## —— The Editor comments ——

### SCIENCE'S TOWER OF BABEL

We are all familar with the Biblical story concerning the Tower of Babel and the considerable confusion which resulted when the builders' "tongues were confounded" (*Genesis, 11*: 4–9).

On the other hand, we usually think of science as being the one area which readily crosses the barriers of language and which is fully intelligible in any tongue. Unfortunately, however, this is not always the case, and the irony of the matter is that the confusion to which we here refer arises even in the individual's native language. This confusion is primarily due to carelessness on the part of authors. Frequently authors are not nearly as precise or consistent as scientists should be in their choice of symbols, abbreviations, and terminology.

A writer will refer to the "activity" of a compound without making it clear whether he means its chemical activity, biological activity, or optical activity. In other instances D- or L- will be used when *d*- or *l*- is meant, and vice versa. The adjectives angular, optical, specific, and observed are often used either incorrectly or inconsistently in discussing the ability of a substance to rotate polarized light. In other instances, for no good reason, different systems of measurement are sometimes used in the same article, such as centigrade and Fahrenheit temperatures, metric and English lengths, or metric and apothecary weights.

A less obvious but more perplexing area of inconsistency pertains to terminology used to express spectrometry nomenclature. This situation has been due, in part, to evolutionary changes in accepted or approved terms and definitions by responsible nomenclature bodies as well as carelessness on the part of some authors. As a guide to our authors and readers we are presenting on page VIII of this issue, a list of the terms and definitions adopted for use in THIS JOURNAL. This information is based upon preferred terminology approved by the American Society for Testing and Materials, "Analytical Chemistry," and "Chemical Abstracts." In the interest of accuracy and clarity, we strongly encourage regular use of this preferred terminology by all of our readers and authors, whenever spectrometry terminology is employed.

*Edward G. Feldmann*

# Effect of Emulsifier Concentration and Type on the Particle Size Distribution of Emulsions

## By E. L. ROWE

Two series of mineral oil/water emulsions containing varying amounts of emulsifier, either sodium dodecyl sulfate or polysorbate 80, were studied over a 2-year period. The Coulter counter was used to determine particle size distributions at various time intervals. For each emulsifier, there is a minimum concentration above which the emulsions are stable for over 2 years with little change in particle size distribution. Increasing surfactant concentration causes decreasing median particle size in both series according to a logarithmic relationship. Some of the theoretical aspects of surfactant adsorption at the oil/water interface are discussed.

EMULSIONS AS disperse systems have an advantage over solid-in-liquid dispersions because the particles are spherical and easier to measure. However, the particle size distribution of emulsions is changed easily by adjustment of the phase volume ratio, method of manufacture, temperature, and viscosity (1). Another important variable is the emulsifier concentration. There have been few emulsion studies where the emulsifier concentration was varied deliberately and the mean particle size measured carefully. The earliest work in this area was done by Langevin (2), in 1933, who varied the proportion of emulsion ingredients and found microscopically that "...increase in the proportion of acacia is accompanied by a decrease in the size of the oil globules...." The lack of experimental work in this area since that time is possibly due to the tedium involved in the measurements.

Recent advances in instrumentation have made the quantitative measurement of particle size distributions of emulsions less tedious. The Coulter counter[1] is becoming a popular instrument for the measurement of particle size distributions of emulsions (3, 4). In the present study, the Coulter counter was used to determine the size distributions of two series of emulsions. In each case, the concentration of emulsifier was varied from 0 to 5.0%. The effect of emulsifier type and concentration on the distribution and the changes in particle size with time were observed over a 2-year period.

### EXPERIMENTAL

**Preparation of Emulsions.**—Two series of ten oil-in-water emulsions were made with varying amounts of surfactant. In both series, 100 ml. of mineral oil U.S.P. (viscosity, 40 centistokes) and 300 ml. of

aqueous surfactant solution were mixed in a Waring Blendor for 10 min. Fifty milliliters of each emulsion was poured into a 50-ml. graduated cylinder for observation of creaming, coalescence, and volume ratio of the phases at 25°. The remainder was stored in bottles for particle size distribution studies. In the series labeled 61A through 61J, sodium dodecyl sulfate[2] (SDS) was used as the sole emulsifier with the concentration varying from 0 to 5.0%. (See Table I.) The 65 series was made with polysorbate 80[3] as the sole emulsifier at the same concentration levels as in the SDS series.

**Particle Size Distributions.**—The Coulter counter (model A) was used with the 100-$\mu$ aperture for all particle size determinations. The instrument is kept in constant calibration by frequent checks with well-characterized monodisperse polystyrene latices and puffball spores. The manufacturer does not recommend measurement of particles with diameter less than 1.5% of the aperture diameter (5). However, in most of the present emulsions, few or no particles were observed below 2-$\mu$ diameter. In the few cases where a significant number of the particles were smaller than 2 $\mu$, the measured contribution to the total weight distribution was less than 2%. Also, the frequency distribution curves generally included at least one point on the small side of the modal (peak) diameter. In any event, the conclusions are not affected by small errors in this region. The emulsions were shaken gently so that a homogeneous 2-ml. sample could be withdrawn by pipet. The 2-ml. sample was diluted to 1 L. with a conductive vehicle (0.1% SDS for the 61 series and standard conductive vehicle[4] for the 65 series) and stirred with a magnetic stirrer in a 25° water bath. A 15-ml. sample of this dilute emulsion then was diluted to 1 L. with the standard conductive vehicle. Solvation of the oil upon dilution was considered to be negligible. The effect, if any, is probably constant for all the emulsions involved, and the relative results would still be meaningful. Cockbain (6) has reported aggregation in SDS-stabilized paraffin emulsions where the SDS concentration exceeded 0.45%. Higuchi (3) found aggregation in 1% hexadecane emulsions containing more than 0.1% dioctyl sodium sulfosuccinate and that the rate of deaggregation was a slow process. However, in the

[2] Marketed as Duponol C by E. I. du Pont de Nemours and Co., Wilmington, Del.
[3] Marketed as Tween 80 by Atlas Chemical Industries, Wilmington, Del.

TABLE I.—COALESCENCE OBSERVED IN TWO SERIES OF MINERAL OIL/WATER EMULSIONS

| Emulsion No. | Emulsifier Type | Concn., % | Visible Coalescence of Oil Phase, % 1 Mo. Old | 1 Yr. Old | 2 Yr. Old |
|---|---|---|---|---|---|
| 61A | SDS | 0 | 94 | 100 | 100 |
| 61B | SDS | 0.001 | 64 | 95 | 100 |
| 61C | SDS | 0.005 | 88 | 95 | 97 |
| 61D | SDS | 0.01 | 79 | 88 | 82 |
| 61E | SDS | 0.05 | 67 | 81 | 82 |
| 61F | SDS | 0.1 | <1 | <1 | <1 |
| 61G | SDS | 0.5 | 0 | <1 | <1 |
| 61H | SDS | 1.0 | 0 | Negligible[a] | Negligible[a] |
| 61I | SDS | 2.0 | 0 | 0 | Negligible |
| 61J | SDS | 5.0 | 0 | 0 | Negligible |
| 65A | Polysorbate 80 | 0 | 75 | 92 | 100 |
| 65B | Polysorbate 80 | 0.001 | 92 | 100 | 100 |
| 65C | Polysorbate 80 | 0.005 | 67 | 95 | 100 |
| 65D | Polysorbate 80 | 0.01 | 34 | 84 | 92 |
| 65E | Polysorbate 80 | 0.05 | <3 | 12 | 11 |
| 65F | Polysorbate 80 | 0.1 | <3 | 7 | 7 |
| 65G | Polysorbate 80 | 0.5 | 0 | 6 | 14 |
| 65H | Polysorbate 80 | 1.0 | 0 | Negligible[a] | 3 |
| 65I | Polysorbate 80 | 2.0 | 0 | Negligible | <1 |
| 65J | Polysorbate 80 | 5.0 | 0 | Negligible | Negligible[a] |

[a] One or 2 small drops.

present systems only a negligible amount of aggregation was noted microscopically in the diluted emulsions prior to particle size determination. Both weight and number distributions were calculated from the raw data.

## RESULTS

The emulsions tend to cream rather quickly to the theoretical cream phase volume of 34%[5] but are easily redispersed. Creaming, of course, is not a criterion of physical stability in the colloidal sense. Growth of the oil particles by coalescence which leads to a separated oil layer (commonly called breaking) is a true measure of physical stability (7). The increase in free coalesced oil which occurs with time (even in the most stable emulsions) is expected since the emulsified state is thermodynamically unstable and, at best, represents a pseudoequilibrium. The two series of emulsions were observed over a 2-year period for visible coalescence. Table I lists three sets of observations made during this time interval. There is a minimum surfactant concentration necessary for physical stability. In the SDS series, this concentration is near the critical micelle concentration (CMC) of 0.18–0.25% w/v reported by Rehfeld (8). The minimum polysorbate 80 concentration for stability is not so clear-cut. In this series, the emulsions that are fairly stable at 1 month have a greater tendency than the SDS stabilized emulsions to coalesce.

The particle size distributions of the 65 series are plotted in Fig. 1 on log probability paper. The 61 series is similar. While the log normal fit is not perfect over-all, the distributions are more closely log normal than normal. The number median ($d_n$) and mass median diameters ($d_m$) were determined from the log probability plots and are reported in Table II. Several anomalous results are marked with an asterisk. The cause is difficult to ascertain since the technique of using the Coulter counter in this study was being developed at the time of the first run. Data acquired in subsequent

determinations did not contain deviations of this magnitude.

Polydispersity or broadness of the distribution can be expressed by the slope of the linear distribution plot on probability or log probability paper. The slope is related to the standard deviation of the median particle size. With curves that deviate somewhat from linearity, the true slope value is difficult to determine. Another easy method to express the polydispersity is the ratio of mass median diameter to number median diameter. A monodisperse system has a $d_m/d_n$ ratio of 1. The broader the distribution, the larger the ratio. As shown in Table II, polydispersity of the SDS-stabilized emulsions decreases with increasing emulsifier, while polysorbate 80 emulsions have increasing polydispersity with increasing surfactant concentration. This is a result of the manner in which the number
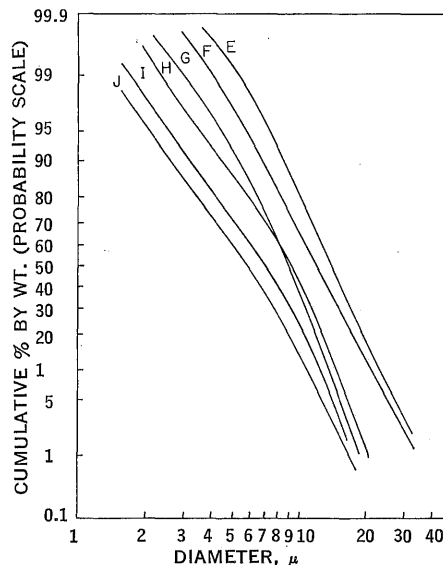


Fig. 1.—Particle size distributions (log probability

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[5] The true volume fraction of oil is 0.25; but in the form

median and mass median diameters change. A large increase in the number of fine emulsion particles with a smaller relative change in the rest of the distribution will decrease the number median diameter more than the mass median diameter because of the small mass contribution. This is apparently the case with the polysorbate 80 emulsions and is substantiated by the increasing turbidity of the aqueous phase of the creamed emulsion as surfactant concentration increases. In the SDS-stabilized emulsions, the aqueous (after creaming) phase becomes clearer with increasing surfactant concentration. The number median diameters of emulsions 61G through 61J do not differ significantly, which can be interpreted to mean there is little change or at least no increase in the small particle end of the distribution with increasing SDS concentration. Decreasing mass median diameters of the same set is an indication of decreasing relative number of large particles.

## DISCUSSION

Although there is some indication of growth of the particles by coalescence with time (Table II), the change is small and possibly within the error of the measurements. Therefore, there is no point in trying to quantitate the kinetics of growth. Vold (9) also found the rate of change of interfacial area, in 50% Nujol–water emulsions stabilized by SDS, to be too slow to afford a criterion for emulsion stability. Experimental evidence by Fischer and Harkins (10) showed that the specific interfacial area of paraffin oil-in-water emulsions decreased by over 30% in the first 50 hr. and thereafter decreased at a much slower almost constant rate. van den Tempel (11) observed a similar effect. His data indicate first-order kinetics with respect to the number of oil particles.

The concept of a fast initial coalescence rate followed by a slow steady rate seems to be reasonable. The high shearing force applied to the oil in the manufacture of these emulsions produces oil droplets of varying stability, depending on the amount of surfactant available for adsorption. Assuming that a condensed monolayer of surfactant is necessary for stability, the initial coalescence rate can be attributed to instability caused by incomplete oil surface coverage. When the oil/water interfacial area is reduced by particle growth (coalescence) so that the available surfactant can form a complete monolayer, a slow rate of coalescence becomes dominant. In a practical sense, this is an ideal situation if generally applicable. The particle size distribution could be observed over a short period of time after manufacture. In the absence of complicating factors, such as chemical instability, this should give enough data to establish the value and constancy of the slow coalescence rate, allowing a fairly accurate prediction of the long range physical stability.

Tables I and II show that a minimum of about 0.1% SDS ($3.5 \times 10^{-3}$ moles/L.) is needed for stability. The interfacial oil/water area in an emulsion can be calculated by

$$S_v = \frac{6 \times 10^{20}}{\bar{d}_{vs}}$$

### Table II.—Median Diameters and Polydispersity of Mineral Oil/Water Emulsions as a Function of Age and Emulsifier Concentration

| Emulsion No. | Emulsifier Concn, % of Aqueous Phase | 2 Wk. Old $d_m^a$ | $d_n^b$ | $d_m/d_n^c$ | 8 Mo. Old $d_m$ | $d_n$ | $d_m/d_n$ | 12 Mo. Old $d_m$ | $d_n$ | $d_m/d_n$ | 16 Mo. Old $d_m$ | $d_n$ | $d_m/d_n$ | 24 Mo. Old $d_m$ | $d_n$ | $d_m/d_n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 61F | SDS 0.1 | 17.5 | 1.8 | 9.7 | 21.3 | 2.1 | 10.1 | 22.8 | 4.9 | 4.7 | 23.5 | 3.5 | 6.7 | 21.4 | 4.7 | 4.6 |
| 61G | SDS 0.5 | 13.0 | 1.8 | 7.2 | 15.3 | 4.2 | 3.6 | 15.5 | 6.4 | 2.4 | 15.6 | 6.1 | 2.6 | 16.1 | 6.5 | 2.5 |
| 61H | SDS 1.0 | 18.5* | 2.2 | 8.4 | 15.5 | 5.7 | 2.7 | 15.9 | 6.9 | 2.3 | 15.6 | 6.3 | 2.5 | 15.6 | 6.3 | 2.5 |
| 61I | SDS 2.0 | 13.3 | 2.1 | 6.3 | 14.0 | 5.5 | 2.5 | 14.4 | 7.6 | 1.9 | 14.3 | 6.9 | 2.1 | 14.3 | 6.5 | 2.2 |
| 61J | SDS 5.0 | 21.0* | 2.0 | 10.5 | 11.4 | 6.1 | 1.9 | 11.7 | 7.1 | 1.6 | 11.6 | 7.1 | 1.6 | 11.4 | 6.6 | 1.7 |
| 65E | Polysorbate 80 0.05 | 13.8 | 8.0 | 1.7 | 13.3 | 8.5 | 1.6 | 13.8 | 7.9 | 1.7 | 14.1 | 8.3 | 1.7 | 14.0 | 8.0 | 1.8 |
| 65F | Polysorbate 80 0.1 | 11.0 | 1.8* | 6.1 | 11.4 | 6.5 | 1.8 | 12.0 | 6.3 | 1.9 | 11.9 | 6.4 | 1.9 | 12.7 | 5.7 | 2.2 |
| 65G | Polysorbate 80 0.5 | 8.4 | 4.2 | 2.0 | 8.6 | 4.7 | 1.8 | 9.0 | 4.6 | 2.0 | 8.8 | 4.7 | 1.9 | 9.0 | 4.6 | 2.0 |
| 65H | Polysorbate 80 1.0 | 7.6 | 2.7 | 2.8 | 9.1 | 3.0 | 3.0 | 9.2 | 3.2 | 2.9 | 9.4 | 3.0 | 3.1 | 9.1 | 3.1 | 2.9 |
| 65I | Polysorbate 80 2.0 | 7.2 | 2.3 | 3.1 | 8.0 | 2.2 | 3.6 | 7.4 | 2.3 | 3.2 | 7.2 | 2.3 | 3.1 | 7.2 | 2.4 | 3.0 |
| 65J | Polysorbate 80 5.0 | 5.4 | 2.1 | 2.6 | 6.1 | 2.0 | 3.0 | 5.7 | 2.1 | 2.7 | 5.8 | 2.1 | 2.8 | 5.6 | 2.1 | 2.7 |

Mass median diameter—50% of the oil droplets (by weight) have a diameter larger than this value, and 50% have a diameter smaller. [b] Number median diameter—50% of the oil droplets (by number) have a diameter larger than this value, and 50% have a diameter smaller. [c] Polydispersity ratio. (See text.)

weighted mean diameter in microns. The mass median diameter, $d_m$, may be substituted for $\bar{d}_{vs}$ with little error. Taking 21.4 $\mu$ as the mass median diameter of emulsion 61F, $S_v$ is $0.28 \times 10^{20}$ Å.²/ml. In 100 ml. of emulsion, there are 25 ml. of oil, and the total oil/water interfacial area is $7 \times 10^{20}$ Å.². There is sufficient SDS present at 0.1% concentration, assuming 25 Å.² surface coverage per molecule, to cover an area of $39 \times 10^{20}$ Å.². Thus, there is more than five times the amount necessary to form a condensed monolayer at the interface.

By comparison, the polysorbate 80 stabilized emulsions are fairly stable after 1 month's aging when the aqueous surfactant concentration is at least 0.05% ($4.1 \times 10^{-4}$ moles/L.). This concentration represents one-tenth the number of molecules as are in 0.1% SDS; but, as shown by Fig. 2, the polysorbate 80 molecule is very bulky and conceivably could cover 10 times as much surface as a SDS molecule. In addition, the surface activity of polysorbate 80 is greater than SDS at low concentrations (12, 13); thus, a greater percentage of polysorbate 80 molecules are adsorbed at the interface. The polysorbate 80 emulsions have a greater tendency to form free oil by coalescence than the SDS-stabilized emulsions (Table I), but the particle size distributions remain essentially constant, indicating perhaps uniform particle growth of all sizes with the number of smallest measured particles being replenished by growth of those too small to measure.

Another point of interest is that stable SDS emulsions have larger median diameters (consequently smaller total interfacial area) than the stable polysorbate 80 emulsions at the same emulsifier concentration. This may be due to a dependency on the kinetics of droplet formation during manufacture, especially at concentrations below the CMC. Smaller droplets may be formed more easily in the polysorbate 80 formulations because of lower dynamic interfacial tensions. On the other hand, coalescence kinetics may be the most important factor. Assuming that equally small droplets are formed by the applied shearing forces regardless of the emulsifier, the polysorbate 80 film could be more resistant to rupture or desorption by shear-induced collisions during formation than the SDS film. The third, and perhaps most logical, explanation is that
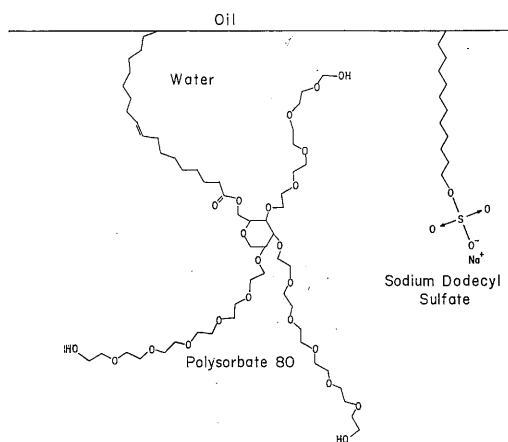


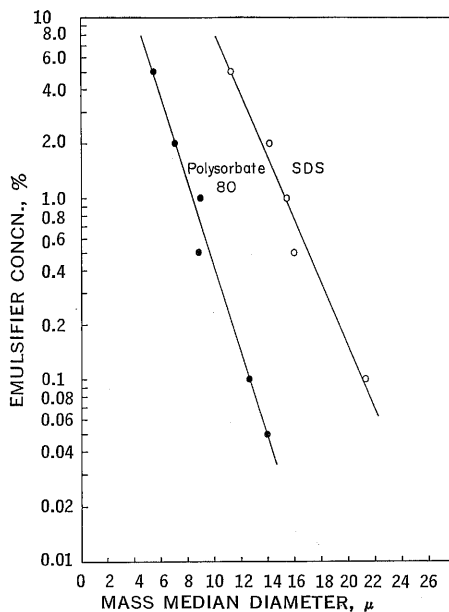Fig. 2.—Schematic representation of a typical



Fig. 3.—Mass median diameter of mineral oil/water emulsions as a function of emulsifier concentration (data from Table II).

SDS can stabilize larger droplets than polysorbate 80. The ionic character of SDS creates an electrical double layer at the oil/water interface adding an electrostatic repulsion factor in addition to the film barrier which reduces effective particle–particle collisions and inhibits coalescence. With this premise, the upper stable diameter limit is higher when SDS is the emulsifier.

As the emulsifier concentration is increased, the mass median diameters of both series tend to decrease (Table II). Increasing surfactant concentration leads to greater adsorption at the oil/water interface (8, 9). Increased surfactant adsorption stabilizes more total oil/water interfacial area; as a result, the particle size distributions have smaller median diameters. Logarithmic plots of surfactant concentration against mass median diameters are linear[6] for both the 61 and 65 series (Fig. 3).

The general equation for these curves is

$$\log C = \log C_0 - k d_m$$

where $k$ is the slope, $C$ is the surfactant concentration, and $\log C_0$ is the intercept. When $C = C_0$, the mass median diameter, $d_m$, is zero.[7] The relationship holds for the emulsions at all ages. For SDS, the equation of the least-squares regression line is

$$\log C = 2.68 - 0.174\, d_m$$

The correlation coefficient for the series is 0.985. In the case of polysorbate 80, the equation is

$$\log C = 2.01 - 0.237\, d_m$$

with a correlation coefficient of 0.991.

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[6] A plot of log surfactant concentration against log interfacial area (related to $1/d_{vs}$) is also linear and may be a more general empirical relationship.
[7] $C_0$ could have significance in terms of complete solubiliza-

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