Kinetics of Flocculation and/or Coalescence of Dilute Oil-in-Water Emulsions

D. F. BERNSTEIN*, W. I. HIGUCHI, and N. F. H. HO

Abstract ☐ The present study was part of a long-range attempt to describe quantitatively the coalescence or flocculation behavior of emulsions. Several baseline experiments of emulsion coalescence kinetics were conducted with stress placed on the elimination of possible artifact effects. Dibutyl phthalate, dioctyl phthalate, ditolyl, and "Unity Oil" were chosen as the oil phases in this investigation. Dilute emulsions of the oils in varying concentrations of sodium lauryl sulfate solutions were prepared ultrasonically, and the changes in the particle number and size distribution with time were studied in electrolyte solutions. The data obtained were treated by plotting the reciprocal of the cumulative number of particles greater than a specified size *versus* time. A theoretical analysis involving the consideration of finite emulsion droplet-size distributions showed that this method of data treatment is valid for the experimental systems in this study. For rapid reaction systems, the slopes of these Smoluchowski-type plots were directly related to the Smoluchowski rate constant. Rapid reaction conditions were found when the surfactant concentration was sufficiently low or when the electrolyte concentration was sufficiently high. The possible influences of wall effects, oil volatility, oil solubility, creaming (or sedimentation), shear, and mixing effects upon the rate constants were investigated. In the cases of ditolyl and the phthalates, it was found that these influences were negligible or could be eliminated by modifying the techniques involved in the procedure. In studies over a 10-fold range of oil concentration, 100-fold range of surfactant concentration, and a 6-fold range of electrolyte concentration, a maximum rate constant for coalescence of 4.0×10^{-12} cm.^{3}/sec. ($\pm 5\%$) was observed. Interestingly, this maximum rate constant is about 70% of the theoretical Smoluchowski rate constant.

Keyphrases ☐ Emulsions, oil/water—flocculation, coalescence kinetics ☐ Flocculation, coalescence behavior—diluted o/w emulsions ☐ Kinetics—o/w emulsion flocculation, coalescence ☐ Particle-size analysis—emulsions ☐ Aging effect, emulsions—particle number, particle-size distribution

The kinetics of coagulation (flocculation or coalescence) is one of the more important problems in the theory of disperse systems. The theory, first proposed by Smoluchowski (1), modified by Fuchs (2), and extended by Verwey, Overbeek, Derjaguin, and Landau (2), has never been completely developed analytically due to the complexities of the mathematical models and to the difficulty in handling the nonlinear integro-differential equation necessary for the analytical treatment.

Difficulties in designing suitable experimental verification of these theories have also been encountered. Little quantitative work has been reported in the literature, and the semiquantitative studies have involved little more than checks of the Schultze–Hardy rule or the effect of surfactant on the particle-size distribution of disperse systems (3, 4). Most work has been performed on solid sols or latex suspensions, since they are relatively monodisperse; few studies have involved emulsions.

Van den Tempel's (5) investigation of the stability of emulsions to the action of electrolyte correlated the rule of Schultze and Hardy, according to which the concentration of a cation necessary to coagulate a negatively charged sol is determined by the charge on the cation.
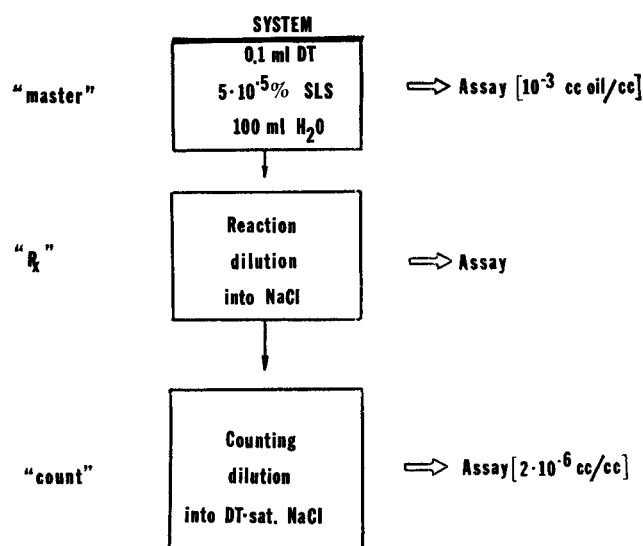

Figure 1—*Schematic representation of dilution steps.*

His system was not monodisperse, and the particles were counted microscopically.

The Coulter counter has been extensively used to characterize colloidal systems. Wachtel and LaMer (6) used the Coulter counter to size o/w emulsions, while Higuchi *et al.* (7, 8) first investigated parameters of emulsion aggregation by differentiating the relative amounts of aggregates. These studies were followed by Lemberger and Mourad (9) and Swift and Friedlander (10), the latter concentrating on the application of similarity or self-preserving functions to the Smoluchowski fundamental equation for aggregation. Rowe (4) and Mima and Kitamori (11) demonstrated the utility of the change in particle-size distribution as a parameter of emulsion stability. Mima and Kitamori (11) found that flocculation of oil droplets stabilized with acacia was dependent on the concentration of the oil and salt and on the size distribution of the primary (original) particles.

Matthews and Rhodes (12, 13) and Higuchi *et al.* (14) demonstrated the use of the Coulter counter in investigating the coagulation of monodisperse latexes. Matthews and Rhodes (12, 13) found coagulation times (or half-lives) to be about twice what the Smoluchowski theory predicted. Thus, the rate constants were also half of the Smoluchowski maximum of 5.6×10^{-12} cm.^{3}/sec. Johnson *et al.* (15), using polyvinyltoluene latex, found rate constants of 4.0×10^{-12} cm.^{3}/sec. for systems at 17°. Ho and Higuchi (16) found a 4% increase in the rate of aggregation of denatured ovalbumin due to the heterogeneity of their system. Their value of 4.148 for the self-preserving A_1 heterogeneity factor compared favorably to Smoluchowski's value of 4.0 for a monodisperse system.
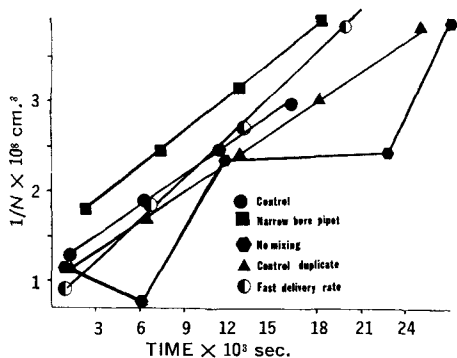
Figure 2—*Effect of artifacts in the dilution steps on the 1/N versus time plot.*

THEORY

Smoluchowski developed a basic theory for aggregation of spherical particles in a colloidal suspension (1, 2, 17). His fundamental equation for the flocculation of a system controlled by Brownian diffusion is

$$\frac{dN_\infty}{dt} = -KN_\infty{}^2 \qquad \text{(Eq. 1)}$$

where N_∞ = the number of particles of all sizes, K = bimolecular rate constant, t = time, and

$$K = \frac{4\pi DR}{W} \qquad \text{(Eq. 2)}$$

and the Stokes–Einstein translational diffusion coefficient

$$D = \frac{kT}{6\pi\mu a} \qquad \text{(Eq. 3)}$$

where R = distance between the centers of the two particles, W = stability factor (= 1.0 for irreversible collision, >1.0 when a potential barrier exists), k = Boltzmann constant, T = Kelvin temperature, μ = viscosity, and a = radius of the particle.

At collision, $R = 2a$ (the particles are assumed to be spherical and conjoin into spheres). Thus the theoretical maximum (W = 1.0) rate constant at 30° in water is

$$K = \frac{4kT}{3\mu W} = 5.62 \times 10^{-12} \text{ cm.}^3/\text{sec.} \qquad \text{(Eq. 4)}$$

Integration of Eq. 1, where N_o is the number of original particles of all sizes,

$$\int_{N_o}^{N} \frac{dN}{N^2} = -K \int_0^t dt \qquad \text{(Eq. 5)}$$

yields Eq. 6:

$$\frac{1}{N} - \frac{1}{N_o} = Kt \qquad \text{(Eq. 6)}$$

Thus, plots of reciprocal numbers of particles *versus* time are linear with slope K and intercept $1/N_o$.

The half-life, τ, is

$$\tau = \left(\frac{4kT}{3\mu}\right)^{-1} \cdot \frac{1}{N_o} \qquad \text{(Eq. 7)}$$

Using Eqs. 4 and 6,

$$\frac{1}{N} - \frac{1}{N_o} = \frac{4kT}{3\mu}t \qquad \text{(Eq. 8)}$$

and Eq. 7:

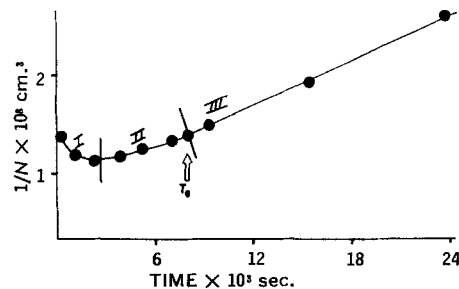$$N_o = \frac{3\mu}{4kT\tau} \qquad \text{(Eq. 9)}$$

Figure 3—*1/N versus time plot indicating the growth of small particles into the Coulter counter range.*

and multiplying Eq. 8 by N_o, the relationship

$$\frac{N_o}{N} - 1 = \frac{4kTN_o}{3\mu}t \qquad \text{(Eq. 10)}$$

is transformed to

$$\frac{N_o}{N} = 1 + \frac{t}{\tau} \qquad \text{(Eq. 11)}$$

Data in this form are said to be normalized. The normalized graph of N_o/N *versus* time/τ allows all systems to be plotted on a common graph. The maximum theoretical system has both slope and intercept of 1.0.

EXPERIMENTAL

Materials—The oil, ditolyl[1], was redistilled under reduced pressure and had a measured density of 0.993 g./ml. at 20°, a n_D^{20} of 1.5940, and a UV maximum at 250 nm. Another oil phase, that of mixtures of dioctyl phthalate[2] and dibutyl phthalate[3], was investigated once the preliminary studies were completed.

The sodium lauryl sulfate surfactant[4] was repurified by recrystallization from ethanol and ethanol–water mixtures. Double-distilled water was used exclusively. Sodium chloride electrolytes were either 5, 0.9, or 0.8% sodium chloride USP solutions or were prepared by dilution of these. Magnesium sulfate was anhydrous analytical reagent grade material. All experiments were performed at room temperature (16–26°).

Preparation of Master Emulsion—The master emulsion was prepared by ultrasonification with the Biosonik II[5], equipped with a 20 kHz. piezoelectric probe. Oil, 0.1 ml., was added to 99.9 ml. of a 5 × 10⁻⁵% solution of sodium lauryl sulfate in water and mechanically shaken prior to irradiation to disperse the larger globules. Emulsification is produced more rapidly and with far more efficiency when the oil and aqueous phase are mechanically agitated so that a gross mixture is first produced. The solution was then subjected to 20 kHz. for 15 sec., followed by 10 kHz. for 10 additional sec. Emulsions so produced were relatively monodisperse with particles in the 0.6–0.8-μ range (diameter).

The reaction dilution was made into a solution containing sufficient quantities of sodium lauryl sulfate and NaCl to give the desired concentration of surfactant and electrolyte. The counting dilution—a further 100-fold dilution to provide a particle concentration suitable for the Coulter counter—was made into saline solution presaturated with the oil under investigation.

Particle-Size Analysis—Particle size was determined using the Coulter counter, model A[6], equipped with a 50-μ aperture tube. A 400-channel RIDL analyzer was used for the distribution determinations. Calibration of the tube was achieved with polyvinyl-toluene latexes[7] of 1.857- or 2.051-μ diameter. The manometer tube apparatus was completely shielded by copper screening to eliminate electronic noise.

[1] Supplied by Aldrich Chemical Co. as 3,3'-dimethylbiphenyl, puriss.
[2] Aldrich Chemical Co., Milwaukee, Wis.
[3] Union Carbide Chemical Co., New York, N. Y.
[4] Maprofix 563, Onyx Chemical Co., Wilmington, Del. (95% C-12).
[5] Bronwill Scientific, Rochester, N. Y.
[6] Coulter Industrial Sales, Hialeah, Fla.
[7] Polyvinyltoluene, Dow Chemical Co., Midland, Mich.

Table I—Ditolyl Initial Rate Constants for Several Salt and Surfactant Concentrations

Percent Sodium Lauryl Sulfate in Reaction	Dilution	Rate Constant $K \times 10^{-12}$ cm.^{3}/sec. 0.9% NaCl	4% NaCl	1% MgSO$_4$
0.6×10^{-6}	1/4	4.169		
0.4×10^{-5}	1/12	3.707		
0.5×10^{-5}	1/10	3.899		
0.6×10^{-5}	1/8	3.787		
1.0×10^{-5}	1/5	3.848		
1.0×10^{-5}	1/5	3.935		
1.0×10^{-5}	1/5	4.077		
1.2×10^{-5}	1/4	4.262		
1.2×10^{-5}	1/4	4.287		
2.5×10^{-5}	1/2	4.318		
9.0×10^{-5}	1/5	4.016		
1.0×10^{-4}	1/5	2.261		
2.5×10^{-4}	1/5	1.315		
1.0×10^{-3}	1/5	0.933	4.187	3.525
1.2×10^{-3}	1/5	0.169	4.154	3.640
1.2×10^{-3}	1/5		4.285	3.740

Table II—Initial Rate Constants as a Function of Oil, Salt, Surfactant, and Temperature

Oil	Reaction Vessel Composition — Sodium Lauryl Sulfate, %	NaCl, %	T	$K \times 10^{-12}$ cm.^{3}/sec. At T	At 25°a
Ditolyl	1.0×10^{-5}	0.9	23°	4.077	4.297
	1.2×10^{-5}	0.9	16°	3.395	4.352
	9.0×10^{-5}	0.9	23°	4.016	4.233
	1.0×10^{-4}	0.9	23°	2.261^b	2.383
	2.5×10^{-4}	0.9	23°	1.315^b	1.386
	1.0×10^{-3}	0.9	23°	0.933^b	0.983
	1.2×10^{-3}	0.9	23°	0.169^b	0.178
Dioctyl phthalate–dibutyl phthalate	1.2×10^{-5}	0.9	18°	3.341	4.042
	1.2×10^{-5}	0.9	16°	3.321	4.257
	1.2×10^{-5}	0.9	16°	2.931	3.757
	9.0×10^{-5}	0.8	27°	2.224	2.112
	3.9×10^{-4}	0.8	27°	0.610	0.579
	8.1×10^{-4}	0.8	16°	0.212	0.272
	3.8×10^{-3}	0.8	27°	0.126	0.120
	8.0×10^{-3}	0.8	16°	0.056	0.072
Hexadecane	1.2×10^{-5}	0.8	16°	2.845	3.647
	1.2×10^{-5}	0.9	16°	3.457	4.431
Unity Oil	1.2×10^{-5}	0.8	17°	2.873	3.576

a Temperature and viscosity corrections applied to obtain K at 25°.
b 4% NaCl gave $K = 4.219\ (\pm 1.5\%) \times 10^{-12}$ cm.^{3}/sec.

Apparatus—All glassware used in these experiments was washed thoroughly and rinsed twice in tap water and once in distilled water before use. Pipets were subjected to four wash–rinse cycles before use.

Preliminary Studies—The first system was a slight modification of van den Tempel's (5) mixture of 57 volumes of chlorobenzene and 43 volumes of paraffin oil, resulting in a density of 1.006 g./ml. By using a ratio of 56 volumes of chlorobenzene and 44 volumes of mineral oil, a mixture was obtained having a density of 1.0027 g./ml. However, the chlorobenzene had some solubility in the aqueous phase and was partially volatilized by the ultrasonic irradiation. Thus, upon loss of the aromatic component from the system, the oil phase had a density of less than unity and quickly creamed. A search of the literature to find a nonpolar, water-insoluble, high boiling point liquid having a density close to unity indicated that ditolyl (3,3'-dimethylbiphenyl) would be suitable.

Early experimental results with ditolyl demonstrated a rapid loss of particles from the counter measuring system[8]. To determine the reason for this phenomenon, a quantitative assay for ditolyl was introduced. This involved extraction of the oil from the emulsion with a small amount of ether, followed by three cyclohexane extractions. It was demonstrated with both control solutions and emulsions that this technique gave quantitative recovery of oil (98.5–101.5%).

The possibility of the following artifacts contributing to the rapid disappearance of particles was examined: (a) unimolecular wall reaction between the oil and vessel wall; (b) volatility of the oil in dilute emulsions; (c) creaming of the oil phase; and (d) solubility of the oil in electrolyte solution.

Assays of aliquots drawn from the bulk emulsion as well as an assay of the residual volume of emulsion were quantitative. Thus the oil was not undergoing a wall reaction; if it were, the bulk assay would have been less than 100% recovery and the remainder (including the wall washing liquor) greater than 100%.

Assay experiments were performed with some tightly sealed beakers and some that were left open to the atmosphere. All assays were quantitative, indicating that (b) was not influencing the disappearance of the oil. Assays were conducted on a reaction system over a period of time to test the effect of creaming. These assays were quantitative over 7–8 hr. (about 3.5–4 τ in the system being investigated), but decreased in percent recovery after that time. However, since the counting procedure is of the order of a minute, the immediate loss of particles could not be explained in this way.

To investigate the solubility of ditolyl in saline solution, a saturated solution was first assayed (both by direct assay and by extraction assay) and the solubility was determined to be 1.5 × 10^{-6} ml. oil/ml. saline. Since the concentration of ditolyl in the dilute counting stage was 2 × 10^{-6} ml. oil/ml. saline, it was evident that some 75% of the oil was solubilized. Emulsions diluted into saline rapidly decreased (about 40%) in counts over 1 min., while an identical

dilution into saline presaturated with the oil showed no decrease in counts over 10 min. All subsequent experiments were conducted using such a presaturated vehicle for the counting dilution. This solubility phenomenon was shown not to be important in the "reaction" dilution, since the emulsion is 100 times as concentrated in oil.

Dilution Technique—The system investigated most closely was a "master" emulsion composed of 0.1 ml. ditolyl, 5 × 10^{-5}% sodium lauryl sulfate, and water to make 100 ml. This master emulsion was diluted into the "reaction" vessel and then diluted into the "counting" vessel such that the total dilution was 500-fold. By diluting the master from 2 to 20 times (denoted $^1/_2$–$^1/_{20}$ dilution), a 10-fold oil concentration range was investigated. With the $^1/_2$ dilution, the counting dilution was $^1/_{250}$; mixing the 1-ml. aliquot with this volume of saline changed the particle-size distribution. Using a $^1/_{20}$ reaction dilution (and $^1/_{25}$ counting dilution) that had a half-life of 10 hr., the creaming effect occurred after 7.5 hr, and quantitative data could not be obtained from so short an experiment. Thus, a $^1/_5$ dilution was chosen as optimum. This system is represented schematically in Fig. 1.

The data obtained (time and the number of particles greater than a specified size) were treated by the typical Smoluchowski rate plot of $1/N$ versus time. While linear curves resulted, a sufficient amount of scatter generated a study of the actual pipeting and dilution steps involved in the procedure.

The technique of the dilution steps is as follows: the reaction dilution was effected by using a 5-ml. wide bore, blowout-type serological pipet (Kimax No. 37034B). Two such 5-ml. aliquots were taken from the master and diluted into 40 ml. of a solution containing the desired amounts of surfactant and electrolyte. The counting dilution was performed by quantitative transfer of 1 ml. of the reaction emulsion into 99 ml. of the presaturated saline. The saline was stirred before the transfer to ensure adequate mixing of the aliquot with the saline without unnecessary shear. The aliquot was introduced just below the surface of the solution and allowed to drain into the counting vessel at a rate of 1 ml. in 10–11 sec. No further mixing was performed. The particles were then immediately counted.

Using this technique, the number of particles in four[9] successive determinations did not differ from the average of the four by more than 3%. Using a 1-ml. "to deliver" pipet (small bore) for the transfer operation, a decrease in the number of counts (as compared to the described procedure) was attributed to shear-induced coalescence of the particles passing the narrow bore. Although the deviations from the average count were 4–7%, rate constants were similar to those obtained from the described procedure.

---

[8] About three orders of magnitude larger than Smoluchowski coalescence.

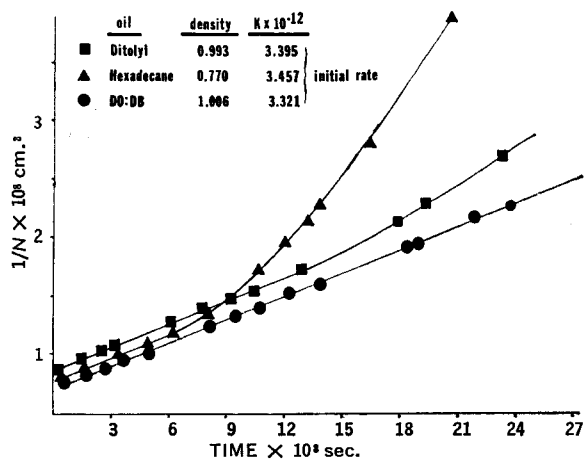[9] Due to electronic polarity effects, an even number of readings must be taken.

Figure 4—$1/N$ versus *time plot of several oils of differing densities.*

When prestirring was not performed, a large amount of scatter was noticed in the $1/N$ *versus* time plot. When the aliquot was allowed to flow out of the wide-bore pipet simply by gravity (1 ml. in 1 sec.), the data obtained yielded a shear-accelerated rate constant. The effect of these artifacts on the treatment of data is shown in Fig. 2. The technique first presented was used in all experiments because of its accuracy and reproducibility.

This double-dilution technique was chosen over the *in situ* system (*e.g.*, one 500-fold dilution from master to counting vessel) so as not to sacrifice volumetric accuracy. To ensure that the two-stage dilution did not change the coalescence pattern at each step, one 500-fold dilution was made simultaneously with the same dilution in two steps. The particle counts in each system were within 7–10% of each other. This variation was also noted in the 500-fold dilution of dialyzed latex particles, and the difference in both cases is attributed to problems associated with mixing a 1-ml. aliquot into the large volume (500 ml.) of saline.

In addition, the second dilution in the two-step procedure was made into saline and into saline-surfactant solutions to check the possibility of desorption at this step. Absolute counts and rate constants determined from each method differed by less than 1%.

Aging of Emulsion—After the master emulsion was ultrasonified, it was allowed to stand undisturbed in its concentrated form for 5 min ; the reaction dilution was then made. Counting determinations at intervals of approximately 0.1 τ demonstrated an initial increase in the number of particles followed by the decrease one normally expects from coalescence (Fig. 3). In Region I of Fig. 3 (early times after dilution), the increase in the number of particles is due to the great number of small particles (small in the sense that they were below the minimum size seen by the Coulter counter) "growing" into the range of the instrument. Region II represents that in which the coalescence of the larger particles is becoming more important. Finally, in Region III, most of the small particles have coalesced to become large enough to be counted and thus represents the situation in which most of the mass of oil is accounted for by the Coulter counter.
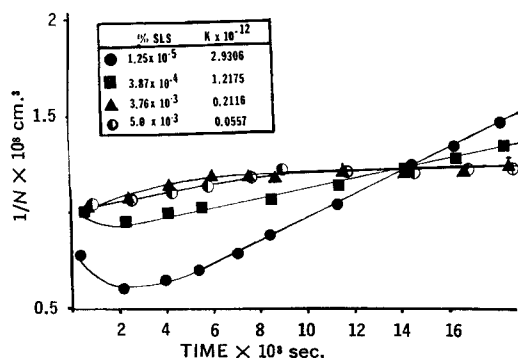

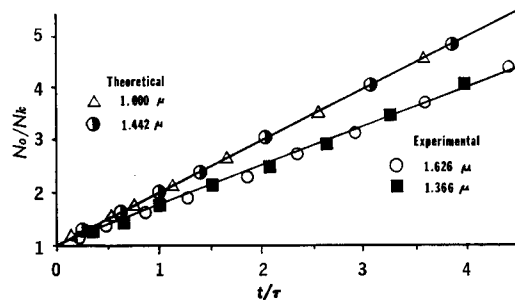**Figure 5**—*Effect of surfactant concentration on the* $1/N$ *versus time plot.*

Coulter Counter Thresholds—Adjustable threshold settings (voltage screenout) in the electronic counting circuit permit a count to be determined for the total number of particles larger than a given size. Experiments run at threshold settings of 3, 4, and 5 (corresponding to all particles larger than 1.366-, 1.509-, and 1.626-μ diameter, respectively) gave similar rate constants. Since linearity was observed in Region III of the Smoluchowski plot, it was accepted that the majority of particles were being counted in this region and that the small effect due to coalescence of small particles into the Coulter counter range could be neglected. Theoretical analyses involving computer studies demonstrated that this assumption was valid.

RESULTS AND DISCUSSION

Over 40 systems utilizing ditolyl were investigated, each being reproduced at least twice with rate constants within 5% of each other for similar systems. These data are summarized in Table I. In studies over 100-fold surfactant, 6-fold sodium salt, 4-fold magnesium salt, and 10-fold oil concentration ranges, a maximum rate constant of 4.0 $\times$ 10^{-12} cm.^{3}/sec. ($\pm 5\%$) was observed. The rate constants were determined by least-squares regression analyses of the linear portion of the $1/N$ *versus* time plot (Region III, Fig. 3). The values reported are initial values only and do not reflect the deviations due to creaming. When the reaction vessel was a $^1/_5$ dilution, graphical deviations (increasing upward slope) were noted after 4 τ (about 35,000 sec.). These graphical deviations were accompanied by a corresponding decrease of the percent oil recovered from the quantitative UV extraction assay. Even swamping the system at this point with surfactant (the stabilized emulsion gave a nearly horizontal slope from that point on) did not inhibit the eventual slight upward trend of the $1/N$ *versus* time plot.

Another series of investigations was directed toward a 2:1 (v/v) mixture of dioctyl and dibutyl phthalates. The resulting density of 1.006 g./ml. was matched to within 0.5% of that of the 0.8% NaCl in the reaction vessel. The creaming effect (detected graphically or by assay) was absent for 7.5–8 τ (about 70,000 sec.)[10]. These experiments were performed at 17 $\pm$ 1°, and the decrease in temperature (resulting in an increase in the viscosity) was believed to be responsible for the decrease in the rate constants to values between 2.8 and 3.3 $\times$ 10^{-12} cm.^{3}/sec. These determinations are summarized in Table II.

Figure 4 shows the similarity of initial rate constants independent of the oil employed, even when hexadecane (with a 23% density difference) systems were investigated. The effect of the density of the oil and, consequently, its importance are noted by the upward curvature of the graphs depicting the coalescence behavior of oils whose density differs from that of the saline vehicle employed.

Figure 5 is a typical surfactant study utilizing the dioctyl phthalate–dibutyl phthalate system. Interestingly, the higher surfactant concentrations permitted some coalescence to occur before a stable system (the horizontal portion of the graph) was reached. Particle-size distribution photographs showed almost no change over this stability period. This "limited coalescence" phenomenon is being pursued further.

Figure 6—*Comparison of theoretical and experimental data on a normalized plot.*

---

[10] Even after 8 τ, the loss of particles from the system due to creaming is primarily due to the increased r^2 term and not the density difference in Stoke's equation.

Table III—Computer Input Data

Dielectric constant	80	Time	$20\,\tau$
Hamaker constant	10^{-13} erg	Number of classes	100
Surface potential	6 mv.	Initial singlets	5%
Kappa (cm.$^{-1}$)	$1.26 \times 10^{+6}$	doublets	10%
Viscosity	1 cp	triplets	50%
kT	4.14×10^{-14}	4-mers	25%
Singlet radius	$0.5\,\mu$	5-mers	10%

COMPUTER STUDIES

The IBM 360/67 computer, utilizing a program (18) involving solutions to the set of nonlinear ordinary differential equations, was used to generate a set of theoretical data. These input data are given in Table III.

To check the validity of determining K from the $1/N$ versus time plot along with the arbitrary choice of threshold (minimum particle size seen), a normalized plot (Fig. 6) of the computer-generated data was made.

When all the particles were counted, the slope was 1.031 (corresponding to a rate constant of 5.794×10^{-12} cm.^{3}/sec.). A similar graph, excluding the 5% singlet contribution, gave a slope of 1.017 (rate constant: 5.715), while the slope of a graph omitting both singlets and doublets was 1.009 (rate constant: 5.671). Similar results were found experimentally; these data are summarized in Table IV.

The computer-generated rate constants were greater than the Smoluchowski maximum (5.62) due to the heterogeneity of the system. The validity of using the $1/N$ versus time plot to determine K was thus established. Also noteworthy was the independence of the rate constant on the minimum size cutoff point.

Studies now in progress include rigorous particle-size distribution determinations, salt–surfactant interplay, electrophoretic mobility studies, and investigations into the region of limited coalescence. By using the analytical tools at hand, experiment and theory can then be compared in a wide range of systems.

REFERENCES

(1) M. von Smoluchowski, *Physik Z.*, **17**, 557(1916).

(2) "Colloid Science," vol. 1, H. R. Kruyt, Ed., Elsevier Publishing Co., Amsterdam, The Netherlands, 1952, chap. 7.

(3) S. Rehfield, *J. Colloid Interface Sci.*, **24**, 358(1967).

(4) E. L. Rowe, *J. Pharm. Sci.*, **54**, 260(1965).

(5) M. van den Tempel, *Rec. Trav. Chim.*, **72**, 419(1953).

(6) R. E. Wachtel and V. K. LaMer, *J. Colloid Interface Sci.*, **17**, 531(1962).

Table IV—Rate Constant as a Function of Omission of Small Particles

Threshold	Corresponding[a] Particle Diameter, μ	$K \times 10^{-12}$ cm.^{3}/sec.	Percent of Maximum Theoretical Rate
Experimental			
3	1.366	4.252	75.65
4	1.509	4.169	74.18
5	1.626	4.077	72.54
Computer Simulation ($W = 1.0$)			
N_k	1.000	5.794	103.1
N_k less singlets	1.260	5.715	101.7
N_k less singlets and doublets	1.442	5.670	100.9

[a] Particles having dimensions less than this are not counted.

(7) W. I. Higuchi, R. Okada, and A. P. Lemberger, *J. Pharm. Sci.*, **51**, 683(1962).

(8) W. I. Higuchi, R. Okada, G. A. Stelter, and A. P. Lemberger, *ibid.*, **52**, 49(1963).

(9) A. P. Lemberger and N. Mourad, *ibid.*, **54**, 229 (1965).

(10) D. L. Swift and S. K. Friedlander, *J. Colloid Interface Sci.*, **19**, 621(1964).

(11) H. Mima and N. Kitamori, *J. Pharm. Sci.*, **55**, 44(1966).

(12) B. A. Matthews and C. T. Rhodes, *J. Colloid Interface Sci.*, **28**, 71(1968).

(13) B. A. Matthews and C. T. Rhodes, *J. Pharm. Sci.*, **57**, 557(1968).

(14) W. I. Higuchi, T. O. Rhee, and D. R. Flanagan, *ibid.*, **54**, 510(1965).

(15) G. A. Johnson, S. M. A. Lecchini, E. G. Smith, J. Clifford, and B. A. Pethica, *Discuss. Faraday Soc.*, **42**, 120(1966).

(16) N. F. H. Ho and W. I. Higuchi, *J. Pharm. Sci.*, **56**, 248(1967).

(17) M. von Smoluchowski, *Z. Physik. Chem. (Leipzig)*, **92**, 129(1917).

(18) A. Suzuki, N. F. H. Ho, and W. I. Higuchi, *J. Colloid Interface Sci.*, **29**, 552(1969).

ACKNOWLEDGMENTS AND ADDRESSES