

STABILITY OF EMULSIONS OF WATER IN OIL

I. THE CORRELATION BETWEEN ELECTROKINETIC POTENTIAL AND STABILITY

W. Albers¹ and J. Th. G. Overbeek

van 't Hoff Laboratory, University of Utrecht, Netherlands

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ABSTRACT

Experiments on W/O emulsions of moderate concentration, stabilized with oil-soluble, ionizing stabilizers, show that in these emulsions no correlation exists between stability against flocculation and electrokinetic potential. Although, according to theoretical calculations, energy barriers of over $15 kT$ are present, if the radius of the dispersed globules is about 1μ and the electrokinetic potential exceeds 25 mv., they apparently do not prevent lasting contact between particles. All our emulsions flocculate rapidly, even in the presence of a surface potential considerably higher than 25 mv.

A rather pronounced anticorrelation exists between the zeta potential and coalescence. It is explained as a consequence of the free mobility of the stabilizing molecules in the interface.

The good stabilization against coalescence caused by some oleates of polyvalent metals is due to the formation of a thick film of partial hydrolyzates in the interface.

INTRODUCTION

As early as 1914 Newman (1, 2) reported that the oleates of barium, magnesium, zinc, and cadmium stabilize W/O emulsions. Shortly afterwards Briggs and Schmidt (3) used Mg-oleate to stabilize W/O emulsions containing up to 90% of water. They were the first to notice that the stabilized water globules were of irregular shape—a fact observed afterwards many times by other investigators. In 1940 Schulman and Cockbain (4) attributed this irregularity to the stiffness of the interfacial film. From their experiments they concluded that W/O emulsions are formed only when the film of stabilizer molecules in the interface is uncharged and stiff as a result of complex formation. In the discussion of their experimental results they argued that a W/O emulsion can not be stabilized against flocculation by charge on the water droplets because, oil being a nonionizing medium, an electrical diffuse layer or ionic atmosphere can not be built up. Further, according to them a charged film is not able to

¹ Present address: Philips' Research Laboratories, Eindhoven, Netherlands.

prevent coalescence because owing to repulsion between the stabilizer molecules in the interface, no interlinked solid condensed film can be formed. In 1951 Moilliet and Collie (5) endorsed this view.

In 1933, however, Fuoss and Kraus (6) had already shown that even in apolar oils a distinct though very small ionization may occur. An ion-forming compound, such as a polyvalent metal salt of an organic acid, dissolved in benzene (for convenience we refer to this liquid) in a concentration of about 10 mmoles per liter possesses a degree of ionization in the order of 10^{-8} . Consequently the ionic concentration is in the order of $10^{-10} N$, so that, in spite of the low dielectric constant of the medium, the electrical double layer is very diffuse, i.e., the corresponding Debye length $1/\kappa$ is several microns. Therefore, as Koelmans and Overbeek (7) remark, the capacity of the double layer in such apolar systems is very low and only very little charge is needed to obtain appreciable surface potentials. The repulsion at the low ionic concentrations involved, is described in good approximation by Coulomb's law

$$V_R = \psi_0^2 \epsilon a^2 / R,$$

in which V_R = energy of interaction, ψ_0 = surface potential, ϵ = dielectric constant, a = radius of the droplet, and R = distance between the centers of the particles. When the Coulomb repulsion is combined with the van der Waals attraction (van der Waals' constant $A = 10^{-12}$ erg, cf. Hamaker (8)) an energy barrier of $15 kT$ is obtained in the case of a radius $a = 1 \mu$ and a surface potential $\psi_0 = 25$ mv. (see Fig. 1). This surprisingly high maximum of about $15 kT$, which value as a rule is sufficiently high to stabilize against flocculation, is due to the very slow decay of the electrical repulsion between the particles with the distance.

On the one hand, these calculations are supported by experiments of van der Minne and Hermanie (9). They observed a carbon suspension of concentration 0.1% in mineral oil and found that stabilization against flocculation is obtained when the electrokinetic potential, ζ , exceeds 20–25 mv. The carbon suspension was stabilized with the calcium salt of diisopropylsalicylic acid, an oil-soluble soap. Similar facts were found by Koelmans (7) for suspensions in xylene.

On the other hand, the above calculation seems to be contradicted by the general experience that W/O emulsions of moderate concentration always flocculate, or as Pink (10) expressed it, that the fundamental difference in the two types of emulsions is reflected in the more rapid creaming which is so characteristic of the oil-continuous type.

In order to try to solve the contradiction pointed out above, we determined the electrokinetic potential and the stability against flocculation and against coalescence of a number of water-in-oil emulsions, stabilized with stabilizers, which ionize to some extent in the oil phase.

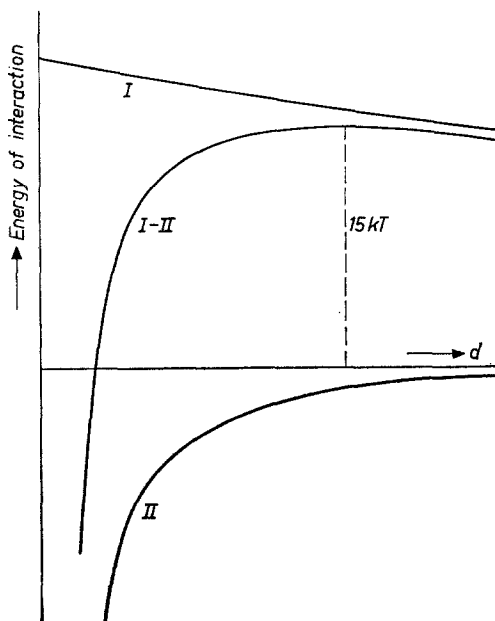


FIG. 1. Potential energy of interaction between two globules with radius $a = 1 \mu$ in oil as a function of the distance d between the surfaces. The surface potential $\psi_0 = 25$ mv.; dielectric constant of the oil $\epsilon = 2.3$. I = Coulomb repulsion; II = van der Waals' attraction.

MATERIALS AND EXPERIMENTAL METHODS

Oleates of polyvalent metals were prepared by double decomposition between inorganic salts of the bi- and trivalent metals and the calculated equivalent amount of sodium oleate, dissolved in water of about 90°C . to prevent enclosure of impurities (11). The precipitated oleates were washed with water, dried first over CaCl_2 in a desiccator, next in a hot air oven during 45 minutes at 105°C .

Ca-didodecylsalicylate and petroleum sulfonates of some bivalent metals were obtained from Koninklijke Shell Laboratorium, Amsterdam. The sulfonates were liberated from mineral oils by dissolving in a hot mixture of 50% ethanol in water, subsequent extraction of the mineral oil with a low-boiling petrol fraction, followed by evaporation of the solvent.

Benzene was thoroughly dried by distillation over sodium to prevent the precipitation of any possible hydrated modification of the soap (12).

Electric conductivity, down to about $10^{-14} \Omega^{-1} \text{ cm.}^{-1}$, was measured by a simple d.-c. method following Koelmans (7). The conductivity cell (see Fig. 2) was treated on the outside with silicons to repel moisture. The distance between the platinum electrodes is small compared with the

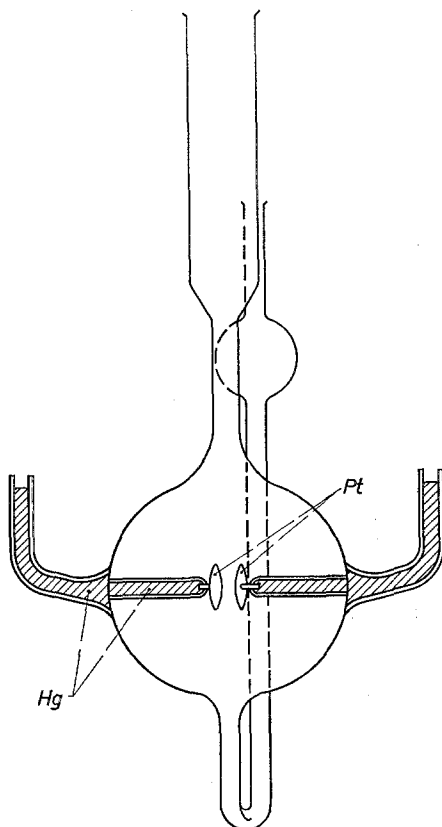


FIG. 2. Conductivity cell for media with low dielectric constant.

distance between the inner wall of the bulb and the electrodes. Thus trouble by conduction of the electric current alongside the glass walls of the cell is diminished. This has been proved to be effective because by measurements on pure benzene a specific conductivity lower than $10^{-14} \Omega^{-1} \text{ cm.}^{-1}$ was obtained. This is small as compared with the specific conductivities of the solutions of soaps of polyvalent metals and other ionic stabilizers in benzene, which are in the order of $10^{-10} \Omega^{-1} \text{ cm.}^{-1}$.

A Philips d.-c.-electronic Voltmeter-pH meter G.M. 4491 was used to determine the potential in the circuit.

The electrophoresis measurements were carried out in the cylindrical cell as described by van der Minne and Hermanie (13). During these measurements the applied voltage never exceeded 100 v./cm. to prevent electrostatic induction effects that would otherwise disturb the electrophoresis measurements.

The emulsions were prepared by adding water slowly to the solution of

stabilizer in benzene under the influence of the vigorous stirring of a centrifugal emulsifier, the IKA Ultra Turrax (type TV 45, Janke and Kunkel, KG, Staufen i. Br.). The concentration of the soap in the oil in most cases amounted to 10 mmoles/l. The W/O emulsions used in the sedimentation or breaking experiments contained 15 volume per cent of water. The percentage of water used in the electrophoresis measurements was about 0.005. This low percentage was obtained from an emulsion containing 15 volume per cent of water by diluting with the oil phase of an identical emulsion. The radii of the water droplets ranged mostly between 1 and 4 μ . Measurements of sedimentation and breaking were carried out in glass-stoppered graduated cylinders.

MEASUREMENTS AND RESULTS

Emulsions of water in benzene have been prepared in the presence of oleates of the metals Al, Ba, Ca, Cd, Cu^{II}, Fe^{III}, Hg^{II}, Mg, Mn, Ni, Pb, Sr, and Zn, petroleum sulfonates of Ba, Mg, and Zn and Ca-didodecylsalicylate. The soaps are soluble in benzene except the oleate of Hg^{II}. They are insoluble in water. When they are dissolved in benzene in concentrations of 10 mmoles/l. their specific conductivity appears to be in the order of $10^{-10} \Omega^{-1} \text{ cm.}^{-1}$. These soaps of polyvalent metals promote water in oil emulsions which, however, all flocculate, as observed by sedimentation velocity and microscopic examination. Some of these flocculated emulsions are stable against coalescence, others are not. In column 1 of Table I a series of oleates has been given, from the top downwards increasing in ability to stabilize emulsions of water in benzene against coalescence. The time interval between the preparation and the breaking of the emulsion is adopted as a measure for stability against coalescence. From Ba-oleate up to and including Sr-oleate the time of coalescence increases from a quarter of an hour to about 20 days. The oleates of Fe^{III}, Mg, Pb, and Cu^{II} stabilize against coalescence for several months and even longer.

Determination of the interfacial tension by stalagmometer showed that the oleate molecules are strongly adsorbed at the interface between water and benzene. The polar head will dip in the water phase; the hydrophobic hydrocarbon chains will point into the oil phase. By ionization of one negative oleate ion from the oleate molecule a positive metal-mono-oleate ion will remain in the interface. It is observed actually from electrophoresis measurements that the water droplets of the water in benzene emulsions are positively charged. Zeta potentials have been calculated from the observed electrophoretic velocities using the equation:

$$v_e = \frac{\epsilon E \zeta}{6\pi\eta},$$

in which v_e = electrophoretic velocity, ϵ = dielectric constant, E = ap-

TABLE I

Correlation between the Electrokinetic Potential ζ and the Stability against Coalescence in Water-in-Benzene Emulsions Stabilized by the Oleates of Polyvalent Metals and Some Other Stabilizers

1	2	3
Sequence of increasing stability against coalescence	ζ -potential = ψ_0 potential (mv.)	Time interval between preparation and beginning of breaking of the emulsion
Ca-didodecylsalicylate	130	A few hours
Ba-oleate	0	
Mn-oleate	70	
Ca-oleate	20	
Zn-oleate	50	
Al-oleate	45	Some days
Mg-petroleum sulfonate	80	
Ba-petroleum sulfonate		
Zn-petroleum sulfonate		
Ni-oleate	32	10-20 days
Cd-oleate	22	
Sr-oleate	10	
Fe ^{III} -oleate	15	Several months
Mg-oleate		
Pb-oleate		
Cu ^{II} -oleate		

plied field strength, ζ = electrokinetic potential, and η = viscosity of the oil phase.

As the double layer in oil is extremely diffuse and therefore the decay of the potential with the distance from the interface slow, the surface potential ψ_0 may be identified with ζ .

Electrophoresis measurements on water in benzene emulsions stabilized with Ca-didodecylsalicylate gave a surface potential of 130 mv. These emulsions broke immediately after preparation. When stabilized with Mg-, Zn-, Ba-petroleum sulfonates a ψ_0 of about 80 mv. was obtained. These emulsions break within a week.

STABILITY AGAINST FLOCCULATION

It is obvious from the experiments described above that a surface potential considerably higher than 25 mv. is not sufficient to stabilize dispersed droplets with a radius equal to or larger than 1μ against flocculation. This is shown on the one side by the high sedimentation velocities, on the other side more spectacularly by the rapid breaking of some such W/O emulsions. For, evidently, coalescence can take place only after introductory flocculation. These observations seem to be in contradiction with the calculations of Koelmans (7) mentioned above, from which it followed that in nonpolar media surface potentials of 25 mv. provide a

sufficiently high energy barrier to prevent flocculation of two particles with radii above 1μ . In a subsequent paper in this journal we shall show that although Koelmans's conception is correct for very dilute suspensions and emulsions it is not applicable to more concentrated emulsions and certainly not to the cream layer. In this paper we direct our attention to stabilization against coalescence.

STABILITY AGAINST COALESCENCE

The specific conductivities of the solutions of the different oleates in benzene have almost the same value, indicating equal degrees of ionization. Nevertheless as shown in Table I surface potentials differ appreciably. The low value observed in water in benzene emulsions stabilized by Cu^{II} —and some other oleates might be due to partial hydrolysis of the soap. The products of hydrolysis are insoluble both in water and in benzene, accumulate at the interface, and interfere with the formation of an electrical double layer in the oil phase.

To test this point of view interfacial films of emulsions with low surface potentials, stabilized by Cu^{II} , Fe^{III} , or Mg-oleate were collected and analyzed. After breaking the emulsions by centrifuging the films were filtered, dried first over CaCl_2 in a desiccator, next in a hot air oven during 45 minutes at 105°C .

The results of the analysis are shown in Table II, together with the calculated compositions of the pure oleates and the calculated compositions of possible products of hydrolysis.

The data for Cu, Fe, C, and H in column 2 of Table II are obtained by polarography, by colorimetry, and via combustion in the conventional gravimetric way, respectively. The percentage of O is acquired by subtraction from 100 %.

Comparison of column 2 and column 3 makes it plausible that these emulsions are stabilized by hydrolysis products.

The notion that soaps which do not stabilize water in benzene emulsions against coalescence do not hydrolyze either is supported by the experiments of Pink (12). He studied the effect of water on benzene solutions of Mg-, Ca-, Sr-, Ni-, and Zn-oleates. Two per cent solutions of the soaps in benzene were shaken with an equal volume of water. After breaking of the resulting emulsions the concentration of soaps remaining in the benzene layer was estimated. It appeared that almost the whole quantity of Mg-oleate had been removed from the benzene phase. Ca- and Sr-oleate had disappeared for the greater part but the oleates of Ni and Zn were found back nearly completely in the benzene phases, indicating that the poor stabilizers, viz., Ni- and Zn-oleate, scarcely hydrolyze.

The stabilizing action of the hydrolysis products may be explained in two ways. They may be considered as small particles, insoluble in both

TABLE II
The Composition of the Hydrolysis Products of the Oleates in the Interfacial Film with Low Potential

1	2	3	
Theoretical oleates	Hydrolysis products	Possible composition of the hydrolysis products	
Mg-oleate:			
Mg 4.14		7.45	
C 73.68	67.06	67.02	
H 11.26	10.41	10.55	
O 10.92		14.98	
Mg-OIOH or Mg(OH) ₂ MgOl ₂ complex			
Cu ^{II} -oleate:			
Cu 10.16	24.25 ± 0.25	23.96	
C 69.06	46.87	45.28	
H 10.55	6.35	6.41	
O 10.23	22.53	24.35	
Cu-OIHCO ₃ ·CuCO ₃ or (CuCO ₃) ₂ ·HOl complex			
Fe ^{III} -oleate:			
		a or b	
Fe 6.21	10.08 ± 0.17	10.75	9.86
C 72.08	53.26	48.37	53.06
H 11.01	7.33	7.10	7.89
O 10.70	29.33	33.78	29.19
(a) Fe(HCO ₃) ₃ ·HOl complex or (b) (Fe(HCO ₃) ₃) ₇ ·(HOl) ₈ complex in which Ol = oleate HOl = oleic acid			

phases and therefore accumulating at the interface. By virtue of their largely hydrocarbon character (see analysis) they will be more easily wetted by benzene than by water, stick out at the oil side, and stabilize the emulsion of water in oil mechanically (14). Alternatively they may be considered as forming a continuous, multimolecular, rather rigid layer separating the two phases by a layer impermeable to water and preventing coalescence of the water droplets.

Table I shows the unexpected fact that an increase in surface potential is roughly correlated with a decrease in stability against coalescence. High charge indicates little hydrolysis. Oleates that give a high charge will probably be present in the interface as a monolayer as contrasted to the multilayer formed by hydrolysis products. The molecules in the monolayer are expected to be quite mobile, because the van der Waals attraction between the hydrocarbon chains, dissolved in the oil side of the interface, will be quite small. After coagulation, the nonhydrolyzed soap molecules may be easily pushed away by the attraction forces between the water droplets and coalescence will follow.

In Table I the position of the oleates of the alkaline earth metals is exceptional. The low electrokinetic potential suggests a pronounced hydrolysis though rapid coalescence is observed. However, the formed hydroxides and hydrocarbonates of these metals are soluble in the water phase of the emulsion globule. Consequently the ability of the interfacial film to stabilize against coalescence is strongly diminished.

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