

# Deaggregation in Oil-in-Water Emulsions I

## Influence of Electrolytes

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An emulsion system of 2 per cent hexadecane in water stabilized by 0.09 per cent dioctyl sodium sulfosuccinate was prepared in an initially highly aggregated state. The rate of deaggregation of this system was found to be constant for approximately 20 days and influenced by electrolytes and temperature. In the presence of various sodium salts, deaggregation rate was reduced. The degree of reduction was found to be dependent upon the sodium ion concentration, an indication that the counter ion effect reduced the particle charge, resulting in a reduction of repulsive forces between particles. Rate of deaggregation increased as the temperature was increased, and the relative increase in rate of deaggregation was found to be greater in those systems containing higher electrolyte concentrations.

WHEN THE PARTICLES of a dispersion approach each other, they become subject to two types of forces—repulsive (electrical or steric) and attractive (London dispersion forces). If the repulsive forces are not so long ranged as the attractive forces, the particles may assume an aggregated state. Such aggregates can be redispersed by a moderate rate of shear, but their presence in the system may alter certain physical properties of the system, such as sedimentation rate, rate of coalescence of an emulsion, and rheology (1, 2).

The addition of electrolytes to emulsions or suspensions has been observed to enhance the aggregation tendency of the particles, evidenced by creaming or sedimentation rates (2-4). This effect is attributed to a reduction in the zeta potential due to an increased concentration of counter ions in the diffuse double layer, thus rendering attractive forces more favorable and/or decreasing the effective soap concentration for aggregation to occur due to film-film attractions. In view of the complex nature of the aggregation-deaggregation phenomenon, it should be studied as directly as possible.

Recently, Higuchi *et al.* (5) reported a technique for the direct study of aggregation and deaggregation in hexadecane in water systems. Relatively narrow size range emulsions were prepared, and the droplets were counted rapidly and sized as a function of time. A reversible deaggregation-aggregation cycle was observed and found dependent upon the concentration of dioctyl sodium sulfosuccinate<sup>1</sup> (AOT) in the sys-

tem. It was felt that the application of this technique to the study of deaggregation in similar systems would provide further information on the nature of particle interactions in dispersions. Of particular interest in this study was the influence of electrolytes on the deaggregation rate of initially highly aggregated hexadecane in water emulsions.

### EXPERIMENTAL

**Materials.**—Components of the emulsion system selected for this study were hexadecane, AOT, and water. The hexadecane was Eastman practical grade, purified by redistillation under reduced pressure. AOT ("100% pure") was purified further by the fractional precipitation method (6)<sup>2</sup> from methanol and water-methanol solvent mixture. The fraction selected for use was that shown capable of solubilizing 40-50 molecules of water (7). Water used was doubly distilled from permanganate in a glass apparatus. All electrolytes employed in this study were analytical reagent grade quality.

**Procedure.**—Emulsions were prepared following the method previously described (5) with a slight modification. A stock emulsion of 40% by volume hexadecane was prepared by the electrical dispersion method described by Nawab and Mason (8). Exactly 1.0 Gm. of AOT was dissolved in 50 ml. of *n*-hexadecane to make the dispersed phase, while another 1.0 Gm. of AOT was dissolved in 60 ml. of water to make the continuous phase. The continuous phase was placed in a beaker with a grounded contact, and exactly 40 ml. of the dispersed phase was added in portions through a 10-ml. syringe fitted with a 25-gauge needle, the tip evenly cut perpendicular to its axis, to which 6 kv. was applied. The height of the liquid in the syringe was kept at a level between the 8-10 ml. mark in order to obtain a steady flow rate, and the distance between the tip of the needle and the surface of the continuous phase was kept at 2.5 cm. These conditions provided the best appearing spray. The emulsion was agitated gently during preparation by means of a magnetic stirrer.

The major portion of particle size obtained by this method was in the order of 1  $\mu$  in diameter. The

<sup>2</sup> With a slight modification of the procedure by Higuchi, W., and Misra, J., private communication.

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<sup>1</sup> Marketed as Aerosol OT by the American Cyanamid Co., Pearl River, N. Y.

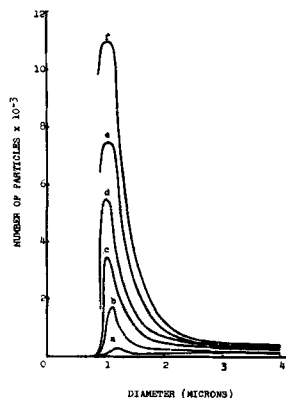


Fig. 1.—Droplet size distribution in a 2% *n*-hexadecane emulsion containing 0.09% AOT. Key: a, initial; b, 4 days; c, 7 days; d, 11 days; e, 15 days; f, 24 days.

stock emulsion was placed in a polyethylene bottle and was aged for 1 week in a rotating wheel type constant-temperature bath at 30° prior to dilution.

For a given experiment the stock emulsion was diluted 1–20 by volume to obtain a 2% *n*-hexadecane emulsion containing 0.09% AOT. Sufficient quantities of concentrated aqueous solutions of the various electrolytes to give the desired final concentration of electrolyte in the emulsion were added to the system during the dilution of the stock emulsion. The concentration of electrolytes in the emulsion varied from  $5 \times 10^{-4}$  to  $3.4 \times 10^{-2}$  *M*. The samples containing the various concentrations of electrolytes were placed in 15-ml. glass vials and tumbled gently in the constant-temperature bath at 30° for a 12–25-day period. Experiments in which sodium chloride was employed as electrolyte were also carried out at 24°, 37.5°, and 45°. The volume in each vial was the same (13 ml.). For each experimental run, all emulsions studied were prepared by dilution of the same stock emulsion. Deaggregation of the particles was followed by the taking of measurements at various intervals of time during the period of tumbling. The time of the dilution of the stock emulsion and addition of electrolytes was considered zero time.

**Measurements.**—Exactly 1 ml. of emulsion was diluted to 100 ml. by addition of water; then 1, 2, 5, or 10 ml.<sup>3</sup> of this dilution was again diluted to 100 ml. by addition of 0.90% saline solution. It has been shown previously that this dilution technique has no significant effect on aggregation or deaggregation in these systems during the course of the size analysis (5). Size analyses were obtained with the Coulter counter<sup>4</sup> employing a 50- $\mu$  aperture tube which had been calibrated with polystyrene latices,<sup>5</sup> 1.17  $\mu$  and 1.305  $\mu$  in diameter, at all sensitivity and attenuator settings used in these studies.

## RESULTS AND DISCUSSION

**Deaggregation.**—Size analysis data obtained for the standard hexadecane in water emulsion used in these studies are shown in Fig. 1, where the number of particles has been plotted against diameter dis-

tribution. The various curves correspond to the particle size distribution within the system at different intervals of time under conditions of gentle tumbling in a constant-temperature bath maintained at 30°. Deaggregation in the system is denoted by the increasing number of particles approximately 1  $\mu$  in diameter which corresponds to the mono-dispersed droplet diameter. This parameter of the system is referred to as the peak population and is used as an index to deaggregation throughout these studies. It should also be noted that although the 50- $\mu$  aperture tube employed in these studies did not permit complete characterization of the particle population after extended periods of deaggregation, in all instances the peak population could be identified accurately. It was felt that inasmuch as similar emulsion systems had been completely characterized previously with a 30- $\mu$  aperture tube (5), advantage could be taken of the increased ease and convenience of using a 50- $\mu$  aperture tube for this work.

That the rate of deaggregation of the initially highly aggregated emulsion system was constant for a significant period of time is shown by Fig. 2, where peak population is plotted against time of deaggregation. Under the experimental conditions employed, the linear relationship held to about 20 days, after which the rate of deaggregation decreased. In all experimental emulsion systems studied, the linear relationship between peak population and time was obtained over the period of observation.

### Inhibition of Deaggregation by Electrolytes.—

Since deaggregation of these emulsions is indicative of a re-equilibration in the state of aggregation of the system upon dilution and is the result of the altered balance between repulsive and attractive forces due to dilution, it was felt that an investigation of factors which modify deaggregation rate would provide further information on the nature of particle interactions in these systems. Of prime interest was the effect of electrolytes upon the deaggregation

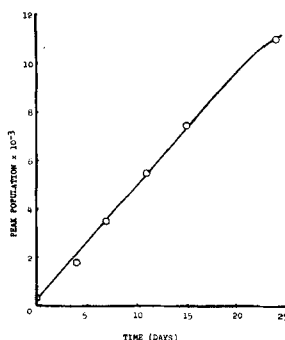


Fig. 2.—Deaggregation of 2% *n*-hexadecane emulsion containing 0.09% AOT as a function of time.

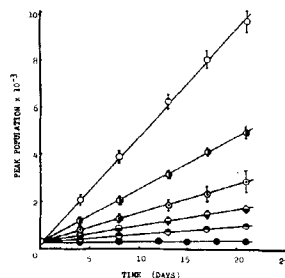


Fig. 3.—Influence of NaCl concentration on the rate of deaggregation. Key: O, no NaCl (control); ●,  $5 \times 10^{-4}$  *M*; ○,  $1 \times 10^{-3}$  *M*; ●,  $1.5 \times 10^{-3}$  *M*; ○,  $2 \times 10^{-3}$  *M*; ●,  $4 \times 10^{-3}$  *M*.

<sup>3</sup> The volume, taken from the first dilution, varied according to the period of tumbling and the amount of inhibitor (electrolytes) present in the system.

<sup>4</sup> Coulter Industrial Sales, Chicago, Ill.

<sup>5</sup> Kindly supplied by J. W. Vanderhoff, Dow Chemical Co., Midland, Mich.

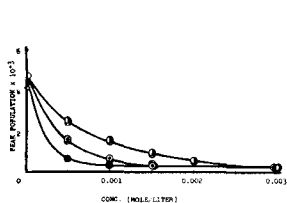


Fig. 4.—Influence of various electrolytes on peak population after deaggregation for a 10-day period. Key: O, NaCl;  $\bullet$ , NaH<sub>2</sub>PO<sub>4</sub>;  $\circ$ , Na<sub>2</sub>HPO<sub>4</sub>;  $\ominus$ , Na<sub>2</sub>SO<sub>4</sub>;  $\bullet$ , Na citrate.

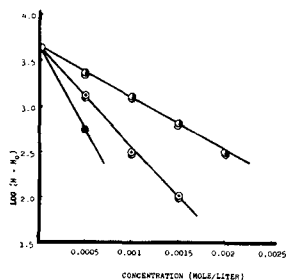


Fig. 5.—Plot of  $\log(H - H_0)$  at 10 days against concentration of electrolyte. Key: O, NaCl;  $\bullet$ , NaH<sub>2</sub>PO<sub>4</sub>;  $\circ$ , Na<sub>2</sub>HPO<sub>4</sub>;  $\ominus$ , Na<sub>2</sub>SO<sub>4</sub>;  $\bullet$ , sodium citrate.

process. Five salts were chosen for study—NaCl, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and sodium citrate. These salts were added to the standard emulsion, and deaggregation was followed for a 12–21 day period.

The influence of various concentrations of NaCl on deaggregation is shown in Fig. 3, where peak population is plotted against time for a series of emulsions containing concentrations of NaCl from  $5 \times 10^{-4}$  to  $4 \times 10^{-3} M$ . These data are representative of the type of data obtained with all electrolytes. Each point represents an average of five determinations, with the standard deviation indicated by the line extended through the point. An exception was in studying those emulsions in which deaggregation essentially was inhibited completely where duplicate determinations were made because of the highly reproducible experimental results. A NaCl concentration of  $4 \times 10^{-3} M$  in the emulsion resulted in complete inhibition of deaggregation. It is interesting that an increase in the concentration of NaCl above  $4 \times 10^{-3} M$  did not aggregate the system further, an indication that aggregation was essentially complete initially in the dilute emulsion under the experimental conditions employed. The NaCl concentration was increased up to  $3.3 \times 10^{-2} M$  (not plotted) without producing a further decrease in the rate of deaggregation.

To demonstrate that inhibition of deaggregation did not involve instability of the emulsion droplets, two samples of emulsion which showed complete inhibition for a period of 10 days (one contained  $4 \times 10^{-3} M$  NaCl, and the other contained  $1.5 \times 10^{-3} M$  Na<sub>2</sub>HPO<sub>4</sub>) were diluted to twice their volume with 0.09% AOT solution. After a period of 2–5 days, the samples showed deaggregation again.

In Fig. 4 peak population after a 10-day deaggregation period is plotted against electrolyte concentration for the five electrolytes used in this study. The inhibition of deaggregation is not only affected by the concentration of an electrolyte but also by the valency of the anion for the series of sodium salts. This is to be expected since the sodium ion represents the counter ion for AOT stabilized droplets, and at equivalent molar concentrations di- and trivalent

anionic salts would give rise to higher sodium ion concentration. Figure 4 shows that peak populations for systems containing  $5 \times 10^{-4} M$  Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> are approximately the same as for systems containing  $1 \times 10^{-3} M$  NaCl or NaH<sub>2</sub>PO<sub>4</sub>. A similar qualitative relationship between divalent anionic sodium salts at  $1 \times 10^{-3} M$  and univalent anionic salts at  $2 \times 10^{-3} M$  also holds.

The data of Fig. 4 also may be plotted in a logarithmic form. Such plots are shown in Fig. 5, where the logarithm of the peak population after 10 days ( $H$ ) less the initial peak population ( $H_0$ ) is plotted against concentration for the various salts. The lines obtained may be represented by an empirical equation of the type

$$H = A e^{-Bc} + H_0 \quad (\text{Eq. 1})$$

where  $A$  and  $B$  are constants. The significance of this equation is not clearly established at the present time.

Over the concentration range employed with sodium citrate, essentially complete inhibition of deaggregation was observed at all but one concentration ( $5 \times 10^{-4} M$ ) of this electrolyte. If linearity can be assumed for this electrolyte in this type of plot, it is interesting to compare the slopes of the lines obtained. The slope for NaCl and NaH<sub>2</sub>PO<sub>4</sub> is  $-5.7 \times 10^4$ ; for Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>, it is  $-11 \times 10^4$ ; and for sodium citrate, it is  $-18 \times 10^4$ . Thus, the ratios of the slopes for the various electrolytes are approximately 1:2:3 for salts giving rise to one, two, and three sodium ions per molecule. In a qualitative fashion, this would imply strongly that the major effect of these electrolytes in reducing deaggregation rate is related to the sodium ion concentration which they contribute to the medium. On this basis, it is reasonable to conclude that reduction in electrokinetic potential of the emulsified droplets is at least in part responsible for the observed inhibition of deaggregation in these systems.

**Effect of Temperature.**—The effect of temperature on the rate of deaggregation of the system was studied employing NaCl as the electrolyte at temperatures of 24°, 30°, and 37.5°. Deaggregation of the standard emulsion was also followed at 21° and 45°. It was observed that sodium chloride became

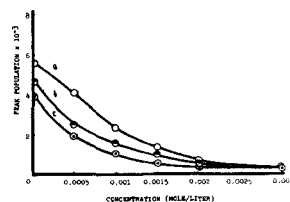


Fig. 6.—Influence of temperature on deaggregation rate in the presence of various concentrations of NaCl. Key: O, at 37.5° C.;  $\bullet$ , at 30° C.;  $\circ$ , at 24° C.

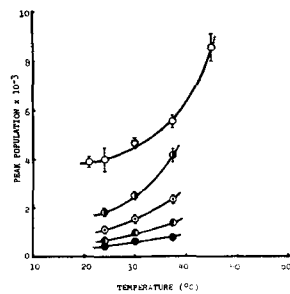


Fig. 7.—Plot of peak population after 10-day deaggregation period against temperature in the presence of NaCl. Key: O, no NaCl (control);  $\bullet$ ,  $5 \times 10^{-4} M$ ;  $\circ$ ,  $1 \times 10^{-4} M$ ;  $\ominus$ ,  $1.5 \times 10^{-3} M$ ;  $\bullet$ ,  $2 \times 10^{-3} M$ .

TABLE I.—RELATIVE RATE OF DEAGGREGATION AT VARIOUS NaCl CONCENTRATIONS

NaCl Concn., <i>M</i>	Relative Rate of Deaggregation <sup>a</sup>	
	30° C.	37.5° C.
0	1.2	1.4
5 × 10 <sup>-4</sup>	1.2	1.4
1 × 10 <sup>-3</sup>	1.6	2.6
1.5 × 10 <sup>-3</sup>	2.0	3.2
2 × 10 <sup>-3</sup>	2.3	3.0

<sup>a</sup> Ratio of rate at temperature of rate at 24° C.

less effective in inhibiting deaggregation of the emulsion upon increasing the temperature. This is shown in Fig. 6, where peak population has been plotted against concentration of NaCl for the three temperatures studied. At 24°, the rate of deaggregation is less than 30°, but the empirical relationship between peak population and electrolyte concentration of Eq. 1 held. The rate of deaggregation increased at 37.5°; the curve shows that some deviation from the exponential relationship of Eq. 1 occurred, particularly at low electrolyte concentration. The relationship between deaggregation rate and temperature for control systems and those containing electrolyte is shown more clearly in Fig. 7, where peak population after 10 days is shown at the several temperatures for systems containing different amounts of electrolyte. At zero and low electrolyte concentrations, the increase in rate of deaggregation as the temperature is raised can be seen readily. It is not quite so apparent from the figure for those systems containing higher concentrations of NaCl. However, if the rate of deaggregation ( $H - H_0$  at 10 days) at 24° is taken as reference point or the relative increase in rate at 30° and 37.5°, the systems containing higher concentrations of NaCl experience a greater increase in relative rate of deaggregation as temperature is increased. This is apparent in Table I.

The rate of deaggregation of the standard emulsion was also determined at 21° and 45°. Attempts to determine deaggregation rates for electrolyte containing systems at 45° were unsuccessful. Reversibility of the inhibition could not be demonstrated, and physical evidence of coalescence was apparent in these systems. If deaggregation may be looked upon as a rate process dependent upon the relative repulsive and attractive forces between particles, the system could possibly adhere to an Arrhenius type relationship. However, Arrhenius type plots were nonlinear, an indication that the mechanism of deaggregation in the system may not be constant over the temperature range studied. Qualitatively, these observations would be in agreement with previous studies on micelle formation (9, 10), in which it has been shown that critical

micelle concentration increases with increasing temperature, with a marked increase above a temperature of 40°. The effect of sodium chloride in decreasing critical micelle concentration has also been shown to diminish with increasing temperature (11). Since the interfacial behavior of AOT in these systems can be attributed to the same physical properties associated with micelle formation, the AOT interfacial film can be expected to vary in certain of its properties as temperature is increased. This film and its properties are implicated clearly in particle interactions; thus, the deaggregation process could be expected to show a variation with temperature.

The possibility of a relationship between particle interactions and micelle formation exists in these systems; therefore, the critical micelle concentration for the purified AOT used in these studies was determined. Two methods of measurement were employed: surface tension determination by the ring method and absorbance determination using a pinacyanol chloride concentration of  $1 \times 10^{-4}$  *M* solution. Both methods gave a value of  $2.5 \times 10^{-3}$  *M*, in agreement with the value reported by Dixon and co-workers (6). In addition, the concentration of NaCl necessary in an 0.09% ( $2 \times 10^{-3}$  *M*) solution of AOT to induce micelle formation was determined by the surface tension method and found to be  $3.1 \times 10^{-3}$  *M*. All determinations were made at a room temperature of approximately 26°.

It is interesting that, at all temperatures studied, essentially complete inhibition of deaggregation could be produced with a NaCl concentration of  $3 \times 10^{-3}$  *M*. (See Fig. 6.) In this concentration range of NaCl, one could expect micellar properties to appear in the system. If film-film interactions occur, they would be enhanced by this behavior. However, further work is necessary to establish whether micelles do indeed form in this system under the conditions of the experiment.

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