or no micelle formation takes place. Such behavior is not unexpected since light scattering experiments[5] have shown that a homologous detergent does not form micelles. Therefore light scattering,[5] and ultracentrifuge data give the same qualitative results. These studies indicate that the number of molecules per micelle is highly dependent on the composition of the detergent.

Although Igepal CO-710 and Surfonic N-95 are similar detergents, the numbers of molecules per micelle are considerably different for the two detergent solutions. This is not unexpected, since the two detergents have been shown to differ markedly in other respects such as adsorption properties.[22]

DISCUSSION

M. E. Ginn (Monsanto Chemical Co.).—Is micellar molecular weight independent of total concentration as a general rule, as the data suggest?

C. W. Dwiggins, Jr.—As a general rule, it would not be expected that micellar molecular weights would be independent of the total concentrations. However, for the low concentrations and experimental conditions involved, the dependence appears to be low for the non-nonic detergents studied. It probably would become quite noticeable as the concentrations necessary for gel formation are approached or at near the critical micelle concentration.

H. B. Klevens (Klevens Associates).—Helix formation

(22) H. N. Dunning, Chem. Eng. Data Series, 2, No 1, 88 (1957).

seems to play a role in ethylene oxide and propylene oxide polymers. With this in mind, it would be easier to accept a value of 2–3 molecules per micelle rather than that of one.

C. W. Dwiggins, Jr.—The Pluronic L-64, detergent was found to contain approximately 1 molecule per micelle, assuming that the molecular weight reported for this detergent is correct. Light scattering experiments of A. M. Mankowich gave an aggregation number of only slightly greater than 1 for a similar detergent.

Donald G. Dobay (B. F. Goodrich Company).—Could you comment further on the great difference in number of molecules per micelle between surfactants of approximately the same chemical structure and composition?

C. W. Dwiggins, Jr.—At the present state of knowledge it would be quite difficult to explain this difference since there are many possible explanations. Rather weak forces are involved in micelle formation. Variation in chain length distribution could be partially responsible, or possibly slight contamination of the detergent by some unknown material. As detergents of higher purity and narrower chain length distribution become available, these questions perhaps can be resolved.

Irwin H. Billick (Esso Research and Engineering).—Did you make any measurements of the critical micelle concentration?

C. W. Dwiggins, Jr.—Not in this work. Surface tension studies by Lun Hsiao, H. N. Dunning and P. B. Lorenz (J. Phys. Chem., 60, 657 (1956)) indicate that the detergents studied, with the exception of Pluronic L-64, have critical micelle concentrations of the order of $10^{-4}M$. No break in the surface tension vs. concentration curve was observed for Pluronic L-64.

BLACK SOAP FILMS[1]

By J. Th. G. Overbeek[2]

Department of Chemistry, University of Southern California, Los Angeles 7, California

During the aging of colored soap films, black spots are formed which are ultrathin parts of the film. They are usually separated from the colored part of the film by a sharp transition and grow spontaneously. The principal forces that govern their thickness are the electrostatic repulsion between the soap ions on the two faces of the film and van der Waals attraction amongst all the molecules of the film. It is essential to take into account the fact that the electrostatic repulsion acts only across the water layer of the film, whereas the water layer and the soap molecules both contribute to the van der Waals forces. The equilibrium thickness of the black films presumably is determined by these forces and by the border suction (surface tension divided by the radius of curvature of the border surface). The rate of formation of black films depends on these forces and on the viscous resistance in the film. An extension of Frankel's theory on the rate of film formation is presented, which takes the influence of electrostatic and van der Waals forces into account. In films formed from solutions of non-ionic detergents both electrostatic repulsion and steric repulsion play a role. Black films do not break spontaneously but breaking may be caused by a number of effects, such as evaporation, dewetting of impurities, local heating, etc.

Introduction

Foams, soap bubbles and soap films are attractive subjects for research, not only from a scientific and technical, but also from an esthetic point of view. It is a pleasure to observe the interesting structures of foams and the beautiful interference colors in not all but most soap lamellae. Freshly formed lamellae may be too thick to show colors, but they all drain under the influence of gravity and when they reach a thickness between a few microns and 0.1 micron the interference colors appear. Given time and enough stability, the films will drain further and become so thin that reflection from the front side and the backside are very nearly

(1) Invited lecture of the Foreign Guest of Honor, 34th National Colloid Symposium, Lehigh University, June 16, 1960.

(2) Van't Hoff Laboratory, State University of Utrecht, Utrecht, The Netherlands.

in counterphase and the film looks *black*. These black regions are often sharply separated from the colored part of the film or bubble. They seem to be holes, and as early as 1672 Hooke[3] reported "On holes in soap bubbles." Newton[4] also studied these "holes" and observed that black films of different thickness could exist next to each other. Gibbs[5] was quite explicit about black films. He described the sudden thinning from colored to black "very much as if there were an attrac-

(3) R. Hooke, Communication to the Royal Society, March 28, 1672; see T. Birch, History of the Royal Society, A. Millard, London, 1757, Vol. III, p. 29.

(4) I. Newton, "Opticks," Book II, Part I, exp. 17, Dover Publ., New York, N. Y., 1952, based upon the 4th edition, W. Innys, London, 1730.

(5) J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances, see "Collected Works," Yale University Press, New Haven, 1948, p. 311 ff.

tion between the surfaces of the film, insensible at greater distances, but becoming sensible when the thickness of the film is sufficiently reduced." He observed a thicker rim between the black and the colored film and concluded that the black part is not simply formed by extension of the film, but by a spontaneous disproportionation of the thicker colored film into black film plus a thick rim around it. Finally he remarked, "That which is most difficult to account for in the formation of the black spots is the arrest of the process by which the film grows thinner. It seems most natural to account for this, *if possible*, by passive resistance to motion, due to a very viscous or gelatinous condition of the film."

We shall see how these very pertinent remarks by Gibbs remain significant for modern soap film research.

The first question to be answered is, Why should we be so much interested in soap films and particularly in the black ones which are certainly not the most beautiful? The main reason is that foams, and in particular isolated soap films, are very simple "colloidal" systems. The thinning seems to indicate that they are on their way to breaking, but in the formation of the black film the breaking is prevented or at least greatly retarded. In soap films we have a simple model for the behavior of very thin liquid layers between solid particles or emulsion droplets, and we may obtain a better understanding of coagulation of suspensions and of breaking of emulsions by studying soap films. Moreover, there is the practical interest in foams. Some people, such as the manufacturers of shaving cream, or beer, or the users of froth flotation, want to stabilize them. Others, such as distillers, or oil producers, look eagerly for ways to destroy foams.

Formation of Black Films.—A black film can be formed in two different ways. It may form spontaneously somewhere in the middle of a colored, usually rather thin, film and grow in area at the expense of the colored film. It may be formed also at the border (called Plateau border, or Gibbs border) which surrounds a soap film, where it is attached to a frame, to other films (in a foam) or to the horizontal surface of a liquid. Due to the curvature of the surface such a border is always a seat of suction (lower pressure) with respect to adjacent flat film. Mysels, Shinoda and Frankel[6] pointed out that this suction acts more strongly on a thick film than on a thin film, and consequently there is a tendency for thicker film to be sucked in and thinner film to be generated at these borders (see Fig. 1). When the film surface is mobile, this is the main process by which a soap film becomes thinner. This idea can be extended to the welt between black and colored film. The welt can be considered as a kind of border, sucking in the colored film and generating more of the black one, the excess liquid accumulating in the welt and usually breaking away from it in two-dimensional droplets, which flow to the lower parts of the film.[7]
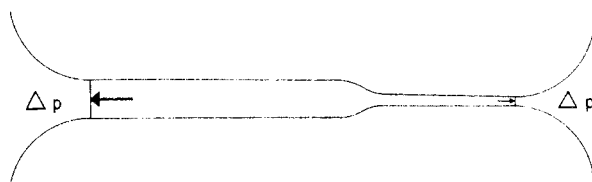
Fig. 1.—Border suction (Δp) acts more strongly on thicker parts of the film, sucks in thick film and generates thinner film.

When the black film is subjected to mild evaporation a second, thinner, black film is formed,[8] but we will limit our discussion nearly exclusively to the first.

Thickness of the Black Film.—The black film is too thin to show interference colors, but it does reflect some light. Light reflected from the front and the back surface has a phase difference slightly exceeding 180°, and thus it is not completely extinguished.

The ratio of reflected and incident light intensities (light beams perpendicular to film) is given by

$$I/I_0 = 4r^2 \sin^2 (2\pi nd/\lambda)$$

where $r^2 = (n - 1)^2/(n + 1)^2$ is the reflection coefficient of one surface, n is the (average) refractive index of the film, d its thickness and λ the wave length in vacuum of the light used. From a measurement of the intensity of the reflected light, the thickness of the film can be determined. It varies between slightly less than 100 Å. and about 500–700 Å. The second black film (the one caused by evaporation) is about 50 Å. thick.

Theoretical Discussion.—We must explain: (a) the great stability of these ultrathin structures, either colored or black; (b) the spontaneous formation of black films, and the fact that they do not thin indefinitely; (c) the multiplicity; (d) the mechanism(s) by which they ultimately break.

The explanation of the fact that soap films can stand a great deal of deformation without rupture has been given by Gibbs.[9] Adsorption of the soap molecules at the water–air interface is accompanied by a lowering of the surface tension. Local extension of the film entails a decrease in the amount of soap adsorbed per unit area and thus leads to an increase in the surface tension, which tends to contract the extended part of the film, thus preventing it from becoming dangerously thin. Variants of Gibbs' theory have been presented by Marangoni,[10] and much more recently by Ewers and Sutherland.[11] The first actual measurement of film elasticity has been made very recently by Mysels, Cox, and Skewis.[12]

As this cause for stability is not a particular property of the black films, we shall not discuss it further.

An attraction between the surfaces of the film as postulated by Gibbs might explain the sudden

(6) K. J. Mysels, K. Shinoda and S. Frankel, "Soap Films, Studies of Their Thinning and a Bibliography," Pergamon Press, New York, N. Y., 1959, p. 20 ff.

(7) Ref. 4, plates III and VI, between pp. 62 and 63.

(8) Ref. 6, p. 70 ff.

(9) Ref. 5, p. 300 ff.

(10) C. Marangoni, Fusi. Agosto, Piave, 1865; *cf. Ann. phys.*, (5) **143**, 337 (1871); *Nuovo Cimento*, (3) **3**, 50, 97, 192 (1879).

(11) W. E. Ewers and K. L. Sutherland, *Australian J. Sci. Res.*, **A5**, 697 (1952).

(12) K. J. Mysels, M. C. Cox and J. Skewis, private communication; see also Abstracts of Papers presented at A. C. S. Meeting, Sept., 1959.
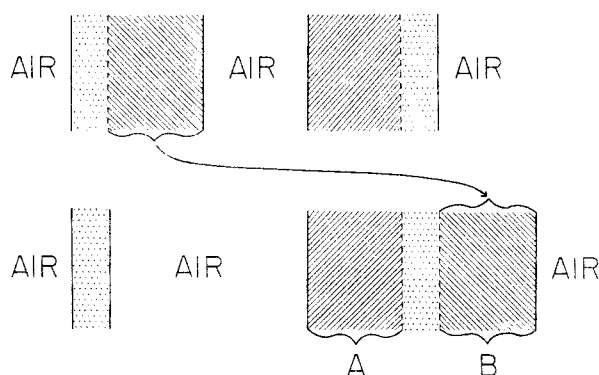
Fig. 2.—Upper part: two thick films far apart; lower part: films rearranged into a thin one and a very thick one. The interaction between the diagonally-marked parts A and B is only present in the lower picture and explains the decrease in potential energy in the rearrangement.
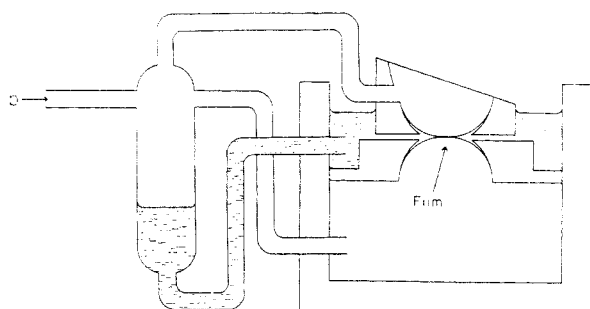

Fig. 3.—Apparatus for studying black films: the pressure p regulates the difference in pressure between the border and the film. The reflection of light projected through the upper window (inclined to avoid undesirable reflections) on the soap film is used to determine its thickness. Apparatus was constructed by Boekelman and Duyvis, and is very similar to that used by Derjaguin and Titijevskaja.

onset of the formation of the black film and the abrupt transition between the black and the colored film. De Vries[13] has proposed that such an attraction may be due to London–van der Waals forces. Indeed, it is well known how the existence of surface tension is explained by the fact that molecules near the surface are attracted toward the interior of the liquid by intermolecular attraction forces. In a very thin film the proximity of the two surfaces makes this inward attraction somewhat weaker or, in other words, lowers the free energy of the film and acts as a factor favoring further thinning of the film. De Vries pointed out that this effect is exactly equivalent to the force between two semi-infinite layers of solution separated by an air gap of the same thickness as the film, and can be treated quantitatively on this basis.

There are different ways in which this effect can be treated. One of them is illustrated in Fig. 2. If a film becomes thinner and the total interface of the system is not changed, the material lost by the film must be added somewhere else in the system, either in the bulk of the liquid or, energetically equivalent, to increase the thickness of an already thick film. The upper part of Fig. 2 depicts two thick films, each divided by an imaginary plane into a thin and a thick layer. The potential energy of each of the thick films is built

(13) A. J. de Vries, Rec. trav. chim., 77, 383 (1958).

up from the interactions between all individual pairs of molecules. After the rearrangement shown in the lower part of the figure, the potential energy of the total system is changed by the interaction between the two diagonally hatched parts of the thick film and this makes the lower situation more stable than the upper one. The actual difference ΔV between the energy of the two situations (per cm.^{2} of thin film formed) is given by[14,15]

$$\Delta V = A/12\pi H^2$$

where A is the Hamaker–van der Waals constant, and H is the thickness of the thin film. Consequently the van der Waals attraction is equivalent to a pressure on the film equal to

$$P = A/6\pi H^3$$

It has been shown both experimentally and theoretically that the above equations require modification when H is of the same order or larger than the wave length connected with the London–van der Waals forces. In that case, *retardation* of these forces plays a role. However, the thickness of the black films is usually such that the van der Waals forces are not affected by retardation, and one of the important aspects of black film research is that it may furnish a tool for the determination of non-retarded van der Waals forces.

Van der Waals forces ultimately would lead to bursting of the film unless some opposing force stops the process. This opposing force has been recognized by different authors—Bikerman,[16] Derjaguin,[17] and others—as being due to the electrostatic repulsion between the layers of adsorbed soap ions. If this is correct, the thickness of the black film ought to depend on the thickness of the electric double layer and consequently on the salt content of the soap solution. Derjaguin and Titijevskaja[18] have devised an ingenious experiment, in which they measure the thickness of black films under different levels of border suction. A sketch of the essential parts of the apparatus is shown in Fig. 3. They find a good agreement between calculated and measured film thickness, considered as an equilibrium between border suction and electrostatic repulsion, calculated on the basis of Gouy–Chapman double layers (see Fig. 4). Van der Waals forces were not taken into account. They would not influence the results perceptibly for thick films, obtained at low ionic strength, but one would expect them to make the thin films still thinner. However, the thin films obtained by Derjaguin at high ionic strength are actually even thicker than the calculated value based on repulsion and border suction. Derjaguin ascribes this to a special structure of the solvent, rather in line with Gibbs' suggestion of a "gelatinous behavior."

The exact nature of this gelatinous layer is not

(14) J. H. De Boer, Trans. Faraday Soc., 32, 21 (1936).

(15) H. C. Hamaker, Physica, 4, 1058 (1937).

(16) B. V. Bikerman, "Foams, Theory and Industrial Applications," Reinhold Publ. Corp., New York, N. Y., 1953, p. 154.

(17) B. V. Derjaguin, Disc. Faraday Soc., 18, 24 (1954).

(18) B. V. Derjaguin and A. S. Titijevskaja, "Gas–Liquid and Liquid–Liquid Interfaces," Proc. 2nd Int. Congr. Surf. Activity, Vol. I, Butterworth, London, 1957, p. 211; see also ref. 17.

clear. There appears to be a contradiction with information derived from electrokinetic phenomena, which, if anything, suggest only a very thin layer of increased viscosity near a phase boundary. Mysels[19] has suggested that the presence of micelles in the film might prevent further collapse. In the author's opinion this question is still unsettled. More experiments, also below the c.m.c., are desirable.

It is, of course, tempting to do similar experiments with soap films between oil layers. They have indeed been done by van den Tempel,[20] although without regulation of the border suction. He found the predicted dependence of the thickness on the ionic strength, but just as in Derjaguin's case, the films at high salt content are thicker than calculated.

If the situation in black soap films can be described as an equilibrium between van der Waals attraction, electrostatic repulsion and some border suction, then this forms an ideal case for the application of the theory of the stability of lyophobic colloids as developed by Derjaguin and Landau[21] and by Verwey and Overbeek,[22] because this theory is based on the same forces. As the van der Waals attraction changes in inverse proportion with some power of the thickness and the electrostatic repulsion varies exponentially with the thickness of the film, a plot of the potential energy of the film against its thickness shows a sharp dip for very small thickness. At intermediate thickness there may be a maximum, which can act as an energy barrier, and there is a shallow minimum at larger thickness (see Fig. 5). The stable black film is supposed to correspond to this shallow minimum.

Experimental information obtained at my laboratory in Utrecht by Duyvis and at the University of Southern California by Skewis is in qualitative agreement with this picture. Recent results obtained by the Bulgarian authors Scheludko and Exerowa[23] even allow the calculation of the Hamaker–van der Waals constant from such experiments. It is found to be equal within a factor 2 or 3 to $A = 5 \times 10^{-13}$ ergs, in good agreement with theoretical predictions.

However, since a hydrophobic colloid usually flocculates at a salt content of about 0.1 molar monovalent electrolyte, one would expect soap films to break at or below that limit. But good soap films do not break, even at 1 molar. This probably should be explained by the fact that electrostatic repulsion acts between the ionic heads of the soap molecules, but van der Waals attraction includes the hydrocarbon tails as well. This is equivalent to a shift between the origins of the attraction and repulsion curves over maybe 10 or 20 Å. In that case the repulsion acts against a less steep part of the attraction as is illustrated in Fig. 6. Calculation shows that a shift of only a few Å. is enough to prevent breaking by even the
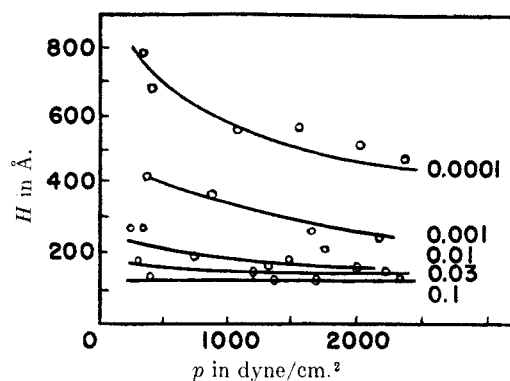
(19) K. J. Mysels, private communication.

(20) M. van den Tempel, J. Colloid Sci., 13, 125 (1958).

(21) B. V. Derjaguin and L. Landau, Acta physicochim. U.R.S.S., 14, 633 (1941).

(22) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.

(23) A. Scheludko and D. Exerowa, Kolloid. Z., 168, 24 (1960).

Fig. 4.—Thickness H of sodium oleate films (in A.) as a function of the border suction (in dynes/cm.^{2}) and sodium chloride content, from Derjaguin and Titijevskaja.[17,18] All solutions contain $10^{-3} M$ sodium oleate. The molarity of sodium chloride was varied from 0.001–0.1 M, and is indicated in the figure.
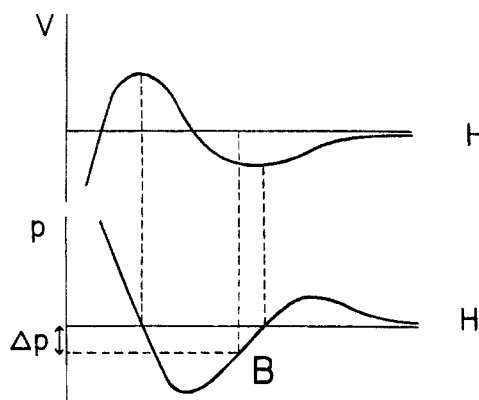

Fig. 5.—General form of potential energy V vs. thickness H and pressure p vs. H for a combination of electrostatic repulsion with van der Waals compression. In equilibrium with a border suction, Δp, the black film would correspond to point B.

highest possible concentration of monovalent electrolyte. This would not be the case for bivalent ions, but lack of solubility of soaps of bivalent metals makes this a difficult point to check.

Another point is connected with the formation of the black film. As this takes place spontaneously and at a finite rate, and requires work against viscous resistance, it is by no means certain that the black film, as usually found, is a true equilibrium structure. Frankel[24] has worked out a theoretical treatment of the relation between the thickness of a soap film and the rate at which it is drawn out of a border, considering the whole process as a steady state.

This theory is based on the idea that when the film is drawn it passes from a region of low pressure (the border) to a region of high pressure (the flat film). The pressure gradient squeezes out some of the solution in viscous laminar flow. The slower the film is drawn, the more efficient this squeezing process and the thinner the film becomes. The predicted proportionality between film thickness and the $^2/_3$ power of the rate of drawing was confirmed for film thicknesses between 0.1 and 6μ. The constant of proportionality agreed with prediction.[12,24]
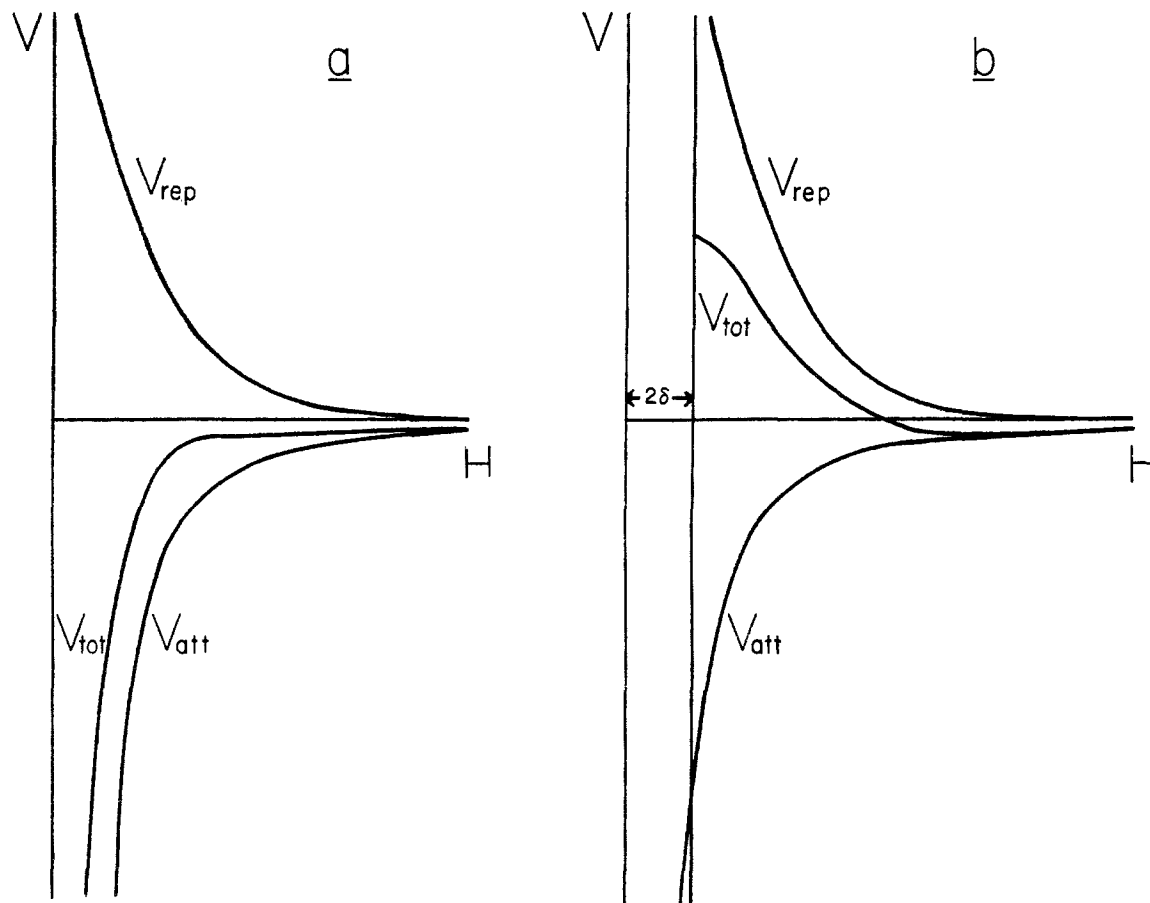
(24) Ref. 6, Chapter V, p. 47 ff.

Fig. 6.—Demonstration of stabilizing influence of a small shift in origin between repulsion curve and attraction curve; (6a) repulsion and attraction have the same origin; (6b) repulsion curve is shifted a distance 2δ (twice the thickness of the hydrocarbon part of the soap layer) to the right.

For very thin films van der Waals forces and electrostatic repulsion also contribute to the pressure gradient. This can be expressed quantitatively in an equation for drawing of a film of thickness $T + 2\delta$, at a rate v

$$vT = 2vy + \frac{2\gamma y^3}{3\eta} \frac{d^3 y}{dx^3} + \frac{2y^3}{3\eta}$$

$$\left\{ \frac{A}{16\pi(y+\delta)^4} - \frac{16\epsilon T'^2\kappa^2\varphi^3\kappa^2 e^{-2\kappa y}}{\pi e^2} \right\} \frac{dy}{dx}$$

where $\varphi = (\exp(ze\psi/2KT) - 1)/(\exp(ze\psi/2KT) +1)$ and $2y + 2\delta$ is the film thickness in the transition region between the border and the flat film, δ is the thickness of the hydrocarbon part of one soap layer, x is the coördinate perpendicular to the border in the direction of drawing, γ is the surface tension, η the viscosity of the solution, A the van der Waals–Hamaker constant, ϵ the dielectric constant in the double layer, K and T the Boltzmann constant and the temperature, e the elementary charge, z the valence of the counter ions, ψ the electric potential at the ionic heads of the soap molecules and κ the reciprocal of the Debye length.

This equation has been solved using the digital computer facilities at the Western Data Processing Center at the University of California at Los Angeles. Due to the large choice of parameters the data are not yet complete. Preliminary results indicate an easily detectable influence of van der

Waals forces and electrostatic repulsion at low rates of drawing and high salt content. They also indicate that the excess tension required to produce black films may be extremely small and in certain cases even negative, pointing to the possibility of spontaneous growth of these films. Moreover, there are regions where the film thickness changes very rapidly with little change in rate or excess tension in agreement with the abrupt transition between black and colored film. It seems also as if the black film formed is not very far from equilibrium, but this conclusion is very definitely a preliminary one. Application of this line of thought to the welt is planned, but will be more difficult, because the welt grows, and thus there is no stationary state. The welt, although qualitatively similar to a double border, is too thin to admit direct quantitative application of the stationary state treatment. This would require that somewhere in the middle of the welt flow is practically loss free, as is the case in a real border far from the film. However, viscous losses cannot be neglected in any part of the welt.

Before finishing this lecture I wish to mention two subjects briefly. The first is that of foams stabilized by non-ionic detergents. My co-worker Duyvis at Utrecht made a number of measurements on films stabilized by polyethylene oxide soaps. He found two "equilibrium thicknesses,"

one at about 700 Å. probably connected with a weak but long range electrostatic repulsion (low ionic strength) and a second one at about 80 Å. where we assume that the repulsion mechanism is the mechanical interference between the polyethylene oxide chains from both sides of the film.

The second topic is concerned with how and why a film breaks. According to our discussion so far, it should not break at all. Electrostatic repulsion keeps the film above a minimum thickness and it can be shown conclusively that the activation energy for the formation of a hole in such a film is extremely large, so that the process does not occur spontaneously.[25]

In practice, however, small amounts of impurity may accumulate on the frame to which the film is attached and break the film by dewetting. Evaporation, driving the film thickness below the thickness of the maximum in the potential energy curve, is another common mechanism leading to breaking. It may also lead to the thinner second black film if this structure, consisting presumably of only two layers of soap with some water of hydration, is stable. In principle a very tall film or one in a very strong gravitational or centrifugal field could break under its own weight, either because the excess surface tension required to carry the weight becomes too large, or because gravity pushes the film over the energy barrier. Figure 7 shows a combination of van der Waals, electrostatic and gravitational energy which would just lead to film breakage because the V–H line has at best a horizontal slope. The gravitational energy is equal to $\rho g h H$, where ρ is the density of the solution, H the film thickness, g the gravitational acceleration and h the height above the surface of the bulk liquid.

Any gradient in the surface tension, caused, e.g., by local heating, local evaporation or local contamination, will lead to an extension of the part of the film with the lower surface tension and lead to rupture.

The study of rupture of the films has as yet not made much progress, but it is obviously important, also for exploiting the parallels between soap films and problems in emulsion and suspension stability.

The subject I have chosen for this lecture is one on which research is by no means finished, but I believe that it is a rich source of information, interesting *per se*, and allowing conclusions which
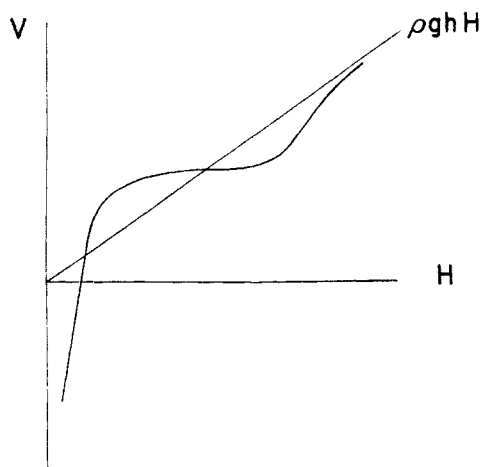
(25) A. J. de Vries, *Rec. trav. chim.*, **77**, 383, 441 (1958).

Fig. 7.—Potential energy curve with horizontal point of inflection due to gravity ($\rho g h H$) combined with van der Waals and electrostatic forces.

are of value to many other fields of colloid science.

To conclude the lecture a movie was shown of a horizontal soap film in which a colored central part was surrounded by a black rim. The movie as shown was accelerated about 60-fold as compared to reality. In the picture the growth of the welt could be seen very clearly, also that the welt detached dropwise and that the "drops" floated downward to the lower and thicker parts of the film. Furthermore it showed some of the complications met with, such as the effect of evaporation.