

parable stability with incompletely and completely substituted ammonium ions (Table I), the more basic 2,6-dihydroxybenzoate and particularly salicylate ion form much more stable ion pairs with incompletely substituted ammonium ions (Table III) than with

quaternary ammonium ions (Table I). Again hydrogen bonding stabilizes the ion pairs in the former case.

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A Study of Double Layer Repulsion and van der Waals Attraction in Soap Films

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Measurements of equilibrium thicknesses of soap films over a range of ionic strengths are presented for mobile and rigid films of sodium lauryl sulfate in the presence of lithium chloride. The forces determining this thickness are discussed in terms of existing theories of van der Waals attractions and of electric double layer repulsion. Some of the problems involved in the experimental testing of these theories are brought out. While there is good qualitative agreement between theory and experiment, definite quantitative discrepancies appear also. It is suggested that some of these could stem from limitations of the double layer theory.

The principal long-range forces between large charged particles in solution are the double layer repulsion due to the interaction of their ionic atmospheres and the van der Waals attraction attributed¹ mainly to electromagnetic dispersion forces as postulated originally by London.² The theory of both effects has been elaborated in considerable detail and most of modern interpretation of the stability and flocculation of colloids is based upon both of them.^{3,4} These theories are derived from basic principles of physics, but the simplifying assumptions that are necessary to keep the mathematics tractable limit the region of strict applicability to low salt concentrations and low surface potentials. Their rigorous application to real systems is not always easy and the treatment of flocculation is particularly difficult because of the complex kinetics and the uncertain geometry of the region of interaction. Hence the value of these theories in this field has occasionally been questioned.⁵

The only early evidence bearing directly upon double layer repulsion was a study⁶ of iridescent (or Schiller) layers of ferric and tungstic oxides which yielded only qualitative agreement as would be expected in view of

the difficulties involved in these systems. Recent experiments involving the direct measurement of the force barrier between two crossed platinum wires,⁷ although much simpler in geometry and minimizing the kinetic factor, can determine only the maximum height of the repulsion barrier, but not its position. The results of these experiments could in general be explained by the theories^{3,4} but suggested the existence of some hitherto unknown, additional repulsive force.

The past decade has produced direct measurements of London interactions between macroscopic plates and lenses under vacuum⁸⁻¹⁰ which agree with the theoretically expected distance dependence as well as with the absolute value. However, the minimum distance accessible to these methods is about 1 μ which is quite large compared with separations involved in colloidal phenomena and the techniques are not readily applicable to measurements in solutions because of the required vacuum.

In recent years it became clear¹¹⁻¹⁵ that a critical test of the theory can be provided in principle by the equilibrium thickness of a thin liquid film—a soap film. This equilibrium thickness varies, depending on the conditions, between some 50 and 1000 Å ., which is just the order of distance between interacting colloidal particles. Qualitatively, when an ionic surfactant is used to stabilize the film, this thickness decreases upon addition of salt, in harmony with the reduced range of double layer repulsion according to the stability theory. Moreover, as the van der Waals forces between all the particles of the liquid film tend to compress the

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(6) H. Zocher and W. Heller, *Z. anorg. allgem. Chem.*, **186**, 75 (1930); P. Bergmann, P. Löw-Beer, and H. Zocher, *Z. physik. Chem.*, **A181**, 303 (1938).

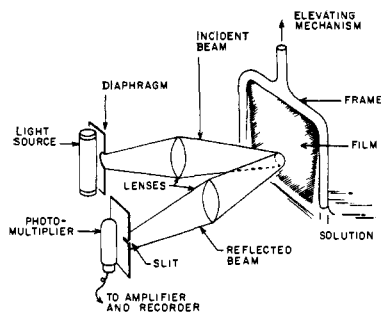


Figure 1. Principle of the experiments. A film is formed by raising the frame at a controlled speed and its thickness determined by measuring the intensity of reflected light.

film,^{12,13,15,16} it appears that the thickness of a soap film is governed by just the same factors that determine colloidal stability. As a tool for the study of double layer repulsion and van der Waals attraction, the soap film has the advantages of its static equilibrium, well-defined geometry, and reasonably well-known structure.

Working along these lines, Scheludko¹² made measurements which seemed to indicate that present theories are even able to account quantitatively for the observed equilibrium thicknesses. These measurements were performed on microscopic circular lamellae formed upon slow withdrawal of liquid held by capillarity in a short glass tube about 3 mm. in diameter and 3 mm. high. More recently, Duyvis¹⁷ has shed doubt upon the validity of this method by reporting a dependence of thickness upon the diameter of the lamella. This latter finding has been disputed by Exerowa, Ivanov, and Scheludko.¹⁸

In this paper we report on the results of an experimental technique which is very different from that of these investigators and measures accurately the equilibrium thickness of large vertical films. The films were formed from solutions of pure ionic surfactants over a wide range of ionic strengths and their equilibrium thicknesses determined under both static (drainage of thick film) and dynamic (slow formation) conditions. Moreover films of different surface viscosity (mobile and rigid films) were compared.

Our experimental results are similar to those of Scheludko and Exerowa¹² and reasonably close to earlier experiments of Deryagin and Titievskaya.¹¹ However, our interpretation differs from the previous ones in that we find a quite significant disagreement with theory.^{3,4,19}

Experimental

The apparatus used is described in detail elsewhere.²⁰ It consists essentially of a vertical rectangular frame (Figure 1) which can be raised at controlled, very slow speeds from a submerged position in the surfactant solution. The intensity of light reflected just above the

meniscus from a small area of the film thus formed is measured photoelectrically. This intensity is compared with the maximum intensity reflected by a film having an optical thickness of a quarter wave length, and from this ratio the thickness is deduced as will be indicated below. Evaporation is prevented by submerging the chamber in which the film is formed in a constant temperature bath and by saturation of the air inside the chamber.

Materials. The dodecyl and tetradecyl alcohols were of very high purity and obtained from Applied Science Laboratory, State College, Pa. The sodium dodecyl sulfate has been described.²¹ The sodium tetradecyl sulfate was prepared in a similar way by Otter and purified by Liulevicius-Palubinskas.²² Its surface tension-concentration curve showed no minimum, the tetradecyl alcohol having been removed by high vacuum sublimation at 100°.²²

Structure of Film

Stable films of appreciable area can be formed only in solutions of surfactants which *eo ipso* give surface layers different from the bulk. Recently Corkill, *et al.*,²³ using radioactive tracers showed that the composition of these surface layers is independent of the thickness of the film.

Some of these surface layers possess a marked surface shear viscosity or even a surface yield value which gives the films a characteristic slow-draining behavior.^{24,25} These are called rigid films. Most solutions of surfactants give rapid-draining mobile films. In the former there exists presumably a two-dimensional mixed surface crystal of fully extended ions and molecules (*e.g.*, lauryl sulfate and lauryl alcohol), and in the latter the surfactant particles are kept apart by either electrostatic or, in the case of nonionic surfactants, by steric factors. The surface layer on each face of a film has a thickness d_1 which for rigid films is about twice that in a mobile film. We have estimated²⁰ the former at 16 Å., the latter at 8.5 Å., for dodecyl sulfate. Two such thicknesses are the difference between the material thickness δ of the film and that, d_2 , of its aqueous core. The optical properties of these surface layers are uncertain, and we have estimated²⁰ their refractive index as 1.45, whereas that of the aqueous core is 1.33 (assumed independent of ionic strength). Fortunately these values for the surface layers are not critical and should be a good first approximation.

Computation of Film Thickness

The determination of thickness has been discussed in detail elsewhere.²⁰ Basically, it involves the measurement of the reflectivity of the film followed by the computation of an equivalent water thickness d_w (that of a homogeneous film consisting only of solution and having the same reflectivity). Then a correction for the different optical properties of the surface layers

(16) A. de Vries, *Rec. trav. chim.*, **77**, 383 (1958).

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

Table I. Equilibrium Thickness of Soap Films of Solutions of Sodium $n\text{-C}_{12}$ and $n\text{-C}_{14}$ Sulfates in the Presence of Lithium Chloride

Length	Surfactant	Mole/l. LiCl	Counterion	Type ^a of film	Å.			P_s , dynes/cm. ²
					d_w	δ	d_2	
12	7.3×10^{-4}	0.905	0.906	M	90	83	66	14
12	2.83×10^{-3}	10^{-1}	0.103	R	137	123	91	6,200
12	2.14×10^{-3}	6.4×10^{-2}	6.6×10^{-2}	S	140	126	94	21,000
12	3.7×10^{-3}	1.6×10^{-2}	1.97×10^{-2}	R	199	185	153	16,000
12	3.7×10^{-3}	1.6×10^{-2}	1.92×10^{-2}	M	203	195	178	5,100
12	1.07×10^{-2}	...	9.0×10^{-3}	M	253	246	229	6,500
12	4.0×10^{-3}	1.92×10^{-3}	5.92×10^{-3}	R	310	296	264	6,800
12	3.48×10^{-3}	...	3.48×10^{-3}	R	400	386	354	3,300
14	3.0×10^{-3}	...	2.3×10^{-3}	M	515	507	487	990
12	1.77×10^{-3}	...	1.77×10^{-3}	R	555	541	509	1,440
12	8.7×10^{-4}	...	8.7×10^{-4}	R	777	763	731	660
14	7.9×10^{-4}	...	7.9×10^{-4}	S	800	784	747	740

^a R, rigid; S, semirigid; M, mobile. The R and S solutions contained the corresponding alcohol in proportion of 2.5% by weight of the dry surfactant.

is applied to give the real thickness δ of the film. On the basis of our assumptions as to this structure (see above), the correction amounts to -13.5 \AA . for rigid films and to -7.25 \AA . for mobile films of dodecyl sulfate. For the tetradecyl system, 2.5 \AA . should be added to the thickness of each monolayer in rigid films and about 1.5 \AA . in mobile films so that the optical correction is increased by 2 and 1 \AA ., respectively. To obtain the thickness of the aqueous core d_2 , one must further subtract from δ twice the thickness d_1 of the surface layer, *i.e.*, 2×16 and $2 \times 8.5 \text{ \AA}$., respectively, for our dodecyl model. The total correction from the equivalent thickness d_w to the core thickness d_2 amounts thus to -45.5 or -24.25 \AA ., respectively, which is quite significant, especially for the thinner films. Some of the early published results do not carry these corrections and are not easily converted because of uncertainties as to the nature of the surface layers. Scheludko has recently^{12b} used a correction of -52 \AA . for the (presumably mobile) sodium oleate system. It should be noted that the equivalent water thickness is certainly an over-estimate of the real thickness of the film and that the corrections used should be of the right order of magnitude, but their exact value is somewhat arbitrary. We estimate our over-all limit of uncertainty in the equivalent water thickness d_w to be about 8 \AA ., in the material thickness δ about 10 \AA ., and in that of the aqueous core d_2 some 13 \AA .

Results

As we reported already,²⁰ when the frame is raised at speeds above some $5 \mu/\text{sec}$. the film thickness increases with increasing frame velocity. This can be interpreted as the result of a competition between the rate of entrainment by the surfaces and the rate of gravitational outflow of the aqueous core. A purely hydrodynamic description of this phenomenon has been given by Frankel²⁶ and for related conditions by Deryagin and Levi.²⁷ Our experiments,²⁰ performed at the same time as the ones to be discussed now, are in excellent agreement with this theory. This shows that the viscosity of the aqueous core does not change significantly to within a few molecular diameters of the surface layers.

(26) S. Frankel, ref. 25, Chapter V.

(27) B. V. Deryagin and S. M. Levi, "Fiziko-Khimiya Naneseniya Tonkikh Sloev na Dvizhushchuyusya Podlozhki," USSR Academy of Science, Moscow, 1959; B. V. Deryagin, *Zh. Eksperim. i Teor. Fiz.*, **15**, 9 (1945).

For frame velocities between ~ 5 and $\sim 2 \mu/\text{sec}$., the behavior can be quite complicated.^{20,28} However, when the rise of the frame is slower than $0.5\text{--}2 \mu/\text{sec}$. the thickness of the film becomes independent of the velocity of the frame as shown in Figure 2. The limiting

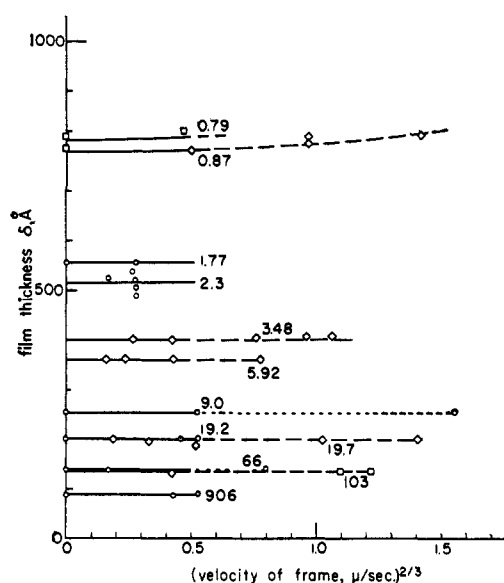


Figure 2. Film thicknesses at low frame velocities are essentially constant and equal to those obtained by static drainage and shown on the vertical axis. The lines correspond to values of Table I: mobile films, O; semirigid, Δ ; rigid, \diamond . Numbers indicate total counterion concentrations in millimoles per liter.

equilibrium values and the corresponding conditions are listed in Table I. That this limiting thickness is really an equilibrium thickness was shown also for mobile films by raising the frame at a rapid rate to form a thicker film and then allowing it to drain. The same equilibrium thickness was obtained within 20 min. and often persisted for 24 hr. or longer. It should be noted that such constancy of thickness is possible only when extreme precautions are taken to avoid evaporation. The thicknesses reported were measured upon a rectangle $0.3 \times 0.04 \text{ mm}$. but were essentially the same over large areas of the film (which was 3 cm. wide and several millimeters or even centimeters high). This was

(28) J. Th. G. Overbeek, unpublished calculations.

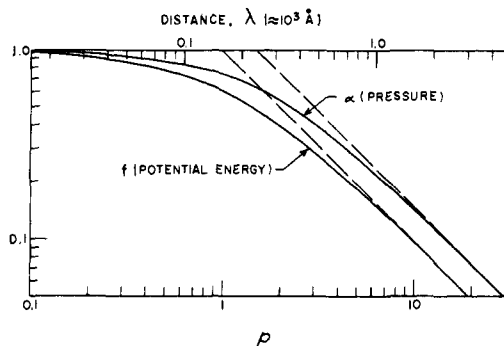


Figure 3. Correction factors to short-range van der Waals potential (f) and pressure (α) as a function of the parameter p and of the approximate thickness for water based on ref. 31a.

evident from the fact that the intensity of reflected light remained the same as the film was raised (provided the speed was slow enough) or lowered (at any speed), or as the optical apparatus was displaced so as to sweep neighboring areas of the film. These thicknesses appear therefore to be true equilibrium values free of size and time effects.

Theoretical

1. *Compressive Forces.* The classical London interaction between two atoms gives a potential energy varying inversely with the sixth power of their separation. When integrated,²⁹ assuming simple additivity, over all atoms of two flat layers it gives an attractive pressure varying inversely with the third power of their distance: $P_v = K'/\delta^3$ for two flat semi-infinite layers at distance δ . Overbeek³⁰ has noted, however, that as the distances involved become comparable to the wave length corresponding to the fluctuations responsible for the London forces, the effect has to decrease or become "retarded." Quantitative estimates of Casimir and Polder,^{31a} confirmed by a different approach by Lifshits,^{31b} and recently by McLachlan,^{31c} show that in this case the power is increased by a unit so that the force between flat layers decreases with the fourth power of the distance: $P_v'' = K''/\delta^4$. It is important to note that the thicknesses involved in soap films lie mainly in the transition region between the two power regimes. Numerical values for the interaction of atoms in this transition region have been given by Casimir and Polder^{31a} and Overbeek²⁹ based on these an evaluation of the energy of interaction, V , between two flat layers. This takes the form

$$V = fV' \quad (1)$$

where V' is the short-range form of the attractive energy, and f is a correction factor whose values are listed and shown²⁹ as a function of the parameter $p = 2\pi\delta/\lambda$, where λ is the wave length of maximum absorption of the material considered. For water λ may be taken as about 10^3 \AA . The variation of f with distance is shown in Figure 3.

(29) See ref. 1, Chapter VI, section 10.

(30) J. Th. G. Overbeek, Symposium Grenslaagverschijnselen, *Verhandel. Koninkl. Vlaam. Acad. Wetenschap., Belg.*, 130 (1947); see also ref. 31a.

(31) (a) H. B. G. Casimir and D. Polder, *Nature*, **158**, 787 (1946); *Phys. Rev.*, **73**, 360 (1948); (b) E. M. Lifshits, *Zh. Eksperim. i Teor. Fiz.*, **29**, 94 (1955); (c) A. D. McLachlan, *Proc. Roy. Soc. (London)*, **A271**, 387 (1963).

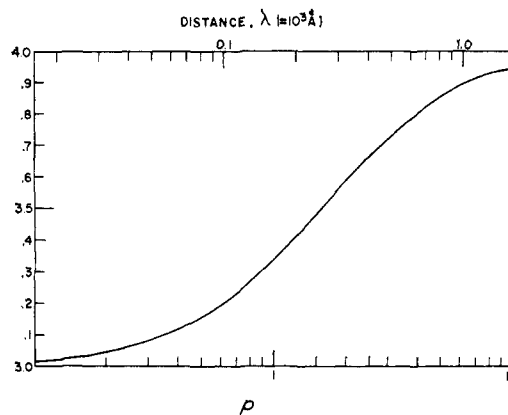


Figure 4. Variation of the exponent of the van der Waals pressure-distance relation in the transition zone as a function of the parameter p and of the approximate thickness for water based on ref. 31a.

The attractive pressure P_v between two flat semi-infinite layers in the transition zone can be obtained from (1) as

$$P_v = -\partial V/\partial \delta = \alpha P_v' \quad (2)$$

where $P_v' = -\partial V'/\partial \delta (= -2V'/\delta)$, and $\alpha = f - 1/2 \cdot \partial f/\partial \ln p$ is a correction factor to be applied to the short-range form of the attraction. The variation of α with distance is also shown in Figure 3 as a function of both p and λ .

The variation of the exponent in the relation between P_v and distance is shown in Figure 4. As may be seen, the transition between the third and fourth power dependence occurs between 10^2 and 10^3 \AA ., which is the range of equilibrium thicknesses of soap films.

For a quantitative calculation of the compression, we need a numerical value for the proportionality constant K' . The lines of Figure 5 are based on the estimate of Kirkwood and Slater³²: $A = 6 \times 10^{-13}$ where A , the so-called Hamaker-van der Waals constant, equals $6\pi K'$. It may be noted that experimental evaluations yielded values of A between about 10^{-12} and 10^{-14} so that the value adopted by us is more or less an average. Figure 5 shows the variation of P_v with distance computed in this way. Here again the transition from the third power to the fourth power regime is indicated.

The above calculations refer to the attraction of two material layers across a thin film of vacuum. It can be easily shown, however,^{12a,13} that exactly the same result is obtained for the reverse situation, the one of interest to us, provided additivity of these forces holds true. In other words, a thin film is subject to a compression due to van der Waals forces which is equal to the pressure pressing together two semi-infinite layers of the same material separated by a distance equal to the thickness of the film.

A soap film is compressed not only by van der Waals forces but also by the hydrostatic suction, P_b , which at the height just above the meniscus, where our measurements were performed, amounted to 255 dynes/cm.² (horizontal line in Figure 5). The total resulting compression $P_c = P_v + P_b$ is also shown in Figure 5 (heavy line). For sufficiently thick films the van der Waals

(32) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

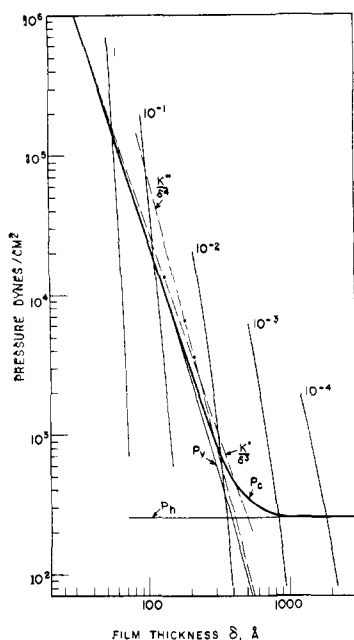


Figure 5. Pressures determining the equilibrium thickness of a soap film: heavy line shows the compressive force P_c resulting from van der Waals attractions P_v changing from third to fourth power regimes and hydrostatic suction P_h ; steep series of lines shows double layer repulsion P_r at indicated ionic strengths (calculated assuming $A = 6 \times 10^{-18}$, $\psi_d = 100$ mv., $d_1 = 15$ Å., and $\lambda = 10^8$ Å.).

pressure is so low that the hydrostatic compression predominates.

2. *Double Layer Repulsion.* The repulsive pressure between two parallel charged planes in an electrolyte solution can be calculated explicitly³³ as a function of the potential of the planes and of their distance provided several simplifying assumptions are made, notably the validity of the Poisson-Boltzmann distribution for smeared out point charges in a homogeneous solvent with no dielectric saturation. For separations larger than twice the double layer thickness κ^{-1} (a condition always fulfilled in our case), the repulsion is given to a very good approximation by

$$P_r = 1.59 \times 10^9 c \gamma^2 e^{-\kappa d_2} \quad (3)$$

In this equation c is the total concentration in moles/liter of the (symmetrical) electrolyte, and γ is a function of the diffuse double layer potential ψ_d

$$\gamma = \frac{\exp \frac{ze\psi_d}{2kT} - 1}{\exp \frac{ze\psi_d}{2kT} + 1} \quad (4)$$

where z is the valency of the electrolyte, e the charge of the electron, k the Boltzmann constant, and T the absolute temperature. γ^2 varies from 0 to 1 as ψ_d changes from 0 to ∞ , and for a monovalent electrolyte $\gamma^2 = 0.33$ for $\psi_d = 65$ mv., 0.58 for 100 mv., and 0.93 for 200 mv. Thus its variation in real systems is relatively limited because of the rather high values of potentials encountered.

Values of P_r computed in this way are plotted also in Figure 5 for several concentrations of a 1:1 electrolyte.

(33) See ref. 1, Chapter VI, section 3.

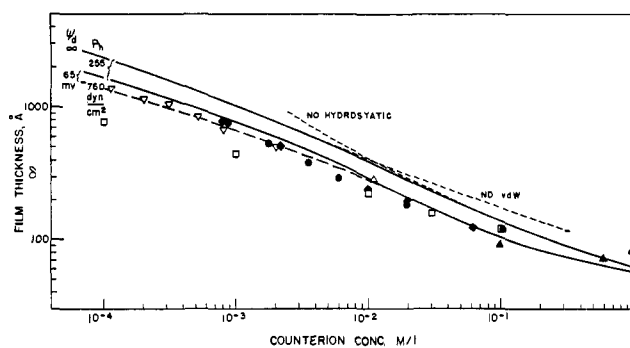


Figure 6. Calculated and experimental thicknesses of soap films as a function of ionic strength. The lines are based on intersection points of Figure 5 with various indicated parameters: filled points show δ including optical correction; open points show the equivalent water thickness d_w (this work: mobile, \diamond ; semi- and rigid, \circ ; Scheludko, ∇^{12a} and ∇^{12b} ; Deryagin and Titievskaya,¹¹ \square).

It may be noted that the slopes of these lines are extremely steep. As a result, small changes in the γ^2 factor in expression 3 which shift these calculated lines vertically have only minor effects on the abscissa of any values of P_r . The lines drawn correspond to $\psi_d = 100$ mv. and would show a barely perceptible shift if ψ_d were taken as infinity (clearly an over-estimate) or as 65 mv. (close to the lower limit of practical values), both corresponding to 75% changes in γ^2 and therefore in P_r .

As already pointed out, the film thickness d_2 entering expression 3 cannot be identified with the total thickness of a soap film δ . It refers only to the thickness of the central aqueous layer, while the total thickness includes also the two adsorbed monolayers which give the film its stability. The van der Waals forces, on the other hand, may be considered as being exerted by all the molecules of the film, any different behavior of the surface layers being equivalent to only a small thickness correction. The difference $2d_1$ between the distance d_2 of the two planes involved in the repulsion and the range δ over which the van der Waals compression is exerted vary with the nature of the surfactant. For the computation of the repulsion lines of Figure 5, we have used the value of 30 Å. which is a good approximation.

3. *Equilibrium Thickness.* The equilibrium thickness is determined by the balance of compressive and repulsive pressures; *i.e.*, the film is at equilibrium when $P_r = P_c$. In terms of Figure 5 the equilibrium thickness is therefore the abscissa of the intersection point of the P_c line with the P_r line corresponding to the proper ionic strength and surface potential. Figure 6 shows the values thus calculated as a function of counterion concentration for a number of parameters and limiting conditions. The complicated shape of these lines is related to the composite nature of the P_c curve in Figure 5, and the dotted branches show the smooth shape which would be given by either hydrostatic or van der Waals forces acting alone to compress the film.

At low ionic strength the equilibrium thickness is sensitive to the hydrostatic pressure, and a dashed line shows the effect of increasing this pressure from the value of 255 dynes/cm.² used in our work to 760 used by Scheludko and Exerowa.^{12a} The variation of the calculated equilibrium thickness with the assumed dou-

ble layer potential is shown in Figure 6 by the two solid lines corresponding to the extreme values of infinity and of 65 mv. The relative insensitivity of the equilibrium thickness to this enormous variation in potential is related to the steepness of the P_r lines in Figure 5 and is fortunate because the independent evaluation of the surface potential is not easy.

The factor that ultimately determines the equilibrium thickness is the range of the double layer repulsion—the abscissa of the P_r line in Figure 5—whose calculated value depends primarily on the decay of potential in the neighborhood of a charged plane. It is this factor which causes most of the 40-fold change in the thickness shown in Figure 6, and it is only if the theory of this effect is accepted as correct that the other parameters—surface potential and attractive forces—can be estimated from the equilibrium thickness.

Experimental Testing

An experimental test of the theory requires the knowledge of a number of factors, the most important being the ionic strength, the surface potential, and the thicknesses of the whole film and of its aqueous core.

If the monomeric surfactant is considered as a simple 1:1 electrolyte,³⁴ the ionic strength is easily determined from the concentration of the surfactant and of any added salt. Above the critical micelle concentration (c.m.c.) there is, however, considerable ambiguity which increases with the concentration of the surfactant and decreases as the proportion of added salt becomes larger. We have assumed where necessary that the contribution of micelles to the ionic strength was equivalent to 20% of the surfactant concentration above the c.m.c. However, the majority of solutions used in our experiments were just below the c.m.c. and obviated this difficulty.

At high dilutions where van der Waals forces are negligible, one can deduce the surface potential from the film thickness. This, however, is based precisely on the theory that one would wish to test. Furthermore it is not applicable at higher ionic strengths and any extrapolation requires additional assumptions. In particular, the assumption of constant potential^{12a} is questionable for a strongly ionized and highly compressed monolayer.

The most straightforward approach is perhaps the direct calculation using the Gouy–Chapman theory, but here again one needs the assumptions of the diffuse double layer theory. Still another possibility is to consider the surface film as akin to the surface of a micelle of the same surfactant and substitute for the surface potential the ζ potential estimated for the micelles. However, the calculation of ζ from the measured electrophoretic mobilities^{36–38} involves several additional assumptions, and the relation between ζ and the diffuse double layer potential ψ_d is not yet known.³⁹

These different approaches give quite diverging results as shown in Table II for two ionic strengths. As already mentioned, it is fortunate that the calculated

Table II. Double Layer Potentials Estimated by Some Different Approaches for Sodium Dodecyl Sulfate Film

	ψ_d , mv. ^a	
	a	b
Gouy–Chapman theory, assuming 52 Å. ² per ion and 100% ionization	224	165
ζ -Potential from ref. 36	108	77
ζ -Potential according to ref. 38 from data of ref. 36	200	92.5
Maximum ζ -potential, calcd. from ref. 39 assuming $f_w = 10.2 \times 10^{-12}$ v. ⁻² cm. ²	93	47
From equilibrium thickness, assuming $A = 5 \times 10^{-13}$	39	..

^a Counterion concentration in moles per liter: a, 5×10^{-3} ; b, 5×10^{-2} .

equilibrium thicknesses are not sensitive to the exact value of ψ_d .

In Figure 6 our experimental equilibrium thicknesses are compared with the theoretical predictions. For the sake of comparison, the results of Deryagin, *et al.*,¹¹ and of Scheludko, *et al.*,¹² are also given, where possible in terms of the material thickness δ .

Discussion

Figure 6 shows that there is essential agreement in thickness measurements between the earlier microscopic methods of Deryagin and of Scheludko and their co-workers^{11,12} and our macroscopic one, except for the two most dilute solutions of Deryagin. Thus it is likely that the “diameter effect” reported by Duyvis¹⁷ is due to an artifact. As already indicated, Exerowa, *et al.*,¹⁸ could not repeat Duyvis’ findings.

Figure 6 shows also that the qualitative agreement between theory and experiment is excellent especially if a relatively low potential is assumed. On the basis of completely independent data about van der Waals forces and double layer structure, the theory predicts equilibrium values of soap films varying by a factor of 40 within the pertinent range of ionic strengths. The experimental points do not deviate from these predictions by more than 20% except for the first measurements of Deryagin in the difficult region of high dilutions which are clearly out of line. Thus there seems to be little doubt that the basic theoretical approach is sound.

On the other hand, there are disturbing quantitative discrepancies such as the tendency of the points to be above the line for an infinite potential at high concentrations, and the close agreement between Scheludko’s and our results despite the difference in hydrostatic pressure and in the materials used.

We will now consider two aspects of this problem in more detail, namely the relative thicknesses of rigid and mobile films and the trend of van der Waals pressure with thickness. As all the pertinent details are only known for our own experiments, we will confine these analyses to our equilibrium thicknesses.

1. Comparison of Mobile and Rigid Films. Figure 6 shows that our mobile films are slightly thicker than rigid films at the same ionic strength. This comparison should be relatively free of experimental uncertainties as all the films were examined under the same conditions. Surface potentials should be no higher in mobile than in

(34) Any dimerization³⁵ involves only the negatively adsorbed co-ions and therefore has no significant effect.

(35) P. Mukerjee, *J. Phys. Chem.*, **62**, 1404 (1958).

(36) D. Stigter and K. J. Mysels, *ibid.*, **59**, 45 (1955).

(37) R. J. Hunter, *ibid.*, **66**, 1367 (1962).

(38) P. H. Wiersema, Thesis, Utrecht, 1964.

(39) J. Lyklema and J. Th. G. Overbeek, *J. Colloid Sci.*, **16**, 501 (1961).

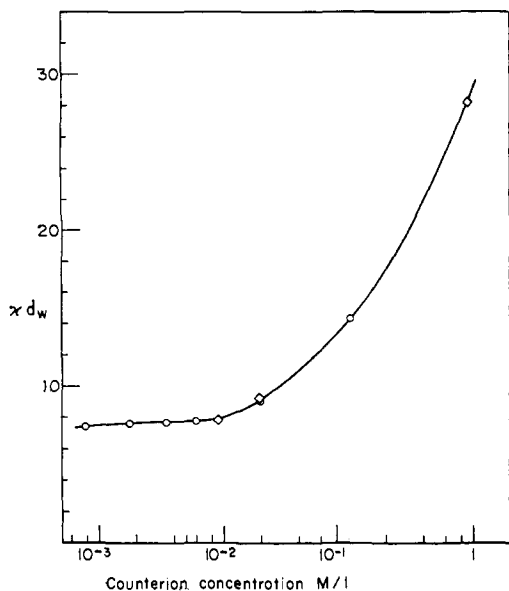


Figure 7. Equivalent water thicknesses of rigid \circ and mobile \diamond films of sodium dodecyl sulfate plotted in terms of the double layer thickness $1/\kappa$.

rigid films since Wilson, *et al.*,⁴⁰ found that addition of lauryl alcohol (which renders the films rigid) has little effect on the adsorption of the lauryl sulfate ion, there being a slight increase if anything. The greater thickness of the mobile films could, however, be the result of an over-correction for the optical effect of the surface layer. Figure 7 therefore shows the equivalent water thicknesses, d_w , of these films. In order to expand the scale, this thickness is measured by comparison with the double layer thickness by plotting the κd_w product. The figure shows that these equivalent water thicknesses are about equal and since the optical correction must be larger for rigid films, it seems certain that the effect is not an artifact.

Yet theory leads one to expect the reverse, a greater thickness for the rigid films unless the van der Waals forces show some very unlikely peculiarities. Qualitatively this can be seen as follows. Let us change from a mobile film to a rigid film by increasing the thickness d_1 of the surface monolayer. If this is done at constant total thickness δ , it results in a reduction of the central aqueous core d_2 , causing a greater compression of the double layers and an increase in P_r . In view of the steepness of the P_r curves (Figure 5) this should lead to a corresponding thickening of the film unless the van der Waals forces would simultaneously increase correspondingly which is very unlikely. Alternatively, let us make the change in d_1 without changing the central core. Thus P_r remains the same but the total thickness is increased. This in turn should lead to a reduction of the van der Waals compression P_v since this decreases in general as the film becomes thicker (Figure 5) and should consequently lead to a new equilibrium at a still larger thickness.

This last argument can be made quantitative if retardation of van der Waals forces is neglected. Duyvis¹⁷ has shown that under these conditions

(40) A. Wilson, M. B. Epstein, and J. Ross, *J. Colloid Sci.*, **12**, 345 (1947).

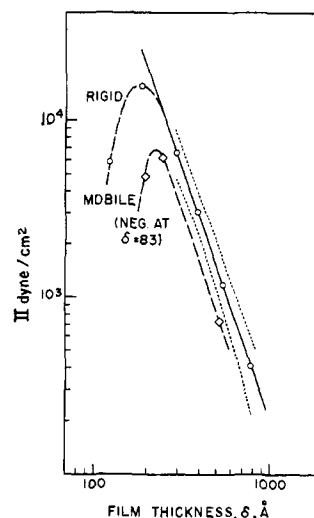


Figure 8. van der Waals pressure as calculated from experimental data and the double layer theory for $\psi_d = 100$ mv.: upper dashed line shows the effect of an error of +25 mv. in potential or of $(5 \text{ \AA.} + 3\%)$ in thickness; lower dashed line for same errors in opposite direction.

$$6\pi P_v = -A_{11}[d_2^{-3} - 2(d_1 + d_2)^{-3} + (2d_1 + d_2)^{-3}] + 2A_{12}[d_2^{-3} - (d_1 + d_2)^{-3}] - A_{22}d_2^{-3}$$

where the subscripts indicate the layers to, or between which, the pertinent Hamaker constants apply. Hence the change in van der Waals pressure as the surfactant layer increases is, neglecting the 6π factor

$$-(\partial P_v / \partial d_1)_{d_2} = A_{11}[(d_1 + d_2)^{-4} - (2d_1 + d_2)^{-4}] - 2A_{12}(d_1 + d_2)^{-4}$$

This is negative (*i.e.*, the compression decreases) unless

$$A_{12} < \frac{A_{11}}{2} \left[1 - \left(\frac{1 + d_1/d_2}{1 + 2d_1/d_2} \right)^4 \right] \approx A_{11} \frac{2d_1}{d_2}$$

which would be the case only if the interaction of surfactant molecules with water molecules would be less (and even much less for thicker films) than that of water molecules with each other. In view of the greater polarizability of hydrocarbons it is the opposite that is to be expected.

The reason for this discrepancy between theory and experiment is not clear. Besides some unlikely experimental error it could lie either in an unexpected effect of van der Waals attractions or in some unsuspected influence of surface structure on the double layer.

2. *The Trend of van der Waals Forces with Distance.* Heretofore we have used the theory of van der Waals forces to calculate an equilibrium thickness which was then compared with the experimental values. We shall now use the reverse approach, utilize the experimental values, in conjunction with the double layer theory to obtain values for the van der Waals pressure Π which can then be compared with the theory. Thus we can set

$$\Pi = P_r - P_b$$

and compare it with P_v , which increases rapidly as the film becomes thinner (Figure 5). The results of this computation are shown in Figure 8. In this calculation

we have used $\psi_d = 100$ mv. which seems a reasonable average of results listed in Table II and whose effect will be discussed further below.

At large thicknesses (and corresponding low ionic strengths) there is indeed a rapid regular increase in Π as the film becomes thinner, but for thicknesses below some 200 Å. there is a maximum followed by a rapid decrease, in clear contradiction to the theoretical expectation because the van der Waals pressure is expected to increase if the film becomes thinner. This means that the repulsive force operative at higher ionic strengths is apparently higher than calculated by the Gouy–Chapman theory. This effect could be accounted for if there were a water structure supporting the film, but we have shown,²⁰ as already mentioned, that no such structure could be detected in kinetic measurements.

Another possible source for this higher repulsive force in thin films was suggested by K. J. M.,^{13b} namely the presence of micelles in the intralamellar solution when films are formed from solutions above the c.m.c. Since the diameter of a micelle with its surrounding double layer is of the same order as the thickness of a film, a significant contribution could be expected. However, this effect could play no role in our experiments as the concentrations used were all below or just above the c.m.c. so that micelles were absent or practically so.

That the Gouy–Chapman calculation, which is based upon an ideal system, breaks down at high ionic strength is generally known. What is surprising, however, is that it breaks down already at ionic strengths of the order of 2×10^{-2} and that the deviations are so great that to bring the 123-Å. point for rigid films upon the rising branch would require an increase of the repulsion by a factor of 10. Although many improvements in the double layer theory have been proposed,⁴¹ and several, in particular the introduction of finite ion size, tend to increase the repulsion, none of them suggest that a change of the magnitude required here is likely.

If one now considers the situation at the other end of the scale where the films are thick, one notices that the points lie on a straight line. The slope of this line is 3.0 which would be the value expected for nonretarded van der Waals interactions. The thicknesses involved here are, however, of the order of 500 Å. so that it is rather the retarded pressure with a slope closer to 4 as shown on Figure 4 that would be expected. Furthermore the constant A calculated from this line assuming nonretarded interaction is 3×10^{-12} which is some seven times larger than expected. Thus it seems that here the calculated repulsion is too high and does not decay as rapidly as expected. Yet we are here in the region of 10^{-3} N solutions where the premises of the theory should be reasonably satisfied.

(41) D. A. Haydon in "Recent Progress in Surface Science," J. F. Danielli, K. G. A. Pankhurst, and A. C. Riddiford, Ed., Academic Press Inc., New York, N. Y., 1964.

These discrepancies in the behavior of thick films cannot be removed by assuming other reasonable values of the potential. The dotted lines in Figure 8 show the effect of changing the potential by 25 mv. This does not affect the slope significantly. It would be reasonable to expect that in fact the potential tends to decrease as the concentration increases as suggested by Table II. This would tend to reduce the slope further instead of raising it as required by the theory.

Large systematic experimental errors can of course account for any discrepancy. However, a reasonable error of $\pm(5 \text{ \AA.} + 3\%)$ would not affect the conclusion as shown by the same dotted lines in Figure 8. Furthermore, the thickness measurements themselves are in relatively good agreement with other similar ones as shown in Figure 6. One is tempted to conclude that for high equilibrium thicknesses the actual repulsion is lower than that predicted by the Gouy–Chapman theory either because ψ_d is considerably lower than usually assumed or because the potential drop in the diffuse layer is much steeper than according to Poisson–Boltzmann statistics. In this respect it is interesting to note that some modern double layer theories that are not based upon a Boltzmann distribution predict a steeper potential decay.^{42, 43}

Finally we want to note that our conclusion that the double layer theory gives less than the desired repulsion at short distances has been reached before, both for soap films¹¹ and for emulsion droplets,⁴⁴ but only now has an additional contribution from the water structure been excluded on the same system.²⁰ Similarly the apparent third power dependence for thick films has been observed earlier^{12a, 19} though the interpretation differed.

Conclusion

Thus it appears that the study of equilibrium films is a sensitive tool for testing theories of interparticle forces in the medium range and that thus far the agreement with theory is only qualitative.

Since the equilibrium thickness depends mainly on the range of the double layer repulsion and on its dependence on ionic strength, it is possible that this is the part of the theory where improvement is to be sought.

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(42) F. P. Buff and F. H. Stillinger, *J. Chem. Phys.*, **39**, 1911 (1963).

(43) H. D. Hurwitz, A. Sanfeld, and A. Steinchen-Sanfeld, *Electrochim. Acta*, **9**, 929 (1964).

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