

## STABILITY OF EMULSIONS OF WATER IN OIL

### II. CHARGE AS A FACTOR OF STABILIZATION AGAINST FLOCCULATION

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*Received January 21, 1959*

#### ABSTRACT

It is shown by theoretical calculations that the energy barrier between charged droplets in water-in-oil emulsions is strongly diminished when the concentration of the emulsion is not extremely low. This is a consequence of the great extension of the diffuse electrical double layer in oil. The high concentration in the sediment (or cream) therefore strongly promotes flocculation. Gravity also promotes flocculation directly in all but the most dilute W/O emulsions because the weight of the particles in higher layers transmitted by the extended double layers presses on those in the lower layers and forces them together.

#### INTRODUCTION

It has been pointed out in a preceding paper (1) that water-in-oil emulsions flocculate rapidly, notwithstanding the presence of a rather high potential on the water droplets. Calculating the energy barrier in the approach of two water droplets with a radius of  $1 \mu$  and a surface potential of 25 mv. a value of  $15 kT$  is found, which ought to retard flocculation quite considerably. It will be shown in this paper that because of the long range of the electrical repulsion the two particle calculations have to be abandoned. By taking interactions between large numbers of particles into account the observed behavior of W/O emulsions with respect to flocculation can be understood.

#### EFFECT OF THE CONCENTRATION OF THE DISPERSE PHASE ON THE STABILITY AGAINST FLOCCULATION IN MEDIA OF LOW DIELECTRIC CONSTANT

In systems in which water is the continuous phase the thickness of the double layer generally equals about  $10^{-3}$ - $10^{-2} \mu$  so that electrical interaction takes place only at very short distances. The potential energy of the charged particles at a mutual distance of a few times  $10^{-2} \mu$  thus equals

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zero with regard to infinite distance. Consequently the total energy barrier has to be crossed before flocculation can occur.

In an oil-continuous system, however, the thickness of the diffuse double layer is several microns. The thickness is of the same order as the distance between the dispersed globules in a moderately concentrated emulsion. The globules therefore possess a potential energy with regard to separation at an infinite distance. Consequently the energy barrier is lowered and the stability against flocculation is diminished. This effect has already been mentioned by Verwey (2). A further lowering of the energy barrier occurs as a consequence of the combined interaction of more than two particles, as has been illustrated schematically in Fig. 1 for a globule *b* under the influence of two neighboring globules *a* and *c*.

The influence, however, of all the globules must be taken into account. The charged globules of the disperse phase are distributed more or less homogeneously in the continuous medium. Very short distances between the globules will rarely occur owing to the double layer repulsion.

To calculate the influence of all the surrounding globules on a particular globule *b* a model for the arrangement of the globules has to be assumed. In this model we consider twelve nearest neighbor globules to be situated on a spherical shell  $R_I$  with radius  $R_I$ , and all the other globules to be homogeneously distributed in the space outside a sphere  $R_{II}$  with radius

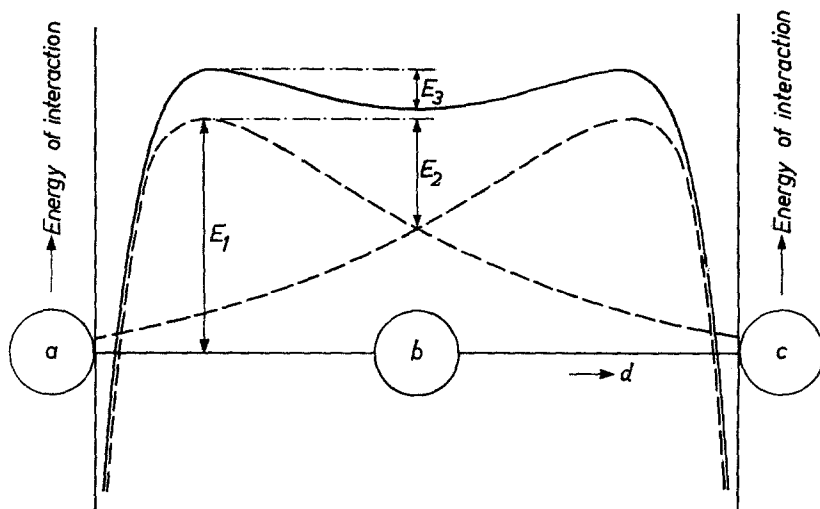


FIG. 1. Reduction of the energy barrier. The broken lines represent the interaction between the globule *a* and *b* in the absence of *c* and between *c* and *b* in the absence of *a*.  $E_1$  is the energy barrier to be surmounted if particle *b* approaches *a* from infinity. It is reduced to  $E_2$  if *b* is assumed to start from the position in the drawing. It is still further reduced to  $E_3$  if the simultaneous interaction with *c* is taken into account. The drawn line is the sum of the two broken lines.

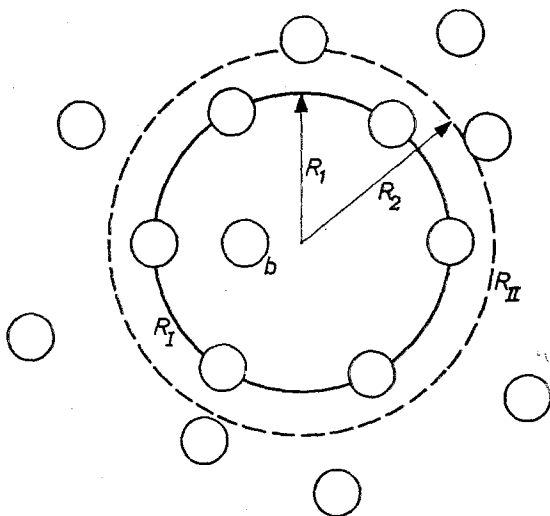


FIG. 2. Distribution of droplets interacting with droplet  $b$ . Twelve droplets on sphere  $R_I$ , all other droplets outside sphere  $R_{II}$ .

$R_2$  as shown in Fig. 2. The radius  $R_I$  is chosen equal to the average distance between the droplets or to the distance they would have in a regular 12 coordinated lattice.

So if  $\varphi$  is the volume fraction of spheres with radius  $a$

$$\varphi = 0.74 \frac{a^3}{\left(\frac{R_I}{2}\right)^3}$$

or

$$R_I = \frac{1.81a}{\sqrt[3]{\varphi}}; \quad [1]$$

and  $R_2$  is chosen in such a way that the volume within  $R_{II}$  just corresponds to the volume available to thirteen particles.

$$\frac{4\pi}{3} R_2^3 = \frac{13}{0.74} \frac{4\pi}{3} \left(\frac{R_I}{2}\right)^3$$

or

$$R_2 = 1.3 R_I = \frac{2.36a}{\sqrt[3]{\varphi}}. \quad [2]$$

The energy of interaction between a pair of globules at a distance  $x$  between the centers is, according to Verwey and Overbeek (3):

$$V_R = \beta \epsilon a^2 \psi_0^2 e^{2ka} \frac{e^{-kx}}{x}, \quad [3]$$

in which  $\psi_0$  is the surface potential,  $\epsilon$  is the dielectric constant of the medium, and  $\kappa$  is the reciprocal thickness of the double layer. Here,  $\beta$  is a factor varying between 0.60 and 1.00 which for simplicity will be put equal to 1.

If the twelve nearest neighbors can occupy any arbitrary position on the sphere  $R_1$  the probability of finding one on unit area of the surface is  $12/4\pi R_1^2$ . Assuming that the droplet  $b$  is situated at a distance  $q$  from the center of the sphere  $R_1$  and using coordinates as given in Fig. 3, the interaction energy of droplet  $b$  with the droplets in the surface element  $P$  is given by

$$dV_R = \frac{12}{4\pi R_1^2} R_1 \sin \alpha d\theta \cdot R_1 d\alpha \cdot \epsilon \psi_0^2 a^2 e^{2\kappa a} \frac{e^{-\kappa x}}{x}. \quad [4]$$

Observing that  $x = \sqrt{R_1^2 + q^2 - 2qR_1 \cos \alpha}$  and integrating over  $\alpha$  and  $\theta$  we find:

$$V_R = 6\epsilon \psi_0^2 a^2 e^{2\kappa a} \frac{e^{-\kappa R_1}}{\kappa R_1} \frac{e^{\kappa q} - e^{-\kappa q}}{q}. \quad [5]$$

The assumption incorporated in Eq. [5] that the twelve nearest neighbors can occupy any position on the sphere  $R_1$  is not correct for one of the twelve neighbors, viz., for the one with which the droplet  $b$  possibly flocculates.

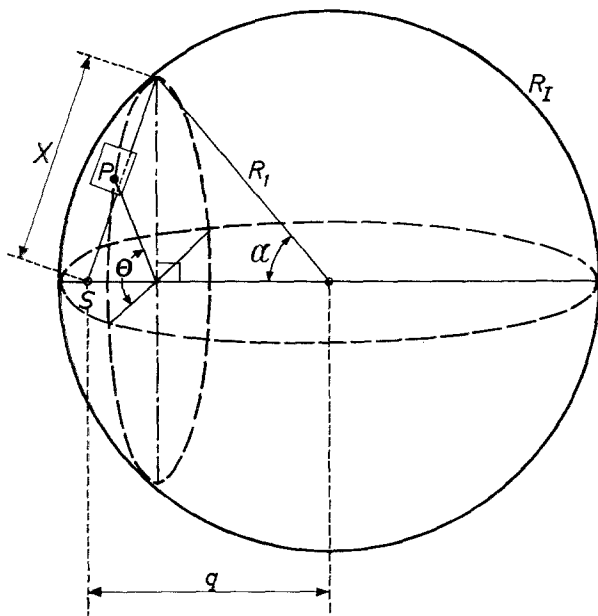


FIG. 3. Interaction of the surface element of the sphere  $R_1$  and globule  $b$  situated in  $S$ . Here  $x$  and  $q$  represent the distances between  $S$  and the element  $P$  and between  $S$  and the center of the sphere, respectively.

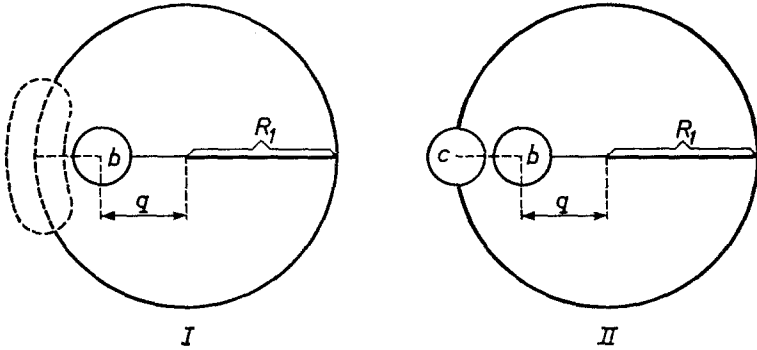


FIG. 4. I. Interaction between globule  $b$  and globule  $c$  spread over the spherical shell. II. Interaction between globule  $b$  and globule  $c$  in fixed position.

If we consider, for simplicity, only head-on collisions, this droplet, which we call  $c$ , has a fixed position as shown in Fig. 4, instead of being spread out over one-twelfth of the surface of the sphere. The interaction with particle  $c$  spread out on one-twelfth of the shell has to be subtracted from Eq. [5] and the interaction with  $c$  in this fixed position to be added.

An expression for the first effect is easily found by integrating Eq. [4] over  $\theta$  from 0 to  $2\pi$  and over  $\alpha$  from 0 to  $\arccos 5/6$ .

The final expression for the interaction with the first twelve neighbors is:

$$V_R = \epsilon\psi_0^2 a^2 e^{2\kappa a} \left[ \frac{e^{-\kappa(R_1-q)}}{R_1 - q} + \frac{6}{\kappa R_1 q} \left\{ e^{-\kappa\sqrt{R_1^2+q^2-5/3R_1q}} - e^{-\kappa(R_1+q)} \right\} \right]. \quad [6]$$

The calculation of the interaction with all nonnearest neighbors is carried out in a similar way by integrating an expression like [4] but now integrating also over the radius of the shell between  $1.3R_1$  and  $\infty$ . The proportionality constant has now to be equal to the number of droplets per unit volume. Consequently

$V_R(\text{nonnearest neighbors}) =$

$$\frac{0.74}{\frac{4\pi}{3}(R_1)^3} \epsilon\psi_0^2 a^2 e^{2\kappa a} \int_{R=1.3R_1}^{\infty} \int_{\alpha=0}^{\pi} \int_{\theta=0}^{2\pi} \frac{e^{-\kappa x}}{x} R^2 dR \sin \alpha d\alpha d\theta, \quad [7]$$

in which  $x = \sqrt{R^2 + q^2 - 2Rq \cos \alpha}$ . After carrying out the integration and adding the result to Eq. [6] the final expression for the interaction energy of droplet  $b$  with all other droplets becomes:

$$V_R(\text{total}) = \epsilon\psi_0^2 a^2 e^{2\kappa a} \left[ 8.88 \frac{1.3\kappa R_1 + 1}{\kappa^3 R_1^3} e^{-1.3\kappa R_1} \frac{e^{\kappa q} - e^{-\kappa q}}{q} + \frac{e^{-\kappa(R_1-q)}}{R_1 - q} - \frac{6}{\kappa R_1 q} \left\{ e^{-\kappa(R_1+q)} - e^{-\kappa\sqrt{R_1^2+q^2-5/3R_1q}} \right\} \right]. \quad [8]$$

In most cases the underlined term representing the interaction between droplets *b* and *c* (see Fig. 4) gives the major effect, but the other terms are by no means negligible. The lowering of the energy barrier in per cent of the value for the simple interaction of two particles is given by:

lowering =

$$\frac{\lim_{R_1 \rightarrow \infty} V_R \text{ total } (q = R_1 - 2a) - \{V_R \text{ total } (q = R_1 - 2a) - V_R \text{ total } (q = 0)\}}{\lim_{R_1 \rightarrow \infty} V_R \text{ total } (q = R_1 - 2a)} \times 100\% = \frac{1200a e^{2\kappa a}}{\kappa R_1 (R_1 - 2a)} \left\{ 1.48 \frac{1.3\kappa R_1 + 1}{\kappa^2 R_1^2} e^{-1.3\kappa R_1} \right. \tag{9}$$

$$\left. (2\kappa(R_1 - 2a) - e^{\kappa(R_1 - 2a)} + e^{-\kappa(R_1 - 2a)}) + 2\kappa(R_1 - 2a)e^{-\kappa R_1} + e^{-2\kappa(R_1 - a)} - e^{-\kappa\sqrt{1/3R_1^2 - 2/3R_1a + 4a^2}} \right\} \% .$$

This lowering is represented in Fig. 5 for different values of the volume fraction  $\varphi$  and the reciprocal thickness of the double layer  $\kappa$ .

Although the calculation is admittedly quite rough, the order of magni-

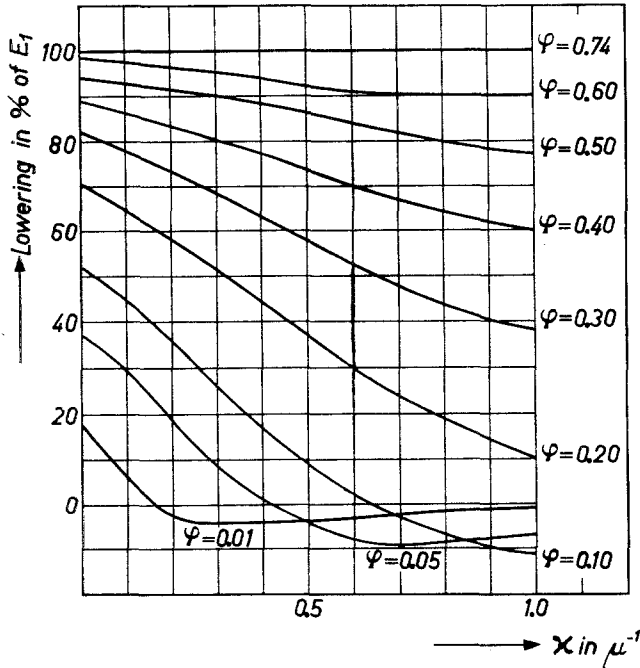


FIG. 5. Lowering of the energy barrier for flocculation in concentrated emulsions expressed in per cent of the energy barrier in an infinitely dilute emulsion. Drop radius  $a = 1\mu$ .

tude of the effect is quite obvious. A more refined calculation, taking account of the van der Waals attraction, would make the lowering of the barrier more pronounced.

It is evident from Fig. 5 that the concentration influence of the dispersed phase diminishes the stability against flocculation already at low concentration of water in oil, when the reciprocal thickness of the double layer is in the order of  $0.1 \mu^{-1}$ . In the cream layer, where the concentration may come close to 74%, the effect is enormous.

#### INFLUENCE OF GRAVITY ON THE STABILITY AGAINST FLOCCULATION

In an emulsion the droplets settle under the influence of a force  $f_g$ , which equals

$$f_g = \frac{4}{3}\pi a^3 g(\rho_i - \rho_e), \quad [10]$$

where  $g$  = acceleration of gravity and  $\rho_i$  and  $\rho_e$  are the densities of the droplets and the continuous phase, respectively.

This force should be compared to the maximal repulsive force between two particles in order to see whether gravity can accelerate flocculation.

An upper limit for the repulsive force,  $f_r$ , can be found by differentiation of Eq. [3].

$$f_r = -\frac{dV_R}{dx} = \epsilon a^2 \psi_0^2 e^{2\kappa a} \frac{e^{-\kappa x}}{x} \left( \kappa + \frac{1}{x} \right),$$

in which the factor  $\beta$  has been put equal to 1. The maximum value of  $f_r$  is obtained for  $x = 2a$ , the minimum possible value of  $x$ :

$$(f_r)_{\max.} = \frac{\epsilon \psi_0^2}{4} (1 + 2\kappa a). \quad [11]$$

TABLE I

*Correlation between the Radius  $a$ , the Gravitational Force  $f_g$  Acting on the Globules, and the Maximum Slope of the Energy Function between Two Globules as Represented in Column 3*

1	2	3	4
$a(\mu)$	$\kappa(\mu^{-1})$	$(f_r)_{\max.}$ (dynes $\times 10^{10}$ )	$f_g$ (dynes $\times 10^{10}$ )
1	0.1	480	5
1	0.3	640	5
1	1.0	1200	5
10	0.1	1200	5000
10	0.3	2800	5000
10	1.0	8400	5000

In Table I  $(f_r)_{\max.}$  and  $f_g$  are compared for a number of relevant cases,  $f_g$  being calculated for water globules of density = 1.00 in benzene of density = 0.88 and  $\epsilon = 2.3$  with  $\psi_0 = 80$  mv.

It is obvious from Table I that in the case of water-in-benzene emulsions flocculation occurs as soon as a few to a few hundred droplets of water are situated above each other. For the cumulative weight of a vertical row of droplets acts on the lowest one as soon as the condition

$$\left(\frac{dV_R}{dx}\right)_{x=2a+d} \cong f_g, \quad [12]$$

where  $d$  is the distance between the surfaces of the droplets, is satisfied. It usually is if the concentration of the disperse phase is not very low. The globules on the bottom of the vessel must therefore flocculate, even if the disperse phase is homogeneously distributed over the continuous phase.

The figures of column 3 are too high. On the one hand, the van der Waals attraction and the factor  $\beta$  (see Eq. [3]) in the formula according to Verwey and Overbeek have not been taken into account. On the other hand, according to Eq. [8] the decay of the energy barrier as a result of the contribution of all the surrounding globules is less steep than in the case of interaction between two globules, for which Eq. [11] has been derived.

#### RATE OF FLOCCULATION IN MEDIA OF LOW DIELECTRIC CONSTANT

Since the distance between the globules is generally not very large compared with the thickness of the double layer in oil continuous systems, every globule possesses a higher potential energy than if it were at infinite distance from all other globules. For this reason after flocculation of a number of globules on the bottom of the vessel, the remaining globules act like an expanding spring which accelerates their migration to the bottom of the vessel.

Moreover, every globule is forced downwards under the action of the cumulative weight of all globules lying above, as has already been pointed out. So the velocity with which the globules sink is some orders higher than the velocity of a globule that settles out under the influence of its own weight alone.

Consequently a very rapid flocculation occurs until the remaining bulk concentration of the disperse phase is very small; i.e., until the distance between the globules has become large with regard to the thickness of the double layer.



## CONCLUSION

Flocculation by Brownian motion as well as under the influence of gravity is strongly promoted and proceeds very rapidly in oil continuous systems, if the concentration of the dispersed charged globules is not very low.

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