

Aggregation in Oil-in-Water Emulsions

Effects of Dioctyl Sodium Sulfosuccinate Concentration

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A procedure was developed which is suitable for the study of aggregation in oil-in-water emulsions. It involves the preparation of a relatively monodispersed emulsion (droplet sizes around 1μ diameter) by the electrical dispersion technique and the determination of the distribution of sizes of the aggregates with the Coulter counter. The method was applied to the study of aggregation in hexadecane-in-water emulsions containing dioctyl sodium sulfosuccinate¹ (AOT) at varying concentrations. It was found that at low AOT concentrations ($\lesssim 0.1\%$) the emulsions were completely deaggregated. As the AOT concentration increased beyond this value, aggregation set in and progressively increased over the entire range of AOT concentration studied (up to 1.5%). In this system, aggregation was found to be completely reversible, the equilibrium being reached in all cases in a few days.

THE AGGREGATION of droplets in an emulsion or of particles in a suspension may alter the dynamic behavior of the system in at least two basic ways. First, the rate of creaming or sedimentation in dilute systems will be very much greater when aggregation is present (1). Since gravitational effects are much greater in creamed or sedimented systems, the rates of coalescence in emulsions and the caking rates in suspensions will be expected to take place more rapidly. Secondly, aggregation may affect the rheology (2) of the system. In general one would expect either thixotropic or pseudoplastic behavior in aggregating systems. The greatest amount of aggregation should be present at zero shear, and as the shear rate increases, deaggregation will increase as the forces of shear tend to pull apart the aggregates. Whether the system will be thixotropic or pseudoplastic depends upon how rapidly the aggregation-deaggregation equilibrium is established.

Since both the physical stability and flow properties of emulsions and suspensions are of great interest to the development pharmacist, a basic quantitative study of aggregation is essential. To the authors' knowledge, all past studies (1, 3, 4) of this problem for particles and droplets in the micron range or greater have not been of direct nature. Generally, creaming or sedimentation rates were followed and the aggregation behavior deduced in a qualitative or semiquantitative fashion. Because the situation in detail is very complex, to understand

truly the important factors involved in aggregation, the phenomenon itself should be studied as directly as possible.

The purpose of this communication is twofold. A main purpose is to present a procedure which is well suited to quantitative studies of emulsion aggregation. It involves the preparation of a relatively narrow size range oil-in-water emulsion and the rapid counting and sizing of the droplets as a function of time. Secondly, the method is applied to the investigation of the effects of the surfactant (dioctyl sodium sulfosuccinate) concentration on aggregation and deaggregation in hexadecane-in-water emulsions.

THEORY AND PAST EXPERIMENTS

Aggregation in emulsion systems is the formation of agglomerates without coalescence, i.e., without the actual rupture of the interfacial film and the subsequent formation of larger droplets. When contact of phases is prevented by a sufficiently high barrier, which may be either electrical or steric in nature, coalescence can be prevented. However, aggregation may take place in these systems if the attractive droplet-droplet forces² predominate at long range.

This long range attraction may be looked upon as arising from either or both of two distinct sources. First of all, two droplets will attract each other appreciably (attractive energies $\gtrsim kT$, where k = Boltzmann's constant and T = absolute temperature) even at distances large compared to molecular dimensions. These forces are the London dispersion forces accentuated as a result of the integration of the molecule-molecule interactions over the volumes of the two droplets. Studies both theoretical (5, 6) and experimental (3) clearly expose the existence of these macroscopic forces. The second contribution to droplet-droplet attraction might arise if, in the region between the two particles, the interfacial film of one droplet attracts the film of the other. This would be expected to be most important when the

² These may include interactions involving adsorbed films when surfactants are present or if surface solvation is important.

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¹ Marketed as Aerosol OT by American Cyanamid Co.

adsorbed surfactant films on oil droplets in water expose relatively hydrophobic and/or nonionizing functional groups toward the water phase. "Soluble" surfactants which, when adsorbed onto oil droplets, are able to expose an abundance of hydrophilic groups to the water should, in general, not contribute to droplet-droplet attraction, and therefore aggregation. On the contrary, by means of their charges or/and hydrophilic bulk, they should contribute to the prevention of close approach of the droplets.

If, then, the repulsive forces (electrical or steric) are not as long ranged as the above attractive forces, the droplets may find themselves energetically more comfortable in the aggregated states.

Cockbain (1) has interpreted his creaming rate studies of benzene- and paraffin-in-water emulsions in the following way: conventional low molecular weight ionic stabilizers, both cationic and anionic, prevent both coalescence and aggregation at low stabilizer concentrations ($\lesssim 0.1\%$ or so), but at higher concentrations (~ 0.1 to 1% or so) aggregation occurs in all cases. At much higher concentrations the droplets deaggregate in some cases. Because without exception aggregation was found with all surfactants studied, the practical importance of Cockbain's observations are clear.

EXPERIMENTAL

General Considerations.—The following novel measures were taken to permit a direct study of aggregation and deaggregation. To eliminate as much as possible the effects of the distribution of sizes, narrow size range emulsions were prepared by the high voltage electrical dispersion method described by Nawab and Mason (7). To follow aggregation, the Coulter counter³ (8) was employed to determine both droplet concentration and size distribution changes as a function of time.

Preparation of Emulsions.—Hexadecane was redistilled Eastman practical grade. The American Cyanamid "100% pure" Aerosol OT (AOT) was specially purified (8) by fractional precipitation from methanol and water-methanol solvent mixture. The water used was doubly distilled.

Hexadecane containing 2.0% by weight AOT was placed in a syringe, as shown in Fig. 1. A No. 25 needle, with the tip evenly cut off perpendicular to its axis, permitted a flow of about 20 drops per second with no applied voltage to the needle. The hexadecane solution was sprayed onto a 1% aqueous AOT solution with 6 kv. applied to the needle. The aqueous solution was grounded as shown and was agitated with a magnetic stirrer. The needle tip-to-solution surface distance was 2.5 cm. These conditions were selected to give the best appearing spray. The spraying was continued until about 40% by volume hexadecane had been emulsified. This was the stock emulsion used in the studies. It was kept in a polystyrene bottle at 30°C. in a rotating wheel type constant temperature bath which provided gentle agitation.

Calibration and Use of the Coulter Counter.—The 30- μ aperture was used throughout these studies. The threshold scale of the instrument was cali-

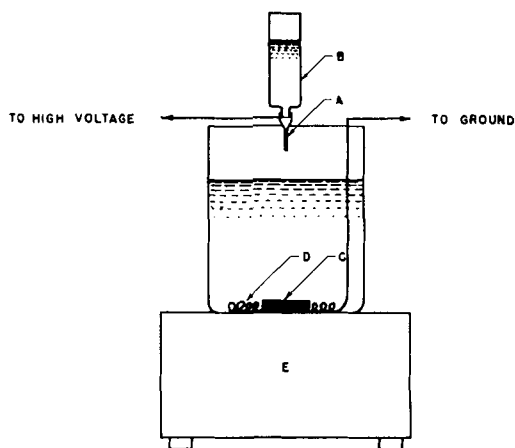


Fig. 1.—Apparatus for the preparation of emulsions by electrical dispersion. A, hypodermic needle; B, syringe; C, stirring bar; D, grounding coil; E, stirrer.

brated with polystyrene latices,⁴ 1.17 and 1.83 μ diameters,⁵ at all sensitivity and attenuator settings used in our studies except for those corresponding to low sensitivities. These latter settings were calibrated by the data themselves by determining the scale factors which gave the same count *vs.* threshold values. It was assumed that the pulse height was proportional to the volume of the particle passing through the aperture. This is the usual assumption which may be justified theoretically in an approximate manner. Also, employing blood cells as a third calibration point this assumption has been approximately verified by us in at least one instance.

In Fig. 2, results of a typical calibration run of a mixture of 1.83 and 1.17 μ latices in 0.90% saline solution are shown. The curve shown is the derivative⁶ of the cumulative count curve (counts *vs.* threshold curve), which is the one directly obtained with the instrument. Since the standard deviation of the latex sizes was known to be considerably less than the peak widths and since these particles did not appear to be agglomerated to any extent, the peak widths are believed to be a measure of the resolving power of the instrument. Thus, it is apparent that the resolving power of the instrument was about 0.2 μ in this range.

Procedure for Deaggregation Studies.—The stock emulsion (see above) was diluted to 1.0 and 2.0% by volume hexadecane with water containing varying amounts of AOT so that the final emulsions contained AOT ranging from about 0.05 to 1.5% by weight. About 10 ml. of these emulsions was pipetted into leak-tight vials of about 15-ml. capacity. The vials were fixed to wheels rotating at 30 r.p.m. in a constant temperature bath maintained at 30°C.

⁴ Kindly supplied by J. W. Vanderhoff, Dow Chemical Co., Midland, Mich.

⁵ These are electron microscope values. It was assumed that the aqueous suspension sizes were the same.

⁶ These and those for the emulsions were obtained by numerical difference methods. While the distribution "curves" should really be histograms for this reason, intervals taken on the x-axis were generally small enough so that the "smoothing" introduced little error for our purposes.

³ Coulter Industrial Sales, Elmhurst, Ill.

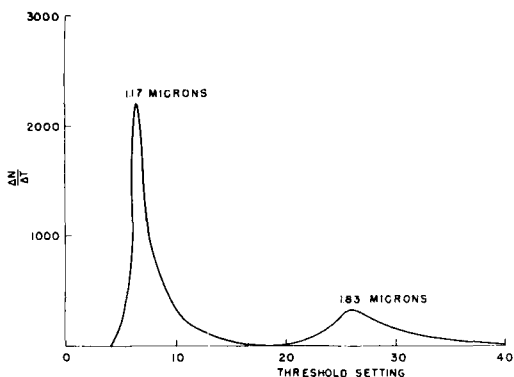


Fig. 2.—Differential count curve for a mixture of 1.17 and 1.83 μ diameter polystyrene spheres obtained with the Coulter counter. The ordinate is the derivative of the cumulative count curve with respect to the threshold setting.

Samples were removed from time to time and the size analyses with the Coulter counter carried out in the following way. The 1.0 and 2.0% hexadecane emulsions were diluted by about a factor of 1000 to provide a low enough concentration suitable for the Counter. To accomplish this without sacrifice of volumetric accuracy, the dilution was carried out in two steps, *viz.*, 1 to 10 with water followed by a 1 to 100 in 0.90% saline.

Procedure for Aggregation Studies.—Emulsions in which aggregation was completely absent (AOT concentrations $\geq 0.09\%$) were aggregated to varying degrees by addition of solid AOT. These were handled in the same manner as in the deaggregation experiments. Samples were taken over a period of about 10 days.

RESULTS

Figure 3 gives the number-diameter distribution curve for the completely deaggregated emulsion. Complete deaggregation was observed for the 1.0 and 2.0% emulsions when the AOT concentration was 0.09% or less. This curve shows the remarkable ability of the high voltage technique to prepare

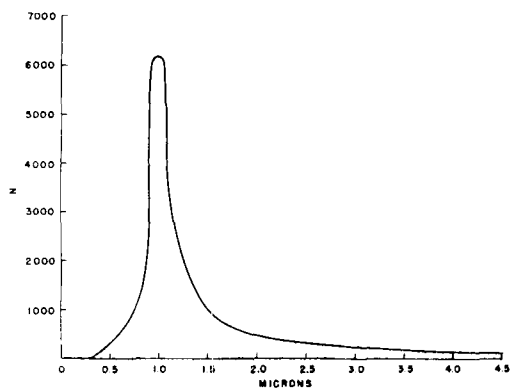


Fig. 3.—The droplet diameter distribution curve for the completely deaggregated hexadecane-in-water emulsion prepared by the electrical dispersion method.

emulsions with a very high population of essentially a single size. It should be emphasized, however, and it is apparent from the curve, that the mass distribution curve will appear considerably different, being much broader. In all cases, at maximum deaggregation the 0–5 μ range accounted for only about 50% of the total hexadecane used in the preparation. Most of this discrepancy could be accounted for by extrapolation of the distribution curve to about 10 μ . Presumably, some of these large droplets were formed not in the spraying but from the portions of the hexadecane which dropped from the needle prior to and after the high voltage was applied and which were subsequently emulsified by the stirring.

Figures 4–7 give the distribution curves showing deaggregation as a function of time for the 1.0% emulsions at different AOT concentrations. After about 10 days, aggregation-deaggregation equilibrium was apparently reached in all cases. Distribution curves obtained at later times did not show further deaggregation. It is noteworthy that only after the stock emulsion had itself equilibrated for about 1 week did the results of the deaggregation experiments become reproducible. Apparently the redistribution kinetics of the AOT was very slow in this concentrated and highly aggregated system.

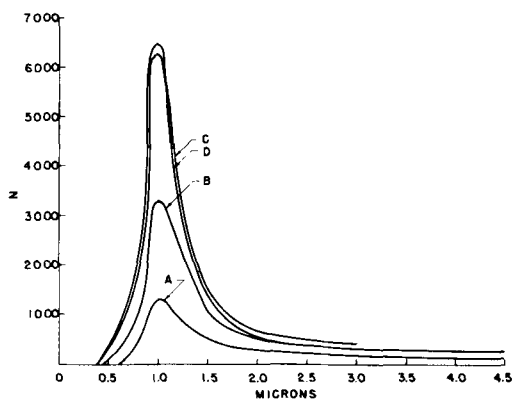


Fig. 4.—Deaggregation in 1.0% hexadecane emulsion containing 0.045% AOT when diluted from stock emulsion. A, initial; B, 3 days; C, 6 days; D, 9 to 12 days.

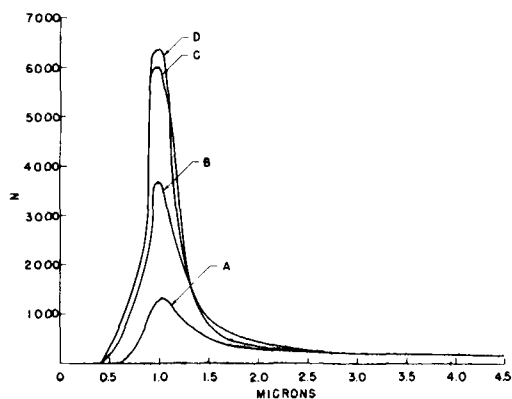


Fig. 5.—Deaggregation in a 1.0% hexadecane emulsion containing 0.09% AOT. A, initial; B, 3 days; C, 6 days; D, 9 to 12 days.

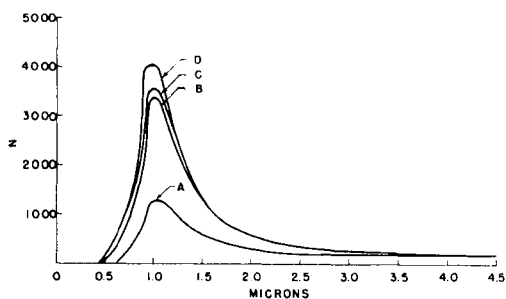


Fig. 6.—Deaggregation in a 1.0% hexadecane emulsion containing 0.50% AOT. A, initial; B, 3 days; C, 6 days; D, 9 to 12 days.

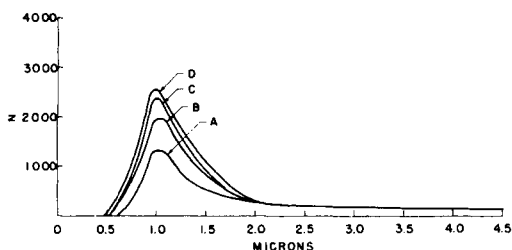


Fig. 7.—Deaggregation in a 1.0% hexadecane emulsion containing 1% AOT. A, initial; B, 3 days; C, 6 days; D, 9 to 12 days.

It can be seen from Figs. 4-7 that during the initial periods of deaggregation not all of the final mass of the completely deaggregated emulsion can be found in the 0-5 μ range. This is in contrast to the aggregation data for the 2.0% emulsions summarized in Figs. 8 to 11, in which cases the disappearance of the single particles in the 1 μ size region may be accounted for by the increases in concentration of particles in the 1.5 to 4 μ size range. The difference in behavior may be explained by the existence of very large aggregates in the stock emulsion. These would be expected to deaggregate much more slowly than the smaller aggregates.

That aggregation-deaggregation was completely reversible was demonstrated by the following experiment. A completely deaggregated 2.0% hexadecane

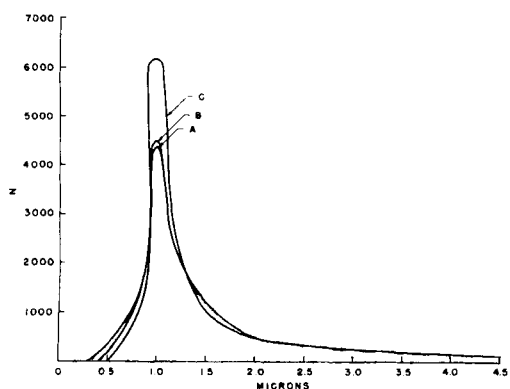


Fig. 8.—Aggregation in an initially completely deaggregated 2.0% hexadecane emulsion containing 0.18% AOT. C, initial; B, 2 days; A, 4 to 7 days.

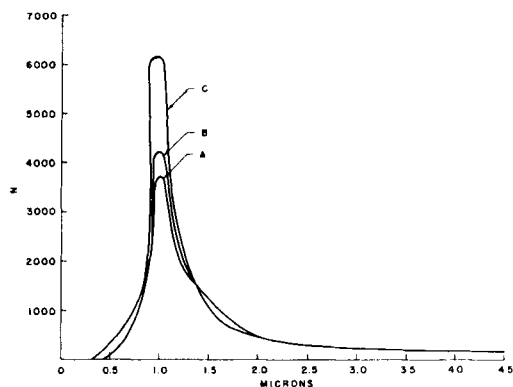


Fig. 9.—Aggregation in a 2.0% hexadecane emulsion containing 0.29% AOT. C, initial; B, 2 days; A, 4 to 7 days.

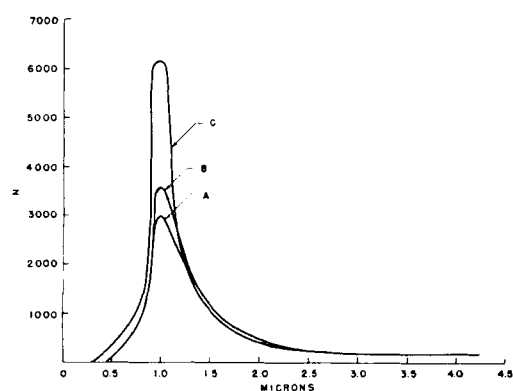


Fig. 10.—Aggregation in a 2.0% hexadecane emulsion containing 0.49% AOT. C, initial; B, 2 days; A, 4 to 7 days.

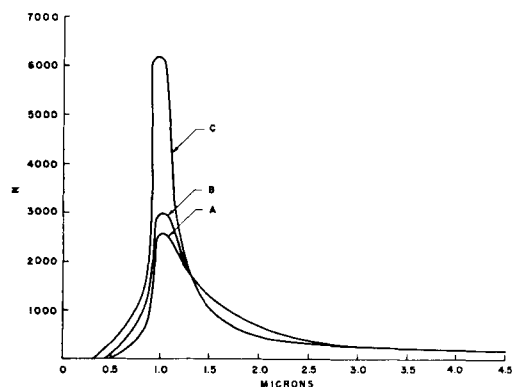


Fig. 11.—Aggregation in a 2.0% hexadecane emulsion containing 0.99% AOT. C, initial; B, 2 days; A, 4 to 7 days.

emulsion containing 0.09% AOT was partially aggregated by addition of enough AOT so that the AOT concentration was 0.18%. This emulsion was then diluted by a factor of two with water. The initial and final emulsions gave identical size distribution curves.

Earlier in these studies there was some concern as to whether the degree of aggregation in the 1.0 and 2.0% emulsions may have been altered by the dilution steps (see *Procedure*) themselves. Specifically, the questions were (a) did the first dilution step deaggregate the emulsions to any extent and (b) did the high salt concentration in the second step of dilution induce coalescence, further aggregation, or deaggregation? By varying the time of mixing from a few minutes to 30 minutes, no effect of the first dilution step on the results was observed. Also for periods up to 1 hour, no change in the counting was observed after the second dilution. Furthermore, the manner of introduction of sample and the degree of stirring during the introduction was unimportant for the second dilution. Thus, true pictures of the 1.0 and 2.0% emulsions were very likely obtained by the procedure employed.

DISCUSSION

Method.—The above results demonstrate that this procedure is suitable for quantitative aggregation studies. It should prove to be useful and practical in the evaluation of additives as to their ability to prevent aggregation and coalescence. The relative rapidity of the measurements permits the determination of the distribution of sizes within minutes. This is not only convenient but allows studies of relatively rapidly changing systems with apparently little disturbance to the systems themselves.

Mechanism of Aggregation in Hexadecane Emulsions Stabilized by AOT.—Cockbain (1) has proposed that aggregation in this system results possibly from polymolecular adsorption of the surfactant on the droplet surface. He suggests that after the formation of a monolayer, which exposes primarily hydrophilic groups to the aqueous phase, a second layer begins in which the molecules are oriented in the reverse direction, i.e., with the hydrophobic groups oriented toward the aqueous phase. Thus, interactions between these hydrophobic portions of the second layer of the droplets may account for aggregation.

While the above picture may be the correct one, the following alternative mechanism similar to that of Greiner and Vold (4) may be proposed which does not invoke the second and hydrophobic layer concept. At sufficiently low surfactant concentrations (<0.1% AOT), a monolayer or less of surfactant is adsorbed and aggregation is prevented by the repulsive long range interaction of the electrical double layers around the droplets. The double layer arises because the sulfonate ion is preferentially adsorbed and the sodium ions are distributed according to the Poisson-Boltzmann equation. If the counterion (Na^+) concentration is low enough, the thickness of the electrical double layer will be great and thus long range repulsion will prevail and cancel out the London attractive forces to within about kT for all interparticle distances. Thus aggregation is prevented at low AOT concentrations.

Now as the AOT concentration increases, the Na^+ concentration increases in the system. This increase in Na^+ concentration is approximately equal

to the AOT concentration increase up to the critical micelle concentration (CMC), beyond which the increase in Na^+ will be slower because the dissociation of the Na^+ from the micelles will be limited. As the Na^+ concentration increases, the thickness of the double layer will decrease by at least, approximately, the inverse square root of the Na^+ concentration. When the thickness of this electrical layer is sufficiently reduced so that the range of the repulsive forces have become sufficiently reduced, the London attractive forces will predominate by more than kT at some interparticle distances. This is the secondary minimum phenomenon (3, 5, 6). Under these conditions aggregation may take place. The depth of this minimum and, hence, the forces of particle-particle attraction will increase with increasing Na^+ concentration. Thus aggregation increases with increase in the AOT concentration.

Recently Schenkel and Kitchener (3) studied the aggregation in water of 10 μ diameter polystyrene spheres, the surfaces of which were fully sulfonated chemically (therefore not unlike our system electrically). They found that aggregation (increased sedimentation rate) became important when the added potassium nitrate concentration exceeded about $3 \times 10^{-4} M$. Aggregation increased to about $4 \times 10^{-3} M$ salt. These investigators point out that this behavior is in accordance with the theoretical predictions of Verwey and Overbeek (6) that coarse particles (micron range) should exhibit a secondary minimum of about 6 kT deep in $1 \times 10^{-4} M$ one-to-one electrolyte. These electrolyte concentrations are approximately in the same range as the Na^+ concentration at which aggregation begins in our hexadecane-water system. In our studies, the Na^+ concentrations were actually a little greater, viz., about 2 to $4 \times 10^{-3} M$ in Na^+ . So, if anything, the conditions in our systems were actually somewhat more conducive to aggregation. Perhaps a smaller London constant is appropriate for the hexadecane-water system. This may account for the difference.

The above discussion shows that it is very likely that the aggregation phenomenon may be basically an electrically induced one and that it appears to be unnecessary to postulate film-film attraction. It is quite possible that both mechanisms are important, since increasing ionic strength invariably increases the tendency for the aggregation of the surfactant itself. More basic studies are needed to provide definite answers to this problem.

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