STABILITY OF EMULSIONS OF WATER IN OIL

III. FLOCCULATION AND REDISPERSION OF WATER DROPLETS COVERED BY AMPHIPOLAR MONOLAYERS

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ABSTRACT

Theoretical calculations demonstrate that emulsions of water in oil cannot be sufficiently protected against flocculation by an adsorbed layer of amphipolar molecules with an oleophilic chain of about 20 A. It is, however, expected that such flocculated emulsions can be redispersed by moderate rates of shear. This is confirmed by viscosity measurements. Non-Newtonian behavior found at low rates of shear is a consequence of flocculation. From the minimum rate of shear to reach the Newtonian region, i.e., to cause complete redispersion, the effective van der Waals' constant between the water droplets can be estimated. The rather low value of $A = 0.4 \times 10^{-14}$ erg is found.

INTRODUCTION

It was shown in a previous communication (1) that electric charges cannot be expected to stabilize water-in-oil (W/O) emulsions of more than extremely low concentration. In this paper we shall investigate whether a layer of oleophilic chains on the water droplets may prevent their flocculation.

When the surface of the water droplets is densely covered with stabilizer molecules of high desorption energy the surfaces of the droplets can approach each other only to a distance that equals twice the length of the stabilizer molecules. If the energy of the van der Waals' attraction at this distance is larger than a few times kT flocculation will occur. If not, the emulsion will be stable.

For the usual stabilizers the oleophilic chain is not longer than 20 A. Consequently the minimum distance between the water droplets is 40 A.

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TABLE I

Van der Waals' Energy between Two Spheres at a Distance of 40 A.
Expressed as Multiples of kT (4×10^{-14} erg)

Radius a	$A = 10^{-12}$ erg	$A = 10^{-13}$ erg	$A = 10^{-14}$ erg
0.1μ	50	5	0.5
1.0μ	500	50	5
$10\ \mu$	5000	500	50

The van der Waals' energy between two spheres of radius a at a distance d is given by:

$$V_{\text{van der Waals}} = -\frac{Aa}{12\,d},$$

when $d \ll a$ and A is the van der Waals' constant (2).

Table I shows that for the usual range of droplet sizes and normal values of the constant A the energy at contact, i.e., $d = 40$ A, is much larger than kT except perhaps for the smallest particles at an exceptionally low value of A. Therefore W/O emulsions are not stabilized against flocculation when the adsorbed stabilizers have a hydrocarbon chain of 20 or less carbon atoms.

CHARGED DROPLETS

It may be argued that if an electric charge or a layer of oleophilic chains are unable to stabilize W/O emulsions a combination of the two may perhaps lead to stabilization. The repulsion due to the electric double layer, however, has a very long range, and the maximum in the potential energy vs. distance curve (*cf.* Fig. 1 of paper I (3) in this series) is always situated at a larger separation than 40 A. Consequently the action of the oleophilic chains does not support that of the double layer and vice versa.

In general W/O emulsions containing droplets with a radius $\geqq 1\mu$ will therefore be either broken or flocculated, depending on their stability against coalescence (1, 3). If they are not stabilized against coalescence, they will flocculate and break. If, however, they are stable against coalescence the flocculation may conceivably be prevented or reversed by mechanical action, e.g., by stirring the emulsion.

BEHAVIOR OF BINARY AGGREGATES IN LAMINAR FLOW

In order to investigate whether a flocculated system can be redispersed to the primary particles by shaking, we shall consider the behavior of aggregates in a laminar field of flow.

Two points have to be considered:

First: what is the minimum rate of shear, D, to surmount the van der

Waals' attraction by which the particles are held together in the aggregate, if the minimum distance between the surfaces of the water droplets equals d (d is twice the length of the hydrocarbon chain of the stabilizing molecule adsorbed at the interface)?

Second: will the period during which the shearing force is acting last long enough to allow the redispersed particle to be removed to such a distance from the aggregate that it will not be caught back during the rotation of the aggregate?

CALCULATION OF THE RATE OF SHEAR NECESSARY TO OVERCOME THE VAN DER WAALS' FORCE IN THE AGGREGATE

Big aggregates may be expected to fall apart more easily than small ones. For a given rate of shear, the redispersing force (see Eq. [4] for $d \ll a$) and the number of contact points to be broken will both on the average be proportional to the $\frac{2}{3}$rd power of the number of primary globules in the aggregate. But the breaking of the aggregate may occur along the weakest plane by breaking the contact points one by one. This wedge effect is absent in a doublet. Consequently the splitting of the smallest aggregate, a complex consisting of two particles only, is the last and the most difficult step to complete redispersion. For this reason we shall investigate the behavior of a two-particle aggregate under the influence of a shearing force.
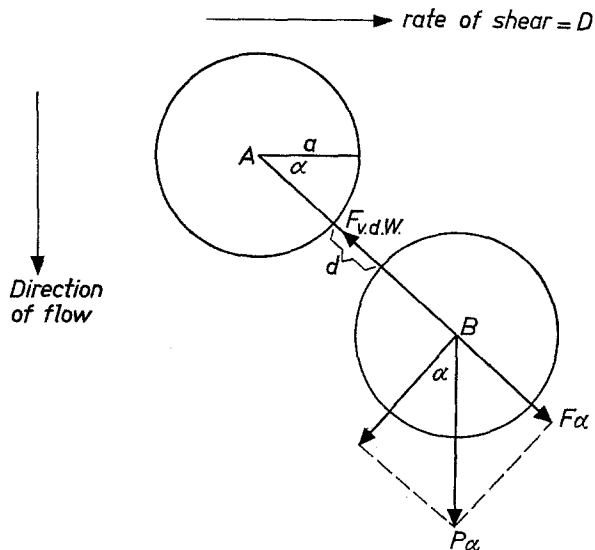

FIG. 1. Rotation of a two-particle aggregate under influence of a shearing force. Here a = radius of the globule, d = distance between the surfaces of the globules, F_{vdW} = van der Waals' force, $F\alpha$ = shearing force acting on particle B, as caused by the hydrodynamic flow.

In general the line connecting the centers of the two droplets will make an angle with the plane defined by the direction of flow and the direction of shear. When the flow starts this line will describe a rather complicated trajectory, but finally it will become parallel to the plane indicated above (at least if the aggregate has not been broken up before). Therefore we shall consider only a binary aggregate AB built up from two spherical droplets A and B, and situated in the plane of flow and shear (see Fig. 1). The line connecting the particles makes an angle α with the direction of shear; the distance between the surfaces is d. The difference in rate of flow between the centers of the droplets A and B is equal to

$$\Delta v = (2a + d)D \cos \alpha. \tag{1}$$

A part of this flow, viz., $\Delta v \cos \alpha$ leads to a rotation of the droplets around their center of gravity with a rate

$$d\alpha/dt = D \cos^2 \alpha. \tag{2}$$

The remaining part of the flow, viz. $\Delta v \sin \alpha$ results in a tension $F_\alpha = P_\alpha \sin \alpha$ tending to force the particles apart.

This tension F_α is determined by the entire flow pattern around the two spheres. As a very first approximation we may put it equal to the force calculated from Stokes' law. This results in

$$F_\alpha = 6\pi\eta a \frac{\Delta v}{2} \sin \alpha = 3\pi\eta a(2a + d)D \sin \alpha \cos \alpha. \tag{3}$$

During the rotation of the aggregate from $\alpha = 0$ to $\alpha = 90°$ the tension F_α increases from zero to a maximum value at $\alpha = 45°$ and decreases again to zero for $\alpha = 90°$. Separation of the aggregate and redispersion may occur when the value of F_α is larger than the van der Waals' attraction F_{vdW}, starting at some angle $\alpha_{\text{crit.}} < 45°$ and extending to $\alpha = 90°$

$$F_{\alpha_{\text{crit.}}} = \tfrac{3}{2}\pi\eta a(2a + d)D \sin (2\alpha_{\text{crit.}}) = F_{\text{vdW}}. \tag{4}$$

We are interested in cases where d starts at a value (e.g., 40 A.) much smaller than a (e.g., 1 μ). In these cases, according to Hamaker (2) the van der Waals' force is given by

$$F_{\text{vdW}} = \frac{Aa}{12 \, d^2}. \tag{5}$$

The condition for redispersion is, therefore, neglecting d in comparison with a

$$3\pi\eta a^2 D \sin (2\alpha_{\text{crit.}}) > \frac{Aa}{12 \, d^2} \tag{6}$$

TABLE II

Critical Rates of Shear in sec.⁻¹ for Redispersion of Particles Separated by a Layer of 40 A. Thickness as a Function of van der Waals' Constant, A, and Particle Radius a.

Radius a	$A = 10^{-12}$ erg	$A = 10^{-13}$ erg	$A = 10^{-14}$ erg
0.1μ	10^6	10^5	10^4
$1\ \mu$	10^5	10^4	10^3
$10\ \mu$	10^4	10^3	10^2

or

$$D > \frac{A}{36\pi\eta a\ d^2 \sin (2\alpha_{crit.})} \ . \qquad [7]$$

Inserting the value 40 A. for d and 0.006 poise for η (e.g., benzene at 25°C.) and 30° for $\alpha_{crit.}$ (see below), we obtain

$$D > \frac{A}{a} \times 10^{13}. \qquad [8]$$

Table II gives values for the critical rate of shear, $D_{crit.}$, calculated with Eq. [7] for a number of representative cases.

ESTIMATION OF THE CRITICAL ANGLE, $\alpha_{crit.}$, FOR DISPERSION

We shall now show that redispersion occurs in a very short time, if the rate of shear is larger than $D_{crit.}$. During rotation of the aggregate between $\alpha = 0$, and $\alpha = 90°$ the excess of the tension F_α over the van der Waals' attraction, F_{vdw}, will force the particles apart. Mooney (4) has calculated the friction factor for the motion of two solid spheres along the line connecting their centers. For small distances, p, between the surfaces the relative axial velocity $v_{rel.}$ under the influence of an axial force F on each of the spheres is given by

$$v_{rel.} = \frac{4p\left(1 + \dfrac{p}{2a}\right)^2}{3\pi\eta a^2}\ F. \qquad [9]$$

If the separation is large Stokes' law holds and then

$$v_{rel.} = \frac{2F}{6\pi\eta a}\ . \qquad [10]$$

The transition between the validity regions of Eqs. [9] and [10] will be situated roughly at

$$\frac{4p\left(1 + \dfrac{p}{2a}\right)^2}{a} \sim 1 \quad \text{or} \quad \frac{p}{a} \sim 0.215. \qquad [11]$$

There are a number of uncertainties in applying Mooney's equation [9] to our case. Emulsion droplets are liquid and so deformation of the particles and flow inside the droplets may play a role. A more serious difficulty is presented by the choice of a relation between p, the gap through which flow with a viscosity η is possible, and d, the distance between the water droplets. The extreme view that p is equal to d minus twice the length of a stabilizer chain would lead to the conclusion that the droplets would not be separated by any finite rate of shear, because then at the start p would be zero and according to Eq. [9] $v_{rel.}$ would be and remain zero as well.

However, the layer of stabilizing chains is certainly not rigid and not impermeable to the oil phase. Consequently we should assume that p at the start has a finite value between 0 and d. If d is 40 A., p will very probably be between 2 and 20 A. In the region where Mooney's expression [9] is applicable the rate of separation of the droplets can be approximately described by

$$\frac{dd}{dt} = \frac{4p}{3\pi\eta a^2}\left[6\pi\eta a^2 D \sin\alpha\cos\alpha - \frac{Aa}{12\,d^2}\right], \qquad [12]$$

with Eq. [2] giving the relation between α and t. We carried out a few numerical integrations of Eq. [12]. They showed that for an initial value of $p = 2$ A. the critical angle $\alpha_{crit.}$ was about 27°; for $p = 6$ A. it was about 32°. In Eq. [7] the critical angle occurs as $\sin 2\alpha$. As $\sin 2\alpha$ is already 0.80 for $\alpha = 27°$ and can never be larger than 1, the precise value of $\alpha_{crit.}$ is of little importance for our problem.

Consequently when the rate of shear exceeds the value given by Eq. [7] agglomerates will be broken up into single particles in less than the time required for half a revolution, i.e., in less than $2\pi/D$ sec. Table II shows that droplets of 1μ, protected by an oleophilic layer of 20 A. each, may be separated by a rate of shear of about 1000 sec.$^{-1}$ when the van der Waals' constant is low. For a high value of this constant the rate of shear must be higher.

DEPENDENCE OF THE VISCOSITY OF AN EMULSION ON THE STATE OF AGGREGATION OF THE DISPERSED PHASE

In a flocculated emulsion part of the continuous phase is immobilized in the aggregates, so that the volume fraction φ of the dispersed phase, and consequently also the viscosity of the emulsion, is increased. Redispersion of an emulsion may therefore be investigated by means of viscosity measurements.

Under the influence of an increasing hydrodynamic force, i.e., by increasing the rate of shear, a flocculated aggregate redisperses gradually as is schematically represented in Fig. 2. During disaggregation, immobilized medium is set free and the viscosity decreases. As soon as all aggregates are redispersed into original globules the viscosity remains constant in spite of further increase in the rate of shear. This is expressed by the $D\tau$
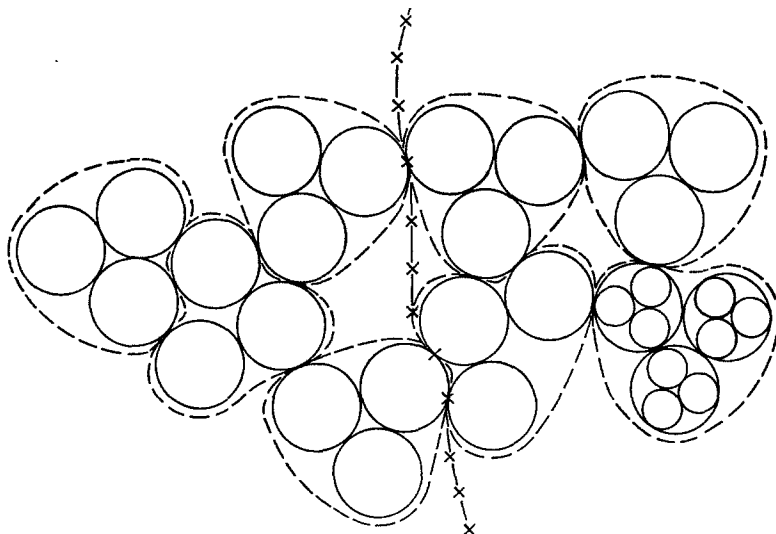
FIG. 2. Under influence of a shearing force the aggregates redisperse first along the crossed line, secondly along the broken lines, and finally along the solid lines.
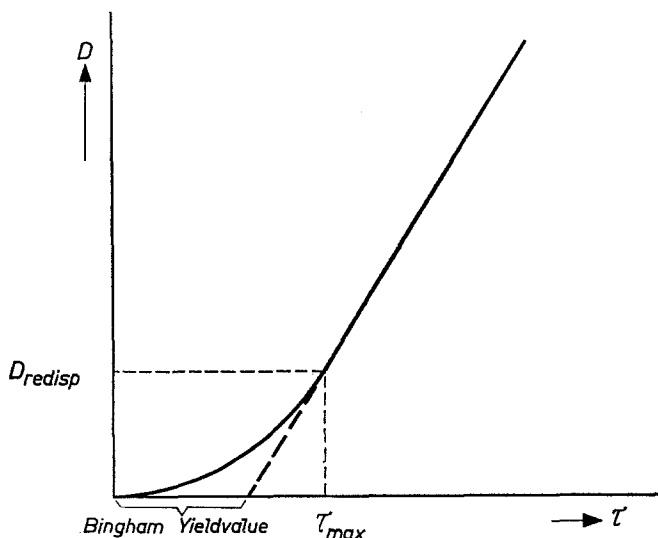

FIG. 3. Schematic representation of the D-τ curve of an agglomerated emulsion, as expected on the basis of the theory presented. Complete redispersion results if D and τ are greater than $D_{\text{redisp.}}$ and $\tau_{\text{max.}}$, respectively.

(rate of shear, shear stress) diagram of Fig. 3, where a straight line is found beyond the critical point $\tau_{\text{max.}}$, $D_{\text{redisp.}}$.[3]

[3] See the discussions on this subject given by J. J. Hermans in "Flow Properties of Disperse Systems," pages 26 and 27. North-Holland Publishing Company, Amsterdam, 1953.

According to Eq. [6]

$$D_{\text{redisp.}} = \frac{A}{36\pi\eta a\, d^2 \sin(2\alpha_{\text{crit.}})}.$$ [13]

To obtain $D_{\text{redisp.}}$ from viscosity measurements the concentration of the emulsion should be high enough to have a sufficiently pronounced non-Newtonian behavior. On the other hand, it should be low enough to allow a redispersing droplet to move away far enough from the rotating aggregate to move out of the van der Waals' attraction field without being caught immediately by a neighboring aggregate. Concentrations between 10 % and 30 % by volume are suitable.

THE VISCOMETER

An Ostwald type viscometer with a capillary of radius $r = 0.032$ cm. and length $L = 17.4$ cm. and with two flow bulbs situated about 10 cm. above each other (see Fig. 4) was used (5). Different levels of filling can be chosen. For each level two different average rates of shear are available. A cathetometer was used to determine the (average) hydrostatic head and to reproduce the levels of filling. Water was used for the calibration. The viscometer was rigidly mounted in a constant-temperature bath at *ca.* 21°C. with a fluctuation of less than 0.02°C.

The flow time, t, varied between 50 and 1000 sec. and was determined with an accuracy of 0.1 sec. No corrections were applied for the influence of surface tension, of incomplete drainage (6), and of the Hagenbach correction (7). The latter equals about 0.5 % in the most unfavorable cases.

In order to prevent creaming of the emulsion during the rather long waiting and measuring periods, the density of the benzene phase was adjusted to the density of water by addition of about 15 % carbon tetrachloride.

Diagrams of D-τ were derived from the data in the following way (8). The shear stress at the wall of the capillary is calculated from

$$\tau = \frac{rgh\rho}{2L},$$ [14]

and the rate of shear at the wall from

$$D = \frac{rg}{8L}\frac{\rho_0 h_0 t_0}{\eta_0}\left[\frac{3}{t} + \frac{h\, d\left(\frac{1}{t}\right)}{dh}\right],$$ [15]

where $g =$ the acceleration due to gravity, $h =$ the average value of the hydrostatic head, and $\rho =$ the density of the emulsion. The values with subscript 0 refer to the calibration experiment with water.
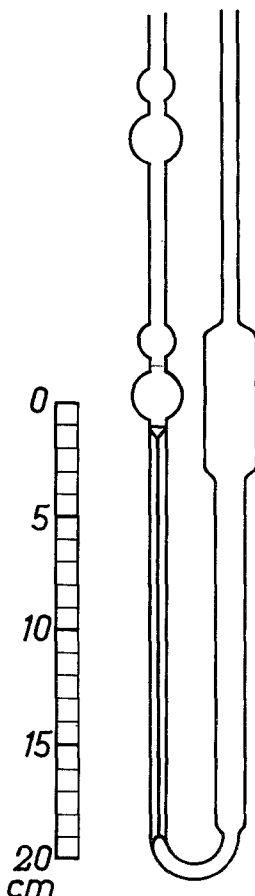
FIG. 4. Viscometer. Radius of capillary $r = 0.032$ cm.

EFFICIENCY OF REDISPERSION IN THE CAPILLARY OF THE VISCOMETER

Equation [15] is based upon the assumption that the rate of shear, D, is a unique function of the shear stress, τ. This implies that, if aggregates are broken up, this disentangling takes place in a short time as compared to the total time of travel in the capillary. It will now be shown that this is the case in our experiments.

It has already been pointed out that fission of a binary aggregate will occur in a fraction of the time of rotation of the aggregate, if it occurs at all. Therefore the time of rotation T_r should be small compared to the traveling time T_c of the aggregate in the capillary. In a field with a rate of shear D, the time of rotation is equal to

$$T_r = \frac{2\pi}{d\alpha/dt} = \frac{2\pi}{D \cos^2 \alpha} = \frac{4\pi}{D}. \tag{16}$$

From the center to the wall of the capillary the velocity decreases and the rate of shear increases. Conditions in the axis are therefore unfavorable for redispersion, whereas they are most favorable near the wall of the capillary. More or less arbitrarily we shall consider the conditions at $\frac{1}{3} r$ from the axis because 80 % of the liquid travels and 90 % of the friction is generated between $\frac{1}{3} r$ and r.

At $\frac{1}{3} r$ from the axis the rate of shear is (assuming for simplicity strict Newtonian behavior)

$$D = \frac{rgh\rho}{6\eta L}.$$ [17]

The velocity v of the liquid at $\frac{1}{3} r$ is given by

$$v = \frac{2r^2 gh\rho}{9\eta L},$$ [18]

and the total time of flow through the capillary

$$T_c = \frac{L}{v} = \frac{9\eta L^2}{2r^2 gh\rho}.$$ [19]

From Eqs. [16], [17], and [19] we find:

$$\frac{T_r}{T_c} = \frac{16\pi r}{3L} = 0.03,$$ [20]

substituting the actual values for $r = 0.032$ cm. and $L = 17.4$ cm.

Consequently, if the rate of shear is high enough to redisperse the aggregates, redispersion will be complete in the first few millimeters of the capillary.

MEASUREMENTS

Emulsions of water in benzene (+15 % carbon tetrachloride) were prepared as described in part I of this series (3). Measurements were made on emulsions in which one of the following stabilizers had been dissolved.

  I. 1 % Cu^{II}-oleate.
 II. 1 % emulgide W.O.L. = partial ester of triglycerol and polycondensed ricinoleic acid.
III. 1 % SPAN 85 = sorbitan trioleate.
 IV. 1 % SPAN 60 = sorbitan monostearate.
  V. 1 % magnesium-petroleumsulfonate = magnesium salt of didodecyl-benzene (naphthene) sulfonic acid.
 VI. 1 % mixture of magnesium-petroleumsulfonate and Ca-didodecyl-salicylate, while at the same time 18 % calcium acetate has been dissolved in the water phase.
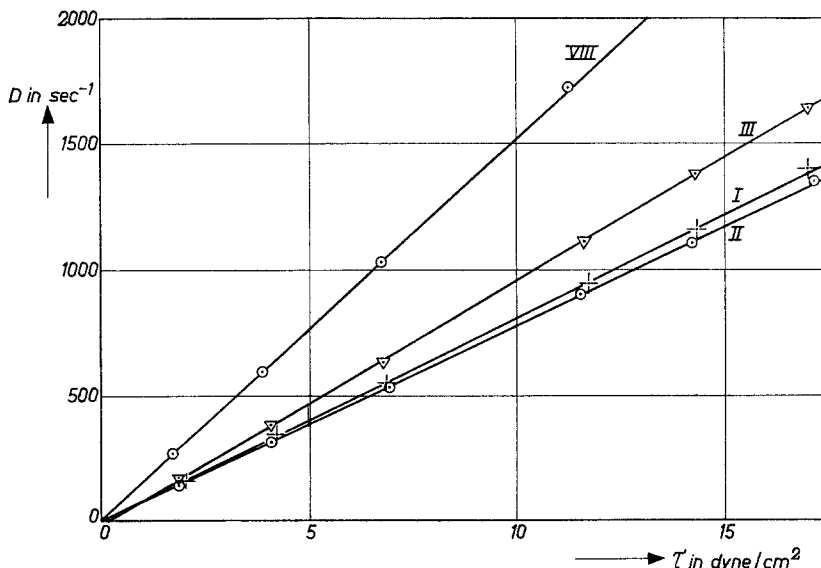VII. Like VI, but a slightly more concentrated emulsion.

FIG. 5. Rheological behavior of benzene and water in benzene (+15% CCl₄) emulsions.

Curves I, II, and III represent water in benzene emulsions stabilized with Cu^II-oleate, emulgide W.O.L., and SPAN 85, respectively. Curve VIII shows the behavior of pure benzene.
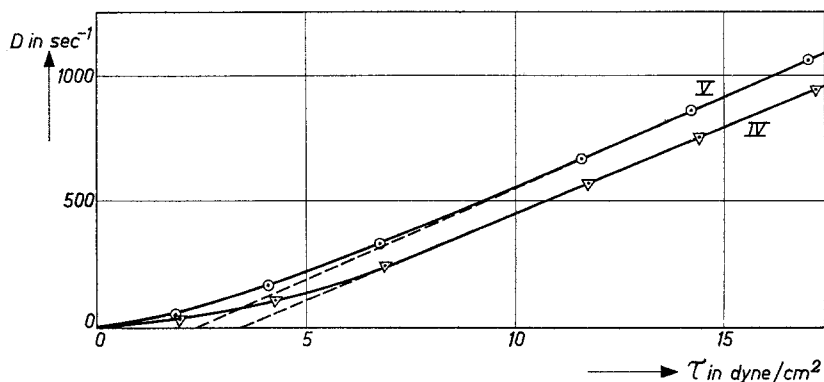

FIG. 6. Rheological behavior of water (+18% Ca-acetate) in benzene (+15% CCl₄) emulsions, stabilized with a mixture of Mg-petroleum-sulfonate and Ca-didodecyl-salicylate.

For comparison viscosity measurements were also done on VIII, pure benzene.

Figures 5, 6, and 7 show the relation between shearing stress τ and rate of shear D for these emulsions as calculated from Eqs. [14] and [15]. The relevant data for these emulsions were collected in Table III.
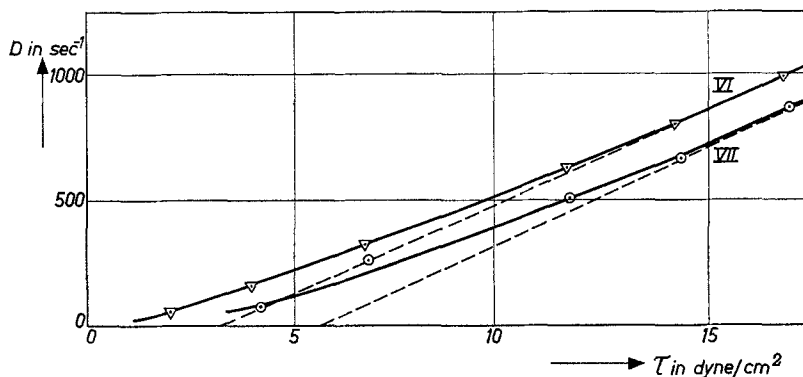
FIG. 7. Rheological behavior of water in benzene (+15% CCl₄) emulsions, stabilized with SPAN 60 (curve IV) and Mg-petroleum-sulfonate (curve V).

TABLE III

Comparison between the Calculated and the Measured Critical Rate of Shear, D_{redisp}.

1	2	3	4	5	6	7
Emulsion number	Volume fraction φ	Most frequent radius a (μ)	$\left(\dfrac{d\tau}{dD}\right)_{lin} = $ (η_{Newton}) (centipoise)	D_{redisp}. observed from D-τ diagram ($sec.^{-1}$)	D_{redisp}. calculated from Eq. [13] ($sec.^{-1}$); $A = 0.4 \times 10^{-14}$ erg	Number of carbon atoms in oleophilic chain of the stabilizer
I	0.17	3.5	1.24	<50	100	17 (but hydrolyzed)
II	0.17	4.5	1.29	<50	4	78
III	0.14	5.5	1.04	<100	70	17
IV	0.175	3.5	1.41	200	100	18
V	0.17	1.5	1.35	550	500	12
VI	0.15	1	ca. 1.27	>1400	750	12
VII	0.17	1	ca. 1.20	>1400	750	12
VIII	0.00	—	0.65	<50	0	—

DISCUSSION OF RESULTS

Figures 5, 6, and 7 indicate that all the curves pass through the origin or come very near to it. There is no yield value or only a very small one. Some of the curves are straight (I, II, and VIII); the others are more or less curved, indicating a plastic behavior of the emulsions. The upper straight parts of the curves indicate situations where the emulsions behave as Newtonian liquids, i.e., where complete redispersion has taken place. The rate of shear where the straight part passes into the curved part is the minimum rate of shear sufficient for complete redispersion, D_{redisp}. .

The theoretical value for D_{redisp}. was calculated from Eq. [13]. The most

frequent radius as mentioned in column 3 of Table III was used for a, and twice the hydrocarbon chain length (1.2 A. per carbon atom) of the stabilizer for d. The value of $\alpha_{crit.}$ was put equal to 30°. A reasonable agreement between the experimental and theoretical values for $D_{redisp.}$ is obtained by choosing $A = 0.4 \times 10^{-14}$ erg for the van der Waals' constant.

The difference between the two values for emulsion I suggests a larger d than the length of an oleate chain can account for. This corresponds with the view that this emulsion is not stabilized by the oleate chains but by products of hydrolysis which act as solid particle stabilizers, as has been pointed out in a preceding paper (3). The experimental value for emulsion III is quite low. However, emulsion III is definitely non-Newtonian, whereas emulsion I is not; this indicates a greater tendency to flocculation in emulsion III, as has been confirmed by microscopic observation.

There is a striking difference between emulsions III and IV, though the hydrocarbon chains are approximately of the same length. However, the rapid flocculation of emulsion IV can easily be explained by the fact that in this case only one stearic chain per sorbitan molecule is present, whereas the stabilizer of emulsion III contains three oleate chains per sorbitan molecule. The surface of the water globules of emulsion III is therefore notably more densely covered with oleophilic chains than that of emulsion IV. Thus, on the mutual approach of the water globules of emulsion IV, the stearic chains may partially double up or slip alongside each other instead of mutually colliding with their extremities as occurs in the case of emulsion III, so that the effective length is less than 18 C-atoms. The experimental value of $D_{redisp.exp.}$ actually appears to be notably higher than the theoretical value of $D_{redisp.th.}$ for 18 C-atoms.

Once more it becomes obvious that water-in-oil emulsions at rest are not stable to flocculation in spite of a surface potential of about 100 mV as is shown clearly by curves V, VI, VII, represented in Figs. 6 and 7. Moreover microscopic observations proved all emulsions except I and II to be aggregated to a large extent.

THE VAN DER WAALS' CONSTANT

A value of the order of 10^{-14} erg has to be taken for the van der Waals' constant A to obtain agreement between experiment and theory in the redispersion experiments (column 5 and 6 of Table III). This is much lower than the values commonly used for suspensions in aqueous media ($A \approx 10^{-12}$ erg) and also lower than the values to be expected from theory, although these are admittedly rather uncertain.

Some possible explanations for the low value of A that have to be considered are:

1. The van der Waals' constants for water and the mixture of benzene and carbon tetrachloride might be nearly the same, so that the mutual

van der Waals' constant would be quite small. This, however, would be quite accidental and would also make it hard to explain why the stability of emulsions with and without CCl_4 is so similar.

2. Double layer repulsions will in principle promote further redispersion and if left out of account simulate too low a van der Waals' constant. Quantitative calculations as given in parts I and II of this series (1, 3) prove that the force of the double layer repulsion is only a small fraction of that of the van der Waals' attraction and could never explain that the van der Waals' constant is one to two orders of magnitude smaller than expected.

3. Incomplete redispersion at the limit where the D-τ curve is already straight might be partly responsible for the discrepancy. It would increase the value of a in Eq. [13] and thus lead to a larger value of A. But more than a factor 2 or 3 would not be expected from this source.

4. The retardation effect. For the relatively large particles and interparticle distances considered here retardation (2) of the van der Waals' force has to be taken into account. However, if the typical retardation wavelength is put equal to 1000 A. the retardation factor is between 1 and 0.5, and again the discrepancy between $A = 10^{-14}$ and $A = 10^{-12}$ remains unexplained.

We must conclude either that the van der Waals' constant in these emulsions is rather low indeed, or that the minimum distance between the emulsion droplets is larger than we realize.

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