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Flocculation and Deflocculation Stability of Colloidal Dispersions

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PART I. GENERAL ASPECTS

Introduction

A good method of obtaining clean sand is to stir dirty sand in a pail of water and allow the suspension to settle. Sand settles much faster than clay and organic contaminants, and, if the water is poured away as soon as most of the sand has settled, the contaminants will still be in suspension and flow away with the water. The explanation of the method is quite simple. Sand grains are considerably larger than clay particles and, as the force of gravity is proportional to the mass (or volume) of the particles, but the hydrodynamic resistance only to the first power of their linear dimensions (Stokes law), the rate of settling increases rapidly with particle size. It is easily calculated that a spherical particle of 2μ diameter and a density of 2 settles in water at room temperature with a velocity of about 1 cm. per hr. Particles 10 times as large settle 100 times as fast, that is, about 1 cm. per min., and for particles smaller than 1μ the settling may usually be neglected.

That this, however, is only part of the story is rather nicely illustrated in a phenomenon that has occured in recent years in the Netherlands (1). One of our rivers, a Rhine arm, used to carry and still carries a certain amount of clay. This river debouched in the Zuider Zee and deposited its clay in the form of a continually growing delta. After the Zuider Zee had been closed off from the North Sea by the building of a long dike, its water became progressively fresher and, simultaneously, the delta stopped growing. Although the river still carried clay and its streaming profile was not substantially changed, the clay was not deposited any more.

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Apparently the rate of settling of the clay is larger in salt water than in fresh water.

Many other examples can be given where the rate of settling of a suspension depends critically on relatively small changes in the composition of the liquid. Fresh milk, in which fat globules are suspended, will cream (fat is less dense than water) very slowly and the milk will easily pass unchanged through ordinary filter paper. If, however, the milk has turned sour, the fat and some of the protein "coagulate," and the floccules do not pass filter paper any more and cream rapidly. Latex flows out of the rubber tree as a stable suspension of small rubber particles in an aqueous solution. It is made to coagulate and form large rubber sheets by addition of certain acids or salts. Egg white coagulates by boiling. Here the amount of suspended material (protein) is so large that all the "floccules" stick together, fill the total available space, and hold the liquid in the remaining interstices.

Similar phenomena occur between particles of different nature. Dirt adheres to the skin or to textile fibers, and the art of washing consists in breaking the bond between dirt and, for example, fiber, which is mainly done by mechanical action, and preventing reformation of the bond, for which purpose soaps and other detergents are used in the washing process.

Stability of Colloids

These phenomena (flocculation, etc.) are perhaps most spectacular in colloid dispersions. The colloid size range is defined in such a way that sedimentation or creaming of individual particles is negligibly slow. But addition of electrolytes and other changes in the dispersion medium may cause *flocculation* or *coagulation,* i.e., the formation of aggregates, followed by macroscopic separation of phases.

For a typical colloid suspension such as a gold sol, a silver iodide sol, or a dilute emulsion, the distinction between the flocculated and the non-flocculated state is easy, but for extremely dilute and for very concentrated systems, especially if the particles are large, the distinction may be less obvious, although it is still quite important.

As aggregates can only be formed by collisions between particles, and as the probability of such collisions is proportional to the square of the particle concentration, the rate of aggregate formation in dilute suspensions may be so low as to escape easy detection. Sedimentation will remain slow in such a case, but in the sediment the particles will become aggregated.

In very concentrated systems, the total volume of aggregates may be so large that they entrap all available liquid, so that no visible sedimentation

occurs. Still, a coagulated and noncoagulated suspension can be easily distinguished by their mechanical properties, and just because of these mechanical effects the state of the system is important from a practical point of view.

A concentrated, coagulated suspension shows plasticity. This means that such a system behaves as a solid when only a small shearing force is applied, but to a larger shearing force, which is strong enough to break the bonds between the particles, it behaves as a liquid. Moulding clay is a good example of plasticity. If, after the deformation, the system remains fluid for some time, returning only slowly to the more rigid state, one speaks of thixotropy (change of state by handling) (2). [Thixotropy is shown very well by a concentrated suspension of ferric oxide flocculated by various amounts of electrolyte. The higher the concentration of electrolyte, the shorter the time during which the system stays fluid after being turned from rigid (gel) to fluid (sol) by shaking.]

On the other hand, a concentrated, nonflocculated suspension flows easily at low rates of shear but shows a progressively larger resistance against deformation at higher rates of shear. This behavior is called dilatancy (3, 4). The explanation is that the individual particles in the concentrated suspension, if given sufficient time, flow around one another quite easily, but if they are forced to hurry, they become "panicky," do not find the easiest way, and pile up, thus preventing further movement. Quicksand is a spectacular example of this kind of behavior, but a concentrated suspension of flour or starch grains also demonstrates it quite well.

This digression about concentrated suspensions has indicated at least some of the practical importance of the distinction between flocculated, flocculating, and nonflocculating, but as the easiest and most complete information on these properties stems from colloid chemistry, we shall now return to colloids in aqueous solutions.

Preparation of Colloidal Suspensions

A very general method of preparing colloidal suspensions of insoluble (or better, slightly soluble) substances is to allow them to be formed from a more soluble state. For example, a gold sol, a suspension of metallic gold, is formed if a solution of the very soluble aurichloric acid is reduced by a suitable reducing agent. A sol of arsenic trisulphide is formed by mixing solutions of H_2S and As_2O_3. A mastic sol is obtained by pouring an alcoholic solution of the resin in water.

In all these cases the highly dispersed colloidal state is obtained if the rate of nucleation of the new phase is large as compared to its rate of

crystallization. But this is not enough. In order to obtain a stable colloid, the final dispersion medium must be such as not to cause coagulation, which implies among other things that the electrolyte content must be low.

Coagulation by Electrolytes

One of the typical properties of the hydrophobic colloids* is their high and fairly uniform sensitivity to salts. An arsenic trisulphide sol, for instance, coagulates after the addition of NaCl to a final concentration of 50 mmol/l (millimoles per liter). Other salts with monovalent cations cause coagulation at roughly the same concentration, but salts with divalent cations cause coagulation at about 1 and those with tervalent cations at about 0.1 mmol/l, as shown in Table I. It is also shown in the table

TABLE I. Coagulation Concentrations for an Aqueous Sol of As_2S_3, in mmol/l (5)

Monovalent Cations		Divalent Cations		Trivalent Cations	
Salt	Coagul. Conc.	Salt	Coagul. Conc.	Salt	Coagul. Conc.
LiCl	58	$MgCl_2$	0.72	$AlCl_3$	0.093
NaCl	51	$MgSO_4$	0.81	$Al(NO_3)_3$	0.095
KCl	49.5	$CaCl_2$	0.65	$\frac{1}{2} Al_2(SO_4)_3$	0.096
KNO_3	50	$SrCl_2$	0.63^5	$Ce(NO_3)_3$	0.080
$\frac{1}{2} K_2SO_4$	65.5	$BaCl_2$	0.69		
HCl	31	$ZnCl_2$	0.68^5		
$\frac{1}{2} H_2SO_4$	30	$(UO_2)(NO_3)_2$	0.64		
Morphine chloride	0.42	Quinine sulphate	0.24		
New fuchsin	0.11	Benzidine nitrate	0.09		

that H^+-ions and many organic cations have a larger coagulating power than corresponds to their valency. Gold sols or silver iodide sols show in general the same coagulation behavior as As_2S_3 sols, although the absolute values of the coagulation concentrations may be somewhat shifted.

*Hydrophobic colloids are dispersions in water of substances that are only slightly soluble, and in which the dispersed particles are in the colloidal size range (about 50 Å to 10,000 Å). They have to be prepared in a roundabout way. Hydrophilic colloids are also dispersions in water of particles in the same size range, but these particles are truly soluble in water. Hydrophilic sols can be formed spontaneously from water and the dry colloid material: for example, gum arabic, many proteins.

A ferric hydroxide sol, as opposed to the ones just mentioned, is sensitive to the valence of the coagulating anions rather than the cations, as shown in Table II. This pronounced influence of the valence of the ions is known as the rule of Schulze and Hardy. It gives a clue to the interpretation of the stability of colloids against flocculation.

TABLE II. Coagulation Concentrations for
an Aqueous $Fe(OH)_3$ Sol, in mmol/l (5)

Monovalent Anions		Divalent Anions	
Salt	Coagul. Conc.	Salt	Coagul. Conc.
NaCl	9.25	K_2SO_4	0.205
KCl	9.0	Tl_2SO_4	0.22
$\frac{1}{2}BaCl_2$	9.65	$MgSO_4$	0.22
KBr	12.5	$K_2Cr_2O_7$	0.195
KI	16	H_2SO_4	~0.5
KNO_3	12		
HCl	>400		
$\frac{1}{2}Ba(OH)_2$	0.42		

The difference between arsenic sulphide, gold, and silver iodide on one hand, and ferric hydroxide on the other is that the particles of the first three sols are negatively charged, as proved by their motion in an electric field (electrophoresis), whereas ferric hydroxyde particles are positively charged. The pronounced influence of the valence according to the rule of Schulze and Hardy applies, therefore, to the ions that are oppositely charged to the particles (the counterions). The valence and nature of ions of the same charge (co-ions) as the particle are unimportant for stability.

Potential-Determining Ions

Which are the factors that determine the sign and magnitude of the charge of particles? In the preparation of colloidal suspensions it is not only necessary to avoid high electrolyte concentration, that is, to keep the electrolyte content below the Schulze-Hardy flocculation limit, but it is also necessary to take care that small concentrations of special ions are present, which are easily adsorbed at the interface. Such ions, which are exceptions to the Schulze and Hardy rule so far as their influence on colloid stability is concerned, are often identical with the "potential-determining ions" which govern the potential difference E between parti-

cles and liquid in accordance with the Nernst equation

$$E = E_o + \frac{RT}{z_i F} \ln a_i \tag{1}$$

in which a_i and z_i are the activity and the valence of the potential-determining ions. Such ions usually fit in or on the crystal lattice of the particles. Examples are Ag^+ and Cl^- for the AgCl sol, Fe^{3+}, OH^-, and also H^+ for the $Fe(OH)_3$ sol, S^- and also H^+ and OH^- for sulphide sols, and H^+ and OH^- for many metal sols (the metal acts more or less as a reversible hydrogen or oxygen electrode). In the case of emulsions of oil in water, surfactants are powerful antiflocculants because the surfactant ions are strongly adsorbed at the water-oil interface on account of their amphipathic nature.

Theoretical Interpretation of Colloid Stability

As mentioned before, aggregates can only be formed by collisions between particles. These collisions are caused by the Brownian motion of the particles and their number may be enhanced by systematic motions such as stirring of the suspension, sedimentation of particles and aggregates, etc. The number of Brownian collisions can be calculated from kinetic theory and proves to be adequate for quite rapid flocculation except in the case of extremely dilute suspensions.

Why then is not every colloidal suspension flocculated after a short time? Obviously, and this is verified by direct observation in the ultramicroscope, the collisions take place, but in stable systems they do not lead to permanent attachment of the colliding particles. The existence of the rule of Schulze and Hardy, i.e., the overwhelming influence of the charge of the ions and the sign of the charge of the particles on stability as compared to more specific effects, points very clearly to the importance of electrical phenomena for colloid stability. The first assumption, then, is that the collisions seen in the ultramicroscope do not actually lead to contact, but that the mutual electrostatic repulsion keeps the particles separated by some small distance. However, the notions of charge and electrostatic repulsion in electrolyte solutions should be handled with caution. The colloidal suspension as a whole must be electrically neutral and, if the particles are charged, an equivalent amount of charge of opposite sign must be present in the solution. Under the influence of electrostatic attraction toward the particle and a diffusion tendency away from it, this "countercharge" will form an ionic atmosphere around each particle very similar to the ionic atmospheres in solutions of strong electrolytes (see Figure 1). The combination of the surface charge
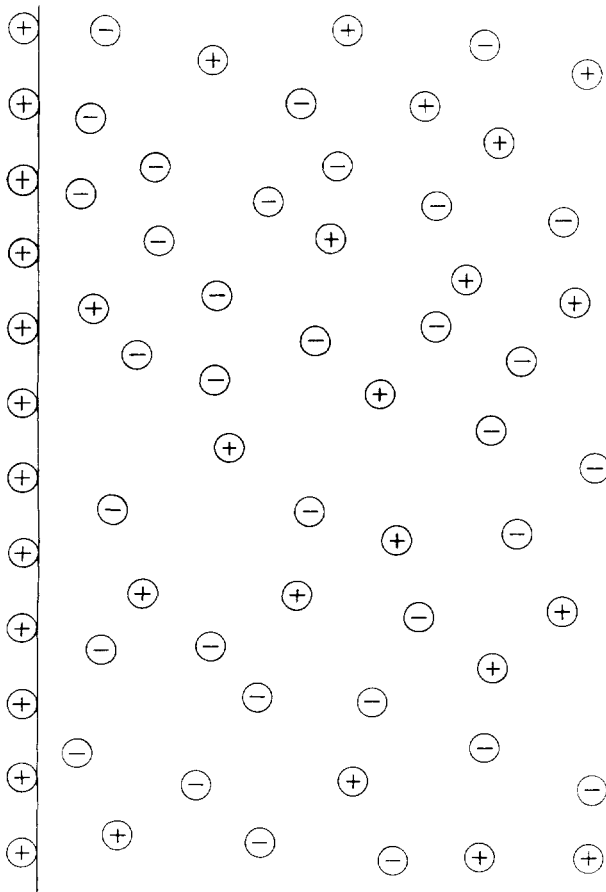
Ionic   atmosphere

FIGURE 1. Schematic representation of electrochemical double layer on a positively charged particle.

on the particle and the space charge in the solution is called electrochemical double layer (or electric double layer). The charge density and the potential in such a double layer decrease more or less exponentially with increasing distance from the surface.

STRUCTURE OF THE ELECTROCHEMICAL DOUBLE LAYER (6)

The average local concentration (n_i) of any type of ion in the double layer is governed by Boltzmann's law. It is a good approximation to take

only electrical effects in the energy into account. Consequently,

$$n_i = n_{io} \exp\left(-\frac{z_i e \varphi}{kT}\right) \approx n_{io} - \frac{z_i e n_{io} \varphi}{kT} \qquad (2)$$

where n_{io} is the concentration far from the surface, z_i is the valence of the ions of type i, e is the elementary charge, k is Boltzmann's constant, T is the absolute temperature, and φ is the local electric potential, with $\varphi = 0$ in the electrolyte solution far from the interface. The expansion of the exponential in only two terms leads to easy mathematics and qualitatively correct results, but in colloid and surface chemistry, this approximation is usually not good enough quantitatively.

The local charge denisty (ρ) is coupled to the local potential by Poisson's equation. This charge density is built up from ionic charges.

$$\rho = \sum_i z_i e n_i \approx - \sum_i \frac{z_i^2 e^2 n_{io} \varphi}{kT} \qquad (3)$$

In ρ the main term of the expansion of the exponential is zero because the solution is electroneutral.

For simplicity we write Poisson's equation for only one direction (x is the axis perpendicular to the interface, which is assumed to be flat)

$$\frac{d^2\varphi}{dx^2} = - \frac{4\pi\rho}{\epsilon} \approx \sum_i \frac{4\pi z_i^2 e^2 n_{io}}{\epsilon kT} \varphi = \kappa^2 \varphi \qquad (4)$$

in which ϵ is the dielectric constant of the solution and the Debye-Hückel length, $1/\kappa$,

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon kT}{\sum_i 4\pi z_i^2 e^2 n_{io}}} \qquad (5)$$

determines the thickness of the ionic atmosphere.

To give an idea of the extension of the ionic atmosphere it may be mentioned that, in water at room temperature and for monovalent ions, $1/\kappa$ is equal to 10 Å for a concentration of 0.1 molar concentration to 100 Å for a millimolar concentration, and to 1000 Å for a concentration of 10^{-5} mol/l.

The solution of Eq. 4 is

$$\varphi \approx \varphi_o \exp(-\kappa x) \qquad (6)$$

where φ_o is the potential at the interface, where $x = 0$.

As mentioned before, the value of φ is determined by the activity of the potential-determining ions. Figure 2 shows the relation between potential
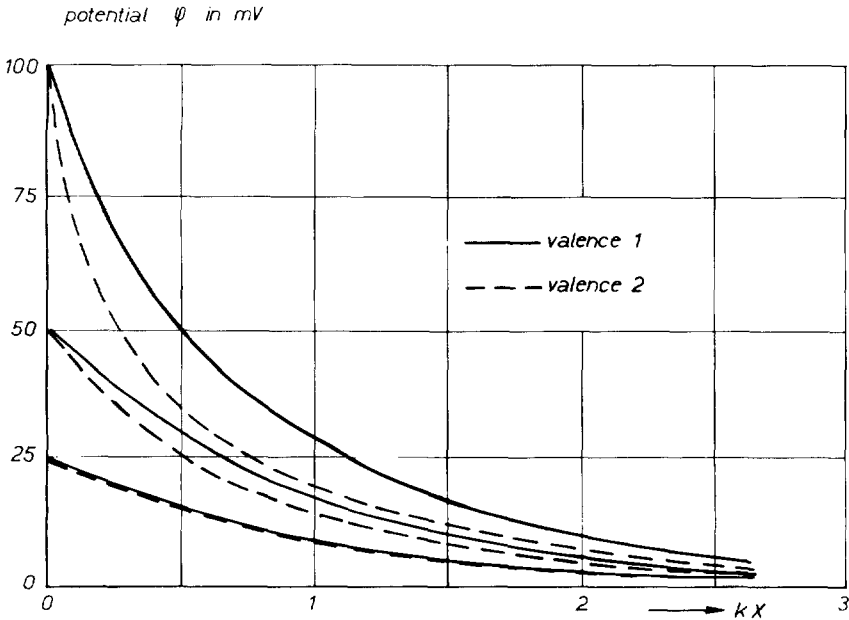
potential φ in mV

FIGURE 2. Potential in the double layer as derived from a nonapproximated solution of the Poisson-Boltzmann equation.

and distance for a more complete treatment of the Poisson-Boltzmann equation.

As a strong repulsion between two particles can only be expected when their double layers overlap to a considerable extent, it is clear that the range of the electrostatic repulsion is of the order of $1/\kappa$. The very long-range Coulomb repulsion is therefore considerably screened off by the countercharge.

Interaction of Two Double Layers

When two double layers interact, this not only affects the space charge in the liquid (the "diffuse double layers"), but also the surface charges. In the most simple case when the concentration of potential-determining ions is not too small, they will be able to keep the value of φ_0 constant under all circumstances, including the close approach of two particles. Between the two particles the double layers cannot develop completely and the potential in the liquid between the particles does not return to zero. This is shown in Figure 3 in which the particles are presented as flat plates at two different distances.
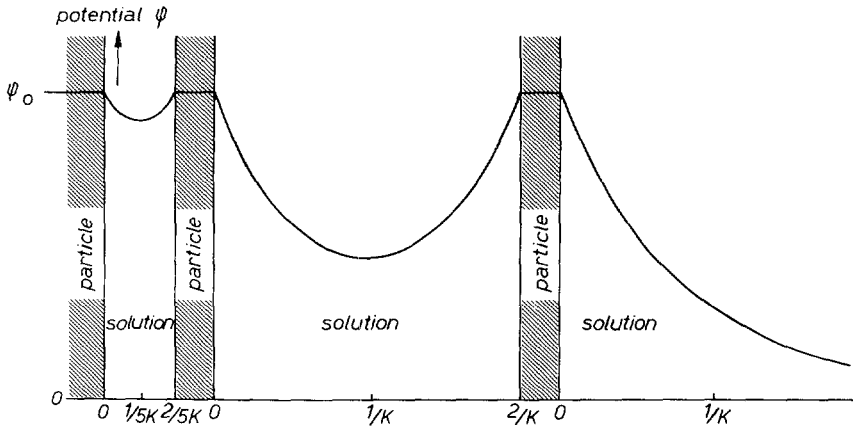
potential φ

Figure 3. Electric potential in overlapping double layers. The interfaces are assumed to be flat, parallel, and infinitely large.

As the original double layers had formed spontaneously, their free energy (their contribution to the free energy of the whole system) is negative, and, as the double layers are "pushed away" when two particles come close together, the free energy of their double layers becomes less negative. Consequently, positive work has to be done to bring the particles together; they repel each other. This repulsion can be estimated quantitatively if the free energy of the double layers in different situations can be calculated. This can be done by using imaginary charging processes very similar to those used in the theory of Debye and Hückel for strong electrolytes.

Without going into details of the derivation [see Verwey and Overbeek (6), pp. 77 ff.], we shall give now the equations for the free energy per cm^2 of a double layer on a flat interface and for the work to bring two of these flat double layers from infinity to a distance H. Since the valence of the co-ions is unimportant, the equations are given for the simple case of a symmetrical electrolyte (valence z, concentration far away from the interface n molecules/cm^3):

$$F_{\text{double layer per cm}^2} = -\frac{2nkT}{\kappa}\left\{4\cosh\frac{ze\varphi_o}{2kT} - 4\right\}$$

$$\approx (\text{for } \varphi_o \ll 25\text{mV}) -\frac{\epsilon\kappa\varphi_o^2}{8\pi} \quad (7)$$

$$V_{\text{repulsion(per cm}^2\text{ of each of the double layers)}} \approx \frac{64nkT}{\kappa}\gamma^2 e^{-\kappa H} \approx \frac{8\epsilon k^2 T^2}{\pi e^2}\frac{\kappa\gamma^2}{z^2}e^{-\kappa H} \quad (8)$$

In which

$$\gamma = \frac{e^{ze\varphi_o/2kT} - 1}{e^{ze\varphi_o/2kT} + 1} = \tanh(ze\,\varphi_o/4kT) \qquad (9)$$

Figure 4 shows the free energy of repulsion for the nonapproximated Poisson-Boltzmann case.

It is rather obvious that the absolute value of F increases strongly with the surface potential and that it is proportional to the dielectric constant and to the inverse thickness of the double layer. It is also not unexpected that the energy of repulsion (and also the force of repulsion) contains a factor $\exp(-\kappa H)$, but it is perhaps not so obvious that energy of repulsion is not very sensitive to the surface potential, if this is high. This is due to the fact that Eq. 8 is primarily a good approximation when the particles are not too close together, and that, upon increasing a surface potential which is already high, most of the countercharge is accumulated very close
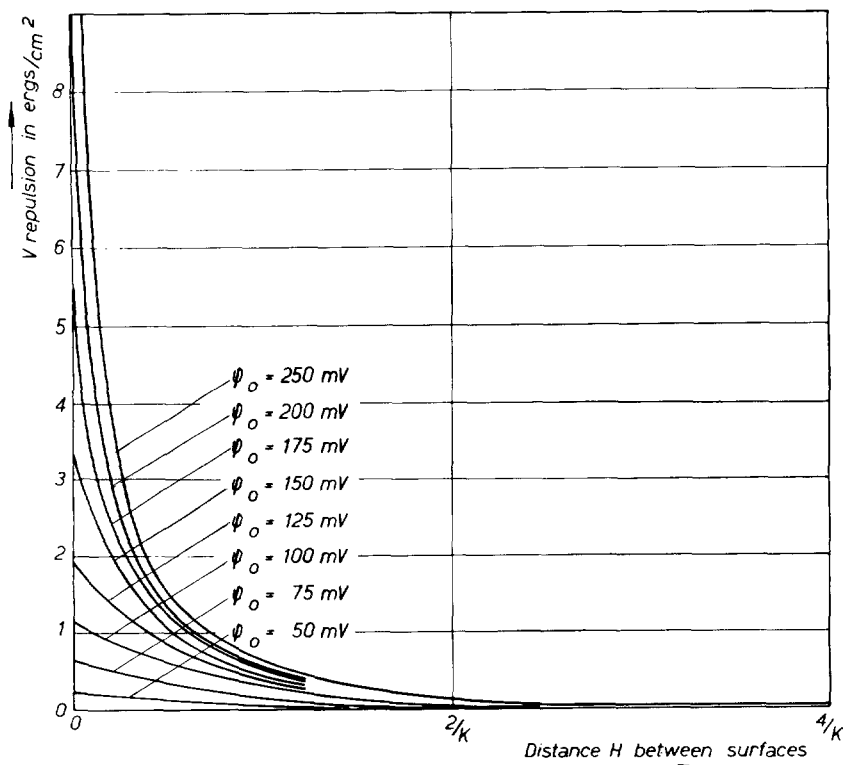

FIGURE 4. Free energy of repulsion per cm^2 between two interacting flat double layers, for a constant value of the potential at the interface in a 0.001 molar solution of a 1–1 electrolyte in water at 25° C.

to the surface, so that the remaining field farther away does not depend strongly on φ_o.

The repulsion equation has been tested by means of the "Schiller layers" (7). These are formed if sols of platelike particles are allowed to settle, in which case the plates are stacked in horizontal positions on the bottom of the container at distances which are determined by the equilibrium between electrostatic repulsion and gravity. Figure 5 shows data for particles of tungstic acid which are flat and very thin ($\approx 0.02\,\mu$). Their distance, which is of the same order as the wave length of light, can be determined from interference colors. The agreement between theory and experiment is quite good, especially considering that no adjustable parameters occur in the theory.
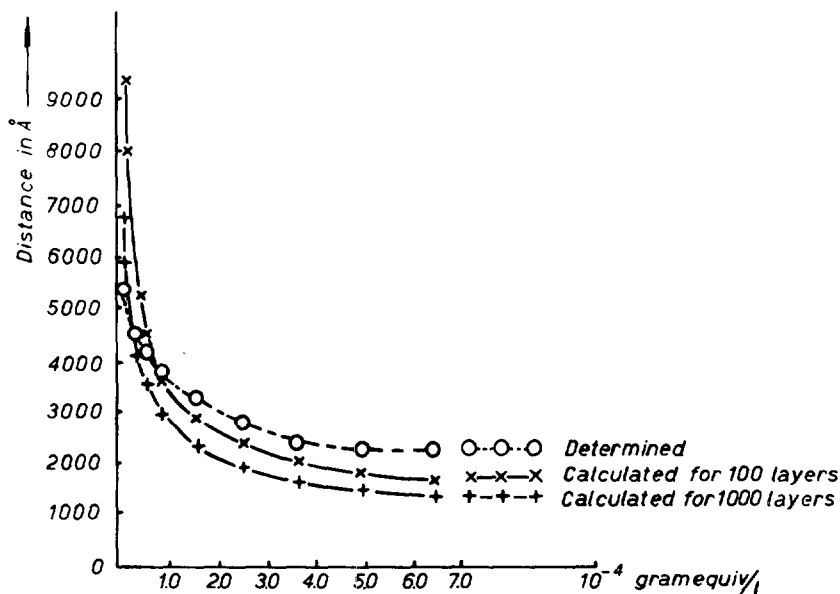

FIGURE 5. Schiller layers of platelike particles of tungstic acid. Distance between two layers as a function of the concentration of monovalent electrolyte. The number of plates in the stack was not accurately known but was certainly between 100 and 1000.

Attraction Between Particles

In adding electrolyte to a sol one obviously compresses the double layer ($1/\kappa \approx 1/\sqrt{n}$), but at the flocculation concentration the repulsion still has a finite range and a finite value.*

*Electrophoresis shows that the charge on the particle is still present and, if anything, has increased as compared to lower concentration of electrolyte.

Flocculation in these circumstances can only be understood if an attraction of at least the same range as the repulsion is present. Kallmann and Willstaetter (8) were the first to suggest that this long-range attraction might be due to London–van der Waals forces. The very generality of these forces would agree with the general occurrence of flocculation. It is easy to show that van der Waals forces have indeed a sufficiently long range and a sufficient strength. Of course the range of a force is something vague, but if we consider that the energy corresponding to this force should be larger than kT in order to make itself felt in practice, then considerations become more definite. Van der Waals energies between pairs of molecules are inversely proportional to the sixth power of their distance and they are additive, or at least approximately so. This means that, if we consider two particles at a given distance and now enlarge all dimensions x-fold, keeping densities constant, the contribution to the van der Waals energy from any pair of volume elements is the same whatever the scale of the case (see Figure 6). Indeed, enlarging each volume element x-fold (linearly) would increase the number of molecules
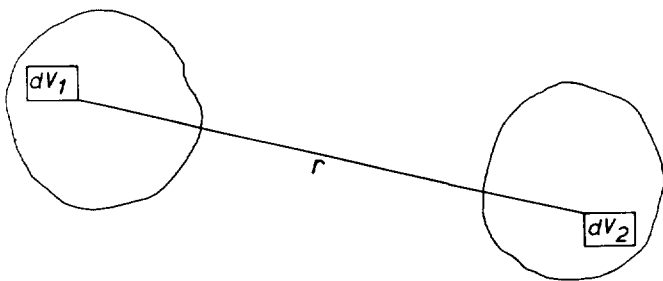

FIGURE 6. The van der Waals energy $V_{\text{att.}}$ between two particles can be built up as a sum or integral of the van der Waals energies between pairs of volume elements:

$$V_{\text{att.}} = - \int_{V_1} \int_{V_2} \frac{\lambda q^2 \, dV_1 \, dV_2}{r^6}$$

in which $-\lambda/r^6$ is the energy between a pair of molecules at a distance r, and q is the number of molecules per unit volume.

participating in the attraction $x^3 \times x^3 = x^6$-fold, but at the same time the distance has increased x-fold, which causes the contribution to the van der Waals energy to decrease with a factor x^6. Consequently, the van der Waals energy is independent of the scale of the picture.

We know that the van der Waals energy between two simple atoms or molecules is of the order kT when the distance between the atoms or molecules is about one atomic diameter. Consequently, the van der Waals energy between two colloidal particles is equal to kT when they are separated by a distance of the order of their diameter, and this implies

that the range of the van der Waals forces in this case is of the order of 100 Å or more, quite comparable to $1/\kappa$, the range of the electrostatic repulsion.

For particles in a liquid, or more generally, in a medium of high density, the van der Waals forces still lead to an attraction, if the two particles consist of the same substance. The proof for this theorem is given by de Boer (9).

Consider two particles of substance 1 separated by a medium, called 2. Then, if the two particles are brought closer together, at the same time two completely comparable volumes of the medium 2 must be brought together and the total change of all the van der Waals energies is proportional to

$$\Delta E = -E_{11} - E_{22} + 2E_{12} \qquad (10)$$

as is illustrated in Figure 7. In this equation, $-E_{ij}$ represents the mutual van der Waals energy between a particle of kind i and a particle of kind j of the shape and size as given in the figure, when they are close together.
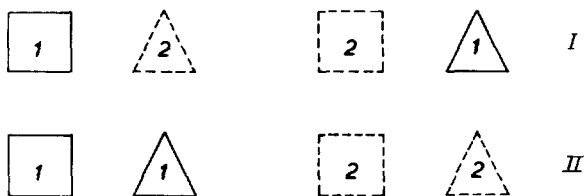

FIGURE 7. Illustrating the net change in van der Waals energy for two particles of substance 1 approaching one another in a medium 2.

If it is assumed, as is often a fair approximation (Van Laar, Hildebrand) that $E_{12} = \sqrt{E_{11} \times E_{22}}$, Eq. 10 can be transformed into

$$\Delta E = -E_{11} - E_{22} + 2\sqrt{E_{11} \times E_{22}} = -\left(\sqrt{E_{11}} - \sqrt{E_{22}}\right)^2 \qquad (11)$$

As this can never become positive, it shows that the van der Waals energy between particles of the same material always leads to an attraction and that the geometrical factor (dependence on shape, distance, and orientation) of this attraction does not depend on the nature of the medium.

[This consideration still holds even for the case of a thin layer of a liquid between two gas spaces. The van der Waals forces will act as if there is an attraction between the gas spaces and lead to further thinning of the layer of liquid. This effect is illustrated in a more realistic way in Figure 8, which shows that a disproportionation of two moderately thin films into a thicker and a thinner one always leads to a decrease in van der Waals energy. This is the main mechanism responsible for the formation

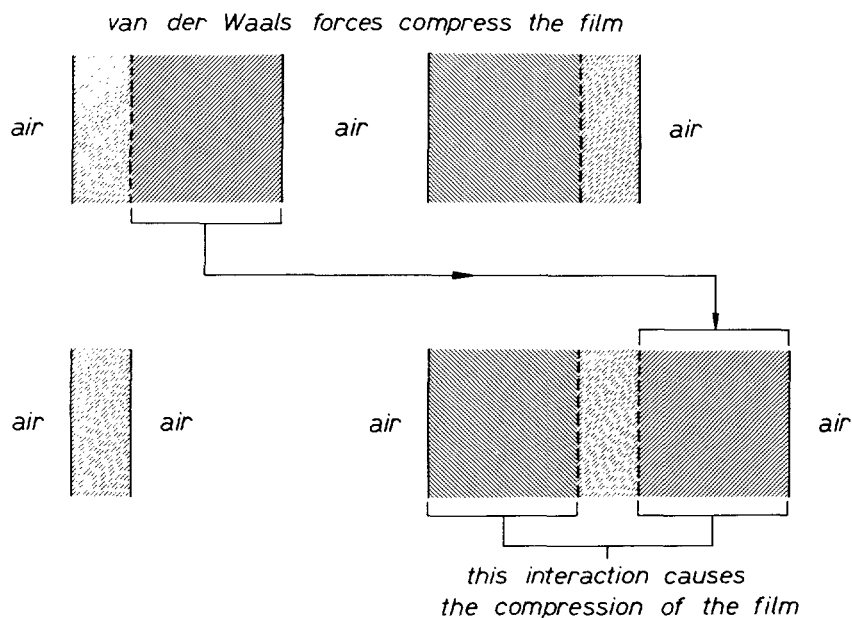*van der Waals forces compress the film*

FIGURE 8. Van der Waals forces lead to further thinning of thin films, as in foams and soap bubbles.

of very thin ("black") soap films, which will be discussed further in Part II.]

The van der Waals energy can be calculated between particles of all kinds of shapes [for spheres, see Hamaker (10); for cylinders, Sparnaay (11), for laths, Vold (12)], but the simplest results are obtained if we consider with de Boer (13) two parallel thick flat plates (two half-spaces) separated by a narrow gap of thickness H. A simple integration of the type shown in the legend to Figure 6 shows that for this case the van der Waals energy per cm^2 cross-section is inversely proportional to H^2, and equal to (10, 13)

$$V_{att.} = -\frac{\pi\lambda q^2}{12H^2} = -\frac{A}{12\pi H^2} \tag{12}$$

in which A, the Hamaker constant, is defined as (10):

$$A \equiv \pi^2 q^2 \lambda \tag{13}$$

Refinements in the Theory of Attraction

In several respects the above theory of attraction forces is only approximately correct. According to London's theory (14), van der Waals

forces are exclusively (or at least to a large extent) due to fluctuating electric moments in the two molecules which are correlated in such a way that, on the average, an attraction results. These fluctuating dipoles are connected with possible transitions between energy levels in the molecules and thus connected with certain wavelengths which are usually situated in the far ultraviolet, at about 1000 Å. [As dielectric and optical dispersions are based on the same transitions, London–van der Waals forces are also called *dispersion forces.*]

As electromagnetic signals travel only at a finite speed, the correlations cannot be fully established, if the distance between the two molecules is larger than the London wavelength (15). Casimir and Polder (16) gave a quantitative theory of this retardation of van der Waals forces and showed that for large separations the energy was inversely proportional to the seventh power of the distance instead of to the sixth power.

Another flaw in the theory is the assumption of additivity of London forces. If the molecules are far apart, as in a gas, additivity is indeed realized. But in condensed media deviations from additivity may be large. Therefore, a theory of attraction forces based on macroscopic properties of condensed bodies is preferable. Such a theory has been given for the attraction between ideal metals in the range of retarded attraction forces by Casimir (17) and in a more general way for dielectrics at any distance by Lifshitz (18). In Lifshitz' theory fluctuations in the local polarization and in the local field are considered. It is shown that for any frequency these fluctuations are related to the imaginary part of the dielectric constant (i.e., to the absorption coefficient) for that frequency. The fluctuations are correlated over distances of the order of the reciprocal absorption coefficient. The correlations in the fluctuations between different bodies lead to an attraction and, for the case of two half-spaces separated by a gap H, the dependence on the separation is identical to that found in the theory based on the additivity of molecular interactions, that is, the free energy is inversely proportional to H^2 for short distances and to H^3 for large distances (short and large measured by the wavelength of the main absorption peak). The proportionality constant in the attraction equation can be calculated as an integral containing the complex dielectric constant over the complete range of frequencies. Unfortunately, the dielectric data are not yet known sufficiently extensively to allow a general quantitative application of Lifshitz' theory. Dzyaloshinskii, Lifshitz, and Pitaevskii (19) extended the theory to the case of a liquid medium between the two half-spaces. Just as in the more simple theory, attraction always results if the two half-spaces contain the same material.

It can be shown (20) that Lifshitz' theory, if applied to the attraction

between two gas masses, is in quantitative agreement with London's value for the dispersion forces.

Experiments on Attraction

In a relatively small number of investigations the relation between the van der Waals attraction force between flat or slightly curved plates has been measured as a function of the distance. These experiments are difficult because very small distances ($<$ 1000 Å) have not been realized due to the roughness of plates and the interference of dust particles and because the forces are small at larger separations. So far only retarded van der Waals forces have been measured. The results are in reasonable agreement with the theory, both with respect to the dependence on the distance and to the absolute value, but the accuracy is poor. Derjaguin *et al.* (21) investigated quartz, thalliumbromide-iodide, and quartz-chromium; Sparnaay (22), metals; Kitchener and Prosser (23), pyrex glass; and Black *et al.* (24), fused silica. Recently, von Silfhout (25) succeeded in improving the accuracy of these measurements considerably so that now a real test of the theory seems possible.

No one has yet succeeded in measuring the attraction as a function of the distance with a liquid medium between the plates. The main difficulty is the viscous resistance of the medium and the very small values of the force (fractions of a dyne), which makes the rate at which equilibrium is reached too small.

Several investigators have made measurements of the attraction force between objects "in contact," in some cases even in the presence of a liquid medium, but the uncertainty in the distance of closest approach and the influence of deformations around the point of contact make quantitative interpretations difficult. The results are in semiquantitative agreement with the expected value for nonretarded van der Waals forces.

Theory of Colloid Stability Based on Electrostatic Repulsion and van der Waals Attraction

If the electrostatic repulsion and the van der Waals attraction are combined, curves of energy against distance are obtained, as illustrated in Figure 9 for flat plates with a narrow gap and in Figure 10 for two spheres. The typical features of these curves are determined by the fact that the electrostatic free energy is an *exponential function* of the distance (at least approximately) and the van der Waals energy an *inverse nth power*
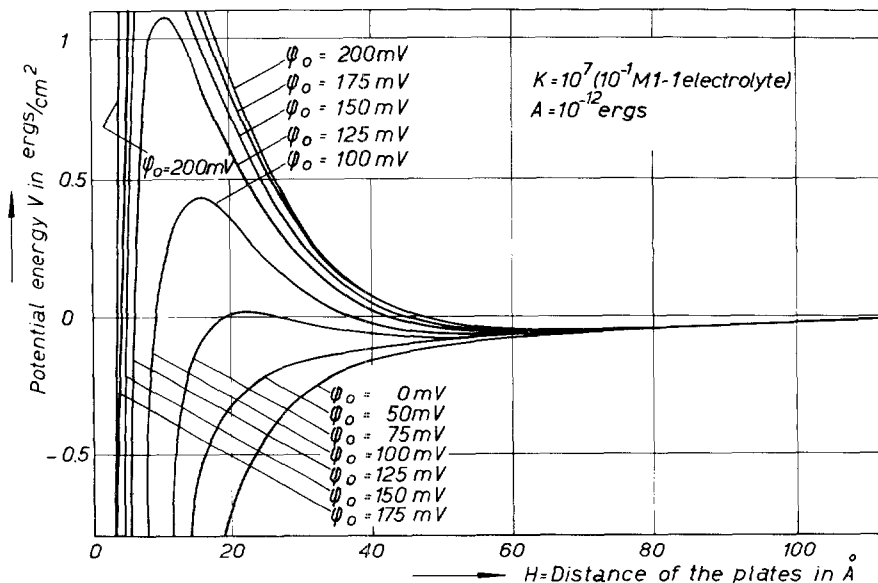
FIGURE 9. Free energy of interaction between flat plates with electric double layers immersed in 0.1 M monovalent electrolyte, for different values of the surface potential and a mutual Hamaker constant $A = 10^{-12}$ ergs. [Verwey and Overbeek (6).]

(second power for the flat plates). Both for very short distances and for very large distances, the inverse nth power is always more important than the exponential function and, consequently, the van der Waals forces prevail always at large and at small distances. In the intermediate range the exponential function may or may not outweigh the inverse nth power, depending on the actual values of the coefficients.

When salt is added to a suspension and causes flocculation, the repulsion curve becomes steeper so that its range is shortened, and the repulsion loses its ability to overcome the van der Waals force which at this shorter distance is so much stronger. This is particularly well illustrated in Figure 10, where the different curves correspond to different electrolyte contents. At the lower electrolyte contents an energy barrier of 10 kT or more keeps the particles separated, but at higher electrolyte content ($\kappa >$ 10^6) this barrier disappears and every Brownian collision leads to permanent contact.

The coagulation concentration must be close to the condition in which the energy barrier just disappears, or in which the energy curve just touches the horizontal axis. This leads, for the case of flat plates, to the following conditions which must be simultaneously satisfied:

$$V_{tot.} = \frac{8\epsilon k^2 T^2}{\pi e^2} \frac{\kappa \gamma^2}{z^2} e^{-\kappa H} - \frac{A}{12\pi H^2} = 0 \quad \text{and} \quad \frac{dV_{tot.}}{dH} = 0 \quad (14)$$
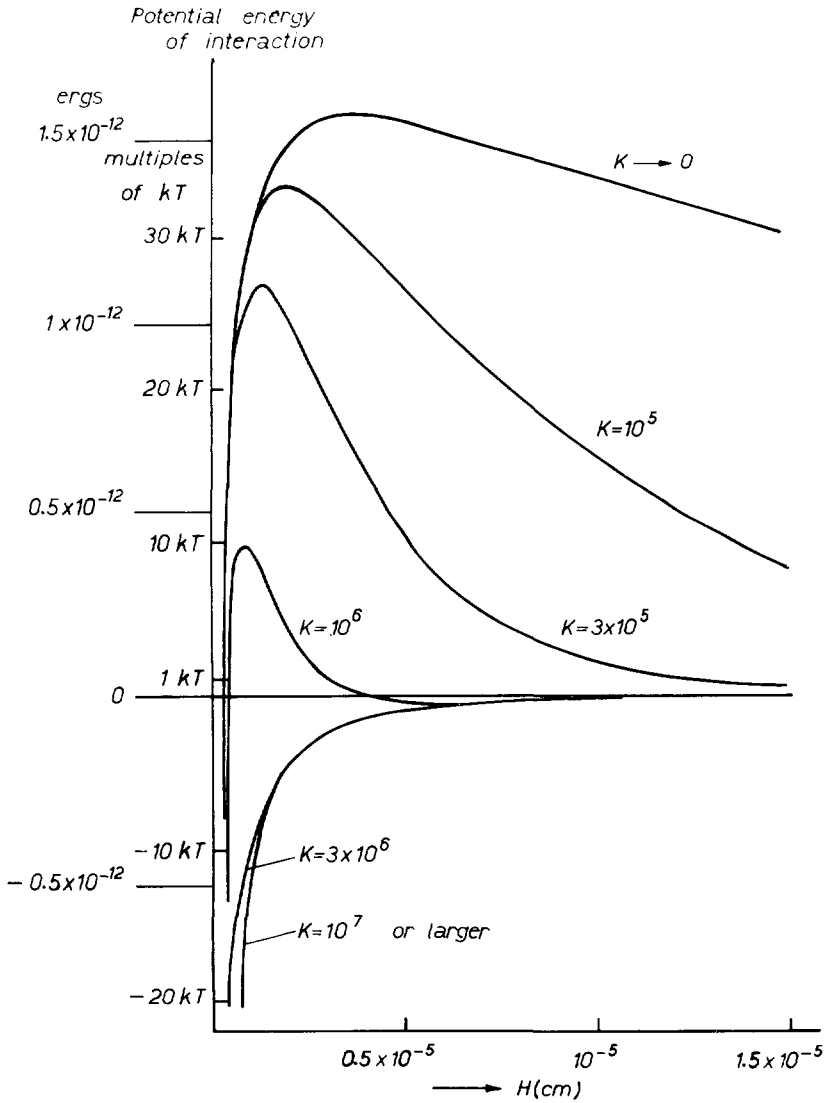
FIGURE 10. Free energy of interaction between spherical particles (radius 1000 Å) in electrolyte solutions of various concentrations ($c \approx 10^{-15}\kappa^2$ mol/1). Surface potential 25.6 mV; $A = 10^{-12}$ ergs. The energy scale is given in multiples of kT and in ergs. [Verwey and Overbeek (6).]

Or, combining constants and less interesting variables such as T and ϵ leads to

$$P\frac{\kappa}{z^2}\gamma^2 e^{-\kappa H} - \frac{Q}{H^2} = 0 \quad \text{and} \quad -P\frac{\kappa^2}{z^2}\gamma^2 e^{-\kappa H} + \frac{2Q}{H^3} = 0 \quad (15)$$

From these two equations it follows directly that

$$\kappa H = 2 \tag{16}$$

Inserting this in one of the Eqs. 15 and rearranging, we find

$$\kappa z^2 = \frac{4 P \gamma^2 \exp(-2)}{Q}$$

or, remembering that (from Eq. 5)

$$\kappa = zC\sqrt{c} \tag{17}$$

where C is a constant, we find

$$z^3\sqrt{c} = \frac{4 P \gamma^2 \exp(-2)}{Q C} = \text{const.} \tag{18}$$

or

$$c \approx \frac{1}{z^6} \tag{19}$$

This relation predicts that for high potentials ($\gamma = \text{constant} \approx 1$) and constant temperature and dielectric constant, the flocculation concentrations are proportional to the inverse sixth power of the valence of the counterion.

Flocculation concentrations for monovalent, divalent, and trivalent ions are in the ratio

$$1 : \frac{1}{2^6} : \frac{1}{3^6} = 100 : 1.56 : 0.137 \tag{20}$$

which is in fair agreement with the experimental data for As_2S_3 (see Table I), $Fe(OH)_3$ (Table II), and many other hydrophobic colloids. The agreement is indeed quite good when one recalls the considerable simplifications that have been used in the derivation of Eq. 19.

These considerations have been independently developed by Derjaguin and Landau (26), by Verwey (27), and by Overbeek (6), and explain the flocculation of colloidal and coarser systems by simple electrolytes quite well.

The shallow minimum in the potential-energy curves at relatively large distances between the particles (see Figures 9 and 10) is not deep enough to play a role for small particles. For large particles and emulsion droplets it may be a cause for flocculation, and it is certainly an important factor for black soap films, as discussed in more detail in the next section.

PART II. PARTICULAR CASES AND APPLICATIONS

Introduction

In the previous section a general framework for understanding the stability of colloidal suspensions against flocculation was given. The simultaneous presence of attractive and repulsive forces is essential for the explanation given. It will be obvious that, when further details are studied, many special systems with special properties can be found.

In the first place, the structure of the electric double layer is complicated by the individual properties of the ions. They are not really point charges, but have a certain volume, a polarizability, adsorbability at the interface, etc. In more detailed quantitative studies of the double layer these properties play a role and they manifest themselves in the stability, for example, in the small values of the coagulation concentrations for certain organic ions as described in Table I. We shall not enter into further details here, though one should not lose sight of such specific effects. In this section, rather, a number of examples of stability and flocculation with special aspects will be examined, and a few of the many practical applications will be considered.

Emulsions and Foams

So far our attention has been mainly directed toward suspensions of solid particles in a liquid (usually water). If we look now at the behavior of small liquid droplets dispersed in another liquid or of gas bubbles in a liquid, i.e., at emulsions and foams, we find that the stability of such systems is really governed by several factors. Small droplets and bubbles are subject to a somewhat larger excess pressure (due to the higher curvature of the interface) than large ones. This drives the material from the small bubbles and droplets to the large ones and leads to a coarsening of these systems. The effect is quite important for foams and not negligible for some emulsions. Second, as the particle in foams and emulsions are usually larger than 1μ, the influence of gravity causes creaming (with emulsions) or drainage (with foams), and the rate of these processes depends strongly on the viscosity of the continuous phase. Figures 11 and 12, taken from work by de Vries (28), demonstrate both effects for foams. The liquid in Figure 12 had a much greater viscosity than that in Figure 11. Therefore, the foam of Figure 11 drains rapidly to a so-called polyhedral foam, but in the same time the foam in Figure 12 has hardly
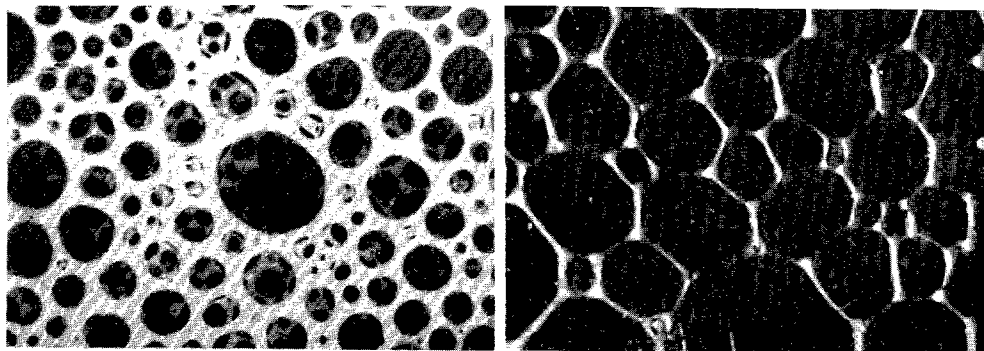
Figure 11. Foam prepared by dispersing gas bubbles in a liquid (an emulsion) of low viscosity (11 centipoise) drains to a polyhedral foam. (a) Immediately after preparation; (b) 15 min. later. [de Vries (28).] (13.5 X, linear)

drained at all. Nevertheless, diffusion of gas from small to large bubbles has visibly coarsened the foam in Figure 12.

Apart from creaming and coarsening by diffusion, an emulsion may be stable in the same sense that a suspension is stable; that is, although Brownian motion brings the emulsion drops together, they do not adhere permanently but retain their independence. If, however, the emulsion flocculates, the droplets form agglomerates ("bunches of grapes"), but in these agglomerates they may still remain individual droplets. As the droplet size of most emulsions is a good deal larger than that of colloidal suspensions, the coagulated droplets can usually be separated again by
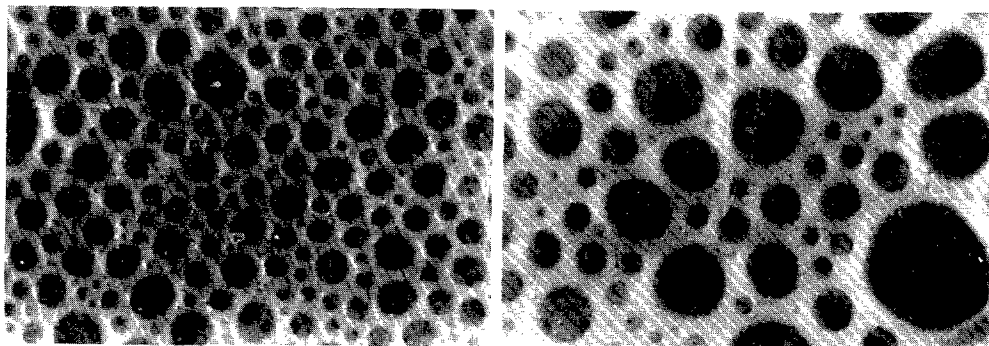

Figure 12. Foam prepared by dispersing gas bubbles in a liquid (an emulsion) of high viscosity (65 centipoise). Hardly any drainage in 15 min., but coarsening by diffusion obvious. (a) Immediately after preparation; (b) 15 min. later. [de Vries (28).] (13.5 X, linear)

shaking or stirring.* But the coagulated droplets may also coalesce; that is, they actually flow together and form one larger drop.

In this two-stage process of coagulation and coalescence, the first stage is very similar to coagulation of suspensions. The second stage, which cannot occur in suspensions, is also found in foams. Coalescence of emulsions and breaking of foams are quite similar processes, and similar also to the coalescence of individual water or oil droplets attached to a fiber. In this coalescence process, the critical stage is the formation of the first small hole in the lamella remaining between two bubbles or drops. This hole will then enlarge rapidly and spontaneously. de Vries (28) has shown that the formation of the first hole requires an activation energy which is very large, a great many times kT, unless the film is extremely thin (< 30 Å). The rate of drainage and the probability of rupture are therefore important properties of the lamellae.

Drainage and Breaking of Soap Films

Since the behavior of foams and emulsions is so largely governed by the properties of thin lamellae of liquid, the study of individual thin liquid films is a promising field, especially since the thickness of such films can be determined quantitatively by observing the interference colors in reflected light. Figure 14 gives an example of a soap film in a glass frame, drawn out of a soap solution and photographed in reflected white light. The correspondence between color and thickness of the film is indicated.

Soap films owe their remarkable stability to the fact that soap molecules (and any other molecules that are composed in a similar way from a large hydrophobic and a hydrophilic part) have a strong tendency to adsorb at the water-air (or water-oil) interface. The hydrophobic part of the molecule has no affinity for water and is driven out of the bulk of the solution to the interface. This adsorption is accompanied by a lowering of the surface tension. A local thinning of the soap film might threaten its permanence, but in local thinning the adsorbed soap molecules are drawn farther apart, exposing more water and thus increasing the surface tension. This increased surface tension will contract the soap film just at the place where it threatened to become thin and break. This self-repairing or damage-preventing effect is called the Gibbs-Marangoni effect (29, 30).

*The ease of redispersion may also be connected with the fact that the emulsion droplets may be flocculated in the shallow minimum of the potential-energy curves, at a relatively large distance between the droplets, rather than in the deep minimum at close contact (cf. Figures 9 and 10).

Soap films can thus be considered as two nearly close-packed mono-layers of soap molecules with a layer of aqueous soap solution between them, as shown schematically in Figure 13.

Under the influence of gravity, such soap films become thinner because the water layer drains away. The rate of this drainage process depends greatly on the mechanical properties of the monomolecular surface layers. If they are rigid, drainage is due to viscous flow of the aqueous layer between virtually solid walls. This is a slow process which takes many hours for soap films of a few centimeters height. But if the surface layers are mobile, turbulent motions in two dimensions are possible. At the places where the soap film is attached to the bulk liquid, to the glass or metal frame, or (in a foam) to other soap films, a thicker region is formed, which is called the *Plateau border*. Thick film is sucked into these borders while, simultaneously, an equal area of thin film is drawn out of them. As a consequence of this process, which has been called *marginal regeneration* by Mysels, *et al.* (31), the thinning of the film as a whole is much more rapid and takes only minutes instead of hours.

Figure 15 and Figure 16 give examples of a slowly draining rigid film and a rapidly, turbulently draining mobile one, respectively. On further draining, "black" parts develop in both types of film. Here the film is so thin that the interference between light reflected from the front and the
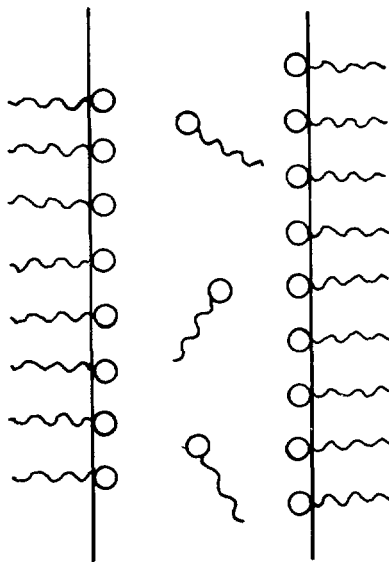

FIGURE 13. Schematic representation of cross-section through a soap film. Polar ends of soap molecules are represented by circles; the apolar tails by wavy lines.

FIGURE 14. Vertical soap film in reflected white light. Layers of constant thickness are horizontal and → arranged in order of increasing thickness in the downward direction due to gravity.
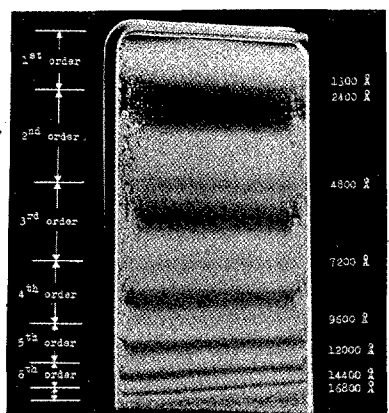

FIGURE 15. Slowly draining rigid soap film. The surface is so stiff that the force of gravity is not enough to smooth out thickness variations at one horizontal level.
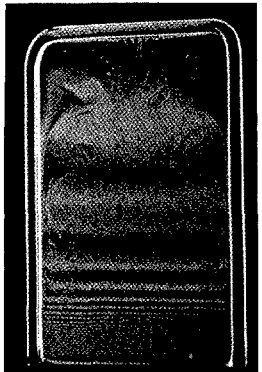

FIGURE 16. Rapidly draining mobile soap film. Note the highly turbulent motion in the top part of the film and the color variations (variations in thickness) all along the vertical borders.
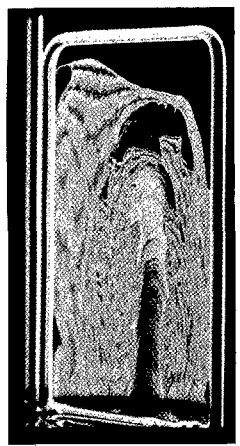
FIGURE. 17. Rigid film after prolonged drainage. Note the sharp boundary between black and colored film and the single rather broad stem of marginal regeneration.
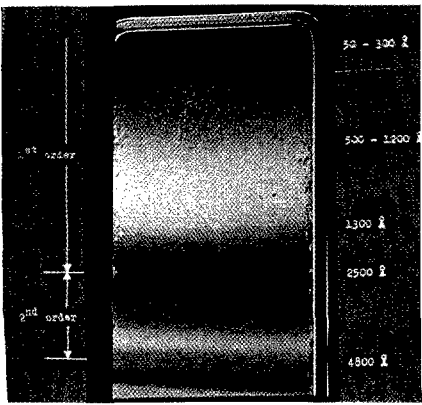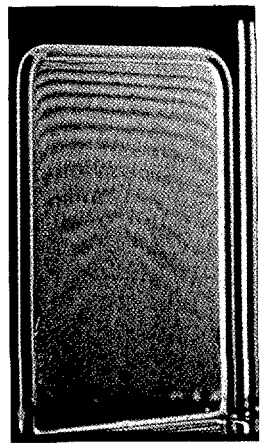

FIGURE 18. Mobile film, the same as that of Figure 14, after longer drainage.

back of the film is nearly completely in counterphase, so that only very little light is reflected. By measuring the small intensity of the reflected light, one can determine the thickness of these *black films*. The thinnest are just two layers of soap molecules with a few molecules of water of hydration between them, but in many cases the black films still contain water layers of 100 Å and thicker. Figures 17 amd 18 show how these black films are sharply separated from the colored films. The thickness of the soap film changes in a nearly discontinuous way from about 500 Å to 1000 Å to 50 Å to 300 Å. The thickness of black films depends on their electrolyte content, and for a sufficiently high electrolyte content the film is reduced to essentially a bimolecular soap layer.

It has already been mentioned in Part I (see Figure 8) that van der Waals forces promote thinning of a film. The van der Waals pressure, proportional to the reciprocal third or fourth (retardation) power of the thickness, becomes stronger, the thinner the film and would rapidly lead to its rupture unless a repulsion were to prevent the further approach of the soap layers. As these soap molecules are ionized they form electric double layers, and, when the repulsion between the two double layers is strong enough, an equilibrium is reached corresponding to the shallow minimum in the energy against distance curves of Figure 9 [cf. Overbeek (32)]. Consequently, the study of these black equilibrium soap films gives information on the van der Waals and electrostatic forces that is useful in considering not only soap bubbles and foams but colloid chemistry as a whole.

Recently, Vrij (33) has shown that the surfaces of soap films are not quite flat but are slightly corrugated due to statistical fluctuations. It is possible to measure the extent of these fluctuations by surface-light scattering and to derive information on the interaction forces in the film from it.

Vrij (34) has further developed this idea of surface fluctuations and has shown that some of these fluctuations will grow spontaneously (essentially by the same mechanism as depicted in Figure 8) and be the cause of breaking of the film.

From the above it will be clear that in the present situation soap film research offers several important methods that may lead to a better understanding of flocculation and stability in general.

Surfactants as Stabilizers

Soaps, and surfactants in general, are powerful stabilizers for suspensions and emulsions, as is evident from their wide application in launder-

ing and detergency. The mechanism of their action is similar to that of potential-determining ions; that is, they are strongly adsorbed at small concentrations and convey a charge to the surface. Their amphipathic nature (amphipathic means having a strongly apolar and a polar part) causes them to adsorb at a great variety of interfaces, including the water-air interface. In this they are superior to the much more specific potential-determining ions.

The reason that they are so strongly adsorbed, nearly independent of the nature of the phase (in contact with the aqueous solution), has already been briefly indicated in the section on soap films. If a hydrocarbon chain is inserted between them, a good deal of energy has to be supplied to break these waterbonds, but, if the surfactant molecule is at the interface, its polar part can be hydrated with gain in free energy without the loss necessary to force the nonpolar part into water. [There are substances that are surface active in less polar liquids than water (in particular, fluorinated hydrocarbon derivatives), but the effects are hardly so pronounced as for water.]

The extent of the adsorption of surfactants is often quite large. More or less compact monolayers may be formed which carry a surface charge on the order of one elementary charge per 50 Å^2 or 25 μ Coulomb/cm^2, and this is at least as great as the charge due to the adsorption of potential-determining ions. Consequently, ionic surfactants may be considered to stabilize by electrostatic repulsion. In the coagulation of such suspensions or emulsions, the rule of Schulze and Hardy applies, except for those ions which form undissociated or insoluble molecules (H^+, Ca^{++}, etc., in the case of ordinary soaps).

In developing synthetic surfactants, not only a great variety of anionic and cationic surfactants have been produced, but also nonionic surfactants; many of these are less prone to reaction with hydrogen ions or multivalent cations. A few examples of both kinds are: sodium lauryl sulphate and other alkyl sulphates and sulphonates ($C_nH_{2n+1}OSO_3Na$, $C_nH_{2n+1}SO_3Na$); cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$) and similar structures; and octylphenol polyglycol ether (C_8H_{17}⟨◯⟩—

($O—CH_2—CH_2)_nOH$) with n varying between 4 and 30. These nonionic surfactants can also stabilize emulsions and suspensions, but obviously the electrostatic mechanism, although not completely absent, is not the main stabilizing factor in these cases. They are strongly adsorbed for the same reasons as ionic surfactants and in the adsorbed state form a hydrophilic layer of considerable thickness which acts more or less as a mechanical buffer around the particles. This type of repulsion is described as steric or entropic; the last term points to the fact that interpenetration

of the layers of hydrophilic groups, even if they are not closely packed, results in a decrease of the entropy (due to the higher local concentration). The range of this repulsion does not extend beyond the length (or rather twice the length) of the polar group, but this may be enough to prevent a very deep van der Waals minimum of energy to be reached. Often such suspensions or emulsions do coagulate in the sense that aggregates are formed, but these aggregates can be redispersed by moderate stirring.

Sensitization and Protective Action

Just as is the case with surfactants, many macromolecules which are soluble in water are easily adsorbed at interfaces. They are therefore also adsorbed on colloidal particles, covering them with a relatively thick layer which can keep the particles separated to such a distance that the van der Waals attraction is not strong enough to bind them together. As the range of this repulsion by macromolecules may be a good deal larger than in the case of nonionic surfactants, they are more effective stabilizers—so effective, that the particles lose their sensitivity to salts and behave as if they were of the same nature as the adsorbed macromolecules. A particle of colloidal gold covered by gelatin behaves as gelatin "with a golden heart." This is called protective action, and it is quite an important method of bringing, or rather keeping, particles of widely varying nature in suspension in solutions of widely varying compositions. Natural latex and milk are both emulsions protected by a layer of protein and, therefore, stable against coagulation.

If the same macromolecular substances, however, are added to a suspension in an amount not great enough to give protection, one usually finds that the suspension is *more* prone to flocculation. It is *sensitized* (35). The coagulation concentration as a function of the concentration of macromolecules first decreases (sensitization) and then increases to very high values (protection), as shown schematically in Figure 19. Sensitization is easily explained. The large molecules obviously have many groups or segments with which they can attach to the adsorbent surface. If the macromolecule is present in sufficient excess, all adsorption sites are covered by individual macromolecules. But if there is no excess, some macromolecules may be attached to two sites on different particles and thus bind these particles together. Loosely built, open flocs with a large sediment volume are formed in this way, and this openness may be a big advantage in the ease of filtration and drying (36). These flocculation aids (e.g., polyacrylamide) are also used as soil improvers by keeping the soil colloids in a flocculated and open state in which air and moisture can circulate easily.
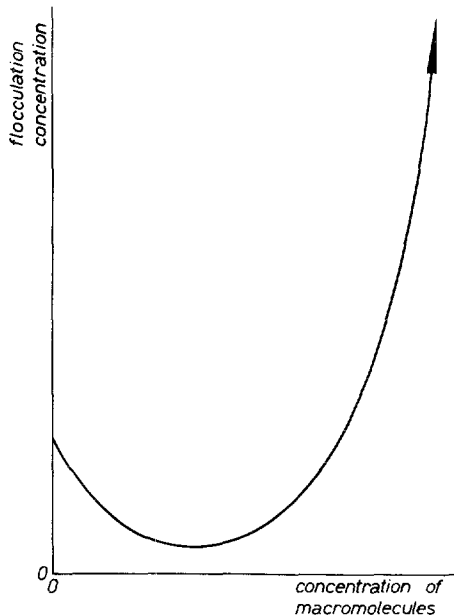
FIGURE 19. Sensitization (lowering of the coagulation concentration) and protection by the same macromolecular substance in different concentrations.

Clays (37)

Clays have a series of special aspects which justify their separate treatment. As found in nature, clays have a particle size in the colloid range. Being silicates with a lamellar lattice structure, they usually have lamellar particles. Their charge is based on two different mechanisms. One is a simple dissociation-association equilibrium of surface oxygen atoms at the broken edges. In acid media these oxygens may adsorb protons and acquire a positive charge. In alkaline media protons may dissociate from hydrated surface groups, leaving a negative charge behind. But apart from this amphoteric mechanism, clays carry a more permanent negative charge as a consequence of isomorphic substitution in the lattice. If, as indeed occurs, a Si-ion in the lattice is replaced by an Al-ion without any further change, then the lattice acquires a negative charge, which is compensated outside the particle by, for example, Na^+-ions forming a diffuse double layer around the clay particle. The same phenomenon occurs if Al^{+++} is replaced by, for example, Mg^{++}. This "permanent charge" may be quite large, amounting to 0.1 to 1 milliequivalent per gram of clay.

The combination of this fixed negative charge and the variable charge on the edges, which is positive in an acid medium, leads to a strong de-

pendence of the flocculation behavior on the pH and to a very special type of flocculation where + and − charges are both present on one particle. Card-house structures, that is, very open flocs, may be formed by attraction between + and − sites.

Suspensions and Emulsions in Nonpolar Media

If a liquid or solid is dispersed in a nonpolar medium, the very general nature of the van der Waals forces leads us to expect that such a dispersion will flocculate, unless some mechanism for repulsion is present. Such a mechanism may, again, be electric or steric in nature. At first sight it may seem rather improbable that enough ionic charges can be present in a medium such as benzene or cyclohexane to give a sufficiently strong repulsion because, as a consequence of the low dielectric constant, dissociation in such a medium is extremely low. It can, however, be shown, for example, by conductance measurements, that salts containing ions with a large nonpolar part attached to the charged group do dissociate (38). Electrophoresis experiments (39) prove that the dissociation products do adsorb at interfaces. In general, the more polar ion is adsorbed; the less polar one stays in the solution. Examples of such salts are tetra-isoamyl ammonium picrate or salts of fatty acids and multivalent cations, which can dissociate into a large positive and a large negative ion:

$$\text{Cu(oleate)}_2 \rightleftharpoons \text{(Cu oleate)}^+ + \text{oleate}^-$$
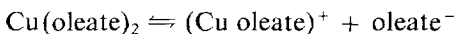
In favorable circumstances the electric charge per particle is large enough to prevent agglomeration. The range of the repulsion is always large because, as a consequence of the low ion content, the thickness of the double layer is very large.

An interesting influence of the size of the particles occurs in this case, as contrasted to the ionic mechanism of stabilization in water where particle size is not an important variable. In water near the flocculation limit the range of the electric forces is usually small as compared to the particle size, and the relevant forces and energies are really concentrated in the region of closest approach of the two particles. Therefore, the over-all size of the particles is only of secondary importance. In nonpolar media we have, as pointed out by Koelmans (40), either an electrostatic repulsion of very long range (essentially Coulomb repulsion, practically unhindered by the countercharge) or a steric repulsion (protection) with a steep gradient at a small distance. The electrostatic repulsion is roughly proportional to the square of the particle charge, and if either the charge per unit area or the surface potential are considered to be constants, the force decreases with decreasing particle size. For small particles it may

TABLE III. Energy of Electrostatic Repulsion in a Medium of Low Dielectric Constant (Xylene, $\varepsilon =$ 2.3) Between Two Particles in Contact ($\varphi_0 =$ 100 mV; $1/\varkappa = 5\,\mu$)

Particle Radius (cm)	$V_{repuls.}/kT$
10^{-4}	200
10^{-5}	20
10^{-6}	2

not be strong enough to counteract the van der Waals forces. Table III shows how, for a surface potential of 100 mV and a double-layer thickness $(1/\kappa)$ of 5 μ, the energy of repulsion will certainly be too small for 100 Å particles and possibly also for particles with a radius of 1000 Å, but is probably strong enough to keep particles of 1 μ separated.

On the other hand, the steric repulsion can at best keep the particles separated by a fixed distance. At that distance the van der Waals force increases with increasing particle size and may, as shown in Table IV for a

TABLE IV. Energy of van der Waals Attraction for a Case of Steric Protection by Two Layers of 20 Å $(H = 40\,Å)$ and a Hamaker Constant, $A = 10^{-13}$ ergs

Particle Radius (cm)	$V_{attr.}/kT$
10^{-4}	51
10^{-5}	4.2
10^{-6}	0.1

distance of separation of 40 Å (two layers of 20 Å thick) and a Hamaker constant of 10^{-13} ergs, lead to flocculation of particles of 1 μ, but leave particles of 100 Å free.

Consequently, for large particles the steric mechanism is less favorable for stabilization than electrostatic repulsion, whereas for small particles the situation is just reversed, as summarized in Table V. These facts have been found in investigations of suspensions of various inorganic solids in oil (40). For dilute emulsions of water in oil, the same reasoning applies, but for more concentrated emulsions, the long range of the electrostatic forces is not effective as in such an emulsion the droplets are already much closer together than the range of the repulsion [cf. Albers and Overbeek (41)].

A third mechanism of stabilization of emulsions was described long ago by Pickering (42). It is based on the introduction of small solid particles in the emulsion.

TABLE V. Particle Size and Stabilizing Mechanism

Particle Size	Stabilizing Mechanism	Stability Against Flocculation
Large	Ionic double layer	Stable
Large	Steric protection	Flocculated
Small	Ionic double layer	Flocculated
Small	Steric protection	Stable

In an oil-water system, the equilibrium position of solid particles depends on the three interfacial tensions. The particles may either be completely wetted by one of the two phases (if the interfacial tension between the solid and the other of the two phases is high enough) or, when there is a finite contact angle, they will accumulate at the interface. Depending on whether the contact angle (as measured in the aqueous phase) is sharp or obtuse, the particles will protrude into the water or protrude into the oil phase. If they protrude into the aqueous phase they will prevent oil-oil contacts and stabilize an oil-in-water emulsion, or, if they protrude into the oil phase, they will promote a water-in-oil emulsion.

Repeptization and Deflocculation

In many cases of practical application one is interested not only in preventing the agglomeration of particles in a suspension, but also in dispersing the particles, starting with the agglomerated state. For this process the terms redispersion, repeptization, or deflocculation have been used almost interchangeably. In cases where the repulsion mechanism is wholly or partly steric (protective action) and where agglomeration has been caused by concentrating the suspension or emulsion by sedimentation or by drying, repeptization is not difficult to understand. In the agglomerates the particles are still separated by a rather thick protective layer, and, if the system is mixed with a larger amount of liquid, redispersion may take place spontaneously by Brownian motion or be promoted by a moderate mechanical action such as stirring or shaking.

It is more difficult to redisperse agglomerates that have been formed by taking away the electrostatic repulsion, although in a number of cases, redispersion occurs, as anybody knows who has ever washed a sulphide precipitate and seen it pass through filter paper when the washing has proceeded far enough. The difficulty in understanding the possibility of redispersion here is that, in the agglomerates, the particles are very close together, at least in the "points of contact," and, therefore, van der Waals attraction is strong. The washing-away of the precipitating elec-

trolyte may restore the potential barrier between the particles (cf. Figure 10), but the particles are now on the wrong side of the barrier and the question is, "How can they overcome this barrier?" The answer is probably complex. Redispersion is the exception rather than the rule, and presumably a number of favorable factors have to coincide to produce it. To begin with, the van der Waals attraction in the agglomerates should not be too strong. Therefore, face-to-face contact between particles is unfavorable and contact only at protuberances or edges is favorable for redispersion. Such protuberances may to a certain extent act as "steric protective layers." The solvent itself may act as a protective agent, as was shown by Mackor (43) to be the case for silver iodide in acetone.

Apart from these geometric and steric factors, the sluggish rate of attainment of the adsorption-desorption equilibrium of the potential-determining system may play an important role.

By changing the salt concentration one changes immediately (say in 10^{-7} sec.) the thickness of the double layer. This changes the ratio between surface charge and surface potential and, therefore, the surface potential is no longer at its equilibrium value; the surface charge has to be adjusted by adsorption or desorption of charge carriers. In repeptization the electrolyte content is suddenly lowered, so that at constant surface charge the potential increases very strongly. This leads to an extra repulsion as compared to the situation where the sol was flocculated. This extra repulsion may be high enough to explain redispersion. Certain metal sols [e.g., silver sols prepared by the citrate method of Lea (44)] which were known to show redispersion have for a long time been considered as protected colloids. In current experiments in the author's laboratory, Frens (45) is showing that the redispersion of these sols and of analogous gold sols depends on the slow attainment of equilibrium of the potential-determining system.

Applications

Before a few of the numerous applications of these considerations on colloid stability are cited, it should be mentioned that, at least in aqueous media, the pH often is a very important variable for flocculation and deflocculation. This is due to the fact that, in so many cases, the pH is directly or indirectly potential-determining, and often an isoelectric point (or point of zero charge) may be found in the attainable pH region. In suspensions of inorganic oxides, charge and surface potential shift to more negative values when the pH is increased. The same is true for metals when they can be considered as oxygen or hydrogen electrodes. Many

protective agents such as proteins, carbohydrates, or synthetic ionized polymers contain carboxyl or other groups which are sensitive to the pH. Even in the apparently simple case where dispersions are flocculated by polyvalent ions such as Th^{4+} or Al^{3+}, the flocculating ions will hydrolyze at higher pH, and the flocculating agent may rather be a complex ion or even a small colloidal particle of the hydroxide with a higher (or lower) charge than the single unhydrolyzed ions.

Emulsions both of oil in water and of water in oil find many applications. A good example is the emulsion polymerization process by which many polymers, among them G.R.S. and other rubbers, are prepared in very large quantities. Here usually a stable, but rather coarse, emulsion of the monomer in an aqueous solution is the starting point. This emulsion is stabilized by soap, which is present in excess. During the polymerization the rubber is produced in the form of a large number of very small latex particles, which are stabilized by the excess soap present in the reaction mixture. The ultimate size of the latex particles depends on the amount of soap available for their protection; the more soap, the smaller and the more numerous the particles. After the polymerization is stopped, the stability of the latex is destroyed by the addition of acid and/or salts so that the rubber can be obtained in massive form and be freed from contaminants present in the reaction mixture, or the latex may be used as such and its colloid stability only destroyed when it has received its definitive shape (dipping process, electrodeposition). One of the advantages of working with emulsified systems is the high fluidity of these emulsions as compared to bulk or dissolved polymers, which allows easy stirring, mixing, and transport, and good heat exchange.

Emulsions are often used for pharmaceutical, cosmetic, and agricultural purposes to disperse oil-compatible substances in water or water-compatible substances in oil. Emulsions of oil in water are easy to stabilize and usually are quite fluid; emulsions of water in oil are more difficult to stabilize, as mentioned previously. They are often flocculated, but not coalesced and, if concentrated, have a pronounced plastic behavior like butter or wet clay.

Foams, which can conveniently be considered as emulsions of gas in water, have found several applications, but sometimes they are a terrible nuisance. One of their assets is a relatively high mechanical strength at a very light weight. This is used in foam rubber, which is usually made by blowing latex into a foam and coagulating it in that state. Another asset of foams is their ability to keep particles suspended in the foam lamellae or at the gas-liquid boundary. This property is essential for the *froth flotation* of minerals and is helpful in preventing redeposition of dirt in the washing process.

The large specific volume of foams is often a nuisance, however, so that defoaming agents are frequently used. Amphipathic substances with a small, nonionized polar group such as octyl alcohol are efficient defoaming agents. They displace the soap (or other foam stabilizer) from the surface but do not build up the electric double layer that is necessary to prevent rupture of the black films.

An application on a very large scale is found in the manipulation of agricultural *soil*. The use of certain macromolecules as soil improvers has already been mentioned. Another application is found in the treatment of clay soils which contain a large amount of salt. A clay soil is normally in the flocculated state, owing to the presence of a sufficient amount of Ca^{++}-ions. If such a soil is flooded by sea water, the Ca^{++}-ions are exchanges against sodium ions; the soil remains flocculated on account of the high sodium chloride concentration, but in this state it cannot be used for agriculture. When the salt is washed away by rain water, the Ca^{++}-ion concentration and the Na^+-ion concentration decrease simultaneously. A state can then easily be reached with such a low Ca^{++} and Na^+ content that the clay deflocculates. If it is mechanically treated in this state, it forms a stable suspension which, under the influence of gravity, settles to a very dense sediment, virtually impermeable to air and water and, for a long period, unsuitable for agriculture. The old practice consisted in leaving such a soil untouched for several years, until the Ca^{++}-ion concentration was slowly restored under the influence of CO_2 and weathering processes, before ploughing or applying other mechanical treatments. If, however, before all the Na^+ is washed away the soil is treated with Ca^{++}—and gypsum is a cheap enough source for Ca^{++}—deflocculation can be prevented and the soil used again after a much shorter period of waiting.

Water treatment is another field in which colloid chemical methods are applied. Water often contains a small, but undesirable, amount of suspended materials that easily forms, because of the low salt content, stable suspensions which do not sediment and pass many conventional filters. Flocculation by addition of large amounts of electrolytes is obviously out of the question, but small amounts of Al^{+++} or Fe^{+++} salts, which by hydrolysis form positively charged colloidal particles, are powerful flocculants for the negatively charged suspended materials. The mutual attraction between + and − charges overcomes the rather slow flocculation which would otherwise result from the small concentration of the contaminants.

In *washing* and *laundering,* deflocculation of dirt particles is one necessary aspect; prevention of redeposition by keeping the deflocculated material in this state is another. As mentioned before, foam may be useful

in helping to prevent the coarser dirt particles from sedimenting, or it may be a nuisance that has to be avoided or at least controlled in mechanical washing processes. If these various properties have to be combined in one detergent, it is usually necessary to make rather complicated mixtures of soaps, other surfactants, salts, etc.

Suspensions used in *paper coating* often contain a mixture of suspended materials such as clays, resins (or latexes), and pigments; the presence of stabilizers, often from the category of macromolecular protective colloids, is essential. During handling, such a suspension has to be stable, otherwise undesirable agglomerates are formed, but, on the paper, the stability has to be diminished to the extent that the suspended materials adhere to the paper fibers. Alum can be used for this purpose.

The final applications that should be mentioned are the great variety of *paints* and *inks* in which particulate pigments are distributed as finely as possible, either in water or in oil, or even in an oil-in-water emulsion, as in the modern emulsion and latex paints. As the general trend is to use finer and finer pigment particles because of their better optical properties and to be very critical about the occurrence of aggregates which spoil the smooth aspect of the painted or inked surface, huge amounts of stabilizing agents, ionic, nonionic, and polymeric surfactants, are used in this field. In these systems, again, easy flow is desirable during handling, brushing, or spraying, but once the coatings are applied on the surface, they should not flow any more; that is, they must have a certain amount of thixotropy. To obtain these properties for often rather complicated mixtures of dispersed materials is quite an art, but in order to find a more systematic way through this maze of difficulties, the very general principles of colloid stability as treated herein will serve as a useful guide.

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