

Kinetic Model for the Simultaneous Processes of Flocculation and Coalescence in Emulsion Systems

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We consider an emulsion system in which the two interrelated processes of flocculation and coalescence take place simultaneously. The flocculation is described in terms of von Smoluchowski's theory, whereas the coalescence is related to the rupture of the liquid films between the drops. Since the latter process takes place in aggregates, we adopt for it a kinetic scheme which formally resembles that of parallel chemical reactions. A set of differential equations governing the overall kinetics is formulated and solved for several particular cases. The rate constants of flocculation and coalescence stand as model parameters. Solutions for the number of single drops vs time are obtained in the asymptotic regimes of fast and slow coalescence. In the case of linearly built aggregates we derive an explicit expression for the total number of drops in the system. For arbitrary aggregates the complete set of kinetic differential equations is solved numerically. The results are compared with those obtained by other authors through particular averaged models of flocculation and coalescence. The theory can be employed to investigate the role of different factors for the emulsion stability: the solubility of the surfactant, the adsorption and the Gibbs elasticity of the layer, the surface viscosity etc. © 1994 Academic Press, Inc.

1. INTRODUCTION

In real emulsions one can distinguish two different physical processes leading to destabilization. The first one is flocculation (reversible aggregation of the drops) which leads to emulsion creaming since the aggregates are subject to buoyancy force. The second process, coalescence, takes place when the thin liquid layer between two neighboring drops is ruptured. This process is irreversible and leads to separation of the dispersed phase. Because of the tremendous practical importance of these phenomena, many studies have been devoted to the kinetic stability of emulsions in view of the flocculation and coalescence processes.

The system without coalescence was explored by Smoluchowski (1, 2). A recent investigation performed by Elminyawati *et al.* (3) accounts for the possible fragmentation of the aggregates—reversible redispersion of the drops into the continuous phase. Bak and Heilmann (4) found a so-

lution of the infinite set of Smoluchowski equations in the particular case when the aggregates cannot grow larger than a given size. A special choice of the rate constants provides an explicit solution (4). The time evolution of drop size distribution in dilute, homogeneous dispersion was analyzed by solving population dynamics equations (5). The effects of Brownian motion, thermocapillary migration, and gravity sedimentation were studied in this article. All these models (1-5) do not account for the coalescence stage and for the possible flat film formation upon droplet aggregation. It was shown theoretically that plane parallel films can be obtained even between droplets of micron and submicron size due to direct interdroplet interaction (6).

Hartland and Gakis (7) and Hartland and Vohra (8) were the first to attempt a model that relates the lifetime of single films to the rate of phase separation in emulsions of fairly large drops (around 1 mm) in the absence of surfactant. Their analysis was extended further by Lobo *et al.* (9) to quantify the coalescence within already creamed or sedimented emulsion (or foam) with drop sizes less than 100 μm and also to account for the presence of surfactants, which are commonly used as stabilizers.

Several authors investigated the simultaneous existence of flocculation and coalescence (10, 11). The treatment was based on the notion that the average number of drops per aggregate changes with time due to both flocculation with other particles (aggregates) and coalescence inside the aggregate (10). Alternatively, the overall rate of change of the number of individual particles (free and in aggregates) was set to be proportional to the average number of contacts between the drops in the aggregates (11).

The role of direct droplet interactions and Brownian motion on the coalescence rate in dilute homogeneous emulsions of micron and submicron size was theoretically studied in Ref. (12). The processes of film formation, thinning, and rupture were included as consecutive stages in the Smoluchowski scheme and the coalescence rate in the beginning of the process was calculated. Expressions for different types of interaction between two deformed droplets were obtained in Ref. (13).

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The approach developed in Refs. (12, 13) allows the calculation of the rate constants of the two consecutive processes: aggregation (flocculation) and film thinning and rupture (coalescence), when only two-particle interactions are considered and the parameters of the system (drop size, interparticle interaction, shear viscosity of the solvent, etc.) are known. The rate constant of flocculation is known to be influenced by the size of the particles or aggregates (5). On the other hand, the rate of coalescence in an aggregate essentially depends on the number of particles inside it and the packing type, i.e., on the number of contacts between the drops. That is why it is too much oversimplified to present the whole process of diffusion, flocculation, and coalescence, including higher order aggregates, by using a single averaged parameter for drop fusion and another constant for aggregation.

For that reason, in this paper we consider a complete kinetic scheme accounting for the possibilities of flocculation and coalescence in and between the aggregates. We assign a rate constant to each elementary act and thus we define a full set of kinetic differential equations describing the system. The scheme of the coalescence in the aggregates formally resembles that of parallel chemical reactions.

2. FORMULATION OF THE PROBLEM AND MATHEMATICAL MODEL

We consider here an emulsion system in which two interrelated processes—flocculation and coalescence—take place. It will be assumed that the flocculation can be described in terms of Smoluchowski's theory (1, 2)—Fig. 1.

Let the coalescence proceed according to the following scheme: Any aggregate (flock) composed of n particles can partially coalesce to become an aggregate of i particles ($1 \leq i < n$), with the rate constant being $k_c^{n,i}$ —Fig. 2. (A single particle can be formed when $i = 1$.) This aggregate i is further involved in the flocculation scheme, which makes the flocculation and coalescence processes interdependent. Therefore, the system exhibiting both flocculation and coalescence

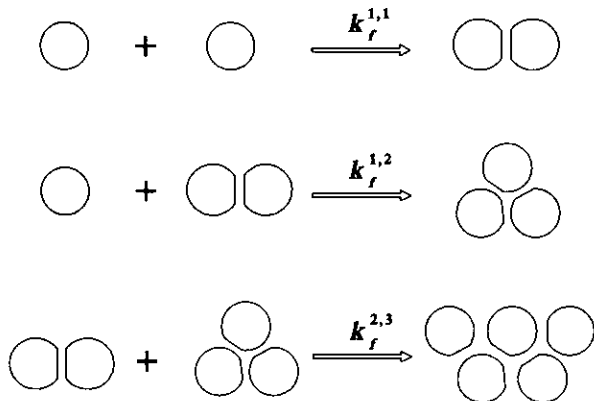


FIG. 1. Model of flocculation according to the Smoluchowski scheme.

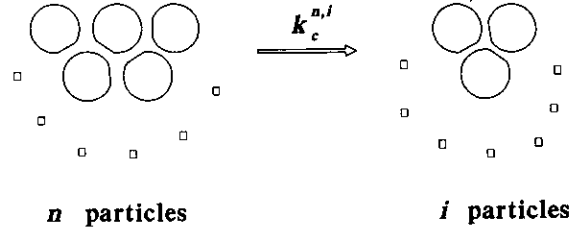


FIG. 2. Coalescence in an aggregate of n particles to become an aggregate of i particles, with a rate constant $k_c^{n,i}$, $1 \leq i < n$.

will be described by a combination of the schemes 1 and 2. In such a system the single particles formed through coalescence, although larger in size, are kinetically equivalent to the initially present single particles. Similarly, no distinction will be made between the aggregates i formed by collision of smaller aggregates and those formed through coalescence in larger ones.

A possible exhausting of the single particles or aggregates can be considered. For example, at a certain size any particle or aggregate can emerge or sink due to buoyancy force. The set of kinetic equations for this model system is

$$\begin{aligned}
 \frac{dv_1}{dt} &= -2 \sum_{i=1}^{\infty} k_f^{1,i} v_1 v_i + \sum_{i=2}^{\infty} k_c^{i,1} v_i - q_1 \\
 \frac{dv_2}{dt} &= k_f^{1,1} v_1^2 - 2 \sum_{i=1}^{\infty} k_f^{2,i} v_2 v_i \\
 &\quad + \sum_{i=3}^{\infty} k_c^{i,2} v_i - k_c^{2,1} v_2 - q_2 \\
 &\quad \vdots \\
 \frac{dv_n}{dt} &= \sum_{i=1}^{n-1} k_f^{i,n-i} v_i v_{n-i} - 2 \sum_{i=1}^{\infty} k_f^{n,i} v_n v_i \\
 &\quad + \sum_{i=n+1}^{\infty} k_c^{i,n} v_i - \sum_{i=1}^{n-1} k_c^{n,i} v_n - q_n \\
 &\quad \vdots
 \end{aligned} \tag{1}$$

We introduce the notation, v_1 , number of the single particles; v_i , number of the aggregates comprising i particles ($i = 2, 3, \dots$); v , total number of single particles plus all kinds of aggregates,

$$v = \sum_{i=1}^{\infty} v_i; \tag{2}$$

$k_f^{i,j}$, the rate constants of collisions of size i drops with size j drops, per unit volume. The collision kernels between drops for Brownian, gravity, and Marangoni-induced collisions are given by Wang and Davis (5) and some models for the relative diffusivity are discussed in Ref. (14). $k_c^{n,i}$ is the rate

constant of coalescence of an aggregate of n particles to one composed of i particles ($1 \leq i < n$) or to a single particle ($i = 1$). q_1 is the flux of single particles out of the system and q_i is the flux of aggregates of i particles ($i = 2, 3, \dots$); t denotes time.

After summing up the equations in the set [1] we obtain the total number of particles and aggregates ν (Eq. [2]),

$$\frac{d\nu}{dt} = -\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_f^{i,j} \nu_i \nu_j - q, \quad [3]$$

where the total flux of single particles and aggregates q is defined as

$$q = \sum_{i=1}^{\infty} q_i. \quad [4]$$

In the particular case of $q = 0$ and equal flocculation rate constants we find the Smoluchowski relation (1, 2)

$$\nu = \frac{\nu_0}{1 + k_f \nu_0 t}, \quad [5]$$

with ν_0 being the total amount of particles in the initial moment $t = 0$ and k_f being the characteristic flocculation rate constant. Equation [1] represents an infinite set of nonlinear differential equations. At infinite time of coalescence ($k_c^{n,i} = 0$) and without flux of particles it coincides with the set of Smoluchowski which has a sole exact solution:

$$\nu_i = \frac{\nu_0 (k_f \nu_0 t)^{i-1}}{(1 + k_f \nu_0 t)^{i+1}}, \quad i = 1, 2, \dots \quad [6]$$

If exhausting of particles takes place due to buoyancy force, then an increase in the aggregate size would lead to a rapidly increasing flux. Therefore, aggregates of size above a given definite size, corresponding to a number of particles N , will not be actually present in the system. Then the problem [1] is reduced to a finite number of equations:

$$\begin{aligned} \frac{d\nu_1}{dt} &= -2 \sum_{i=1}^{N-1} k_f^{1,i} \nu_1 \nu_i + \sum_{i=2}^N k_c^{1,i} \nu_i - q_1 \\ \frac{d\nu_2}{dt} &= k_f^{1,1} \nu_1^2 - 2 \sum_{i=1}^{N-2} k_f^{2,i} \nu_2 \nu_i + \sum_{i=3}^N k_c^{2,i} \nu_i - k_c^{2,1} \nu_2 - q_2 \\ &\vdots \\ \frac{d\nu_N}{dt} &= \sum_{i=1}^{N-1} k_f^{i,N-i} \nu_i \nu_{N-i} - \sum_{i=1}^{N-1} k_c^{N,i} \nu_N - q_N. \end{aligned} \quad [7]$$

The set [7] is to be processed under initial conditions

$$\nu_i(0) = \nu_0, \nu_i(0) = 0, i = 2, 3, \dots, N. \quad [8]$$

Given the values of the parameters, the problem [7], [8] can be solved numerically with the desired precision (17, 18). Elminyawi *et al.* (3) have proposed numerical solutions to the Smoluchowski aggregation-fragmentation equation in the absence of particle exhausting. The method allows solving the set [7] up to $N = 100$.

The time dependence of the total number of particles in the system, ν_T , is of major importance when emulsions are under consideration. ν_T comprises the number of individual particles moving freely plus the number of particles included in all kind of aggregates:

$$\nu_T = \sum_{i=1}^{\infty} i \nu_i. \quad [9]$$

We multiply the k th equation in [1] by k and sum up for all k .

If i and j are arbitrary indices, then at $i \neq j$ the equation $i + j$ will contain a flocculation production of aggregates

$$k_f^{i,j} (i + j) (\nu_i \nu_j + \nu_j \nu_i).$$

The loss of aggregates according to the i th equation is

$$-2k_f^{i,j} i \nu_i \nu_j$$

and from the j th equation

$$-2k_f^{i,j} j \nu_i \nu_j.$$

Therefore,

$$k_f^{i,j} (i + j) (\nu_i \nu_j + \nu_j \nu_i) - 2k_f^{i,j} i \nu_i \nu_j - 2k_f^{i,j} j \nu_i \nu_j = 0.$$

At $i = j$ the flocculation production from the $2i$ th equation is

$$2k_f^{i,i} i \nu_i^2,$$

and the loss from the i th equation is

$$-2k_f^{i,i} i \nu_i^2,$$

so

$$2k_f^{i,i} i \nu_i^2 - 2k_f^{i,i} i \nu_i^2 = 0.$$

As a result of these considerations we come to the conclusion that the flocculation terms will disappear from the equation for ν_T . Namely,

$$\frac{d\nu_T}{dt} = \sum_{k=1}^{\infty} k \sum_{i=k+1}^{\infty} k_c^{k,i} \nu_i - \sum_{k=2}^{\infty} k \sum_{i=1}^{k-1} k_c^{k,i} \nu_k - q_T, \quad [10]$$

where the total flux of particles, q_T , defined as the flux of individual particles plus the flux of all particles included in aggregates, is given by

$$q_T = \sum_{i=1}^{\infty} i q_i. \quad [11]$$

Let us introduce a total rate constant referring to complete coalescence of the i th aggregate:

$$k_{c,T}^i = \sum_{k=1}^{i-1} (i-k) k_c^{i,k}, \quad i = 2, 3, \dots \quad [12]$$

After rearranging the sums in Eq. [10] we find

$$\frac{dv_T}{dt} = -\sum_{i=2}^{\infty} k_{c,T}^i v_i - q_T. \quad [13]$$

It should be noted that in the theory of Smoluchowski the total number of particles ν_T remains constant and equal to the initial number ν_0 . Here Eq. [13] reflects the decrease in ν_T owing to (i) coalescence and (ii) exhausting of particles through the flux.

Equations [12, 13] allow obtaining a solution for ν_T provided the coalescence constants $k_c^{i,k}$ are known. Explicit expression for these constants can be written if the aggregates are built up linearly. Such an assumption was used in Refs. (10, 11) for small aggregates, and it also holds if the drops form a fractal-like structure—see, e.g., Fig. 2 in Ref. (15). In a linearly built aggregate consisting of i drops there will be $(i-1)$ liquid films between neighboring drops. Correspondingly, a simultaneous rupture of $(i-k)$ films will lead to a disappearance of $(i-k)$ drops and an aggregate comprising k individual drops will be produced. Hence,

$$k_c^{i,k} = a \binom{i-1}{i-k} P^{i-k} (1-P)^{k-1}, \quad [14]$$

where P is the probability for rupture of a single film. a is a constant of proportionality between $k_c^{i,k}$ and the probability for simultaneous rupture of $(i-k)$ films chosen arbitrarily, when the rest of $(k-1)$ films in the aggregate remain stable.

$$k_c^{2,1} = aP. \quad [15]$$

From Eqs. [12], [14], and [15] we have

$$k_{c,T}^i = k_c^{2,1} (i-1). \quad [16]$$

With this expression for $k_{c,T}^i$, using also Eqs. [2] and [9], we transform Eq. [13] to read

$$\frac{dv_T}{dt} = -k_c^{2,1} (\nu_T - \nu). \quad [17]$$

This differential equation can be solved if we recall that $\nu(t)$ is given by Eq. [5]. The result is

$$\nu_T(t) = \nu_0 \exp(-k_c^{2,1} t) \left\{ 1 + \frac{k_c^{2,1}}{k_f \nu_0} \exp\left(-\frac{k_c^{2,1}}{k_f \nu_0}\right) \times \int_1^{1+k_f \nu_0 t} \frac{1}{y} \exp\left(\frac{k_c^{2,1}}{k_f \nu_0} y\right) dy \right\}. \quad [18]$$

The rate constant for coalescence of a doublet, $k_c^{2,1}$, has the meaning of inverse lifetime of the liquid film between the drops.

We can avoid the assumption of linearly built aggregates by introducing an alternative expression for $k_c^{i,k}$, instead of Eq. [14]. If all acts of coalescence between two drops in an arbitrary aggregate have equal probability, we can write

$$k_c^{i,k} = aP^{i-k}. \quad [19]$$

For $k_c^{2,1}$ we recover Eq. [15]. From Eq. [12] it follows that

$$\begin{aligned} k_{c,T}^i &= a \sum_{k=1}^{i-1} (i-k) P^{i-k} \\ &= \frac{k_c^{2,1}}{(1-P)^2} [1 - iP^{i-1} + (i-1)P^i]. \end{aligned} \quad [20]$$

In the limiting case of small probabilities, $P \ll 1$, Eq. [20] gives that all coalescence rate constants are equal, $k_{c,T}^i \sim k_c^{2,1}$. Conversely, if P is close to unity, then we have $k_{c,T}^i \sim k_c^{2,1} i(i-1)/2$ with a sufficient accuracy, and the rate constants $k_{c,T}^i$ do not depend on the probability P .

3. TIME DEPENDENCE OF THE NUMBER OF SINGLE PARTICLES AT FAST AND SLOW COALESCENCE

For the rate constants $k_c^{i,1}$ both Eqs. [14] and [19] give

$$k_c^{i,1} = k_c^{2,1} P^{i-2}, \quad [21]$$

where Eq. [15] was also used. If there are no fluxes due to buoyancy and all the flocculation rate constants are about the characteristic flocculation rate k_f , then we can combine the first equation in the set [1] with Eq. [21]:

$$\frac{dv_1}{dt} = -2k_f \nu_1 \nu + k_c^{2,1} \sum_{i=2}^{\infty} \nu_i P^{i-2}. \quad [22]$$

Two limiting cases can be distinguished:

- (1) Rate of coalescence much greater than that of flocculation, $k_c^{n,i} \gg k_f \nu_0$ (rapid coalescence);
- (2) rate of flocculation much greater than that of coalescence, $k_f \nu_0 \gg k_c^{n,i}$ (slow coalescence).

3.1. Fast Coalescence

We can admissibly suppose the probability for coalescence of two particles to be very close to 1. Then Eq. [22] becomes

$$\frac{dv_1}{dt} = -2k_f v_1 \nu + k_c^{2,1} (\nu - v_1), \quad [23]$$

where the total number of single particles and aggregates ν is expressed through Eq. [5]. The differential equation [23] along with the initial condition [8] can be solved to give

$$v_1 = \nu \left[1 - \frac{k_f \nu_0}{k_c^{2,1}} \cdot \frac{1 - \exp(-k_c^{2,1} t)}{1 + k_f \nu_0 t} \right] \quad [24]$$

At short times, when $k_c^{2,1} t \ll 1$, v_1 is given by the approximate equation

$$v_1 \sim \frac{\nu_0}{(1 + k_f \nu_0 t)^2} (1 + \frac{1}{2} k_f \nu_0 k_c^{2,1} t^2), \quad [25]$$

and at large time intervals we have from Eq. [24] that v_1 is close to ν .

Since Eq. [24] is very important, we develop below another physical interpretation for it. Let us assume that aggregates composed of three, four, etc., particles cannot be formed just because of the rapid coalescence inside the aggregates. From the set [7] at $N = 2$ and without fluxes, $q_1 = 0$, $q_2 = 0$, we obtain

$$\begin{aligned} \frac{dv_1}{dt} &= -2k_f v_1^2 + k_c^{2,1} v_2 \\ \frac{dv_2}{dt} &= k_f v_1^2 - k_c^{2,1} v_2. \end{aligned} \quad [26]$$

We now introduce here a small parameter $\epsilon = k_f \nu_0 / k_c^{2,1} \ll 1$, dimensionless time $\tau = k_c^{2,1} t$, and dimensionless variables $\nu'_1 = v_1 / \nu_0$, $\nu'_2 = v_2 / \nu_0$. The problem [26] with initial conditions [8] is then expressed in an alternative form:

$$\begin{aligned} \frac{d\nu'_1}{d\tau} &= -2\epsilon(\nu'_1)^2 + \nu'_2, & \frac{d\nu'_2}{d\tau} &= \epsilon(\nu'_1)^2 - \nu'_2, \\ \nu'_1(0) &= 1, & \nu'_2(0) &= 0. \end{aligned} \quad [27]$$

In the set [27] the small parameter ϵ multiplies the nonlinear terms and consequently we can apply the scaling method (16): We define a local time scale $\tau_1 = \tau$ and a global scale $\tau_2 = \epsilon\tau$. The solution is being sought as an asymptotic series with respect to the small parameter:

$$\begin{aligned} \nu'_1 &= \nu'_{1,0}(\tau_1, \tau_2) + \epsilon \nu'_{1,1}(\tau_1, \tau_2) + \dots, \\ \nu'_2 &= \epsilon \nu'_{2,1}(\tau_1, \tau_2) + \dots \end{aligned} \quad [28]$$

After substituting the series [28] in [27] and equating the first-order terms containing ϵ we find the set of equations for the first asymptotic approximation

$$\begin{aligned} \frac{\partial \nu'_{1,0}}{\partial \tau_1} &= 0, & \frac{\partial \nu'_{2,1}}{\partial \tau_1} &= (\nu'_{1,0})^2 - \nu'_{2,1}, \\ \nu'_{1,0}(0, 0) &= 1, & \nu'_{2,1}(0, 0) &= 0. \end{aligned} \quad [29]$$

The general solution of [29] can be determined up to an arbitrary function $A(\tau_2)$ for which $A(0) = 1$ and

$$\nu'_{1,0} = A(\tau_2), \quad \nu'_{2,1} = A^2(\tau_2)[1 - \exp(-\tau_1)]. \quad [30]$$

The equations for the second approximation with respect to the small parameter, $\nu'_{i,1}$, are found to be

$$\begin{aligned} \frac{\partial \nu'_{1,1}}{\partial \tau_1} + \frac{\partial \nu'_{1,0}}{\partial \tau_2} &= -2(\nu'_{1,0})^2 + \nu'_{2,1}, \\ \nu'_{1,1}(0, 0) &= 0. \end{aligned} \quad [31]$$

From [30] the general solution of [31] is obtained as

$$\nu'_{1,1} = -\left(\frac{dA}{d\tau_2} + A^2\right)\tau_1 + A^2[\exp(-\tau_1) - 1]. \quad [32]$$

It tends to infinity as $\tau_1 \rightarrow \infty$ and therefore it should be

$$\frac{dA}{d\tau} + A^2 = 0, \quad A(0) = 1. \quad [33]$$

The solution of Eq. [33] is

$$A(\tau_2) = \frac{1}{1 + \tau_2}. \quad [34]$$

From Eqs. [28], [30], [32], and [34] it follows that up to a second order with respect to ϵ we have

$$\nu'_1 = \frac{1}{(1 + \tau_2)} + \frac{\epsilon}{(1 + \tau_2)^2} [\exp(-\tau_1) - 1]. \quad [35]$$

It can be pointed out that returning to physical variables in Eq. [35] gives exactly the result [24]. Consequently, the first and the second physical interpretations mentioned above are equivalent (within a reasonable accuracy). The second approach provides also the asymptotics at long times, ν_1 close to ν . Therefore, for rapid coalescence, if the aggregates in the system are only doublets, Eq. [24] gives the correct solution for ν_1 both at short and at long times (the assumption $P = 1$ put forward to derive Eq. [24] is justified).

3.2. Slow Coalescence

In this case the general relation between the rates of the two processes is $k_f \nu_0 \gg k_c^{n,i}$. If the exhausting of particles

can be neglected, $q_1 = q_2 = \dots = 0$, we can present the set [1] in the following way:

$$\begin{aligned} \frac{dv_1}{dt} + 2k_f v_1 v &= k_f v_0 \sum_{i=2}^{\infty} \frac{k_c^{i,1}}{k_f v_0} v_i \\ \frac{dv_2}{dt} - k_f v_1^2 + 2k_f v_2 v &= k_f v_0 \sum_{i=3}^{\infty} \frac{k_c^{i,2}}{k_f v_0} v_i \\ &\quad - k_f v_0 \frac{k_c^{2,1}}{k_f v_0} v_2 \\ &\quad \vdots \\ \frac{dv_n}{dt} - k_f \sum_{i=1}^{n-1} v_i v_{n-i} + 2k_f v_n v &= k_f v_0 \sum_{i=n+1}^{\infty} \frac{k_c^{i,n}}{k_f v_0} v_i \\ &\quad - k_f v_0 \sum_{i=1}^{n-1} \frac{k_c^{n,i}}{k_f v_0} v_n \\ &\quad \vdots \end{aligned} \quad [36]$$

On the right-hand side of Eq. [36] we put the terms of higher order with respect to the small quantity $k_c^{i,n}/(k_f v_0)$. The left-hand side coincides with the set of Smoluchowski. Therefore, the solution of Eq. [36] can be sought as a small correction to the solution of Smoluchowski—Eq. [6]:

$$v_i = \frac{v_0 (k_f v_0 t)^{i-1}}{(1 + k_f v_0 t)^{i+1}} + v_i'. \quad [37]$$

From the first equation [36] and from [37] we can derive an equation for the perturbation in the number of individual particles

$$\frac{dv_1'}{dt} + 2k_f v_1' v = k_f v_0 \sum_{i=2}^{\infty} \frac{k_c^{i,1}}{k_f v_0} \frac{v_0 (k_f v_0 t)^{i-1}}{(1 + k_f v_0 t)^{i+1}}, \quad [38]$$

which is being solved under the initial condition

$$v_1' = 0. \quad [39]$$

We apply here the method of variation of arbitrary constant (16) and seek for a solution of Eq. [38] in the form

$$v_1' = \frac{v_0}{(1 + k_f v_0 t)^2} f(t). \quad [40]$$

The function $f(t)$ should obey the differential equation

$$\frac{df}{dt} = \sum_{i=2}^{\infty} k_c^{i,1} \left(\frac{k_f v_0 t}{1 + k_f v_0 t} \right)^{i-1}. \quad [41]$$

From Eqs. [39] and [40] we find the initial condition for $f(t)$

$$f(0) = 0. \quad [42]$$

If $k_c^{i,1}$ is given by Eq. [21], then the right-hand side of Eq. [41] can be summed up analytically and the differential equation considerably simplifies:

$$\frac{df}{dt} = k_c^{2,1} \frac{k_f v_0 t}{1 + (1 - P)k_f v_0 t}. \quad [43]$$

After solving Eq. [43] with the initial condition Eq. [42], inserting into Eq. [40] and after that substituting in Eq. [37] at $i = 1$, we finally come to the following result for the number of single particles in the case of slow coalescence:

$$v_1 = \frac{v_0}{(1 + k_f v_0 t)^2} \left\{ 1 + \frac{k_c^{2,1} t}{1 - P} - \frac{k_c^{2,1}}{(1 - P)^2 k_f v_0} \times \ln[1 + (1 - P)k_f v_0 t] \right\}. \quad [44]$$

From Eq. [44] it follows that at short times, $k_f v_0 t \ll 1$, the relation [25] holds. In other words, irrespective of whether the coalescence is fast or slow, the behavior of v_1 at short times is one and the same—the flocculation is rate-determining. This is physically understandable since before any coalescence can take place, the particles should first flocculate. In the limit of long times, $k_c^{2,1} t \gg 1$, the asymptotic expression

$$v_1 \approx v_0 \frac{1}{k_f v_0} \frac{1}{t} \frac{k_c^{2,1}}{k_f v_0 (1 - P)} \quad [45]$$

is applicable. The number of individual particles is essentially dependent on both the coalescence and the flocculation rate constants.

4. AVERAGED MODELS FOR A SYSTEM WITH FLOCCULATION AND COALESCENCE

We compare below three averaged models developed by van den Tempel (10) and Borwankar *et al.* (11) with the predictions of our model. The conditions under which our theory reduces to the averaged models and the relation between the rate constants in the models are discussed.

4.1. Model of van den Tempel (10)

It falls within the most cited and widely accepted models for flocculating and coalescing systems. We investigate here what the conditions for its applicability are. According to van den Tempel, if

$$m = \frac{v_T - v_1^S}{v - v_1^S} \quad [46]$$

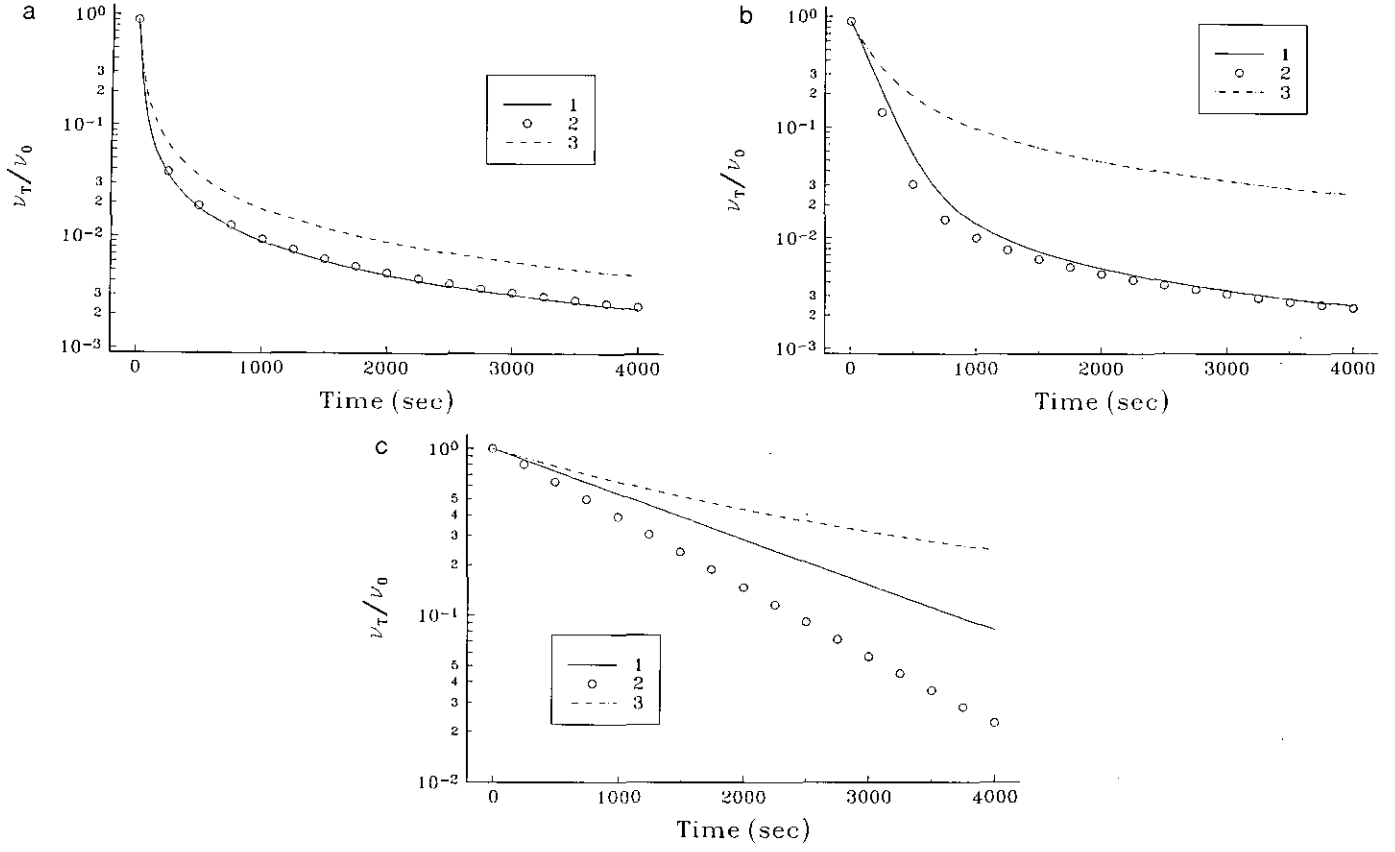


FIG. 3. Relative change in the total number of drops vs time: initial number of primary particles $\nu_0 = 1 \times 10^{10} \text{ cm}^{-3}$; flocculation rate constant $k_f = 1 \times 10^{-11} \text{ cm}^3/\text{s}$; curve 1, the numerical solution of the set [1] with $P = 0.5$ in Eq. [20]; curve 2, the model of Borwankar *et al.* (11) for diluted emulsions; curve 3, the model of van den Tempel (10), Eq. [48]; (a) coalescence rate constant $k_c^{2,1} = 1 \times 10^{-1} \text{ s}^{-1}$; (b) $k_c^{2,1} = 1 \times 10^{-2} \text{ s}^{-1}$; (c) $k_c^{2,1} = 1 \times 10^{-3} \text{ s}^{-1}$.

is the average number of particles per aggregate, corresponding to the Smoluchowski theory (the index "S" denotes Smoluchowski distribution), then

$$\frac{dm}{dt} = k_f \nu_0 - k_c^a (m - 1). \quad [47]$$

k_c^a measures the rate of coalescence (10). The assumption of linearly built aggregates (see Section 2 above) was used in Ref. (10) to establish Eq. [47]. The latter can be rearranged by substituting for m and accounting for ν from Eq. [5] and for ν_1^S from Eq. [6]:

$$\frac{d\nu_T}{dt} = k_f \nu_0 \frac{k_f \nu_0 t - 1}{k_f \nu_0 t + 1} \nu - (\nu_T - \nu) \times \left[k_c^a + \frac{1}{t} \frac{k_f \nu_0 t - 1}{k_f \nu_0 t + 1} \right]. \quad [48]$$

Up to a second order (inclusive) and at short times, $k_f \nu_0 t \ll 1$, the solution of Eq. [48] reduces to

$$\nu_T = \nu_0 (1 - k_f \nu_0 k_c^a t^2). \quad [49]$$

At long times, $k_f \nu_0 t \gg 1$, and for fast coalescence, $k_c^a \gg k_f \nu_0$, Eq. [48] can be simplified to give

$$\frac{d\nu_T}{dt} = -k_c^a (\nu_T - \nu). \quad [50]$$

On comparison of Eqs. [13], [17], and [50] we come to the conclusion that in van den Tempel's theory a certain hypothesis has been set up. When the coalescence is fast, and at long times, $k_f \nu_0 t \gg 1$, the total rate of coalescence k_c^a is an averaged constant parameter:

$$k_c^a = \frac{\sum_{i=2}^{\infty} k_{c,T}^i \nu_i}{\nu_T - \nu} = \text{const} = k_c^{2,1}. \quad [51]$$

This parameter characterizes the relative change in the total number of particles ν_T with time. The oversimplification put forward by van den Tempel lies in using ν_1^S from the Smoluchowski distribution to define m —Eq. [46].

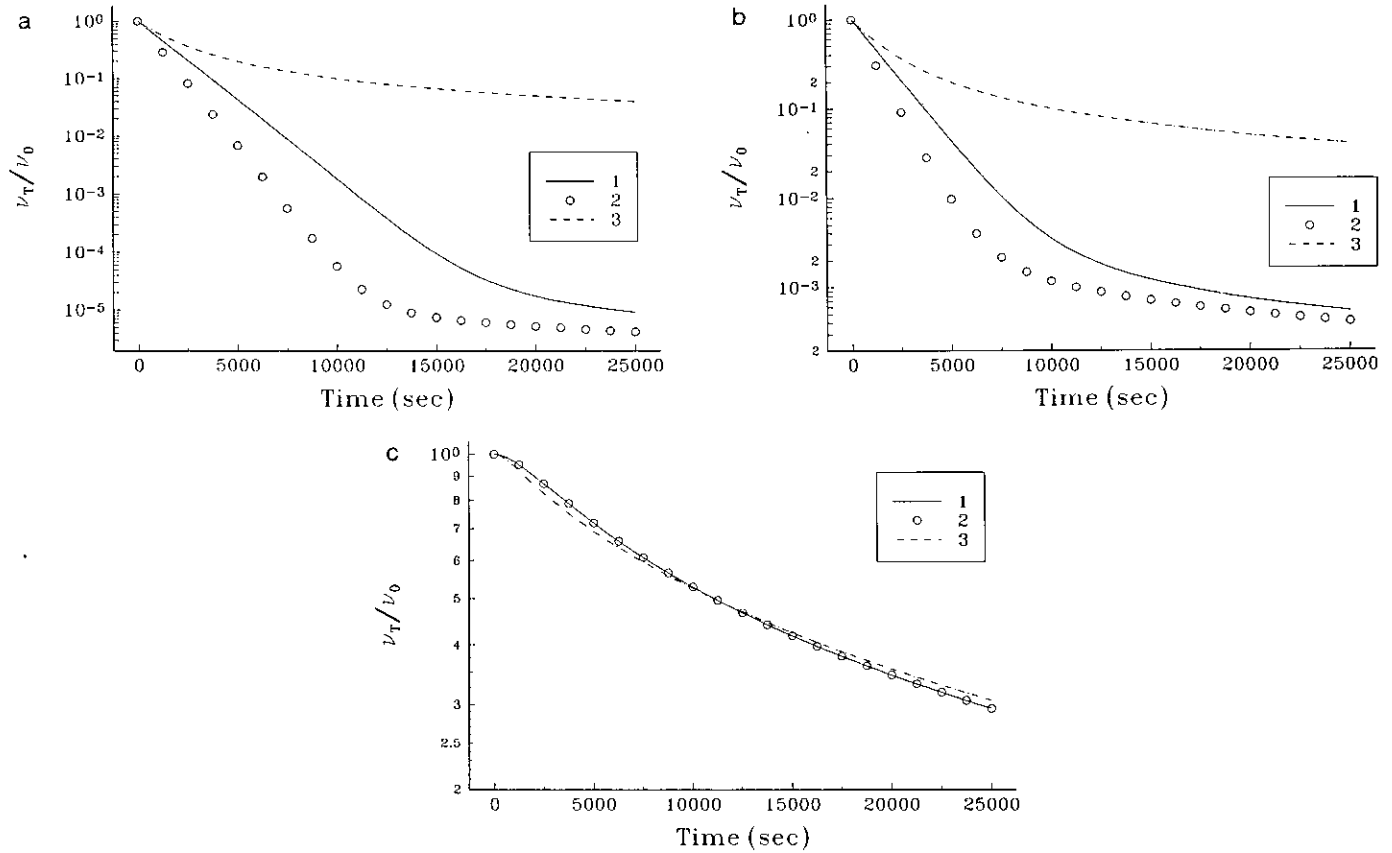


FIG. 4. Relative change in the total number of drops vs time: initial number of primary particles $\nu_0 = 1 \times 10^{12} \text{ cm}^{-3}$; coalescence rate constant $k_c^{2,1} = 1 \times 10^{-3} \text{ s}^{-1}$; curve 1, the numerical solution of the set [1] with $P = 0.5$ in Eq. [20]; curve 2, the model of Borwankar *et al.* (11) for diluted emulsions; curve 3, the model of van den Tempel (10), Eq. [48]: (a) flocculation rate constant $k_f = 1 \times 10^{-11} \text{ cm}^3/\text{s}$; (b) $k_f = 1 \times 10^{-13} \text{ cm}^3/\text{s}$; (c) $k_f = 1 \times 10^{-16} \text{ cm}^3/\text{s}$.

4.2. Models of Borwankar *et al.* (11)

These authors propose two separate models of coalescence: (a) in emulsions of low volume fraction (diluted systems), and (b) in concentrated emulsions. As in Ref. (10), the treatment is based on considering the average number of particles in aggregates, but the assumption of ν_1^S put in Eq. [46] is avoided.

(a) In diluted emulsions, if particles are not exhausted due to fluxes, Borwankar *et al.* (11) suppose the hypothesis [51] to be valid during the whole process of flocculation and coalescence. When $k_{c,T}^i$ is proportional to the number of particles in the i th aggregate minus one, $k_{c,T}^i = k_c^a(i-1)$, Eq. [51] holds identically. We see from Eq. [16] that this is exactly the case of linearly built aggregates, with $k_c^a = k_c^{2,1}$. Therefore, the model proposed in Ref. (11) is in accordance with the general treatment developed here as long as linear aggregates are under consideration. The numerical solution for ν_T found in Ref. (11) coincides with our Eq. [18]. In addition, it is evident from Eq. [50] that for rapid coalescence the models of van den Tempel and Borwankar *et al.* give the same results. This fact is illustrated in Fig. 4c (see next section).

(b) Another hypothesis has been raised by Borwankar *et al.* (11) for concentrated emulsions when considering coalescence without exhausting of particles due to fluxes. This hypothesis states that the mean rate of coalescence with respect to the number of particles engaged in aggregates keeps constant value,

$$kp = \frac{\sum_{i=2}^{\infty} k_{c,T}^i \nu_i}{\nu_T - \nu_1}, \quad [52]$$

where p is the average number of films per particle.

In particular, if $k_{c,T}^i = kpi$, Eq. [52] is identically satisfied. In other words, the total coalescence rate constant of an aggregate composed of i particles is set to be proportional to the number of particles in this aggregate. Such an assumption can be conceived by analogy with Eq. [16], since within the approach of Ref. (11) ($p.i$) corresponds to the number of contacts between neighboring particles in the i th aggregate. From Eqs. [13] and [52] it follows that

$$\frac{d\nu_T}{dt} = -kp(\nu_T - \nu_1) \quad [53]$$

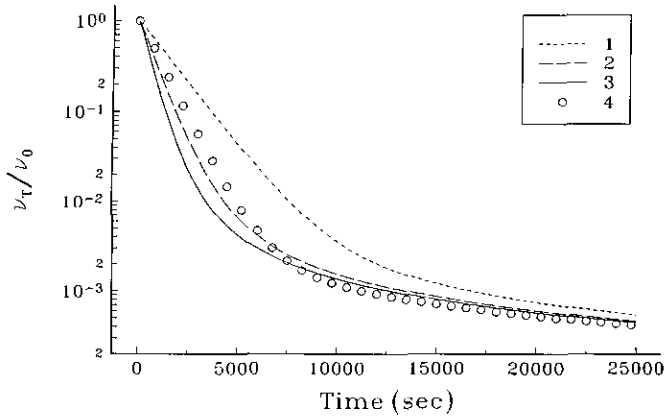


FIG. 5. Relative change in the total number of drops vs time: initial number of primary particles $\nu_0 = 1 \times 10^{12} \text{ cm}^{-3}$; flocculation rate constant $k_f = 1 \times 10^{-13} \text{ cm}^3/\text{s}$; coalescence rate constant $k_c^{2,1} = 1 \times 10^{-3} \text{ s}^{-1}$; curve 1, the numerical solution of the set [1] with $P = 0.50$ in Eq. [20]; curve 2, $P = 0.80$; curve 3, $P = 0.95$; curve 4, the model of Borwankar *et al.* (11) for diluted emulsions.

—see Eq. [18] in (11). Equation [53] can be solved with the initial condition $\nu_T(0) = \nu_0$. The exact solution is easily found provided that $\nu_1(t)$ is known:

$$\nu_T = \nu_0 \exp(-kpt) + kp \int_0^t \nu_1(\tau) \times \exp[-kp(t - \tau)] d\tau. \quad [54]$$

Up to the second order (inclusive) and at short times, $k_f \nu_0 t \ll 1$, the solution [54] acquires the form

$$\nu_T = \nu_0 (1 - k_f \nu_0 k p t^2). \quad [55]$$

We have used the method of the infinite asymptotics (4) to obtain that at long times, $kpt \gg 1$, Eq. [54] becomes

$$\nu_T \sim \nu_1(t). \quad [56]$$

5. NUMERICAL COMPARISON BETWEEN DIFFERENT MODELS OF FLOCCULATION AND COALESCENCE

We present here numerical solutions of the complete set of kinetic differential equations [1] at various values of the rate constants of flocculation and coalescence. In fact, we have two independent parameters to describe the coalescence process in the case of arbitrary aggregates: $k_c^{2,1}$ and the probability for film rupture, P —see Eqs. [19], [20]. Once $k_c^{2,1}$ and P are known, all the rate constants $k_c^{i,k}$ in the set [1] are unambiguously defined via Eq. [19].

We make numerical comparison using the results of van den Tempel (10) and those of Borwankar *et al.* (11) which correspond to low volume fraction emulsions. In order to choose the parameters properly, we apply the relation

$$k_c^a = k_c^{2,1} \quad [57]$$

found in Section 4.2 for linearly built aggregates. The same values of $k_c^{2,1}$ are considered as those used by Borwankar *et al.* (11) for k_c^a . The rate constant of flocculation can be estimated as (10)

$$k_f \sim \frac{4kT}{3\eta} \sim 1 \times 10^{-11} \text{ cm}^3/\text{s}. \quad [58]$$

More precisely, Eq. [58] gives the characteristic value for k_f , which is actually operative when the flocculation process does not include passing through a potential barrier. In the case of barrier flocculation k_f could be smaller by several orders of magnitude.

We present in Figs. 3–5 data for the relative change in the total number of emulsion drops, ν_T/ν_0 (or n/n_0 in the notation of Borwankar *et al.* (11)) as a function of time. Figures 3a–3c refer to $k_f \nu_0 = 0.1 \text{ s}^{-1}$ and the coalescence constant $k_c^{2,1}$ varies between 0.1 s^{-1} (Fig. 3a) and 0.001 s^{-1} (Fig. 3c). It is seen that the agreement between the exact solution and the results of Borwankar *et al.* (11) is better for faster coalescence. The van den Tempel curves deviate considerably from the other two solutions.

Figure 3b shows that at long times the data of Borwankar *et al.* (11) coincide with the solution of the set [1]. No coincidence is observed in Fig. 3c because in that case the time is not long with respect to the coalescence, $0 < k_c^{2,1} t < 4$. Figure 4b presents ν_T/ν_0 for the same values of $k_f \nu_0$ and $k_c^{2,1}$ as in Fig. 3c, but up to very long times. Under these conditions, the agreement between curves 1 and 2 is confirmed.

Figures 4a–4c illustrate the influence of the flocculation rate constant at fixed $k_c^{2,1}$. If the flocculation is very fast compared to the coalescence, the differences between the

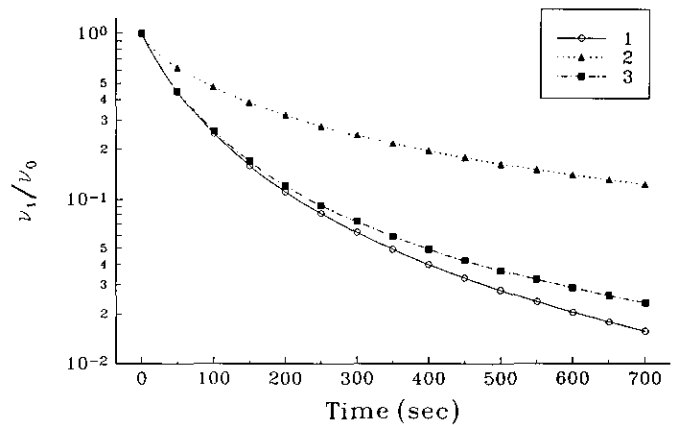


FIG. 6. Relative change in the number of single drops vs time: $k_f \nu_0 = 1 \times 10^{-2} \text{ s}^{-1}$; curve 1, solution of Smoluchowski, Eq. [6]; curve 2, fast coalescence, $k_c^{2,1} = 1 \times 10^{-1} \text{ s}^{-1}$, Eq. [24]; curve 3, slow coalescence, $k_c^{2,1} = 1 \times 10^{-3} \text{ s}^{-1}$, Eq. [44] with $P \leq 1$.

predictions of the three models are tremendous—Fig. 4a. At moderate times the curves deviate by orders of magnitude. On the contrary, if the coalescence is faster than the flocculation, then all the data exhibit a perfect agreement—Fig. 4c. Indeed, it was proved in the previous section that for fast coalescence the theories of van den Tempel, Borwankar *et al.*, and the present one should give identical results. In this case the structure of the aggregates becomes irrelevant and the predictions of the model (11), which are strictly applicable to linearly built aggregates, match the numerical solution of [1].

We have chosen the probability for a film rupture, P , to be 0.5 for our curves in Figs. 3 and 4. This choice is somewhat arbitrary. The question about the connection between P and the hydrodynamics of the thinning interdroplet films is to be investigated in a future work.

Figure 5 illustrates the role of the parameter P for the behavior of the numerical solution. Obviously, at very long times P is uninfluential. We mention that $P = 0$ means complete absence of coalescence and $k_c^{ik} = 0$, then the set [1] is reduced to that of Smoluchowski.

Figure 6 shows the solutions for the normalized number of single particles, ν_1/ν_0 , referring to fast and slow coalescence. We use Eqs. [24] and [44] with $P \ll 1$, respectively. The Smoluchowski result is given by Eq. [6]. It is evident that the effect of the coalescence is well pronounced even if the process is slow. At times shorter than the characteristic time for coalescence there still exists an appreciable deviation of ν_1 from the Smoluchowski curve.

6. CONCLUSIONS

In this work we develop a kinetic model for the simultaneous processes of flocculation and coalescence in emulsion systems. A set of differential equations is formulated and the analytical solution is analyzed in several asymptotic cases. For linearly built aggregates, explicit expression for the total number of individual drops results from the theory. In the case of arbitrary aggregates we solve the kinetic equations numerically, using three model parameters—the rate constants of flocculation and coalescence, and the probability for rupture of an interdroplet film.

We discuss the averaged models proposed by other authors. They do not assign rate constants to each possibility for coalescence in the aggregates, but deal with certain av-

eraged characteristics of the process. Nevertheless, for the particular case of linear aggregates the existing theory (Ref. (11)) is in complete agreement with the general treatment proposed here. For aggregates of more complex structure, we compare the numerical solutions of the complete set of kinetic equations with the outcome of the averaged theories.

It turns out that if the coalescence is much faster than the flocculation, the predictions of the different models coincide. This finding is in consonance with the fact that in the case of rapid coalescence the flocculation is rate-determining and the structure of the aggregates is immaterial—large aggregates cannot form. Conversely, for slow coalescence the results of the averaged models considerably deviate from the exact solution. At very long times and irrespective of the values of the kinetic parameters, the model of Borwankar *et al.* (11) is close to the numerical solution.

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