STABILITY OF OIL-IN-WATER EMULSIONS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAP AAN DE TECHNISCHE HOGESCHOOL TE DELFT OP GEZAG VAN DE RECTOR MAGNIFICUS Dr O. BOTTEMA, HOOGLERAAR IN DE FACULTEIT DER ALGEMENE WETENSCHAPPEN, VOOR EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 25 MAART 1953, DES NAMIDDAGS TE 4 UUR,

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promotor Prof. Ir H. EILERS

STELLINGEN

I

De stabiliteit van een olie-in-water emulsie tegen agglomeratie of vlokvorming kan beschreven worden met behulp van electrostatische afstoting en van der Waals attractie, als bij de hydrophobe solen van vaste deeltjes.

Dit proefschrift, Hoofdstuk III.

II

Het door *Cockbain* gevonden verband tussen de oproomcapaciteit en de zeepconcentratie in een olie-in-water emulsie kan beter verklaard worden met behulp van het „tweede minimum" in de potentiaalkromme dan met adsorptie van zeepionen met de koolwaterstofketen van het oppervlak af gekeerd.

E. G. Cockbain, Trans. Faraday Soc. **48,** 185 (1952).

III

De directe meting van het potentiaalverval aan het grensvlak olie–water levert slechts niet-evenwichtswaarden, welke grotendeels bepaald worden door diffusie van ionen in de olielaag.

B. D. Powell en *A. E. Alexander,* J. Coll. Sci. **7,** 482 (1952).

IV

De hoge waarden der zeta-potentiaal van oliedruppels gedispergeerd in zuiver water kunnen nog steeds niet bevredigend verklaard worden.

H. Limburg, Rec. trav. chim. **45,** 772 (1926).
E. J. W. Verwey en *K. F. Niessen,* Phil. Mag. **28,** 435 (1939).

V

In de door *Brinkman* opgestelde viscositeitsformule voor dispersies is de overeenstemming van de hogere orde termen met die uit de formule van Eilers een toevallige omstandigheid.

H. C. Brinkman, J. Chem. Phys. **20,** 571 (1952).
H. Eilers, Kolloid-Z. **102,** 154 (1943).

VI

De grootte-verdeling der rubberbolletjes, zoals deze in de latexvaten van Hevea Braziliensis voorkomen, is in overeenstemming met de veronderstelling dat de vorming van de rubber in de latexvaten plaats vindt.

M. van den Tempel, Trans. Inst. Rub. Ind. **28,** 303 (1952).

VII

Dat de vulcanisatie van rubber met zwavel in tegenwoordigheid van vulcanisatieversnellers aanleiding geeft tot de vorming van een driedimensionaal netwerk door zwavelbruggen tussen verschillende rubbermoleculen, is nog nergens overtuigend bewezen.

P. Schidrowitz, India Rubber J. **73,** 221 (1952).
R. D. Stiehler en *J. H. Wakelin,* Ind. Eng. Chem. **39,** 1647 (1947).

VIII

De bijzondere moeilijkheden welke ondervonden worden bij het streven naar internationale unificatie van het octrooirecht worden veroorzaakt doordat verschillen in de nationale regelingen in het algemeen geen aanleiding blijken te geven tot een verschillende mate van bevordering der industrie.

IX

De door *Henne* vermelde grote stabiliteit van het fluor-stearinezuur behoeft geen verwondering te wekken, daar mono-fluoralkanen bij afwezigheid van sterke zuren aanmerkelijk stabieler zijn dan de overeenkomstige chloriden.

A. L. Henne; in *Gilman,* Organic Chemistry I, Chapter 11, pag. 948.
N. B. Chapman en *J. L. Levy,* J. Chem. Soc. (London) **1952,** 1673.

X

Bij de polarografische bepaling van de zinkconcentratie in ammoniakale oplossing dient in rekening te worden gebracht dat de samenstelling van het zink-complex, en dus ook de hoogte van de polarografische golf, afhankelijk zijn van de ammoniakconcentratie en de pH der oplossing.

P. Cassagne, Rev. Gén. Caoutchouc **28,** 105 (1951).

XI

Bij de bepaling van het koolzuurgehalte van physiologische vloeistoffen verdient een directe titratie de voorkeur boven de manometrische methode van van Slijke.

F. C Koch en *M. E. Hanke*, Practical methods in biochemistry. Baltimore 1948, pag. 234.

XII

De verklaring van *Salomon* voor het optreden van een maximum temperatuur waarboven de reactie van SO_2 met olefinen niet meer plaats vindt, verschilt niet wezenlijk met die van *Dainton* en *Ivin*.

G. Salomon, Disc. Faraday Soc. 1947 (2) p. 356.
F. S. Dainton en *K. J. Ivin*, Nature **162,** 705 (1948).

XIII

De voorspelling van de toekomstige ontwikkeling van chemische industrieën met behulp van een drie-parameter vergelijking zal in het algemeen geen bruikbare resultaten opleveren.

R. H. Ewell en *B. Scheuerman*, Chem. & Eng. News **30,** 3516 (1952).

XIV

Het is te verwachten dat de verdere ontwikkeling van de chromatografische methodiek steeds meer in de richting der zuivere verdelingschromatografie zal gaan.

XV

Wat *Wheland* op pag. 28 van „The theory of resonance" zegt betreffende de resonantietheorie geldt mutatis mutandis voor elke „man-made" theorie.

C. W. Wheland, The theory of resonance. New York 1947.

Van deze plaats wil ik gaarne mijn dank betuigen aan allen, die tot de totstandkoming van dit proefschrift hebben bijgedragen. Bijzondere dank ben ik verschuldigd aan de Directie van de Rubber-Stichting, Delft, voor de wijze waarop zij mij in de gelegenheid stelde de in dit proefschrift verwerkte onderzoekingen in haar laboratoria uit te voeren en te publiceren.

CONTENTS.

CHAPTER I.

LITERATURE ON THE STABILITY OF OIL-IN-WATER EMULSIONS.

A critical survey is given of the literature concerning the coagulation of oil-in-water emulsions. A relation between the stability and the electrical charge of the oil droplets has sometimes been found, but in many cases such a relation appears to be non-existent.

The theories describing the action of emulsifying agents are discussed.

A satisfactory explanation of the experimental results recorded in the literature can in most cases be given by taking into account that flocculation and coalescence are different reactions, which can be controlled separately. The results of several investigations suggest that flocculation is governed by electrostatic repulsion as in the case of the hydrophobic sols of solid particles, whereas coalescence appears to be affected by the structure of the interfacial film.

1. Charge and stability.

An oil-in-water emulsion is a two-phase system in which the oil phase is present in small drops, dispersed in the continuous aqueous phase. The "oil"-phase is characterised by being liquid, immiscible with water, and by having a very low specific conductivity.

The stability of an oil-in-water emulsion is generally considered to represent the tendency of the emulsion to remain in an unaltered condition for a certain time. The condition of an emulsion can be changed in a variety of ways, which will generally be influenced by different factors. Sedimentation — or creaming — may occur without change in particle size, but this phenomenon may be profoundly influenced by aggregation of the particles. On the other hand, sedimentation — or creaming — may be entirely avoided by properly adjusting the densities, but even then aggregation and particle growth remain possible.

Coagulation of an emulsion comprises both aggregation (or flocculation) and particle growth by coalescence. The coagulation of an emulsion will ultimately lead to the appearance of a separate oil layer, i.e. breaking.

At the beginning of this century it had been suggested almost simultaneously by *Hardy* and *Donnan* that the stability of colloidal systems against coagulation might be the result of an electrostatic repulsion of the particles, carrying charges of the same sign. Based on this suggestion, extensive theoretical and experimental investigations

led to the conclusion that the behaviour of hydrophobic sols of solid particles can be fairly well explained in terms of an electrostatic repulsion of the charged particles, which repulsion may be more or less counteracted by an attractive force of the Van der Waals–London type [1].

On several occasions it has been proposed to study an emulsion as a model system in the investigation of the behaviour of hydrophobic colloids. The stability conditions of emulsions are, according to a theory developed by *Verwey* and *Niessen* [2], not fundamentally different from those of the hydrophobic sols. In both cases, the stability would be primarily controlled by the electrostatic potential on the aqueous side of the interface. The difference in behaviour is connected with the different mechanism giving rise to a potential at the interface.

2. Electrostatic potential at the interface.

In the case of two immiscible liquids in contact, the potential difference between the interiors of the liquids arises from an unequal distribution coefficient of the positive and negative ions. Generally, the anions will be more soluble in the oil phase than the cations, which explains the well-known rule of *Coehn* [3].

The potential drop on both sides of the interface can be calculated as a function of the electrolyte concentrations, and it is found that the potential drop on the aqueous side is generally only a small fraction of the total potential difference between the interiors of the phases. Moreover, the smallness of the oil droplets in an oil-in-water emulsion will prevent the diffuse double layer in the oil phase from developing to its full extent, and this will still further decrease the magnitude of the potential drop in the aqueous phase.

As in this case the total potential drop across the interface is only determined by the kind of electrolyte used, and not by its concentration, it is impossible to increase the potential drop in the aqueous phase by changing the electrolyte concentration.

The influence of capillary-active ions on the stability of an oil-in-water emulsion is explained by *Verwey* [4] as caused by the much larger potential drop in the aqueous phase in the presence of a film of adsorbed soap ions. The influence of the amount of adsorbed soap ions on the potential drop in the aqueous phase has been calculated,

[1] *E. J. W. Verwey* and *J. Th. G. Overbeek*, Theory of the Stability of Lyophobic Colloids. Amsterdam 1948.
[2] *E. J. W. Verwey* and *K. F. Niessen*, Phil. Mag. **28**, 435 (1939).
[3] *Coehn*, Wied. Ann. **64**, 227 (1898).
[4] *E. J. W. Verwey*, Trans. Faraday Soc. **36**, 192 (1940).

and it is found that one ion per 1000 sq.A. of interface may already increase the potential drop to about 100 mV, if the electrolyte concentration is sufficiently low.

This may be compared with an observation of *Powney* and *Wood*[5] who found that the electrophoretic mobility of oil drops in soap solutions of varying concentration reaches a maximum at a soap concentration much lower than the Critical Micellar Concentration.

The conditions which give rise to the development of a potential difference between two immiscible phases have been studied by *Dean, Gatty* and *Rideal*[6]. At the interface oil-water there will be a layer of oriented dipoles, producing a difference of electric potential between the phases. This potential difference can be neutralised by the separation of pairs of ions across the interface to form diffuse Gouy-layers in each phase. Changing the layer of adsorbed dipoles, either by further adsorption of a capillary-active substance, or by sweeping the interface with partical removal of the Gouy-layers, will result in a quick change in the potential. However, it is found that this change in potential decays to zero with a velocity depending upon the specific resistance of the oil phase. This becomes evident when it is considered that the time required to neutralise the dipole field will be a function of the concentration of ions in the oil phase and of the viscosity of the oil, and these factors determine also the specific resistance of the oil.

The adsorption of a substance in the interface between two bulk phases cannot permanently alter the potential difference between the two phases, unless the adsorbed substance is soluble in at least one of the phases and its concentration in that phase is changed by the adsorption. In that case the magnitude of the change in the potential difference depends on the dissolution of the substance in the bulk phases rather than on its adsorption in the interface.

Experiments with alcohols, ethers and esters as the oil phase indicate a time constant (i.e. time in which the change in potential on adsorption falls to 1/e of its initial value) of the order of 10 minutes. It may be expected that this time constant would be very much larger when hydrocarbons are used as the oil phase. From these results it appears that in oil hydrosols of paraffin oil it will take a considerable time before equilibrium has been established, after changing the electrolyte concentration.

As soon as a certain amount of capillary-active ions has been

[5] *J. Powney* and *L. J. Wood*, Trans. Faraday Soc. **37**, 152, 220 (1941); ibid. **36**, 57 (1940).

[6] *R. B. Dean, O. Gatty* and *E. K. Rideal*, Trans. Faraday Soc. **36**, 161 (1940).

adsorbed at the interface paraffin–water, the contribution of the diffuse double layer in the oil phase may be neglected as compared with that of the layer in the aqueous phase. The concentration of ions in the paraffin is too low to furnish a perceptible contribution to the total charge of the double layer system.

3. Early experiments with dilute emulsions.

In experimental investigations with the purpose of establishing a relationship between charge and stability in oil-in-water emulsions, the particle charge was generally believed to be indicated by the electrophoretic mobility of the oil droplets. The amount of non-coagulated oil was estimated from turbidity measurements.

The correlation between the zeta-potential and the stability was extensively studied by *Powis* [7] and by *Limburg* [8]. These investigators used oil hydrosols, obtained by shaking a small amount of pure paraffin oil with the purest water available. Nevertheless, their results differ considerably.

The zeta-potential was measured by *Powis* by a microscopic method, whereas *Limburg* used the macroscopic U-tube method. The electrophoretic mobility in the pure oil hydrosol, without any electrolyte added, has been shown [9] to be dependent on the presence of extremely small amounts of impurities, the concentration of which can hardly be ascertained. It is, therefore, not alarming that all investigators who determined this mobility found different values [9, 10]. It might be expected, however, that the influence of electrolytes on the electrophoretic mobility would be more reproducible. This is not the case.

Both *Powis* and *Limburg* found a maximum in the electrophoretic mobility upon the addition of KCl to a concentration of about 0.001 M. It is doubtful whether an increase in the zeta-potential by an initial addition of electrolyte really exists [11] unless some capillary-active ion is present, the adsorption of which may be increased by the addition of electrolyte [12]. This would be in accordance with *Powis*'s observation regarding an increased stability in the presence of this same amount of KCl. The existence of a stability maximum, however, has not been confirmed by *Limburg*.

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[7] *F. Powis*, Z. physik. Chem. **89**, 186 (1915).
[8] *H. Limburg*, Rec. trav. chim. **45**, 772, 854, 875 (1926). Diss. Delft 1924.
[9] *W. Dickinson*, Trans. Faraday Soc. **37**, 140 (1941).
[10] *A. J. Ham* and *E. D. M. Dean*, Trans. Faraday Soc. **36**, 52 (1940).
[11] *H. R. Kruyt* and *J. Th. G. Overbeek*, Trans. Faraday Soc. **36**, 110 (1940).
[12] *J. Powney* and *L. J. Wood*, Trans. Faraday Soc. **36**, 420 (1940).
[13] *A. King* and *G. W. Wrzeszinski*, J. Chem. Soc. **1940**, 1513.

The maximum in mobility on the addition of a monovalent electrolyte has not been recorded by other investigators [5, 10, 13].

The well-known statement of *Powis*, according to which the rate of coagulation of an oil hydrosol suddenly increases as soon as the absolute value of the zeta-potential becomes less than 30 mV, has not been proved by his experiments on the influence of monovalent electrolytes. Both *Powis* and *Limburg* found a steady decrease in the absolute values of the zeta-potential and a steady increase in rate of coagulation, upon the addition of KCl in amounts exceeding that necessary to obtain the maximum in electrophoretic mobility. There is no sharp fall in stability when the potential of —30 mV is reached. However, *Powney* and *Wood* [5] confirm that coagulation by NaCl becomes particularly rapid at the zeta-potential of about —30 mV.

Evidence in favour of *Powis*'s statement concerning the existence of a critical potential has been derived from his experiments with the chlorides of Ba, Al and La. Addition of these electrolytes in increasing amounts caused a steady decrease in the zeta-potential, and a sudden fall in stability as soon as the absolute value of this potential becomes less than 30 mV. Charge reversal was possible with Al and with La, but only with the latter the positive charge became larger than 30 mV, leading again to a stable sol.

Limburg, however, found no decrease in electrophoretic mobility upon the addition of $BaCl_2$ in amounts up to 0.005 M, and the stability became already very low at a concentration of 0.002 M. Addition of $AlCl_3$ causes, according to *Limburg*, charge reversal which may well lead to a sufficiently high positive charge to impart a high stability to the emulsion.

Summarising the comparison of these investigations, it may be said that the theory of the "critical potential" as developed by *Powis* for non-stabilised emulsions, is not confirmed by the experiments of *Limburg*. This may perhaps be attributed to the discordant results of the electrophoresis experiments, which appear to be different in all the experiments recorded.

Limburg extended his measurements to oil hydrosols containing HCl and potassium carbonate. The influence of the pH, at a nearly constant value of the ionic strength, has more recently been investigated by *Williams* [14] and *Dickinson* [9]. They found that the electrophoretic mobility of oil droplets increases almost proportional to the pH, between pH 2 and 10. *Limburg* records a steady rise in mobility upon addition of increasing amounts of potassium carbonate, but HCl had

[14] *G. C. Williams*, Trans. Faraday Soc. **36**, 1042 (1940).

no influence. Nevertheless, both electrolytes cause coagulation at concentrations of about 0.005 respectively 0.0001 M. These results indicate clearly, according to *Limburg*, that a direct correlation between particle charge and stability does not exist.

Some other interesting conclusions, of a more qualitative nature, may be drawn from the work of *Powis*. He determined the stability of an emulsion by comparing its turbidity with that of a set of standards, obtained by diluting the original emulsion with pure water. Comparison was only made visually; no difference in appearance could be detected between an emulsion obtained by diluting and an emulsion obtained by coagulation, unless the oil concentration became less than 20 per cent. of the original concentration. It was observed that the standard emulsion containing only 25 per cent. of the original amount of oil lost its turbidity much faster than the original emulsion. The correlation of this turbidity with the concentration and size of the oil droplets, and especially with the concentration of aggregates, is unknown, but this might be the first example of an influence of the particle concentration on the rate of coagulation recorded.

This influence of the concentration of particles upon the rate of coagulation becomes only clearly perceptible when the rate of flocculation and the rate of coalescence are of the same order of magnitude. That this condition has been satisfied in several of *Powis*'s experiments is shown by the results of his microscopical examination of a coagulated emulsion. It is stated that the decrease in turbidity of a coagulated emulsion appears to be due to the formation of aggregates consisting of between 2 and 200 particles; furthermore that the tendency of two adjacent particles to coalesce is somewhat larger in the absence of electrolyte, though even in this case many particles remain in aggregates without coalescing.

The last part of *Limburg*'s paper describes the influence of surfaceative agents on the stability and zeta-potential of these very dilute oil emulsions. Oleic acid, dissolved in the paraffin, nor saponin, dissolved in the aqueous phase, had an appreciable influence on the electrophoretic mobility in the presence of electrolytes. The influence of the electrolytes on the stability was, however, profoundly altered in the presence of these agents. Thus, the presence of 5 per cent. of oleic acid in the paraffin prevented coagulation by potassium carbonate in concentrations up to 0.075 M. Even in rather acid solutions (0.010 M. HCl) the presence of oleic acid retards the coagulation. In the presence of saponin no coagulation could be observed, even with 0.1 M. electrolytes (KCl, HCl and K_2CO_3). The experiments with saponin were conducted without slowly rotating the coagulating

emulsion, as had been done in all other experiments, because the presence of saponin caused the formation of foam upon stirring. The avoidance of stirring made agglomeration clearly visible in this case, even to the naked eye, and it is stated that the aggregates can be easily redispersed by shaking. It is evident that the stabilising effect of the saponin must be attributed to a considerable lowering of the rate of coalescence, whereas the rate of flocculation appears to be hardly affected by the agent.

The experiments with gelatin have only been recorded with regard to the influence of the pH, without the addition of neutral electrolytes. It was found that near the iso-electric point of the gelatin the addition of a very small amount of this agent sufficed to suppress the electrophoretic mobility entirely. The stability was extremely low at a gelatin concentration slightly below that necessary to obtain a mobility = 0. Increasing the gelatin concentration did not cause a change in the mobility, but the stability increased until no more coagulation could be observed with 100 mg per liter. This shows that neutralisation of the charge may occur by the adsorption of a very small amount of gelatin, which has practically no influence on the rate of coalescence. The latter can only be retarded by the adsorption of a much larger amount of the gelatin. Agglomeration is liable to occur in these emulsions stabilised with gelatin, but this could not be observed as they were continually rotated.

It is noteworthy that the existence of "stable" emulsions of uncharged oil globules appears to be possible in the presence of gelatin. This is confirmed by the measurements of *Friedman* and *Evans* [15], using concentrated emulsions.

A direct correlation between the electrophoretic mobility and the stability, in the presence of a very small amount of gelatin, was also found at a pH 2.8. There is a sharp minimum in the stability at exactly the gelatin concentration which is necessary to suppress the mobility.

Limburg concludes from his experiments that the influence of the charge on the stability is sometimes evident. Generally, however, the charge has only a minor effect as compared to the structure of the interfacial layer.

Eilers and *Korff* [16], taking into account that Powis's hypothesis of a "critical potential" proved not well founded, considered that the stabilising influence of the electrostatic potential at the surface of the particle will be only roughly expressed by the zeta-potential. They introduced a quantity having the dimension of an energy, and

[15] *L. Friedman* and *D. N. Evans*, J. Am. Chem. Soc. **53**, 2898 (1931).
[16] *H. Eilers* and *J. Korff*, Trans. Faraday Soc. **36**, 229 (1940).

containing the zeta-potential and the characteristic lenght $1/\varkappa$ of the Debye-Hückel theory. The value of this new quantity will determine whether the sol is stable or coagulates, "as far as this depends on boundary electric phenomena".

Application of this theory to the data published in *Powis*'s and *Limburg*'s papers largely confirms their views. This, however, holds only for the unstabilised oil hydrosols. Extension of their theory to *Limburg*'s data pertaining to the influence of potassium carbonate on an emulsion containing oleic acid proved only possible when the influence of still other factors was taken into account.

4. Action of emulsifying agent.

In 1917 both *Langmuir* [17] and *Harkins* [18] advanced a theory of emulsifier action, according to which the stabilisation of an emulsion by soap has to be attributed to adsorption of soap molecules at the interface. *Langmuir*'s experiments at an air–water interface had shown that fatty acid molecules occupy a well-defined area in a tightly compressed monomolecular layer on the surface of water. It was assumed that the stabilising action of the soap would become evident as soon as the amount present would be sufficient to produce a monomolecular layer at the interface with an area per soap molecule about equal to that found with the fatty acids at an air–water interface. An excess of soap would remain in the aqueous phase. An unstable emulsion would result if the amount of soap present were insufficient to cover the entire interface with a sufficiently dense layer.

To test this theory, several authors determined the amount of soap adsorbed by chemical analysis of the serum obtained by creaming the emulsion. The specific interface was determined at the same time by microscopic measurement. The emulsifying agents used were in all cases fatty acid soaps, and the pH of the emulsions was usually not sufficiently high to suppress hydrolysis entirely. The fatty acid formed by hydrolysis dissolves in the oil phase, and thus the decrease in concentration in the aqueous phase exceeds the amount of soap adsorbed. *Griffin* [19] determined also the amount of fatty acid dissolved in the oil phase, and showed that the cations of the soap were not present in the oil. In the presence of an excess of alkali in the emulsion, he found an area of 44 sq.A. per molecule of sodium oleate, which

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[17] *I. Langmuir*, J. Am. Chem. Soc. **39**, 1896 (1917).
[18] *W. D. Harkins, E. C. H. Davies* and *G. L. Clark*, J. Am. Chem. Soc. **39**, 541 (1917).
[19] *E. L. Griffin*, J. Am. Chem. Soc. **45**, 1648 (1923).

compares well with the area of 46 sq.A. found for oleic acid on the Langmuir trough.

Harkins and *Beeman* [20] and *Fischer* and *Harkins* [21] confirmed this result, and state that an emulsion having too low a soap concentration to build up a monomolecular layer at the interface would coagulate until the interfacial area had decreased to a sufficiently low value. The resulting emulsion would be infinitely stable.

Van der Meulen and *Rieman* [22], using sodium ricinoleate in very concentrated emulsions of a solution of phenol in toluene, obtained quite different results. According to their experiments, the area per adsorbed soap molecule decreases steadily when the soap concentration in the aqueous phase is increased. An excess of alkali had no influence. Their values for the interfacial area, however, were derived from the measurement of only a very small number of particles.

The relationship between the amount of adsorbed soap and the stability was explained by *Robinson* [23] as due to the mobility of the soap ions in the gaseous film. This will enable the soap ions on two neighbouring oil droplets to flow away from the parts of the surfaces facing each other, thereby decreasing the electrostatic repulsion. The stability conferred by the soap ions reaches a maximum as soon as the film has become sufficiently condensed to restrict the mobility of the ions along the surface. This will occur at the Critical Micellar Concentration.

In the theory developed by *Verwey* [24] the effect of emulsifying agents consists of giving the liquid drops properties more or less comparable with those of solid particles, and of increasing the potential drop at the aqueous side of the interface. An increased electrostatic repulsion retarding the flocculation may result from the presence of adsorbed emulsifying agent.

5. Concentrated emulsions.

Whereas the electrical double layer is apparently of no importance in stabilising the emulsions containing a hydrophilic colloid, other emulsons have been prepared in which it plays a predominant part [25]. Both oil-in-water and water-in-oil emulsions could be produced by shaking oil with an electrolyte solution. Fairly concentrated emulsions

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[20] *W. D. Harkins* and *N. Beeman*, J. Am. Chem. Soc. **51**, 1674 (1929).
[21] *E. K. Fischer* and *W. D. Harkins*, J. Phys. Chem. **36**, 98 (1932).
[22] *P. A. v. d. Meulen* and *W. Rieman*, J. Am. Chem. Soc. **46**, 876 (1924).
[23] *C. Robinson*, Trans. Faraday Soc. **32**, 1424 (1936).
[24] *E. J. W. Verwey*, Proc. Koninkl. Nederland. Akad. Wetenschap. **53**, 376 (1950).
[25] *D. F. Cheesman* and *A. King*, Trans. Faraday Soc. **36**, 241 (1940).

showing some stability were obtained by using oils having a relatively high specific conductivity, such as alcohols and ketones, but when benzene is used as the oil phase, electrolytes do not confer an appreciable stability on the emulsions [26].

From the experiments it appears that the anions dissolve preferentially in the oil phase, the more so when they are less hydrated. They impart a negative charge to the oil droplets. Excess of salt decreases the stability, but an optimum concentration appears necessary to build up a sufficiently high potential. From the theory as developed by *Verwey* [2] it would follow that the magnitude of the potential at an oil–water interface cannot be changed by varying the electrolyte concentration, but in an emulsion containing droplets which are small as compared with the thickness of the double layer in their interior, increasing the electrolyte concentration will decrease the thickness of this diffuse layer and therefore the potential difference across the interface will increase.

Bhatnagar [27] tried to explain the phase-inversion which may occur on adding polyvalent cations to an oil-in-water emulsion by a preferential adsorption of these polyvalent ions, leading initially to an inversion of the sign of the charge. He regarded the charge as a factor which not only determined the stability but also the type of an emulsion.

This theory was disproved by *King* and *Wrzeszinski* [28], who were unable to change the type of an emulsion when it contained an emulsifying agent which did not form a water-insoluble salt with the polyvalent cation added. Their conclusion is that "in the case of emulsifying agents incapable of forming water-insoluble salts with polyvalent metals, electrolytes have little influence on emulsion type and stability, except when the emulsifying action of the agent is destroyed by some chemical change". Here the occurrence of phase inversion is regarded as indicating a low stability of the original emulsion. It is evident that this statement holds only when coalescence is the rate-determining reaction.

The stability of oil-in-water emulsions stabilised with various kinds of emulsifying agents was studied in a more quantitative way by *King* and *Mukherjee* [29]. They calculated the total interfacial area of one ml of emulsified oil from a microscopically determined size-frequency

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[26] *T. Isemura* and *R. Tachibana*, Chem. Abstr. **45**, 7408 d (1951).
[27] *S. S. Bhatnagar*, J. Chem. Soc. **117**, 542 (1920); ibid. **119**, 61, 1760 (1921).
[28] *A. King* and *G. W. Wrzeszinski*, Trans. Faraday Soc. **35**, 741 (1939).
[29] *A. King* and *L. N. Mukherjee*, J. Soc. Chem. Ind. (London) **58**, 243 (1939); ibid. **59**, 185 (1940).

distribution curve, and the rate of decrease of this interfacial area was taken as indicating the instability. The emulsions studied contained 40 per cent. of oil and had a rather low stability, because either a low concentration of emulsifying agent was used or electrolytes were added which reacted chemically with the agent. The authors state that their method of size-frequency determination is not sufficiently exact for accurate theoretical calculations and, in a later paper [30], admit that it even may sometimes give misleading results.

From the data obtained with soap-stabilised emulsions it is concluded that the specific interface decreases almost linearly with time. If, however, the published data are used to calculate approximate values for the number of particles, the curves representing the resulting decrease in particle number as a function of time are found to contain a point of inflexion. It is probable that the considerable number of hardly visible particles which are present in the fresh emulsion contributes more to the specific interface than has been assumed by *King* and *Mukherjee*. This would lead to a more rapid decrease of the interfacial area in the first days after the preparation of the emulsion, a behaviour as has been found in the emulsions stabilised with hydrophilic colloids such as gelatin and various vegetable gums.

In the latter kind of emulsions the number of very small particles is much less than in the soap-stabilised emulsions, and the published values of the specific interface may, therefore, be regarded as more accurate. The specific interface decreases at first rapidly and afterwards very slowly. Approximate values for the number of particles can be calculated, and it is found that this number decreases almost exponentially with time. This is what may be expected when it is taken into account that the rate of coagulation of these concentrated emulsions is determined by the very slow coalescence of the oil droplets, which is a first order reaction. The specific interface itself should also decrease exponentially with time; this was confirmed by the measurements of *Lotzkar* and *Maclay* [31] on emulsions stabilised with vegetable gums.

Though these emulsions were regarded as very stable against coagulation, their heavy consistency shows a considerable interaction between the particles. Thus, in these concentrated systems, a high rate of flocculation does not lead to coagulation because coalescence is very slow.

It is stated by *King* and *Mukherjee* [29] that the high viscosity would contribute to the stability because this "would seem to prevent

[30] *A. King,* Trans. Faraday Soc. **37,** 168 (1941).
[31] *H. Lotzkar* and *W. D. Maclay,* Ind. Eng. Chem. **35,** 1294 (1943).

coalescence". In fact, the high viscosity indicates a low stability against flocculation, and emulsions can only be produced in this case when the emulsifying agent has a strong retarding action on coalescence.

The relationship between charge and stability of stabilised emulsions, as investigated by *Limburg* [8], was further studied by *King* and *Wrzeszinski* [13], using several other emulsifying agents and rather concentrated emulsions. The stability was estimated by measuring the amount of oil separated in a given time. With saponin as the emulsifying agent, the results of *Limburg* could be confirmed: the addition of electrolytes, even in concentrations which entirely suppressed the electrophoretic mobility, had no influence on the rate of oil separation. The treated emulsions, however, showed a tendency to "creaming and clumping", indicating that stability was only controlled by the very slow coalescence. Generally no simple correlation was found between electrophoretic mobility and stability. Very concentrated emulsions could be broken by saturating the aqueous phase with electrolytes, even in cases where no water-insoluble salt was formed by interaction of the salt with the emulsifying agent. In this case the action of the salt is determined by the position of its anion in the lyotropic series.

As in these concentrated emulsions, saturated with salt, the stability will be determined by the rate of coalescence, it appears that the resistance against rupture offered by the film of the emulsifying agent can be influenced by ions having a charge of the same sign as the interfacial film.

An influence of the electric charge on the rigidity of the interfacial film, and thus on the rate of coalsecence rather than on the rate of flocculation, was postulated by *Schulman* and *Cockbain* [32]. A highly stable emulsion will be formed if the interfacial film consists of a stable complex of a water-soluble and an oil-soluble compound. The existence of a complex of two molecular species is derived from the behaviour of a monomolecular layer of the mixture at an air–water interface. If the layer surrounding the oil droplets is electrically charged, it will be in a "liquid condensed" state, which favours stability. The electrical charge of the ions in the interface causes them to repel each other, thus preventing the formation of a solid state. If the charge of the components in the film is taken away, a solid film is formed and the stability of the oil-in-water emulsion is diminished.

In a subsequent paper [33] it is shown that the specific interaction

[32] *J. H. Schulman* and *E. G. Cockbain,* Trans. Faraday Soc. **36,** 651 (1940).
[33] *E. G. Cockbain* and *A. J. McMullen,* Trans. Faraday Soc. **47,** 322 (1951).

between oil-soluble alcohol molecules and water-soluble soap ions, which was supposed to contribute to the stability, does not exist.

A clear indication of the possibility for influencing the coalescence and the flocculation separately was obtained by *Elkes, Frazer, Schulman* and *Stewart* [34]. They mixed a protein, dissolved in a buffer solution, with an emulsion stabilised by an anionic or a cationic soap. The presence of a cationic soap confers a positive charge on the emulsified oil globules. The net charge of the protein can be made positive or negative by adjusting the pH of the buffer solution.

Mixing an emulsion with a protein solution has no appreciable influence on the stability when the net charge of the protein molecule has the same sign as that of the oil droplets. If, however, the protein molecules have a charge opposite to that of the oil droplets, flocculation or breaking will be observed, depending on the amount of protein present in the final emulsion. If its concentration exceeds a certain minimum value, only flocculation occurs, obviously because the coalescence has been enormously retarded by the layer of adsorbed protein. If the amount of protein added is less than about 2 mg per m^2 of interface, its influence on the rate of coalescence is insufficient to avoid breaking. This critical concentration can be slightly decreased by adding neutral electrolytes.

The influence of the formation of water-insoluble salts of the soap ions on the rate of coalescence was studied by *Martin* and *Hermann* [35]. They measured the rate of oil separation upon centrifuging a concentrated emulsion containing a reactive cation in an amount smaller than required, or just sufficient, to react with all the soap ions present. The amount of oil separated depended only on the proportion of the soap which had reacted with the cation, and not on the specific nature or even the valency of the cation. Only the action of H-ions was stronger than that of other cations. However, unknown ionic concentrations and the effect of the centrifugal field render a more exact treatment difficult.

Finally, it must be mentioned that *Ross* [36] advanced a different theory of emulsion stability, by stressing the analogy with the collapse of a foam. First, a concentrated cream layer has to be formed as a consequence of a difference in density. The rate of drainage of the water contained in the thin layer between the oil globules in this cream will determine the rate of oil separation.

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[34] *J. J. Elkes, A. C. Frazer, J. H. Schulman* and *H. C. Stewart*, Proc. Roy. Soc. (London) **A 184**, 104 (1945).

[35] *R. A. Martin* and *R. N. Hermann*, Trans. Faraday Soc. **37**, 25 (1941).

[36] *S. Ross*, J. Phys. Chem. **47**, 266 (1943).

A somewhat similar mechanism was proposed by *Lederer* [37] and by *Dobroswky* [38]), who calculated the volume of oil separated in a given time while assuming that coagulation (coalescence) only occurs at the upper surface of the emulsion. This upper surface soon becomes covered with a layer of oil, and it is postulated that the rate of coagulation is determined by the number of oil droplets which reach this interface in a given time. It is not clear why coalescence should occur immediately at the water–oil interface, but not in aggregates which might have formed in the bulk of the emulsion. Experiments of *Cheesman* and *King* [39], using water-in-oil emulsions, showed only in a few cases agreement with Lederer's formula. According to these theories, no coagulation would occur in an emulsion of an oil having the same density as the continuous phase. It is possible that a mechanism as proposed by *Ross* has some influence on the rate of coagulation of emulsions which are relatively stable against flocculation, but cream rapidly.

6. Conclusion.

The stabilising action of the electrical charge in emulsions of non-polar oils manifests itself only in non-stabilised, very dilute emulsions, but even in this case the evidence is not convincing. In concentrated emulsions of a non-polar oil — which must always contain a stabilising agent — removal of the charge leads sometimes to a mere thickening and only in a few cases to breaking of the emulsion.

Concentrated emulsions without a stabilising agent can only be produced if a highly polar oil is used as the oil phase. They have a rather low stability, which is influenced by electrolytes in a way indicating that the electrostatic repulsion contributes to the stability.

If the amount of emulsifying agent in an emulsion is sufficient to form a "coherent film" around the oil globules, electrostatic repulsion as measured by the zeta-potential plays only a subordinate part in the stabilisation against coagulation. A perceptible influence on the rate of coagulation by the addition of electrolytes to such an emulsion occurs only, when the electrolytes react chemically with the emulsifying agent.

Coalescence is often the rate-determining reaction in the coagulation of technical emulsions. If, however, the rate of flocculation is

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[37] *E. L. Lederer,* Kolloid-Z. **71,** 61 (1935).
[38] *A. Dobrowsky,* Kolloid-Z. **95,** 286 (1941).
[39] *D. F. Cheesman* and *A. King,* Kolloid-Z. **83,** 33 (1938).

sufficiently low to avoid the formation of aggregates, a very stable and concentrated emulsion can be prepared in which no specific agents retarding the coalescence are present. This is the case in emulsions stabilised by ionic soaps, in which flocculation, accompanied by thickening, leads immediately to breaking.

CHAPTER II.

THE ELECTRICAL DOUBLE LAYER AT THE OIL-WATER INTERFACE.

The electrostatic interaction between charged oil globules in water is determined by the potential drop at the aqueous side of the interface. This potential drop is, under the conditions of the present investigation, practically entirely determined by the amount of adsorbed soap ions and the electrolyte concentration in the aqueous phase. A model is described according to which the charge in the diffuse layer is compensated by the charge of the adsorbed soap anions *minus* the charge of the counter-ions situated between the ionic heads of the adsorbed soap ions. The capacity of the double layer in the oil phase may be neglected.

The amount of adsorbed soap ions has been determined by measuring the dependency of the interfacial tension on the soap concentration, followed by application of the Gibbs adsorption isotherm. The potential drop at the aqueous side of the interface has been calculated; it was found to be practically independent on the soap concentration in the range of concentrations investigated. The potential drop is decreased by increasing the salt concentration; the effect of an addition of salt on the potential drop is strongly dependent on the valency of the counter ions.

Determination of the zeta-potential by measurement of electrophoretic mobility of oil droplets indicates that the values of the surface potential as calculated in the present chapter are of the right order of magnitude.

1. Model of the double layer.

An investigation of the interaction between dispersed oil globules involves a study of the electrostatic phenomena at the oil–water interface. A potential difference will generally exist between the interiors of an oil and a water layer in contact, the magnitude of which, ΔV, is determined by the distribution equilibrium of the dissolved ions (fig. 2.1a) [1]. The potential function arising from the unequal ionic distribution, in the absence of specifically adsorbed ions, has been investigated by *Verwey* and *Niessen* [2]. It is found that diffuse double layers are present on both sides of the interface, and the potential drop occurs partly in the oil phase and partly in the aqueous phase. Moreover, at the interface itself a "boundary potential drop" χ is present, caused by the orientation of dipoles. The adsorption of capillary-active ions at the interface will not affect the magnitude of the potential difference between the interiors of the phases, so long as the ionic concentrations in the bulk phases are not changed by the

[1] *E. J. W. Verwey*, Trans. Faraday Soc. **36**, 192 (1940).
[2] *E. J. W. Verwey* and *K. F. Niessen*, Phil. Mag. **28**, 435 (1939).

adsorption process [3]. The initial change in the potential difference caused by the adsorption of ions is compensated by a rearrangement of the dissolved ions across the interface (fig. 2.1b).

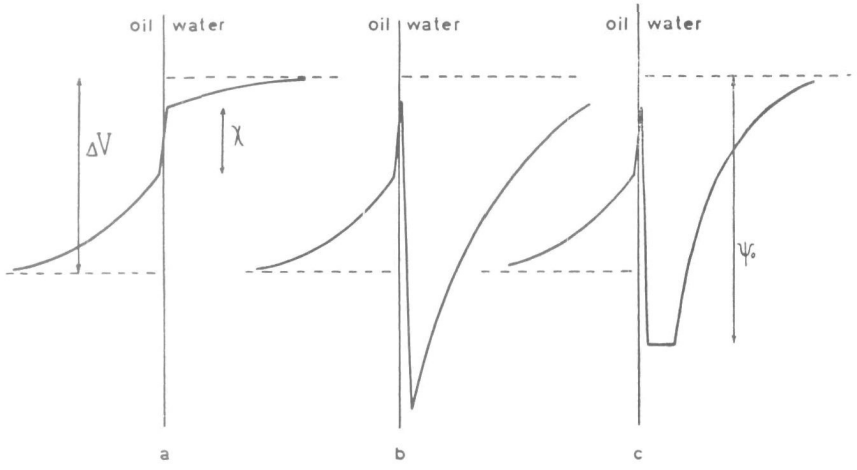

Fig. 2.1. The potential at an oil—water interface.
a. in the absence of surface-active ions;
b. after addition of soap ions, in solution of very low ionic strength;
c. in the presence of soap ions and a large amount of salt.

The interaction of dispersed oil droplets, and therefore the colloidal stability of an emulsion, is controlled by the potential drop at the aqueous side of the interface. *Verwey* [4] calculated the influence of the amout of adsorbed soap ions on the magnitude of the potential drop in the aqueous phase, using the assumptions that the total potential drop across the interface is not affected by the adsorption of soap and that the ionic concentration even in the immediate neighbourhood of the interface remains sufficiently low to allow the ions to be treated as point charges without finite dimensions.

In the emulsions considered in this investigation, and also in technically important emulsions, in which the oil phase has a very low electric conductivity and which are stabilised by the presence of ionic soaps, the potential drop at the aqueous side of the interface depends only on the amount of soap ions adsorbed, and on the electrolyte concentration in the aqueous phase. This follows from the electric neutrality of the whole interface, which implies that the charge of the adsorbed soap ions is compensated by the charges in the diffuse double

[3] *R. B. Dean, O. Gatty* and *E. K. Rideal,* Trans. Faraday Soc. **36,** 161 (1940).
[4] *E. J. W. Verwey,* Proc. Koninkl. Nederland. Akad. Wetenschap. **53,** 376 (1950).

layers at both sides of the interface. The contribution of each of these diffuse layers is proportional to

$$\sqrt{n_i \varepsilon_i} \sin h \left(\frac{e\psi_i}{2\,kT} \right)$$

in which n_i is the ionic concentration, ε_i the dielectric constant and ψ_i the potential drop in phase i. The value of $\sqrt{n_i \varepsilon_i}$ in the aqueous phase will be at least 10^3 times the value in the oil phase, whereas the sin h terms are of the same order of magnitude. This shows that the capacity of the diffuse double layer in the oil phase can be neglected, even though the potential drop in this double layer may have a fairly high value.

It follows that, under the conditions mentioned, the total potential difference between the interiors of the phases is determined by the unequal distribution of the ions, and not by the adsorption of soap, whereas the reverse is true for that part of the potential drop which controls the stability of the emulsion against flocculation.

The structure of the double layer can only be discussed after the introduction of a suitable model. In the case of the mercury–water and the AgI–water interfaces models have been proposed allowing a satisfactory treatment of the phenomena occurring at these interfaces [5, 6]. In the case of an oil–water interface, on which soap ions are adsorbed, a slightly different model will prove more useful.

In the model which will be adopted here [7], part of the counter ions are considered to be situated *between* the ionic heads of the soap molecules, which will project some distance into the aqueous phase. The layer containing the soap ions and part of the counter ions is situated in the immediate neighbourhood of the interface and has a depth of only several times 10^{-8} cm. The potential in this layer is assumed to have uniformly the value ψ_0 with respect to a point far away in the aqueous phase (fig. 2.1c). This layer will be called the Stern-layer, though its structure is more in accordance with the views expressed by *Müller* [8] and by *de Bruyn* [9] than with those of *Stern* [10].

It will be assumed in the calculation of the following sections that the soap concentration in the aqueous phase is always below the critical micellar concentration.

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[5] *D. C. Grahame,* Chem. Rev. **41,** 441 (1947).
[6] *E. L. Mackor,* Rec. trav. chim. **70,** 663, 747, 763, 841 (1951)
[7] *J. T. Davies,* Trans. Faraday Soc. **47,** 414 (1951).
[8] *H. Müller,* Kolloidchem. Beih. **26,** 274 (1928).
[9] *H. de Bruyn,* Rec. trav. chim. **61,** 193 (1942).
[10] *O. Stern,* Z. f. Elektrochemie **30,** 508 (1924).

2. Determination of surfaces charge.

The only quantity that can be measured at an oil–water interface is the interfacial free energy. The surface charge σ can be found from such measurements by application of Gibbs's theorem, according to which at constant temperature and pressure [11]:

$$-\mathrm{d}\gamma = \sum_i \Gamma_i \mathrm{d}\mu_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

in which γ is the interfacial tension, Γ_i is the surface excess of component i, defined as:

$$\Gamma_i = \left(\frac{\partial n_i}{\partial \omega}\right)_{\substack{p;\ T;\ n_1;\ n_2 \\ \mu_1 \text{———} \mu_i}} = \frac{1}{\omega}\left(n_i - m_i \frac{18}{1000} n_{H_2O}\right) . \quad . \quad . \quad (2.2)$$

μ_i is the thermodynamic potential of the component i;
n_i is the number of moles i in the system;
m_i is the molality of i in the homogeneous solution;
ω is the area of the interface.

In using equation (2) it is assumed that the solubility of each of the components in the oil phase may be neglected, as well as the solubility of the oil in the aqueous phase. Components 1 and 2 are chosen as water respectively oil. The constancy of n_1 and n_2 in equation (2) implies that the surface excesses of water and oil molecules are considered zero.

Application of equation (1) to a system containing the salt BA and the anionic soap DS, both supposed to be completely dissociated in the solution, gives under the conditions mentioned:

$$\mathrm{d}\gamma = -\Gamma_{B+}\mathrm{d}\mu_{B+} - \Gamma_{A^-}\mathrm{d}\mu_{A^-} - \Gamma_{H+}\mathrm{d}\mu_{H+} - \Gamma_{OH^-}\mathrm{d}\mu_{OH^-} - \\ - \Gamma_{D+}\mathrm{d}\mu_{D+} - \Gamma_{S^-}\mathrm{d}\mu_{S^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

The number of independent variables is much lower than the number of terms in equation (3), as relations exist between them. However, it is now assumed that none of the ions present, except S^-, is specifically adsorbed at the interface. The term containing Γ_{H^+} may be neglected as compared with the adsorption of the other cations, as it was found that no change in interfacial tension could be detected upon varying the pH between 10.6 and 2.9 in a 0.004 M solution of Aerosol MA containing 0.1 M sodium chloride. Similarly, the (negative) surface excess of OH^- at the negatively charged interface

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[11] *E. A. Guggenheim*, Trans. Faraday Soc. **36**, 397 (1940); ibid. "Thermodynamics". North-Holland Publishing Co. Amsterdam, 1949.

will be neglected, as the concentration of OH^- in the solution is only a small fraction of that of the other anions. Together with the neutrality condition, this gives the equations:

$$\begin{aligned} -\Gamma_{A^-} + \Gamma_{B^+} + \Gamma_{D^+} &= \Gamma_{S^-} \\ \Gamma_{H^+} = \Gamma_{OH^-} &= 0 \end{aligned} \quad \ldots \quad (2.4)$$

Taking further into account that:

$$\begin{aligned} d\mu_{AB} &= d\mu_{A^-} + d\mu_{B^+} \\ d\mu_{DS} &= d\mu_{D^+} + d\mu_{S^-} \end{aligned} \quad \ldots \quad (2.5)$$

equation (3) can be transformed into:

$$-d\gamma = \Gamma_{S^-} d\mu_{DS} + \Gamma_{A^-} d\mu_{AB} + (\Gamma_{A^-} - \Gamma_{B^+})(d\mu_{D^+} - d\mu_{B^+}) \quad . \quad (2.6)$$

This equation will be applied to experimental data in which the interfacial tension is given between an oil layer and an aqueous soap solution containing varying amounts of soap. If the soap solution contained a non-surface active electrolyte AB, the concentration of this salt was high with respect to the soap concentration and remained constant when the soap concentration was varied. In the absence of salt, equ. (6) yields:

$$-d\gamma = \Gamma_{S^-} d\mu_{DS} = 2\,\Gamma_{S^-} d\mu_{S^-} = 2\,\Gamma_{S^-} RT\, d\ \ln\ c_{S^-} f_{S^-} \quad . \quad (2.7)$$

If an excess of salt is present, a distinction may be made between experiments in which B^+ and D^+ are identical, say Na^+, and those in which the cations are different. In the first case, the last term of equation (6) vanishes. Moreover, the thermodynamic potential of the sodium ions will hardly be affected by varying the soap concentration, so long as this remains low as compared with the salt concentration. The resulting equation is;

$$-d\gamma = \Gamma_{S^-}\, d\mu_{S^-} = \Gamma_{S^-} RT\, d\ \ln\ c_{S^-} f_{S^-} \quad \ldots \quad (2.8)$$

If the cations are different, variation of the soap concentration will result in:

$$\begin{aligned} d\mu_{AB} &= 0 \\ d\mu_{B^+} &= 0 \\ d\mu_{D^+} &= d\mu_{S^-} \end{aligned}$$

whence:

$$-d\gamma = \Gamma_{S^-} d\mu_{S^-} + \Gamma_{D^+} d\mu_{D^+} \quad \ldots \quad (2.9)$$

The large excess of the cation B^+ ensures that Γ_{B^+} will be of the same order of magnitude as Γ_{S^-}, whereas Γ_{D^+} is only a small fraction

$$\frac{\sigma_1}{\text{v.e.}} = \frac{N_1}{1 + \frac{0.6 \times 10^{24}}{18 \times n} \exp\left(\frac{ve\psi_0}{kT}\right)} \quad . \quad . \quad . \quad . \quad (2.12)$$

where N_1 is the number of available positions in 1 cm² of the Stern layer; n is the number of counter ions of valency v in 1 cm³ of the homogeneous solution; e is the elementary charge; ψ_0 is the potential in the Stern layer with respect to a point in the aqueous phase far from the interface.

The factor $\frac{0.6 \times 10^{24}}{18}$ represents the number of positions available to the counter ions in 1 cm³ of the homogeneous solution; an estimation of the corresponding number N_1 in the Stern layer leads to a value of 10^{15} when the depth of this layer is taken as 3×10^{-8} cm.

The diffuse part of the double layer has a charge σ_2 which is related to the potential at the boundary between the Stern and the Gouy layers, ψ_0, by the equation:

$$\sigma_2 = \sqrt{\frac{\varepsilon kT}{\pi} \Sigma nv^2} \sinh\left(\frac{ve\psi_0}{2kT}\right) \quad . \quad . \quad . \quad . \quad (2.13)$$

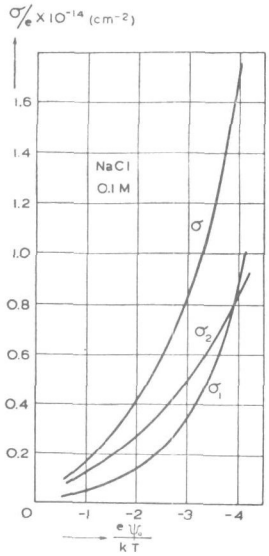

Fig. 2.2. Relation between the potential in the Stern layer, ψ_0, the amount of adsorbed soap σ/e, and the partition of the counter ions between Stern- and Gouy-layer, in a 0.100 M solution of a 1—1 valent electrolyte.

of it. Thus, no appreciable error will be made in neglecting the second term of equation (9), and the resulting equation is identical with (8). If the cation B^+ has a valency $v > 1$, a much smaller excess of the salt is sufficient to make $\Gamma_{B^{v+}} \gg \Gamma_{D^+}$, as the ratio between the concentrations of B^{v+} and D^+ in the double layer is much higher than in the bulk of the solution [12].

It has been shown by *McBain* and *Bolduan* [13] that in soap solutions the theory of strong electrolytes, as developed by *Debye* and *Hückel*, may be safely applied so long as the soap concentration does not surpass the critical micellar concentration. The activity coefficient f_{S^-} can be obtained with sufficient accuracy from this theory:

$$\ln f_{S^-} = -1.1 \sqrt{c_S}$$

Substitution in equation (7) gives finally:

$$-d\gamma = 2\Gamma_{S^-} RT (1 - 0.55 \sqrt{c_{S^-}}) d \ln c_{S^-} \quad . \quad . \quad (2.10)$$

In equation (8), the activity coefficient does not change appreciably by varying the soap concentration, whence:

$$-d\gamma = \Gamma_{S^-} RT \, d \ln c_{S^-} \quad . \quad . \quad . \quad . \quad . \quad (2.11)$$

Values of Γ_{S^-} can be calculated from equations (10) or (11) after the relationship between the interfacial tension and the soap concentration has been determined experimentally. In solutions containing a large excess of neutral electrolyte, this Γ_{S^-} may, according to equation (2) be identified with the amount of soap ions adsorbed at 1 cm^2 of the interface. The surface charge follows from:

$$\sigma = e.v. \Gamma_{S^-}$$

If no excess of electrolyte is present, Γ_{S^-} will not correspond exactly with σ/v.e, because there is a deficiency of soap anions in the diffuse part of the double layer. This deficiency, however, amounts to only a few percent of σ.

3. **The potential function in the aqueous phase.**

In the model described in section I of this Chapter, part of the cations will be situated in the Stern layer, between the ionic heads of the soap anions, and the remaining part in the diffuse or Gouy layer. The fraction of the counter ions present in the Stern layer is found by application of the Langmuir-Stern equation [10]:

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[12] *J. F. Danielli*, Surface Chemistry, London 1949, p. 87.

[13] *J. W. McBain* and *O. E. A. Bolduan*. J. Phys. Chem. **47**, 94 (1943).

A further equation is found by taking into account the electric neutrality of the whole double layer system:

$$\sigma_1 + \sigma_2 = \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.14)$$

Equations (12), (13) and (14) suffice to calculate ψ_0 as a function of n and σ. Fig. 2.2 gives the result in a 0.100 M solution of a 1–1 valent electrolyte.

4. Experimental.

The oil phase consisted of a mixture of equal volumes of monochlorobenzene and paraffin oil. The resulting density of 0.988 g per cm^3 at 20° C is slightly lower than that of the oil phase used in the emulsions investigated, in which the density of the dispersed phase (1.006 g per cm^3 at 20° C) corresponded closely with that of the aqueous serum. It was however, considered desirable to carry out the measurements of interfacial tension with the oil phase as the upper layer, and this proved only possible when its density was decreased to the value given. The slight difference in density and composition, as compared with the oil phase used in the preparation of the emulsions, will probably be without perceptible influence on the adsorption of soap ions.

Paraffin oil was a water-white medical grade, supplied by Brocades (Den Haag, Holland). It had a density of 0.875 g per cm^3 and a viscosity of 0.90 poise, both at 20° C. Purification by shaking with aluminium hydroxide and subsequent drying had no perceptible influence on its surface properties. Monochlorobenzene "pure" from Brocades was used without further purification, after tests had indicated the absence of surface-active impurities.

The Aerosol OT and Aerosol MA were anhydrous samples obtained through the courtesy of American Cyanamid Company (Bound Brook, N.J., U.S.A.). Aerosol OT is stated to be the sodium salt of di-(ethylhexyl)-sulphosuccinic acid and Aerosol MA the corresponding di-(methylamyl) derivative. Sodium laurate solutions were prepared by dissolving lauric acid, supplied by Hess Products Ltd., Leeds, England, in a sufficient excess of aqueous carbon dioxide-free NaOH solution to give a pH of 10.5. This lauric acid is stated to contain about 9 per cent. of myristic acid and has a m.p. of 43—44° C. It was considered unnecessary to separate the constituents for the purpose of the present investigation. The inorganic salts used were of reagent quality.

The Wilhelmy plate method was used to measure the interfacial tension between the aqueous solution and the oil phase. A glass slide, suspended in a vertical plane from the arm of a torsion balance, hangs with its lower part in the aqueous layer and with its upper part in the oil layer. The interface between the layers must cut the vertical surface of the plate. Because of the small difference between the densities of the phases the capillary rise of the aqueous layer at the wall of the plate reaches a value of several cm at an interfacial tension of 20 dynes/cm. The height of the plate was 2.8 cm. Values of the interfacial tension surpassing 20 dynes/cm could, therefore, not be measured. The correction for buoyancy is very simple in this case, as it is practically independent on the depth of submerging in the lower layer and, consequently, on the shape of the meniscus. Care was taken to adjust the interface at the same level in all experiments.

Zero contact angle could easily be obtained, at sufficiently low values of the interfacial tension, by wetting the slide in the aqueous layer before rising it in the interface. After a reading had been taken, part of the aqueous layer was

removed and replaced by an equal volume of a concentrated soap solution, thereby keeping the salt concentration constant. This was carried out without disturbing the interface.

All measurements were carried out at room temperature (18—20° C). Only in the case of the sodium laurate solutions at soap concentrations somewhat below the critical micellar concentration, the reproducibility was unsatisfactory. Presumably this was caused by the low solubility of the soap under the conditions of the experiments.

In all measurements equilibrium appeared to be established within about one minute. When, in some experiments, equilibrium was attained more slowly, a repetition with carefully purified solutions eliminated this time effect.

5. Results and discussion.

Interfacial tensions against the oil layer, of Aerosol MA solutions containing varying amounts of salts are shown in fig. 2.3 and 2.4; in fig. 2.5 the data for sodium laurate have been assembled. Bivalent cations could only be used in solutions containing Aerosol MA, as the other soaps were precipitated from their solutions by the addition of even small amounts of magnesium salts. In the case of Aerosol OT the solubility becomes even very low in the presence of monovalent electrolytes.

The surface excess of the soap has been calculated by means of equation (10) or (11) and the results are shown in fig. 2.6. Generally, the addition of salt to a soap solution causes an increased adsorption of

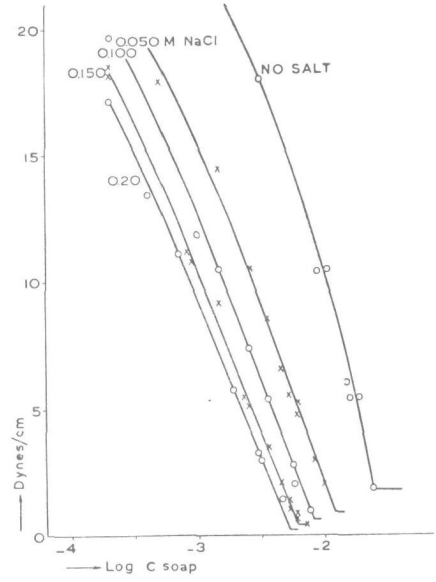

Fig. 2.3. Interfacial tension of Aerosol MA solutions containing sodium chloride, against oil mixture.

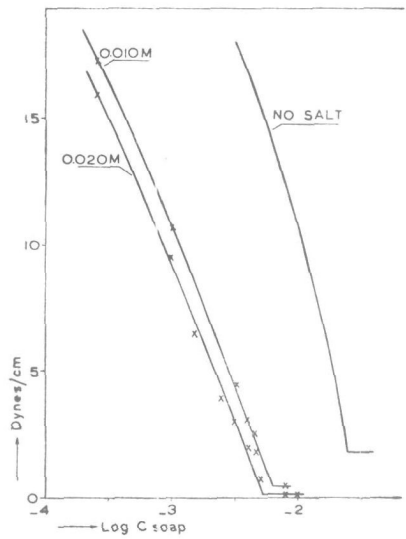

Fig. 2.4. Interfacial tension of Aerosol MA solutions containing magnesium chloride, against oil mixture.

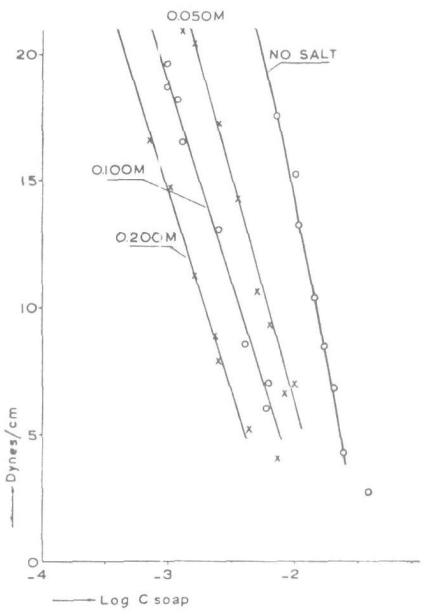

Fig. 2.5. Interfacial tension of sodium laurate solutions containing sodium chloride, at pH = 11.0, against oil mixture.

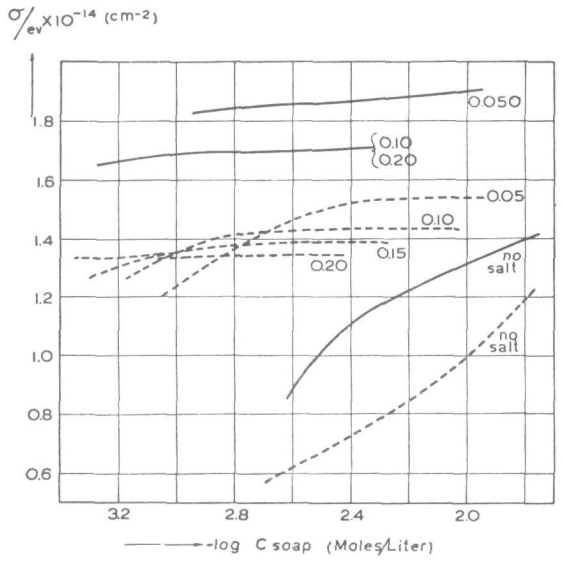

Fig. 2.6. Surface excess of the soap ions as a function of the soap concentration in the aqueous phase. Numbers give concentration of sodium chloride in moles/liter. Curves for 0.010 M and 0.020 M magnesium chloride coincide with curves for 0.100 M and 0.150 M sodium chloride, respectively. Dotted curves: Aerosol MA. Fully drawn curves: sodium laurate.

soap, which may be explained by the decreasing electrostatic repulsion of the ionic heads in a more concentrated salt solution. At fairly high salt and soap concentrations, however, though still below the critical micellar concentration, a further increase of the salt concentration appears to decrease the amount of adsorbed soap. It is possible that the values for σ given in fig. 6 in the 0.05 M salt solution are somewhat too high, because the thermodynamic potential of the cation has been assumed to remain constant when the soap concentration was varied (equ. 8), which is not strictly valid at this relatively low salt concentration.

It follows from fig. 2.3; 2.4 and 2.5 that, in the presence of a sufficient amount of salt the interfacial tension decreases linearly with the logarithm of the soap concentration, showing that the amount of adsorbed soap is not affected by the soap concentration, under these circumstances. This behaviour might seem somewhat unexpected, as it is generally believed that a decreasing interfacial tension must necessarily be caused by an increased adsorption of soap. It can be explained by considering that the interfacial tension measures the

amount of energy required to extend the surface with one cm^2, and this amount will be lower in a more concentrated soap solution because in this case more ions are available for occupying positions in the newly formed interface.

The adsorption of laurate ions is always larger than of Aerosol MA anions, under comparable conditions, whereas both contain hydrophobic groups of twelve carbon atoms. By transferring a hydrocarbon chain from an aqueous to an oil medium more energy can, apparently, be gained when the hydrocarbon has a straight chain than when it consist of several branched chains. The "bulkiness" of the hydrocarbon chain itself will offer little resistance to closer packing, as the area available for one laurate ion is always larger than 50 sq.A., and this hydrocarbon chain can be packed in an area of 20 sq.A. in a dense monolayer of the undissociated molecules [14].

The potential ψ_0 has been calculated from the amount of adsorbed soap, and the electrolyte concentration, by comparison with graphs similar to fig. 2.2. The results are shown in fig. 2.7 in which the potential is seen to decrease nearly linearly with increasing salt concentration. It is practically independent on the soap concentration in the range from 0.001 to 0.004 M for Aerosol MA and from 0.0014 to 0.006 M for sodium laurate. At Aerosol MA concentrations below 0.001 M the potential ψ_0 in a salt solution is only slightly lower than has been indicated in fig. 2.7. The influence of bivalent cations on

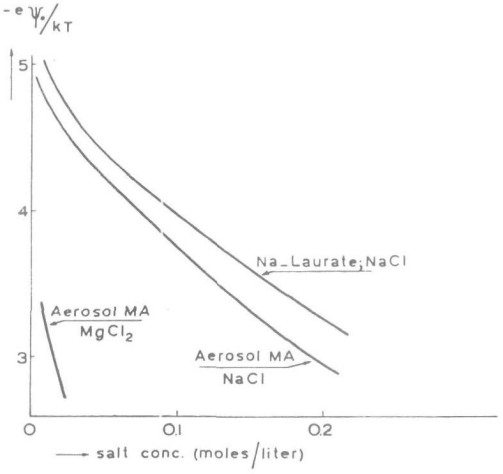

Fig. 2.7. Relation between the potential in the Stern-layer and the salt concentration in the aqueous phase.

[14] *I. Langmuir*, J. Am. Chem. Soc. **39**, 1848 (1917).

the potential has also been given in fig. 2.7; it appears that the same decrease in potential can be obtained with a concentration of bivalent cations which is roughly ten times as low as the concentration of monovalent cations necessary to obtain this effect.

The exact values of the surface potential obtained according to the model used in this investigation depend to a considerable extent on the values assigned to the constants entering in these equations. The values of these constants have been chosen in accordance with evidence obtained from various investigations; the resulting value of the surface potential shows reasonable agreement with that of the zeta-potential measured by means of electrophoresis. Application of the theory of *Verwey* [4], however, in which the dimensions of the ions are neglected, would result in much higher values of the surface potential.

6. Electrophoresis measurements.

The electrophoretic mobility of the oil droplets was measured in a U-tube apparatus against a clear solution containing soap and salt in the same concentration as the aqueous phase of the emulsions investigated. The clear solution contained also 5 per cent. of glucose which appeared necessary to obtain a sharp boundary. The side tubes containing the electrodes had a sufficiently large cross-section to avoid interference by evolution of gas.

From the velocity u of the boundary in a field E of about 2 V/cm the zeta-potential was calculated by means of the Helmholtz equation:

$$\zeta = \frac{4\pi\eta u}{\varepsilon E}$$

The effect of the electrophoretic retardation on these large, non-conducting spheres has been taken into account in this equation, whereas the relaxation effect may be neglected because $\varkappa R \gg 1$. The estimation of electrophoretic mobility of these fairly large spheres in a concentrated electrolyte solution presents an example of a case in which the calculation of the zeta-potential from the mobility data offers no difficulty. It would have been possible to obtain relatively accurate values of the zeta-potential in this case. In view of the fact that the relation between ζ and ψ_0 is not known and a knowledge of an approximate value of ζ is sufficient for the present purpose, no attempt has been made to obtain this high accuracy.

The results are summarised in table 2.I:

Table 2.I.

Zeta-potential of oil drops emulsified in aqueous Aerosol MA solution, Oil. conc. 0.4 %.

soap conc. mol/l	electrolyte	conc. mol/l	ζ (mV)
0.00031	—	—	103
,,	NaCl	0.050	131
,,	,,	0.100	124
,,	,,	0.150	114
,,	,,	0.200	117
0.00088	—	—	140
,,	NaCl	0.100	126
,,	,,	0.150	105
0.00088	$MgCl_2$	0.005	66
,,	,,	0.010	58
0.00088	Luteo-cobaltic	0.0002	15
,,	chloride	0.0003	12

The values of the zeta-potential in the presence of bi- or tervalent cations are somewhat lower than would follow from fig. 2.7. This may be attributed to specific adsorption in the Stern layer, which makes the concentration of the counter ions in this layer slightly higher than would follow from equ. (12) considering only electrostatic forces.

CHAPTER III.

FLOCCULATION IN AN OIL-IN-WATER EMULSION.

The stability of an emulsion against coagulation is partly determined by such trivial factors as density of the dispersed phase and viscosity of the continuous phase, and partly by specific colloidal phenoma controlled by particle interaction. Colloidal stability shoud be studied in a system in which the influence of a difference in density is eliminated.

Analogous to the behaviour of the hydrophobic sols of solid particles, the colloidal stability of an oil-in-water emulsion may be assumed to be controlled by the rate of flocculation. The existence of a relationship between the rate of flocculation and the electrostatic repulsion of the oil droplets would follow from an effect of the valency of the counter ions as expressed by the rule of *Schulze* and *Hardy*. The influence of the valency, however, manifests itself not only through the thickness of the double layer but also through the value of the surface potential.

The potential energy of interaction for two oil droplets of equal size has been calculated as a function of the distance between the particles. The values of the surface potential calculated with the aid of the model introduced in Chapter II give rise to an energy barrier sufficiently high to prevent flocculation to a distance between the particles of only a few A. Lower values of the surface potential would result in a potential barrier sufficiently low to allow particles to cross it at a measurable rate. The low values of the surface potential can be accounted for by introducing specific adsorption of the counter ions in the Stern layer. Such low values, however, are not consistent with evidence obtained from electrophoresis measurements.

A mechanism explaining the flocculation of emulsified oil droplets is suggested in which a high potential barrier does not prevent flocculation in the "secondary minimum" of the potential energy. Coalescence would, in this case, be controlled by the formation of an oil bridge across the barrier. Some evidence is brought forward showing that a perceptible influence of the "secondary minimum" occurs in the emulsions studied here.

The influence of the particle size on the rate of flocculation is discussed.

1. Introduction.

The coagulation of the hydrophobic sols of solid particles involves only a flocculation process, while recrystallisation and particle rearrangements may occur after the formation of the coagulum has taken place. The stability of the sol itself, however, depends only on the rate of flocculation. In the same sense the stability of an oil-in-water emulsion against coagulation will depend primarily on the rate of flocculation, as coalescence cannot take place before flocculation has occured.

The stability of the hydrophobic sols has been explained in a satisfactory way by taking into account the electrostatic repulsion and the *Van der Waals* attraction [1] between the dispersed particles. The rate of flocculation can be calculated, by means of this theory, as a function of the potential drop in the double layer and the electrolyte concentration. The influence of the valency of the coagulating ions, known as the rule of *Schulze* and *Hardy*, has been shown to be a consequence of the large potential drop in the double layer surrounding the colloidal particle.

In this chapter an attempt will be made to correlate the behaviour of an oil-in-water emulsion with respect to flocculation by electrolytes, with the electric conditions at the interface. In the first place the influence of the valency of the coagulating ions may be used to investigate whether electrostatic repulsion contributes to the stability of an oil-in-water emulsion. A more quantitative estimation of the effect of electrostatic repulsion is, however, possible by the application of the theory developed by *Verwey* and *Overbeek* [1].

2. Effect of valency of the counter ions.

The applicability of the rule of *Schulze* and *Hardy*, showing that electrostatic repulsion is responsible for the stability of the sol against flocculation is, in the case of the hydrophobic sols of solid particles, usually investigated by means of flocculation experiments in which the accelerated sedimentation of the flocs is taken as an indication of the occurrence of flocculation. These experiments proved rather unsuccessful in the case of the oil-in-water emulsions. This may be attributed to the particle-size distribution of the emulsified oil droplets, in which small particles are often prevailing but relatively large particles, in a colloid-chemical sense, also occur. The aggregates produced in the flocculation process will cream faster than the separate particles, but the very small particles and their aggregates remain in the serum. Thus, a clear serum which is often taken as an indication of the occurrence of flocculation in a sol of solid particles is not produced in an emulsion unless the stability becomes so low that even the very small particles aggregate and cream in the time of the experiment. At the relatively high electrolyte concentration, however, which is necessary to obtain a sufficiently low stability, the small particles are more stable than the larger drops [2]. It follows that the occurrence of a sharply defined electrolyte concentration

[1] *E. J. W. Verwey* and *J. Th. G. Overbeek*, Theory of the Stability of Lyophobic Colloids. Amsterdam 1948.

[2] Reference 1, p. 177.

producing flocculation in a predetermined time will not be found in emulsions having a large range of particle sizes.

Moreover, by shaking the flocculating sol after a suitable time, the aggregates of solid particles can be made to grow, thereby increasing their rate of sedimentation. In the case of emulsions the aggregates in which coalescence has not yet occurred will be redispersed by even relatively slight stirring.

In the present investigation the influence of the valency of the coagulating cation has been found to follow the rule of *Schulze* and *Hardy* [3], suggesting a close analogy with the stability of the hydrophobic sols of solid particles. However, an important difference exists. The calculation of the potential drop at the aqueous side of an oil–water interface which was carried out in Chapter II shows that this potential drop depends to a considerable extent on the valency of the cation present [4]. In fact, the concentration of bivalent (magnesium) ions necessary to reduce the potential drop to a given value proved to be about one-tenth of the concentration of sodium ions which had to be present to obtain the same effect. As the rates of flocculation caused by the addition of these ions in this same ratio are also practically identical, it may be argued that the influence of the valency of the coagulating ions manifests itself through the potential drop, and not only through the thickness of the double layer.

If the potential drop across the double layer becomes sufficiently small, the specific effect of the valency on the interaction vanishes. Such low values might occur at the interfaces studied in this investigation, but even then the behaviour as predicted by the rule of *Schulze* and *Hardy* will be observed because the potential itself is sensitive to the valency of the counter ions.

3. Interaction of large spherical particles with a thin double layer.

Even in an emulsion containing no indifferent salt, the counter ions of the soap are usually present in a sufficiently high concentration to reduce the tickness of the double layer $1/\varkappa$ to less than 10^{-6} cm. The oil drops have, generally, a radius (R) exceeding 50×10^{-6} cm, thus $\varkappa R > 50$.

When the double layer is thin as compared with the radius of the particles, the method introduced by *Derjaguin* [5] may be used to calculate the potential energy of the electrostatic interaction of the

[3] Chapter V, section 3.
[4] Chapter II, section 5.
[5] *B. Derjaguin*, Kolloid-Z. **69**, 155 (1934). Acta physicochimica URSS **10**, 333 (1939).

two double layers around colliding spheres. The surface of the spheres are divided into a number of infinitisemal parallel rings, and the contribution of each pair of rings is found by considering them as parts of two infinitely large planes. When using this method, it is assumed that the interaction of a given pair of rings is not influenced by adjacent elements having either a larger or a smaller distance from each other.

The total contributions of all pairs of rings gives the repulsive energy of the two spheres of equal size, as a function of the distance between the surfaces, H_0:

$$V_R = \frac{2\pi R}{v^2} \int_{H_0}^{\infty} f(u, z)\, d\frac{\varkappa H_0}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

where f is the free energy of the double layer system per cm^2 as a function of $z = ve\psi_0/kT$ and $u = ve\psi_d/kT$ in which ψ_d is the potential half-way between the centres of the particles.

An analytical expression giving f as a function of u and z, and which is valid in all cases of practical importance, has not been found, but values of f may be obtained from tables [6]. Approximations may be used when the surface potential ψ_0 is small; the introduction of a suitable approximation leads to:

$$V_R = 4.62 \times 10^{-6} \frac{R}{v^2} \gamma^2 e^{-\varkappa H_0} \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

in which:

$$\gamma = \frac{e^{z/2} - 1}{e^{z/2} + 1}$$

The potential energy of the Van der Waals attraction is given by the approximation, valid when $H_0 \ll a$;

$$V_A = -\frac{1}{12} A \frac{R}{H_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

in which the value of the constant A depends upon the polarizability of the atoms constituting the material in the droplets. In assigning a value to A, it must be taken into account that each droplet of oil replaces an equal volume of water, and that the polarizability of the atoms in the oil is not very different from that of the water atoms. This will result in a lower value for the constant A than has been

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[6] Reference 1, p. 141.

found between solid particles in water [7] or between glass plates in vacuum [8]. A value of 10^{-13} erg will be used here.

The potential energy of interaction, given by:

$$V = V_R + V_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

is represented in fig. 3.1 as a function of the distance between the spheres. The rate of flocculation can, according to the method introduced by *Fuchs* [9], be obtained from this curve by defining a function W:

$$W = 2 \int_2^\infty e^{V/kT} \frac{ds}{s^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

($s = H_0/R + 2$) and considering that the rate of flocculation of the system is $1/W$ times the rate of *rapid* flocculation of a system having the same particle concentration.

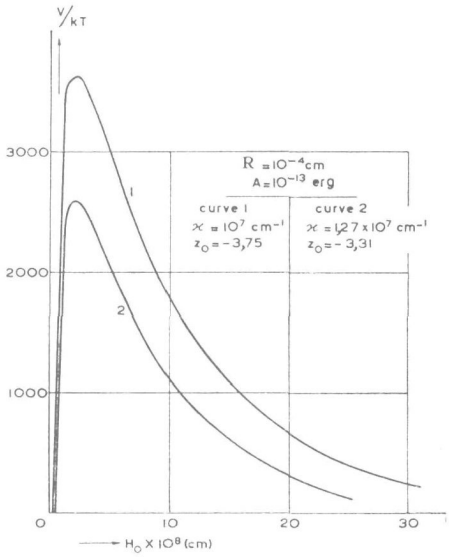

Fig. 3.1. Potential energy of interaction for two identical oil globulus, as a function of the distance between the surfaces

In calculating the curves of fig. 3.1 it has been assumed that two droplets having a diameter of 2 microns are in interaction, and both have a surface potential ψ_0 as calculated for an emulsion stabilised

[7] *H. Reerink*, Diss. Utrecht 1952.
[8] *M. J. Sparnaay*, Diss. Utrecht 1952.
[9] *N. Fuchs*, Z. Physik. **89**, 736 (1934).

with Aerosol MA in a 0.100 resp. 0.150 M solution of sodium chloride. According to fig. 7 of Chapter II, these surface potentials are 95 and 84 mV, respectively. The potential barrier which opposes collision is only a few Angstrom units wide but its height is sufficient to give the "stability ratio" W an extremely high value, showing that no flocculation will occur. Nevertheless, flocculation has been observed to occur in these systems, at an appreciable rate. It will be necessary to investigate whether flocculation is possible in the presence of a high potential barrier.

The presence of a very high potential barrier between the emulsified oil droplets is caused by the large size of these droplets, as both the repulsive and the attractive energy are proportional to the particle size. A potential barrier with a height of only several times kT will lead to a value for W indicating flocculation to occur with a measurable rate. Such values of W can be obtained if the surface potential ψ_0 would have a value of about 25 mV at particles having a diameter of 2 microns (fig. 3.2). Values of ψ_0 as low as this are not inconsistent with the theory given in Chapter II: by the introduction of a specific adsorption energy of the cations in the Stern layer the charge of the particles, including the Stern layer, can be made sufficiently small to account for a surface potential of only 25 mV. Comparison with the experimentally determined zeta-potential, however, shows that ψ_0 in a flocculating emulsion containing only monovalent cations will probably have a value not lower than about 75 mV.

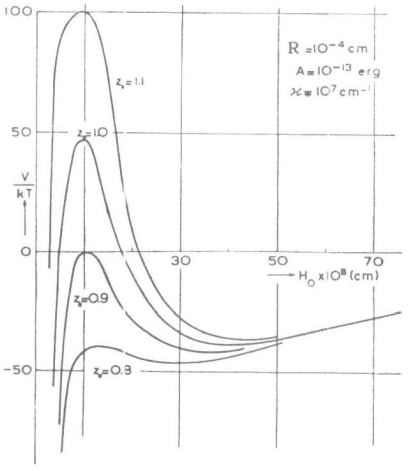

Fig. 3.2. Potential energy of interaction for two identical oil globules, as a function of the distance between the surfaces, at low values of the surface potential.

The zeta-potential in the systems in which flocculation has been observed to occur is often higher than 100 mV (section 6 of Chapter II). It is generally assumed that the zeta-potential ζ will have a value slightly lower than the surface potential ψ_0 as the "slipping plane" will be situated at a small distance from the outer plane of the Stern layer towards the interior of the bulk liquid. At the interface of emulsified oil droplets, however, it is by no means evident that this same relation between ζ and ψ_0 will hold. If several of the counter ions of the Stern layer do not take part in the electrophoretic motion of the particle the value of ζ will even be higher than that of ψ_0. A considerable difference between ζ and ψ_0 would, however, appear improbable.

Moreover, in the case of the small surface potentials the height of the potential barrier is very senstive to the absolute value of the surface potential, and it would be proportional to the particle size. Experimental evidence has shown that the rate of flocculation is remarkably insensitive to changes in the kind and concentration of the emulsifying agent, from which it appears probable that the influence of small changes in the surface potential is not as large as would follow from the curves given in fig. 3.2. A considerable influence of the particle size on the rate of flocculation, which would also follow from the curves given in fig. 3.2, could hardly have escaped attention but has never been observed.

An explanation for the flocculation of an emulsion in the presence of a very high potential barrier, in which the effect of the particle size on the rate of flocculation has been eliminated, will be suggested in the next section.

4. Flocculation in the "secondary minimum".

A characteristic feature of the potential curves calculated by means of the equations given before is the presence of a "secondary minimum", i.e. a region of negative values of the potential energy at fairly large distances between the particles (fig. 3.3). The existence of such a "secondary minimum" has not yet been fully established experimentally, mainly because a pronounced minimum occurs only in systems containing relatively large particles, and in these systems the influence of gravity outweighs all other effects [10]. In the emulsions used in the present investigation, however, the effect of a "secondary minimum" in the potential energy must become particularly evident. It may be expected that easily reversible flocculation will occur in this minimum.

[10] *H. R. Kruyt*, Colloid Science I (Elsevier 1952) p. 324.

Evidence concerning this effect was obtained from the behaviour of stock emulsions containing 40 per cent. of oil and no electrolyte

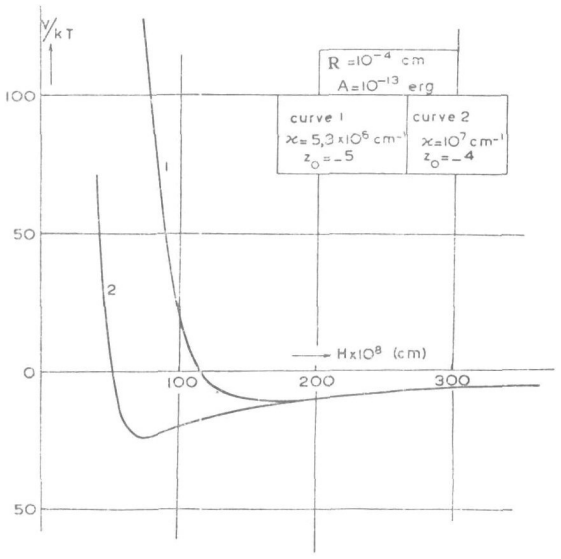

Fig. 3.3. Secondary minimum in the potential energy curve at fairly large interparticle distance.

other than the ionisable soap. After several days these emulsions had separated into two distinct layers, with a *sharp* boundary there between. The less concentrated top layer contained only the smaller particles. From the fact that a sharp boundary always occurs, it follows that individual sedimentation of the droplets cannot be made responsible for this phenomenon, as the size-frequency distribution has the continuous shape which is generally found in emulsions of this kind [11]. Aggregation will have occurred which affects only the larger particles and which must be completely and easily reversible. The energy which keeps these aggregates together depends on the particle size in such a way that up to a certain particle size this energy is insufficient to cause aggregation. It may be assumed that this aggregation occurs in the "secondary minimum", which, in emulsions without added salt, is situated at a distance between the particles of about 250 A and the depth of which is proportional to the particle size.

[11] *A. King* and *L. N. Mukherjee*, J. Soc. Chem. Ind. (London) **58**, 243 (1939); ibid. **59**, 185 (1940).

The theory of *Onsager* [12] explaining the phase-separation by the formation of tactoids in colloidal systems containing anisodimensional particles is, evidently, not applicable in this case.

Insertion of the approximate equations (2) and (3) in (4) and differentiation with respect to H_0 results in an equation (6) from which the interparticle distance H_m at wich the potential energy has a minimum value, may be derived:

$$H_m^2 \cdot e^{-\varkappa H_m} = 1.80 \times 10^{-9} \cdot \frac{v^2}{\varkappa \gamma^2} \cdot \quad . \quad . \quad . \quad . \quad . \quad (3.6)$$

It is noticed that the position of the "secondary minimum" does not depend on the particle size, in the approximation used.

The relation between H_m and the electrolyte concentration, as expressed by $\varkappa$, is represented in fig. 3.4 for two values of the surface potential. It is found that variation of the surface potential, within the range investigated, has hardly any influence on the position of the "secondary minimum". The distance between the particles at this minimum potential energy decreases to a value as low as 60 A by increasing the concentration of 1–1 valent electrolyte to 0.150 M.

The valency of the counter ions has a profound influence on the position of the "secondary minimum", because it affects also v and

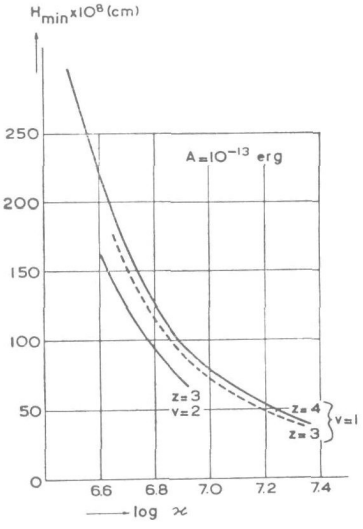

Fig. 3.4. Interparticle distance at the "secondary minimum" of the potential energy, as a function of the electrolyte concentration.

[12] *L. Onsager,* Ann. N.Y. Acad. Sci. **51,** 627 (1949).

$\varkappa$ of equation (6). Fig. 3.4 shows that a minimum at the same particle distance as in a 0.100 M solution of a 1–1 valent electrolyte is obtained at a concentration of 0.020 M for a salt containing a bivalent cation.

The (negative) value of the potential energy in the "secondary minimum" is practically entirely determined by the value of the Van der Waals attraction; it follows from equ. (3) that the depth is about inversely proportional with H_m.

If it is assumed that flocculation of emulsified oil droplets occurs in the "secondary minimum", the rate of flocculation would always have a value slightly higher than that corresponding with "rapid" flocculation. The latter occurs when no forces act between the particles and collisions take place only as a consequence of Brownian motion. There is no energy barrier preventing flocculation in the "secondary minimum", and attraction prevails at relatively large distances between the particles.

If flocculation is always "rapid" the stability of an emulsion would not be controlled by its rate but by subsequent coalescence, which may be described as the formation of a connection between the two globules through the potential barrier, over a distance of, say, 60 A. Once the connection has been formed, the droplets will merge together in a very short time, depending upon the viscosity of the oil phase, the interfacial tension and the particle size [13].

The formation of relatively narrow "oil bridges" between two adjacent particles may be assumed to be a consequence of deformations of the particle surfaces, which are liable to occur in the strong field of force prevailing between the particles. A protrusion of the surface of one of the particles may have a lower potential energy at its extreme end if the motion of the surface is sufficiently rapid to prevent the establishment of equilibrium between the adsorbed soap ions and the counter ions in the diffuse double layer. The energy necessary to extend the interface with a half-sphere having a radius of 50 A is about 100 kT at an interfacial tension of 5 dynes/cm, which may be regarded as an upper limit. It would follow that the rate of coalescence depends not only on the "rigidity" of the interfacial layer but mainly on the distance between the particles when they are in the "secondary minimum" of the potential energy. A lower interfacial tension would, according to this model, promote coalescence and thus have the rather unexpected effect of decreasing the stability of the emulsion. Finally, the height of the

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[13] *J. Frenkel,* J. Phys. U.S.S.R. IX (5), 383 (1945); *R. E. Dillon, L. A. Matheson* and *E. B. Bradford,* J. Coll. Sci. **6,** 108 (1951).

potential barrier will probably have some influence on the rate of coalescence.

5. Influence of particle size.

Equations (2), (3) and (4) show that the total energy of interaction, at a given distance between the particles, is proportional to the particle radius. The height of the potential barrier between colliding particles of equal size is, therefore, also proportional with the particle radius. In the case of "slow" flocculation through the potential barrier this would imply that the smaller particles coagulate more rapidly than the larger ones, and it might be expected that this would lead to an observable decrease in the concentration of the smaller particles whereas the formation of very large droplets by coalescence of several of the larger drops would be improbable. No such effect has been observed in oil-in-water emulsions.

The size-frequency distribution of the oil drops in the emulsions in which coagulation has proceeded to such an extent that the particle concentration has decreased to one-half of its original value, differs from the original distribution mainly in a general shift towards the larger sizes. The maximum in the distribution, which remains near one micron, becomes slightly lower. The size of the larger particles in the coagulated emulsion is notably higher than in the original one.

A quantitative estimation of the influence of the particle size on the stability is hardly possible in oil-in-water emulsions, in which the larger particles may have a diameter 20 times as large as that of the smallest drops. Several effects cooperating in decreasing the effect of the particle size on the rate of flocculation will be discussed in section 4 of Chapter V.

In the case of collisions between particles having unequal diameters, both the repulsive [7] and the attractive [14] energy have values intermediate between those for equal particles of either the larger or the smaller size. The values are obtained by replacing R in equations (2) and (3) by:

$$\frac{d_1 d_2}{d_1 + d_2}$$

It appears that in the case of "slow" flocculation the probability for the formation of an aggregate containing a large particle is, on the one hand, lower because a higher energy barrier has to be overcome, but this effect may partially be compensated by the more

[14] *H. C. Hamaker,* Rec. trav. chim. **57,** 61 (1938).

frequent collisions involving large particles. In hydrophobic sols of solid particles the surface potential may become very low at high electrolyte concentrations, and the electrostatic repulsion may then be disregarded. In this case the attraction between larger particles will be higher than between smaller ones, and consequently the larger particles will flocculate more rapidly [2]. It is doubtful, however, whether sufficiently low values of the surface potential can be obtained at an oil–water interface without having recourse to polyvalent cations.

If flocculation is assumed to occur in the "secondary minimum" its rate will be determined mainly by the initial particle concentration. After a sufficiently long time an equilibrium is established in which the number of flocculated particles is determined by the depth of the minimum. At a given electrolyte concentration this depth is approximately proportional to the particle size. Aggregates in which no large particle is present will, therefore, be improbable, the more so the lower the electrolyte concentration. This would be in accordance with the suggested explanation of the behaviour of the stock emulsions discussed in section 4.

CHAPTER IV.

MECHANISM OF THE COAGULATION OF AN EMULSION.

The colloidal stability of an oil-in-water emulsion can be correlated with the well-known behaviour of the hydrophobic sols of solid particles if the rate of coagulation is expressed in terms of a decrease in particle concentration.

Coagulation of an emulsion occurs in two stages, called flocculation and coalescence. Flocculation is assumed to occur according to the second order reaction process applied by *Von Smoluchowski* to the similar phenomenon in the hydrophobic sols of solid particles. Coalescence is a first order reaction and will only occur between adjacent drops in an aggregate.

An equation is derived in which the particle concentration is expressed as a function of both the rate of flocculation and the rate of coalescence, and the time of coagulation. The rate of coagulation appears to depend upon the particle concentration, in such a way that the rate of increase of 1/n increases with decreasing initial particle concentration. Approximations are given which may be applied to cases of practical importance.

1. The mechanism of coagulation.

An emulsion, in which creaming is avoided by adjustment of the densities may show instability in two ways:

a. The formation of more or less reversible aggregates. In sufficiently concentrated emulsions this leads to a clearly perceptible increase in viscosity, which is often the only indication of the occurrence of this kind of instability recorded.

b. Coalescing of two drops after they have combined to an aggregate. This is essentially an irreversible process, leading to a decrease in the number of oil droplets and finally to "breaking".

Limburg [1] made already a distinction between a "reversible" and an "irreversible" part in the coagulation process of an emulsion; he states that "irreversible" coagulation can only occur after the "reversible" coagulation has taken place. He intended to study especially the "irreversible" part of the coagulation process, but his measurements do not allow to distinguish between flocculation and coalescence.

The flocculation process is, in the case of the hydrophobic sols of solid particles, a second order reaction to which the theory of *Von Smoluchowski* [2] can be applied. It may be assumed that this

[1] *H. Limburg,* Rec. trav. chim. **45,** 772, 854, 875 (1926).

[2] *M. v. Smoluchowski,* Physik. Zeitschr. **17,** 557, 583 (1916); Z. physik. Chem. **92,** 129 (1917).

theory can also be used to describe the kinetics of the flocculation of an emulsion. Coalescence, however, will be a first oder reaction, as it may be assumed that the chance of two adjacent drops in an aggregate to coalesce will not depend upon the number of drops in the aggregate.

If a process is found to consist of two consecutive reactions, the overall reaction rate is mainly determined by the slower of the two. In a very dilute oil-in-water emulsion the rate of flocculation can be made smaller than the rate of coalescence. In this case the stability of the emulsion against coagulation will be influenced by factors which affect the rate of flocculation. Increasing the initial concentration of oil droplets in the emulsion will result in a slowly increasing rate of coalescence and a much faster increasing rate of flocculation. In highly concentrated emulsions, the coalescence can be made the rate-determining reaction. In a certain range of concentrations both rates will be of the same order of magnitude, and in this same range, the peculiar effect of the particle concentration on the rate of coagulation must become particularly evident. That the factors affecting stability were different in dilute and in concentrated emulsions was mentioned by *Van der Minne* [3].

Even in the most dilute emulsions studied, however, it is easy to decrease the rate of coalescence to such a low value that coalescence becomes the rate-determining reaction. This can be achieved by adding surface-active agents which sometimes may have little or no influence on the rate of flocculation, but a retarding action on coalescence.

2. Measurement of stability.

The rate of coagulation of a sufficiently concentrated emulsion has often been estimated by determining the amount of oil separating in a given time. The rate of oil separation, however, will not only be influenced by the interaction of the droplets but also by the difference between the densities of the two phases and by the viscosity of the aqueous phase. To obtain an insight into the various factors which control the stability against coagulation, it will be useful to exclude the influence of such trivial factors as difference in density. This can easily be achieved by using an oil phase having the same density as the aqueous phase.

In dilute emulsions, estimation of the stability has often been carried out by means of turbidity measurements [4]. In this case it is apparently

[3] *J. L. v. d. Minne*, Symposium Hydrophobic Colloids, 1937, p. 138.
[4] *F. Powis*, Z. physik. Chem. **89**, 186 (1915).

assumed that the amount of reflected light is proportional to the number of particles, including flocs. This may be true in a certain range of concentrations and of particle sizes, but in a coagulating emulsion containing particles of widely varying diameters this assumption can hardly be regarded as correct.

The most exact measurements recorded in the literature of the rate of coagulation of an emulsion use the decrease of the specific interface with time [5]. It can, however, easily be shown that the determination of the number of particles, as a function of time, is a much more sensitive method to measure the rate of coagulation, than the specific interface method. A 10 per cent. decrease in interfacial area is accompanied with a 27 per cent. decrease in the number of particles, provided that the general shape of the size-frequency distribution curve does not change appreciably during coagulation.

Moreover, the coagulation of hydrophobic sols has been extensively studied by the method using the decrease in particle number. A theory has been developed correlating the rate of decrease in particle number with the conditions at the interface [6]. Application of this method will provide a means for comparing the coagulation of an emulsion with that of a hydrophobic sol.

3. Decrease of the particle concentration with time.

When investigating the coagulation of a hydrophobic sol (which is usually called flocculation), the particle concentration is generally determined by counting the number of light-spots produced by the particles in an ultra-microscope. A light-spot may be produced by a single primary particle, or by an aggregate containing a number of primary particles. As a rule, it is not possible to distinguish between the two, and each light-spot is counted as a single particle.

The number of such particles in unite volume, n, found at a time t, is given by *Von Smoluchowski*'s theory as:

$$n = \frac{n_0}{1 + an_0t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where n_0 is the number of particles at $t = 0$ and a is a rate-determining constant which, in the case of "rapid" coagulation of a monodisperse sol has the value:

$$a = 8\pi\, DR \approx 8\pi \frac{kT}{6\pi\eta R} .R \approx 10^{-11}\ cm^3\ sec^{-1} \quad . \quad . \quad (4.2)$$

[5] *A. King* and *L. Mukherjee*, J. Soc. Chem. Ind. (London) **58**, 243 (1939); ibid. **59**, 185 (1940).

[6] *E. J. W. Verwey* and *J. Th. G. Overbeek*, Theory of the Stability of Lyophobic Colloids. Amsterdam 1948.

in which D is the diffusion constant of a particle having a radius R; T is the absolute temperature and k is Boltzmann's constant.

In deriving equation (1) it is assumed that the coagulation has proceeded for a sufficiently long time to establish a "nearly stationary state" around each particle; i.e. the number of particles diffusing in unit time through a sphere surrounding one central particle equals the number of particles adhering to this central particle, in unit time. This state has been reached after a time $t > R^2/D$. All experimental coagulation times should, therefore, be large as compared with R^2/D [7].

When applying this theory to the coagulation of an emulsion, it should be taken into account that the flocculation of oil drops is often easily reversible. In many cases is has been found that the aggregates can be redispersed by stirring, and this action of shearing forces may still be enhanced by diluting with a solution of a suitable surface-active agent.

The coagulation of an emulsion is not only determined by the formation of more or less reversible aggregates, but also by the number of particles which coalesce to form larger drops. The number of particles existing after a time t can be found by taking into account that only the particles in an aggregate may combine to form larger particles. The average number of primary particles in an aggregate at time t, called n_a, is obtained by application of *Von Smoluchowski*'s theory. This gives for the number of primary particles which have not yet combined into aggregates, at time t:

$$n_1 = \frac{n_0}{(1 + an_0t)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.3)$$

and for the number of aggregates:

$$n_v = \frac{an_0^2 \cdot t}{(1 + an_0t)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.4)$$

The total number of primary particles in all aggregates is, in unit volume:

$$n_0 - n_1 = n_0 \left\{ 1 - \frac{1}{(1 + an_0t)^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (4.5),$$

hence;

$$n_a = \frac{n_0 - n_1}{n_v} = 2 + an_0t \quad . \quad . \quad . \quad . \quad . \quad (4.6)$$

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[7] *F. C. Collins* and *G. E. Kimball*, J. Coll. Sci. **4**, 425 (1949). See also reference 2.

The average number of separate particles existing in an aggregate at time t is called m. This number will always be smaller than n_a because a certain amount of coalescence will have occurred. The number m will be only slightly lower than n_a if coalescence is very slow, whereas it will have a value very near to 1 if coalescence is very rapid.

The rate of coalescence is assumed to be proportional to the number of points of contact between the particles in an aggregate, which is $(m - 1)$ if the aggregates consist only of a relatively small number of particles. Observation has shown that, in sufficiently dilute emulsions, small aggregates generally contain one large particle together with one or two small ones, and are built up linearly. Thus, m decreases proportional to $(m - 1)$ whereas m increases at the same time by adherance of other particles. The rate of increase of m caused by flocculation follows from equation (6). This gives:

$$\frac{dm}{dt} = an_0 - K(m - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.7)$$

where K measures the rate of coalescence.

Integrating equation (7) gives:

$$m - 1 = \frac{an_0}{K} + \left\{ 1 - \frac{an_0}{K} \right\} e^{-Kt} \quad . \quad . \quad . \quad . \quad (4.8)$$

where the boundary condition $m = 2$ when $t = 0$ has been used. The total number of particles, whether flocculated or not, in a coagulating emulsion at a time t is found by adding the number of unreacted primary particles to the number of particles in the aggregates:

$$n = n_1 + n_v \cdot m = \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

$$= \frac{n_0}{1 + an_0 t} + \frac{an_0^2 \cdot t}{(1 + an_0 t)^2} \left\{ \frac{an_0}{K} + \left(1 - \frac{an_0}{K}\right) e^{-Kt} \right\}$$

In this equation, the first term represents the number of particles which would have been found if each aggregate had been counted as one single particle (compare equation 1). The second term gives the number of particles which comes in addition to that of the classical theory when the composition of the aggregates is taken into account. With $K = \infty$, meaning immediate coalescence, the second term vanishes and n has the value given by equation (1); with $K = O$, which means that no coalescence occurs, equation (9) gives $n = n_0$ for every value of t.

If $O < K < \infty$, the effect of a change in particle concentration on

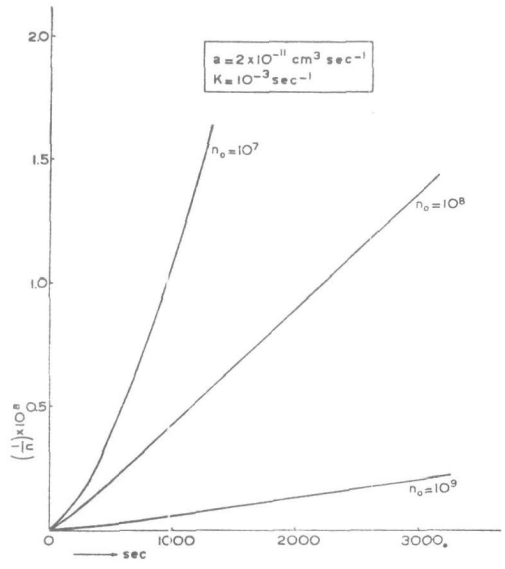

Fig. 4.1. Increase of average particle volume with time, for various initial concentrations.

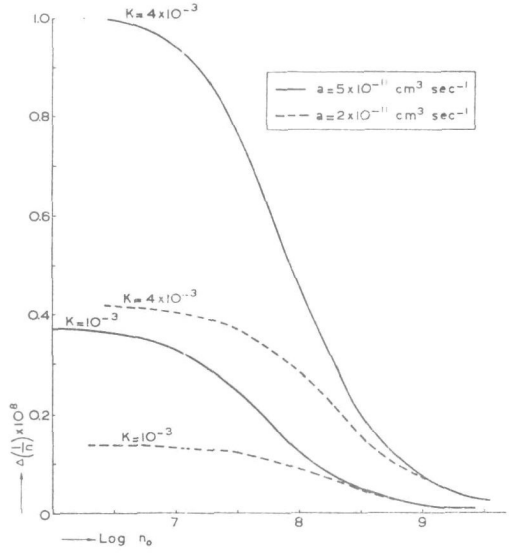

Fig. 4.2. Decrease of particle number after five minutes coagulation, as a function of the initial particle concentration.

the rate of coagulation, which was discussed in section 1, follows from equation (9). This can be shown by writing equation (1) as:

$$\frac{1}{n} - \frac{1}{n_0} = at \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

showing that the rate of increase of 1/n in a coagulating hydrophobic sol is independent on the particle concentration. This no longer holds for an emulsion. Fig. 4.1 shows the rate of increase of 1/n calculated by means of equation (9) for several values of n_0. It appears that 1/n increases less rapidly, the more concentrated the emulsion.

The influence of the particle concentration is shown more clearly in fig. 4.2, from which it appears that in very dilute emulsions, and in concentrated emulsions, the rate of coagulation as measured by the value of 1/n after a predetermined time is not appreciably changed by increasing the particle concentration. In the region where an_0/K is of the order of magnitude 1, however, the rate of coagulation falls sharply with increasing n_0.

4. Approximations.

(i) In a flocculating *concentrated* emulsion it is possible to make $an_0/K \gg 1$. In actual systems K has generally a value much smaller than 1, and it will be sufficient to make $an_0 \geqq 1$ to satisfy the condition. In this case an_0t will rapidly become $\gg 1$, and the contribution of the unreacted primary particles may then be neglected. It follows:

$$n = \frac{an_0^2 \cdot t}{(1 + an_0t)^2} \left\{ \frac{an_0}{K} (1 - e^{-Kt}) \right\} \quad . \quad . \quad . \quad . \quad (4.11)$$

A further approximation may be obtained by putting $1 + an_0t \backsim an_0t$, whence:

$$n = \frac{n_0}{Kt} (1 - e^{-Kt}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.12)$$

It is found that, in concentrated emulsions, the rate of coagulation no longer depends upon the rate of flocculation. Fig. 4.3. shows that, under the conditions chosen, equations (11) and (12) yield practically the same results as the "exact" equation (9) as soon as $n_0 > 10^{10}$. Moreover, the particle number is found to decrease nearly exponentially with time, until Kt becomes large as compared with unity. This is confirmed by the experiments of *Lotzkar* and *Maclay* [8].

It has been assumed in deriving equation (7) that the number of

[8] *H. Lotzkar* and *W. D. Maclay,* Ind. Eng. Chem. **35,** 1294 (1943).

points of contact between m particles in an aggregate would be $(m - 1)$. This, however, no longer holds if the aggregate consists of a very large number of particles, as is the case when flocculating a concentrated emulsion. In a tightly packed aggregate of spheres, all having the same size, each particles touches 12 other particles. Moreover, the number of points of contact in such an aggregate will be proportional to m rather than to $(m - 1)$. In a heterodisperse system, one particle may touch even more than 12 other particles. This can be taken into account by writing equation (7) as:

$$\frac{dm}{dt} = an_0 - p \,.\, K \,.\, m \quad . \quad . \quad . \quad . \quad . \quad (4.13)$$

in which p has a value between 1 and about 6. This equation gives after integrating:

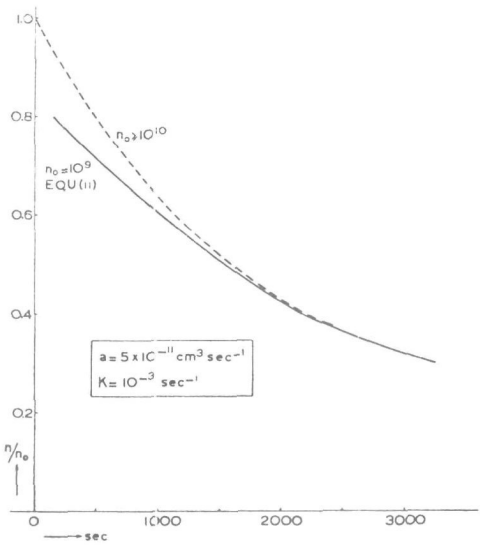

Fig. 4.3. Decrease of particle number in concentrated emulsions. The dotted line follows from equ. (9), (11) or (12) without perceptible difference. The fully drawn curve shows that equ. (11) cannot be applied to dilute emulsions under the conditions chosen.

$$m = \frac{an_0}{p \,.\, K} + \left(2 - \frac{an_0}{p \,.\, K}\right) e^{-pKt} \quad . \quad . \quad . \quad . \quad (4.14)$$

which has to be used instead of equation (8) when dealing with concentrated emulsions. This would mean that the apparent rate of

coalescence increases with the particle concentration, in a way depending upon the particle size distribution, the degree of packing and the size of the aggregates.

(ii) In a very *dilute* emulsion an_0/K can be made $\ll 1$ if coalescence occurs sufficiently rapidly. After coagulation has proceeded for such a long time that $Kt \gg 1$, the second term in the right-hand member of equation (9) may be neglected as compared with the first term. The resulting equation (1) no longer contains K and the rate of coagulation does not depend upon coalescence.

(iii) If coalescence is very slow, the exponential term may be expanded in a power series, of which the first two terms are only used when $Kt \ll 1$. In this case:

$$n = n_0 \left\{ 1 - \frac{Kt}{1 + an_0t} + \frac{Kt}{(1 + an_0t)^2} \right\} \quad . \quad . \quad . \quad (4.15)$$

As could be expected, this equation gives only a very small decrease in particle number, as the last terms are both $\ll 1$.

(iv) After coagulating for a sufficiently long time, it will always be possible to make $Kt \gg 1$, in which case the exponential term may be neglected. In the denominator we will then have $an_0t \gg 1$, and the resulting approximation is:

$$n = \frac{n_0}{Kt} + \frac{1}{at} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.16)$$

With large n_0, the first term predominates over the last one, and by disregarding the term containing a an equation is finally obtained which may also be derived from equation (12) by neglecting its exponential term.

CHAPTER V.

MEASUREMENT OF THE RATE OF COAGULATION OF AN OIL-IN-WATER EMULSION.

Dilute oil-in-water emulsions stabilised with anionic soaps were coagulated by the addition of salt. After a predetermined time coagulation was stopped by diluting with a solution of a nonionic surface active agent. The rate of coagulation was measured by counting, after varying times of coagulation, the number of oil drops under a microscope.

The rate of coagulation increases with increasing salt concentration. An upper limit in the rate of coagulation, where "rapid" flocculation occurs, was observed when salts with polyvalent cations were used as the coagulating electrolyte.

Increasing the concentration of Aerosol OT caused a higher rate of coagulation in dilute salt solutions and a lower rate at higher salt concentrations. Variation of the concentration of the more soluble soaps had little effect on the rate of coagulation.

The influence of the valency of the coagulating cation was investigated in emulsions stabilised with a soap giving no insoluble compounds with the cations used. A behaviour as predicted by the rule of *Schulze* and *Hardy* was observed. Variation of the anion in the coagulating electrolyte had no effect on the rate of coagulation.

The rate of coagulation decreases with increasing initial particle concentration. This is explained by considering coagulation as caused by flocculation followed by coalescence. From experiments in which the initial particle concentration was varied, estimations could be made of both the rate of flocculation and of coalescence. The rate of coalescence had a value of the order of 0.001 per second. For the rate of flocculation a higher value was found than that predicted by *Von Smoluchowski*'s theory for "rapid" flocculation. Several effects are present which operate simultaneously to increase the measured rate of flocculation; the influence of these effects is discussed.

1. Introduction.

According to the theory developed in Chapter IV the rate of coagulation of an emulsion is mainly determined by the rate of flocculation of the oil globules, if the particle concentration is low and coalescence occurs sufficiently rapidly. On the other hand, coalescence is the rate-determining reaction in concentrated emulsions, especially if its rate has been decreased by the addition of a suitable emulsifying agent. The rate of flocculation can only be measured in very dilute emulsions in which coalescence occurs rapidly; even in this case it will be necessary to take into account that coalescence occurs with a finite velocity.

The influence of electrolytes on the rate of coagulation of dilute oil-in-water emulsions has been investigated by counting the number of oil droplets as a function of the time of coagulation. The composition of the emulsions has been adjusted in such a way that creaming or sedimentation, during the time of an experiment, was avoided.

2. Experimental method.

The materials used were the same as those described in Chapter II. The "oil"-phase was made up by mixing 57 volumes of monochlorobenzene with 43 volumes of paraffin oil. The resulting density of 1.006 g per cm^3 at 20° C corresponds closely with the density of the aqueous salt solutions used in the coagulation experiments.

Stock emulsions were prepared by stirring 40 volumes of "oil" into 60 volumes of the aqueous soap solution. The crude emulsions were homogenised by several passings through an apparatus as described by *Briggs* [1]. In this apparatus the emulsion flows through a capillary glass tube into a flask to which suction is applied. The particle size of the homogenised emulsion can be controlled by a suitable choice of the pressure gradient and the diameter of the capillary.

In the emulsions used in the coagulation experiments the large majority of the particles has a diameter between 0.5 and 10 microns. Droplets having a diameter of up to 20 microns were sometimes observed. Particles smaller than about 0.5 microns are not visible in the microscope used for counting; the number of these particles should, therefore, be as small as possible. This was verified by observing the diluted emulsion in a microscope fitted with a cardiod condensor and comparing the number of light spots with the particle concentration known from counting in incident light. In all emulsions used for coagulation experiments the difference between the two measurements was negligible.

Weighed portions of the stock emulsion were diluted with water and, if desired, soap solution. At $t = 0$ each of the diluted emulsions was carefully mixed with the amount of salt solution necessary to obtain the desired concentrations. Experiments have been performed in which the oil concentration was in the range of from 0.1 to 10 per cent.; the soap concentration was of the order of 0.1 per cent. and salts were present in such an amount that coagulation occurred at a measurable rate. When sodium laurate was used as the emulsifying agent, caustic soda was also added in an amount sufficient to give a pH of 11.0 ($\pm$ 0.1) in the final emulsion. The emulsions were then allowed to coagulate for a predetermined time, after which they were mixed with a solution of a non-ionic emulsifying agent.

The non-ionic agent used throughout was Emulphor 0 (Badische Anilin- & Soda-Fabrik), which is stated to be the reaction product of a fatty alcohol with poly-ethylene oxide. By diluting the emulsion with the solution of the non-ionic agent the salt concentration was considerably reduced. Moreover, it had been found in previous experiments that the addition of about 1 per cent. of Emulphor 0 to an emulsion prevents further coagulation, even in the presence of a considerable amount of electrolyte. Microscopic examination revealed that the aggregates which have formed during the coagulation are completely redispersed after the addition of the Emulphor 0 solution. The number of oil droplets in this emulsion is the number which has been denoted by n in equation (9) of Chapter IV.

[1] *T. R. Briggs*, J. Phys. Chem. **19**, 210, 478 (1915).

Determination of the particle concentration was carried out within the next few hours by transferring a drop of the diluted emulsion to a hemacytometer of the Bürker model, and counting the number of particles in 60 squares, each defining a volume of 0.25×10^{-6} cm^3. A duplicate determination was always carried out with a fresh drop of the emulsion agreement was usually to within 10 per cent. The average of the two determinations was used to calculate n.

The distribution of these droplets among the 120 squares was found to follow quite closely a Poisson distribution curve. With the high value of the Poisson parameter this may be treated approximately as a normal distribution. In this case it is possible to calculate the probability that 10 per cent. less particles are found in a second determination starting with the same particle concentration. This probability is 0.15 when the total number of particles counted in each determination is 200. As the number of particles counted was always more than 200, it may be concluded that a decrease in the particle concentration of at least 10 per cent. can be estimated with sufficient accuracy.

In determining the value of n_0 the stock emulsion was immediately diluted with a sufficient amount of the Emulphor O solution to obtain a particle concentration suitable for counting.

All experiments were carried out at room temperature, which was between 17 and 21° C.

3. **Results.**

Influence of soap and salt concentration.

According to *Von Smoluchowski*'s theory [2] for the flocculation of a hydrophobic sol, 1/n should increase linearly with time (compare equation (10) of Chapter IV). In experiments on hydrophobic sols in which "slow" flocculation was studied, however, it has often been observed that the slope of the curve giving 1/n as a function of time decreases as the flocculation proceeds [3]. Apparently, the aggregates formed during "slow" flocculation are more stable than the original particles. An explanation of this effect may be given by considering the influence of the particle size on the attractive and repulsive forces (Chapter III section 3). It may be expected that emulsions will show a similar behaviour.

In several experiments with rather low salt concentrations, a slowly decreasing rate of coagulation was actually observed, but in other experiments this rate appeared to increase or remained substantially constant. This can be explained by considering that the number of

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[2] *M. von Smoluchowski*, Physik. Zeitschr. **17**, 557, 583 (1916); Z. physik. Chem. **92**, 129 (1917).

[3] *H. R. Kruyt* and *A. E. van Arkel*, Rec. trav. chim. **39**, 656 (1920); ibid. **40**, 169 (1921).

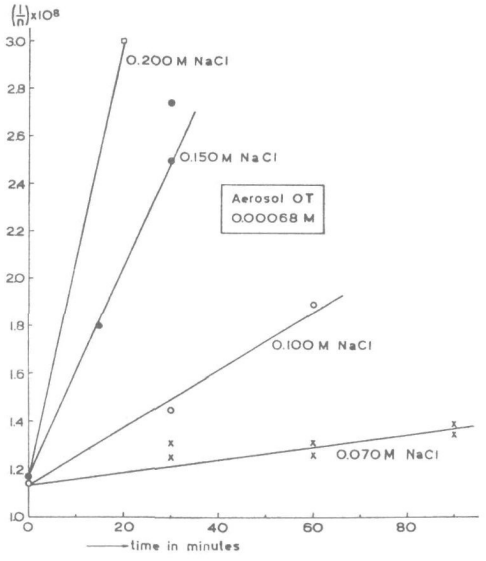

Fig. 5.1. Influence of the concentration of sodium chloride on the rate of coagulation of emulsions stabilised with Aerosol OT.

particles will decrease during coagulation, which, according to equation (9) of Chapter IV, will cause the rate of coagulation to increase if both the rates of flocculation and of coalescence remain unchanged. The limited accuracy of the measurements, however, together with the smallness of this effect, made it difficult to draw a sharp distinction between experiments with an increasing or with a decreasing rate of coagulation. (Compare fig. 5.1 as an example). A straight line was therefore drawn approximately through the experimental points, and the rate of coagulation obtained from the slope of this line.

A number of experimental results obtained in this way have been assembled in fig. 5.2, in which the rate of coagulation of an emulsion containing Aerosol OT is plotted against the concentration of the coagulating electrolyte. The position of several of the points represented in fig. 5.2 has been repeatedly checked, and it may be assumed that the general shape of the curves given is representative of the actual behaviour of the emulsions.

The shape of the curves shows that the rate of coagulation increases rapidly with the electrolyte concentration. This is the behaviour which would be expected, at least qualitatively, from considerations regarding the influence of electrolytes on the rate of *flocculation*, if this were controlled by electrostatic forces.

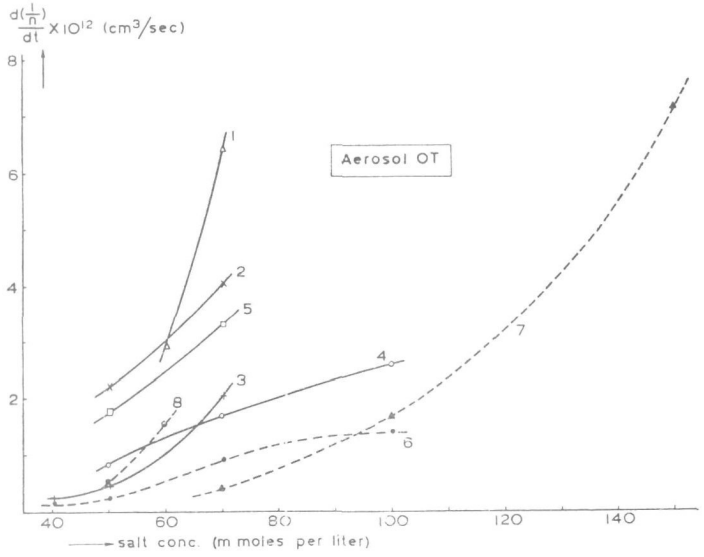

Fig. 5.2. Rate of coagulation with varying amounts of monovalent electrolytes.

Symbol		curve	soap conc.	salt	$n_0 \times 10^{-8}$
Emulsion a	△	1	0.00035 M	KCl	0.77
	×	2	0.00064 M	KCl	0.77
	+	3	0.00071 M	KCl	1.54
	○	4	0.0013 M	KCl	1.54
	□	5	0.0024 M	KCl	1.54
Emulsion b	●	6	0.00069 M	KCl	0.80
	▲	7	0.00069 M	NaCl	0.88
	◕	8	0.0013 M	KCl	0.80

In the coagulation of the hydrophobic sols, the rate of flocculation increases with the salt concentration up to a certain limit, where "rapid" flocculation occurs. A further increase of the electrolyte concentration has no influence on the rate of flocculation. The existence of such an upper limit in the rate of coagulation has not been established in the case of emulsions coagulated with salts containing a monovalent cation. The rather high concentration of these salts which appears to be necessary to obtain "rapid" flocculation in an emulsion increased the density of the aqueous phase, and the resulting creaming of the relatively large oil droplets manifests itself as a

further increase of the rate of coagulation. Moreover, it has to be borne in mind that the rate of coagulation, which is recorded in fig. 5.2, cannot be used to study the flocculation reaction without taking into account the influence of the coalescence.

When salts containing polyvalent cations are used, the salt concentration necessary to obtain "rapid" flocculation is sufficiently low to avoid a high difference in density. With luteo cobaltic chloride in concentrations of 0.0005 and 0.001 M, the rates of coagulation were a = 1.3 and 1.2×10^{-11} cm^3 sec^{-1}, respectively, in an emulsion stabilised with 0.0008 M Aerosol MA. These practically identical rates of coagulation must be attributed to identical rates of flocculation, as the initial particle concentrations in these experiments were sufficienlty low (0.3×10^8 cm^{-3}) to avoid an appreciable influence of the rate of coalescence.

The slope of the curves in fig. 5.2 indicates that the effect of an increasing salt concentration on the rate of coagulation depends upon the amount of soap present. Generally a higher salt concentration causes a more pronounced increase in the rate of coagulation, the lower the soap concentration. This is in accordance with the observation, according to which an increasing concentration of Aerosol OT causes a higher rate of coagulation at fairly low salt concentrations, whereas at higher salt concentrations the reverse is true.

In emulsions stabilised with Aerosol MA the influence of the soap concentration on the rate of coagulation was much less. Several of the experimental results have been collected in table 5.I and fig. 5.3, showing that the influence of the concentration of Aerosol MA never exceeds the experimental error. The effect of the initial particle concentration on the rate of coagulation, which appears from the data given in table 5.I, will be discussed below.

It appears probable that the influence of the concentration of Aerosol OT on the rate of coagulation must be attributed to the fact that both the solubility and the critical micellar concentration of the soap are at about 0.001 M in a 0.050 M potassium chloride solution. In all experiments with Aerosol OT at a salt concentration exceeding 0.050 M there was some insoluble soap present. The solubility and the critical micellar concentration of Aerosol MA in salt solutions are much higher, and have not been reached in these experiments.

The two different emulsions stabilised with Aerosol OT are not strictly comparable, as emulsion b was always found to coagulate somewhat more slowly than emulsion a under the same conditions. Such a difference has never been observed with emulsions containing Aerosol MA or sodium laurate. This behaviour, as well as some other

particular features of the curves given in fig. 5.2, can be explained by considering the influence of the adsorbed soap film on the rate of coalescence. In the case of fatty acids adsorbed at an air–water interface, the properties of the film can be profoundly altered by allowing very small amounts of polyvalent cations to react with the adsorbed soap molecules [4]. These polyvalent cations are preferentially adsorbed at the interface, and, if they form a water-insoluble salt with the soap present, this reaction will increase the "rigidity" of the interfacial film. It may be assumed that traces of polyvalent cations, the concentration of which is not easily reproducible, retard the coalescence in emulsions stabilised with Aerosol OT. The solubility of the corresponding salts of Aerosol MA and probably also of lauric acid is sufficiently high to avoid this difficulty.

In both emulsions containing Aerosol OT the rate of coagulation with 0.100 M potassium chloride is somewhat lower than might be expected. This may also be due to a decreased rate of coalescence, whereas the rate of flocculation increases in the usual way with the salt concentration. This explanation is in accordance with the fact that the potassium salts of these soaps are generally less soluble than the sodium salts. That "rapid" flocculation does not occur in these experiments follows from the data obtained with sodium chloride: the rate of coagulation increases continuously with the concentration of sodium chloride and reaches a value of 17.5×10^{-12} cm^3 sec^{-1} in a 0.200 M salt solution (fig. 5.1).

The importance of the electrical double layer in the stabilisation of an emulsion against coagulation is shown by the applicability of the rule of *Schulze* and *Hardy*, according to which the concentration of a cation necessary to obtain a predetermined rate of coagulation of a sol with negatively charged particles is mainly determined by the valency of the cation, whereas its specific nature is far less important.

The behaviour as predicted by the rule of *Schulze* and *Hardy* is actually observed in the coagulation of an emulsion, but only when the coagulating electrolyte has no appreciable effect on the rate of coalescence. This is the case when no insoluble soap is formed at the interface. Fig. 5.3 shows that the same rate of coagulation is obtained with a magnesium concentration about one-tenth of the potassium concentration, if Aerosol MA is used as the emulsifying agent. Fig. 5.4 shows that all monovalent cations tested have practically the same effect on the rate of coagulation, independent on the anion used.

It may be assumed that the rate of coalescence will be hardly

[4] *I. Langmuir* and *V. J. Schaefer*, J. Am. Chem. Soc. **58**, 284 (1936); ibid. **59**, 2400 (1937).

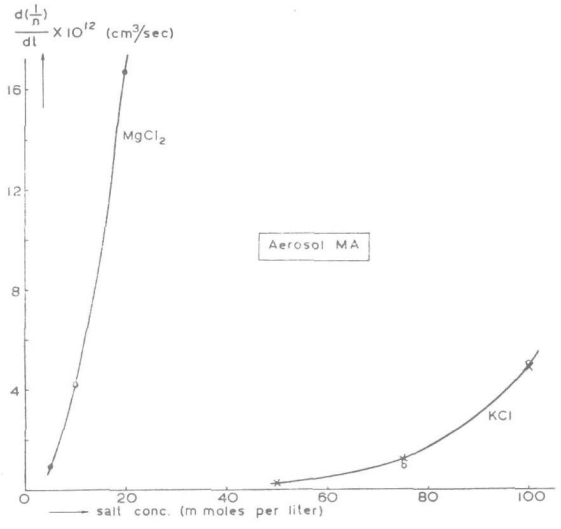

Fig. 5.3. Rate of coagulation with varying amounts of mono- and divalent cations.

Symbol	soap conc.	salt	$n_0 \times 10^{-8}$
●	0.0016 M	$MgCl_2$	1.38
×	0.0016 M	KCl	1.38
○	0.0008 M	KCl	0.67

Table 5.I.

Effect of concentration of Aerosol MA on rate of coagulation by 0.075 M sodium- or potassium chloride.

No. of experiment	Initial particle conc. $\times 10^{-8}$	Soap conc. M	Rate of coag. $a \times 10^{12}$ (cm³/sec)
98	0.3	0.00028	3.0
100	,,	,,	10.0
102	,,	0.0006	5.0
89	0.67	0.0006	1.6
92	,,	,,	0.8
81	,,	0.00077	1.6
85	,,	0.0039	0.5
88	3.2	0.0029	0.3
80	,,	0.0039	0.2

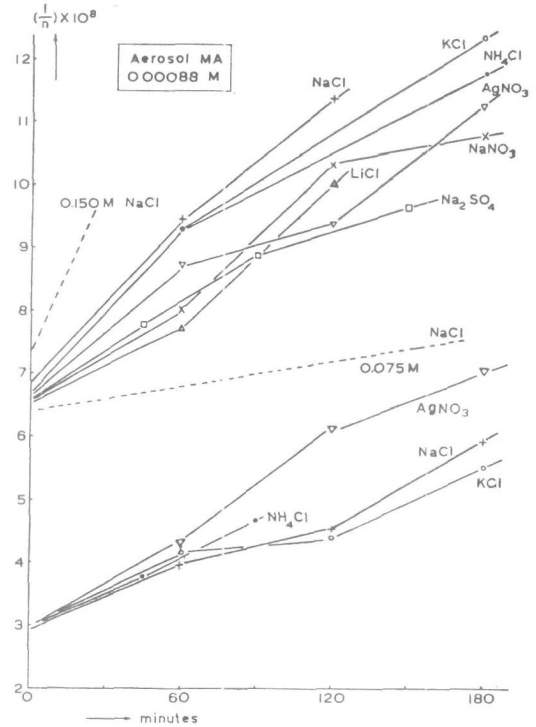

Fig. 5.4. Coagulation of Aerosol MA stabilised emulsions with 0.100 M monovalent cations, for two different initial particle concentrations.

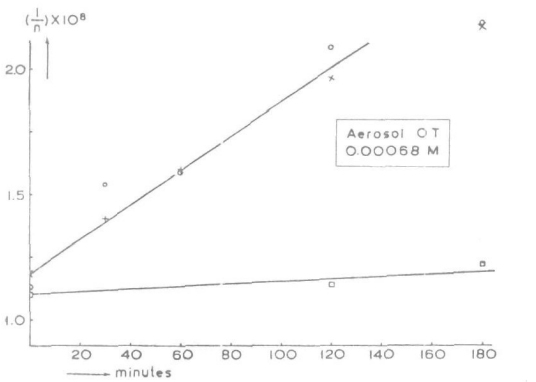

Fig. 5.5. Coagulation of Aerosol OT stabilised emulsions with various salts.

+ ×	NaCl	0.100 M
○	Na_2SO_4	0.050 M
□	$MgCl_2$	0.005 M

affected by substituting one electrolyte for another, as the influence of the various monovalent cations on the surface-active properties of a dissolved soap is practically independent on the specific nature of the cation [5]. The somewhat slower coagulation with the lithium salt, as compared with the sodium and potassium salts, is in accordance with the fact that it has slightly less influence on the surface-activity and is also less active in flocculation. The differences between the behaviour of the other salts are not reproducible, and are probably due to accidental differences in the experimental technique.

In the presence of Aerosol OT, the effect of the nature of the coagulating ion follows from fig. 5.5. Substituting one anion for another has no effect, but with 0.005 M magnesium chloride the rate of coagulation was only 0.10×10^{-12} cm^3 sec^{-1}. This low rate of coagulation must be attributed to the retarding action on coalescence, caused by the formation of insoluble soap at the oil–water interface.

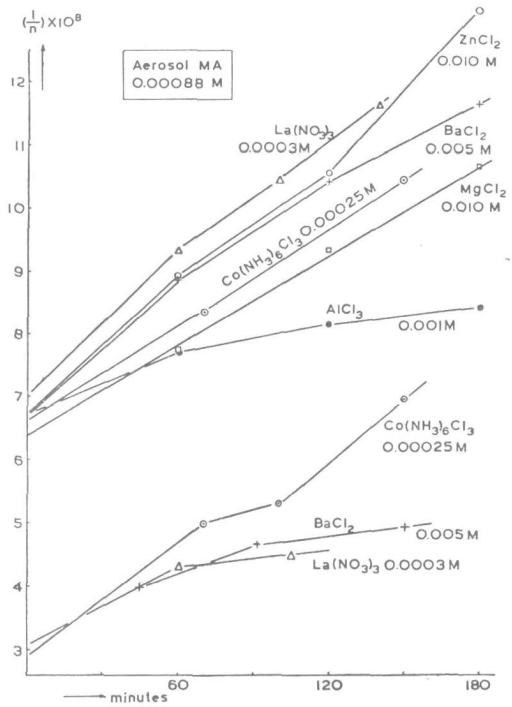

Fig. 5.6. Coagulation of Aerosol MA stabilised emulsions with polyvalent cations, for two different initial particle concentrations.

[5] *R. G. Aickin* and *R. C. Palmer*, Trans. Faraday Soc. **40**, 116 (1944).

That the magnesium ions react with the soap adsorbed at the interface and not only with the soap micelles or crystals which may be present in the aqueous phase follows from the decreased electrophoretic mobility caused by the presence of the magnesium ions. In the experiment recorded in fig. 5.5 the zeta-potential, determined according to the method described in section 6 of Chapter II, had decreased to about 60 mV. Experiments with a higher concentration of bivalent cations were not possible because the formation of insoluble soap interfered with the counting.

Even in the presence of Aerosol MA the concentration of bivalent cations necessary to obtain a certain rate of coagulation varies slightly with the nature of the cation (fig. 5.6).

Increasing the initial particle concentration resulted in the same lowering of the rate of coagulation, independent on the salt used. It is highly probable that identical rates of coagulation and identical influence of the initial particle concentration can only be obtained if both the rate of flocculation and the rate of coalescence are the same in all experiments recorded in fig. 5.4 and 5.6. Moreover, a 0.005 M solution of Aerosol MA containing salts of bivalent cations in a concentration up to 0.1 M shows no sign of turbidity. No insoluble soap, which might affect the rate of coalescence, is therefore formed in the emulsions containing Aerosol MA.

When sodium laurate is used as the emulsifying agent, much higher salt concentrations have to be used to obtain a satisfactory rate of coagulation. Mixing of the emulsion with such a fairly concentrated salt solution causes a very rapid coagulation as long as the turbulent motion persists. After about one minute this motion of the liquid ceases and normal coagulation sets in, the rate of which can be measured by comparing the number of oil droplets after varying times of coagulation with the number existing one minute after mixing. At this moment, however, an unknown amount of aggregates is already present. Accurate values for the various reaction rates could only be obtained if the influence of the aggregation in the mixing period were excluded.

The results of measurements with various concentrations of sodium laurate are shown in fig. 5.7. The value of n_0 found by extrapolating in an $1/n$ vs. time plot was well below the value calculated from the known particle concentration of the stock emulsion. It is found that the soap concentration has hardly any influence on the rate of coagulation as measured by the slope of the curves between 7 and 15 minutes. The decrease in particle concentration caused by stirring, however, depends to a considerable extent on the amount of soap

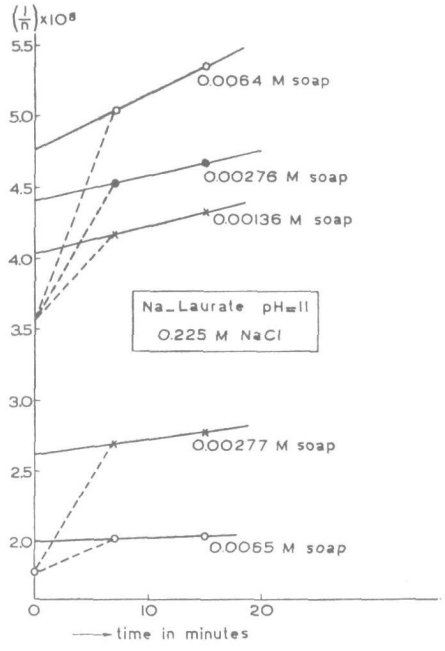

Fig. 5.7. Effect of sodium laurate concentration, and of initial particle concentration, on the rate of coagulation of emulsions containing 0.225 M sodium chloride.

present, and also on the initial particle concentration. No attempt has been made to study this phenomenon further, as it proved very difficult to perform the mixing in a reproducible way.

The rate of coagulation of emulsions containing sodium laurate at a pH = 11.0 in the presence of sodium chloride is shown in fig. 5.8. The results obtained with these fairly high salt concentrations were generally less reproducible than in the case of the emulsions stabilised with the Aerosol-type soaps. This is attributed to the occurrence of orthokinetic flocculation. The large influence of the orthokinetic flocculation in the emulsions stabilised with sodium laurate may partly be due to the occurrence of larger particles in these emulsions than in emulsions containing Aerosol-type soaps. Average particle concentrations in the stock emulsions containing 40 per cent. of oil were with Aerosol OT 50×10^8; with Aerosol MA 20×10^8 and with sodium laurate 3×10^8 per cm^3.

The decrease in the rate of coagulation upon increasing the salt concentration from 0.175 to 0.200 M (curve 2 in fig. 5.8) proved to

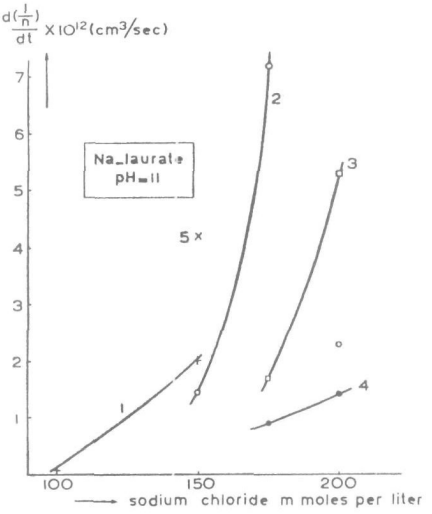

Fig. 5.8. Rate of coagulation of emulsions stabilised with sodium laurate, as a function of salt concentration.

symbol	curve	soap conc.	$n_0 \times 10^{-8}$
+	1	0.00276 M	0.493
○	2	0.00276 M	0.40
□	3	0.00136 M	0.40
●	4	0.0055 M	1.53
×	5	0.00276 M	0.38

be reproducible, though the exact values obtained in duplicate experiments differed to a considerable extent. It appears that this effect must be attributed to the formation of insoluble soap, as the critical micellar concentration in a 0.200 M solution of sodium chloride is at 0.006 M sodium laurate [6]. Exact data for the solubility of sodium laurate in the solutions used are not available, but extrapolation of data obtained at higher temperatures [7] indicate that the solubility in water at 18° will be about 0.005 M. The value in a solution of sodium chloride is still much lower.

[6] *M. L. Corrin* and *W. D. Harkins*, J. Am. Chem. Soc. **69**, 679, 683 (1947).
[7] *J. W. McBain, G. C. Brock, R. D. Vold* and *M. J. Vold*, J. Am. Chem. Soc. **60**, 1870 (1938).

Influence of the initial particle concentration.

A conspicuous effect following from the data assembled in fig. 5.2 and table 5.I concerns the influence of the initial particle concentration on the rate of coagulation. This effect must be investigated by comparing experiments in which the rate constants for both flocculation and coalescence remain unchanged. This condition implies that an increase of the interfacial area per unit volume of the emulsion should not affect the structure of the double layer. As the amount of electrolyte dissolved in the oil phase may be neglected in all cases, experiments should be compared in which both the soap and the electrolyte concentrations in the aqueous phase are the same. In the rather crude emulsions considered here, the amount of adsorbed soap may even be neglected, leading to the condition that the total soap concentration in comparable experiments should be the same.

Taking for the surface–average diameter of the oil droplets the value 10^{-4} cm, the interfacial area in 1 cm^3 of an emulsion containing 10^9 oil drops is 31.4 cm^2, and the number of soap ions adsorbed on that area will be about 30×10^{15}. This is less than 1 per cent. of the number present in 1 cm^3 of a 0.0007 M soap solution. The effect of a variation in the soap concentration of less than 1 per cent. on the rate of coagulation is far below the experimental error.

The influence of the initial particle concentration on the rate of coagulation is shown in fig. 5.9 and 5.10. The data for Aerosol OT have been obtained from experiments in which the initial particle concentration was the only variable. In fig. 5.10 data have been included in which also the concentration of the Aerosol MA was varied, as it had been found that a change in the soap concentration alone had little influence on the rate of coagulation, in this case. Values for the various reaction rates have been obtained from these curves by comparison with a number of graphs similar to fig. 4.2 (Chapter IV). The results are summarised in table 5.II.

In table 5.II data have also been included for an emulsion stabilised with sodium laurate at pH = 11.0, coagulated with 0.175 M sodium chloride (fig. 5.11). These data were obtained by coagulating first a rather crude emulsion ($n_0 = 0.31 \times 10^8$ at an oil concentration of 4 per cent.). Another sample of the same stock emulsion was thereupon homogenised until the particle concentration in the 4 per cent. emulsion amounted to 0.775×10^8 per cm^3. This second emulsion was coagulated under exactly the same conditions. The increase of the particle concentration appears to have a considerable influence on the rate of coagulation.

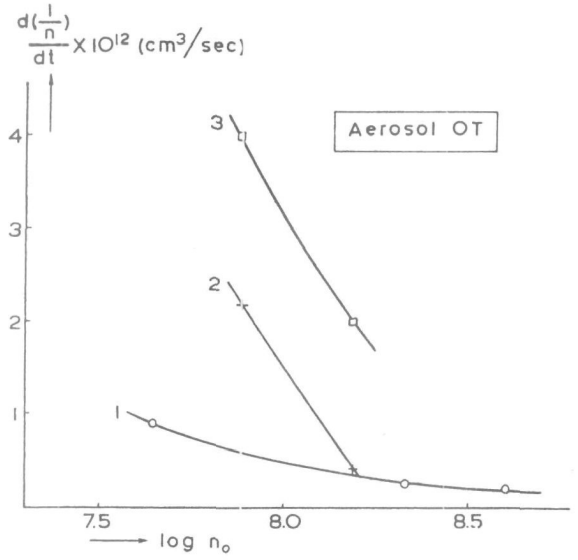

Fig. 5.9. Influence of initial particle concentration on the rate of coagulation.

symbol	curve	salt	soap conc.
○	1	0.070 M NaCl	0.0035 M
+	2	0.050 M KCl	0.0007 M
□	3	0.070 M KCl	0.0007 M

4. Discussion.

When every collision between particles is effective in removing one separate particle from the system, the rate of flocculation has a value of about 10^{-11} cm^3 sec^{-1} in a monodisperse system of spherical particles. Higher values can only occur if collisions are caused by still other forces than those responsible for Brownian motion. The high values obtained for the rate of flocculation in the present investigation may be explained by considering that several mechanisms acting in the direction of an increased rate of flocculation, are operating in the emulsions considered here. These are:

(i) The Van der Waals attraction causing an increased rate of diffusion towards a central particle as soon as a droplet coagulating with it has approached it to a distance of about one particle radius.

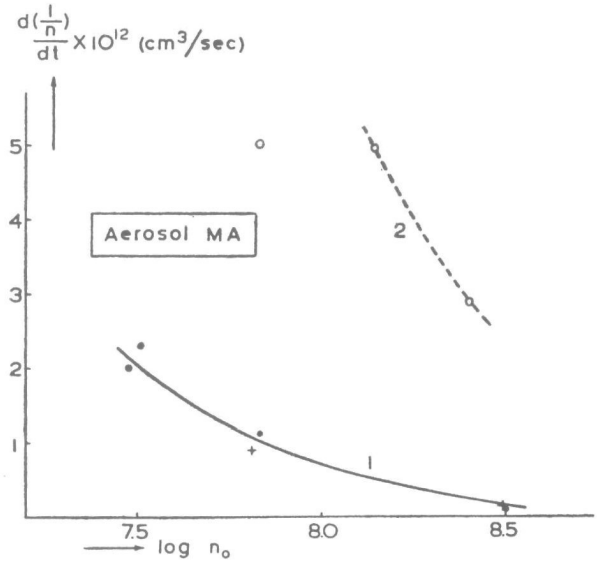

Fig. 5.10. Influence of initial particle concentration on the rate of coagulation.

symbol	curve	salt	soap conc.
+ ●	1	0.075 M NaCl	variable
○	2	0.100 M KCl	„

(ii) The particle size distribution which, if it is not strictly uniform, will cause an increased rate of flocculation. Calculations by *Müller*[8] indicate that the rate of flocculation may increase by 15 per cent. if the particle size distribution is symmetrical . With asymmetrical distribution an increase of 50 per cent. appears to be possible.

(iii) The flocculation occurring during the mixing of the salt solution with the emulsion. The inevitable stirring will increase the number of collisions, but the shearing forces operating in the liquid will also tend to disrupt any aggregate formed. Finally, an equilibrium will be established in which the amount and the size of the aggregates depend, among others, upon the motion of the liquid and the particle size distribution of the droplets. As the liquid motion is necessarily turbulent, and therefore irreproducible, it is at present not possible

[8] *H. Müller*, Kolloidchem. Beih. **26**, 257 (1928); ibid. **27**, 223 (1928).

Table 5.II.

Reaction rates in soap-stabilised emulsions, obtained from the dependence of the rate of coagulation on the initial particle concentration.

Soap	Salt	Rate of flocculation $cm^3/sec \times 10^{11}$ a	Rate of coalescence $sec^{-1} \times 10^3$ K
Aerosol OT			
0.0035 M	0.070 M NaCl	1	0.5
0.0007 M	0.050 M KCl	(30)	(0.1)
0.0007 M	0.070 M KCl	30	0.6
Aerosol MA			
—	0.075 M NaCl	5	0.1
—	0.100 M KCl	30	2
Na-laurate pH = 11.0			
0.0028 M	0.175 M NaCl	25	1

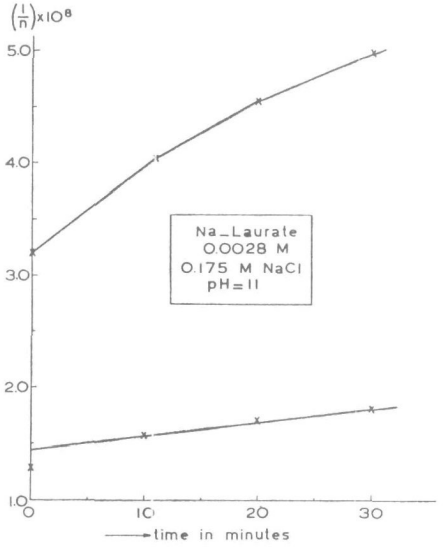

Fig. 5.11. Showing increased rate of coagulation upon decreasing the initial particle concentration.

to consider this effect more quantitatively. Its magnitude may be estimated from calculations made by *Von Smoluchowski* [2], according to which the frequency of collisions is proportional to the velocity gradient in the liquid and to the third power of the particle radius. A velocity gradient of 1 sec^{-1} will increase the rate of flocculation about 15-fold, when particles of 10^{-3} cm diameter are considered. The influence on the smaller particles is much less. Nothing can be said, however, concerning the aggregates surviving after the motion of the liquid has ceased.

From the results obtained with the Aerosol-stabilised emulsions it may be deduced that the influence of this effect, if it contributes significantly to the measured rate of coagulation of these emulsions, can be made sufficiently reproducible to allow it to be eliminated when studying the effect of other variables. An obvious condition is that the mixing is always carried out in the same way, and that the particles are not too large. The less satisfactory reproducibility in the emulsions containing sodium laurate is attributed to this effect.

(iv) The orthokinetic flocculation caused by creaming or sedimentation. *Müller* [8] has shown that a significant effect occurs only if particles are present larger than

$$R \geqslant \sqrt[4]{\frac{40\,kT}{\pi g d}}$$

(d is the difference in density between oil and aqueous phase; $g = 981$ cm sec^{-2}). A density difference of 0.5 per cent. may have occurred in several experiments with a low or a high salt concentration, and a difference of 0.1 per cent. can hardly be avoided. The corresponding minimum particle sizes are 5.6 and 8.5 microns. Particles larger than these were present in all emulsions used.

An estimation of the influence of the effect can be made by means of a theory developed by *Müller*, according to which the rate of flocculation between particles having a diameter ratio $R_1/R_2 = \alpha$ is given by:

$$\frac{\sin h\ C}{C}$$

where $C = \frac{4\pi gd}{3kT} \cdot R_2^4 \cdot f(\alpha)$. The value of $f(\alpha)$ depends only on the diameter ratio, and may be obtained from a table in *Müller*'s paper. Inserting the values $R_2 = 10^{-3}$ cm and $\alpha = 0.8$ results in $f(\alpha) = 0.0146$; $C = 1.53$ and $\frac{\sinh C}{C} = 1.44$. For a diameter ratio different from 0.8 and for smaller particles the effect would be smaller.

A complete discussion of this effect would involve the calculation of the contributions of particles of all sizes present, which is not possible without the knowledge of a suitable function describing the size-frequency distribution. From the fact that the frequency of collisions between particles of 20 and 16 microns is 1.44 times the frequency which would be observed with $d = 0$, whereas for nearly all other possible particle combinations the effect is much smaller, it would appear that the total increase in the rate of flocculation caused by this effect is of the order of ten per cent. or less. On the other hand, C is proportional to the density difference which may become as large as 0.005 in exceptional cases. The influence of this effect is then much larger.

Summing up, it may be said that several factors cooperate in increasing the observed rate of flocculation, though it is still doubtful whether the high values given in table I can be quantitatively accounted for. The highest values for the rate of *coagulation* measured were 2.5×10^{-11} cm^3 sec^{-1} (Aerosol MA and 0.030 M magnesium chloride) and 1.75×10^{-11} cm^3 sec^{-1} (Aerosol MA and 0.200 M sodium chloride). As nothing indicated these rates to be the highest possible, and the rate of flocculation has to be still larger, the values given in table 5.II may be considered to have the right order of magnitude.

The coagulation experiments have to be extended for a time sufficiently long compared with the time in which equilibrium is established. Diffusion equilibrium, in which the number of particles diffusing in unit time through a sphere surrounding a central particle equals the number of particles adhering to this central particle, is obtained after a coagulating time of the order of R^2/D, in which R is the particle radius and D its diffusion constant. With $D = kT/6\pi\eta R$, this condition is satisfied if $t \gg 4.7 \times 10^{12} \cdot R^3$ sec. For the larger particles present in the emulsions, especially those containing sodium laurate, it may take one hour before equilibrium has been established. Moreover, reproducible results can only be obtained if the flocculation caused by stirring can be neglected as compared with the flocculation caused by diffusion in the quiescent emulsion, which will only be the case after sufficiently long coagulation times.

On the other hand, the coagulation experiments cannot be extended for such a long time that a concentration gradient results from creaming. In the experiments with emulsions containing sodium laurate these two conditions contradict each other, as the relatively large particle size implies a long time before equilibrium has been established, but creaming of the large drops, and especially of their

aggregates, cannot be avoided entirely. As in this case estimates of the various reaction rates cannot be made without taking into account the agglomeration in the mixing period, no attempt was made to study the coagulation of these emulsions more quantitatively.

CHAPTER VI.

CONCLUSION.

From a study of the literature concerning the stability of oil-in-water emulsions the conclusion has been drawn that electrostatic respulsion may contribute to the stability. By making a distinction between flocculation and coalescence it becomes evident that especially the flocculation reaction will be controlled by electrostatic forces. The influence of the electrical double layer on the flocculation of emulsified oil droplets is the subject of the Chapters II and III.

An investigation of the influence of the electrical double layer necessitates a study of its structure. Direct measurement of the potential drop at the aqueous side of the interface, which proved extremely useful in the investigation of the AgI-sol, is not possible in the case of an oil–water interface. An indirect method has been used to obtain the necessary information about the magnitude of this potential drop. This method uses measurements of the interfacial free energy at an oil–water interface at which soap ions have been adsorbed. The results of these measurements give, after the application of surface-thermodynamics, the amount of soap ions adsorbed at unit area of the interface. The magnitude of the potential drop at the aqueous side of the interface can be obtained from the soap-adsorption data after the introduction of a suitable model of the double layer.

The potential drop at the aqueous side of the oil–water interface appears to be of the order of 100 mV under the conditions of the present experiments. This value is in perfect agreement with that obtained from measurements of the electrophoretic mobility of the dispersed oil droplets, but is too high to allow an explanation of the flocculation of these droplets analogous to the flocculation in hydrophobic sols of solid particles. The relatively large size of the oil droplets results in an extremely high potential barrier between colliding drops. Flocculation of the oil drops by crossing the barrier would seem improbable; moreover, if this kind of flocculation would occur it might be expected to be practically irreversible and coalescence would appear to occur immediately after flocculation, as the distance between the surfaces of the oil globules becomes less than 1 A after the barrier has been crossed. Reversible flocculation which does not result in immediate coalescence can, however, easily be realised experimentally. It is suggested that this reversible flocculation will

occur in the "secondary minimum" of the potential energy of interaction.

Experimental determination of the rate of coagulation of emulsified oil droplets has been carried out by counting the number of oil droplets present after a predetermined time of coagulation. The rate of flocculation has been calculated from the results of these experiments by considering the influence of the initial particle concentration on the rate of coagulation. Experiments have been carried out in the range of particle concentrations where the influence of a variation of this concentration becomes particularly evident.

The influence of the valency of the coagulating cations on the rate of coagulation is in accordance with the rule of *Schulze* and *Hardy*, showing that the stability of the emulsion against coagulation is controlled by the electrical double layer. In the experiments using polyvalent cations the initial particle concentration was sufficiently low to ensure that the rate of coagulation was mainly determined by the flocculation reaction. Moreover, a change in the initial particle concentration brought about a change in the rate of coagulation which proved independent on the kind of salt used. It may be concluded that the rate of flocculation is affected by the valency of the counter ions in the same way as the rate of coagulation.

The applicability of the rule of *Schulze* and *Hardy* in the flocculation of hydrophobic sols has been shown to be connected with the high value of the potential drop in the diffuse double layer [1]. The influence of the valency of the counter ions on the interaction of diffuse double layers of colliding particles is connected with the fact that, at sufficiently high values of the surface potential, the excess of counter ions in the double layer exceeds the deficiency of the ions having a charge of the same sign as the interface. As a rule, the value of the surface potential itself is practically independent on the amount and kind of "indifferent" electrolyte present in the sol. In the case of oil-in-water emulsions, however, another explanation of the effect of the valency of the counter ions presents itself, as the value of the surface potential at an oil–water interface appears to be highly sensitive to the concentration and kind of the counter ions. This, however, strengthens the argument concerning the effect of the electrostatic repulsion on the rate of flocculation.

If flocculation would occur in the "secondary minimum" of the potential energy of interaction, the effect of the valency of the counter ions must be explained in a slightly different way. Addition of poly-

[1] *E. J. W. Verwey* and *J. Th. G. Overbeek*, Theory of the Stability of Lyophobic Colloids. Amsterdam 1948.

valent cations results in a decreased distance between the particles in the "secondary minimum", and hence in an increased depth of the minimum. The rate of flocculation, however, which would in all cases correspond with "rapid" flocculation in the sense of Von Smoluchowski's theory, would hardly be affected by the addition of electrolytes. It is possible that the "degree" of flocculation, which may be defined as that portion of the globules for which the "secondary minimum" is sufficiently deep to prevent escape of the particles after flocculation has occurred, is increased in the presence of electrolytes. This explanation would be acceptable if the "secondary minimum" for particles of a certain size present in sufficient amount would have a depth of the order of kT. Accurate values for the depth of this minimum cannot be given at present, as the value of the constant A entering into equation (3.3) has not been determined with sufficient accuracy, and the relation between the magnitude of the Van der Waals attraction and the distance between the particles has not yet been fully established [2, 3]. It appears probable, however, that particles will generally be present the size of which is just sufficient to make the depth of the "secondary minimum" about kT, upon mutual approach. Addition of salt would, in that case, result in an increased number of particles for which the depth is larger than kT, i.e. an increased "degree" of flocculation. In the present experiments this cannot be distinguished from an increased "rate" of flocculation.

An important objection against the assumption of flocculation in the "secondary minimum" is that it would result in a preferential flocculation of the larger particles. This effect could be used to explain the sedimentation of the stock emulsions, but it has not been found in the coagulation experiments.

It follows that the experimentally determined effect of the valency of the counter ions shows that the electrostatic repulsion contributes to the stability, but it cannot be used to decide whether flocculation occurs in the "secondary minimum" or not.

The experimentally determined rate of flocculation had in all cases a value higher than that predicted by the theory of Von Smoluchowski for "rapid" flocculation. Even at salt concentrations sufficiently low to expect "slow" flocculation to occur the rate of flocculation was found to have a value higher than 10^{-11} cm^3 sec^{-1}. Though both the large particle size and the particle size distribution cooperate to increase the value of the rate of flocculation as compared with that resulting from Von Smoluchowski's theory, the experimentally

[2] *M. J. Sparnaay,* Diss. Utrecht 1952.
[3] *E. L. Mackor,* Rec. trav. chim. **70,** 841 (1951).

determined rates of flocculation may be considered as substantiating the theory of flocculation in the "secondary minimum".

The rate of coalescence has also been determined from the dependency of the rate of coagulation on the initial particle concentration. The value of about 10^{-3} sec^{-1}, showing that out of every 1000 oil globules contained in aggregates two will coalesce per second, is rather low if it is taken into account that no "rigid" film of adsorbed molecules was present in these experiments. The presence of such a monomolecular layer showing rigidity may be expected to have a retarding action on coalescence. Experimental evidence obtained is not in contradiction with the theory, according to which the rate of coalescence is mainly controlled by the interparticle distance at the "secondary minimum" of the potential energy. The effect of an increasing salt concentration on the rate of coagulation would, in this case, have to be explained as an accelerating of coalescence caused by a decreased interparticle distance at the "secondary minimum".