

Coupling of Coalescence and Flocculation in Dilute O/W Emulsions

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1. GENERAL

A. Kinetic and Thermodynamic Stability in Macroemulsions and Miniemulsions

The majority of emulsion-technology problems relate to the stabilization and destabilization of emulsions (1-7). Despite the existence of many fundamental studies related to the stability of emulsions, the extreme variability and complexity of the systems involved in any specific application often pushes the oil industry to achieve technologically applicable results without developing a detailed understanding of the fundamental processes. Nevertheless, since in most cases technological success requires the design of emulsions with a very delicate equilibrium between stability and instability, a better understanding of the mechanisms of stabilization and destabilization might lead to significant breakthroughs in technology.

Notwithstanding their thermodynamic instability, many emulsions are kinetically stable and do not change appreciably for a prolonged period. These systems exist in the metastable state (8-15). The fundamentals of emulsion sta-

bility (destabilization) comprise emulsion surface chemistry and physicochemical kinetics.

In contrast to the large success in industrial applications of emulsion surface chemistry the potential of physicochemical kinetics as a basis for emulsion dynamics modeling is almost never used in emulsion technology. This situation has started to change during the last decade. Although the coupling of the subprocesses in emulsion dynamics modeling (EDM) continues to represent a large problem not yet solved, models are elaborated for (1) macroemulsions (10, 16-22); and (2) miniemulsions (23-30), for long and short lifetimes of thin emulsion films.

1 For large droplets (larger than 10-30 μm) in macroemulsions the rate of thinning of the emulsion film formed between two approaching droplets is rather low, and correspondingly, the entire lifetime of an emulsion need not be short, even without surfactant stabilization of the film. For this case the notion of *kinetic stability* is introduced (10, 16-19) to denote the resistance of the film against *rupture during thinning*. The droplet deformation and flattening cause this strong resistance, which is described by the Reynolds equation (31, 32). According to theory, the role

of this deformation (33-35) decreases rapidly with decreasing droplet dimension.

2 For small droplets (smaller than 5-10 μm) in miniemulsions droplet deformation can be neglected, because the Reynolds drainage rate increases as R^{-5}_d (10, 36) (R_d , the Reynolds film radius) and because the smaller the droplets, the smaller is their deformation (33—35).

In distinction from macroemulsions, where the kinetic stability is the manifestation of droplet-droplet hydrodynamic interaction and droplet deformation, in miniemulsions the kinetic stability is the manifestation of the interplay between surface forces and Brownian movement (23). As the molecular forces of attraction decrease linearly with decreasing droplet dimension, namely, approximately 10 times at the transition from macroemulsions to miniemulsions, the potential minimum of droplet-droplet interaction (secondary minimum) decreases, and for miniemulsions this depth can be evaluated as 1—5 kT (12, 37). At this low energy, Brownian movement causes droplet doublet disaggregation after a short time (the doublet fragmentation time, T_d). If this time is shorter than the lifetime of the thin film, rapid decrease in the total droplet concentration (t.d.c.) is prevented (restricted by the coalescence time, T_c), i.e., stability is achieved due to this kinetic mechanism (23).

B. Current State of Emulsion Stability Science

A large disparity exists between knowledge concerning kinetic stability and thermodynamic stability. The main attention has been paid to *kinetic stability* for both macroemulsions (16-22) and miniemulsions (23-30). As a result, the droplet-droplet interaction and the collective processes in dilute emulsions are quantified (38, 39) and important experimental investigations are made (27, 28, 40). Some models are elaborated for the entire process of coalescence in concentrated emulsions as well (41, 42). Given thermodynamic stability, a thin interdroplet film can be metastable.

In contrast to the large achievements in investigations of kinetic stability, modest attention has been paid to the fundamentals of thermodynamic stability in emulsions, especially regarding the surfactant adsorption layer's influence on the coalescence time. There are several investigations devoted to the surface chemistry of adsorption related to emulsification and demulsification. However, the link between the chemical nature of an adsorption layer, its structure, and the coalescence time is not yet quantified.

A premiss for such quantification is the theory of a foam-bilayer lifetime (43). The main notions of this theory are similar to the theory of Derjaguin and coworkers (44, 45). However, the theory (43) is specified for amphiphile foam films, it is elaborated in detail, and is proven by experiment with water-soluble amphiphiles, such as sodium dodecyl sulfate (47). As the dependence of the rupture of the emulsion film on surfactant concentration is similar to that for a foam film, the modification of theory with respect to emulsions may be possible. Although this modification is desirable the specification of a theory for a given surfactant will not be trivial, since the parameters in the equation for the lifetime (45) are unknown and their determination is not easy. As the theory (43, 47) is proposed for amphiphiles and since a wider class of chemical compounds can stabilize, emulsions, the film-rupture mechanism (44) is not universal regarding emulsions.

Thus, in contrast to the quantification of kinetic stability, the empirical approach continues to predominate regarding thermodynamic stability. Meanwhile, thermodynamic stability provides greater opportunity for long-term stabilization of emulsions, than does kinetic. This means that the experimental characterization of thermodynamic stability, i.e., the measurement of coalescence time, is of major importance.

C. Specificity of Emulsion Characterization

Generalized emulsion characterization, i.e., measurement of droplet size distribution, electrokinetic potentials, Hamaker constant, etc., is not always sufficient. Thermodynamic stability with respect to bilayer rupture cannot be quantified with such a characterization procedure alone. Consequently, measurement of the coalescence time T_c is of major importance for an evaluation of emulsion stability; it is an important and specific parameter of emulsion characterization.

The current state of miniemulsion characterization neglects the importance of T_c measurement. A practice for T_c measurement is practically absent with the exception of only a few papers considered in this chapter. Meanwhile, many papers devoted to issues more or less related to emulsion stability do not discuss T_c measurement. One reason for this scientifically and technologically unfavorable situation in which emulsions are incompletely characterized may originate from a lack of devices enabling T_c measurements to be made.

D. Scope of the Chapter

This chapter is focused on kinetic stability in miniemulsions with emphasis on the coupled destabilizing subprocesses, in distinction from other chapters in the *Encyclopedia* describing other aspects of emulsion stability.

In general there are three coupled subprocesses that will influence the rate of destabilization and phase separation in emulsions. These are aggregation, coalescence, and floe fragmentation. Often, irreversible aggregation is called coagulation and the term flocculation is used for reversible aggregation (13, 48). Ostwald ripening (49, 50) coupled (24) with aggregation and fragmentation is a separate topic which will be not considered here.

A simplified theory is available for the coupling of coalescence and flocculation in emulsions void of larger floes. This theory is considered in Sec. II and will assist in the consideration of the more complicated theory of coupling of coalescence and coagulation (Sec. III). The experimental investigations are described in parallel. Section IV is devoted to the theory of doublet fragmentation time and its measurement, as this characterizes an emulsion regarding fragmentation and because its measurement is an important source of information about surface forces and the pair interaction potential. The discrimination between conditions for coupling of coalescence with coagulation or with flocculation is considered in Sec. V. The quantification of kinetic stability creates new opportunities for long-term prediction of miniemulsion stability, for stability optimization, and for characterization with the standardization of T_c and T_d measurements. This forms the basis for emulsion dynamics modeling (Sec. VI).

II. COUPLING OF COALESCENCE AND FLOCCULATION

A. Singlet-Doublet Quasiequilibrium

Each process among the three processes under consideration is characterized by a characteristic time, namely, T_{Sm} , T_d , and T_c . The Smoluchowski time (51), T_{Sm} , gives the average time between droplet collisions. If the time between two collisions is shorter than T_d a doublet can transform into a triplet before it spontaneously disrupts. In the opposite case, i.e., at

$$\tau_{Sm} \gg \tau_d \quad (1)$$

the probability for a doublet to transform into a triplet is very low because the disruption of the doublet occurs much earlier than its collision with a singlet. The rate of multiplet formation is very low for

$$\text{Rev} = \tau_d / \tau_{Sm} \ll 1 \quad (2)$$

where we introduce the notation “Rev” for small values of the ratio corresponding to the reversibility of aggregation and a singlet-doublet quasiequilibrium.

The kinetic equation for reversible flocculation in a dilute monodisperse o/w emulsion when neglecting coalescence is [52–54]

$$\frac{dn_2}{dt} = \frac{n_1^2}{\tau_{Sm}} - \frac{n_2}{\tau_d} \quad (3)$$

where n_1 and n_2 are the dimensionless concentrations of doublets and singlets, $n_1 = N_1/N_{10}$, $n_2 = N_2/N_{10}$, N_1 and N_2 are the concentrations of singlets and doublets, and N_{10} is the initial concentration, and

$$\tau_{Sm} = \left(\frac{4kT}{3\eta} N_{10} \right)^{-1} = (K_f N_{10})^{-1} \quad (4)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of water. For aqueous dis-

persions at 25°C , $K_f = \frac{4kT}{3\eta} = 6 \times 10^{-18} \text{m}^3 \text{s}^{-1}$

The singlet concentration decreases with time due to doublet formation, while the doublet concentration increases. As a result, the rates of aggregation and floe fragmentation will approach each other. Correspondingly, the change in the number of doublets $dn_2/dt = 0$. Thus, a dynamic singlet-doublet equilibrium (s.d.e.) is established:

$$n_{2eq} = \frac{\tau_d}{\tau_{Sm}} n_{1eq}^2 \quad (5)$$

Under condition (2) it follows from Eq. (2.5) that

$$n_{1eq} \cong 1, N_{1eq} = N_{10} \quad (6)$$

$$N_2 = \text{Rev} \cdot N_{10} \text{ or } n_2 \ll 1 \quad (7)$$

Thus, at small values of Rev the s.d.e. is established with only small deviations in the singlet equilibrium concentration from the initial concentration [Eq. (6)] The doublet concentration is very low compared to the singlet concentration, and the multiplet concentration is very low compared to the doublet concentration. The last statement follows from a comparison of the production rates of doublets and triplets. The doublets appear due to singlet-singlet collisions, while the triplets appear due to singlet-doublet collisions. The latter rate is lower owing to the low doublet

concentration. The ratio of the number of singlet-doublet collisions to the number of singlet-singlet collisions is proportional to Rev .

B. Kinetic Equation for Coupling of Flocculation and Intradoublet Coalescence in Monodisperse Emulsions

Both the rate of doublet disaggregation and the rate of intradoublet coalescence are proportional to the momentary doublet concentration. This leads (23, 29) to a generalization of Eq. (3):

$$\frac{dn_2}{dt} = \frac{n_1^2}{\tau_{Sm}} - n_2 \left(\frac{1}{\tau_d} + \frac{1}{\tau_c} \right) \quad (8)$$

There are two unknown functions in Eq. (8), so an additional equation is needed. This equation describes the decrease in the droplet concentration caused by coalescence:

$$\frac{d}{dt}(n_1 + 2n_2) = -\frac{n_2}{\tau_c} \quad (9)$$

The initial conditions are

$$n_2 \Big|_{t=0} = 0 \quad (10)$$

$$\frac{dn_2}{dt} \Big|_{t=0} = \frac{n_{10}}{\tau_{Sm}} \quad (11)$$

Condition (11) follows from Eqs (8) and (9). The solution of the set of Eqs (8) and (9), taking into account boundary conditions (10) and (11), is a superposition of two exponents (23, 29). In the case

$$\tau_c \gg \tau_d \quad (12)$$

the solution simplifies (23, 29) to

$$n_2(t) = \frac{\tau_d}{\tau_{Sm}} \left[\exp\left(-\frac{2\tau_d t}{\tau_{Sm}\tau_c}\right) - \exp\left(-\frac{t}{\tau_d}\right) \right] \quad (13)$$

Equation (13), as compared to Eqs (5) and (6), corresponds to the s.d.e. if the expression in the second brackets equals unity. In the time interval:

$$\tau_d < t < \tau \quad (14)$$

where

$$\tau = \tau_c \frac{\tau_{Sm}}{2\tau_d} \quad (15)$$

the first term in the second brackets is approximately equal to 1, while the second one decreases from 1 to a very small

value. Thus, the s.d.e. is established during the time T_d and is preserved during the longer time interval [Eq. (14)].

For times longer than T there is no reason to apply Eq. (13) since the condition to linearize Eq. (8) is no longer valid with the concentration decrease. At the beginning of the process the doublet concentration increases, while later coalescence predominates and the doublet concentration decreases. Thus, function (13) has a maximum (23, 29).

C. Coalescence in a Singlet-Doublet System at Quasiequilibrium

After a time t_{\max} a slow decrease in the doublet concentration takes place simultaneously with the more rapid processes of aggregation and disaggregation. Naturally, an exact singlet-doublet equilibrium is not valid owing to the continuous decrease in the doublet concentration. However, the slower the coalescence, the smaller is the deviation from the momentary dynamic equilibrium with respect to the aggregation-disaggregation processes.

It is reasonable to neglect the deviation from the momentary doublet-singlet equilibrium with the condition:

$$\frac{dn_2}{dt} \ll \frac{n_2}{\tau_d} \quad (16)$$

Indeed, for this condition the derivative in Eq. (3) can be omitted, which corresponds to s.d.e. characterized by Eq. (5).

It turns out (23, 27-29) that the deviation from s.d.e. is negligible as the condition (13) is valid, i.e., for conditions (2) and (12). For these conditions the fragmentation of flocs influences the coalescence kinetics which can be represented as a three-stage process, as illustrated in Fig. 1. During a rather short time T_d the approach to s.d.e. takes place, i.e., a rather rapid increase in the doublet concentration (stage 1). During the next time interval $T_d < t < t_{\max}$ the same process continues. However, the rate of doublet formation declines due to coalescence (stage 2). The exact equilibrium between the doublet formation and their disappearance due to coalescence takes place at the time t_{\max} when the doublet concentration reaches its maximum value $n_2(t_{\max})$. During the third stage, when $t > t_{\max}$, the rate of doublet fragmentation is lower than the rate of formation, because of the coalescence within doublets. This causes a slow monotonic decrease in the concentration. Taking

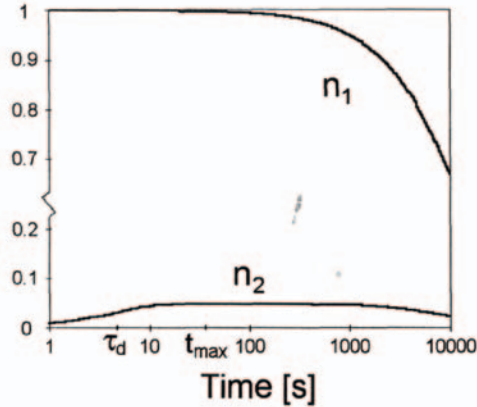


Figure 1 Three stages in the coupling of aggregation, fragmentation, and coalescence under the condition $\tau_d \ll \tau_{Sm} \ll \tau_c$. Initially, the doublet concentration n_2 is very low and the rates of doublet fragmentation and of coalescence are correspondingly low compared to the rate of aggregation (first stage, no coupling). Owing to increasing n_2 the fragmentation rate increases and equals the aggregation rate at t_{max} (exact s.d.e.). The growth in n_2 stops at t_{max} (second stage, coupling of aggregation and fragmentation). Intradoublet coalescence causes a slight deviation from exact s.d.e. to arise at $t > t_{max}$, and the singlet concentration n_1 and the doublet concentration decrease due to intradoublet coalescence (third stage, coupling of aggregation, fragmentation, and coalescence); n_1 and n_2 are dimensionless, $n_1 = N_1/N_{10}$; $n_2 = N_2/N_{10}$; N_{10} is the initial singlet concentration. (From Ref. 23.)

into account the s.d.e. [Eqs (5) and (7)], Eq. (9) can be expressed as

The result of the integration of Eq. (17) can be simplified

$$\frac{dn_1}{dt} = -\frac{\tau_d}{\tau_{Sm}\tau_c} n_1^2 \quad (17)$$

to

$$n_1(t) = \frac{n_1(t_{max})}{1 + n_1(t_{max})\frac{t}{2\tau}} \cong \left(1 + \frac{t}{2\tau}\right)^{-1} \quad (18)$$

with a small deviation in $n_{d1}(t_{max})$ from unity. As opposed to the preceding stages when the decrease in droplet concentration caused by coalescence is small, a large decrease is now possible during the third stage. Thus, this is the most important stage of the coalescence kinetics.

D. Reduced Role of Fragmentation with Decreasing τ_c

With decreasing τ_c , condition (12) is violated and new qualitative features of the destabilization process, not discussed in Refs 27-29, arise. As the ratio τ_c/τ_d diminishes and

$$\tau_c < \tau_d \quad (19)$$

the s.d.e. is violated because a larger part of the doublets disappear due to coalescence. Correspondingly, the smaller the ratio τ_c/τ_d the smaller is the fragmentation rate in comparison with the aggregation rate, i.e., the larger the deviation from s.d.e. In the extreme case:

$$\tau_c \ll \tau_d \quad (20)$$

the fragmentation role in s.d.e. can be neglected. This means that almost any act of aggregation is accompanied by coalescence after the short doublet lifetime. Neglecting this time in comparison with τ_{Sm} , in agreement with condition (1), one concludes that any act of aggregation is accompanied by the disappearance of one singlet:

$$\frac{dn_1}{dt} = -\frac{n_1^2}{\tau_{Sm}} \quad (21)$$

This leads to a decrease in the singlet concentration described by an equation similar to the Smoluchowski equation for rapid coagulation:

$$n_1(t) = (1 + t/\tau_{Sm})^{-1} \quad (22)$$

The Smoluchowski equation describing the singlet time evolution does not coincide with Eq. (22). The peculiarity of Eq. (22) is that it describes the kinetics of coupled aggregation and coalescence with a negligible fragmentation rate. Due to fragmentation, doublet transformation into multiplets is almost impossible under condition (1).

The coupling of aggregation, fragmentation, and coalescence in the more general case described by condition (19) leads to equation:

$$n_1(t) = \frac{n_1(t_{max})}{1 + n_1(t_{max})t/2\tau_g} \cong (1 + t/2\tau_g)^{-1} \quad (23)$$

$(t > \tau_d + \tau_c)$

with a small deviation of $n_1(t_{max})$ from unity and

$$\tau_g = \frac{\tau_{Sm}(\tau_d + \tau_c)}{2\tau_d} \quad (24)$$

Under conditions (1) and (12) $\tau_g \approx \tau$ and Eq. (23) transforms into Eq. (18). Under conditions (1) and (20) $\tau_g \approx \tau_{Sm}$ and Eq. (23) transforms into Eq. (22). Equation (24) demonstrates the reduction of the role of fragmentation with decreasing τ_c . It is seen that at the transition from condition (19) to condition (20) τ_d cancels out in Eq. (24), i.e., the fragmentation role diminishes.

E. Experimental

1. Application of Video-enhanced Microscopy Combined with the Microslide Technique for Investigation of Singlet-Doublet Equilibrium and Intradoublet Coalescence (27-29)

Direct observation of doublets in the emulsion bulk is difficult because the doublets tend to move away from the focal plane. The microslide preparative technique can, however, be successfully applied, providing pseudobulk conditions. A microslide is a plane-parallel glass capillary of rectangular cross-section. The bottom and top sides of the capillary are horizontal, and the gravity-induced formation of a sediment or cream on one of the inner normal surfaces is rapidly completed owing to the modest inner diameter of the slide. If both the volume fraction of droplets in an emulsion and the capillary height are small, the droplet coverage on the inside surface amounts to a few per cent, and the analysis of results is rather simple. It can be seen through the microscope that the droplets which have sedimented on to the capillary surface participate in chaotic motion along the surface. This indicates that a thin layer of water separating the surface of the microslide from the droplets is preventing the main portion of droplets from adhering to the microslide surface, an action which would stop their Brownian motion.

During diffusion along the microslide ceiling the droplets collide. Some collisions lead to the formation of doublets. Direct visual observation permits evaluation of the doublet-fragmentation time which varies in a broad range (25). Another approach to doublet-fragmentation time determination is based on evaluation of the average concentration of singlets and doublets and using the theory outlined above.

Application of the microslide preparative technique combined with video microscopy is promising and has allowed the measurement of the coupling of reversible flocculation and coalescence (27, 29). However, some experimental difficulties were encountered: droplets could sometimes be seen sticking to the glass surface of the microslide.

2. Improving the Experimental Technique with Use of Low-density Contrast Emulsions (28)

The sticking of droplets indicates a droplet-wall attraction and the existence of a secondary potential pit as that for the droplet-droplet attraction in a doublet. The droplet concentration within the pit is proportional to the concentration on its boundary. The latter decreases with a decrease in the density contrast.

The electrostatic barrier between the potential pit and the wall retards the rate of sticking. The lower the droplet flux through this barrier, the lower is the potential pit occupancy by droplets. Thus, an essential decrease in the rate of sticking is possible with decreasing density contrast.

Oil/water emulsions were prepared (28) by mixing dichlorodecane (DCD, volume fraction 1%) into a 5×10^{-5} M sodium dodecyl sulfate (SDS) solution with a Silverson homogenizer. The oil phase was a 70:1 mixture of DCD, which is characterized by an extremely low density contrast to water, and decane.

The droplet distribution along and across the slide was uniform (28). This indicates that there was no gravity-induced rolling either. One slide among four was examined for two weeks without any sticking being observed (28). The absence of the rolling and sticking phenomena allowed acquisition of quite accurate data concerning the time dependence of the droplet size distribution.

3. The Measurement of Coalescence Time and Doublet-fragmentation Time

The doublet-fragmentation time was measured by direct real-time observation of the doublets on the screen and by analysis of a series of images acquired at 1-3 min intervals (25). The formation and disruption/coalescence of a doublet could thus be determined.

The general form of the concentration dependence agrees with the theory. At $C \sim 3 \times 10^{-3}$ M, both theory and experiment yield times of about 1 min; at $C = 9 \times 10^{-3}$ M, these times exceed 10 min. For calculation of the doublet-fragmentation time the electrokinetic potential was measured (29, 46).

In experiments with different droplet concentrations it was established that the higher the initial droplet concentration, the higher the doublet concentration. This corresponds to the notion of singlet-doublet equilibrium. However, if the initial droplet concentration exceeds 200-300 per observed section of the microslide, multipliants predominate. Both the initial droplet concentration and size affect the rate of decrease in the droplet concentration. The larger the

droplets, the smaller the concentration sufficient for the measurement of the rate of decrease in the droplet concentration. This agrees with the theory of doublet-fragmentation time which increases with droplet dimension. Correspondingly, the probability for coalescence increases. These first series of experiments (27, 29) were accomplished using toluene-in-water emulsions without the addition of a surfactant and decane-in-water emulsions stabilized by SDS. The data obtained, concerning the influence of the electrolyte concentration and surface charge density, were in agreement with the existing notions about the mechanism of coalescence. With increasing SDS concentration, and correspondingly increasing surface potential, the rate of decrease in the droplet concentration was reduced.

Two methods were used for the measurement of the coalescence time (28, 29). Measurement of the time dependence for the concentrations of singlets and doublets and a comparison with Eq. (9) enables an evaluation of the coalescence time to be made. Further, information about the time dependence for singlets and the doublet-fragmentation time may be used as well. These results, in combination with Eqs (15) and (18), determine the coalescence time. The good agreement between results obtained by these very different methods indicates that the exactness of the theory and experiments is not low.

In recent years several research groups have improved significantly the theoretical understanding of coalescence of droplets or bubbles. The newer results (53—57), together with results of earlier investigations (58—62), have clarified the role of double-layer interaction in the elementary act of coalescence.

DLVO theory was applied (63, 64) for the description of “spontaneous” and “forced” thinning of the liquid film separating the droplets. These experimental results and DLVO theory were used (63) for the interpretation of the reported visual study of coalescence of oil droplets 70—140 μm in diameter in water over a wide pH interval. A comparison based on DLVO theory and these experimental data led the authors to conclude (63) that “if the total interaction energy is close to zero or has a positive slope in the critical thickness range, i.e., between 30 and 50 nm, the oil drops should be expected to coalesce.” In the second paper (64), where both ionic strength and pH effects were studied, coalescence was observed at constant pH values of 5.7 and 10.9, when the Debye thickness was less than 5 nm. The main trend in our experiments and in Refs 63 and 64 were in accordance, because it was difficult to establish the decrease in t.d.c at NaCl concentrations lower than 5×10^{-3} M, i.e., double-layer (DL) thicknesses larger than 5 nm. An almost quantitative coincidence in the double-layer influence on

coalescence, established in our work for micrometer-sized droplets and in Refs 63 and 64 for almost 100 times larger droplets, is important for general knowledge on coalescence.

F. Perspective for Generalization of the Theory for Coupling of Coalescence and Flocculation

The proposed theory for coupling of coalescence and flocculation at s.d.e. permits the proposal of some important applications (Sec. VI). At the same time generalized theory is necessary, since the role of multiplets increases after a long time or with a higher initial concentration. At least two approaches to this difficult task are seen.

According to our videomicroscopic observations there are large peculiarities in the structure and behavior of multiplets arising at conditions near to s.d.e. These peculiarities can be interpreted as the manifestation of quasiequilibrium, comprising singlets, doublets, and multiplets. Similar to doublets, the lifetime of triplets, tetraplets, etc., can be short due to fragmentation and coalescence. This can be valid for multiplets with an “open” structure, in distinction from another structure which can be called “closed.” In open multiplets any droplet has no more than one or two contacts with other droplets, which corresponds to a linear chain-like structure. This causes easy fragmentation, especially for the extreme droplets within a chain. The “closed” aggregates have a more dense and isometric structure, in which droplets may have more than two contacts with neighboring droplets. As result, fragmentation is more difficult and the frequency is lower.

Progress in the theory of aggregation with fragmentation (65-69) for a suspension creates a premiss for a theoretical extension towards emulsions. However, the necessity in accounting for coalescence makes this task a difficult one.

III. COUPLING OF COALESCENCE AND COAGULATION

A. General

For emulsion characterization the notation n_1 represents the number density of single droplets and n_i the number density of aggregates comprising i droplets ($i = 2, 3, \dots$). The

total number density of single droplets and all kinds of aggregates is given by

$$n = \sum_{i=1}^{\infty} n_i \quad (25)$$

This characterization corresponds with Smoluchowski theory (51). To characterize coalescence, the total number of individual droplets moving freely, plus the number of droplets included in all kinds of aggregates, n_T :

$$n_T = \sum_{i=1}^{\infty} in_i \quad (26)$$

is introduced as well.

As distinct from the Smoluchowski theory for suspensions, which predicts the time dependence of the concentration of all kinds of aggregates, the time dependence for the total droplet number can be predicted at the current state of emulsion dynamics theory.

The quantification of coagulation within the theory of coupled coagulation and coalescence (CCC theory) is based on the Smoluchowski theory of perikinetic coagulation. Correspondingly, all restrictions inherent in the Smoluchowski theory of Brownian coagulation are preserved in the CCC theory. This means that creaming and gravitational coagulation are not accounted for. A variant of the Smoluchowski theory specified with regard for gravitational coagulation is well known (70). However, its application is very difficult because the rate constant of collisions induced by gravity depends on droplet dimension (12). Owing to the weak particle (aggregate) dimension dependence of the rate constants for Brownian collisions the Smoluchowski theory is valid for polydisperse suspensions and remains valid as polydisperse aggregates arise. Unfortunately, this advantage of the Smoluchowski theory can almost disappear when combined with the coalescence theory, because the coalescence rate coefficients are sensitive to droplet dimension. Thus, droplet and aggregate polydispersity does not strongly decrease the exactness of the description of coagulation in the CCC theory, while the exactness of coalescence description can be severely reduced.

Although the coalescence influence on the Brownian coagulation rate coefficient can be neglected, its influence on the final equations of the Smoluchowski theory remains. It can be shown that Smoluchowski's equation for the total number of particles:

$$n(t) = \left(1 + \frac{t}{\tau_{Sm}}\right)^{-1} \quad (27)$$

remains valid, while in parallel the equations for the singlet and aggregate concentrations cannot be used to account for coalescence. Regarding coupled coagulation and coalescence, the Smoluchowski equation for $n_1(t)$ is not exact because it does not take into account the singlet formation caused by coalescence within doublets.

The coalescence within an aggregate consisting of i droplet is accompanied by the aggregate transforming into an aggregate consisting of $(i - 1)$ droplets. As coalescence changes the aggregate type only, the total quantity of aggregates and singlets does not change. This means that the Smoluchowski function $n(t)$ does not change during coalescence, since Smoluchowski defined the total quantity of particles as consisting of aggregates and singlets.

B. Average Models

Average models do not assign rate constants to each possibility for coalescence within the aggregates, but deal with certain averaged characteristics of the process. The models in Refs 38 and 71 introduce the average number of drops in an aggregate m , because the number of films in an aggregate n_f and m are interconnected. For a linear aggregate:

$$n_f = m - 1 \quad (28)$$

As the coalescence rate for one film is characterized by τ_c^{-1} , the decrease in the average droplet quantity in an aggregate is n_f times larger. This is taken into account in the model of van den Tempel (71) for simultaneous droplet quantity increase due to aggregation and decrease due to coalescence. Van den Tempel formulates the equation which describes the time dependence for the average number of droplets in an aggregate as where the first term is de-

$$\frac{dm}{dt} = K_f N_{10} - \tau_c^{-1}(m - 1) \quad (29)$$

rived using Smoluchowski theory.

The total number of droplets n_T is the sum of single droplets $n_1(t)$ and the droplets within aggregates:

$$n_T(t) = n_1(t) + n_v(t)m(t) \quad (30)$$

where n_v is the aggregate number. The latter can be expressed as

$$n_v(t) = n(t) - n_1(t) \quad (31)$$

Both terms are expressed by Smoluchowski theory. The integration of Eq. (29) and the substitution of the result into Eq. (30) yields the time dependence $n_T(t)$ according to the van den Tempel model.

1. The Model of Borwankar *et al.*

In Ref 38 the van den Tempel model is criticized and improved through the elimination of Eq. (29). The authors point out that the “incoming” aggregates which cause the increase in m have themselves undergone coalescence. This is not taken into account in the first term on the right-hand side of Eq. (29). Instead of taking a balance on each aggregate (as van den Tempel did) Borwankar *et al.* took an overall balance on all particles in the emulsion. For linear aggregates, the total number of films in the emulsion is given by

$$n_f n_v = (m - 1) n_v \quad (32)$$

Thus, instead of Eq. (29) the differential equation for n_T follows:

$$-\frac{dn_T}{dt} = \tau_c^{-1} (m - 1) n_v \quad (33)$$

where m can be expressed through n_T using Eq. (30). The advantage of this equation in comparison with Eq. (29) is obvious. However, there is a disadvantage common to both theories, caused by the use of the Smoluchowski equation for $n_1(t)$. Coalescence does not change the total particle concentration $n(t)$, but changes $n_1(t)$ and correspondingly $n_v(t)$, according to Eq. (31).

The application of Smoluchowski theory in the quantification of the coupling of coalescence and coagulation has to be restricted with the use of the total particle concentration $n(t)$ only. The average models of van den Tempel and Borwankar *et al.* (38) do not meet this demand.

The theory of Danov *et al.* (39) does not contradict this demand, which makes it more correct than the preceding theories. Among the Smoluchowski results the function $n(t)$ is only present in the final equations of this theory. Although the exactness of averaged models is reduced due to the violation of the restriction in the use of Smoluchowski theory, results for some limiting cases are not erroneous.

2. The Limiting Cases of Fast and Slow Coalescence

Two limiting cases can be distinguished: the rate of coalescence is much greater than that of flocculation (rapid coalescence):

$$\tau_c^{-1} \gg \tau_{Sm}^{-1} \quad (34)$$

and the rate of flocculation is much greater than that of coalescence (slow coalescence):

$$\tau_c^{-1} \ll \tau_{Sm}^{-1} \quad (35)$$

According to the general rules of physicochemical kinetics the slowest process is rate controlling. If the coagulation step is rate controlling, namely, when condition (34) is valid, then the coalescence is rapid and the general equation of the theory in Ref. 38 is reduced to second-order kinetics, i.e., to Smoluchowski's equation [Eq. (27)]. Floes composed of three, four, etc., droplets cannot be formed, because of rapid coalescence within the floe. In this case the structure of the floes becomes irrelevant.

At first glance the coagulation rate has not manifested itself in the entire destabilization process in the case of slow coalescence [condition (35)]. At any given moment the decrease in the total droplet concentration is proportional to the momentary total droplet concentration (first-order kinetics), which causes an exponential decrease with time:

$$n = \exp\left(-\frac{t}{\tau_c}\right) \quad (36)$$

However, this equation cannot be valid for an initial short period, because at the initial moment there are no aggregates and their quantity continues to be low during a short time. This means that the coagulation is limiting during an initial time at any slow coalescence rate. This example illustrates the necessity of a more exact approach than that which uses average models. This was done by Danov *et al.* (39).

C. DIGB Model for the Simultaneous Processes of Coagulation and Coalescence

This kinetic model, proposed by Danov, Ivanov, Gurkov, and Borwankar, is called the DIGB model for the sake of brevity. Danov *et al.* (39) generalized the Smoluchowski scheme (Fig. 2a) to account for droplet coalescence within floes. Any aggregate (floe) composed of k particles can partially coalesce to become an aggregate of i particles ($1 < i < k$), with the rate constant being $K_c^{k,i}$ (Fig. 2b). This aggregate is further involved in the flocculation scheme, which makes the flocculation and coalescence processes interdependent. Therefore, the system exhibiting both flocculation and coalescence is described by a combination of schemes 1 and 2.

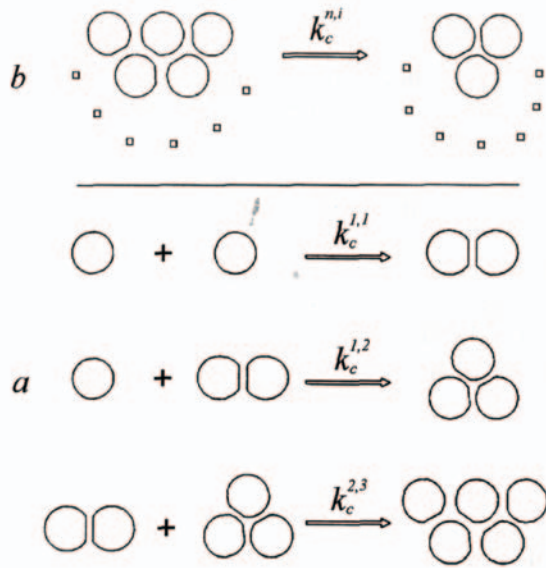


Figure 2 (a) Model of flocculation according to the Smoluchowski scheme; (b) coalescence in an aggregate of k particles to become an aggregate of i particles, with a rate constant $K_c^{k,i}$, $1 < i < k$. (From Ref. 39.)

$$\frac{dn_k}{dt} = \sum_{i=1}^{k-1} K_f^{i,k-i} n_i n_{k-i} - 2 \sum_{i=1}^{\infty} K_f^{k,i} n_k n_i + \sum_{i=k+1}^{\infty} K_c^{i,k} n_i - \sum_{i=1}^{k-1} K_c^{k,i} n_k \quad (37)$$

Equation (37) is multiplied by k and summed up for all k ; this yields the equation for n_T which is expressed through double sums. The change of the operation sequence in these sums leads to the important and convenient equation:

$$\frac{dn_T}{dt} = \sum_{k=1}^{\infty} k \sum_{i=k+1}^{\infty} K_c^{i,k} n_i - \sum_{i=2}^{\infty} k \sum_{i=1}^{k-1} K_c^{k,i} n_k \quad (38)$$

Afterwards, a total rate coefficient referring to complete coalescence of the i th aggregate:

$$K_{c,T}^i = \sum_{k=1}^{i-1} (i-k) K_c^{i,k} \quad (39)$$

$i = 2, 3, \dots$

is introduced. For linearly built aggregates the following expression is derived:

$$K_{c,T}^i = K_c^{2,1} (i-1) \quad (40)$$

With the expression for $K_{c,T}^i$ using also Eqs (25) and (26), Eq. (40) is transformed into

$$\frac{dn_T}{dt} = -K_c^{2,1} (n_T - n) \quad (41)$$

The integration result of this first-order linear differential equation is well known and is represented in general form without specification of $n(t)$ [Eq. (18) in Ref. 39]. An interesting peculiarity of this important derivation is the disappearance of terms, related to coagulation at the transition, from the equation set [Eq. (37)] to the main Eq. (38). This corresponds to the fact that the total quantity of droplets does not change due to coagulation; it decreases due to coalescence only.

The coagulation regularity manifests itself in the $n(t)$ dependence, arising in Eq. (41). It creates the illusion that Eq. (41) can be specified for any $n(t)$ function corresponding to any subprocess affecting the droplet aggregate distribution. For example, the gravitational coagulation theory leads to a function $n_g(t)$ (70), but it does not create the opportunity to describe the gravitational coagulation coupling with coalescence by means of substituting $n_g(t)$ into the integral of Eq. (41). As the coalescence influences the gravitational coagulation another function has to be substituted into Eq. (41) instead of $n_g(t)$. This function has to be derived accounting for the coupling of coalescence and coagulation. One concludes that Eq. (41) cannot be used, because its derivation assumes that the coupling of gravitational coagulation (or another process) and coalescence is already quantified.

A happy exception is Brownian coagulation and its modeling by Smoluchowski with the coagulation rate coefficients, of which sensitivity to aggregate structure and coalescence is low. The substitution of function (27) into the integral of Eq. (41) yields the equation characterizing the coupling of coalescence and Brownian coagulation (39).

In fractal theory (72) it is established that diffusion-limited aggregates and diffusion-limited cluster-cluster aggregates are built up linearly. This can simplify application of the DIGB model. However, the diffusivity of fractal aggregates (73) cannot be described by simple equations and Smoluchowski theory. This will cause coagulation-rate coefficient dependence on aggregate structure, decreasing the exactness of Eq. (41) when applied to fractal aggregates. However, there is no alternative to the DIGB model, which can be used as a crude but useful approximation in this case as well. In the absence of an alternative the DIGB model can be recommended for evaluation in the case of gravitational coagulation.

Danov et al. (39) compares their theory with the predictions of averaged models for identical conditions. It turns out that if coalescence is much faster than flocculation, the predictions of the different models coincide. Conversely, for slow coalescence the results of the averaged models deviate considerably from the exact solution. These two results of the comparison are in agreement with the qualitative considerations in Sec. III.B.

Data for the relative change in the total number of droplets as a function of time are presented in Fig. 3 from Ref. 39. Figure 3 a-c refers to $K_F N_{10} = 0.1 \text{ s}^{-1}$ and the coalescence constant $K_C^{2,1}$ varies between 0.1 s^{-1} (a) and 0.001 s^{-1} (c). It is seen that the agreement between the Danov *et al.* and Borwankar *et al.* models is better the faster the coalescence, as was explained qualitatively above. The van den Tempel curves deviate considerably from the other two solutions.

For very long times, and irrespective of the values of the kinetic parameters, the model of Borwankar *et al.* (38) is

close to the numerical solution. This is probably because the longer the time, the smaller is the concentration of single droplets. In this extreme case the error caused in the average models due to the influence of coalescence on the singlet concentration [not taken into account in the equation for $n(t)$] is negligible.

The shortcomings of the averaged models (38, 71) and the advantages of the DIGB model are demonstrated in Ref. 39. However, the range of applicability of this model is restricted by many simplifications and the neglect of other subprocesses (see Sec. II.A). An efficient analytical approach was made possible due to the neglect of the coalescence rate coefficient's dependence on the dimensions of both interacting droplets.

The model of Borwankar *et al.* was examined experimentally in Ref. 40. The emulsions were oil-in-water with soybean oil as the dispersed phase, volume fraction 30% and number concentration 10^7 - 10^{10} cm^{-3} . The emulsions were gently stirred to prevent creaming during the aging

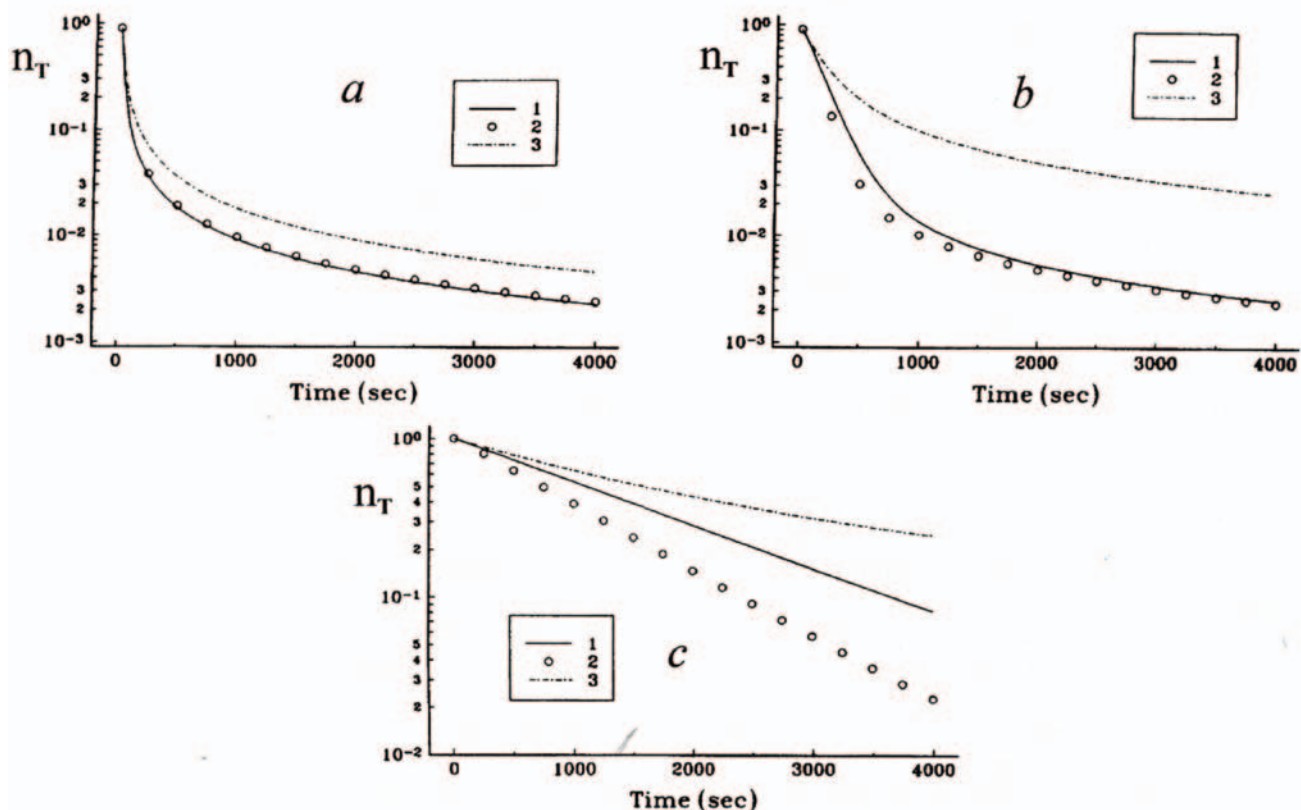


Figure 3 Relative change in the total number of droplets vs. time: initial number of primary particles $N_{10} = 1 \times 10^{10} \text{ cm}^{-3}$; flocculation rate constant $K_F = 1 \times 10^{-11} \text{ cm}^3/\text{s}$; curve 1, the numerical solution of the set Eq. (37); curve 2, the model of Borwankar *et al.* (38) for diluted emulsions; curve 3, the model of van den Tempel (71): (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) $K_C^{2,1} = 1 \times 10^{-3} \text{ s}^{-1}$. (From Ref. 39.)

study. A sample was placed on a glass slide, all aggregates were broken up, and the size of the individual droplets was measured. A quite good agreement with the theory was established. However, the fitting of the experimental data was accomplished using two model parameters, namely, the coalescence and coagulation rate coefficients. For the latter coefficient optimal values (different for two emulsions) were obtained, strongly exceeding the Smoluchowski theory value (Sec. II.A). An interpretation is that orthokinetic and perikinetic coagulation took place simultaneously as a result of stirring. Several experiments are known (discussed in Ref. 54) which demonstrate better agreement with the value for the coagulation constant predicted in Smoluchowski theory.

IV. DOUBLET-FRAGMENTATION TIME

A. Theory of Doublet-fragmentation Time

A doublet fragmentation was described by Chandrasekhar (74) as the diffusion of its droplets from the potential minimum, characterizing their attraction. The time scale for this process takes the form (75):

$$\tau_d = \frac{6\pi\eta a^3}{kT} \exp(-U_{\min}/kT) \quad (42)$$

where U_{\min} is the depth of the potential minimum, k is the Boltzmann constant, and η is water dynamic viscosity.

To derive the formula for the average lifetime of doublets, Muller (76) considered the equilibrium in a system of doublets and singlets: that is, the number of doublets decomposing and forming are equal. Both processes are described by the standard diffusion flux J of particles in the force field of the particle that is regarded as central.

Each doublet is represented as an immovable particle with the second singlet "spread" around the central one over a spherical layer, which corresponds to the region of the potential well. The diffusion flux J of "escaping" particles is described by equations used in Fuchs' theory of slow coagulation. The first boundary condition corresponds to the assumption that the escaping particles do not interact with other singlets. The second condition reflects the fact that the potential well contains exactly one particle.

At small separation between the droplets in a doublet the droplet diffusivity reduces because of the increasing hydrodynamic resistance during the droplet approach. A convenient interpolation formula was used (76) for the description of the influence of hydro-dynamic interaction on the mutual

diffusivity. The difference between the more exact Muller equation and Eq. (42) is caused mainly on account of this hydrodynamic interaction.

B. Doublet-fragmentation Time of Uncharged Droplets

In this section we consider a doublet consisting of droplets with a nonionic adsorption layer. The closest separation between two droplet surfaces h_0 exceeds the double thickness of the adsorption layer ($2h_a$). As a crude approximation h_0 can be identified with $2h_a$. In the case of small surfactant molecules $2h_a \approx 2$ nm.

In this case, the potential well has a sharp and deep minimum. This means that the vicinity of this minimum determines the value of the integral in the more exact Muller (76) equation. For examination of this assumption, this integral was calculated numerically and according to the ap-

$$\int_a^{\beta} \varphi(t) \exp[f(t)] dt = \left[\frac{2\pi}{f''(t_m)} \right]^{1/2} \varphi(t_m) \exp[f(t_m)] \quad (43)$$

proximate equation (26):

where t_m corresponds to the potential well minimum.

The difference in results was small and enabled applica-

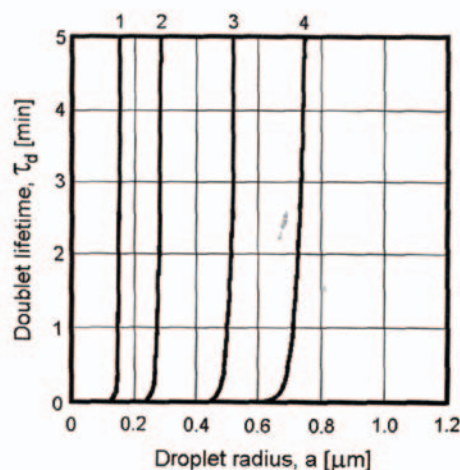
$$U(h) = -\frac{A}{12} \cdot \frac{a}{h} \quad (44)$$

tion of Eq. (43) to the calculation and substitution of the asymptotic expression (11, 14):

which is valid at small distances to the surface. The result of calculations according to Eqs (43) and (44) (the Hamaker constant $A = 1.3 \times 10^{-20}$ J) are shown in Fig. 4. The chosen value of the Hamaker constant is consistent with those reported elsewhere (77, 78). In addition to the value of $A = 1.3 \times 10^{-20}$ J, we mention other values of the Hamaker constant which were employed elsewhere. For example, in food emulsions (78) the Hamaker constant lies within the range 3×10^{-21} - 10^{-20} J. The results of calculations for smaller Hamaker constants are also presented in Fig. 4.

The influence of the adsorption layer thickness on doublet lifetime is shown in Fig. 5 for one value of the Hamaker constant. There is high specificity in the thickness of a polymer adsorption layer. β -Casein adsorbed on to polystyrene latex causes an increase in the radius of the particle of 10-15 nm (79). A layer of β -Mactoglo-bulin appears to be in the order of 1-2 nm thick, as compared to 10 nm for the caseins (80).

When adsorbed layers of a hydrophilic nature are present



the repulsive hydration forces must be taken into account. **Figure 4** Dependence of doublet lifetime on droplet dimension at different values of the Hamaker constant A : (1) $A = A_1 = 1.33 \times 10^{-20}$ J; (2) $A = 0.5 \times A_1$; (3) $A = 0.35 \times A_1$; (4) $A = 0.25 \times A_1$; (5) $A = 0.1 \times A_1$. The shortest interdroplet distance is 2 nm. (From Ref. 26.)

At low ionic strengths, the repulsion follows the expected exponential form for double-layer interaction:

$$U(h) = K_s e^{-(h/h_s)} \tag{45}$$

In Ref. 81 the authors emphasize that the surface charge in food emulsions is low, electrolyte concentrations are high,

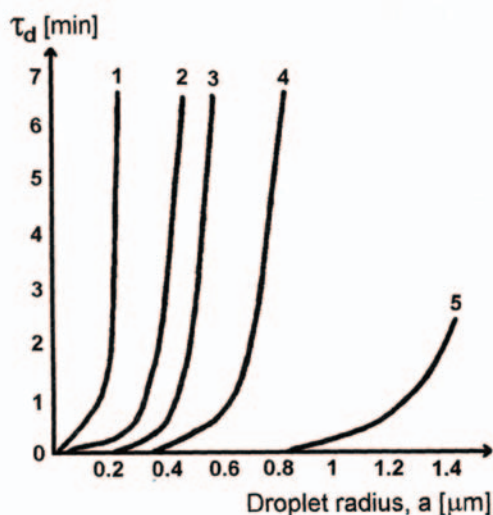


Figure 5 Influence of adsorption layer thickness on the droplet lifetime of an uncharged droplet. Adsorption layer thickness: (1) $h_0 = 1$ nm; (2) $h_0 = 2$ nm; (3) $h_0 = 4$ nm; (4) $h_0 = 6$ nm. $A = 1.33 \times 10^{-20}$ J. (From Ref. 26.)

and hence, the DL is not responsible for emulsion stability. The stabilization can be caused by hydration forces. However, flocculation to the secondary minimum remains. Meanwhile, this conclusion must be specified to account for droplet dimension.

C. Lifetime of a Doublet of Charged Droplets and Coagulation/Flocculation

As seen in Fig. 1 of Ref. 37 the coordinates of the secondary minimum corresponds to $Kh_{\min} = 5-12$ nm. Owing to this rather large distance the frequency dependence of the Hamaker constant may be of importance, and the Hamaker function $A(h)$ characterizing molecular interaction should be introduced.

In Ref. 82 the distance-independent interaction at zero frequency and interaction at nonzero frequency is considered separately:

$$A(h) = A_0 + [A(h) - A_0] \tag{46}$$

The result from 36 systems in Ref. 82 are in quite good accordance with the calculations of other papers. According to Churaev, the system polystyrene-water-polystyrene can be used to estimate the Hamaker function for oil-water systems. However, with increasing droplet separation the importance of A_0 increases on account of $[A(h) - A_0]$. The component A_0 is screened in electrolyte concentrations, because of dielectric dispersion (83-85). At a distance of $kh_{\min} = 3-5$ nm the authors (84) found that molecular interaction disappeared at zero frequency. Experimental evidence concerning this statement is discussed in Ref. 14. When evaluating the secondary minimum coagulation, A_0 can be omitted, as illustrated in Ref. 85.

For illustration of the influence of electrolyte concentration, Stern potential, and particle dimension some calculations of doublet lifetime are made and their results are presented in Fig. 6. The potential well depth increases and in parallel doublet lifetime increases with increasing particle dimension and electrolyte concentration and decreasing surface potential.

V. COALESCENCE COUPLED WITH EITHER COAGULATION OR FLOCCULATION IN DILUTE EMULSIONS

Limited attention is paid to the role of fragmentation in emulsion science. A comparison of the prediction of coalescence with and without accounting for fragmentation (Sec. II and III) enables evaluation of the fragmentation signifi-

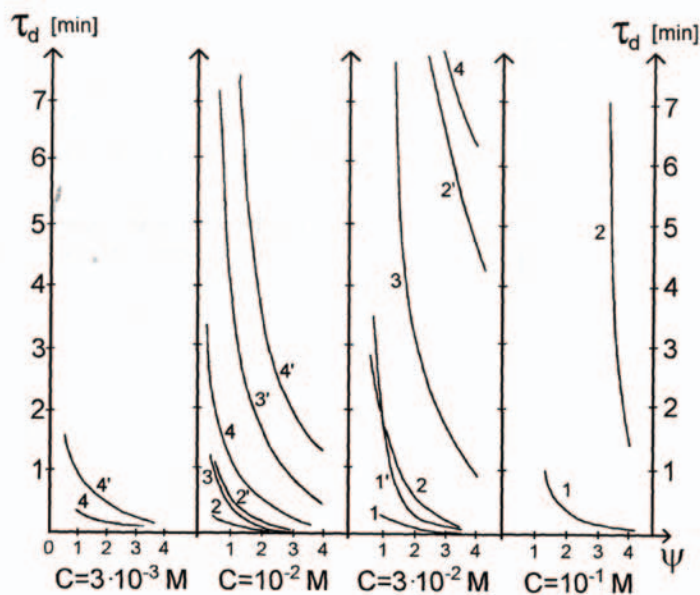


Figure 6 Dependence of doublet lifetime on the Stern potential for different electrolyte concentrations and droplet dimensions. Numbers near curves correspond to droplet radius. (1) Curves 1'-4' without account for retardation of molecular forces of attraction, $\Psi = e\psi/kT$; (2) curves 1-4 with account for retardation. (From Ref. 26.)

cance to be made. This comparison will be carried out in Sec. V. A.

The theories (39) and (23) have different areas of applicability (not specified in the papers) and are complementary. Naturally, this complicates the choice between these theories when taking into account the concrete conditions for experiments. An approximate evaluation of the aforesaid areas of applicability is given in Sec. V.B.

A. Fragmentation of Primary Flocs in Emulsions and the Subsequent Reduction of Coalescence

Floc fragmentation decreases the quantity of inter-droplet films and correspondingly reduces the entire coalescence process. This reduction can be characterized by comparison of Eq. (18) with theory (39), which neglects fragmentation. The longer the time, the greater the reduction, which allows the use of the simpler theory (38) for comparison. The results for longer times coincide with the predictions of the more exact theory (39).

The results of theory (39) concerning slow coalescence are illustrated by curve 1 in Fig. 3c in Ref. 39, which is redrawn in Fig. 7a. It can be seen that for a low value of the

coalescence rate constant, the semi-logarithmic plot is linear, indicating that the process follows a coalescence rate-controlled mechanism according to Eq. (36). As opposed to the simple exponential time dependence in Eq. (36), second-order kinetics dominate at rapid doublet fragmentation, even if coalescence is very slow. The physical reason becomes clear when considering how Eq. (18) is derived. As seen from Eq. (17) the rate of decline in the droplet concentration is proportional to the doublet concentration. The latter is proportional to the square of the singlet concentration at s.d.e., which causes second-order kinetics. Thus, at slow coalescence the disaggregation drastically changes the kinetic law of coalescence, i.e., from the exponential law to second-order kinetics.

In the second stage, coagulation becomes the rate-controlling process because of the decrease in the collision rate accompanying the decrease in the droplet concentration. Thus, at sufficiently long times, second-order kinetics characterize both reversible and irreversible aggregation. Nevertheless, a large difference exists even when identical functions describe the time dependence, as the characteristic times are expressed through different equations for irreversible and reversible aggregation. In the first case it is the Smoluchowski time, in the second case it is the combination of three characteristic times, i.e., Eq. (18).

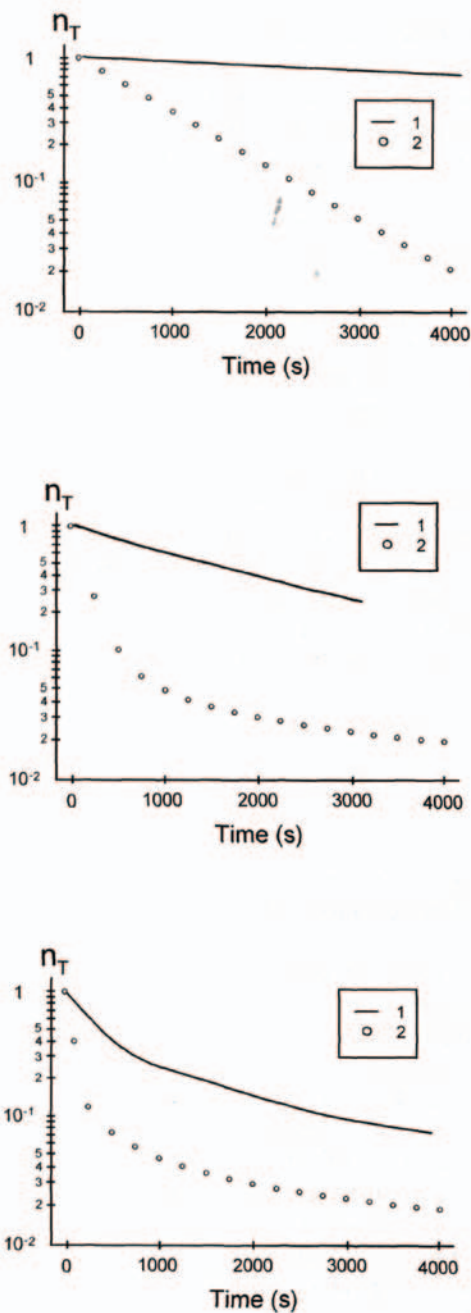


Figure 7 Relative change in the total number of droplets vs. time; initial number of droplets $N_{10} = 1 \times 10^{10} \text{ cm}^{-3}$; flocculation rate constant $K_f = 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; curve 1 - calculations according to Eq. (18); curve 2 - the model of Borwankar *et al* [38] for dilute emulsions, coalescence rate constant (a) $K_c^{2,1} = 1 \times 10^{-1} \text{ s}^{-1}$, (b) $K_c^{2,1} = 1 \times 10^{-2} \text{ s}^{-1}$ (c) $K_c^{2,1} = 1 \times 10^{-3} \text{ s}^{-1}$. Coalescence time $\tau_c = 10^3 \text{ s}$ (a); $\tau_c = 10^2 \text{ s}$ (b); $\tau_c = 10 \text{ s}$ (c). Smoluchowski time $\tau_{Sm} = 10 \text{ s}$. Doublet lifetime $\tau_d = 0.5 \text{ s}$; n_T is the dimensionless total droplet concentration, $n_T = N_T/N_{10}$. (From Ref. 23.).

Let us now try to characterize quantitatively the reduction in coalescence caused by doublet disintegration. For this purpose the calculations are performed according to Eq. (18) at $\tau_{Sm} = 10 \text{ s}$ and $\tau_C = 10^3 \text{ s}$ (Fig. 7a), 10^2 s (Fig. 7b), and 10 s (Fig. 7c). For all figures the same value of the ratio $2\tau_d/\tau_{Sm} = 0.1$ is accepted, satisfying condition (2). In all these figures the calculations according to Eq. (18) are illustrated by curve 1.

The comparison of curves 1 and 2 characterizes the reduction of coalescence caused by doublet disintegration; the lower the Rev values, the stronger the reduction. The simple curve 1 in Fig. 7a can be used also for higher τ_C values, because then the condition of Eq. (31) is even better satisfied. Thus, if τ_{c1} and t_1 correspond to the data in Fig. 7a, and $\tau_{c2} = m\tau_{c1}$ with $m \gg 1$, the identity:

$$\tau_{c2}t_2 = \tau_{c1}m\frac{t_1}{m} \tag{47}$$

is useful. This means that

$$\frac{n_T}{n_o}\left(\tau_{c1}m, \frac{t_1}{m}\right) = \frac{n_T}{n_o}(\tau_{c1}, t_1) \tag{48}$$

i.e., $t_2 = t_1/m$ where the right-hand side of Eq. (48) is drawn in Fig. 8. For example, Fig. 8 is similar to Fig. 7a and can be used for a 100-fold longer time, as shown on the abscissa. The increase in τ_c enables us to increase τ_{Sm} without violating condition (35) and with Eq. (36) valid. Thus, $\tau_{Sm} = 1000 \text{ s}$ or lower can be chosen as the condition for Fig. 8. Curve 1, characterizing the rate of doublet disinte-

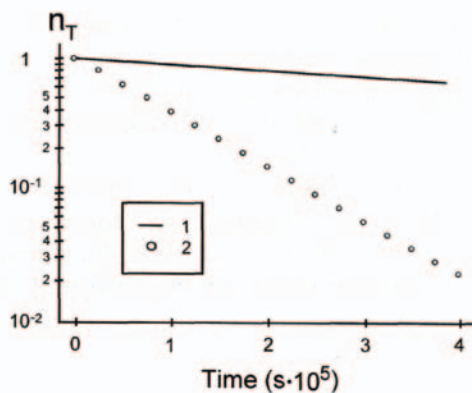


Figure 8 Similar to Fig. 7, with other values for the characteristic times. Coalescence time $\tau_c = 10^5 \text{ s}$; Smoluchowski time $\tau_{Sm} = 10^3 \text{ s}$; doublet-fragmentation lifetime $\tau_d = 50 \text{ s}$. (From Ref. 23.)

gration, is preserved as well if the value of $2\tau_d/\tau_{Sm} = 0.1$ remains; now it corresponds to a higher τ_d value of 5 s.

B. Domains of Coalescence Coupled Either with Coagulation or with Flocculation

The condition:

$$\text{Rev} \gg 1 \quad (49)$$

corresponds to coagulation. The theory for the intermediate case:

$$\text{Rev} \sim 1 \quad (50)$$

when part of the droplets participate in flocculation and another coagulate is absent. To specify the conditions (2) and (49) the doublet lifetime must be expressed through surface-force characteristics, namely, through the surface electric potential, the Hamaker function, and droplet dimension, as was described in [Sec. IV](#).

In the equation for the Smoluchowski time [Eq. (4)] the droplet numerical concentration N_{10} can easily be expressed through the droplet volume fraction φ and the average droplet radius a (we replace a polydisperse emulsion by an “equivalent” monodisperse emulsion). The resulting analysis respective to a and φ is easier than relating to N_{10} because the boundary of application of different regularities are usually formulated with respect to a and φ . The Smoluchowski time is

$$\tau_{Sm} = \kappa_F^{-1} \varphi^{-1} \frac{4}{3} \pi a^3 \quad (51)$$

We exclude from consideration a special case of extremely dilute emulsions. Comparing [Fig. 6](#) with the results of calculations according to Eq. (51) one concludes that condition (49) is mainly satisfied. It can be violated if simultaneously the droplet volume fraction and the droplet dimension are very small. This occurs if $\varphi < 10^{-2}$ and $a < (0.2-0.3) \mu\text{m}$. Discussing this case we exclude from consideration the situation when $a < 0.1 \mu\text{m}$, corresponding to microemulsions and $\varphi \ll 10^{-2}$. With this exception one concludes that, for uncharged droplets, flocculation is almost impossible because condition (2) cannot be satisfied. A second conclusion is that at

$$a < (0.2-0.3) \mu\text{m} \quad (52)$$

theory (39) cannot be applied without some corrections made necessary by the partially reversible character of the aggregation. The main conclusion is that when

$$a > 0.2 \mu\text{m} \text{ and } \varphi > 10^{-2} \quad (53)$$

theory (39) does not need corrections in respect of the reversibility of flocculation. However, this conclusion will change at the transition to a thicker adsorption layer. As described in [Sec. IV](#), the thicker the adsorption layer, the shorter is the doublet-fragmentation time.

The electrostatic repulsion decreases the depth of the potential well and correspondingly decreases the doublet lifetime. As a result, flocculation becomes possible for submicrometer droplets as well as for micrometer-sized droplets, if the electrolyte concentration is not too high, the surface potential is rather high, and the droplet volume fraction is not too high. This is seen from [Fig. 6](#).

The reversibility criterion depends on many parameters in the case of charged droplets. To discriminate and to quantify the conditions of coagulation and flocculation let us consider Rev values lower than 0.3 as low and values higher than 3 as high. In other words, coagulation takes place when $\text{Rev} > 3$, while at $\text{Rev} < 0.3$ there is flocculation; that is, the conditions:

$$\text{Rev} = \frac{\tau_d(c_o, \varphi, a)}{\tau_{Sm}(a, \varphi)} > 3 \quad (54)$$

$$\text{Rev} < 0.3 \quad (55)$$

determine the boundaries for the domains of coagulation and flocculation. These domains are characterized by [Fig. 9](#) and correspond to fixed values of the droplet volume fraction. In addition, a definite and rather large droplet dimension $2a = 4 \mu\text{m}$ is fixed. After fixation of the values of volume fraction and droplet dimension the domains are characterized in coordinates Ψ and C .

In [Fig. 9](#), the domain of flocculation is located above and to the left of curve 2; the domain of coagulation is located beneath and to the right of curve 1. To characterize the sensitivity of the domain boundaries to the Hamaker function value, curves 1' and 2' are calculated using values twice as high as those of curves 1 and 2.

As distinct from uncharged droplets, flocculation in the range of micrometer-sized droplets is possible. As seen in [Fig. 9](#), even rather large droplets ($4 \mu\text{m}$) aggregate reversibly if the electrolyte concentration is lower than $(1-5) \times 10^{-2} \text{ M}$ and the Stern potential is higher than 25 mV. For smaller droplets the domain of flocculation will extend while the domain of coagulation will shrink. For submicrometer droplets, flocculation takes place even at high electrolyte concentrations (0.1 M).

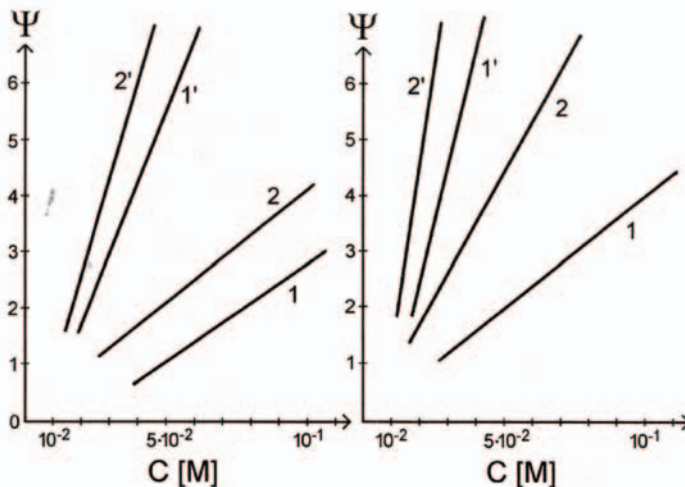


Figure 9 Domains of coagulation and flocculation. Curves 1 and 2 are calculated with the Rabinovich-Churaev Hamaker function; a twice higher value is used for calculation of curves 1' and 2'. The domain of flocculation is located above curve 1, while the domain of coagulation is located beneath curve 2. Volume fraction $\phi = 0.01$ (a); $\phi = 0.1$ (b). Particle dimension $2a = 4 \mu\text{m}$. (From Ref. 26.)

C. Hydration Forces Initiate Flocculation

Due to the similarity of the exponential distance (h) dependence of hydration forces and that for the electrostatic interaction the decrease in the doublet lifetime caused by hydration forces of repulsion can be calculated on account of this similarity. It is sufficient to use the substitution h_s for K^{-1} and K_s for

$$16\epsilon \left(\frac{kT}{e}\right)^2 \tanh\left(\frac{e\psi}{kT}\right)^2 \tag{56}$$

where k is the Boltzmann constant, T is the absolute temperature, ϵ is the dielectric permittivity of water, and e is the elementary charge. The doublet lifetime can be determined with use of the results presented in Fig. 6. For the sake of brevity, a similar figure with K_s and h_s as the abscissa is not shown. It turns out that the decrease in τ_d caused by hydration forces leads to reversible aggregation of submicrometer droplets. As to micrometer-sized droplets, coagulation takes place except for the case when both h_s and K_s are rather large.

VI. APPLICATIONS

The restrictions in Eqs (1) and (12) corresponding to strong retardation of the rate of multiplet formation and slow in-

tradoublet coalescence are not frequently satisfied. Nevertheless, these conditions are important because they correspond to the case of very stable emulsions. As the kinetics of the retarded destabilization of fairly stable emulsions is of interest, attention has to be paid to provide these conditions and thus the problem of coupled coalescence and flocculation arises.

There are large qualitative distinctions in the destabilization processes for the coupling of coalescence and coagulation, and coalescence and flocculation. In the first case, rapid aggregation causes rapid creaming and further coalescence within aggregates. In the second case, the creaming is hampered owing to the low concentration of multiplets, and coalescence takes place both before and after creaming. Before creaming, singlets predominate for a fairly long period of gradual growth of droplet dimensions due to coalescence within doublets. The discrimination of conditions for coupling of coalescence with either flocculation or coagulation is accomplished in Ref. 26.

The creaming time is much shorter in the coagulation case and correspondingly the equation describing the coupling of coalescence and flocculation preserves its physical sense for a longer time than is the case for coagulation. One concludes that the theory of the coupling of coalescence and flocculation provides a new opportunity for long-term prediction of emulsion stability, although creaming restricts the application of this theory as well. Note that this restriction weakens in the emulsions of low-density contrast and in W/O emulsions with a high viscosity continuum.

Long-term prediction is a two-step procedure. The first step is the determination of whether an emulsion exhibits coagulation or flocculation. It means that the characteristic time τ_d must be measured and compared with τ_{Sm} , the value of which is easily evaluated with account taken for the measured concentration using Eq. (4). A comparison of these times allows a choice between condition (1) and the opposite condition ($\tau_{Sm} \ll \tau_d$). The second step is the prediction of the evolution in time for the t.d.c. If condition (1) is valid, Eq. (18) has to be used for the prediction; τ in Eq. (18) has to be specified in accordance with Eq. (15). In the opposite case DIGB theory must be used.

A. Long-term Prediction of Emulsion Stability

It is possible, in principle, to give a long-term prediction of emulsion stability based on the first indications of aggregation and coalescence. The next example clarifies the principal difficulty in a reliable long-term prediction if a dynamic model of the emulsion is not available.

The first signs of aggregation and coalescence can always be characterized by a linear dependence, if the investigation time t is small in comparison with a characteristic time τ for the evolution of the total droplet concentration $n(t)$:

$$n(t) = n_0 \left(1 - \frac{t}{\tau}\right) \quad (57)$$

This short time asymptotic corresponds to many functions, for example, to Eq. (18) or (36). The first can arise in the case of coalescence coupled with coagulation (39), while the second can arise for coalescence coupled with flocculation (29). The discrimination between irreversible and reversible aggregation is only one component of emulsion dynamics modeling (EDM) and it is seen that without this discrimination the difference in the prediction of the time necessary for a droplet concentration decrease, for example, 1000 times, can be 7τ and 1000τ .

B. Perfection of Methods for Emulsion Stabilization (Destabilization) by Means of the Effect on Both Coalescence and Flocculation

Stability (instability) of an emulsion is caused by the coupling of coalescence and flocculation. Meanwhile, for emulsifiers (or demulsifiers) the elaboration of their influence on the elementary act of coalescence only is mainly

taken into account. The coupling of coalescence and flocculation is reflected in Eq. (15) and one concludes that it follows the multiplicativity rule and not the additivity rule. This means that the total result of the application of a stabilizer (destabilizer) depends very much on both flocculation and fragmentation. The development of a more efficient technology for emulsion stabilization (destabilization) is possible by taking into account the joint effect on both the coalescence and the aggregation (disaggregation) processes.

1. Combining Surfactants and Polymers in Emulsion Stabilization

The coalescence rate depends mainly on the thin (black) film stability and correspondingly on the short-range forces. The flocculation depends on the long-range surface forces. Owing to this large difference, synergism in the dependence of these processes on the different factors can be absent.

The use of one surfactant only may not provide both the optimal fragmentation and optimal stability of an emulsion film. Probably the use of a binary surfactant mixture with one component which provides the film stability, and a second one which prevents the flocculation may provide perfect emulsion stabilization. Naturally their coadsorption is necessary. For such an investigation a measurement method for both the doublet-fragmentation time and the coalescence time is necessary.

2. Strong Influence of Low Concentrations of Ionic Surfactant on Doublet-fragmentation Time and Coalescence Time

Let us consider the situation when an emulsion is stabilized against coalescence by means of an adsorption layer of nonionic surfactant and is strongly coagulated because of the subcritical value of the Stern potential that is usual for inorganic electrolytes (46) at moderate pH. In a large floc any droplet has many neighbors, meaning a rather high number of interdroplet films per droplet. The coalescence rate is proportional to the total number of films and can be quite high. It can be strongly decreased by adding a low concentration of an ionic surfactant. This can be sufficient to provide a supercritical Stern potential value that will be accompanied by a drastic decrease in the doublet lifetime compared to that of weakly charged droplets.

At shorter doublet lifetimes flocculation can become reversible and it can stop at the stage of singlet-doublet equilibrium. It will provide a strong decrease in the coalescence

rate because coalescence occurs within doublets only and their concentration can be very low.

Thus, a small addition of an ionic surfactant to a higher concentration of a nonionic surfactant, sufficient to provide an almost saturated adsorption layer, can make the overall emulsion stabilization more efficient. The nonionic surfactant suppresses coalescence but cannot prevent flocculation, while the ionic surfactant retards the development of flocculation.

We can give an example when both coalescence and flocculation are affected by an ionic surfactant (SDS). In Ref 86 it is established that coalescence is suppressed at SDS concentrations exceeding 6×10^{-5} M. Meanwhile, the CCC is 2×10^{-2} M NaCl at 10^{-6} M SDS. Thus, SDS concentrations slightly above 10^{-6} M are sufficient to retard flocculation. In this example it is essential that the concentrations needed to retard flocculation are very low compared to those needed to prevent coalescence.

It is noteworthy that low concentrations of an ionic surfactant can increase emulsion stability as a result of the simultaneous manifestation of three mechanisms. First, the depth of the secondary potential minimum decreases owing to the electrostatic repulsion that is accompanied by a τ_d decrease. Second, the transition from the secondary minimum through an electrostatic barrier and into the primary minimum extends the coalescence time. Third, the time of true coalescence, i.e., the time necessary for thin-film rupture increases because of electrostatic repulsion as well (27, 63).

C. Standardization of the Measurement of τ_c and τ_d

Direct investigation of the coalescence subprocess in emulsions is difficult. Instead, the entire destabilization process is usually investigated. Meanwhile, the rate of the destabilization process depends on the rates of both flocculation and disaggregation and on the floc structure as well. All these characteristics vary in a broad range. At a given unknown value for the time of the elementary act of coalescence τ_c the different times can be measured for the integrated process and different evaluations of τ_c are possible.

The rate of coalescence in an aggregate essentially depends on the number of droplets within it and the packing type, i.e., on the number of films between the droplets. This complication is absent when considering the case of the s.d.e.

The possible advantage of τ_c measurement at s.d.e. is in avoiding the difficulty caused by polydispersity of droplets

appearing during preceding coalescence within large flocs. At the s.d.e. the initial stage of the entire coalescence process can be investigated when the narrow size distribution of an emulsion is preserved.

At s.d.e. the determination of the time dependence of the t.d.c. is sufficient for the investigation of coalescence. In Refs 27 and 28 this was accomplished through direct visual observation. By using video-enhanced microscopy and computerized image analysis the determination of t.d.c. can be automated. Such automated determination of total droplet number in a dilute DCD-in-water emulsion at the s.d.e. can be recommended as a standard method for the characterization of the elementary act of coalescence.

In parallel, the second important characteristic, namely, the doublet-fragmentation time is determined by the substitution of τ_c , τ_{Sm} , and measured τ_d into Eq. (18).

D. Experimental-Theoretical Emulsion Dynamics Modeling

1. General

To predict the evolution of the droplet (floc) size distribution is the central problem in emulsion stability. It is possible, in principle, to predict the time dependence of the distribution of droplets (flocs) if information concerning the main subprocesses (flocculation, floc fragmentation, coalescence, creaming), constituting the whole phenomenon, is available. This prediction is based on consideration of the population balance equation (PBE).

The PBE concept was proposed by Smoluchowski (70). He specified this concept for suspensions and did not take into account the possibility of floc fragmentation. Even with this restriction he succeeded in the analytical solution, neglecting gravitational coagulation and creaming, and obtained the analytical time dependence for a number of aggregates n_1 comprising i particles ($i = 2, 3 \dots$).

In the most general case the equation for the evolution of the total droplet number takes into account the role of aggregation, fragmentation, creaming, and coalescence. There is no attempt to propose an algorithm even for a numerical solution to such a problem.

The usual approach in the modeling of an extremely complicated process is the consideration of some extreme cases with further synthesis of the results obtained. The next three main simplifications are inherent in the current state of emulsion dynamics modeling: the neglect of the influence of the gravitational field, i.e., neglect of

creaming/sedimentation; in a first approximation it is possible to consider either coagulation or flocculation; finally, the neglect of the rate-constant dependence on droplet dimension.

2. Combined Approach in Investigations of Dilute and Concentrated Emulsions

The modeling of collective processes in concentrated emulsions is extremely complicated. Recently, the efficiency of computer simulation in the systematic study of aggregates, gels, and creams has been demonstrated (48). Monte Carlo and Brownian dynamics are particularly suited to the simulation of concentrated emulsions. However, information about droplet-droplet interaction is necessary. The reliability of this information is very important in providing reasonable results concerning concentrated emulsions. In other words, the assumption concerning pair additive potentials for droplet/droplet interaction and the thin emulsion film stability must be experimentally confirmed. The extraction of this information from experiments with concentrated emulsions is very difficult. On the other hand, measurement of the doublet-fragmentation time in dilute emulsions is a convenient method for obtaining information about pair additive potentials. Information about pair potentials and the elementary act of coalescence obtained in experiments with dilute emulsions preserves its significance for concentrated emulsions as well.

One concludes that modeling of concentrated emulsions becomes possible by combining experimental investigation of the simplest emulsion model system with computer simulation accounting for the characteristics of a concentrated emulsion (high droplet-volume fraction, etc.).

3. Kernel Determination Is the Main Task that Must Be Solved to Transform the PBE in an Efficient Method for Emulsion Dynamics Modeling

The levels of knowledge concerning kernels describing different subprocesses differ strongly. There exists a possibility for quantification of kernels related to aggregation and fragmentation (12, 37, 76). On the other hand, the current state of knowledge is not sufficient for prediction of the thin film disruption time.

The deficit in knowledge of thin-film stability makes purely theoretical modeling of emulsion dynamics impos-

sible. As a result a complex semi-theoretical approach to EDM is necessary. The PBE is the main component of both the experimental and the theoretical stages of this approach. In the experimental stage the PBE, simplified with regard to s.d.e., provides the background for determination of the coalescence kernels with use of the experimental data (27, 28).

For determination of the coalescence kernels the more complicated reverse task must be solved, namely, their determination based on comparison of the experimental data on the emulsion evolution in time with the PBE solution. In the absence of an analytical solution the reverse task is usually very difficult. The most efficient way to overcome this difficulty is experimental realization with the use of the universally simplest conditions for emulsion time evolution, which can be described analytically.

4. Singlet-Doublet Quasiequilibrium with Slow Coalescence within Doublets Is the Simplest Emulsion State for which Investigation Can Provide Information about Coalescence

The simplest singlet-doublet emulsion can exist at singlet-doublet quasiequilibrium and with slow coalescence within doublets. Its simplicity results in a very simple kinetic law for the entire kinetics of coupled flocculation and coalescence, namely, Eq. (18). Thus, s.d.e. provides the most convenient conditions for investigations of the elementary act of coalescence and the doublet-fragmentation time.

The main simplification in all existing models for emulsion dynamics (23, 39) is the neglect of the coalescence time dependence on droplet dimensions. This simplification is not justified and decreases very much the value of the prediction, which can now be made with use of the PBE. For elimination of this unjustified simplification it is necessary to determine the coalescence time for emulsion films between droplets of different dimensions i and j , namely, τ_{cij} , similar to the existing analytical expressions for the doublet-fragmentation time, τ_{dij} (12). The determination of a large set of τ_{cij} values by means of a comparison of experimental data obtained for an emulsion consisting of different multiplets and the PBE numerical solutions for it is impossible. On the other hand, this paramount experimental-theoretical task can be solved for a dilute emulsion at s.d.e. and slow intradoublet coalescence.

5. Substitution of the Coalescence Kernels Makes the PBE Equation Definite and Ready for Prediction of Emulsion Time Evolution with the Restriction of Low-density Contrast and without Account for Gravitational Coagulation and Creaming

With application of the scaling procedure for the representation of the kinetic rate constants for creaming and gravitational coagulation the PBE is solved analytically in Ref. 87. This scaling theory creates a perspective for the incorporation of creaming in the emulsion dynamics model in parallel with coalescence, aggregation, and fragmentation.

VII. SUMMARY

The mechanisms of kinetic stability in macroemulsions and miniemulsions are completely different. The strong droplet deformation and flattening in a macro-emulsion cause the Reynolds mode of drainage which prolongs the life of the emulsions. This mechanism is not important for miniemulsion droplet interaction, because either the deformation and flattening are weak (charged droplets) or the Reynolds drainage is rapid owing to the small dimensions of the interdroplet film (uncharged droplets). The kinetic stability of a miniemulsion can be caused by floe fragmentation if the electrokinetic potential is not too low and the electrolyte concentration is not too high, corresponding to some electrostatic repulsion.

The potential strength of physicochemical kinetics with respect to emulsions is the PBE, allowing prediction of the time evolution of the droplet size distribution (d.s.d.) when the subprocesses [including droplet aggregation, aggregate fragmentation, droplet coalescence, and droplet (floe) creaming] are quantified. The subprocesses are characterized in the PBE by the kinetic coefficients. The coupling of the four subprocesses, the droplet polydispersity, and the immense variety of droplet aggregate configurations causes extreme difficulty in EDM. The processes of aggregation, fragmentation, and creaming can be quantified. In contrast, only the experimental approach is now available for efficient accumulation of information concerning emulsion-film stability and coalescence kernel quantification for EDM.

Correspondingly, EDM may be accomplished by combining experiment and theory: (1) determination of coalescence and fragmentation kernels with the use of emulsion stability experiments at low-density contrast (l.d.c.) and s.d.e., because this permits the omission of creaming and

gravitational terms in PBE, simplifying it and making solution of the reverse task possible; and (2) prediction of the droplet size evolution with time by means of solution of the PBE, specified for the determined coalescence and fragmentation kernels. This mathematical model has to be based on the PBE supplemented by terms accounting for the role of creaming and gravitational coagulation in the aggregation kinetics.

EDM with experiments using l.d.c. emulsions and s.d.e. may result in: (1) the quantification of emulsion film stability, namely, the establishment of the coalescence time dependence on the physicochemical specificity of the adsorption layer of a surfactant (polymer), its structure, and the droplet dimensions. This quantification can form a basis for the optimization of emulsifier and demulsifier selection and synthesis for emulsion technology applications, instead of the current empirical level applied in this area; and (2) the elaboration of a commercial device for coalescence-time measurement, which in combination with EDM will represent a useful approach to the optimization of emulsion technology with respect to stabilization and destabilization.

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