}] \quad (5)$$

$$y_3 = 2 y_2 / 3 (1 + t_{r3}) \quad (6)$$

$$y_4 = 3 y_3 / 4 (1 + t_{r4}) \quad (7)$$

$$y_5 = 4 y_4 / 5 (1 + t_{r5}) \quad (8)$$

$$y_6 = 1 - y_1 - y_2 - y_3 - y_4 - y_5 \quad (9)$$

Here: $t_{r2} = 2t_r/3$, $t_{r3} = t_r/3$, $t_{r4} = 3t_r/4$, $t_{r5} = 4t_r/5$.

An additional condition is that $y_p \geq y_{p+1}$ must be always valid. If for the values calculated using equations (5) to (9) $y_{p,\text{old}} < y_{p+1,\text{old}}$ holds, then the corrected values should be calculated using $y_{p+1} = y_{p,\text{old}}$ and $y_{p+2} = y_{p+2,\text{old}} + y_{p+1,\text{old}} - y_{p,\text{old}}$. This means that, if $y_5 = y_1 < y_6$, the surplus was incorporated in sizes $6 < p < p_{\max}$.

Equations (1) to (4) are a logical consequence of the assumed reaction of second order. Equation (5) was obtained assuming that the reactant concentration is the

TABLE I

Time evolution of primary particle number, n_p , in aggregate sizes from $p = 1$ over $p_0 = 6$ to $p = p_0^3 \times 7 = 1512$

$p_{\max} = 6 \quad n_{\max} = 36$									
(A)	t_1	n_p	S_p	n_1	n_2	n_3	n_4	n_5	n_6
	0	0	36	36	0	0	0	0	0
	0.2	6	30	30	5	0	0	0	0
	0.5	12	24	24	9	2	1	0	0
	1	18	18	18	11	4	2	1	0
	2	12	6	12	10	6	5	4	0
	3	18	6	9	9	7	6	5	0
	4	24	6	7	7	6	6	6	3
	5	30	6	6	6	6	6	6	6
	6	36	6	5	5	5	5	5	10
	7	42	6	5	5	5	5	5	14
	8	48	6	4	4	4	4	4	16
	9	54	6	4	4	4	4	4	18
	10	60	6	3	3	3	3	3	20
	11	66	6	3	3	3	3	3	21

$n_6 = 7 \times n_1$ is distributed in $p = 6$ to $p = 2 \times p_0 = 12$

$n_{\max} = 1512$															
(B)	t_r	n_{pr}	n_{re}	n_1	n_2	n_3	n_4	n_5	n_6	n_7	n_8	n_9	n_{10}	n_{11}	n_{12}
	0.105	144	1368	12	12	12	12	12	12	12	12	12	12	12	12
	0.212	264	1248		12	12	12	12	12	12	12	12	12	12	
	0.432	456	1056			24	24	24	24	24	24	24	24	24	
	0.432	744	768				48	48	48	48	48	48	48	48	
	2.938	1128	384					96	96	96	96	96	96	96	
	62	1488	24						180	180					
	251	1506	6						6	6					
	1511	1511	1						6	5					

$n_p = p_0 \times 2^I$																
				1	$\leftarrow I \rightarrow$			p_0	p_0	$\leftarrow I \rightarrow$			1			
				$n_p =$	12	24	48	96	192	384	384	192	96	48	24	12

(C)	t_c	n_{pr}	n_{re}	p_{\min}	p_{av}	p_{\max}
	2	252	126	246	252	258
	4	504	126	498	504	510
	6	756	126	750	756	762
	8	1008	126	1002	1008	1014
	10	1260	126	1254	1260	1266
	12	1512	126	1506	1512	1518

singlet concentration defined by (4.2) and that the doublet concentration is the product concentration defined by (4.1), but with the relative time $t_2 = 2 t_r/3$. The reactant concentration is now defined with the variable fraction, γ_1 . The result is equation (5).

The assumption that $t_{rp} = (p - 1) \times t_r/p$ can be explained like the isotope effect. The reaction rate constant of the heavier isotope is smaller than that of the lighter one, or the half-life of the heavier is bigger than that of the lighter one.

TABLE II

Time evolution of primary particle fraction, y_p , in aggregate sizes from $p = 2$ over $p_0 = 6$ to $p = p_0^3 \times 7 = 1512$

		$p_0 = p_{\max} = 6, \quad n_{\max} = p_0^2 = 36, \quad t_r = n_{pr}/n_{re}$													
(A)	t_r	n_{pr}	n_{re}	y_1	y_2	y_3	y_4	y_5	y_6						
	0	0	36	1000	0	0	0	0	0						
	0.2	6	30	833	147	14	6	3	0						
	0.5	12	24	667	250	54	19	6	0						
	1	18	18	500	300	112	64	24	0						
	2	12	6	333	286	171	137	73	0						
$n_{pr} = t_r \times p_0; \quad n_{re} = p_0$															
	3	18	6	250	250	188	173	141	0						
	4	24	6	200	200	187	187	178	30						
	5	30	6	167	167	167	167	167	165						
	6	36	6	143	143	143	143	143	185						
	7	42	6	125	125	125	125	125	375						
	8	48	6	111	111	111	111	111	445						
	9	54	6	100	100	100	100	100	500						
	10	60	6	91	91	91	91	91	545						
	11	66	6	83	83	83	83	83	583						
$y_6 = 7 \times y_1 = 7 \times 83.3 = 583$ is distributed in $6 \leq p \leq 2 \times p_0 = 12$															
(B)	t_r	n_{pr}	n_{re}	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	y_{10}	y_{11}	y_{12}
			$n_{\max} = 1512 \quad S_6 = 1$				$= 1000 y_p$								
	0.105	144	1368	79	79	79	79	79	79	79	79	79	79	79	79
	0.212	264	1248		79	79	79	79	79	79	79	79	79	79	
	0.432	456	1056			159	159	159	159	159	159	159	159		
	0.432	744	768				317	317	317	317	317	317			
	2.94	1128	384					635	635	635	635				
	62	1488	24						1189	1189					
	251	1506	6						40	40					
	1511	1511	1						40	33					
(C)	t_c	n_{pr}	n_{re}	P_{\min}	P_{av}	P_{\max}									
	1	252	252	246	252	258									
	2	504	252	498	504	510									
	3	756	252	750	756	762									
	4	1008	252	1002	1008	1014									
	5	1260	252	1254	1260	1266									
	6	1512	252	1506	1512	1518									

Factors $p/(p - 1)$ in equations (4), (5), (6) can be explained by the fact that n_{p-1} singlets in size p can be produced from n_p singlets in size $p - 1$. Namely, $n_p \times (p - 1) = n_{p-1} \times p$ and $n_{p-1} = p$ and $n_p = p - 1$ must always hold.

If, instead of y_p , one inserts the corresponding terms $n_p = y_p/S_0$, one obtains the number, n_p , of primary particles distribution in aggregates of sizes $2 \leq p \leq p_{\max}$.

For the start of the process, the simplest calculation can be performed if one uses the value $p_{\max} = 6$ and $n_{p_{\max}} = 6$. Then, the number of primary particles is incorporated in aggregates of size, p , defined by $n_p = y_p \times p_{\max}$ (See Tables I and II, (A), (B), upper part).

The tables elucidate in characteristic steps the time evolution of the numbers, n_p (Table I), and fractions, y_p (Table II) resp., of primary particles in aggregates of sizes $1 \leq p \leq p_{\max}$.

In parts (A) $n_{\max} = p_0^2 = 36$, in parts (B) $n_{\max} = (2 \times p_0)^2 = 144$, in parts (C) $n_{\max} = p_0^3 \times 7 = 1512$.

It is demonstrated in Table I (A), that $n_{\max} = 36$ singlets coagulate to aggregates of sizes $1 \leq p \leq 6$, in times of formation $0 < t_r \leq p_0 - 1 = 5$. In times $5 < t_r \leq 11$ the corresponding values $p = 6$ increase to $p = 12$ and also values $6 > n_p$ to $n_p \leq 2 \times p_0 = 12$. This means that, at the end of this period, $n_p = 2 \times p_0 = 12$ singlets were incorporated in each of the aggregates of size $1 \leq p \leq 12$.

If further progress of coagulation is possible, the size distribution, defined by the histogram, will be established as shown in parts (B). The formation of the histogram of part (B) was explained in reference [1], Tables I and II. By selection of any value $3 \leq p_0$, the histogram of any width can be obtained. In the present paper, $p_0 = 6$ was chosen as an example. There are many possibilities of the sequence of formation of the aggregate sizes, *i.e.* of the formation of the histogram. Here, the assumed sequence was $12 \times 2 \times p_0 + 10 \times 2 p_0 + 8 \times 4 \times p_0 + 6 \times 8 \times p_0 + 4 \times 16 \times p_0 + 2 \times 15 \times p_0 + 31 \times p_0 + 2 \times p_0 - 1$. That of Table I¹ is certainly physically realistic.

After the singlets have been distributed in the histogram, further progress of coagulation can be represented by the increase of the average size, p_{av} , with time or/and by the width of the histogram defined with p_0 or by the absolute value of p_{av} . In Table I (C), at the coagulation time $t_c = 1$, $p_{av} = n_{\max} / 2p_0 = 126$, and in Table II (C) $p_{av} = n_{\max} / p_0 = 252$ were selected as examples. The time evolution was in accordance with equation (2.1).

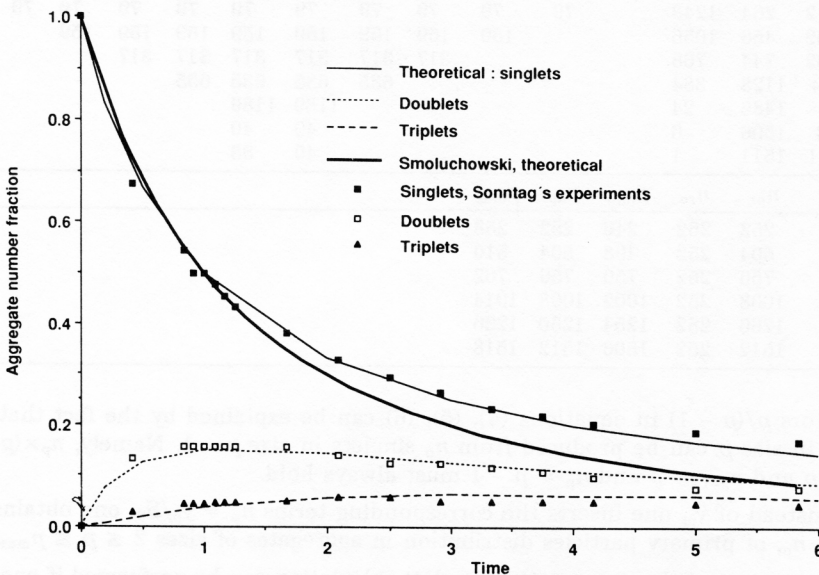


Figure 1. Time evolution of aggregate number fraction. Thermodynamic theory: - - -, Smoluchowski's theory: —, Experiments of reference [2]: points. Abscissa: relative time, t_r . Ordinate: aggregate number fraction: singlets, y_1 , doublets, y_2 , triplets, y_3 .

By a proper choice of the parameters, t_a , p_0 , p_{\max} , $t_{1/2}$, of the theory it is possible to fit the plots to any possible, experimentally observable, second order time evolution plot and to any possible histogram.

Figure 1 exemplifies the theoretical plots for singlets, (4.2), doublets (5), triplets, (6) and the experimental points of Figure 1, reference [2] and the corresponding plot of von Smoluchowski's theory (See below!).

The maximum on the y_2 plot is at $t_r = (2/3)^{1/2}$ (First derivative of equation (5) equals zero). At $t_3 = 3$, $y_2 = y_3$, at $t_r = 6$ all, n_1 to n_6 and y_1 to y_6 resp. become equal.

Von Smoluchowski's Theory of Coagulation Kinetics

In reference [1], p. 124, the theory of von Smoluchowski,⁴ is critically analyzed. Six arguments are quoted, proving that the same theory cannot be valid for experimental systems.

Von Smoluchowski's equation (24), in ref. [4], p. 146 in the notation of the present paper reads:

$$y_p(t_s) = \frac{t_s^{p-1}}{(1 + t_s)^{p+1}} \quad (10.1)$$

Its elementary, therefore simpler, form reads:

$$y_p(t_s) = \frac{t_s^{-2}}{(1 + t_s)^{p+1}} \quad (10.2)$$

Equation (10.2) was obtained by division of the nominator and denominator of (10.1) by t_s^{p+1} . In this form of equation, the computation is not limited by the capacity of the computer. Its relative time is $t_s = t_a \alpha \nu_0$, where α is the collision probability and ν_0 is the sum, $\sum y_p = 1$, for $1 \leq p \rightarrow \infty$. The half life is $t_{1/2} = 1/(\alpha \nu_0)$. According to the same equations (10), for any value of time, $0 \leq t_s \leq \infty$, there is an exact result of $y_p(t_s)$ for each value $1 \leq p \leq \infty$. The histogram consists, at any time, of an infinite number of sizes p . The same postulate of the equation is physically impossible because, at definite times, there must be a definite minimal, average and maximal size p . The bigger is the p , the smaller are the n_p values. It is also impossible that the formation of aggregates of hundreds of singlets should require hundreds of halflives.

The time necessary to transform half of the singlets, $p = 1$, into aggregates of $p \geq 2$, i.e. to calculate the value $y_p(t_s) = 0.5$ for $p = 1$ is consequently $t_s = 2^{1/2} - 1$ (insert into (10.2) $p = 1$ and $y_1(t_s) = 0.5$; the result is $t_s = 2^{1/2} - 1$). The fraction y_1 is, namely, the decreasing reactant, i.e. the singlet concentration fraction. However, the thermodynamic definition of $t_{1/2}$ which follows from equation (4.2) requires that $t_r = 1$ when $y_1 = 0.5$. In order to satisfy this requirement, it is necessary to replace all values $0 < t_s < \infty$ by $t_r = t_s/(2^{1/2} - 1) = t_s/0.414$. Then, only the points (y_1, t_r) , = (1,0) and = (0.5,1) of the plots (3), (4), (10) coincide.

By point 1 in reference [1], p. 124, the conclusion was made that in times $t_s \leq 2^{1/2} - 1 = 0.414$, the particles must be $p < 1$. This is impossible if the addition of the coagulator changes neither the size (number concentration) nor the form of the singlets. The experiments from reference [2] represent this case, i.e. the case when the addition of the coagulator directly induces coagulation. Prior to addition of the coagulator, the singlets are in the size and form in which, if hard spherules, they will

form irregular spongy aggregates, or, if soft (polyvinyl acetate) spherules, probably bigger spheres. The theoretical plot defined by equation (10) describes the same case and is represented in Figure 1.

*Experiments on Coagulation of Singlets to form Doublets, Triplets, by H. Lichtenfeld, H. Sonntag and, Ch Düerr.*²

Reference [2] describes coagulation experiments performed with monodisperse polystyrene, hard, and polyvinyl acetate, soft, sols. The results are presented as » z_1/z_0 , z_2/z_0 , z_3/z_0 vs. t_a or t_r « plots.

Since Smoluchowski's second order coagulation kinetics equation (24) in ref. [4] as used in ref. [2] could not, in its original form, be fitted to the experimental plots by selecting an »aggregation« rate constant, a second equation was introduced with a selected »deaggregation« rate constant. The plots obtained with adjusted aggregation and deaggregation rate constants, fitted, if observed visually, the experimental values well. However, the unacceptable and impossible result, which follows from Figures 7, 8, 9, and 10, was that the half-life, $t_r = t_a/t_{1/2} = 1$, of the coagulation process is reached when $0.25 < y_1 = z_1/z_0 < 0.34$. There can be no doubt that it must be $y_1 = z_1/z_0 = 0.5$, when $t_r = t_a/t_{1/2} = 1$, i.e. when half of the singlets have reacted to form doublets, triplets ... etc. The singlets can be the only particles acting as the reactant component defining [reactant] in eq. (1). This postulate is inherent with the definition of the term »half-life«.

Apart from the latter argument, the principle of scientific reasoning is against the procedure of reference [2]: If a theory offers an algorithm, the plot of which cannot be fitted to experimental plots, then the introduction of a second algorithm, correcting the result of the first, does not improve the first and the inapplicable algorithm and it does not correct the theory. Only an algorithm that can be fitted to experimental plots can be accepted for the confirmation of the correctness of the theory by which it was deduced.

The estimated points of the plots of the ten figures were inserted in the figures with the theoretical y_1 , y_2 , y_3 plots. All points (except Figure 2) fitted, if observed visually, excellently the theoretical plots. In the present Figure 1, the values of Figure 1² were inserted as an example.

It is obvious that von Smoluchowski's theory^{3,4} cannot be considered confirmed by the experiments reported in reference [2].

The Linearized Second Order Coagulation Kinetics Plot

It was demonstrated in reference [1] by Figure 3 that equations (4) can be transformed into the following form:

$$1/(1 - y_1) = 1 + 1/t_r \quad (4.3)$$

The same function is graphically presented in Figure 2. Thus, a linear experimental plot » $1/(1 - y_1)$ vs. $1/t_a$ « in a time period of sufficiently precise and reliable measurements, proves that the process is of second order.

The most precise value of $t_{1/2}$ can be obtained by the least square regression of the plots. The half-life $t_{1/2} = t_a$ ($y_1 = 0.5$) is determined by the ordinate value $y_1 = 1 - y_1 = 0.5$. The extrapolation of the plot to $1/t_a = 0$ determines the unit of the ordinate and the slope, $1/t_a$, of the plot.

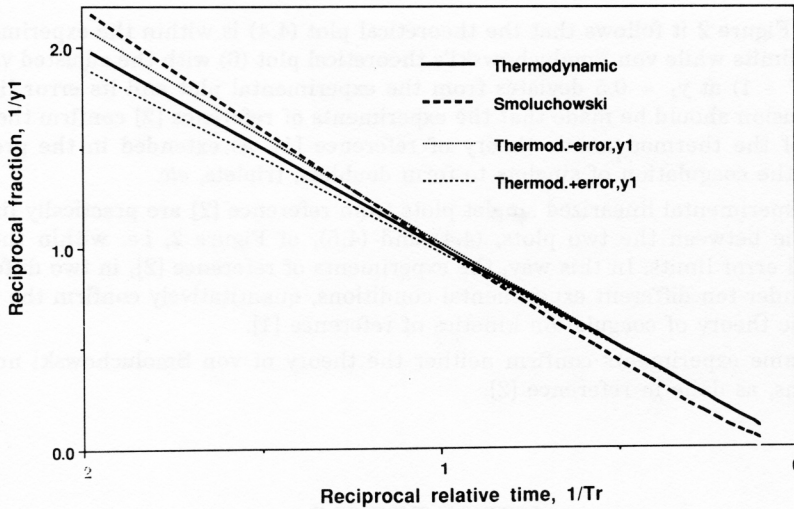


Figure 2. Linearized singlet coagulation kinetics plots. Thermodynamic theoretical: — ; error -0.25: — — ; error +0.25: · · · ; Smoluchowski's theory plot: - - -. Abscissa: reciprocal relative time, $1/t_r$. Ordinate reciprocal singlet fraction, $1/y_1$.

A satisfactory value $t_{1/2}$ can be obtained by the following interpolation equation:

$$t_{1/2} = \frac{1}{(1/t_a - A \times B/C)} \tag{4.4}$$

Its parameters are defined by: t_a if $y_1 = z_1/z_0 < 0.5$ is the bigger, t_b if $y_b = z_1/z_0 > 0.5$ is the smaller fraction of singlets compared with the fraction of $y_1 = 0.5$; $A = 1/t_a - 1/t_b$, $B = 1/(1 - y_1) - 2$ and $C = 1/(1 - y_1) - 1/(1 - y_b)$.

From the ordinate and abscissa values of the ten figures of reference [2], the t_a , or t_r , (abscissa) and $z_1/z_0 = y_1$, (ordinate) values were estimated by the present author with ± 0.5 mm precision. The $t_{1/2}$ values were obtained using equation (5) and by using equation (4) the corresponding plots were drawn. Determination of $t_{1/2}$ was not made by the least square regression method because of the relatively low precision of the estimated y_1 and t_r values from the published figures.

It follows from Figures 3, 5, 6, and 7 in ref. [2] that the scatter of the measurements is $y_1 \pm 0.025$ or app. $\pm 5\%$ in the optimal precision range. The two plots representing equation (4.4) with the estimated absolute error of $\Delta y_1 = \pm 0.025$ read:

$$\frac{1}{(1 - y_1 - 0.025)} = 1 + \frac{t_{1/2}}{t_a} = 1 + \frac{1}{t_r} \tag{4.5}$$

and

$$\frac{1}{(1 - y_1 + 0.025)} = 1 + \frac{t_{1/2}}{t_a} = 1 + \frac{1}{t_r} \tag{4.6}$$

From Figure 2 it follows that the theoretical plot (4.4) is within the experimental tolerance limits while von Smoluchowski's theoretical plot (6) with the adjusted values $t_r = t_s(2^{1/2} - 1)$ at $y_1 = 0.5$ deviates from the experimental plot and its error limits. The conclusion should be made that the experiments of reference [2] confirm the correctness of the thermodynamic theory of reference [1], as extended in the present paper for the coagulation of singlets to form doublets, triplets, etc.

The experimental linearized singlet plots from reference [2] are practically linear. They all lie between the two plots, (4.4) and (4.5), of Figure 2, i.e. within the experimental error limits. In this way, the experiments of reference [2], in two different systems under ten different experimental conditions, quantitatively confirm the thermodynamic theory of coagulation kinetics of reference [1].

The same experiments confirm neither the theory of von Smoluchowski nor its applications, as done in reference [2].

LIST OF SYMBOLS

A, B, C	constants
n_{pr}, n_{re} , [product], [reactant]	singlet number of product, reactant in a defined volume
$n_1, n_2, \dots, n_p, n_{pmax}$	number of singlets in aggregates of sizes 1, 2, ... p , ..., p_{max}
$p, p_{min}, p_{av}, p_0, p_{max}$	sizes of aggregates: variable, minimal, average, defining the histogram width, maximal
S_p, S_0, S_2	sum of singlets in aggregates up to size p , of all, in sizes $2 \leq p \leq p_{max}$
$t_a, t_{1/2}, t_r, t_{r2}, \dots, t_{rp}, t_{rpm}$	time: absolute, half-life, relative time of singlets, doublets, of size p , of maximal size p_{max}
z_0, z_1, \dots, z_p	number concentration of: singlets at $t = 0$, at t variable, of aggregates of size p
y_1, y_2, \dots, y_p	primary particle fraction in: singlets, doublets, ... aggregates of size p .

REFERENCES

1. M. Mirnik, *Croat. Chem. Acta* **63** (1990) 113.
2. H. Lichtenfled, H. Sonntag, and Ch. Düerr, *Colloids and Surfaces* **54** (1991) 267.
3. M. von Smoluchowski, *Phys. Z.* **17** (1916) 557. *ibid.* 585.
4. M. von Smoluchowski, *Z. Phys. Chem.* **92** (1917) 129.
5. M. Mirnik, *Croat. Chem. Acta* **64** (1991) 253.
6. M. Mirnik, P. Strohal, M. Wrischer, and B. Težak, *Kolloid-Z.* **160** (1958) 46.
7. M. Mirnik, *Croat. Chm. Acta* **61** (1988) 81.

SAŽETAK

Teorija koagulacije malih agregata

M. Mirnik

Termodinamska teorija kinetike koagulacije¹ proširena je na koagulaciju jediničnih primarnih čestica koje prelaze u agregate, t.j. nakupine od dvije, tri, ... , itd. takve jedinične čestice. Eksperimenti koagulacije primarnih čestica u agregate od dvije i tri jedinične čestice polistirenskih i polivinil acetatnih solova s vremenom, objavljene u ref. [2] potvrđuju teoriju na više načina: (a) teorijske krivulje jednake su za sve tri vrste čestica eksperimentalnim krivuljama, (b) maksimum na krivuljama agregata s dvije čestice leži na predskazanoj vrijednosti 1.2 vremena polukoagulacije, (c) krivulja agregata s dvije čestice postane jednaka onoj s tri kod predskazanog vremena 3, (d) krivulje »recipročni omjer nestajanja jediničnih čestica vs. recipročno vrijeme« su linearne, (e) krivulje von Smoluchowskog³ ne mogu se izjednačiti s eksperimentalnim krivuljama, (f) postupak analize istih rezultata primijenjen u citatu² daje neprihvatljive vrijednosti vremena polukoagulacije. Umjesto 0.5 je kod vremena polukoagulacije¹ frakcija jedinica pretvorenih u agregate 0.2 do 0.3.