

Destabilization of emulsions through deformation of the droplets

Citation for published version (APA):

Hofman, J. A. M. H., & Stein, H. N. (1991). Destabilization of emulsions through deformation of the droplets. *Journal of Colloid and Interface Science*, 147(2), 508-516. <https://doi.org/10.1016/0021-9797%2891%2990184-A>, [https://doi.org/10.1016/0021-9797\(91\)90184-A](https://doi.org/10.1016/0021-9797(91)90184-A)

DOI:

[10.1016/0021-9797%2891%2990184-A](https://doi.org/10.1016/0021-9797%2891%2990184-A)
[10.1016/0021-9797\(91\)90184-A](https://doi.org/10.1016/0021-9797(91)90184-A)

Document status and date:

Published: 01/01/1991

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Destabilization of Emulsions through Deformation of the Droplets

J. A. M. H. HOFMAN AND H. N. STEIN¹

Laboratory of Colloid Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

Received January 2, 1991; accepted May 6, 1991

Differences between emulsions of decane + CCl₄ in water, stabilized by Na oleate and Aerosol OT, respectively, cannot be accounted for by differences in electrostatic repulsion as long as spherical droplets are considered only. However, electrostatic repulsion may be suppressed when the deformation of droplets upon approach is taken into consideration. This is energetically feasible when the interfacial tension is lower than about 0.1 mN/m. © 1991 Academic Press, Inc.

INTRODUCTION

In the course of an investigation on transport of dilute oil in water emulsions through porous media (1, 2) we noticed a distinct difference in behavior between emulsions stabilized by Na oleate on the one hand, or by Aerosol OT (AOT) on the other. This difference could be accounted for most easily by assuming a much lower stability of the AOT stabilized emulsions than of the Na oleate stabilized emulsions. However, this difference was not expected in view of the far-going resemblance in composition of the disperse phases and in electrokinetic behavior of the emulsions concerned, making substantial differences in Hamaker constants and in electrostatic repulsion unlikely.

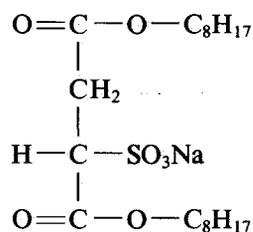
The present investigation substantiates the differences in emulsion stability between the emulsions concerned by experiments performed on their stability in the absence of a porous medium and investigates the possibility of droplet deformation upon approach as an explanation for the differences observed.

EXPERIMENTAL

Prior to the preparation of an emulsion the dispersed phase was made by mixing *n*-decane

(Janssen Chemica, 99+ %, purified on an alumina column, or Merck, zur Synthese, purified by distillation followed by purification on an alumina column) and tetrachloromethane (Merck, pro analysi) such as to give to the mixture a specified density. In the case of sodium oleate, an amount of oleic acid (Merck, reinst) was dissolved in the decane + CCl₄ mixture.

For the AOT stabilized emulsion, a solution of Aerosol OT (= the Na salt of di-octyl-sulphosuccinic acid,



from Sigma Chemical Company, 10% w/v solution, used as received) in water was used with a concentration such that after preparation of the emulsion the desired concentration was reached.

For preparation of a sodium oleate (NaOl) stabilized emulsion, a solution was made of sodium hydroxide (Merck Titrisol) in such a concentration that after the emulsion preparation all the oleic acid dissolved in the oil

¹ To whom correspondence should be addressed.

phase would be neutralized and the pH of the emulsion would be about 10.

To prepare an emulsion, 5 ml of the oil mixture was dispersed in 495 ml water phase (AOT solution or NaOH solution) using an Ystral X40 dispersing unit with a generator for media with low viscosities (diameter 20 mm). The resulting emulsions had a logarithmic normal distribution between 1 μm and 8 μm . The average particle size was 2.5 μm .

The demulsification process was started by adding 5 ml of a concentrated solution of sodium chloride (Merck, pro analysi) to 25 ml of the previously prepared emulsion. The emulsions then were left standing. The change of the particle concentration and the particle size distribution as a function of time was measured using a Coulter Counter (Model ZM, equipped with a Channelyzer 256 and a Coulter Range Expander). At specific times a 400 μl sample of the emulsion was taken and diluted in 25 ml Isoton II (electrolyte solution for Coulter Counter measurements). Because the densities of the dispersed phase and the continuous phase do not exactly match, it was necessary to homogenize the emulsion before it was sampled by shaking it very cautiously for a few seconds.

Checks were made on the occurrence of changes in droplet concentration, after dilution in the Isoton II solution. No detectable changes within the experimental times used were detected, presumably because of the low emulsion droplet concentration.

The concentration of the particles in the diluted sample was determined by counting the number of droplets in 500 μl diluted emulsion. This particle concentration was then used to calculate the particle concentration of the original emulsion.

The Coulter Counter technique has the advantage that a single large particle and a flocculated particle with the same volume give the same response at the instrument. This results in a measurement of the coagulation kinetics which is not affected by the coalescence rate.

Interfacial tensions of the emulsions were measured using a Krüss Spinning Drop Ten-

siometer. The dimensions of the oil droplet in the rotating capillary of the tensiometer were measured by photography.

Zeta-potentials of NaOl stabilized emulsions used, were measured with a Malvern Zetasizer III.

The densities of the decane + CCl_4 mixtures were determined with a Mettler/ Paar DMA55 digital densitometer at 25°C.

RESULTS

Typical values for the reciprocal value of n , the droplet concentration, as a function of the time t are shown in Fig. 1.

The results on stability measurements are expressed through the parameter a in the von Smoluchowski equation on coagulation kinetics,

$$n = \frac{n_0}{1 + an_0t}, \quad [1]$$

where

n = number of emulsion droplets per unit volume, m^{-3} ,

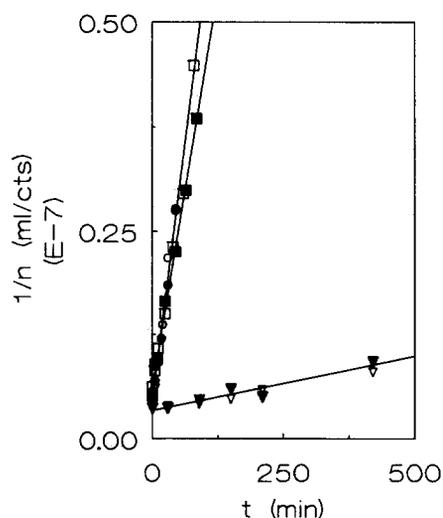


FIG. 1. Reciprocal values of the droplet concentration, vs. time, for a typical AOT stabilized emulsion. Volume fraction of disperse phase: 0.01; [AOT] = 0.00035 mole/l; ∇ [NaCl] = 0.1057 mole/l; \bullet [NaCl] = 0.2114 mole/l; \square [NaCl] = 0.2476 mole/l.

t = time, s;
 $n_0 = n$ at $t = 0$;
 $a = \text{constant}$ (independent of time and n_0),
 $\text{cm}^3 \text{s}^{-1}$.

This equation is derived on the basis of absence of colloid chemical and hydrodynamical interactions, for monodisperse emulsions (3). The parameter a then equals $8\pi D r_p$ for perikinetic coagulation (with $D =$ diffusion constant, r_p radius of particles), while it is equal to $16/3 \cdot \gamma \cdot r_p^3$ for orthokinetic coagulation ($\gamma =$ shear rate).

The hydrodynamical and colloid chemical interactions can be introduced by applying a correction factor K for the coagulation rate (4), equal to:

$$K = \frac{1}{\frac{(r_1 + r_2)}{r_1} \int_{s=\frac{r_1+r_2}{r_1}}^{\infty} \frac{D_{12}^{\infty} \exp(V/kT)}{D_{12} s^2} ds} \quad [2]$$

Here,

V = the interaction energy;
 $s = r/r_1$;
 r = the distance between the particle centers;
 r_1, r_2 = particle radii involved in a collision;
 D_{12} = the mutual diffusion constant of the particles when at distance r ;
 D_{12}^{∞} = the diffusion constant of the particles when at infinite distance.

The quotient D_{12}^{∞}/D_{12} can be calculated from the Spielman theory (4), while V is, for spherical particles, given by the DLVO theory (6).

K can be calculated numerically, and is found generally to be lower than 1. It varies in the case of rapid coagulation (absence of electrostatic repulsion) in most cases between 0.5 and 1. Values of K which are substantially larger than 1 could be expected when V is negative (predominant attraction between the particles); however, for this to be pronounced the particles should be so close together that values of $\exp(V/kT)$ smaller than 1 are overruled by values of the diffusion constant quotient D_{12}^{∞}/D_{12} being much larger than 1.

Thus, the values calculated for the collision frequency a in Eq. [1] from the von Smoluchowski theory are, for all practical purposes, maximum values.

The values of the parameter a describing the droplet concentration as a function of the electrolyte concentration, in the case of the emulsions investigated, are shown in Fig. 2.

Two conclusions appear from this graph:

- The values of parameter a calculated from the experiments substantially surpass the value calculated from the von Smoluchowski theory for perikinetic coagulation;
- The stability toward coagulation differs, AOT stabilized emulsions being significantly less stable than Na oleate stabilized ones, in the field of slow coagulation.

Thus, perikinetic conditions apparently are not completely obeyed: with the particle sizes concerned, the homogenization of the emulsions necessitated by the requirement of obtaining representative samples for the particle counting apparently leads to a substantial increase of coagulation rate over that expected for perikinetic coagulation. It should be noted,

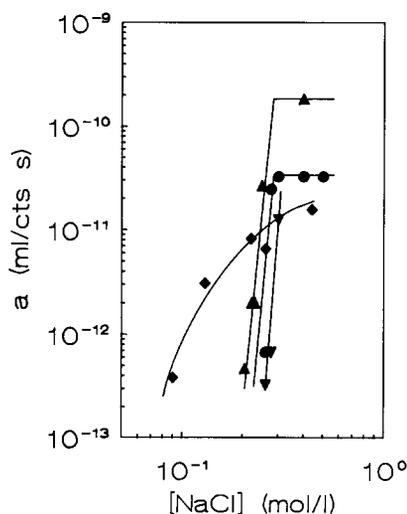


FIG. 2. Values of the collision frequency (parameter a from Eq. [1]), for various types of emulsions: \blacktriangle [NaOl] = 0.5 mmol/l; \bullet [NaOl] = 1.0 mmol/l; \blacktriangledown [NaOl] = 2.0 mmol/l; \blacklozenge [AOT] = 0.42 mmol/l.

however, that both types of emulsions were subjected to the same treatment, which makes the comparison of the coagulation rates free from doubts.

Figure 3 shows the zeta potentials at different electrolyte concentrations for the emulsions concerned, while figure 4 shows the values of the interfacial tension of the AOT stabilized emulsions which agree with the values reported for similar systems by Aveyard (7). The interfacial tension of the Na oleate stabilized emulsions was 0.1 mN/m, and was within the precision of the measurements independent of the NaCl concentration.

DISCUSSION

The experimental results confirm that emulsions stabilized by AOT are less stable than emulsions stabilized by Na oleate, in the field of slow coagulation. The a values (from Eq. [1]) for Na oleate stabilized emulsions show a rapid decrease when the electrolyte concentration drops below the critical coagulation (which is about 0.3 M in the case at hand, see Fig. 2); this is similar to phenomena found in dispersions with solid particles. In the case of AOT stabilized emulsions, the

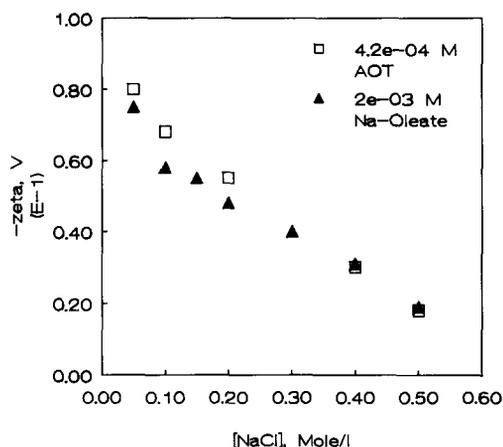


FIG. 3. Zeta potential vs. [NaCl], for AOT and Na oleate stabilized emulsions: \square [AOT] = 0.00043 mole/l; \blacktriangle [Na oleate] = 0.002 mole/l.

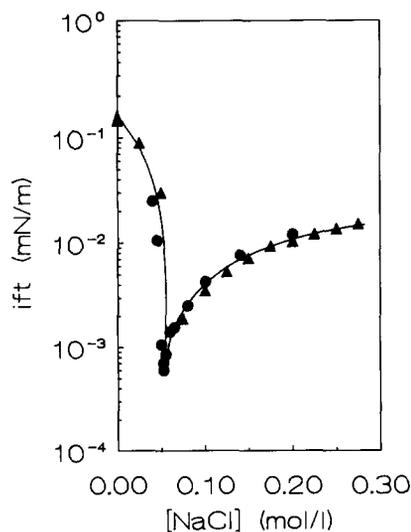


FIG. 4. Interfacial tension vs. [NaCl] for 0.00043 M AOT stabilized emulsions: ift = interfacial tension; different symbols indicate measurements on duplicate series.

transition from rapid to slow coagulation is much more gradual.

In order to explain this, first of all the Hamaker constant must be established. In view of the similarity in composition of the disperse phases, this is expected to be equal for both types of emulsion studied.

The behaviour of Na oleate stabilized emulsions (critical coagulation concentration 0.3 M 1:1 electrolyte; the ζ potential at this concentration being -0.025 V) can be described with a Hamaker constant of $1.1 \cdot 10^{-20}$. In this calculation, a distance between the electrokinetic slipping plane (at which the ζ potential is located) and the L_1/L_2 phase boundary (at which the polarizabilities of the atoms concerned change) of $2 \cdot 10^{-10}$ m has been introduced. Other values for this distance do not lead to significantly other final conclusions (though the absolute values for the parameters concerned change). The ζ potential has been used as an indication for the potential at the border of the diffuse double layer, since in the case of the emulsions investigated other effects than electrostatic ones for repulsion, and of London-van der Waals attraction are improbable (no adsorbed

polymer layers). This is in agreement with coagulation experiments (see, e.g., ref. (8)). Differences in this respect between the types of emulsion studied here are very unlikely.

Retarded London-van der Waals attraction for spherical droplets was calculated according to Clayfield (9). Electrostatic repulsion was calculated by numerical integration of the repulsion contributions from slices into which two approaching spheres may be divided (the planes forming the slices being perpendicular to the axis joining the centers of the particles); the repulsion contribution from one pair of circular surface elements was obtained by interpolation between the values of Overbeek's table for flat surfaces (10), thus avoiding the use of the Derjaguin (11) formula which is applicable to low surface potentials only.

The calculations gave the expected results: for large negative ζ potentials a pronounced repulsive energy barrier prevents coagulation for all practical observation times (see Fig. 5,

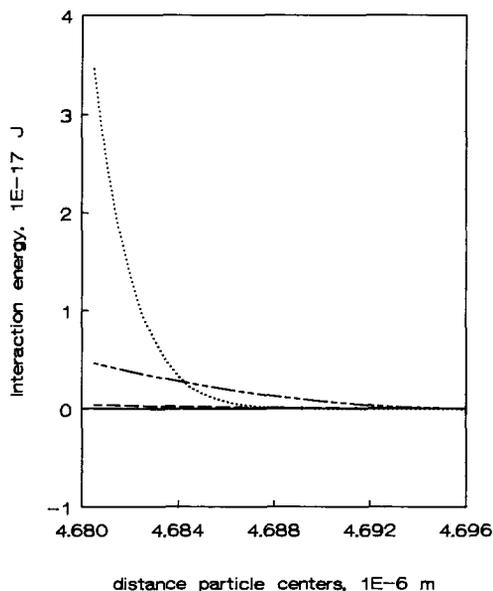


FIG. 5. Potential energy vs. distance between particle centers. Particle radii: $2.34 \cdot 10^{-6}$ m; [NaCl]: 0.05 M; ζ : -0.08 V; Hamaker constant: $1.1 \cdot 10^{-20}$ J; distance between slipping plane and L_1L_2 phase boundary: $2 \cdot 10^{-10}$ m. Interfacial tension: - · · · · 0.01 N/m; --- 0.001 N/m; · · · · undeformed droplets.

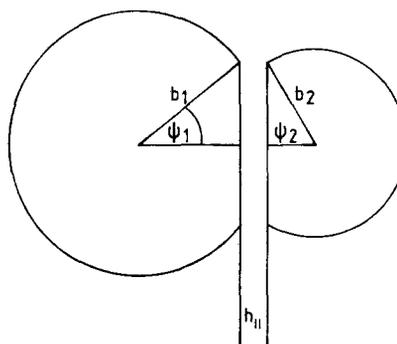


FIG. 6. Deformation of droplets during an encounter, forming a flat contact plane. b_1, b_2 : radii of droplets after deformation; h_{11} : distance between flat plates at secondary minimum.

curve for undeformed droplets, in which the potential energy for $\zeta = -0.08$ V is shown).

This is indeed in agreement with experimental observations for the Na oleate stabilized emulsions. In order to explain the slow but measurable coagulation at large $|\zeta|$ values for AOT stabilized emulsions, we investigated the possibility of droplet deformation. This phenomenon should be taken into account especially for systems with a low interfacial tension, in which droplet deformation is not accompanied by large additional energy values.

Hydrodynamical interaction and electrostatic repulsion will lead to a flattening of two approaching droplets near the contact region. The ultimate situation is expected to resemble that depicted in Fig. 6, with the two droplets sharing a flat contact area in which they are separated by a distance corresponding with the secondary minimum in the potential energy vs. distance curve for flat plates.

It will be noted that droplet pairs as depicted in Fig. 6 will be counted as one single, coagulated particle in the experimental method employed in this investigation.

In this case,

$$r = h_{11} + b_1 \cos \psi_1 + b_2 \cos \psi_2, \quad [3]$$

where

h_{11} = the distance between two flat surfaces in the secondary minimum of the $V(r)$ graph (6);

b_1, b_2 = the radii of the droplets after deformation;
 ψ_1, ψ_2 = angles describing the flattened section of the drops (see Fig. 7).

The flattened section of the droplets must have the same radius for both particles, therefore,

$$b_1 \sin \psi_1 - b_2 \sin \psi_2 = 0. \quad [4]$$

Two additional equations are derived from the condition that the volumes of the deformed particles must be equal to that of the undeformed ones:

$$\begin{aligned} 4/3\pi a_1^3 \\ = 1/3\pi b_1^3(2 + 3 \cos \psi_1 - \cos^3 \psi_1) \end{aligned} \quad [5]$$

$$\begin{aligned} 4/3\pi a_2^3 \\ = 1/3\pi b_2^3(2 + 3 \cos \psi_2 - \cos^3 \psi_2). \end{aligned} \quad [6]$$

Thus, when a_1, a_2, h_{II} , and r are given, Eqs. [3] through [6] can be used to calculate b_1, b_2, ψ_1 , and ψ_2 . But this enables us to calculate the total interaction energy between two droplets after the deformation described in Fig. 7,

$$\begin{aligned} V_{\text{interaction}} = \gamma \Delta A \\ + \pi(b_1 \sin \psi_1)^2 V_{\text{secmin}} \end{aligned} \quad [7]$$

where

- γ = the interfacial tension;
- ΔA = the area change due to the deformation;
- V_{secmin} = the flat surface interaction energy per unit area at the secondary minimum.

Equation [7] can be derived by considering the droplet deformation to be realized when the droplets are still far apart, resulting in the term $\gamma \Delta A$, and then letting the droplets approach until the contacting parts of the surfaces are separated by the distance of the secondary minimum for flat plates. The latter process is accompanied by an energy change

$$\pi(b_1 \sin \psi_1)^2 V_{\text{secmin}}$$

Although the actual development of such contact areas will take a different course, this does not make any difference for the energy.

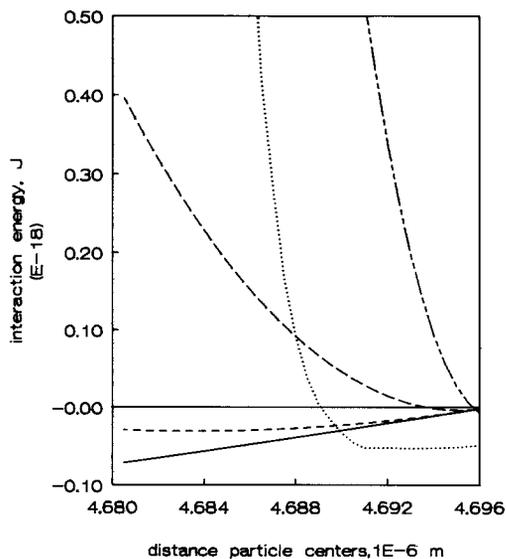


FIG. 7 As Fig. 5, on a different scale for better view on details. undeformed droplets; - . - . interfacial tension 0.01 N/m - - - interfacial tension 0.001 N/m; - - - - interfacial tension 0.0001 N/m — interfacial tension 0.00001 N/m.

In Eq. [7], the interaction between the parts of the deformed spheres outside their contact is neglected. This is a negative contribution to the potential energy which will be smaller (in absolute sense) than the energy of undeformed droplets at the secondary minimum. There are two reasons for this statement:

- (a) If we calculate this interaction energy by a Derjaguin type calculation, dividing the spheres into slices parallel to the flat contact zone, the distance between the surface elements at one distance from the central axis is larger than the distance of the secondary minimum;
- (b) the central part of the spheres is taken into account in Eq. [7], and is therefore missing in the correction term.

We considered the possibility of whether the change in Laplace pressure on droplet deformation should be taken into account in Eq. [7]; this might lead to an elastic restoring force similar to that calculated by Muller (12) for the case of elastic particles approaching a flat

surface. However, on closer examination this appears to be a duplicate calculation of the work required for the increase of the interfacial area on deformation: since it is not possible to deform the droplets without a change in the Laplace pressure, the energy required for the latter effect is already taken into account by the term $\gamma\Delta A$ of Eq. [7].

In calculations using Eq. [7], the value for the interfacial tension γ was taken which had been measured for interfaces in the absence of a nearby other L_1L_2 interface. It has been argued (see, e.g., ref. (13)), that the interaction energy should be incorporated into γ . Whether γ does include the interaction energy, or whether for γ the undisturbed interfacial tension should be used while taking interaction with a nearby L_1L_2 interface into account separately, is a matter of taste. In the present paper, we have chosen the latter approach because it appeared to us to lead to an easier surveyable energy expression.

The area change due to the deformation is:

$$\begin{aligned}\Delta A = & 2\pi b_1^2(1 + \cos \psi_1) \\ & + 2\pi b_2^2(1 + \cos \psi_2) \\ & + 2\pi(b_1 \sin \psi_1)^2 - 4\pi a_1^2 - 4\pi a_2^2.\end{aligned}$$

The interaction energies calculated through this equation are plotted, for $\zeta = -0.08$ V, a Hamaker constant = $1.1 \cdot 10^{-20}$ J, and a value for the distance between slipping plane and

phase boundary = $2 \cdot 10^{-10}$ m, for various values of the interfacial tension, in Fig. 5 and (on a different scale for better seeing some details) in Fig. 7. The values of these parameters introduced are representative for the AOT stabilized emulsion, but do not differ greatly for the NaOl stabilized emulsion.

It is seen that for the lowest value of the interfacial tension ($1 \cdot 10^{-5}$ N/m), there is no energy barrier against coagulation. This value of the interfacial tension corresponds to the value found with most AOT stabilized emulsions (see Fig. 4). A minimum is found in the potential energy for appreciable deformation of the droplets (see Table I); this occurs when the particle centers are much closer than their distance when touching, in the case of undeformed droplets ($4.68 \mu\text{m}$).

Similarly, no electrostatic repulsion is found for the next higher value of the interfacial tension ($1 \cdot 10^{-4}$ N/m), when the droplets are being deformed. This value of the interfacial tension corresponds to the value found for Na oleate stabilized emulsions (Fig. 4). However, the effect is less pronounced in this case, and a minimum is found in the potential energy at larger distance between particle centers than with $\gamma = 1 \cdot 10^{-5}$ N/m.

With values of the interfacial tensions of $1 \cdot 10^{-3}$ N/m, the energy barrier due to electrostatic repulsion is replaced by a much less pronounced barrier in the state obtained by coagulation in the secondary minimum after

TABLE I

Data on the State of Minimum Potential Energy, between Two Equal Emulsion Droplets, Radius = $2.34 \mu\text{m}$

γ (N/m)	Deformation ^b	Distance between particle centers (μ)	$V_{\text{interaction}}$ (J)
Undeformed ^a	—	4.693	$-5.314 \cdot 10^{-20}$
$1 \cdot 10^{-2}$	—	—	— ^c
$1 \cdot 10^{-3}$	$2.45 \cdot 10^{-8}$	4.695	$-3.346 \cdot 10^{-21}$
$1 \cdot 10^{-4}$	$2.26 \cdot 10^{-6}$	4.684	$-3.081 \cdot 10^{-20}$
$1 \cdot 10^{-5}$	$2.22 \cdot 10^{-4}$	4.568	$-3.052 \cdot 10^{-19}$

^a Position of secondary minimum of undeformed droplets (independent of γ).

^b Deformation of droplets in the position of the minimum potential energy, expressed as (additional surface)/(surface of undeformed droplets).

^c No minimum in the potential energy found on deformation.

deformation. It will be noticed that the largest value of the interfacial tension used in the present calculations is of the order of that found for many L_1L_2 interfaces in the presence of only very small amounts of emulsifier.

On comparing the different potential energy minimum values (Table I) and the potential energy vs. distance between particle centers curves (Figs. 5 and 7), we see that when the interfacial tension becomes lower than $1 \cdot 10^{-4}$ N/m, there is only a slight additional energy required (starting from the secondary minimum) for two emulsion droplets to assume a deformed state with a flat contact area. Especially at interfacial tension values of $1 \cdot 10^{-5}$ N/m, there is even a substantial potential energy gain to be obtained on deformation.

Thus, if the state of lowest potential energy could be realized during coagulation conditions, at $\gamma \leq 1 \cdot 10^{-4}$ N/m no electrostatic repulsion would be noticed. At large values of the interfacial tension, a repulsion could be developed, but this is much lower than expected for electrostatic repulsion.

The fact that nevertheless our emulsions show distinct electrolyte concentration effects on emulsion stability (Fig. 2) means that kinetic factors prevent the state of lowest potential energy to be reached during an encounter of two droplets. The flat character of the interface between two adjacent droplets, introduced into our calculations, is the extreme end of a continuous transition starting from undeformed droplets; under kinetic circumstances a "dimple" will develop as, e.g., in the experiments of the Sheludko group (see, e.g., ref. (14)) on horizontal thin liquid films.

The differences between the stabilities of Na oleate and AOT stabilized emulsions, however, which cannot be explained when the droplets remain spherical, indicate that destabilization through deformation of droplets upon encounters takes place, at least in part of the encounters. It is in line with this effect that the AOT stabilized emulsions, showing the smallest values of the interfacial tension and therefore the least potential energies when

being deformed, show a more gradual transition from electrostatically stabilized to not stabilized conditions.

The present treatment is based on the assumption that the stabilizer is present, in both types of emulsions investigated, as an adsorbed monolayer at the L_1L_2 interface. We considered in addition the possibility that the AOT might be present in the form of thick crystal liquid layers, which could in principle lead to droplet attachment without droplet deformation. However, this possibility was considered unlikely since it appears to be incomprehensible how with such a mechanism, at the large negative ζ potential values observed, the liquid crystal layers surrounding two droplets could approach toward each other sufficiently close for attachment of liquid crystals to occur.

The possibility was also considered of microemulsion formation in the case of the AOT containing emulsion. Since there was only a very small specific mass difference between the disperse and the continuous phases (if any), creaming or sedimentation was nearly completely suppressed. Thus, there is no separation between emulsion and microemulsion, and if any microemulsion droplets would occur then the microemulsion droplets were expected to be positioned between the emulsion droplets. Any specific effect of this on the stability of the emulsion would be unexpected (cf. the absence of an influence on the presence of micelles on the stability of emulsions, apart from supplying sufficient surfactant for adsorption on the phase boundaries). This paper shows that it is possible to understand the stability differences between Na oleate and AOT stabilized emulsions without having to take recourse to some unknown effect of microemulsion droplets.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support for this study by Stichting Technische Wetenschappen and by Royal Dutch Shell Exploration and Production Laboratories (Rijswijk).

REFERENCES

1. Hofman, J. A. M. H., "Flow of Dilute Emulsions Through Porous Media," Ph. D. Thesis, Eindhoven, 1990.
2. Hofman, J. A. M. H., and Stein, H. N., to be published.
3. von Smoluchowski, M., *Phys. Z.* **17**, 557 (1916); **17**, 583 (1916).
4. Spielman, L. A., *Chem. Eng. J.* **7**, 129 (1974).
5. Spielman, L. A., in "Mathematical Models and Design Methods in Solid-Liquid Separation" (A. Rushton, Ed), NATO ASI Series E Vol. 88, p. 207. Kluwer Academic, Netherlands, 1985.
6. J. Th. G. Overbeek, in "Colloid Science" (H. R. Kruyt, Ed), Vol. 1, p. 278. Elsevier, Amsterdam, 1952.
7. Aveyard, R., Binks, B. P., Clark, S., and Mead, J., *J. Chem. Soc. Faraday Trans 1* **82**, 125 (1986); **82**, 2169 (1986).
8. McGown, D. N. L., and Parfitt, G. D., *Discuss. Faraday Soc.* **42**, 225 (1966).
9. Clayfield, E. J., Lumb, E. C., and Mackey, P. H., *J. Colloid Interface Sci.* **37**, 382 (1971).
10. Overbeek, J. Th. G., in "Colloid Science" (H. R. Kruyt, Ed.), Vol. 1, p. 254 (Table 2). Elsevier, Amsterdam, 1952.
11. Derjaguin, B. V., and Landau, L., *Acta Physicochim. URSS* **14**, 633 (1941).
12. Muller, V. M., Yushchenko, V. S., and Derjaguin, B. V., *J. Colloid Interface Sci.* **77**, 91 (1980).
13. Huisman, R., and Mysels, K. J., *J. Phys. Chem.* **73**, 489 (1969).
14. Scheludko, A., *Adv. Colloid Interface Sci.* **1**, 391 (1967).