technique resulted from a) the use of Vycor glass which has a lower coefficient of expansion and may have eliminated some of the variations in glass corrections, and b) the use of a solidification procedure which should have eliminated most of the microscopic cracks or vacuoles in the sample. A more rapid equilibration was obtained by the use of a dilatometer bulb with an expanded section which allowed the fat sample to float freely in the mercury and prevented the sample from adhering to the walls of the bulb. Using Vycor dilatometers of 14.0-ml. capacity and a 1.0-g. sample, the error of measurement was ±0.00005 ml. per gram while using Pyrex dilatometers of a similar size and a 1.0-g. sample the error was ±0.00008 ml. The standard error was less for measurements in the liquid state than in the solid state.

The decrease in specific volume after each equilibration at 35°C. was anticipated from previous work, but a numerical value was difficult to obtain since specific volumes were not used. The present work shows that a change in the melting dilation could be expected from the continual decrease in specific volume after each equilibration. The variation in coefficient of expansion for the solid state has a small effect on melting dilation if the decrease in specific volume is neglected. For dilatometer 5, the maximum difference in coefficients of expansion for the solid state (0.000171 and 0.000187) is 0.00016, and if one assumed an equivalent specific volume at —38° C., this would make a difference in melting dilation of 0.0012 ml. per gram.

No explanation is offered for the differences found in the specific volumes of methyl stearate in the solid state. These differences were anticipated from the previous work (1), in which different curves were found for the heating and cooling cycles. The specific volume at a given temperature would depend on the temperature to which the sample was cooled before making the measurement. The present study could be enlarged to include other heating and cooling cycles, but it is expected that a family of curves would be found and the position of each curve would depend on the temperature at which the measurements were started.

The melting dilations and coefficient of expansion in the liquid state are of the same order of magnitude as the previous study (1). The coefficient of expansion for the solid state (0.00018) is lower than previously reported (0.00022 ml.). From the present data it would appear that a dilatometer constructed from Vycor glass containing 100–125 g. of mercury and a 2–3 g. sample should yield data in which the standard error was equal to or less than the standard error found in the present work.

Summary

The dilatometric curves representing heating and cooling cycles for methyl stearate between —38°C. and +35°C. are the same shape as found in the previous study. Cooling cycles which are started from points on the heating curve yield curves which are different from each other and from curves representing the complete heating and cooling cycles. Curves for heating cycles which are started from points on the curve representing the complete cooling cycle will also be different from the curves representing either the heating or cooling cycles in the same temperature region. The specific volumes at any temperature in the solid region depend on the previous history of the sample even though the sample is not melted between determinations. A continual reduction in specific volume was found for successive runs after equilibration at +35°C. This reduction had no apparent effect on the coefficient of expansion of the solid state but did increase the melting dilation. Using the present Vycor dilatometers, the standard error of measurements in the solid state are around ±0.00005 ml. per gram in terms of specific volume. The use of a platinum resistance thermometer and Mueller bridge did not significantly improve the precision of the measurements.

Acknowledgment

The assistance of T. M. Mallard in taking measurements and in calculations of the data is gratefully acknowledged.

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Emulsion Stability[1]

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THE LITERATURE dealing with emulsions is very extensive, and many theories have been expressed concerning their stability (1, 3). It is now generally accepted that a tenuous interfacial film is required for a stable emulsion. This tenuous film has been expressed in terms of surface viscosity (9), condensed films (13), films of considerable thickness (1), and so forth. It is frequently suggested that electric repulsion contributes to the stability of O/W emulsions containing ionic emulsifiers (12, 14), but it is of minor importance with emulsions stabilized with nonionic surfactants (4). The lack of a relationship between electric repulsion and stability has also been noted (2).

It is known that O/W emulsions are best prepared with water-soluble emulsifiers while the oil-soluble emulsifiers are used for stable W/O emulsions. The type of emulsion produced with solids depends upon whether the solid emulsifier is more readily wetted by water or by oil (4). These observations have been extended to relate the degree of stability of emulsions to the non-wetting of the interfacial film by the discontinuous phase (4).

On the basis of insight provided by other investigators, it is possible to present a theory which will account for many observations concerning emulsion stability. That described here concerns emulsion stability only insofar as it relates to coalescence. An emulsion which has creamed or flocculated is considered stable if coalescence does not occur. Minor

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factors such as the density and viscosity of the phases are not considered.

It is emphasized that the function of an emulsifying agent is to provide an energy barrier to the coalescence of droplets coming into contact through Brownian movement or sedimentation (10). Maximum emulsion stability cannot be obtained until the concentration of emulsifier is sufficient for a completed monomolecular film (7). In order for globules to coalesce it is necessary to displace part of this interfacial film. Desorption of the emulsifier into the continuous phase is hindered by the juxtaposition of the interfaces of adjacent globules (4). No such steric hindrance to displacement into the dispersed phase exists. Consequently solubility of the emulsifier in the discontinuous phase is adverse to emulsion stability.

Coalescence is encouraged by the energy of collision and the decrease in free energy occasioned by the decrease in interfacial area resulting from coalescence. The electric repulsion resulting from the interaction of double layers at the interfaces of approaching globules causes the ionic emulsifier to be displaced from opposing faces (11, 12). An analogous factor may be assumed to be present with non-ionic emulsifiers. To account for the fact that micelles of non-ionic surfactants do not grow in size, without limit, it is necessary to assume some hindrance operating between the polar portions of these molecules. A steric effect is usually considered to be responsible.

That these concepts are in agreement with most recorded observations concerning emulsion stability can be seen from the following:

1. The emulsion type (W/O or O/W) is determined by the solubility characteristics of the emulsifier. If the emulsifier is soluble in the dispersed phase, the emulsion will not be stable. This stresses the importance of the steric effect on desorption into the continuous phase, as opposed to unhindered desorption into the globules.
2. With ionic emulsifiers, O/W emulsion stability increases with an increase in emulsifier concentration up to the critical micelle concentration (CMC). At higher concentrations, stability decreases (4). The energy barrier contributed by the interfacial film can be expected to increase with an increased concentration below the CMC because of increased adsorption. Above the CMC the presence of micelles between juxtaposed interfacial films would increase electric repulsion and favor desorption of the ionic emulsifier.
3. The addition of electrolyte to O/W emulsions stabilized by the ionic emulsifier causes a decrease in emulsion stability followed by an increase in stability with increasing electrolyte concentration, as shown by limited studies conducted here. The initial decrease in stability is presumably caused by a reduction in the double layer potential, which would increase the rate of flocculation. Further additions of salt increase adsorption of surfactant ions and cause the formation of a condensed surface film.
4. The addition of long-chain alcohols, acids, and amides, to O/W emulsions containing ionic emulsifiers frequently stabilizes the emulsions through the formation of film complexes (13) which increases the energy barrier. Further additions reduce stability by increasing the solubility of the interfacial film in the oil phase.
5. The addition of liquids soluble in both phases of an emulsion reduces emulsion stability (6), probably by increasing the solubility of the emulsifier in the dispersed phase.
6. For O/W emulsions stabilized with non-ionic emulsifiers there is an optimum size to the polar portion of the emulsifier that is required for maximum emulsion stability. This is generally the minimum size necessary for insolubility of the emulsifier in the oil phase. The reduced effectiveness of molecules containing larger polar groups, in spite of equivalent lowering of interfacial tension, may be caused by some form of repulsion between polar groups on adjacent interfaces.
7. For W/O emulsions stabilized with non-ionic emulsifiers, there is also an optimum size polar grouping required for maximum emulsion stability. The polar group must be sufficiently small for the molecule to be substantially water-insoluble. It must be large enough to exhibit pronounced surface-activity from solution in the oil phase, *i.e.*, concentrate at the oil-water interface.

Emulsions Stabilized with Ionic Surfactants

Desorption of the emulsifier is considered essential for the coalescence of emulsion droplets. The energy required for desorption must then be equal to the potential energy barrier to coalescence contributed by the emulsifier. For oil droplets stabilized with ionic surfactant it is not unreasonable to relate this energy barrier to the free energy of the double layer. The case of O/W emulsions stabilized by an homologous series of ionic surfactants, in the absence of other electrolyte, is considered here.

It can be shown that the electric charge density at an interface containing adsorbed surfactant anions can be expressed in the form (5):

$$\sigma^2 = \frac{DkT}{2\pi} \sum A_i n_{io} \left(\exp\left[(\phi_i - Z_i e\psi_o)/kT\right] - 1\right) \qquad \text{(I)}$$

where

σ = surface-charge density
D = dielectric constant of the medium
k = Boltzmann constant
T = absolute temperature
A_i = the ratio of available sites for ion i where the potential is ψ_o as compared with a comparable volume far removed from the interface
n_{io} = molecular concentration of ions of specie i in the bulk of the solution
ϕ_i = adsorption potential for specie i due to non-Coulombic forces
Z_i = valence of ions of specie i
e = electronic charge
ψ_o = potential at the interface

For the special case where the only solute present is an anionic surfactant, where $Z_- = -Z_+ = -1$, the non-Coulombic adsorption potential for the cation is $\phi_+ = 0$, the ratio of adsorption sites to sites in the bulk of the solution is the same for both types of ions, $A_- = A_+ = A$, and $n_{-o} = n_{+o} = n$, then

$$\sigma^2 = \frac{DkTAn}{2\pi} \left(\exp\left[(\phi_- + e\psi_o)/kT\right] + \exp(-e\psi_o/kT) - 2\right) \qquad \text{(II)}$$

The relation between ϕ_- and ψ_o is readily established.

$$\gamma_- = n_{-o} A_- \exp\left[(\phi_- + e\psi_o)/kT\right] \qquad \text{(III)}$$

$$\gamma_+ = n_{+o} A_+ \exp(-e\psi_o/kT) \qquad \text{(IV)}$$

where γ_- and γ_+ are the surface excess (molecules/cm.^{2}) of surfactant anion and counter-ion, respectively. For the condition that $n_{-o}A_- = n_{+o}A_+ = nA$ in

$$-\frac{\sigma}{e} = \gamma_- - \gamma_+ = nA\left[\exp\left[(\phi_- + e\psi_o)/kT\right] - \exp(-e\psi_o/kT)\right] \qquad \text{(V)}$$

Since $(r_- - r_+)$ is small as compared with r_- or r_+

$$\phi_- \cong -2e\psi_o \qquad \text{(VI)}$$

Substituting VI in II gives

$$\sigma^2 = \frac{DkTAn}{\pi}\left[\exp(-e\psi_o/kT) - 1\right] \qquad \text{(VII)}$$

Since $(-e\psi_o/kT) >> 1$

$$\sigma = -\sqrt{\frac{DkTAn}{\pi}} \cdot \exp(-e\psi_o/2kT) \qquad \text{(VIII)}$$

The free energy of the double layer, *i.e.*, the change in free energy on charging the surface,

$$G = -\int_0^{\psi_0} \sigma \, d\psi_0 \qquad \text{(IX)}$$

$$G = \sqrt{\frac{DkTAn}{\pi}} \int_0^{\psi_0} \exp\left(-e\psi_0/2kT\right) d\psi_0 \qquad \text{(X)}$$

$$G = \sqrt{\frac{DkTAn}{\pi}} \left(\frac{-2kT}{e}\right) \left[\exp\left(-e\psi_0/2kT\right) - 1\right] \qquad \text{(XI)}$$

Since exp $(-e\psi_0/2kT) >> 1$

$$G \sim -\sqrt{n} \left[\exp\left(-e\psi_0/2kT\right)\right] \qquad \text{(XII)}$$

$$\phi_- = X\beta \qquad \text{(XIII)}$$

where

β = attraction per CH_2 group
x = number of CH_2 groups in the hydrocarbon chain

From equation VI

$$-e\psi_0 = \phi_-/2 = X\beta/2 \qquad \text{(XIV)}$$

$$G \sim -\sqrt{n} \left[\exp\left(X\beta/4kT\right)\right] \qquad \text{(XV)}$$

From equations III and IV

$$\Gamma_- + \Gamma_+ = nA \exp\left[\left(\phi_- + e\psi_0/kT\right)\right] + nA \exp\left(-e\psi_0/kT\right) \qquad \text{(XVI)}$$

$$\ln \Gamma_- + \ln \Gamma_+ = 2 \ln n + 2 \ln A + X\beta/kT \qquad \text{(XVII)}$$

At the CMC

$$2\Delta \ln n = -\left(\beta/kT\right)\Delta X \qquad \text{(XVIII)}$$

$$2 \ln\left(\frac{n_1}{n_2}\right) = -\left(\beta/kT\right)\Delta X \qquad \text{(XIX)}$$

For members of a homologous series the CMC decreases with an increase in the number of CH_2 groups in the hydrocarbon chain in accordance with the relationship:

$$\frac{n_1}{n_2} = 2^{-\Delta X} \qquad \text{(XX)}$$

then

$$2 \ln 2^{\Delta X} = \left(\beta/kT\right)\Delta X \qquad \text{(XXI)}$$

$$\beta/kT = 2 \ln 2 \qquad \text{(XXII)}$$

This value, corresponding to 822 calories per mole for the attraction per CH_2 group, is in agreement with published values (5).

Substituting in XV, and replacing n by the molar concentration C

$$G \sim -\left(C \cdot 2^{X}\right)^{\frac{1}{2}} \qquad \text{(XXIII)}$$

The ratio of the free energies of the double layer for members of a homologous series is

$$\frac{G_1}{G_2} = \left[\frac{C_1}{C_2} \cdot 2^{\left(X_1 - X_2\right)}\right]^{\frac{1}{2}} \qquad \text{(XXIV)}$$

Since

$$\frac{C_{01}}{C_{02}} = 2^{\left(X_2 - X_1\right)} \qquad \text{(XXV)}$$

where C_{01} and C_{02} refer to the CMC values of members of a homologous series, then

$$\frac{G_1}{G_2} = \left[\frac{C_1/C_{01}}{C_2/C_{02}}\right]^{\frac{1}{2}} \qquad \text{(XXVI)}$$

If the free energy of the double layer is expressed as an energy barrier to coalescence, then

$$W \sim \exp\left(-G/kT\right) \qquad \text{(XXVII)}$$

$$\ln W \sim -G \qquad \text{(XXVIII)}$$

where the time of coalescence for flocculated globules is increased by a factor W.

$$\ln W \sim \left(C/C_0\right)^{\frac{1}{2}} \qquad \text{(XXIX)}$$

That is, below the CMC for an homologous series of ionic surfactants the stability of an emulsion increases exponentially with the square root of the ratio of concentration to the CMC.

Experimental

Materials. Straight-chain, normal alcohols rated at 90% minimum purity (supplied by Humphrey-Wilkinson Inc., North Haven, Conn.) were fractionated in a Todd Distillation Column, 42 theoretical plate, at 7-mm. mercury pressure and a reflux ratio of 8 to 1. The refractive indices and melting points of the middle portions, as compared with literature values, were as follows: n-dodecanol r.i. 1.4400 at 24.5°C. (lit. 1.4408 at 24.5°C.), m.p. 24°C. (lit. 24°C.); n-tetradecanol r.i. 1.4387 at 40°C. (lit. 1.4283), m.p. 36.6°C. (lit 37.6°C.); n-hexadecanol r.i. 1.4348 at 60° C. (lit. 1.4283 at 78.9°C.), m.p. 49.2°C. (lit. 49.3°C.). The n-octadecanol was better than 95% pure and was not treated.

The purified alcohols were sulfated in hexane at 20°–25°C. with 20% oleum, neutralized in water-ethanol solution with sodium hydroxide, and extracted with ethyl ether. The sodium alkyl sulfates were crystallized once from n-butanol, followed by six recrystallizations from ethanol-ether solution in the range of 75:25 and 25:75. All solvents were of C. P. purity. Absence of a minimum in surface tension-concentration curves indicated that the sodium alkyl sulfates were of high purity. N-Tetradecane, rated at 95% minimum purity, was used as received, except for coalescence measurements on elementary drops. Here the n-tetradecane was passed through a column of activated silica and alumina immediately before use. All glassware was cleaned in boiling nitric acid and rinsed thoroughly in freshly distilled water.

Preparation of Emulsions. The emulsions were prepared by placing 0.1 ml. of n-tetradecane and 10.0 ml. of the appropriate solution in a hypodermic syringe and forcing the mixture through a 23-gauge needle, the end of the needle having previously been cut perpendicular to the sides. Five passes through the needle produced the emulsion. Five ml. of this emulsion were then bulked to 25 ml. with the appropriate solution to produce the final emulsion used in these studies. The particle size of the oil droplets ranged between 0.5 and 5.0 microns. The emulsions were stored in glass bottles at 24°C. ± 2°C. Before each optical density measurement the emulsions were redispersed by gently rotating their glass containers.

Measurement of Optical Density. The optical density of the emulsions was measured by a Duboscq colorimeter. A glass-backed, tinted paper disc served as a primary standard. A very stable emulsion, prepared more than one year previously, which yielded a shade of transmitted light corresponding closely with that of the experimental emulsions, was selected as a secondary standard. As judged by the paper standard, this emulsion did not change significantly throughout this study. The depth of the standard emulsion which gave the same transmittance as a 35.3-mm. depth of the test emulsion was measured. Corrections were made for the light absorption of the dispersing medium. The resulting values represent the depth of a hypothetical column of liquid whose transmittance is that of a 35.3-mm. depth of the test emulsion. These values are proportional to the optical density.

Measurement of the Stability of Individual Droplets. A modification of a previously reported apparatus (4) was employed, as shown in Figure 1. This consisted of a glass tube containing a bulb and stopcock at one end and curved upward at the lower end, where it was drawn to an orifice of 0.37-mm. diameter and ground flat. A platinum ring, 2.0 cm. in diameter, was fixed 1.5 cm. directly above the tip. The droplets formed were generally between 2.0 and 2.6 mm. in diameter. In use the tip was placed in a beaker containing the test solution and n-tetradecane. The interface was sucked clean, and the platinum ring was brought to the interface and then lowered slightly to give a completely flat interface within the ring. The glass tube contained n-tetradecane. About 90% of the drop volume was formed at the tip and aged two minutes before the drop was released. The time was recorded from the moment a drop contacted the interface until it collapsed. Droplets which broke free of the interface within a shorter period than two minutes were discarded. It was observed that during coalescence large droplets frequently left a residue of smaller droplets behind. Coalescence of a droplet set the interface into motion, and this vibration was probably responsible for the formation of the small drops. Since these small drops appeared to affect the stability of the larger drops, the interface was swept clean whenever they appeared. The entire apparatus was placed in a thermostatted Lucite box maintained at 35 ± 2°C. The atmosphere was saturated with water at all times. For each set of conditions, collapse times were measured for a minimum of 50 drops. Reproducibility was not always good, and it was frequently necessary to run a number of replicates under the same experimental conditions.

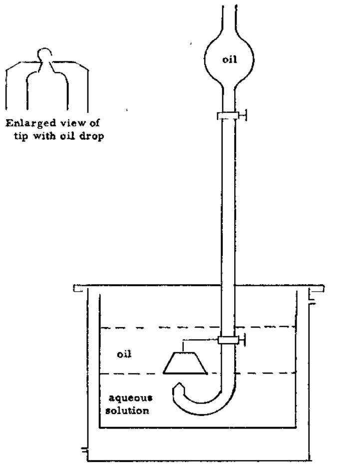

FIG. 1. Apparatus for measuring the stability of elementary drops.

Results

Figures 2 and 3 show typical plots of the percentage decrease in optical density with time for 0.2 volume percentage n-tetradecane in solutions of sodium lauryl sulfate and sodium cetyl sulfate. For the more stable emulsions the curves are linear. The relatively unstable emulsions show an initially rapid and then a slow decrease in optical density with time.

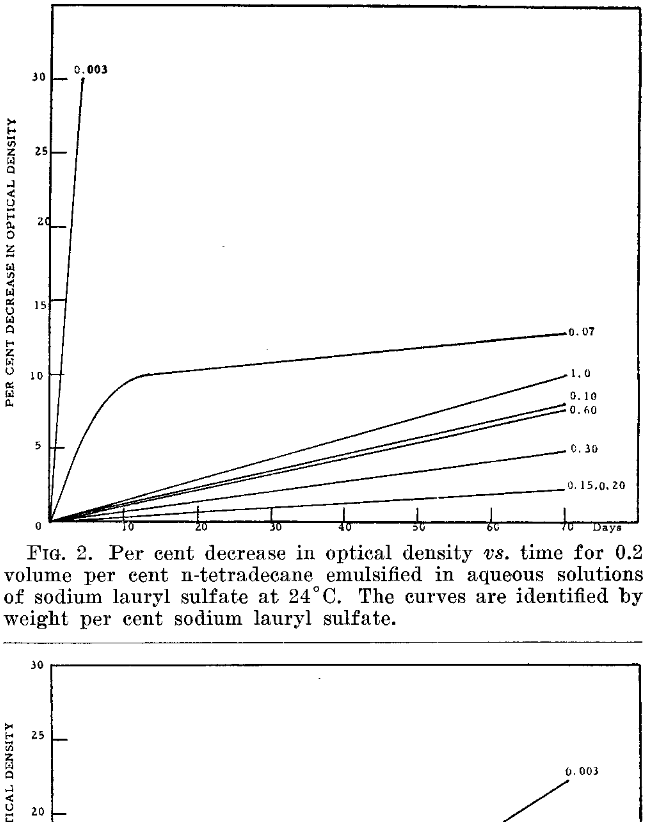

FIG. 2. Per cent decrease in optical density *vs.* time for 0.2 volume per cent n-tetradecane emulsified in aqueous solutions of sodium lauryl sulfate at 24°C. The curves are identified by weight per cent sodium lauryl sulfate.

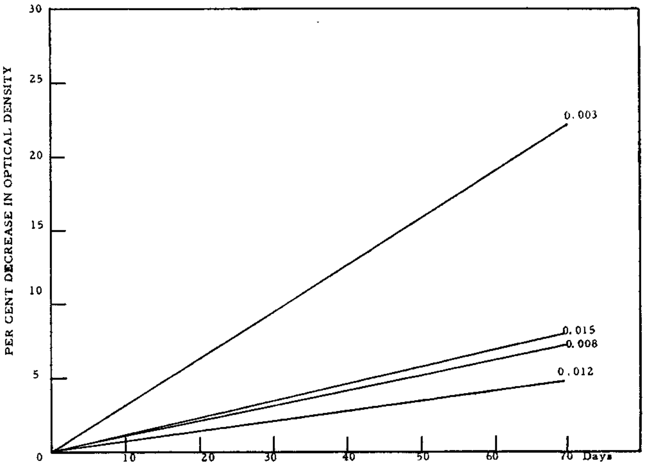

FIG. 3. Per cent decrease in optical density *vs.* time for 0.2 volume per cent n-tetradecane emulsified in aqueous solutions of sodium cetyl sulfate at 24°C. The curves are identified by weight per cent sodium cetyl sulfate.

Data for the percentage decrease in optical density after 70 days were obtained in all cases from the best smooth curve plots of optical density *versus* time. Figure 4 shows this percentage decrease in optical density as a function of concentration for 0.2 volume percentage n-tetradecane in solutions of sodium lauryl sulfate and sodium cetyl sulfate. Both plots give smooth curves. With each sulfate the stability of the emulsion increased with an increase in surfactant concentration up to about the CMC. Above the CMC the emulsion stability decreased with an increase in surfactant concentration.

A typical plot of the results obtained in the measurement of the coalescence time of individual droplets is shown in Figure 5. In general, the number of droplets which did not coalesce within a given time was a linear function of the log of the time. This is contrary to previous observations (4), and suggests that the two-minute aging period was inadequate for adsorbed surfactant ions to reach equilibrium. Values for the half-life of n-tetradecane in sodium alkyl sulfate solutions, employed in Figure 7, were obtained in all cases from a plot of this semi-log function.

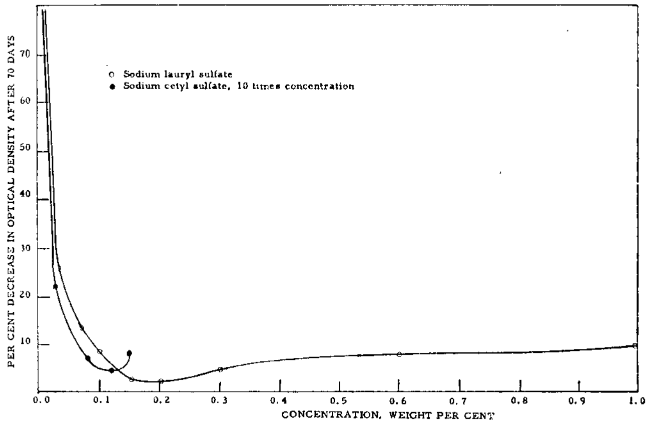

FIG. 4. Percentage decrease in optical density after 70 days *vs.* concentration of sodium alkyl sulfate. Values are for emulsions containing 0.2 volume per cent n-tetradecane stored at 24°C.

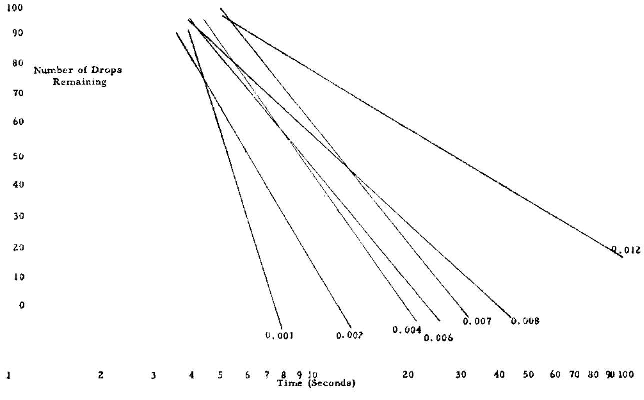

FIG. 5. Number of n-tetradecane drops remaining *vs.* log of time in aqueous solutions of sodium cetyl sulfate at 35°C. The curves are identified by weight per cent sodium cetyl sulfate.

Discussion

Equation XXIX, relating the log of the rate of coalescence to the square root of the ratio of concentration to CMC for members of a homologous series, is tested in Figures 6 and 7. Figure 6 is a plot of log (percentage decrease in optical density after 70 days) vs. $(C/C_o)^{1/2}$ for actual emulsions stabilized with sodium lauryl sulfate and sodium cetyl sulfate. The agreement with equation XXIX is excellent.

A plot of the log of the half-life of elementary droplets of n-tetradecane *vs.* $(C/C_o)^{1/2}$ for aqueous solutions of sodium alkyl sulfates is shown in Figure 7. The scatter of points is magnificent. On the average the points fall on a single straight line. Thus the results are not inconsistent with equation XXIX. In plotting these curves, 0.234% concentration was taken for the CMC of sodium lauryl sulfate. The CMC values for the other sodium alkyl sulfates were calculated from this value and equation XXV.

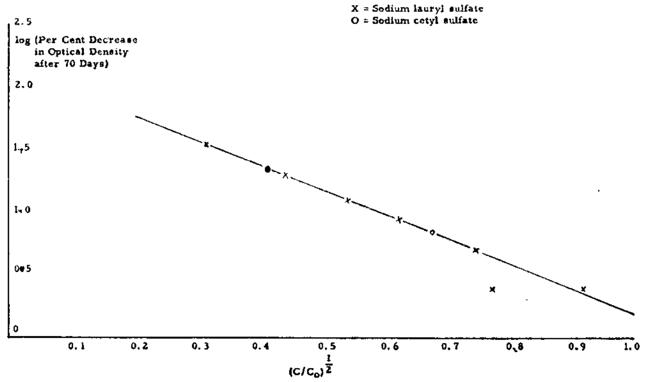

FIG. 6. Log of the per cent decrease in optical density after 70 days *vs.* $(C/C_o)^{1/2}$ for aqueous solutions of sodium alkyl sulfates at 24°C.

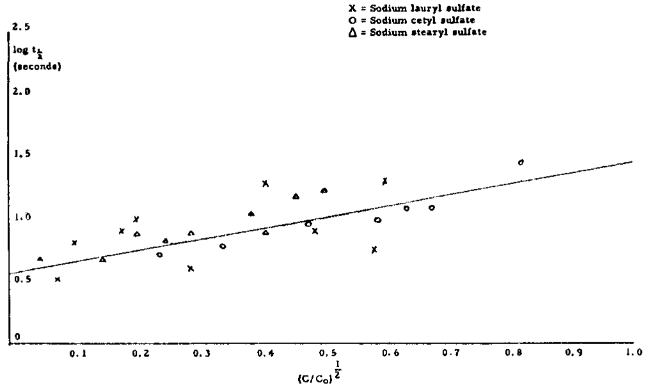

FIG. 7. Lot of the half-life of single droplets of n-tetradecane *vs.* $(C/C_o)^{1/2}$ for aqueous solutions of sodium alkyl sulfates at 35°C.

Conclusions

The interfacial film can be regarded as an energy barrier to coalescence. The derived equation relating the log of emulsion stability to $(C/C_0)^{1/2}$ is shown to be in accordance with experimental findings.

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