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by

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The reversible aggregation and disaggregation of oil particles (benzene or paraffin hydrocarbons) in soap-stabilized emulsions has been studied, employing rate of creaming data as the chief criterion of aggregation. In all the systems examined, aggregation of the oil particles commences at a soap concentration equal to, or a little greater than, the critical micellar concentration of the soap. In many cases, states of maximum and minimum particle aggregation occur at soap concentrations considerably higher than the critical micellar concentration. These maxima and minima are most pronounced with benzene as the disperse phase and unbranched hydrocarbon chain soaps as stabilizer. The results are explained on the basis of polymolecular adsorption which is considered to occur at soap concentrations greater than the critical micellar value.

A correlation exists between the effect of aliphatic alcohols (hydrocarbon chain $< C_6$) in reducing the concentration of soap required for aggregation of the emulsion particles and their effect on the critical micellar concentration of soaps. Addition of inorganic salts prevents disaggregation of the emulsion particles and reduces the soap concentration at which aggregation commences. The latter process is independent of the nature of the salt anion when an anionic soap is used as stabilizer.

Few detailed investigations of particle aggregation in emulsion systems appear to have been carried out, in spite of the practical importance and theoretical interest of the process. In the present work, the rate of creaming of emulsions and the cream volume after a suitable time period have been taken as the main criterion of particle aggregation. Microscopic examination of the emulsions and qualitative observations of turbidity changes in the sera (" skim ") after creaming have been made, in most cases, for comparison with the creaming data.

None of these measurements would be expected to give more than semi-quantitative information concerning the aggregate size distribution in the emulsions. For example, the rate of creaming will be affected, presumably, by the structure of the aggregates and the amount of continuous phase which moves with them, as for suspensions. In addition, it is likely to be influenced by the "sedimentation" potential of the system. The main object of the present investigation, however, was to determine the effect of the nature and concentration of the stabilizing agent on the aggregation of emulsion particles. Preliminary experiments showed that small changes in concentration of a given agent often caused very large changes in the degree of aggregation, enabling the concentration of agent necessary for particle aggregation or dispersion to be defined within narrow limits. (The terms aggregation or cluster formation do not include particle coalescence; evidence will be given that in most of the systems studied coalescence is negligible during the periods of the experiments.)

The type of creaming behaviour observed depends on the particle size distribution. With polydisperse emulsions in which microscopic examination indicates no appreciable aggregation of the oil particles, creaming normally results in the formation of a visible boundary at the top of the emulsion, the boundary moving downwards as the primary particles cream. When a great majority of the particles are present as large aggregates (as determined, for example, microscopically) a high oil concentration gradient is usually set up at the bottom of the emulsion owing to the rapid creaming of the aggregates and the paucity of primary particles; a well-defined boundary is therefore formed which moves upward as creaming progresses. When the aggregates present are small or when many of the primary particles are unaggregated, the creaming characteristics are modified accordingly. Thus, creaming of small aggregates commonly results in a visible boundary near the top of the emulsion, the boundary moving downwards with further creaming of the aggregates. Redistribution of primary particles within the aggregates or redistribution of the latter relative to each other may then result in an upward movement of the boundary, followed by a final downward movement due to the comparatively slow creaming of the unaggregated particles. The rates of creaming described below are based on the above changes in cream volume with time.

EXPERIMENTAL

MATERIALS.—The paraffin hydrocarbon used throughout was a colourless light petroleum fraction (*ex* Manchester Oil Refinery Ltd.) consisting of paraffin and cycloparaffin hydrocarbons. No ethylenic, aromatic or other unsaturation could be detected by infrared spectral analysis.* The benzene was of A.R. quality.

Potassium laurate solutions were prepared by dissolving pure lauric acid in a sufficient excess of caustic potash to give a pH of 11·0, measured with the glass electrode. The Aerosol OT and Aerosol MA were anhydrous samples obtained through the courtesy of American Cyanamid Company. Aerosol OT is stated to be the sodium salt of di(ethylhexyl) sulpho-succinic acid and Aerosol MA the corresponding di(methylamyl) derivative. The cetyltrimethyl ammonium bromide, kindly supplied by I.C.I. Ltd., was recrystallized twice from acetone. Two pure samples of sodium dodecyl sulphate were available, one provided by Dr. R. Matalon and the other prepared in our own laboratories; the same results were obtained with both samples. All inorganic salts were of A.R. quality and the aliphatic alcohols were of laboratory reagent standard.

PROCEDURE.—In each series of experiments, a stock oil-in-water emulsion containing 40 % or 50 % oil was prepared with a hand operated valve homogenizer, using the minimum quantity of emulsifying agent necessary to obtain an emulsion of suitable particle size, i.e. with the large majority of particles $0{\cdot}5\mu$ to 20μ in diameter. Some creaming could then be observed over a period of a few hours even when aggregation of the primary particles was negligible. Aliquots of the stock emulsion were diluted immediately (usually to 10 % oil content) with aqueous solutions of the emulsifying agent already present and containing, if desired, inorganic salts, auxiliary stabilizers, etc. The rates of creaming of the emulsions in any particular series could thus be compared under identical conditions of primary particle size distribution. Very small quantities of emulsifying

* Our thanks are due to Miss J. M. Fabian for determining the spectra.

agent (*ca.* 0·05 %) were usually sufficient to prepare the stock emulsions and to prevent any detectable coalescence of particles during the short time required for dilution.

In all cases, the oil content of the emulsion is expressed as volume of oil per 100 cm³ emulsion and the soap concentration as weight of soap per 100 cm³ of the aqueous phase. All experiments were carried out at room temperature (20°-25° C).

RESULTS

SODIUM DODECYL SULPHATE.—Fig. 1 shows the effect of sodium dodecyl sulphate (NaLS) concentration on the rate of creaming of 10 % benzene emulsions. At concentrations of 0·265 % and 0·18 % NaLS, the creaming rate is slow owing to the absence of aggregates (confirmed microscopically). The slightly higher creaming rate at 0·09 % soap, or less, is probably due to a small degree of particle coalescence which, at these very low soap concentrations, may not be negligible after about 30 min creaming. In the concentration range 0·36 % to 0·8 % NaLS, the rate of creaming increases very rapidly; that this is due to aggregation of the oil particles can be confirmed by microscopic examination or even by the appearance of the emulsion as a whole, which does not possess the uniformly smooth appearance of the unaggregated systems. In the emulsions containing 0·485 % to 0·8 % soap (curves E, F, G of fig. 1) the aggregates are larger than in the emulsion stabilized with 0·36 % soap (D), as indicated by their much faster rate of creaming, and by the appearance of the cream boundary at the bottom of the emulsion and the decrease in cream volume with time. In the presence of 0·97 % NaLS (Curve H) the creaming rate is reduced to a value not greatly different from that of the unaggregated emulsions A, B and C and it is evident from microscopic examination that there is little aggregation of the particles. Further increase in soap concentration results again in a marked increase in the rate of creaming and in the size of the aggregates.

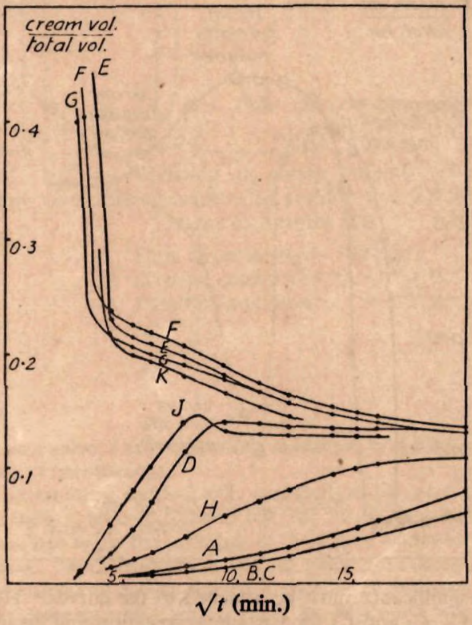

FIG. 1.—Rate of creaming of 10 % benzene emulsions stabilized with sodium dodecyl sulphate.

Sodium dodecyl sulphate.
A. 0·09 %
B. 0·18 %
C. 0·265 %
D. 0·36 %
E. 0·485 % } serum turbidity minimal
F. 0·57 % }
G. 0·8 %
H. 0·97 % serum turbidity maximal
J. 1·15 %
K. 1·75 %

Changes in the turbidity of the emulsion sera as a function of soap concentration (after equal creaming periods) confirm the above conclusions. The serum turbidity shows a pronounced minimum at 0·485 % to 0·57 % and an equally definite maximum at 0·97 % soap.

When aggregation occurs, the rapid creaming of the aggregates is followed by a much slower change in cream volume which is due partly to the slow creaming of primary particles (or very small aggregates) and partly to the redistribution of particles and aggregates into a more closely packed configuration. The essential features of the rate of creaming curves were well represented by plotting the cream volume against soap concentration after a time (e.g. 100 min) sufficient for completion of the initial rapid creaming of aggregates. The choice of a much longer creaming time is not advisable since differences between the systems are then diminished (see fig. 1), e.g. by redistribution of the aggregated particles. A section of fig. 1 corresponding to t = 100 min is given in fig. 2 which shows clearly the influence of NaLS concentration on aggregation of the emulsion particles. C_1 is the soap concentration below which the particles are unaggregated, C_2 the concentration at which aggregation is maximal and C_3 that at which it is minimal (always excepting concentrations below C_1).

The behaviour of paraffin hydrocarbon emulsions stabilized by NaLS (fig. 2) differs from that of the benzene emulsions in two notable respects. The decrease in cream volume corresponding to the soap concentration C_3 is relatively small and the corresponding maximum in serum turbidity (occurring at approximately 1·6 %) is much less pronounced. Secondly, the soap concentrations for the commencement of aggregation and maximum aggregation are a little higher than in the benzene emulsions.

CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB.).—The influence of CTAB concentration on the cream volume of benzene emulsions after 100 min creaming (fig. 3) is very similar, qualitatively, to the effect of sodium dodecyl sulphate on benzene emulsions, and the same significance must be attached to the curves. However, the limiting soap concentrations C_1, C_2 and C_3 for particle aggregation and disaggregation are all considerably lower than the corresponding values for dodecyl sulphate. Paraffin emulsions stabilized with CTAB show the same behaviour as the benzene emulsions in that states of maximum aggregation (with minimum turbidity) and minimum aggregation (maximum turbidity) are very pronounced (fig. 3).

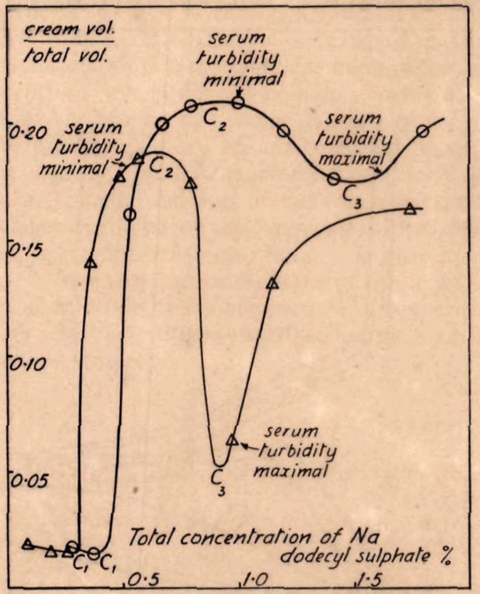

FIG. 2.—Variation in cream volume of 10 % benzene or paraffin emulsions with concentration of sodium dodecyl sulphate.

Time of creaming = 100 min

△ Benzene emulsions $\begin{cases} C_1 = 0{\cdot}30\ \% \\ C_2 = 0{\cdot}65\ \% \\ C_3 = 1{\cdot}05\ \% \end{cases}$

○ Paraffin emulsions $\begin{cases} C_1 = 0{\cdot}45\ \% \\ C_2 = 0{\cdot}95\ \% \\ C_3 = ca.\ 1{\cdot}6\ \% \end{cases}$

AEROSOL MA.—The effect of Aerosol MA concentration on the cream volume of benzene and paraffin emulsions is shown in fig. 4. The limiting concentration C_1 for particle aggregation is well defined, as with all the soaps examined in the present work. In both series of emulsions the cream volume rises rapidly as the soap concentration increases to 2·6 % (for benzene) or 3·2 % (for paraffin). The increase in volume is accompanied by a decrease in turbidity of the sera. At soap concentrations higher than 2·6 % or 3·2 % the changes in cream volume are small. The turbidity of the sera decreases gradually with increasing soap concentrations except that, with benzene, there is a possible small maximum in turbidity between 3·1 % and 3·7 % soap.

POTASSIUM LAURATE (pH 11·0).—In paraffin emulsions stabilized by potassium laurate, particle aggregation increases greatly between 0·95 % and 1·6 % soap (fig. 5). Above this concentration, the cream volume increases slightly and the turbidity of the serum decreases gradually with increasing soap concentration. With benzene emulsions, the cream volume reaches a maximum at 1·4 % soap and gives a fairly shallow minimum at ap-

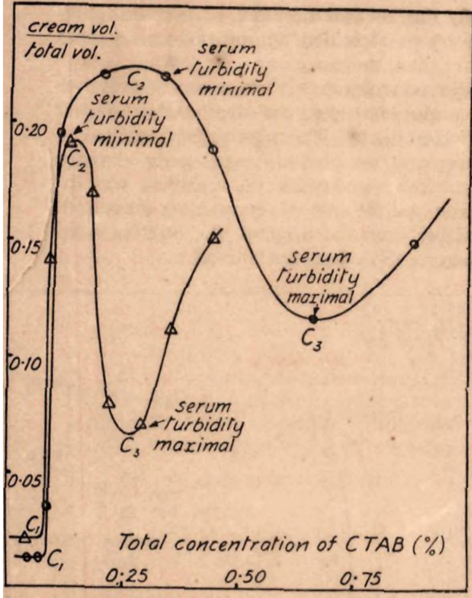

FIG. 3.—Variation in cream volume of 10 % benzene or paraffin emulsions with concentration of CTAB.

Time of creaming = 100 min

△ Benzene emulsions $\begin{cases} C_1 = 0{\cdot}07\ \% \\ C_2 = 0{\cdot}14\ \% \\ C_3 = 0{\cdot}26\ \% \end{cases}$

○ Paraffin emulsions $\begin{cases} C_1 = 0{\cdot}08\ \% \\ C_2 = 0{\cdot}27\ \% \\ C_3 = 0{\cdot}67\ \% \end{cases}$

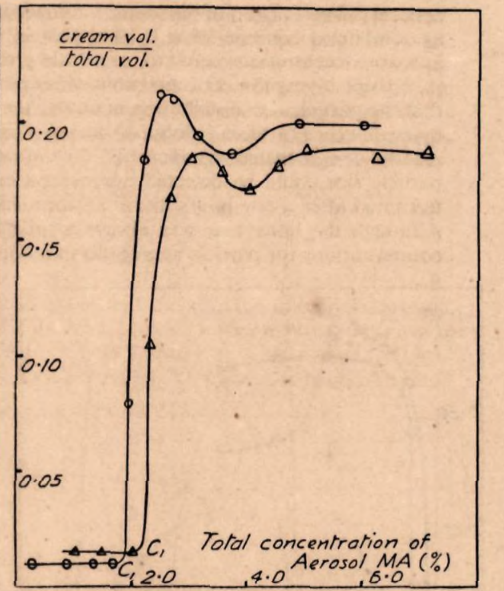

FIG. 4.—Variation in cream volume of 10 % emulsions of benzene or paraffin with concentrations of Aerosol MA.

Time of creaming = 100 min

○ Benzene emulsions: $C_1 = 1{\cdot}9$ %

△ Paraffin emulsions: $C_1 = 2{\cdot}2$ %

proximately 3·0 % soap. The emulsion sera show a corresponding minimum and maximum turbidity at approximately the same concentrations.

AEROSOL OT.—In paraffin emulsions containing Aerosol OT, aggregation of the oil particles increases markedly in the range 0·30 % to 0·40 % soap (fig. 6); at higher concentrations the cream volume is almost constant while the turbidity of the serum decreases slightly as the soap concentration increases. With benzene as the oil phase, the cream volume shows a maximum and the serum turbidity a well-defined minimum at approximately 0·55 % soap. The range of soap concentration which could be examined was limited by the relatively low solubility of Aerosol OT in water (*ca.* 1·2 %).

CORRELATION OF RESULTS WITH CRITICAL MICELLAR CONCENTRATIONS.—The soap concentrations at which aggregation of the oil globules commences, reaches a maximum and falls to a minimum are summarized in table 1, together with the critical micellar

TABLE 1.—INFLUENCE OF SOAPS ON PARTICLE AGGREGATION IN 10 % BENZENE OR PARAFFIN EMULSIONS

Soap	C.M.C. (%)	Conc. of soap (%) for					
		Initial aggregn.	Max. aggregn.	Dis-aggregn.	Initial aggregn.	Max. aggregn.	Dis-aggregn.
		In benzene emulsions			In paraffin emulsions		
CTAB	0·03 [1]	*ca.* 0·07	0·14	0·26	*ca.* 0·08	0·27	0·67
NaLS	0·21 [2]	0·30	0·65	1·05	0·45	0·95	*ca.* 1·6
K laurate	0·57 [3]	0·80	1·4	3·0	0·95	—	—
Aerosol MA	1·6 [4]	1·9	—	—	2·2	—	—
Aerosol OT	0·18 [4]	0·20	0·55	—	0·30	—	—

concentrations (c.m.c.) of the soaps. Allowing for the fact that the c.m.c. is lowered slightly by solubilized benzene,[5, 6] it is clear that in every case particle aggregation commences at soap concentrations equal to, or a little greater than, the c.m.c.

Except at very low concentrations of soap (referred to previously) there was no evidence that the particle size distribution in any of the emulsions studied was significantly affected by coalescence of the oil globules, during a period of 2-3 h. The aggregated particles are readily disaggregated, temporarily, by agitation and no obvious increase in primary particle size could be detected microscopically. In several cases, the creaming was interrupted after a few hours, the emulsions shaken and the rate of re-creaming measured. Although the latter rate was always a little higher than the original, the limiting soap concentrations for particle aggregation and disaggregation were not altered.

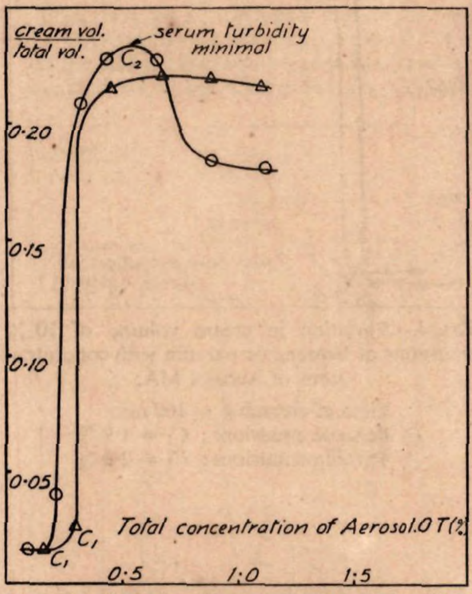

FIG. 5.—Variation in cream volume of 10 % emulsions of benzene or paraffin with concentration of K laurate (pH 11·0).

Time of creaming = 100 min

○ Benzene emulsions $\begin{cases} C_1 = 0{\cdot}8\ \% \\ C_2 = 1{\cdot}4\ \% \\ C_3 = ca.\ 3{\cdot}0\ \% \end{cases}$

△ Paraffin emulsions $C_1 = 0{\cdot}95\ \%$

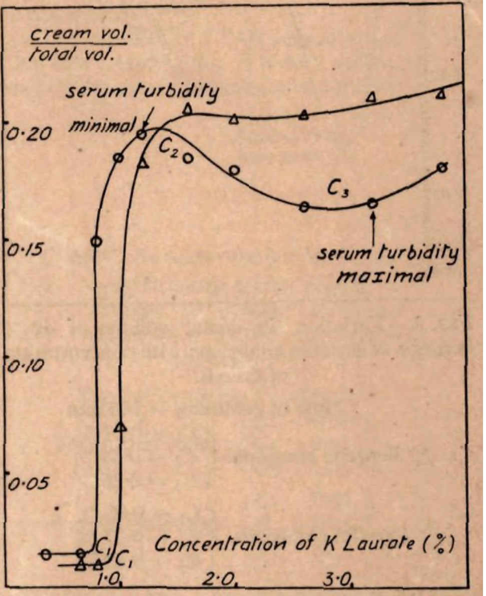

FIG. 6.—Variation in cream volume of 10 % emulsions of benzene or paraffin with concentration of Aerosol OT.

Time of creaming = 100 min

△ Paraffin emulsions $C_1 = 0{\cdot}30\ \%$

○ Benzene emulsions $\begin{cases} C_1 = 0{\cdot}20\ \% \\ C_2 = 0{\cdot}55\ \% \end{cases}$

EFFECT OF PHASE VOLUME RATIO AND PARTICLE SIZE.—Preliminary experiments with 25 % and 10 % paraffin emulsions, prepared from the same stock and stabilized with Aerosol MA, showed that the soap concentration C_1 at which particle aggregation commenced was not appreciably affected by the oil content of the emulsions. Thus, values of $C_1 = 2{\cdot}4\ \%$ and $2{\cdot}2\ \%$ were obtained for the 25 % and 10 % emulsions respectively and part of this difference at least, will be due to the difference in total interfacial area of the emulsions. By direct analysis of the sera of emulsions (particle size $0{\cdot}5\mu$ to 20μ) stabilized by sodium dodecyl sulphate or CTAB, at concentrations between the c.m.c. and the concentration C_2 corresponding to maximum aggregation, it was estimated that not more than 0·01 g of soap were adsorbed per cm^3 of paraffin or benzene. This value, which was obtained by centrifuging the emulsions to give clear sera and analyzing gravimetrically for soap corresponds to a decrease in the initial soap concentration of only 0·1 %, for a 10 % oil emulsion. The difference between the initial and "equilibrium" soap concentrations is thus too small to affect the significance of the data summarized in table 1.

The influence of particle size in Aerosol MA stabilized emulsions was examined qualitatively by comparing the creaming of two 10 % benzene emulsions of estimated particle diameter 0·5μ to 40μ and 0·3μ to 2μ. In both emulsions aggregation commenced at an Aerosol MA concentration of 1·9 ± 0·1 % showing that the effect of particle size in the range studied was very small.

Effect of aliphatic alcohols.—The influence of ethyl and *n*-butyl alcohol on the cream volume of 10 % benzene emulsions stabilized with sodium dodecyl sulphate is shown in fig. 7. The soap concentration C_1 corresponding to the onset of particle aggregation is lowered from 0·3 % to approximately 0·07 % by the presence of 0·53 M butyl alcohol. The soap concentrations C_2 and C_3, corresponding to maximum and minimum states of particle aggregation, are likewise lowered from 0·6 % and 1·0 % to 0·2 % and 0·45 % respectively. The influence of ethyl alcohol is much less marked, the values of C_1, C_2 and C_3 being 0·23 %, 0·4 % and 1·0 % soap respectively at an ethanol concentration of 3·0 M. In all cases, the emulsion sera showed a minimum turbidity at the concentration C_2 and a maximum turbidity in the region of C_3.

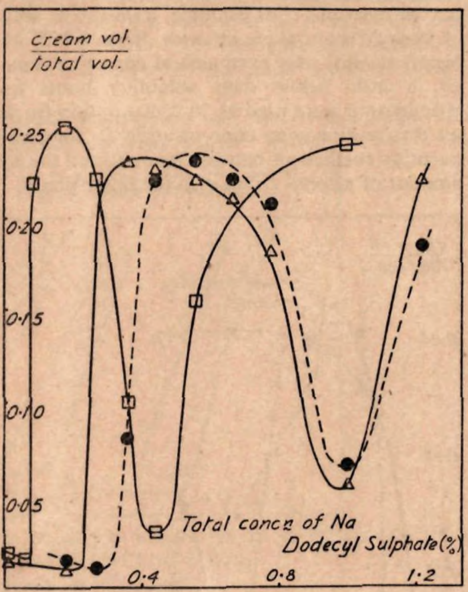

Fig. 7.—Effect of alcohols on the cream volume of 10 % benzene emulsions stabilized with sodium dodecyl sulphate.

Time of creaming = 100 min

- ● No alcohol
- ☐ 0·53 M *n*-butyl alcohol
- △ 3·0 M ethyl alcohol

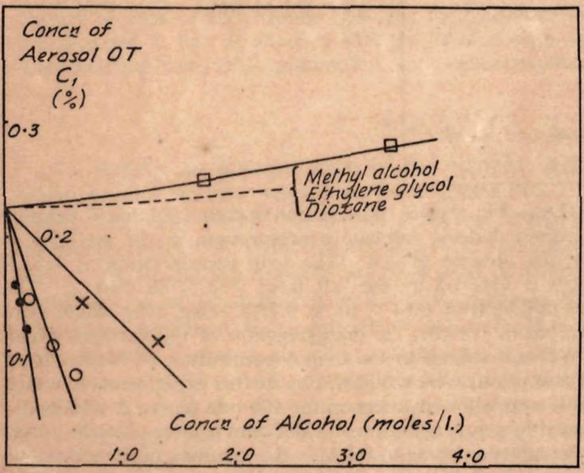

Fig. 8.—Effect of alcohols on the limiting soap concentration C_1 for particle aggregation in 10 % benzene emulsion stabilized with Aerosol OT.

- ☐ ethyl alcohol
- × *n*-propyl alcohol
- ○ *n*-butyl alcohol
- ● *n*-amyl alcohol

More detailed results on the effect of chain length of the alcohol are shown in fig. 8, in which the limiting soap concentration C_1 is shown as a function of alcohol concentration C_a in benzene emulsions stabilized by Aerosol OT, C_a being calculated on the volume of aqueous phase. The influence on particle aggregation of methyl and ethyl alcohol, ethylene glycol and 1 : 4-dioxane was very small. In the presence of *n*-propyl, *n*-butyl and *n*-amyl alcohols, C_1 decreases with alcohol concentration, the rate $-\, \mathrm{d}C_1/\mathrm{d}C_a$ increasing with the number of carbon atoms in the alcohol. Except for the fact that ethyl alcohol increases C_1 slightly, the above results follow closely the effect of the same alcohols on the c.m.c. of dodecylammonium chloride [7] or decyltrimethylammonium bromide.[8] However, addition of the higher aliphatic alcohols ($> C_5$) to the same emulsions gave no detectable decrease in the value of C_1 although their effect on the c.m.c. of the above cationic soaps is very marked. For example, a 0·0196 M solution of *n*-hexyl alcohol reduces the c.m.c. of dodecylammonium chloride from 0·0127 M to 0·0084 M. Normal hexyl and *sec*-heptyl alcohol were examined at concentrations of 0·036 and 0·0155 moles/l. respectively, i.e. a little below their solubility limits in water. 2-ethyl-hexanol, *n*-decanol and *n*-dodecanol were used at 70 % saturation (in water) at 20° C. The absence of any effect on the limiting soap concentration C_1 for particle aggregation is presumably due to the partition coefficients between benzene and the aqueous phase being so high that a negligible amount of alcohol remains in the latter phase.

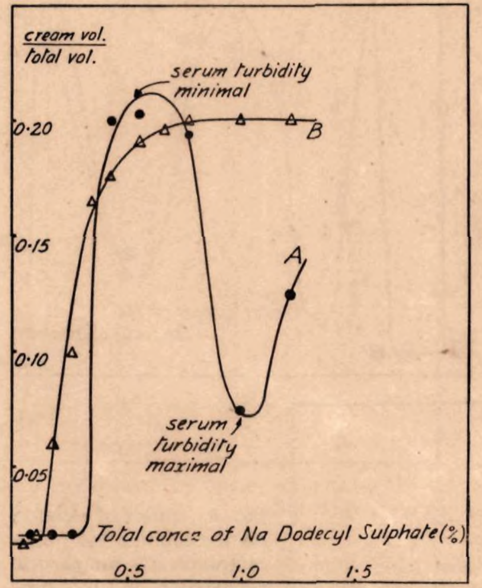

FIG. 9.—Effect of sodium chloride on the cream volume of 10 % benzene emulsions stabilized with sodium dodecyl sulphate.

Time of creaming = 100 min

$$\text{A.}\quad \text{Zero NaCl} \left\{ \begin{array}{l} C_1 = 0{\cdot}33\ \% \\ C_2 = 0{\cdot}6\ \% \\ C_3 = ca.\ 1{\cdot}0\ \% \end{array} \right.$$

$$\text{B.}\quad 0{\cdot}1\ \text{M NaCl}\quad C_1 = 0{\cdot}14\ \%$$

INFLUENCE OF INORGANIC SALTS.—Fig. 9 gives the variation in cream volume of benzene emulsions as a function of sodium dodecyl sulphate concentration, in the presence of 0·1 M sodium chloride and in the absence of salt. The soap concentration at which particle aggregation commences is lowered by the salt from 0·33 % to 0·14 %. The degree of aggregation increases rapidly from 0·14 % to *ca.* 0·75 % soap, after which there is no noticeable change in the cream volume, i.e. disaggregation of the particles which normally results in a minimum cream volume at the soap concentration C_3 is eliminated by 0·1 M sodium chloride. These results were confirmed by further experiments in which the emulsions containing no salt were allowed to cream for 100 min (curve A obtained); the particles were then redispersed by gentle agitation and sufficient sodium chloride added to bring the concentration in the aqueous phase to 0·1 M. Re-creaming of the emulsions followed curve B, fig. 9.

Further work on the salt effect was carried out using paraffin emulsions stabilized with potassium laurate at pH 11·0 ± 0·2. The influence of potassium chloride over a range of concentrations is shown in fig. 10. Variations in rate of creaming and cream volume are not due to changes in primary particle size such as would be caused by coalescence, since on re-dispersing the creamed emulsions the rate of re-creaming was only slightly greater than that of the first creaming. The aggregation process is readily reversible in all cases.

The limiting concentration C_1 of soap at which particle aggregation commences decreases almost linearly with salt concentration in the range investigated (fig. 11). The critical micellar concentration (c.m.c.) of the soap, on the other hand, varies with salt concentration according to the relation

$$\log(\text{c.m.c.}) = -k_1 \log C_g + k_2 \qquad (1)$$

where C_g is the total concentration of counter ions in the solution. The validity of this relation for potassium laurate solutions in the presence of potassium chloride has been established experimentally by Corrin and Harkins[9] and Kolthoff and Stricks.[10] Merrill and Getty's data[11] for the decrease in the c.m.c. of sodium laurate effected by sodium chloride is also given in fig. 11, their data having been extended to 0·16 M sodium chloride by means of eqn. (1). The change of counter ion from sodium to potassium has no significant effect on the c.m.c. The difference $[C_1 - (\text{c.m.c.})]$ is approximately constant at salt concentrations less than about 0·05 M; thereafter the difference decreases with increasing salt concentration.

The influence of the salt anion on particle aggregation was studied using equivalent concentrations of potassium chloride, sulphate and thiocyanate. The last two salts were chosen because of the extreme positions of the anions in the lyotropic series. Results are included in fig. 10, showing that the limiting soap concentration for aggregation is effectively the same in the presence of equivalent concentrations of these three salts.

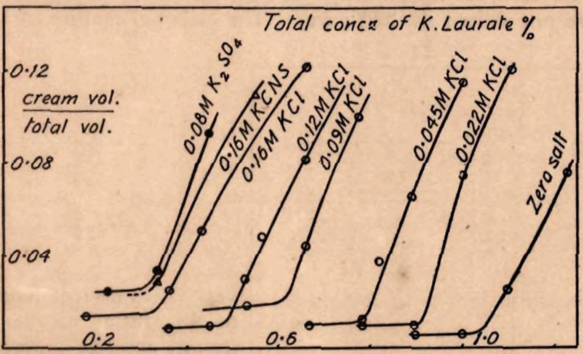

FIG. 10.—Effect of potassium salts on the cream volume of 10 % paraffin emulsions stabilized with K laurate (pH 11·0 ± 0·2).
Time of creaming = 60 min.

DISCUSSION

In seeking an interpretation of the complex aggregation and disaggregation phenomena described above, we have considered a number of possibilities. Of these, the most plausible, in our opinion, rests on the assumption that polymolecular adsorbed films are formed when the soap concentration exceeds the c.m.c. A similar assumption has been used to interpret data[12] on the sedimentation rates of solids stabilized by colloidal electrolytes, where it has been shown[13] that sharp increases of rate can occur without significant changes in zeta potential. Experimental support for this assumption is provided by the recent work of Dixon *et al.*[14, 15] on the adsorption of di-*n*-octyl sodium sulphosuccinate and a cationic soap at the air-water surface. Using a radiotracer method they show that the adsorption of both soaps, at concentrations above the c.m.c., is considerably greater than can be accounted for by a monomolecular film. Measurements by Harkins and collaborators[16] also show that the adsorption of sodium dodecyl sulphate and potassium myristate on graphite continues to increase at concentrations above the c.m.c.

The existence of a state of particle disaggregation between two well-defined states of aggregation in many of the emulsion systems studied can be accounted for if the further adsorption of soap as a secondary layer (at concentrations above the c.m.c.) occurs as single molecules or micelles according to the relative concentration of these species in solution. Thus, at concentrations just above the c.m.c., where the number of micelles is small, it is suggested that single molecules are adsorbed with their hydrocarbon chains oriented towards the aqueous phase. Such particles in an aqueous medium are unstable and aggregation of the particles should therefore occur, as found experimentally in the concentration region C_1 to C_2. At higher concentrations competitive adsorption of the soap in the form of micelles, which leave the outer surface of the particles hydrophilic, results in disaggregation of the particles (region C_2 to C_3). At still higher concentrations, forces of attraction between adsorbed micelles on neighbouring particles can again cause aggregation, particularly when the soap possesses an unbranched hydrocarbon chain. In this final state the oil particles are linked together by an oriented multilayer of soap. Possibly only a small fraction of the surface of each particle contains adsorbed micelles and it will be at these points that aggregation occurs when the soap concentration is greater than C_3. A diagrammatic representation of the adsorbed soap films, based on the above theory, is given in fig. 12 (gegenions are not shown in the figure). The essential feature of the diagram is

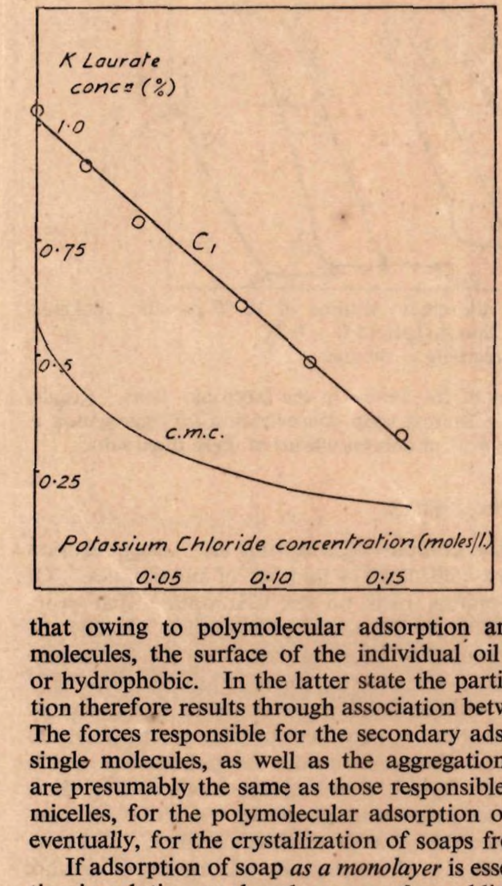

FIG. 11.—Effect of potassium chloride on the critical micellar concentration (c.m.c.) and the limiting soap concentration C_1 for particle aggregation in 10 % paraffin emulsions stabilized with potassium laurate; pH 11·0 ± 0·2.

that owing to polymolecular adsorption and the amphipathic nature of soap molecules, the surface of the individual oil particles may be either hydrophilic or hydrophobic. In the latter state the particles are highly unstable and aggregation therefore results through association between the exposed hydrocarbon chains. The forces responsible for the secondary adsorption of soap either as micelles or single molecules, as well as the aggregation at concentrations greater than C_3, are presumably the same as those responsible for the formation of lamellar (Hess) micelles, for the polymolecular adsorption of soap as found by Dixon[14, 15] and, eventually, for the crystallization of soaps from solution.

If adsorption of soap *as a monolayer* is essentially complete when the concentration in solution reaches the c.m.c., then additives to the soap solution which lower the c.m.c. may be expected to reduce the limiting concentration C_1 at which particle aggregation commences. This occurs in the presence of aliphatic alcohols containing three to five carbon atoms; the close analogy between the effect of alcohols (up to C_5) on the initial aggregation of emulsions and their influence on the c.m.c. of soaps has been referred to in the previous section. The reduction caused by butyl alcohol in the values of C_2 and C_3 for sodium dodecyl sulphate stabilized emulsions (fig. 7) implies that adsorption of micelles and interlinking of particles occur more readily in the presence of butyl alcohol, some of which will be incorporated in the micelles. In the emulsions containing sodium dodecyl sulphate and inorganic salt (fig. 9), the absence of a soap concentration region above the c.m.c. in which disaggregation of the particles can be detected eliminates the need for any distinction to be made between aggregation due to secondary adsorption of single molecules and the direct aggregation of particles covered with a primary layer of soap—or, indeed, aggregation due to the interlinking of particles by micelles. Possibly all three processes occur. However, up to a potassium chloride concentration of at least 0·16 M, the limiting soap concentration C_1 for particle aggregation in emulsions stabilized by potassium laurate is higher

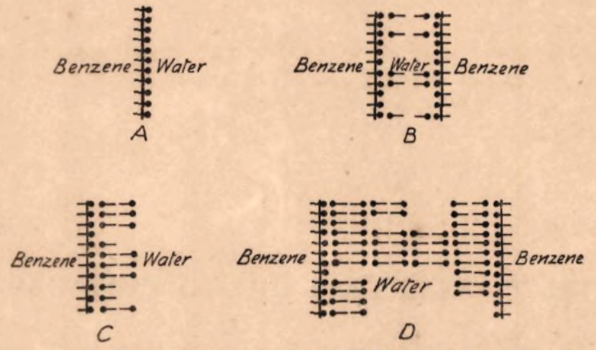

FIG. 12.—Diagrammatic representation of adsorbed films of sodium dodecyl sulphate at the benzene-water interface.

A. Surface of benzene drops hydrophilic.
No aggregation of particles.
Soap concentration $<$ c.m.c.
B. Surface of benzene drops hydrophobic.
Particles highly aggregated.
Soap concentration $>$ c.m.c.
C. Surfaces of benzene drops mainly hydrophilic.
Particles only slightly aggregated.
Soap concentration $>$ c.m.c.
D. Surface of benzene drops still hydrophilic but concentration of soap sufficient to build up multilayers which link benzene particles (cf. lamellar micelle formation in solution).
Soap concentration $\gg$ c.m.c.

than the c.m.c. (fig. 11), showing the necessity for at least one " complete " monolayer of adsorbed soap if reversible aggregation is to take place. The negligible influence of the nature of the salt anion is a property common to both micelle formation[9] in potassium laurate solutions and the aggregation of emulsion particles stabilized with potassium laurate.

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