SPECIFIC IONIC EFFECTS
IN FREE LIQUID FILMS

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CONTENTS

1. INTRODUCTION

In order to test and extend the theory of the stability of lyophobic colloids, developed by DERYAGIN and LANDAU (1) and by VERWEY and OVERBEEK (2), the silver iodide sol has been used for many years (3–7). Much important information about the stability of lyophobic colloids was obtained by means of this model. Beside this system other models like polystyrene sols became the fashion because these can be produced in a high degree of monodispersity and over a wide spherical particle range. Also the charge determining groups of these systems can be varied and controlled (8–10).

During the last twenty to thirty years the interest in foams and emulsions has grown strongly (11–14). Parallel with this has been the development of the soap film as a model for the study of several colloid chemical phenomena, because it became clear that the same factors which play a role in the stability of lyophobic colloidal systems are of importance in the behaviour (stability, specificity, equilibrium thickness) of both isolated and non-isolated soap films (15–26). In these systems the electrical double layer repulsion and the VAN DER WAALS attraction contribute to the forces which control their stability and equilibrium thickness.

An advantage of the soap film over the silver iodide sol as a model is the fact that its geometry is well defined. In addition, and this is of paramount importance, the equilibrium thickness can be determined experimentally. One of the disadvantages, however, is that insufficient information exists about the value of the double layer potential.

A considerable amount of research on the properties of negatively charged silver iodide sols in the presence of electrolytes has established the existence of a lyotropic series with respect to the double layer capacities and to the flocculation values of, for example, the alkali ions (5, 27, 28). Especially the combination of these two quantities indicates specific adsorption of the counterions. Here specific adsorption is defined as adsorption by other then Coulombic forces originating from the surface charge. In studying this specificity one may gain insight into the extent of deviations from the classical GOUY-CHAPMAN theory of the diffuse double layer (29, 30) and from the theory of DERYAGIN-LANDAU (1) and of VERWEY-OVERBEEK (2) because these theories largely neglect finite ion size and specific adsorption.

Counterion specificity is also encountered in the double layer at the mercury interface (31) and at the silica interface (32). It is demonstrated as well in the critical micelle concentration of, for example, the alkali dodecyl sulphates (33) and in the interaction of the alkali ions with different types of monolayers (34, 35). In many of these systems – but not in all of them – the sequence of the interaction of the counterions with the substrate can be interpreted in terms of a stronger binding of the ion, having the smaller hydrated radius.

Research on soap films has shown that specific effects also occur in these systems. The equilibrium thickness of films containing lithium counterions

turns out to be about five percent bigger than those containing sodium counterions (22, 36), which is a small but measurable and significant difference. As a corollary of the research on specificity in stability and the above-mentioned double layer and monolayer systems it is therefore important and logical to study the specificity in soap films further. For that purpose the influence of several alkali counterions, co-ions and non-electrolytes on the equilibrium thickness of free soap films was measured and discussed. As at room temperature the limited solubility of some of the surfactants restricts the number of counterions that can be studied, measurements have been included at higher temperatures, where these surfactants have better solubility. Finally in this thesis some investigations on the so-called stratified films are reported.

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2. FREE LIQUID FILMS

2.1. PHENOMENOLOGY

Under free liquid films we understand those structures that are moulded when a frame immersed in a surfactant solution is withdrawn vertically.

The films are very thin and show beautiful colours in reflected light. This phenomenon, which is due to the interference of light reflected from the front and back faces, can be used to obtain their thicknesses. When the film thickness is $(2n+1) \lambda/4$ ($n=0, 1, 2...$; λ is wavelength in the film) there is maximum reinforcement at normal incidence so that the film looks silvery. Extinction occurs at film thicknesses $2n\lambda/4$ ($n=0, 1, 2...$).

As a rule the thickness of vertical films decreases with time because of drainage due to gravity. Upon draining, the reflected intensity passes through a series of maxima and minima, as schematically depicted in fig. 2–1.

Once a draining film has passed its first, but last observed, interference maximum (number 3 in fig. 2–1) then on further thinning the intensity can only decrease. If the film is stable, the thickness eventually reaches a constant (equilibrium) value. These films can then be so thin that practically no light is reflected: they look gray or black.

One can distinguish two types of film by virtue of their drainage behaviour, rigid and mobile films (1–4).

    a. The rigid film thins so slowly that it takes hours or even days before the equilibrium thickness is reached. It is formed from surfactant solutions with a high surface viscosity. The occurrence of rigidity was attributed to a high surface shear viscosity by SCHICK (5). On the other hand, PRINS and VAN DEN TEMPEL (4) showed that in rigid films the elasticity and the high dilational viscosity are responsible for the slow draining. This type of film shows irregularly curved, closely spaced interference fringes and is formed by, for example,
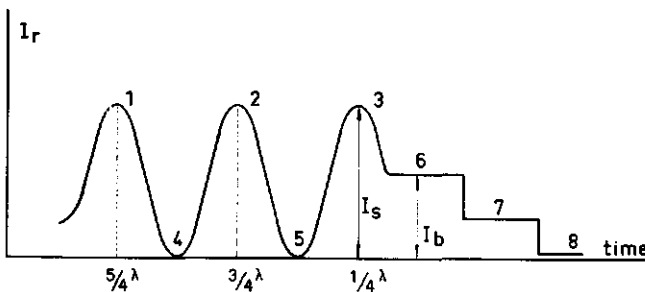

FIG. 2-1. Recorded reflected intensity as a function of time. 1,2,3: interference maxima, I_s = intensity, reflected by silvery film. 4,5: interference minima. 6: reflected intensity from the first black equilibrium film, I_b. 7: reflected intensity from the second black equilibrium film. 8: background intensity.

saponine (6) and sodium dodecyl sulphate solutions, containing slight amounts of dodecyl alcohol. The rigidity in the latter system is probably induced by co-adsorption of the dodecyl alcohol (7).

b. The mobile film, the most common type, thins very rapidly. It is formed from surfactant solutions with normal surface viscosity. Usually in the course of drainage turbulent motion of film material occurs along the borders of the film. In the central part of the film, horizontal bands having the same colour are formed and the boundary between silver coloured and black film is regular and sharp. These films are formed by almost all surfactant solutions, for example by sodium dodecyl sulphate and dodecyl amine hydrochloride solutions (with or without electrolytes).

Finally, it should be mentioned that in some systems more than one equilibrium thickness can be observed (1,8). Films drawn from certain surfactant solutions drain initially like mobile films until they become gray or black (first black film), after which a second thinning process occurs. The presence of the second black film can be deduced from the very slight, constant light intensity, as depicted schematically in fig.2-1. The thickness of this second black film can also be determined photometrically.

2.2. Experimental approach

It is possible to distinguish between two methods for studying soap films, the macroscopic method, in which films of several cm² area are studied and the microscopic method with films of less than one mm² area.

In the present study as well as in references (9-15) the macroscopic approach was applied. The advantages of this method may be summarized as follows:

a. the film is plane parallel and does not contain dimples (16),

b. large surface areas can be realized, so that disturbing effects due to the presence of the borders are minimal. Moreover, the light spot on the film is much smaller than the film dimensions so that scanning of the surface is possible,

c. the film formation is reproducible,

d. the set-up allows the equilibrium films to be produced in two different ways. First, a thick film may be drawn from the solution. By drainage a black equilibrium film is formed in course of time. This is called the static procedure. The second way involves pulling the film very slowly from the solution. This dynamic method was used for the first time by LYKLEMA et al. (11). They found that at very low pulling velocities the thickness of the film is independent of velocity and that the thickness determined in this way is identical to the thickness, found after draining of an initially thick film (static method). Hence, these two different approaches provide an additional check on the reliability of the obtained equilibrium thicknesses.

A disadvantage of the macroscopic method is that because of their large surface areas the films are sometimes unstable.

In the microscopic method, described in references (9, 17-24) a very small

circular film is exposed to an external pressure. The advantage of this method is the long range of films, including non-aqueous ones, and thicknesses which can be studied. This method has the disadvantage that dimpling may occur and that the light spot on the film is not much smaller than the whole film area, so that border effects may influence the reliability of the measured equilibrium thicknesses.

2.3. FORCES IN SOAP FILMS

When the film has stopped draining, equilibrium exists between the forces tending to thin the film further, and those opposing this trend. In other words, equilibrium is characterized by the condition that the sum of all forces is zero. This means that from a knowledge of the equilibrium thickness information about the interplay of forces in soap films can be obtained.

Two groups of forces can be distinguished:
a. attractive forces, such as VAN DER WAALS (Π_{vdW}), capillary (Π_c), and hydrostatic (Π_h) forces,
b. repulsive forces, which include electrical double layer repulsion (Π_{el}), BORN repulsion and forces due to steric hindrance (Π_s).

2.3.1. *Van der Waals forces*

Initially DE VRIES (25) and later OVERBEEK (26) have pointed out the great importance of VAN DER WAALS forces in soap films. They demonstrated that the compressive force on a film of thickness d in air is equivalent to the force which two semi-infinite liquid layers of the same composition as the film, separated by an air gap of thickness d, exert on each other ($\Pi_{film} = \Pi_{gap}$).

The VAN DER WAALS forces have been evaluated quantitatively with the help of two theories.

In their microscopic theory, HAMAKER (27) and DE BOER (28) calculated for the force between two semi-infinite plates separated by a distance d

$$\Pi_{vdW} = - \frac{A}{6\pi d^3} \tag{2-1}$$

where A is the HAMAKER – VAN DER WAALS constant of the material, determined by the expression

$$A = \pi^2 q^2 \beta \tag{2-2}$$

where q = number of molecules per cm³
β = interaction constant for two molecules, defined by the LONDON equation:

$$V = - \frac{\beta}{r^6} \tag{2-3}$$

with $V =$ energy of attraction between two molecules,
$r =$ distance between the centres of these two molecules.

One of the assumptions of the microscopic theory concerns the additivity of the intermolecular dispersion forces. Furthermore, the total force between two bodies is found by integration over their total mass in stead of by summation of the forces between pairs of individual atoms. Moreover, this theory considers the interactions to occur in a vacuum in stead of in a medium and the treatment of attraction between colloidal particles in a condensed medium is only approximative. Finally retardation of the forces for large distances between the atoms is not accounted for. (Distances are assumed large when comparable with the characteristic wavelength, about 1000 Å for water). CASIMIR and POLDER (29) treated quantitatively the retardation of the dispersion forces. Their calculations predict a gradual change of the d^{-3} power law to a d^{-4} power law.

In the macroscopic theory, developed by DZYALOSHINSKII et al. and by LIFSHITS (30–32) the influence of the medium is automatically included. For the force between two semi-infinite bodies at short distances they also arrive at an inverse third power law in the distance. With increasing distances their theory predicts a gradual change from non-retarded to retarded forces. The equivalence of Π_{film} and Π_{gap} according to this theory does not hold at large d, but 'film' and 'gap' are equivalent for d small with respect to the characteristic wavelength.

Further comparison of both theories may be made on the basis of the calculated HAMAKER – VAN DER WAALS constant. Calculation of this constant for water by the microscopic theory according to SLATER and KIRKWOOD (33) yields a value of 6×10^{-13} erg, whereas by the macroscopic theory, using optical data for water vapour, a value of 5.4×10^{-13} erg was calculated by KRUPP (34). Similar calculations made by VAN SILFHOUT (35) for quartz indicate that both theories yield HAMAKER – VAN DER WAALS constants that are well comparable, with the macroscopic theory giving slightly lower results.

Direct application of equation (2–1) to soap films is not permitted, because the films are not homogeneous. They consist of an aqueous core, flanked by two surfactant monolayers with a HAMAKER – VAN DER WAALS constant usually different from that of the surfactant solution. For this composite structure DUYVIS (9) calculated the attractive force

$$\Pi_{vdW} = -\frac{A_{11}}{6\pi} \left[\frac{1}{d_2^3} - \frac{2}{(d_1+d_2)^3} + \frac{1}{(2d_1+d_2)^3} \right] +$$

$$+2\frac{A_{12}}{6\pi} \left[\frac{1}{d_2^3} - \frac{1}{(d_1+d_2)^3} \right] - \frac{A_{22}}{6\pi} \frac{1}{d_2^3} \qquad (2\text{-}4)$$

where (see fig. 2–5, page 14)
$d_1 =$ thickness of the surfactant monolayer,
$d_2 =$ thickness of the aqueous core of the film,
$A_{11} =$ HAMAKER – VAN DER WAALS constant of the monolayer,

A_{22} = HAMAKER – VAN DER WAALS constant of the aqueous core,
A_{12} = composite HAMAKER – VAN DER WAALS constant, approximately equal to $\sqrt{A_{11}.A_{22}}$ Π_{vdW} is always negative if $A_{12} = \sqrt{A_{11}.A_{22}}$ as was proved by DUYVIS (9). As may be seen, equation (2–4) reduces to equation (2–1) for $d_1 = 0$ and $A_{11} = A_{22} = A_{12} = A$ (homogeneous film).

Direct measurement of the VAN DER WAALS force between two macroscopic bodies (35–37) generally yields the d^{-4} law because of the large distances involved, whereas in adhesion experiments the forces obey the d^{-3} law (KRUPP, 34). When it is realized that the equilibrium thickness of soap films can cover a range of about 50–1000 Å, the importance of these systems is evident. The VAN DER WAALS forces can be studied in the transition region of non-retardation to retardation.

The contribution of the VAN DER WAALS forces to the interpretation of the equilibrium thickness was discussed by DUYVIS (9) and by LYKLEMA and MYSELS (12). The rate of thinning of soap films was discussed in terms of the VAN DER WAALS forces by SHELUDKO (18). SHELUDKO (21) and MANEV (23) claimed experimental evidence for retarded VAN DER WAALS forces in films of benzene, chlorobenzene and aniline.

2.3.2. *Hydrostatic pressure*

The second type of force, which has an attractive nature is the hydrostatic pressure. It is the pressure difference between the surface of the bulk solution, in equilibrium with the film, and the outer phase and is determined by the relation

$$\Pi_h = -\rho g h \tag{2-5}$$

where ρ = density difference between the film phase and the outer phase (water vapour and air)

g = gravitational constant

h = height difference between the part of the film under consideration and the surface of the bulk solution

The hydrostatic pressure must be added to the capillary or LAPLACE pressure on the film, the latter being the result of the suction at the PLATEAU-border (the
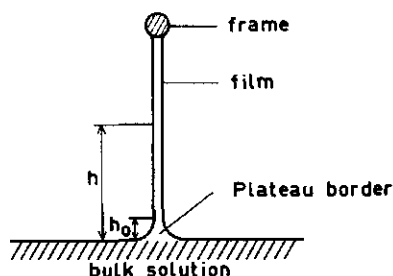

FIG. 2-2. Film in contact with bulk solution.

part of liquid at the boundary between the film and the frame or the solution, Fig. 2–2). At the top of the border this capillary pressure is given by the relation

$$\Pi_c = -\rho g h_0 \tag{2-6}$$

The magnitude of h_0 – the height where the meniscus becomes vertical – has been formulated by MYSELS et al. (1) as

$$h_0 = \sqrt{\frac{2\sigma}{\rho g}} \tag{2-7}$$

where σ is surface tension of the solution.

2.3.3. *Electrical double layer repulsion*

If ionic surfactants have been used to stabilize the film, the walls bear a charge, the sign of which depends on the nature of the ionized group of the surfactant molecule. For example, anionic surfactants like sodium dodecyl sulphate (NaDS) give the walls a negative charge. Together with the positive charge due to the counterions in the aqueous core an electrical double layer is built up similar to that occurring at the surface of a particle in a colloidal dispersion or around electrodes in solution.

As is shown by the colloid stability theory of VERWEY and OVERBEEK (38) overlap of diffuse double layers results in a repulsive force which for soap films tends to prevent thinning. The electrical double layer repulsive force is given to a good approximation by the expression.

$$\Pi_{el} = 64 \, nkT\gamma_d^2 e^{-\kappa d_2} \tag{2-8}$$

where n = number of counterions /cm³ bulksolution
 k = BOLTZMANN constant
 T = absolute temperature
 $\gamma_d = \tanh \left(\dfrac{ze\psi_d}{4kT} \right)$
 z = valency of the counterion
 e = elementary charge
 ψ_d = diffuse double layer potential
 $\kappa = \sqrt{\dfrac{8\pi z^2 e^2 n}{\varepsilon kT}}$ (reciprocal Debye length)
 ε = dielectric constant of the medium
 d_2 = thickness of the aqueous core of the film, flanked by the surfactant monolayers

Formula (2–8) is applicable provided $\kappa d_2 > 1$, a condition which is as a rule fulfilled in soap films. In deriving this equation one of the assumptions is that

the ions are point charges, as a result of which this formula can not account for specific effects.

It should be remarked that the electrical double layer repulsion acts over a distance equal to the distance between the starting points of the two interacting double layers. This distance is slightly less than the aqueous film core. On the other hand the equation for Π_{vdW} contains the aqueous core as well as the monolayers because also these surface layers contribute to the VAN DER WAALS compression. This explains the experimental fact that soap films are stable at concentrations of monovalent electrolytes exceeding very much the flocculation values of these electrolytes for hydrophobic colloidal solutions (26). Therefore this interplay of forces can be studied under conditions where colloidal stability can no longer be used as a tool to study double layer repulsion and VAN DER WAALS attraction.

2.3.4. *Born repulsion and steric hindrance*

When the film becomes very thin BORN repulsion and repulsion due to steric hindrance (Π_s) between the hydrophilic groups of the surfactant monolayers must be considered. BORN repulsion only becomes an important contribution to the total repulsive force when the film is so thin that overlap of the electronic shells in the head groups occurs. However, the thinnest films have thicknesses of about 40 Å, so that the BORN repulsion can be neglected. With respect to the steric hindrance it should be remarked that in our case there are no loops or dangling chains of the two surfactant layers interfering with each other, hence we will pay no attention to this type of stabilization.

2.3.5. *Free energy of soap films*

For the film in equilibrium with its surroundings (bulk solution and atmosphere) the sum of all forces, Π, must be zero,

$$\Pi = \Pi_{vdW} + \Pi_h + \Pi_{el} + \Pi_s = 0 \tag{2-9}$$

Denoting the GIBBS free energy per unit surface area of the film by G, the differential of this quantity becomes

$$dG = -SdT + Vdp + \sigma_f dA + \sum_i \mu_i dc_i \tag{2-10}$$

where S = entropy of the film
T = absolute temperature
V = volume of the film
p = pressure of the film
σ_f = surface tension of the film
A = film surface area
μ_i = thermodynamic potential of component i
c_i = concentration of component i

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The pressures Π being the negative derivatives of the corresponding free energies per unit film area, an equivalent way of formulating the equilibrium condition is therefore

$$-\left(\frac{\partial G}{\partial d}\right)_{p,T,A,c_i's} = \Pi = 0 \tag{2-11}$$

The components of the total free energy per unit surface can be calculated using the expressions $(2-1)$, $(2-5)$ and $(2-8)$:

$$G_{vdW} = -\frac{A}{12\pi d^2} \tag{2-12}$$

$$G_h = \rho\, ghd \tag{2-13}$$

$$G_{el} = \frac{64nkT}{\kappa}\gamma_d^2 e^{-\kappa d_2} \tag{2-14}$$

With respect to the contribution of the steric hindrance to the total free energy (G_s), it can be stated that this component is zero at film thicknesses larger than about twice the surfactant monolayer thickness. It increases markedly to a very high value when the film thickness becomes smaller than this critical value.

The variation of G and that of its component parts as a function of the film thickness is schematically given in fig. 2–3.
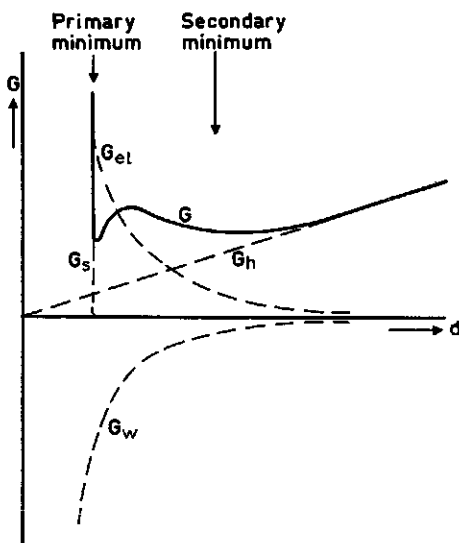

FIG. 2-3. Schematic picture of the free energy of a soap film as a function of its thickness.
G = total GIBBS free energy.
G_{vdW} = GIBBS free energy due to VAN DER WAALS attraction.
G_{el} = GIBBS free energy due to electrical double layer repulsion.
G_h = GIBBS free energy due to hydrostatic pressure.
G_s = GIBBS free energy due to steric hindrance.

When the hydrostatic pressure is zero, the secondary minimum is lower than the primary one. By decreasing the hydrostatic pressure both minima can be brought to the same level. In this case the film has two equilibrium thicknesses. The primary minimum corresponds to the second black film of about 40 Å and is mainly determined by steric hindrance; the secondary minimum corresponds to the first black film of greater and variable thickness. The magnitude of the free energy of the first black film is mainly governed by the VAN DER WAALS attraction and double layer repulsion.

Further quantitative discussion of the forces in soap films will be given in the chapter about the interpretation of the experimental results (page 31). In the light of the results it would appear possible that still other kinds of forces are present which are not accounted for thus far.

2.4. LIGHT REFLECTION

The thin films are never absolutely black but always reflect a fraction R of the incident light.
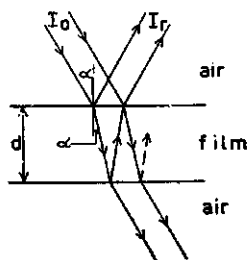
FIG. 2-4. Reflection of light by a homogeneous film.

When the film is conceived as a transparant, homogeneous and isotropic medium, R is given by the formula of RAYLEIGH (39),

$$R = \frac{I_r}{I_0} = \frac{4r^2 \sin^2 \Delta}{1 - 2r^2 + 4r^2 \sin^2 \Delta + r^4} \tag{2-15}$$

where I_0 = intensity of the incident beam
I_r = intensity of the reflected beam
r = FRESNEL coefficient =

$$\frac{n \cos \alpha - n_0 \cos \alpha'}{n \cos \alpha + n_0 \cos \alpha'}; \text{ for nonpolarized light and}$$

angles $< 30°$, $r = \dfrac{n - n_0}{n + n_0}$ to a good approximation

n_0 = refractive index of air
n = refractive index of the film material

$$\Delta = \frac{2\pi nd \cos \alpha}{\lambda} = \text{phase difference between the beams}$$

reflected at the top and the bottom surface of the film

α = angle of refraction
α' = angle of incidence
λ = wavelength of the light in vacuum
d = film thickness

$$\frac{\sin \alpha'}{\sin \alpha} = \frac{n}{n_0}$$

For $n_0 = 1$ and $n = 1.33$ (i.e. a water film in air), the term r^4 is about $1/2500$. Neglecting this term, (2–15) can be simplified to

$$\frac{I_r}{I_0} = \frac{4r^2 \sin^2 \Delta}{1 - 2r^2 + 4r^2 \sin^2 \Delta} \tag{2-16}$$

One can see that the refractive index is an important quantity. This factor occurs five times in formula (2–16): three times in the FRESNEL coefficient and twice in the sine term. It is reasonable to suppose that r is independent of the film thickness, but only a function of the structure of the surface layers of the film. In other words, it is the same for black and silvery films.

The film thicknesses at which maximum reflection occurs (silvery films) are given by the equation

$$d_s = \frac{p\lambda}{4n \cos \alpha} \tag{2-17}$$

where p = the order of interference ($p = 1, 3, 5.....$)

Now we may rewrite formula (2–16) for the last silvery film (index s) and for the black equilibrium film (index b). Furthermore, as $r_s = r_b = r$, it follows that

$$\frac{I_s}{I_0} = \frac{4r^2 \sin^2 \Delta_s}{1 - 2r^2 + 4r^2 \sin^2 \Delta_s} \tag{2-18}$$

where I_s = reflected intensity from the silvery film and

$$\frac{I_b}{I_0} = \frac{4r^2 \sin^2 \Delta_b}{1 - 2r^2 + 4r^2 \sin^2 \Delta_b} \tag{2-19}$$

where I_b = reflected intensity from the black film.

Realizing that $\sin^2 \Delta_s = 1$, then on dividing (2–19) by (2–18)

$$\frac{I_b}{I_s} = \left(\frac{1+2r^2}{1-2r^2+4r^2\sin^2\varDelta_b}\right)\sin^2\varDelta_b \tag{2-20}$$

or

$$\frac{I_b}{I_s} = \left(\frac{1+2r^2}{1-2r^2+4r^2\sin^2\dfrac{2\pi nd_b\cos\alpha}{\lambda}}\right)\sin^2\frac{2\pi nd_b\cos\alpha}{\lambda} \tag{2-20a}$$

where d_b = thickness of the black film

Equation (2–20a) shows how from the reflected intensities I_s and I_b the thickness of the black equilibrium film can be calculated.

However, the above equations apply to a liquid film of homogeneous composition, but soap films should be considered as three-layer systems, an aqueous solution (thickness d_2, refractive index n_2) flanked by two surfactant monolayers (thickness d_1, refractive index n_1) (40, 41), see fig. (2–5).

The light reflection of a homogeneous, isotropic film and that of a sandwich-like structure are different. The problem of the reflection of light by a multilayer system is discussed in detail by several authors (9, 11, 42, 43). It turns out that the total thickness d can be obtained from the equivalent water thickness d_w (that is the thickness calculated using equation (2–20a) after correcting for the different optical properties of the surface layers and the consequent multiple reflections. In order to evaluate this correction quantitatively a model for the soap film must be accepted. LYKLEMA et al. (11), working with films stabilized by sodium dodecyl sulphate (NaDS), base their corrections on two models of the film:

1. The surfactant molecules are oriented perpendicularly to the film surface. The magnitude of d_1 is estimated to be 16 Å (44). This picture is reasonable for rigid films. However, VAN DEN TEMPEL (45) inferred from elasticity of rigid films that here the surfactant molecules lie more or less flat.

2. The surfactant molecules occupy a surface area of 52 Å²/molecule (46). When the density of the monolayer is taken to be unity, this results in a
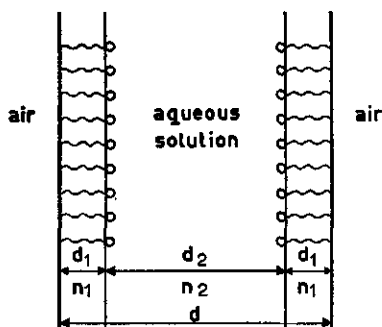
FIG. 2-5. Schematic model of a soap film.

monolayer thickness of 8.5 Å. This picture, in which the surfactant molecules lie more or less flat, is reasonable for mobile films. However, CORKILL et al. (10) studied mobile films and concluded from the simultaneous measurement of the total film thickness and the thickness of the aqueous core that the surfactant molecules are oriented perpendicularly to the film surface.

Choosing $n_1 = 1.45$ and $n_2 = 1.33$ the calculations of LYKLEMA et al. (11) show that the true film thickness is smaller than the equivalent water thickness by a constant amount (independent of water core thickness), which turned out to be 13.5 and 7.3 Å for models 1. and 2. respectively.

The same approach of the problem outlined above was presented earlier by DUYVIS (9) and later a more general theory was formulated by FRANKEL and MYSELS (43) corroborating the conclusion that the correction to be applied to the equivalent water thickness (d^*) is negative $(n_1 > n_2)$ and independent of the thickness of the aqueous core (d_2). Moreover, the theory of FRANKEL and MYSELS can easily be extended to cover reflection from multilayer systems.

It should be noted that the correction is relatively more important in thin films than in thick films.

In fig. 2–6 the magnitude of d^* is given as a function of d_1 ($n_1 = 1.43$; $n_2 = 1.33$). For the calculation, the FRANKEL-MYSELS equation

$$d^* = 2d_1 \frac{n_2^2 - n_1^2}{n_2{}^2 - 1} \qquad (2.21)$$

is used. As may be seen, d* is always negative. An uncertainty of 1 Å in d_1 results in an uncertainty of 0.7 Å in d^*.

In fig. 2–7 the influence of the magnitude of n_1 at fixed n_2 on d^* is given ($n_2 = 1.33$; $d_1 = 10.6$ Å). Here, d* may be positive or negative, for $n_1 < n_2$ and $n_1 > n_2$ respectively. An uncertainty of 0.01 in n_1 implies an uncertainty of almost 0.8 Å in d^*.

The value of d^* applied by the author is based on a surface concentration of one NaDS molecule/41.5 Å² (47–49), $n_1 = 1.43$ and $n_2 = 1.33$ (50). The calculated surfactant monolayer thickness $d_1 = 10.6$ Å and d^* becomes –7.6 Å.
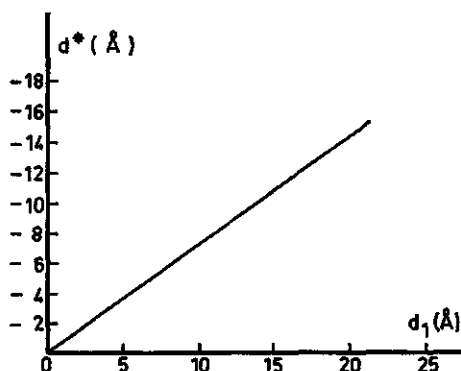

FIG. 2-6. Correction (d^*) to be applied to the equivalent water thickness (d_w) as a function of the surfactant monolayer thickness (d_1). $n_1 = 1.43$ $n_2 = 1.33$.
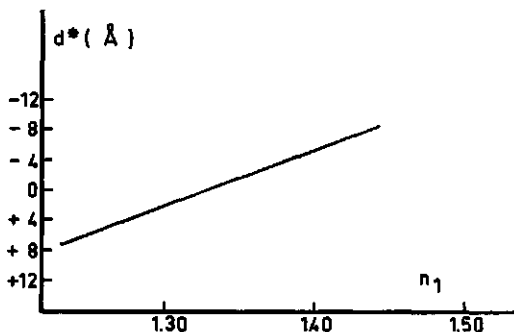
FIG. 2-7. Correction (d^*) to be applied to the equivalent water thickness (d_w) as a function of the refractive index of the surfactant monolayer (n_1). $d_1 = 10.6$ Å $n_2 = 1.33$.

The actual choice made for the parameters characterizing the film affects the interpretation of both the absolute and relative measurements of the equilibrium thicknesses. The absolute measurements are much more sensitive to this choice than the relative ones. The drainage behaviour of all the films studied is the same (mobile). On this basis the model for all the films is the same and so are the corrections.

As will be discussed in more detail, it turns out that the equilibrium films stabilized by lithium dodecyl sulphate (LiDS) are over a large thickness range about five percent thicker than those stabilized by sodium dodecyl sulphate (NaDS), which means a thickness difference of about 5 Å. The magnitude of the thickness and of the refractive index of the surfactant monolayer are well established, so that the difference in film thickness is real and can not be attributed to slight optical differences.

SUMMARY

In this chapter the phenomenology of soap films is briefly described. Two different groups of films can be distinguished: rigid films and mobile films.

The forces which determine the equilibrium thickness of soap films have been discussed. They can be divided into two groups: attractive forces, which promote thinning of the films (VAN DER WAALS forces and hydrostatic forces) and repulsive forces, which retard thinning of the films (the electrical double layer repulsion and forces due to steric hindrance between the hydrophilic groups of the surfactant monolayers). When the film has reached its equilibrium thickness, the sum of all these forces must be zero or the free energy of the film as a function of its thickness must be minimal.

Two methods to study soap films are mentioned: the macroscopic and the microscopic method.

The equilibrium thicknesses of soap films can be measured by means of light reflection. This technique and the consequences of the layered film structure for the light reflection are discussed in detail.

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3. EXPERIMENTAL PART

3.1. THE PREPARATION OF THE SURFACTANTS

Li-, Na-, K-, Rb- and Cs-dodecyl sulphates were prepared according to the procedure of DREGER et al. (1). A surface tension – log concentration curve of NaDS which showed a minimum of 0.2 dyne/cm and a microchemical analysis of all the surfactants revealed that they were pure (difference between experimental and theoretical metal content less than 0.03 %.)

LiDS and NaDS are soluble in water at 25 °C, whereas KDS, RbDS and CsDS are insoluble at 25 °C. However, the latter are soluble above 40 °C.

The non-ionic surfactant OP-11 (octylphenol with an average of eleven ethoxygroups) was obtained from Shell Nederland Chemie N.V., Rotterdam and was not further purified. The specific conductivity of a 0.1 % solution in water at 25 °C was 7×10^{-6} ohm^{-1} cm^{-1}, that of water at 25 °C being 5×10^{-6} ohm^{-1} cm^{-1}. The pH of a 1 % solution of OP-11 in water at 25 °C was 7.0.

3.2. APPARATUS

The apparatus was essentially similar to that constructed and used by LYKLEMA et al (2).

3.2.1. *Frame*

The films were formed in glass frames which were so constructed that the vertical films were about 1.5 cm wide and 2 cm high. For some measurements a Cr-Ni wire having a diameter of 0.0005 inch was attached to the frame by means of glass knobs. If the pulling velocity did not exceed 0.001 mm/sec, this construction of the frame enabled the black equilibrium films to be pulled directly out of the solution (dynamic method) (2, 3).

3.2.2. *Mechanical Part*

The films were formed in the frame which was initially immersed in the surfactant solution contained in a fully filled glass cuvette. Cuvette and frame were set up in a brass box, completely immersed in a constant temperature water bath. In the front walls of the brass box and of the water bath glass
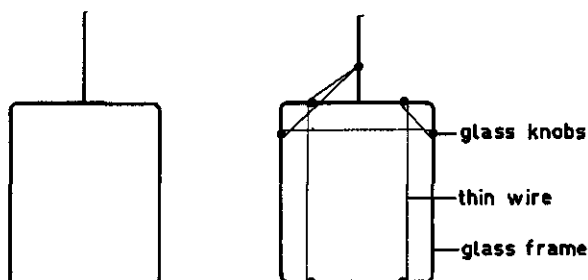
FIG. 3-1. Frames for soap films.

glass knobs

thin wire

glass frame

1 light beam projected onto the film.
2 light beam reflected by the film.
3 lenses (f=10cm).
4 glass windows.
5 cuvette containing surfactant solution.
6 film.
7 glass frame.
8 micrometer.
9 gear box.
10 motor.

windows were constructed. Behind the frame there was room for black perspex plates (light trap) to prevent stray light. The frame was attached to a Cr-Ni rod which could be connected with a screw micrometer. The spindle of this micrometer was attached to a gear box, coupled to a synchronous motor. By variation of the transmission ratio a large range of constant pulling velocities (0.1 μm – 100 μm/sec) of the frame could be achieved.

3.2.3. *Optical and electronic part*

The light source was a high pressure mercury lamp (Osram, HBO 100 W/2) which was fed by a stabilized, variable voltage supply, developed and constructed by the Technical and Physical Engineering Research Service, Wageningen, The Netherlands. The lamp was fitted in a housing having a circular opening ($\varnothing$ 2 cm). The light beam, screened by photographic bellows, was directed horizontally at an angle of about 10° with the normal to the vertical film, via some diaphragms and a biconvex lens ($f=10$ cm). The light spot on the film had a diameter of about 1 mm and was 5 mm above the meniscus of the bulk solution and equidistant from both vertical sides. The reflected beam, screened by bellows, was directed via a lens ($f=10$ cm) onto a diaphragm to form an

1 Servogor recorder	8 removable mirrors
2 voltage supply	9 lenses (f = 10 cm)
3 photomultiplier	10 high pressure mercury lamp
4 diffusers	11 voltage supply
5 interference filter	12 stabiliser
6 slit	13 alternating voltage (220 V)
7 diaphragms	
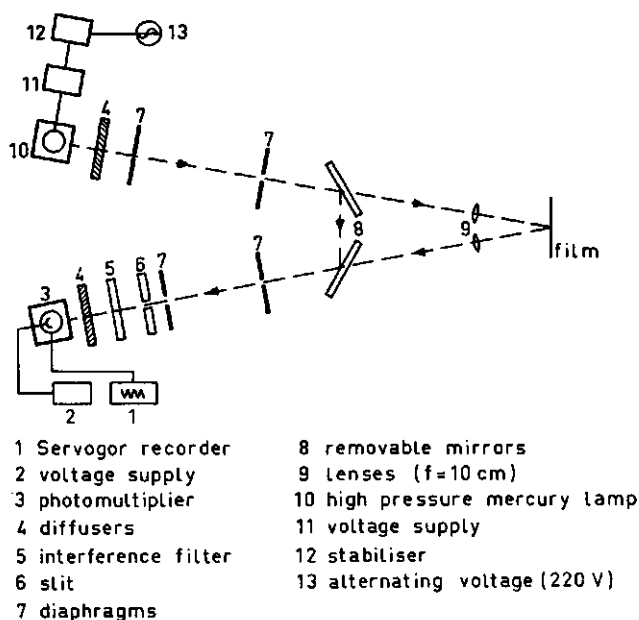
Fig. 3-3. Apparatus for the measurement of the thickness of soap films. Optical and electronic part.

enlarged picture of the illuminated film area. A horizontal slit (0.1 mm wide, 5 mm long) thus selected a rectangle of about 0.01×0.5 mm² out of the illuminated area of the film. Via an interference filter ($\lambda = 5460$ Å or 4360 Å) and an opaque glass the beam was received at the cathode of a photomultiplier (RCA 1 P 21). The photomultiplier operated at a stabilized voltage of 1000 V. The current from this multiplier was registered by a Servogor recorder (RE 511).

After switching on the mercury lamp, a constant light intensity was produced after about half an hour. This could be checked by directing the light beam by means of two mirrors onto the cathode of the multiplier.

Some scanning of the film was possible by adjustment of the lenses, the slit and the photomultiplier. Because it was found that the thickness was constant over large areas of the film, the thickness of all the films was measured at the same height, namely 5 mm above the meniscus.

3.3. PERFORMANCE OF THE MEASUREMENTS

After the cuvette was filled to the top with the surfactant solution and the glass frame had been immersed, the whole equipment was thermostatted in the brass box at 25.00 ±0.01 or 45.00±0.01 °C. Within one hour after the first films were pulled there was evidence that some evaporation of the film occurred. This conclusion is based on the observation that the light intensity from the black film decreased continuously and, that if a solution of NaDS + NaCl was used, formation of second black films occurred. After approximately fifteen

hours evaporation was no longer observed. This was concluded from the constant reflectivity of the black equilibrium films. Only after this time reliable measurements could be performed.

As indicated already in section 2–2d, our experimental set up allowed for two independent methods for obtaining equilibrium films.

In the first method the film was raised manually through the micrometer over a distance of 2 cm. The construction was such, that rotation of the frame about its axis was impossible, so that during this pulling of the film the angle of incidence (10°) of the light beam remained constant. This could also be checked from the fixed position of the image of the film on the slit. The thick film, thus produced, already showed after some seconds interference fringes. After an interval of time (which was shorter the higher the electrolyte content) the black equilibrium film formed, as could be concluded from the constant intensity of the reflected light. The recorded reflected intensity was a function of film thickness (or time of drainage) is schematically depicted in fig. 2.1. Because the interference maxima had the same magnitude, *these maxima I_s were used as standard*. With the help of formula (2–20a), d_w of the black equilibrium film could be calculated.

In the second method the frame was pulled very slowly from the immersed position by means of the synchronous motor and the gear box. The pulling velocity was 0.001 mm/sec or even less. Under these conditions black equilibrium films formed directly, their thickness being independent of the pulling velocity (3). Fig. 3–4 depicts schematically the reflected intensity as a function of time of pulling. After recording the reflected intensity from the black equilibrium film the glass frame was re-immersed and a thick, fresh film was pulled manually in order to determine the intensity I_s of the interference maximum, necessary to calculate d_w of the black equilibrium film from equation (2–20a).

It appeared that films, raised manually and having reached equilibrium in course of time by drainage had the same thicknesses as films, which were continuously raised very slowly, that is to say the thicknesses agreed within 1 Å (table 4–1). This experimental fact proves that both films are equilibrium films.

The thicknesses measured at $\lambda = 5460$ Å and at $\lambda = 4360$ Å agreed within 1 Å. The reported measurements are based on $\lambda = 5460$ Å because the green light emitted from the mercury lamp has a greater intensity than the violet light.

In conclusion, it may be stressed that the present apparatus has the great
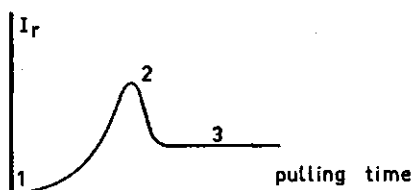
FIG. 3-4. Recorded reflected intensity as a function of pulling time for very slowly formed soap films.
1: pulling starts.
2: reflected intensity from the glass frame.
3: reflected intensity from the black equilibrium film.

advantage in that it allows the thickness of the films to be measured by two different methods, a static and a dynamic one. It turns out that the results of the measurements at 25 °C on the basis of these two methods agree well within 1 Å, implying a reproducibility of 1 % or better over the whole range of film thicknesses.

SUMMARY

After mention has been made of the preparation of the necessary surfactants, in this chapter a description is given of the apparatus with which the thickness of equilibrium films is determined experimentally.

The performance of the measurements on the basis of a static and a dynamic method is discussed and both methods are compared with each other.

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RESULTS AND DISCUSSION

4. FILMS STABILIZED BY IONIC SURFACTANTS. INFLUENCE OF NATURE AND CONCENTRATION OF COUNTERIONS, CO-IONS AND TEMPERATURE

The equilibrium thickness of films stabilized by the following ionic surfactants was measured: LiDS and NaDS at 25 °C and 45 °C and KDS, RbDS and CsDS at 45 °C. The thickness of films stabilized by the second group of surfactants could not be measured at 25° due to insolubility of these surfactants. The surfactant concentrations were in all cases 0.01 mole/l. Films stabilized by solutions of a lower surfactant concentration were not stable enough and, therefore, their equilibrium thickness could not be measured.

Increasing amounts of LiCl, NaCl, KCl, RbCl and CsCl were added to the surfactant solutions mentioned above, after which the thickness of the equilibrium films was measured.

TABLE 4–1. Equilibrium thickness d (Å) of films stabilized by alkali dodecyl sulphates. Influence of type and concentration of the counterion. T = 25 °C. The I_b/I_s values belonging to the thickness in brackets are not reported. * denotes thickness of second black film, formed besides the first.

Ion	Li+		Na+		NH$_4$+		C$_6$H$_5$(CH$_3$)$_3$N+	
c (eq/l)	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d
0.01	0.0781	172	0.0802	175 (172)				
0.02	0.0673	159	0.0682	160				
0.03	0.0592	148	0.0591	148 (147)				
0.04	0.0530	139	0.0537	140 (138)				
0.05	0.0433	125	0.0448	127 (130)				
0.06	0.0448	127	0.0420	123 (123)				
0.07	0.0390	118						
0.08	0.0393	119 (119)	0.0358	112 (111)				
0.09	0.0350	111						
0.10	0.0352	112 (110)	0.0312	105 (103)	0.0320	106	0.0350	111
0.11	0.0341	109						
0.12	0.0300	102 (102)	0.0292	101 (100)	0.0296	101	0.0314	105
0.14	0.0299	102 (102)	0.0267	95 (94)	0.0276	97	0.0301	102
0.16	0.0267	95 (95)	0.0265	95	0.0267	95	0.0275	97
0.18	0.0265	95 (97)	0.0257	94 (94)	0.0250	92.4	0.0273	97
0.20	0.0262	95 (96)	0.0242	90.8	0.0267	95	0.0255	93
0.22	0.0240	90.4 (90.5)	0.0218	85.5	0.0236	89.4	0.0235	89.3
0.24	0.0220	86.4 (89.5)	0.0217	85.4 (37.9*)	0.0236	89.4	0.0229	87.7
0.26	0.0219	85.8 (87.4)	0.0204	83.3 (37.1*)	0.0236	89.4	0.0223	86.8
0.28	0.0204	83.3 (86.1)	0.0186	78.8 (40.0*)	0.0209	84.0	0.0222	86.7
0.30	0.0207	83.4	0.0187	79.1 (40.0*)	0.0206	83.5	0.0208	83.9
0.40	0.0173	76.1						
0.50	0.0150	70.2						
0.60	0.0137	67.2						
0.80	0.0111	59.3						
1.00	0.0091	53.6						
1.20	0.0082	50.0						
1.80	0.0070	45.9						

TABLE 4–2. Equilibrium thickness d (Å) of films stabilized by alkali dodecyl sulphates. Influence of type and concentration of the counterion. T=45°C. The I_b/I_s values belonging to the thickness in brackets are not reported. * denotes thickness of second black film, formed besides the first.

Ion c (eq/l)	Li+		Na+		K+		Rb+		Cs+	
	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d
0.01	–	–	–	–	–	–	–	–	–	–
0.02	0.0253	93.4	0.0233	89.2	0.0207	83.5	0.0224	87.2	0.0270	96.4
0.03					0.0250	92.4				
0.04	0.0237	89.5	0.0220	86.2	0.0228	87.6	0.0238	89.9	0.0280	98.4
0.05					0.0228	87.6 (35.9*)	0.0235	89.4		
0.06	0.0246	91.5	0.0254	93.4	0.0220	86.2	0.0223	87.2	0.0275	97.5
0.07					0.0218	85.5 (35.9*)				
0.08	0.0244	91.2	0.0235	89.4	0.0216	85.4 (35.6*)	0.0237	89.4	0.0266	95.3
0.09									0.0272	97.4
0.10	0.0237	89.6	0.0215	85.4	0.0253	93.4	0.0219	85.7	0.0259	94.4
0.12	0.0220	86.4	0.0205	83.4	0.0230	88.2 (36.6*)	0.0241	90.6	0.0258	94.3
0.14	0.0230	88.4	0.0212	84.8	0.0227	87.4	0.0221	86.4	0.0264	95.4
0.16	0.0209	84.0	0.0207	83.5	0.0242	90.9	0.0226	87.4	0.0271	97.2
0.18	0.0234	89.3	0.0223	87.3	0.0233	88.9	0.0214	85.2	0.0274	97.4
0.20	0.0234	89.3	0.0200	82.2	0.0214	85.1	0.0240	90.4	0.0260	94.5
0.22	0.0232	89.1	0.0205	83.4	0.0206	83.4 (37.1*)	0.0236	89.4	0.0242	90.7
0.24	0.0245	91.3	0.0224	87.3	0.0202	82.8	0.0234	89.3 (37.5*)	0.0226	87.4
0.26	0.0215	85.3	0.0195	81.0	0.0195	81.0	0.0212	84.8 (39.4*)	0.0222	86.6
0.28	0.0224	87.3	0.0172	75.7			0.0240	90.4 (37.1*)	0.0204	83.3
0.30	0.0194	80.9	0.0183	78.4			0.0223	87.2 (36.7*)	0.0214	85.2
0.40									0.0188	79.1
0.50									0.0173	76.2

Also some measurements were performed with films stabilized by 0.01 mole/1 NaDS to which was added NH_4Cl or $C_6H_5(CH_3)_3NCl$.

All these films are mobile and thin regularly and rapidly. At low electrolyte concentration it took several hours and with high electrolyte concentrations only a few minutes for equilibrium to be reached.

The equilibrium film thickness was calculated according to the procedure outlined in chapter 2–4.

Tables 4–1 and 4–2 summarize the experimental results. For all systems $n_1 = 1.43$, $n_2 = 1.33$, $d_1 = 10.6$ Å and $d^* = -7.6$ Å. The concentration of the counterions c was set equal to $c = c$ (surfactant) $+ c$ (added salt). Thus 'c = 0.08' is built up from 0.01 mole/1 surfactant plus 0.07 mole/1 electrolyte solution etc. Actually the counterion concentration should be equal to c.m.c. (surfactant) $+ c$ (added salt). But the c.m.c. of NaDS and LiDS in water at 25 °C is about 0.01 mole/1 (0.0083 and 0.0089 mole/1 respectively) and the contribution of the micelles to the ionic strength is difficult to assess.

The tabulated film thicknesses are the average of at least three measurements. The values in brackets refer to the first black films which have been obtained by very slow pulling. The reproducibility of the measurements at 25 °C is better than one percent over the whole range of thicknesses.

It appeared that the mobile, fast draining films at 45 °C were not very stable.

Fig. 4-1. Equilibrium thickness (Å) of films stabilized by lithium- and sodium dodecyl sulphate. Influence of type and concentration of the counterion. T = 25 °C and 45 °C.
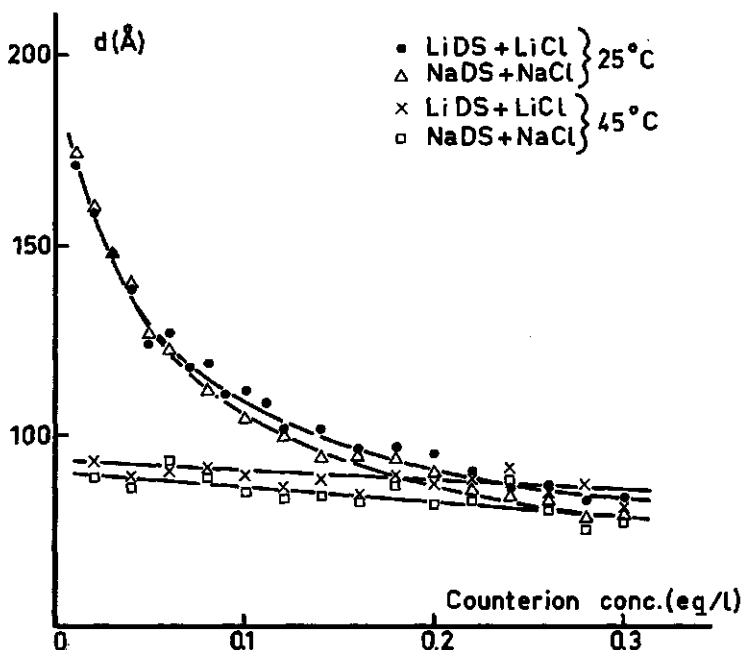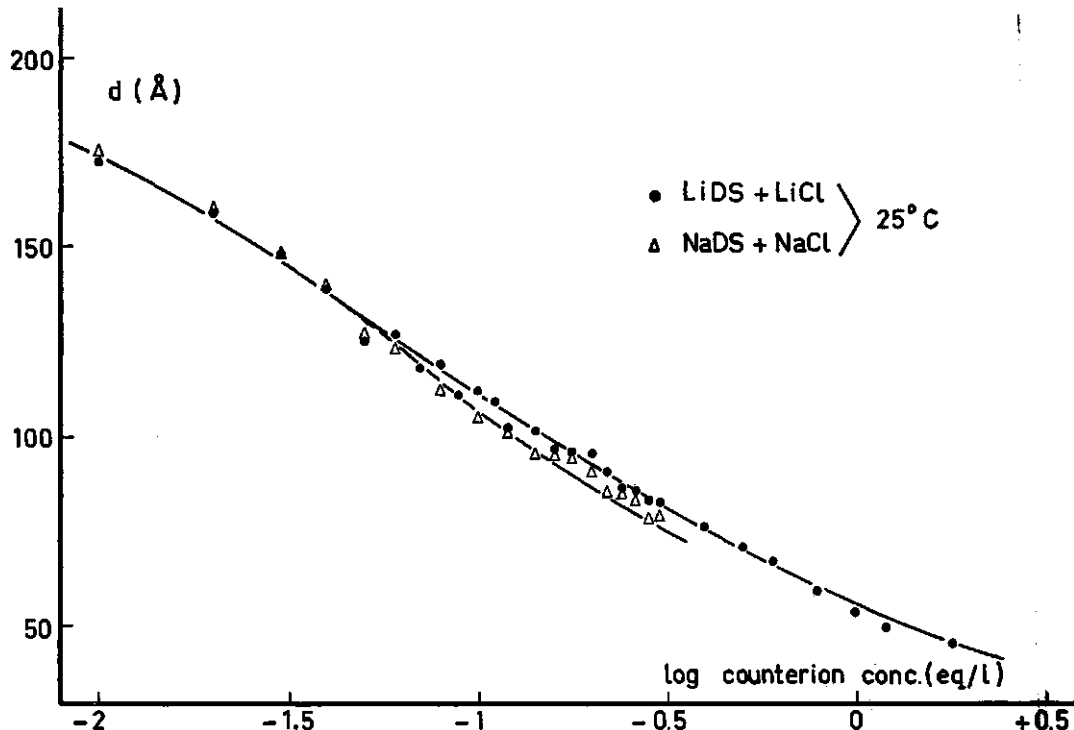
FIG. 4-2. Equilibrium thickness (Å) of films stabilized by lithium- and sodium dodecyl sulphate. Influence of type and concentration of the counterion. T = 25 °C.
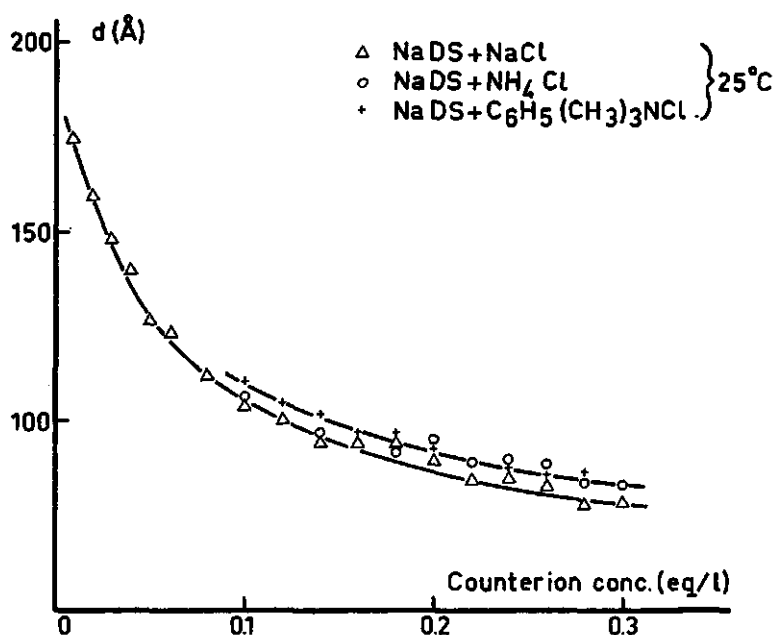
FIG. 4-3. Equilibrium thickness (Å) of films stabilized by sodium dodecyl sulphate. Influence of type and concentration of counterions. T = 25 °C.
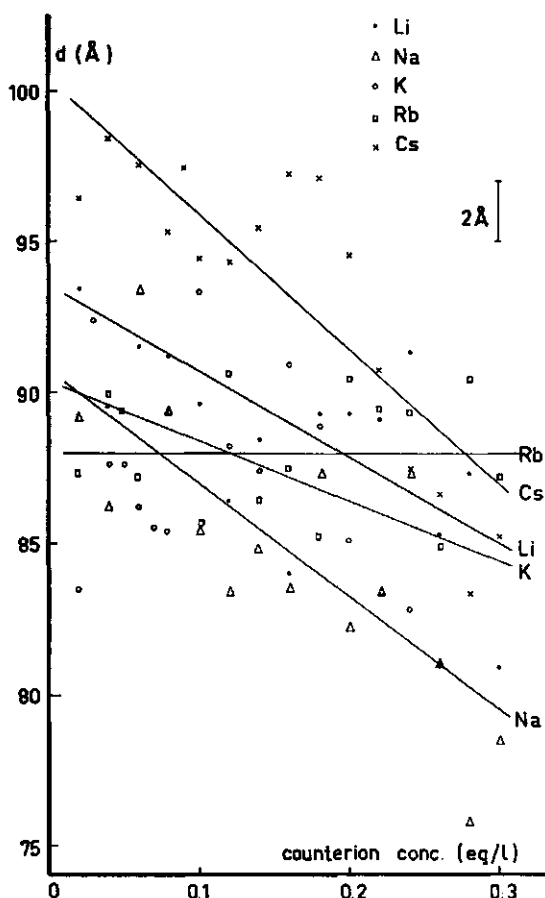
FIG. 4-4. Equilibrium thickness (Å) of films stabilized by alkali dodecyl sulphate. Influence of type and concentration of the counterion. T = 45 °C. Straight lines determined according to the method of least squares.

Films, stabilized by 0.01 mole/l surfactant alone were not stable enough to allow measurements of the equilibrium thickness. The measurements at 45 °C had a reproducibility of ± 2 Å. It was impossible to pull films very slowly at 45 °C because they always burst before thickness measurements could be made.

The tabulated thicknesses of the first black films are plotted in figures 4–1, 4–2, 4–3 and 4–4.

To study the influence of co-ions on the equilibrium thickness, at 25 °C a few measurements were performed on films stabilized by 0.01 mole/l NaDS to which were added $NaNO_3$ and Na_2SO_4 respectively. Table 4–3 summarizes these measurements. Also, see table 4–1.

Although only a few measurements have been performed, one may deduce that the influence of the co-ion on the equilibrium thickness is negligible. However, it was observed that in those cases where both first and second films could be measured, the second black film was formed less rapidly in the $NaNO_3$ -system than in systems with NaCl and Na_2SO_4. In the presence of $NaNO_3$ the lifetime of first black films was about one hour, while with NaCl or Na_2SO_4

TABLE 4–3. Equilibrium thickness $d(\text{Å})$ of films stabilized by NaDS.
Influence of co-ions. $T=25\,°C$.
* denotes that second black films are formed.
$c=0.01$ mole/l NaDS$+c$ (electrolyte).

coion	Cl^-		NO_3^-		$SO_4^=$	
$c(eq/l)$	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d
0.12	0.0296	101	0.0286	99		
0.21	0.0230	88.2			0.0243	90.8
0.31		*	0.0188	79.1*	0.0186	78.8*
0.41		*		*	0.0172	76.1*
0.51		*		*		*

of the same normality, the second black films were formed within a few minutes or even seconds. In other words, the nature of the co-ions does not affect the equilibrium thickness (abscissae axis position of primary and secondary minimum in fig. 2–3) but it does affect the rate of transformation (height of the maximum between primary and secondary minimum) of first to second black films.

4.1. COMPARISON WITH OTHER RESULTS

In order to compare the present results with previous measurements on the same systems, using the same procedures, the corresponding results of LYKLEMA and MYSELS (1), JONES, MYSELS and SCHOLTEN (2) and of JONES (3) are summarized in table 4–4.

TABLE 4–4. Equivalent water thickness d_w (Å) of films stabilized by LiDS and NaDS. Influence of counterion concentration. $T=25\,°C$.

LiCl (eq/l)	d_w		NaCl (eq/l)	d_w	
0.009	253	(1)	0.100	124	(2)
0.0192	203	(1)	0.142	114	(2)
0.0197	199	(1)	0.235	102.9	(2)
0.066	140	(1)	0.246	99.5	(2)
0.10	120	(3)	0.260	95.4	(2)
0.103	137	(1)	0.300	93.6	(2)
0.20	110	(3)			
0.25	97.0	(3)			
0.30	102	(2)			
0.30	89.9	(3)			
0.40	83.8	(3)			
0.50	92	(2)			
0.80	67.6	(3)			
0.906	90	(1)			
1.00	63.1	(3)			

The numbers in brackets refer to the references LYKLEMA and MYSELS (1965), JONES, MYSELS and SCHOLTEN (1966) and JONES (1968).

The authors first mentioned measured, at 25 °C, the equilibrium thickness of macroscopic, vertical films (a few cm²) stabilized by different amounts of NaDS (concentrations below the c.m.c.) to which LiCl had been added.

The *second group of investigators* measured, at 25 °C, *the equilibrium thickness of macroscopic, vertical films (a few cm²) stabilized by* 0.05 % (1.74 × 10⁻³ mole/l) solutions of NaDS to which were added NaCl, LiCl or mixtures of both electrolytes.

JONES (3) measured, at 25 °C, the equilibrium thickness of macroscopic, vertical films stabilized by 0.05 % LiDS (1.84 × 10⁻³ mole/l) plus different amounts of LiCl.

In figure 4–5 the equivalent water thicknesses (d_w) from table 4–4 and our d_w values have been plotted.
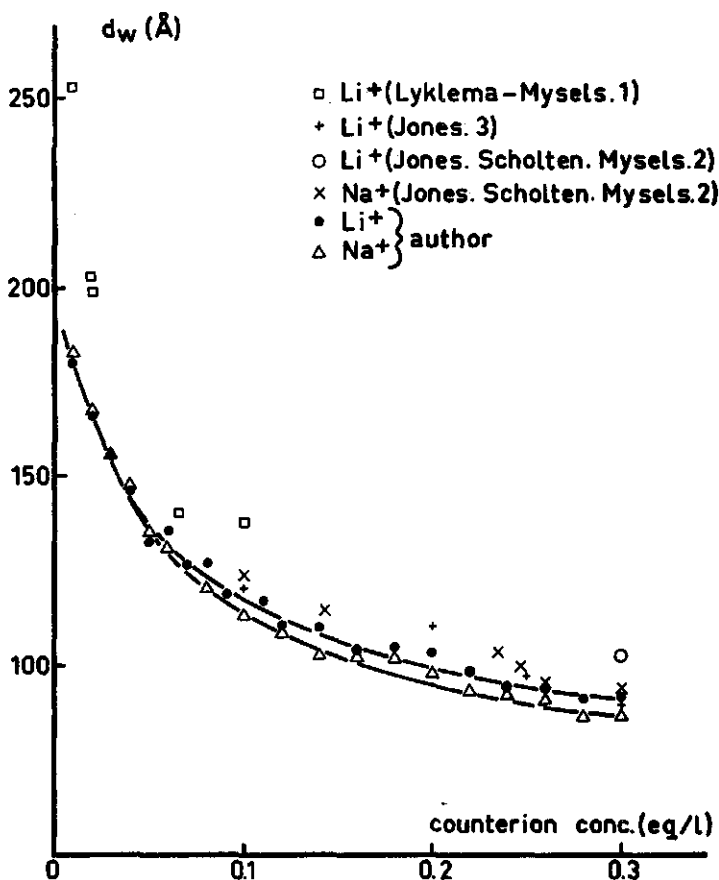

FIG. 4-5. Equivalent water thickness (Å) of films stabilized by LiDS or NaDS. Influence of type and concentration of the counterion. T = 25 °C.

Comparison of the data of tables 4–1 and 4–4 and figure 4–5 shows that, although the general trend is comparable in all systems, a number of disturbing discrepancies occur:

1. at low LiCl-concentrations, much higher values of the equilibrium thickness were measured by LYKLEMA and MYSELS than in the present study (difference about 35% at $c=0.01$ mole/l; about 19% at $c=0.02$ mole/l and about 14% at $c=0.10$ mole/l),

2. at high LiCl-concentrations LYKLEMA and MYSELS, and JONES, MYSELS and SCHOLTEN measured higher values as well. For example, their extrapolated curve yields a value of about 80 Å at a LiCl-concentration of 1.5 mole/l, whereas a thickness of about 48 Å, at the same concentration, was found by the author (by interpolation, see table 4–1 and figure 4–2),

3. there is good agreement between the measurements of JONES and those in the present study for the Li-system,

4. for films with NaCl, over the whole concentration range, the thicknesses reported by JONES, MYSELS and SCHOLTEN are about 10% higher than the present values.

Although it is difficult to account for the experimental differences the following can be noted. In the present study the thickness of the equilibrium films was measured at a fixed position of the light spot on the film, namely 5 mm above the meniscus and equidistant to both vertical sides of the frame so that border effects were absent. Some scanning of the films indicated that they were homogeneous, except for areas close to the meniscus (about 0.5 mm or lower above the surface of the bulk solution) where the films were thicker due to curvature of the meniscus. This thickness, however, was not measured accurately.

One might argue that the films measured in this thesis are too thin as a result of evaporation. However, the thicknesses determined according to the static method were equal to those obtained by the dynamic method. This experimental result and the good reproducibility of the measurements indicate that the present thicknesses are real equilibrium thicknesses. A further discussion and interpretation based on the current values is therefore warranted.

4.2. INTERPRETATION OF EQUILIBRIUM THICKNESSES IN TERMS OF DOUBLE LAYER REPULSION AND VAN DER WAALS ATTRACTION

The experimentally determined equilibrium thicknesses decrease with increasing counterion concentrations. This trend is in accordance with the electrical double layer repulsion which decreases with increasing electrolyte concentration as predicted and formulated by the theory of VERWEY and OVERBEEK (4).

When a soap film has attained its equilibrium thickness, the sum of all forces must be zero. When all forces, except the VAN DER WAALS force, are known, the latter can be calculated as a function of the equilibrium thickness so that the magnitude of the HAMAKER – VAN DER WAALS constant A and the exponent in the power law can be obtained.

As will be shown in section 4.3 in connection with the discussion on ion specificity, the specific effects in the STERN layer outweigh those in the diffuse part of the double layer. Therefore, it is logical to apply the GOUY-STERN picture of the electrical double layer without corrections for ion specificity in the diffuse part of the double layer. The important parameter in this picture is ψ_d, the potential of the diffuse part of the double layer.

The electrical double layer repulsion was formulated by VERWEY and OVERBEEK and is represented by $\Pi_{el} = 64nkT\gamma_d^2 e^{-\kappa d2}$. In deriving this formula they assumed the validity of the POISSON-BOLTZMANN distribution for smeared out point charges in a homogeneous solvent without dielectric saturation. Furthermore they assumed that for weak interaction the potential between the charged walls is given by a linear superposition of the potentials of the two individual double layers. As the film thicknesses were always several times larger than the double layer thickness, this assumption is certainly valid for soap films.

In the equation for the double layer repulsion the potential comes in through the factor

$\gamma_d^2 = \tanh^2 \left(\dfrac{ze\psi_d}{4kT}\right)$ which varies from zero to one as ψ_d varies from zero

to infinity. For (1–1) electrolytes at 25 °C $\gamma_d^2 = 0.33$ at $\psi_d = 65$ mV and $\gamma_d^2 = 0.93$ at $\psi_d = 200$ mV.

Because there is no unambiguous procedure for finding ψ_d, in stability studies the ς-potential is frequently used in stead of ψ_d. We shall do this likewise and take the ς-potentials for NaDS micelles in aqueous solutions of sodium chloride, calculated by WIERSEMA (5) from the electrophoretic mobilities measured by STIGTER and MYSELS (6). The ς-potentials calculated by WIERSEMA up to 0.1 mole/1 NaCl were extrapolated for concentrations up to 0.3 mole/1 NaCl, which is the maximum electrolyte concentration in our system.

As stated above, the total repulsive force in the equilibrium film must be equal to the total compressive force. The latter consists of Π_{vdw} and Π_h. Since the height in the film where the equilibrium thickness was measured was 5 mm above the meniscus, the value of Π_h is 500 dyne/cm². The relation between Π_{vdw} and the equilibrium film thickness is obtained from the equation $\Pi_{vdw} = \Pi_{el} - \Pi_h$, or

$$\frac{A}{6\pi d^3} = 64nkT\gamma_d^2 e^{-\kappa d2} - \Pi_h \qquad (4\text{-}1)$$

The results of these calculations for the films stabilized by NaDS + NaCl at 25 °C are plotted in figure 4–6. As a comparison the theoretical curve for a HAMAKER constant of 5×10^{-13} erg is drawn in the same figure.

It may be remarked that the calculated attractive force increases with increasing film thickness, whereas theoretically for VAN DER WAALS forces the contrary is to be expected. From these two curves one may conclude that at $d = 175$ Å for the chosen HAMAKER constant Π_{el} is about 16 times too high and about a
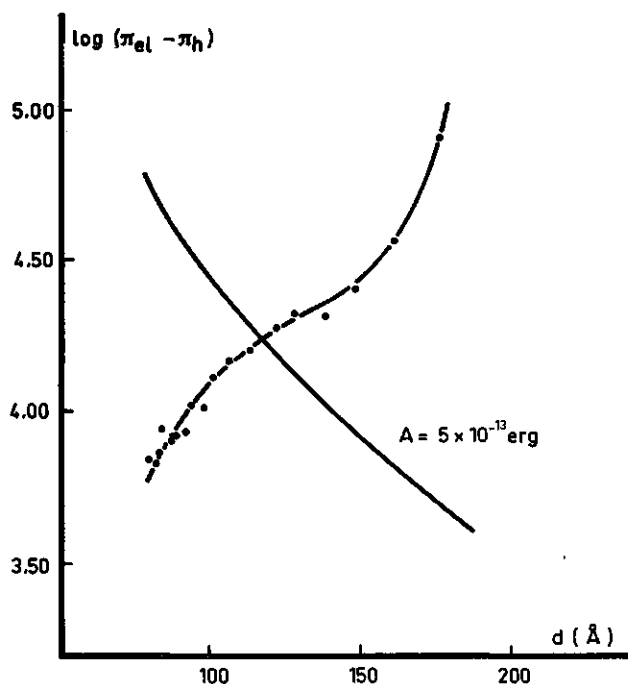
FIG. 4-6. VAN DER WAALS attractive force as a function of the film thickness, calculated from the experimentally determined film thickness using the equation $\Pi_{vdW} = \Pi_{el} - \Pi_h$. As a comparison, the theoretical curve for $A = 5 \times 10^{-13}$ erg is plotted also. System: NaDS + NaCl. $T = 25\,^{\circ}C$.

factor 4 too low at $d = 90$ Å. In other words, the thin films are too thick. There is either a repulsion which we do not know, or the attraction is much lower than we suppose.

In the thickness region below 200 Å the same trend for the attractive force was found by LYKLEMA and MYSELS (1) for films stabilized by NaDS + LiCl. (For films thicker than 200 Å these authors found at least qualitatively the theoretically observed trend. However, in our apparatus no stable films thicker than 200 Å could be obtained). VAN DEN TEMPEL (7), studying the influence of NaCl on the equilibrium distance of paraffin-oil droplets stabilized by NaDS, also found a decreasing attractive force with decreasing distance at distances between the droplets shorter than about 125 Å.

An equilibrium thickness of 123 Å, in addition to that at $c = 0.06$ mole/l, was sometimes observed at $c = 0.01$ mole/l. Also, one time at $c = 0.02$ mole/l, next to $d = 160$ Å, $d = 120$ Å and $d = 84$ Å were measured (NaDS + NaCl system, see table 4-1). Apparently there is some indication of the existence of a multiplicity of the films, which will be treated in more detail in chapter 7 about the stratified films. This in turn would mean that already in the 90–150 Å region some structure formation would occur, which may or may not be comparable to stratification.

The next possibility that must be considered is whether or not theoretical values for Π_{vdW} can be obtained by substitution of other reasonable values for the various parameters determining Π_{el}.

The most important factors which govern the magnitude of Π_{el} at a given d are

1. ψ_d, the potential of the diffuse part of the double layer, or σ_d, the charge of the diffuse part of the double layer, which is directly related to ψ_d according to the GOUY-CHAPMAN equation (4–2) (8),

$$\sigma_d = \sqrt{\frac{\varepsilon n k T}{2\pi}} \left(\exp. \frac{z e \psi_d}{2kT} - \exp. \frac{-z e \psi_d}{2kT} \right) \tag{4-2}$$

2. the thicknesses of the surfactant monolayer, d_1, and of the STERN layer,
3. the counterion concentration in the film.

1. Putting $A = 5 \times 10^{-13}$ erg, ignoring retardation, and setting the surfactant monolayer thickness d_1 equal to 10.6 Å the adapted ψ_d and σ_d values can be calculated at each experimentally determined film thickness and counterion concentration, using equations (4–1) and (4–2). From the reciprocal surface concentration $a_o = 41.5$ Å²/molecule NaDS the surface charge σ_o is calculated as 38.5 $\mu C/cm^2$. By subtraction the charge σ_m of the non-diffuse part of the double layer is thus found. Table 4–5 summarizes some calculations.

It follows that, in order to explain the theoretical trend of Π_{vdW}, σ_m should decrease with increasing concentration. In other words, the adsorption of counterions should decrease with increasing concentration. This is at variance with all physical experience and consequently this possible explanation must be rejected.

2. Similar calculations show that any reasonable choice of d_1, the surfactant monolayer thickness, is insufficient to alter the trend of Π_{vdW} as a function of the equilibrium thickness significantly.

TABLE 4–5. Required values of ψ_d, σ_d and σ_m for some equilibrium films stabilized by NaDS + NaCl (25 °C) in order to interpret the thickness in terms of the equality $\Pi_{vdW} = \Pi_{el} - \Pi_h$ with $A = 5 \times 10^{-13}$ erg.

d(Å)	c(eq/l)	ψ_d(mV)	$\sigma_d(\mu C/cm^2)$	$\sigma_m(\mu C/cm^2)$
175	0.01	22	0.5	38.0
160	0.02	35	1.2	37.3
148	0.03	49	2.2	36.3
140	0.04	63	3.6	34.9
127	0.05	65	4.2	34.3
112	0.08	95	9.8	28.7
105	0.10	130	23.2	15.3
101	0.12	180	67	−28.5
95	0.14	–	–	–

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3. The counterion concentration is one of the most important factors influencing Π_{el}. Therefore, it is useful to question oneself what the counterion concentration in the film should be in order that the required Π_{vdW} is achieved. In answering this question, again the parameter values $A = 5 \times 10^{-13}$ erg and $d_1 = 10.6$ Å were chosen. The result of the calculations is that at $d = 175$Å (bulk concentration 0.01 mole/1) a film concentration of 7×10^{-6} mole/1 and at $d = 79$ Å (bulk concentration 0.30 mole/1) a film concentration of about 1×10^{-5} mole/1 are necessary. Such low film concentrations are unacceptable. Experiments by VAN DER WAARDE (9) and CLUNIE et al. (10, 11) showed that if anything, the electrolyte concentration in the film is rather higher than that of the bulk solution from which the film was pulled. We will revert to this problem below. Furthermore the diffuse double layer thickness at these very low ionic strengths would be several times larger than the film thickness itself.

Further calculations showed that d_1, ψ_d, and A can not be adjusted to give acceptable values for the film concentration. Nor can ion volume, polarization, dielectric saturation and self-atmosphere of the counterions through their influence on the potential essentially lead to an acceptable film concentration.

Interpretation of the film thickness at 45 °C in terms of VAN DER WAALS attraction and double layer repulsion is likewise impossible. The same difficulties are encountered here as was the case with the systems at 25 °C, showing again that still other forces govern the equilibrium thickness of these types of film.

In view of the experimentally observed specificity, it would finally be more exact to extrapolate the measured film thicknesses to a counterion radius of zero. This must be performed on the basis of the curves for Li^+ and Na^+. The problem is, which radius for the counterions should be used. Taking for this value the radii of the hydrated ions (12), 'new' thickness-concentration curves can again be plotted. Calculations with these 'new' thicknesses result again in an increasing attraction with increasing thickness.

From the above discussion and from the analysis by LYKLEMA and MYSELS (1) it is clear that it is impossible to interpret the experimentally obtained equilibrium thicknesses solely on basis of the balance of Π_{vdW} and Π_{el}. In seeking an explanation for this problem one would wonder, in the first place, if the equilibrium salt concentration inside the film is really attained. With respect to this question the following experimental facts may be mentioned.

1. From the measurements of the conductance of films, stabilized by NaDS + varying amounts of NaCl, by VAN DER WAARDE (9) it can be concluded that the electrolyte concentration inside the film is higher than in the bulk solution from which the films are pulled.

2. CLUNIE et al. (10) measured the conductance of films stabilized by decyltrimethylammonium decylsulphate + Na_2SO_4 or $MgSO_4$ and determined the electrolyte content in the films by a radiotracer technique. They calculated

that the electrolyte concentration inside the film is greater than that in the bulk solution for $c_{bulk} < 0.12$ mole/1 but that it is smaller for $c_{bulk} > 0.12$ mole/1.

3. Much information has been accumulated in recent years about the permeability and transport of small molecules (CO_2, H_2O, etc.) through monolayers of long-chain fatty acids, alcohols etc. (13). The overall conclusion of these experiments is that the monolayers are more or less permeable for small molecules. The magnitude of this permeability is a function of the nature of the monolayers and of the permeating molecules.

Regarding these findings one may think in terms of a possible evaporation of the thin soap films. This problem was also considered by PRINS (14). The result of transport of solvent molecules through the vapour phase would imply that an excess electrolyte concentration inside the film exists. Finally this would give rise to an additional repulsive (osmotic) pressure.

If indeed at a temperature of 25 °C evaporation plays a role, one would expect that it is greater at a higher temperature of 45 °C. An indication of this is the fact that at 45 °C the films become thinner much faster than at 25 °C, especially at the lower electrolyte concentrations.

In conclusion, it may be said that the problem concerning the electrolyte content inside the films is not unambiguously dissolved as yet. Therefore, it is worth while to measure this content in the present film systems.

An alternative method to formulate an extra repulsive force in the films might be with the help of a theory developed by BELL and LEVINE (15). These authors examined the nature of the electrical force between a pair of parallel, uncharged plates of infinite thickness and low dielectric constant, immersed in an aqueous (1–1) electrolyte solution. The force is caused by the electrostatic ion-image self-atmosphere potentials and the consequent rearrangement of the electrolyte ions in the neighbourhood of the planes. They only considered point ions and neglected corrections due to ion size, except for introducing a distance of closest approach of the ions to the plates. The result of their calculations is that this force is attractive at small separations and repulsive at larger plate distances. This repulsion takes the same form as the VAN DER WAALS attraction (inverse cube law dependence on the distance) with a HAMAKER – VAN DER WAALS constant of about 3×10^{-14} erg at 25 °C. Between two plates ($\varepsilon = 2.5$) of infinite thickness immersed in a 0.1 mole/1 (1–1) electrolyte ($\varepsilon = 78.3$) at 25 °C they calculated the total force and found that this is of an attractive nature at plate distances of less than about 20 Å; at about 25 Å, the force now having become repulsive, reached a maximum of about 6×10^5 dyne/cm². Having passed this maximum, the repulsive force decreases inversely with the third power of the plate distance and has become practically zero at distances larger than about 100 Å. It turns out that for soap films in air ($\varepsilon = 1$) the results differ slightly with respect to those for the above mentioned system, so that this theory is not important for the interpretation of our film thicknesses.

There is a large discrepancy between existing theories and the results of the experiments on soap films in the present study. The experimental results in the

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work by HUISMAN and MYSELS (16) also show the same feature. These authors calculated the depth of the free energy minimum corresponding to an equilibrium soap film by measuring the contact angle between the film and bulk solution. They found poor agreement between the experimental results and the theories of the VAN DER WAALS forces and double layer repulsion. It is impossible drawing general conclusions about the origin of the deviations from the theory for the film systems studied by them. But it is clear from HUISMAN's and MYSELS' work that for the second black films the attractive forces, calculated from the experimental results, are several times larger than the VAN DER WAALS forces. For the first black films the extent of the discrepancy between theory and experiment depends strongly on the nature of the counterion. For example, for films containing Na^+ ions the attractive force calculated from the experiments is several times smaller than the theoretical value, whereas for films with Li^+ ions the attractive forces are several times greater than those according to theory. These results are very puzzling. In conclusion, also from the contact angle work no satisfactory explanation of the discrepancy between the existing theories and the experimental results is offered.

4.3. Ion Specificity

Several colloid-chemical phenomena depend not only on the valency of the counterion but also on its nature. In these cases it is customary to speak of specific ionic effects.

An example where the interaction of Rb^+ ions with the substrate is stronger than that of Li^+ ions is the negatively charged silver iodide sol (17, 18) where, as a consequence of the stronger adsorption of Rb^+ ions the flocculation value for $LiNO_3$ (165 mmole/l at 25 °C) is higher than that for $RbNO_3$ (126 mmole/l at 25 °C). Although the actual values are somewhat dependent on the method of measurement, their ratio is not very sensitive to the experimental determination. At 65 °C this specificity is reduced to about 12 % (18). The same sequence of interaction is present both in the double layer at the mercury/solution (19) and at the silica/solution interface (20). In general in these systems the specificity is progressive, that is it increases with increasing electrolyte concentrations. The stronger binding of the Cs^+ ions with the substrate is also reflected in the critical micelle concentrations of the alkali dodecyl sulphates (12) and in the interaction of the alkali ions with negatively charged monolayers of docosyl sulphate (21) and dodecyl sulphate (22). The observed order of interaction in all these systems can be interpreted in terms of the stronger binding of the counterion with the smaller hydrated radius.

An example where the interaction of Li^+ ions with the substrate is stronger than that of Cs^+ ions is the adsorption of alkali ions on negatively charged haematite (23). The adsorption is virtually an interaction with the hydroxyl groups in the haematite surface layer and the sequence is in accordance with the sequence of the activity coefficients of the alkali hydroxides. STRAUSS and ROSS (24) measured the binding of monovalent cations by phosphate groups of poly-

phosphates and found that the binding constants decreased in the order $Li^+ >$ Cs^+. Probably here the interaction occurs also with hydroxyl groups on the phosphate surface. The same sequence was observed for the interaction with carboxylate-ion ion exchangers (25) and their swelling (26). Finally, SEARS and SCHULMAN (27) reported for the interaction of alkali ions with carboxylates the sequence $Li^+ > K^+$.

Also in bulk solutions similar sequences of ion interactions are observed. For example, the interactions as deduced from activity coefficients increase in the order $Li^+ < Rb^+$ in the acetate series, which is characteristic for the carboxylates, but decrease in the order $Li^+ > Rb^+$ for the chlorides, nitrates and sulphates, which are characteristic for the dodecyl sulphates etc. This indicates that the observed specificity of ions at surfaces is not only an effect due to the counterion proper, but reflects also the interaction between the counterion and head group in a way that may to a large extent be similar to the corresponding interaction in bulk solution.

Returning to the current experiment it is clear that the counterion specificity for the films is reflected in the equilibrium thicknesses. The equilibrium thicknesses, d, of all the films were obtained by correcting the equivalent water thicknesses, d_w, by -7.6 Å (d^*). The value of the refractive index, n_2, of the aqueous film core was assumed to be equal to that of pure water, 1.33. At a concentration of 0.3 mole/l the difference in refractive index for LiCl and NaCl solutions is less than 0.01. This implies a difference in correction of d_w of less than 0.8 Å, which can be neglected.

Thus, it can be concluded from the experimental data at 25 °C that any specificity for the ions Li^+, NH_4^+ and $C_6H_5(CH_3)_3N^+$ is either absent or the same. The films containing Na^+ counterions are definitely a few percent thinner than the corresponding Li^+ containing films. In view of the above discussion this would suggest that Na^+ ions are more strongly adsorbed in the STERN layer than Li^+ ions and the other ions. This agrees with the experiments of MUKERJEE (12), GODDARD (21) and WEIL (22). At 25 °C the Li^+-Na^+ specificity disappears at a concentration below about 0.05 mole/l. (figure 4–1). Closer inspection of the curves at 25 °C shows that, at increasing electrolyte concentration, the specificity does not increase progressively. It seems that there is a compensating effect.

Except to specific effects in the STERN layer, attention must also be paid to possible specific effects in the *diffuse part* of the double layer.

Several authors have calculated the influence of size, dielectric saturation, ion polarization and self-atmosphere effects of the counterions on the relation between σ_d and ψ_d, and have corrected the POISSON-BOLTZMANN equation for those factors. BRODOWSKY and STREHLOW (28) calculated the influence of ion size and dielectric saturation on ψ_d, whilst BOLT (29) calculated the effect of ion size, dielectric saturation, ion polarization and self-atmosphere effects. SPARNAAY (30) considered ion size, dielectric saturation and polarization corrections to the equation. LEVINE and BELL (31) corrected the POISSON–BOLTZMANN

equation for ion size, dielectric saturation and self-atmosphere effects; they also considered the effect of medium compressibility and cavity potentials. The overall conclusion from these studies is that all these corrections are small and tend to compensate each other (see also ref. 32). Calculations by SANFELD (33) on the influence of counterion size on the diffuse double layer repulsion show that films containing Li^+ ions should be somewhat thinner than those having Na^+ ions, in contrast with the current experimental results. Thus, an interpretation of the Li^+–Na^+ specificity *solely* in terms of the ion size is difficult. The films with the very large phenyl trimethyl ammonium ions (radius is 7.2 Å, ref. 34), with the much smaller ammonium ions (radius is 1.40 Å, ref. 12) and those containing lithium ions (radius is 2.31 Å, ref. 34) have the same thickness, whereas the thickness of the films with sodium ions (radius is 1.78 Å, ref. 34) is definitely smaller.

In view of the above discussion it can be stated that the specificity encountered in soap films can not be attributed very well to effects in the diffuse part of the double layer but is mainly due to specific adsorption in the STERN layer, which in turn is related to the interactions in the electrolyte solution.

As a further conclusive argument to consider specific effects in the STERN layer only it can be noted that a large part of the countercharge – and consequently a considerable part of the total potential drop – is situated in the STERN layer. For example, in the well-studied case of negatively charged silver iodide sols for surface potentials around -300 mV ψ_d is only about -30 mV in 0.1 mole/l (1–1) electrolytes, indicating that 90% of the potential drop occurs in the STERN layer (32a).

4.4. INFLUENCE OF TEMPERATURE

In order to extend the study of the specificity of counterions to K^+, Rb^+ and Cs^+ ions, it turned out to be necessary to perform the experiments at higher temperatures, because the K^+, Rb^+ and Cs^+ dodecyl sulphates do not dissolve at 25 °C. These surfactants dissolve well at 45 °C. For comparison, the thicknesses of the equilibrium films stabilized by LiDS and NaDS were measured at 45 °C as well. Moreover, by means of these experiments the influence of temperature on the Li^+–Na^+ specificity could be studied, as was done by LYKLEMA on the silver iodide system (18), where it appeared that the counterion specificity decreased with increasing temperatures.

Hitherto little research has been done on free liquid films at high temperatures, DERYAGIN et al. (35) found that the equilibrium thickness of films stabilized by solutions with very low electrolyte concentrations (greater film thickness) decreased with increasing temperatures (system: 10^{-3} mole/l Na-oleate $+ 10^{-3}$ mole/l NaCl, $T = 23$ °C, $d = 300$ Å; $T = 50$ °C, $d = 100$ Å), which is in qualitative agreement with the results in the present study. However, they did not interpret this temperature influence. JONES et al. (2) studied the influence of temperature on the formation of second black films stabilized by NaDS $+$ NaCl. This is not relevant to the present point of discussion but we shall revert to it in the next section.

The results at 45 °C are given in figures 4–1 and 4–4 in which straight lines have been drawn, using the method of least squares.

It is obvious that at 45 °C all film thicknesses are smaller than those at 25 °C, especially at the lower electrolyte concentrations. This can not be accounted for by the very small temperature dependence of Π_{el}. Possibly the difference in the thickness at 25 °C and 45 °C can be attributed to evaporation which is greater at higher temperature and at lower electrolyte concentrations.

It appears that no clear lyotropic sequence is obtained although the difference between Li^+ and Na^+, observed at 25 °C, persists at 45 °C. Rather the thickness passes through a minimum going from Cs^+ to Li^+, again suggesting that the equilibrium thickness is determined by two opposing trends. The somewhat greater thickness of the films containing Cs^+ ions might be attributed to strong specific adsorption of these ions, resulting in a compact monolayer so that evaporation is relatively inhibited.

In order to extend the investigations about specific effects in soap films, the influence of non-electrolytes on the equilibrium thickness was also investigated. This problem will be treated in chapter 5.

4.5. SECOND BLACK FILMS

From some studies on the influence of temperature and nature and concentration of counterions on the formation of second black films it is clear that this formation obeys certain rules, but the backgrounds of these rules are still rather obscure.

JONES et al. (2) studied the influence of temperature on the formation of second black films stabilized by NaDS + NaCl. It appeared that at higher temperature the NaCl concentration required to induce formation of second black films had also to be increased. The same trend was observed in the present study but not further investigated. JONES et al. observed also that Li^+ ions above certain minimum concentrations inhibit the formation. IBBOTSON and JONES (36) have studied the influence of the valency of negative counterions on the critical concentration at which second black films are formed. They drew a parallel between the formation of the second black film and the flocculation of a colloidal dispersion and related the critical concentration for second black film formation to the rule of SCHULZE and HARDY. However, the differences in critical concentrations of the counterions having the same valency were rather large.

The results of all these investigations have not yet answered the question: under what conditions does the second black film form?

In table 4–6 a summary is given of the conditions under which the second black films formed in our work. The concentrations in the third column indicate the minimum values of the electrolyte concentrations for which black films are formed.

The second black films are very stable at 25 °C, but less so at 45 °C. Their thickness, is 37.4±1.5 Å. It is independent of temperature, nature and concen-

TABLE 4–6. Formation of second black films.

System	T (°C)	2nd black film	Max. conc. studied
LiDS+LiCl	14, 25, 45	no	0.30 mole/l at 45 °C
			1.80 mole/l at 25 °C
NaDS+NaCl	25	yes, $c=0.24\ m$	
	45	yes, $c=0.45\ m$	
KDS+KCl	45	yes, $c=0.05\ m$	
RbDS+RbCl	45	yes, $c=0.25\ m$	
CsDS+CsCl	45	no	0.50 mole/l
NaDS+NH$_4$Cl	25	no	0.30 mole/l
NaDS+			
+C$_6$H$_5$(CH$_3$)$_3$NCl	25	no	0.30 mole/l
NaDS+NaNO$_3$	25	yes	
NaDS+Na$_2$SO$_4$	25	yes	

tration of counterions and co-ions within experimental error. JONES et al. (2) measured thicknesses of about 44 Å.

Although the rules for second black film formation are not very clear, some trends seem to emerge (see also tables 4–1 and 4–2).

1. The critical concentration at which second black films are formed by the NaDS system increases about linearly with increasing temperature, in accordance with the findings of JONES et al. (2).

2. Potassium ions in very small concentrations promote the formation of second black films, also in accordance with the results of JONES et al.

3. The critical concentration as a function of the radius of the counterion shows an extreme value for potassium. This might indicate that the formation of second black films is governed by two opposing effects. An interpretation of this phenomenon exclusively in terms of the counterion radius is therefore impossible. It could be argued that with Li$^+$ ions and C$_6$H$_5$(CH$_3$)$_3$N$^+$ ions the formation of second black films is impossible because there is no room for these relatively large hydrated ions in an ultrathin film, but on the other hand second black film formation for the systems with the smaller NH$_4^+$ ions and Cs$^+$ ions does not occur.

As pointed out already in this chapter, an interesting difference exists between NO$_3^-$ ions on the one hand and Cl$^-$ and SO$_4^=$ ions on the other: the rate of second black film formation in the presence of NO$_3^-$ions is much smaller than in the systems containing Cl$^-$ or SO$_4^=$ ions.

From the experimental results it can be concluded that the question whether or not, and with the rate at which, the second black film is formed is not related to the thickness of the first black film from which it is formed, nor to the thickness of the second black film itself. Thus one is inclined to interpret the formation of second black films from first black films not in terms of the free energies of both film systems, but on the basis of an activation energy, which apparently is very high in the cases where second black films are not formed. With respect to the magnitude of this activation energy sensitive structural effects evidently play an important role.

SUMMARY

It turns out that the equilibrium thickness of soap films at 25 °C decreases with increasing counterion concentration.

At 25 °C, films containing Na^+ counterions ($c > 0.05$ mole/1) are slightly thinner than films containing Li^+, NH_4^+ or $C_6H_5(CH_3)_3N^+$ counterions. This specificity is not progressive and is mainly due to specific counterion effects in the STERN layer. There is no detectable influence of co-ions on the equilibrium thickness.

Interpretation of the film thicknesses in terms of the electrical double layer repulsion and VAN DER WAALS attraction justifies the conclusion that there must be an additional repulsive force in these film systems. Alternatively, the possibility is not excluded that some evaporation did occur, leading to too high concentrations in the film and to too low thicknesses.

At 45 °C the equilibrium thickness of the films containing the alkali counterions is practically independent of the concentration. The Li-Na specificity, present at 25 °C, is maintained at 45 °C.

The influence of the nature of the counterions on the critical concentration at which second black films are formed has been investigated at 25 °C and 45 °C. Pronounced differences in this concentration are observed.

The overall conclusion from the experimental results is that with respect to the specificity there emerge mutually opposing factors in three cases, 1. the Li-Na specificity is not progressive with increasing counterion concentration, 2. the promoting-inhibiting effect on second black film formation shows a trend and 3. there is a lyotropic sequence in the film thicknesses at 45 °C(hereevaporation could play a part but in spite of that the mutually opposing effect must be maintained). All these trends must be ultimately accounted for by the slight differences in the physicochemical properties of the counterions.

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5. FILMS STABILIZED BY IONIC SURFACTANTS INFLUENCE OF NON-ELECTROLYTES

5.1. INTRODUCTION

Besides the extensive study of colloidal solutions in water, much attention has been paid to sols in other dispersion media. A few examples may be mentioned here. MACKOR (1) studied the stability of silver iodide sols in water-acetone mixtures and found that the flocculation value of $NaClO_4$ in pure acetone ($\varepsilon = 21.0$) was about a hundred times lower than in pure water ($\varepsilon = 78.5$). DAWSON (2) found that the arsenic trisulphide sol stability is much greater in N-methylacetamide ($\varepsilon = 166$) than in water and MATIJEVIC et al. (3) concluded that silver bromide sols in N-methyl-propionamide ($\varepsilon = 140$)-water mixtures showed an abrupt increase in stability at $\varepsilon > 120$. Recently BIJSTERBOSCH et al. (4) found that the stability of silver iodide sols passes through a maximum due to the presence of n-butylalcohol ($\varepsilon = 17.1$). Further literature about the colloid stability in aqueous and non-aqueous media is given in ref. 5, 6.

The influence of non-ionic admixtures on the electrical double layer and hence on sol stability stems mainly from two effects, (a) the dielectric constant of the medium is altered, (b) due to competitive adsorption in the STERN layer

TABLE 5–1.Equilibrium thickness (Å) of films stabilized by NaDS+NaCl.
Influence of urea and sucrose. T=25 °C. $c=0.08$ mole/l means: 0.01 mole/l NaDS+0.07 mole/l NaCl etc.
Column 1: NaDS+NaCl. No urea
Column 2 : NaDS+NaCl +0.25 mole/l urea
Column 3 : NaDS+NaCl +0.50 mole/l urea
Column 4 : NaDS+NaCl +0.50 mole/l sucrose
* denotes second black film formation

	1		2		3		4	
c (mole/l)	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d
0.01	0.0802	175	0.225	308	0.314	372	0.290	355
0.02	0.0682	160	0.126	223	0.167	260	0.170	263
0.03	0.0591	148	0.098	194	0.114	211	0.110	206
0.04	0.0537	140	0.075	168	0.0839	179	0.0876	183
0.06	0.0420	123	0.060	149	0.0710	163	0.0631	153
0.08	0.0358	112	0.0492	134	0.0540	141	0.0505	136
0.10	0.0312	105	0.0362	113	0.0462	130	0.0420	123
0.12	0.0292	101	0.0333	108	0.0337	108	0.0346	110
0.14	0.0267	95	0.0294	101	0.0295	101	0.0280	98
0.16	0.0265	95	0.0268	96	0.0273	97	0.0271	96
0.18	0.0257	94	0.0234	89.4	0.0250	92	0.0255	93
0.20	0.0242	90.8			0.0267	95	0.0223	87.3*
0.22	0.0218	85.5	0.0222	86.7	0.0260	94		*
0.24	0.0217	85.4			0.0195	81.1		
0.26	0.0204	83.3*	0.0203	83.0	0.0212	84.7		*
0.28	0.0186	78.8*			0.0195	81.1		
0.30	0.0187	79.1*		*	0.0198	81.7*		*

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TABLE 5-2. Equilibrium thickness (Å) of films stabilized by LiDS or NaDS. Influence of urea and nature and concentration of counterions.
T = 25 °C.
c_u = urea concentration, mole/l
Column 1:0.01 mole/l NaDS. No NaCl
Column 2:0.01 mole/l NaDS + 0.01 mole/l NaCl
Column 3:0.01 mole/l NaDS + 0.09 mole/l NaCl
Column 4:0.01 mole/l LiDS + 0.09 mole/l LiCl

c_u (mole/l)	1		2		3		4	
	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d	I_b/I_s	d
0	0.0802	175	0.0682	160	0.0312	105	0.0352	112
0.25	0.225	308	0.126	223	0.0362	113	0.0400	120
0.50	0.314	372	0.167	260	0.0462	130	0.0428	124
0.75	0.300	362	0.178	270	0.0473	131	0.0433	125
1.0	0.304	365	0.179	271	0.0469	130	0.0468	130
1.5	0.307	367	0.183	274	0.0443	127	0.0452	128
2.0	0.313	372	0.194	283	0.0462	130	0.0473	131

counterions desorb, that is the double layer becomes more diffuse. Effect (a) will occur mainly with non-adsorbing soluble admixtures, whereas effect (b) will be dominant for strongly adsorbing substances.

In the underlying study the influence of the addition of urea or sucrose on the equilibrium thickness of films stabilized by NaDS was studied. The principal aim was to modify the properties of the STERN layer and investigate its consequences on the electrostatic repulsion. In this sense a parallel with colloidal stability could be drawn.

5.2. EXPERIMENTS AND RESULTS

All measurements were performed at 25 °C and had a reproducibility of 1 %. It turned out that urea and sucrose gave the mobile films stabilized by LiDS or NaDS a great stability. For the calculation of the equilibrium thickness, d, the following parameter values were chosen: $n_1 = 1.43$, $n_2 = 1.33$ (value of water), and $d_1 = 10.6$ Å, which implies that $d^* = -7.6$ Å.

The results are summarized in tables 5-1 and 5-2 and plotted in figures 5-1 and 5-2.

From the measurements the following can be concluded.
1. The equilibrium thickness increases with increasing non-electrolyte concentration. A plateau is attained at a concentration of about 0.5 mole/l urea. Further increase of the urea concentration has no effect on the equilibrium thickness.
2. The slight Li-Na specificity is lost at urea concentrations higher than about 0.5 mole/l.
3. There is no observable effect of urea at high electrolyte concentrations. For NaCl concentrations of about 0.15 mole/l and upwards the films have the same thickness as those without urea.

4. There is no significant difference between the influence of urea and sucrose on the equilibrium thickness.
5. Urea is a slight inhibitor with respect to the formation of the second black film; this was also observed by JONES et al. (7). On the other hand, sucrose is a slight promotor.
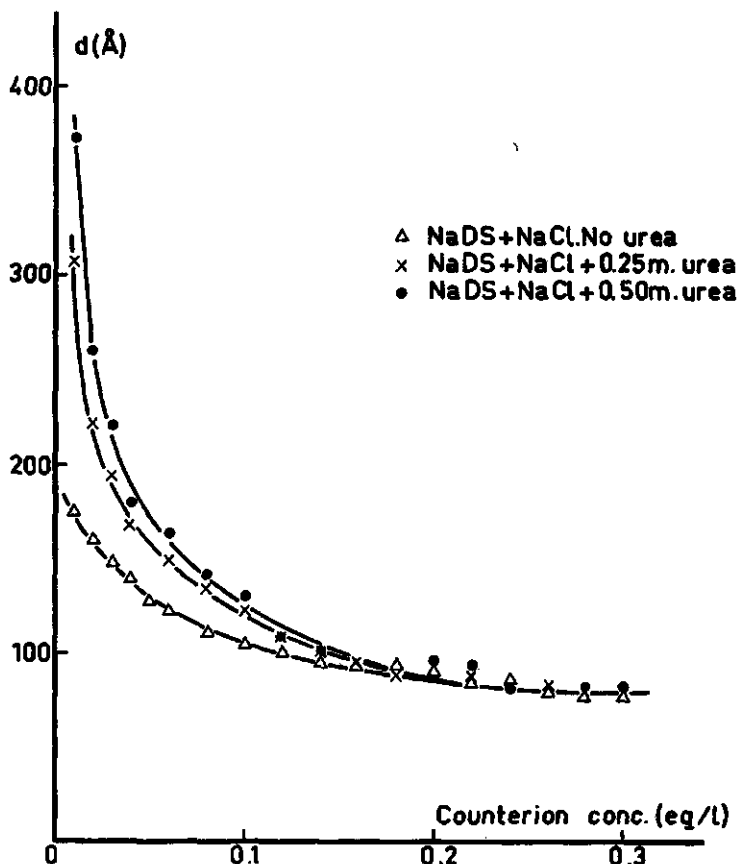

FIG. 5-1. Equilibrium thickness (Å) of films stabilized by NaDS. Influence of NaCl and urea. T = 25 °C.

5.3. DISCUSSION

A possible interpretation of the effect of urea in the present films may be, that with increasing amounts of urea the STERN ions are desorbed and replaced by urea molecules. This causes an increase of ψ_d, which results in a greater Π_{el} and consequently in a greater film thickness. Apparently, as soon as the urea concentration reaches a value of about 0.5 mole/l, all STERN ions are desorbed and replaced by urea molecules. Consequently, ψ_d will not increase further, neither does the film thickness.
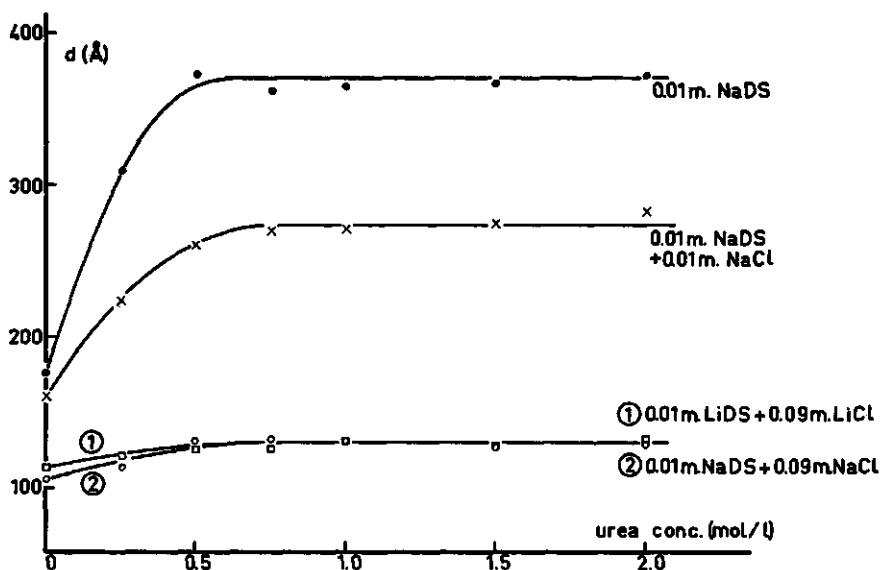
FIG. 5-2. Equilibrium thickness (Å) of films stabilized by LiDS or NaDS. Influence of urea and nature of the counterions. T = 25 °C.

The composition of the STERN layer depends on the urea concentration and on the electrolyte concentration. High electrolyte concentrations promote the adsorption of counterions, whereas high urea contents favour adsorption of urea at the expense of counterions. In view of this picture the decreasing influence of urea with increasing electrolyte content can be understood. The disappearance of the small Li-Na specificity at high urea concentrations agrees also with this picture.

Another effect, brought about by urea could be that if there is some evaporation (for which there is no clear indication) this effect might be reduced because the saturated vapour pressure is lowered. Also, if this mechanism would be operative the effect of addition of urea would be to increase the film thickness.

Assuming that for high urea concentrations no counterions are present in the STERN layer then ψ_d can be calculated using the method outlined in section 4–2, which in turn leads to Π_{vdW} as a function of the film thickness. The results thus obtained as well as those for films containing sucrose are plotted in figure 5–3.

The trend of Π_{vdW} as a function of d is in accordance with the theory. The slope of the straight line is 3. The HAMAKER – VAN DER WAALS constant for these film systems is 1.7×10^{-13} erg which is at least of the right order of magnitude. This outcome supports the idea that film thicknesses in the presence of
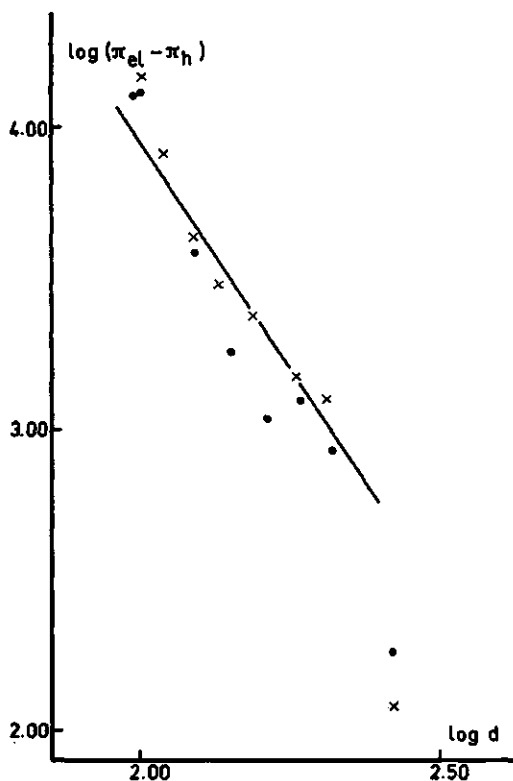
FIG. 5-3. Attractive force as a function of film thickness. System: NaDS + NaCl + urea●●● NaDS + NaCl + sucrose × × × T = 25 °C. The drawn line has a third power slope and yields A = 1.7×10^{-13} erg.

the non-electrolytes urea and sucrose follow relatively well the classical picture of double layer repulsion and VAN DER WAALS attraction because the double layers tend to be more diffuse and/or evaporation is reduced which would lead to better equilibrium thicknesses.

SUMMARY

The equilibrium thicknesses of films stabilized by LiDS (+LiCl) or NaDS (+NaCl) and containing the non-electrolytes urea or sucrose are greater than those of films in the absence of these admixtures, especially at relatively low electrolyte concentrations.

Arguments can be given leading to the expectation that films with urea or sucrose fit better in the classical DERYAGIN-LANDAU and VERWEY-OVERBEEK picture than films without these additives. The experimental results corroborate this. The VAN DER WAALS force follows a third power law between 100 and 400 Å and the obtained HAMAKER-VAN DER WAALS constant amounts to 1.7×10^{-13} erg, in reasonable agreement with theoretical predictions.

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6. FILMS STABILIZED BY NONIONIC SURFACTANTS INFLUENCE OF ELECTROLYTES AND IONIC SURFACTANTS

6.1. EFFECT OF ELECTROLYTES ON EQUILIBRIUM FILM THICKNESS

Because our attempts to make thick equilibrium films ($d > 400$ Å), stabilized by ionic surfactant solutions did not succeed and because this thickness region is theoretically particularly interesting in view of the onset of retardation, we tried to stabilize thick films by nonionic surfactant solutions.

To this purpose we used the nonionic surfactant OP-11 (nC_8H_{17}–C_6H_4O $(CH_2CH_2O)_{11}H$. Some characteristics are: c.m.c. 3×10^{-4} mole/l, specific conductivity of 0.1 % solution in water at 25°C 7×10^{-6} ohm^{-1}cm^{-1}, pH of 1 % solution in water at 25°C 7.0; it is free of electrolytes. A disadvantage, however, is the low double layer potential (1), which nullifies, more or less, the favorable effect of the absence of electrolytes.

Measurements were made at 25°C. The static method was used. The films are mobile and very stable. After less than half an hour the equilibrium thickness was attained. The reproducibility of the measurements was ±1 Å.

The equivalent water thicknesses, d_w, are reported in table 6–1 and plotted in figure 6–1.

The influence of several inorganic electrolytes on the equilibrium thickness was also measured. The results of these measurements are summarized in table 6–2 and also plotted in figure 6–1.

6.1.1. Discussion

The effect of surfactant concentration as well as that of nature and concentration of electrolyte on the equilibrium thickness is very small. The slight increase of the film thickness on adding electrolyte could perhaps be attributed to preferential absorption of one of the ionic species in the surfactant layers, thus creating a kind of double layer. CORKILL et al. (2) did not observe any influence of the electrolyte concentration on the equilibrium thickness of films stabilized by n-dodecyl hexaoxyethylene glycol monoether.

Apparently the double layer potential in these types of film and in consequence also the double layer repulsion are small, especially since there is no effect of the valency of the electrolyte ions. From this it can be concluded that there must be a repulsive force of a non-electrostatic nature which counterbalances

TABLE 6–1. Equivalent water thickness, d_w (Å), of films stabilized by the nonionic surfactant OP-11. Influence of surfactant concentration. T = 25°C.

conc. (%)	0.05	0.1	0.2	0.3	0.4	0.5	1.0	5.0	10.0
I_b/I_s	0.0220	0.0238	0.0234	0.0235	0.0240	0.0242	0.0233	0.0235	0.0216
d_w (Å)	93.9	97.5	96.9	97.0	98.0	98.5	96.4	97.0	93.0

TABLE 6-2. Equivalent water thickness, d_w (Å), of films stabilized by 0.1% OP-11. Influence of type and concentration of electrolytes. T=25°C.

NaCl (mole/l)	I_b/I_s	d_w	MgCl$_2$ (mole/l)	I_b/I_s	d_w	La(NO$_3$)$_3$ (mole/l)	I_b/I_s	d_w
0	0.0238	97.5	0	0.0238	97.5	0	0.0238	97.5
0.02	0.0274	105						
0.04	0.0278	106						
0.06	0.0272	105						
0.08	0.0272	105						
0.10	0.0288	108	0.10	0.0314	113	0.10	0.0313	113
0.125	0.0300	110						
0.15	0.0314	113						
0.20	0.0288	108	0.20	0.0336	116.5	0.20	0.0333	117
0.30	0.0316	113				0.30	0.0326	115
0.40	0.0325	114.5						
0.50	0.0314	113	0.50	0.0320	114			

the VAN DER WAALS attractive force and which is largely independent of the concentrations of the surfactant and electrolyte. Presumably in these types of film the stabilization mechanism is of entropic nature.

In order to discuss the equilibrium thickness quantitatively, d_w's have still to be converted into real thicknesses, d. For that purpose the film is thought to be composed of an aqueous core, in which the electrolytes and the polyoxyethylene chains of the surfactant molecules are dissolved, flanked by the octylphenol chains. Taking $n_1 = 1.45$, $n_2 = 1.33$ and $d_1 = 12$ Å (4), the correction d^* to d_w becomes −10 Å. Thus the equilibrium thicknesses of the films stabilized by
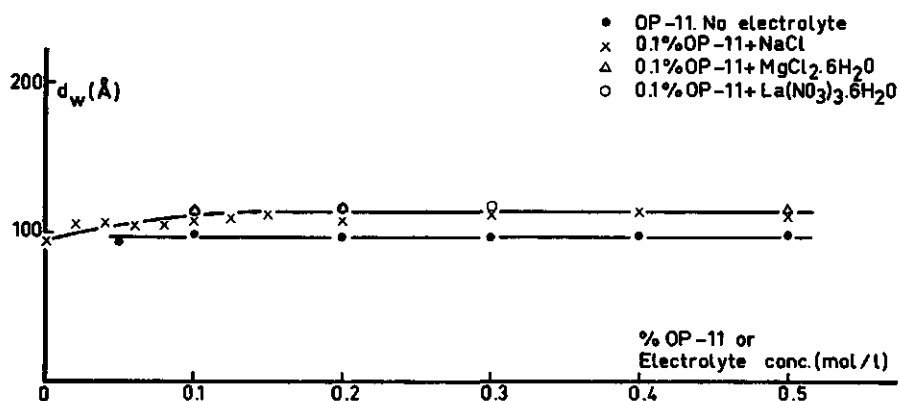

FIG. 6-1. Equivalent water thickness of equilibrium films stabilized by the nonionic surfactant OP-11. Influence of surfactant concentration and nature and concentration of electrolytes. T = 25°C.

OP-11 in the absence of electrolytes will be about 88 Å. On addition of electrolytes, the corrected equilibrium thicknesses are about 104 Å. The length of an extended OP-11 molecule is about 53 Å (4).

The following physical pictures of these types of film can be imagines.

1. The chains of the surfactant molecules stand perpendicularly to the film surface and are extended. Then the film thickness must be at least $2 \times 53 =$ 106 Å. This picture is not acceptable for films without electrolytes but is acceptable for films containing electrolytes. There is good analogy between the equilibrium films stabilized by non-ionic surfactants and the second black films of PERRIN, which under certain conditions are formed by ionic surfactants. In both cases the thickness is hardly or not affected by electrolytes and the aqueous layer is presumably thin.

2. The chains of the surfactant molecules are in an oblique position to the film surface or are coiled. This coil may play a part in a possible entropic stabilization of the films and its extent of expansion determines the space which is available for an aqueous layer between the surfactant monolayers. This aqueous layer is presumably thin.

Finally it would be interesting to compare the behaviour of electrolytes in the present nonionic soap films with the effect of electrolytes on nonionic surfactants in bulk solution.

### 6.2. EFFECT OF IONIC SURFACTANTS ON EQUILIBRIUM FILM THICKNESS

Another possibility for obtaining thick equilibrium films lies in achieving a greater surface charge and potential by adding small amounts of an ionic surfactant to the non-ionic surfactant solution, from which the films were drawn.

A few experiments were performed at 25 °C with films stabilized by mixtures of 0.1 % OP-11 and 10^{-4} mole/l NaDS, to which were added small quantities of NaCl. The films thinned very slowly, in contrast with those, stabilized by OP-11 alone. The slow thinning may be attributed to a high surface viscosity of the mixed surfactant monolayer. The correction d^* applied to d_w was again -10 Å. Table 6–3 and figure 6–2 summarize the results of the measurements.

TABLE 6–3. Equilibrium thickness (Å) of films stabilized by 0.1 % OP-11 + 10^{-4} mole/l NaDS. Influence of NaCl. T = 25 °C.

NaCl (mole/l)	I_b/I_s	d_w(Å)	d(Å)
1×10^{-3}	0.488	498	488
2×10^{-3}	0.0978	202	192
3×10^{-3}	0.1025	206	196
4×10^{-3}	0.0638	162	152
10×10^{-3}	0.0322	114	104

FIG. 6-2. Equilibrium thickness (Å) of films stabilized by 0.1% OP-11 + 10^{-4} mole/l NaDS. Influence of concentration of NaCl. T = 25°C. Drawn curve holds for combinations of ψ_d (assumed constant) and A, given in inset.
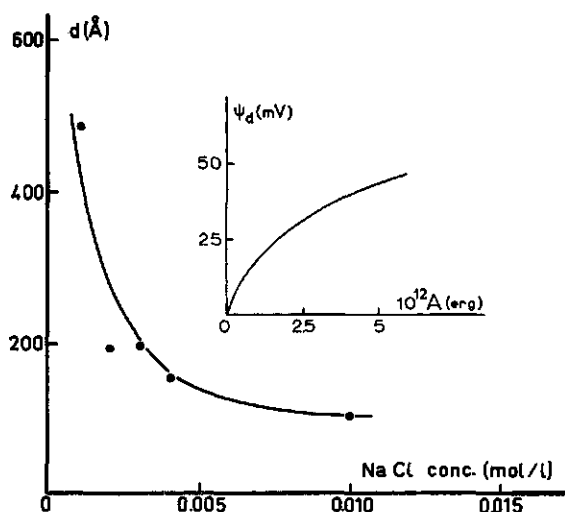
6.2.1. *Discussion*

The experimental fact that the films swell on adding a trace of ionic surfactant shows that the charging of the film surfaces has a great influence.

Taking 12 Å for the monolayer thickness and using equation (4–1), combinations of ψ_d and A can be calculated, agreeing with the observed thickness. In figure 6–2 these are graphically presented in the inset, from which can be concluded that for $A = 5 \times 10^{-13}$ erg, ψ_d becomes about 13 mV. This rather low value for ψ_d suggests that the films are somewhat thinner than is predicted by the theory.

SUMMARY

Equilibrium films stabilized by nonionic surfactants are comparable with the second black films or PERRIN films. There is no significant influence of electrolytes on their thickness and both types of film contain only small amounts of water. This may be attributed to a low diffuse double layer potential.

The equilibrium thickness of films which are stabilized by mixtures of nonionic and ionic surfactants decreases with increasing electrolyte concentrations. Interpretation of this thickness in terms of double layer repulsion and VAN DER WAALS attraction leads to the conclusion that these films are somewhat thinner than is predicted by the theory.

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7. STRATIFIED FILMS

7.1. INTRODUCTION

All experiments described so far are concerned with films which were stabilized by surfactant solutions of low concentrations, usually 0.01 mole/1.

The question was posed, whether equilibrium films stabilized by NaDS (0.01 mole/1) + NaCl (total bulk concentration of counterions x mole/1) would be as thick as films stabilized by pure NaDS (total bulk concentration x mole/1). This question was also asked with respect to films containing only Li^+ counterions.

7.2. EXPERIMENTS AND RESULTS

At 25 °C films stabilized by pure NaDS or pure LiDS have been made. These films were mobile. Unlike the other films, discussed hitherto, they did not thin continuously till the final value was attained but rather showed a number of consecutive thickness steps, henceforth called 'equilibrium thickness' for sake of simplicity though we really have to do with metastable films. The higher the surfactant concentration, the more of these steps could be observed. Visually this multiplicity or stratification was observed as follows. Directly after the film was drawn manually, a mobile, fast draining film formed, which after a few minutes reached an equilibrium thickness with a lifetime of about forty five seconds. After that, at the top of the film a thinner film slowly formed, which in course of time completely replaced the thicker film. This second equilibrium film had a lifetime of about five minutes, after which in the same manner a third, still thinner film with a lifetime of at least one hour was generated. Since the transition of thick film to a thinner one occurs irreversibly, the thick film must have a higher free energy per unit surface. It must be stressed that this stratification only occurred if films were drawn manually (static method). By pulling the films slowly (dynamic method) only the thinnest films formed.
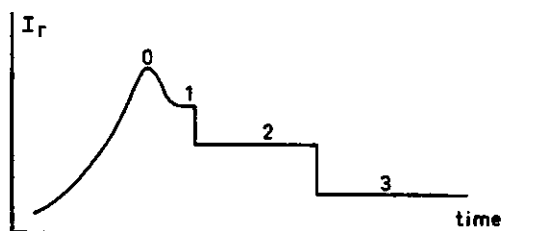

FIG. 7-1. Recorded reflected intensity as a function of time.
0: first interference maximum.
1: first equilibrium film, d'_3.
2: second equilibrium film, d'_2.
3: third equilibrium film, d'_1.

TABLE 7–1. Equilibrium thicknesses, d_1', d_2' and d_3' (Å), of stratified films stabilized by LiDS. T = 25 °C. The equivalent water thicknesses are also tabulated.

conc. (mole/l)	I_b/I_s	d_w'	d_1'	I_b/I_s	d_w''	d_2'	I_b/I_s	d_w'''	d_3'
0.01	0.0781	180	172						
0.02	0.0673	167	159						
0.03	0.0600	157	149						
0.04	0.0490	142	134						
0.06	0.0401	128	120						
0.08	0.0366	122	114						
0.10	0.0309	112	104						
0.12	0.0320	113	105						
0.14	0.0306	111	103						
0.16	0.0294	109	101	0.0853	188	173			
0.18	0.0267	104	96	0.0800	182	167			
0.20	0.0261	102	94	0.0782	180	165			
0.22	0.0219	93.5	86	0.0752	177	162			
0.24	0.0219	93.5	86	0.0694	169	154			
0.26	0.0197	89.1	81.5	0.0580	154	139			
0.28	0.0196	88.9	81.3	0.0613	159	144			
0.30	0.0178	84.5	77	0.0617	159	144	0.129	234	211

Figure 7–1 shows schematically the recorded reflected intensity as a function of time.

Tables 7–1 and 7–2 and figure 7–2 summarize the results of the experiments.

TABLE 7–2. Equilibrium thicknesses, d_1', d_2', d_3' and d_4' (Å), of stratified films stabilized by NaDS. T = 25 °C. The equivalent water thicknesses are also tabulated.

| conc. (mole/l)	I_b/I_s	d_w'	d_1'	I_b/I_s	d_w''	d_2'	I_b/I_s	d_w'''	d_3'	I_b/I_s	d_w''''	d_4'
0.01	0.0811	183	175									
0.02	0.0680	168	160									
0.03	0.0600	157	149									
0.04	0.0497	143	135									
0.06	0.0392	127	119									
0.08	0.0363	122	114									
0.10	0.0316	113	105									
0.12	0.0298	110	102	0.1081	212	197						
0.14	0.0282	107	99	0.0950	198	183						
0.16	0.0286	107	99	0.0847	187	172	0.190	288	265			
0.18	0.0233	96.5	89	0.0767	178	163						
0.20	0.0259	102	94	0.0768	179	164	0.174	274	251			
0.22	0.0223	94.9	87	0.0680	168	153						
0.24	0.0232	96.4	89	0.0721	173	158	0.156	259	236			
0.26	0.0203	90.8	83	0.0645	163	148						
0.28	0.0190	87.8	80	0.0622	160	145						
0.30	0.0184	86	78	0.0576	154	139	0.149	252	229			
0.50	0.0133	73.5	66	0.0465	138	123	0.101	205	182	0.171	272	242
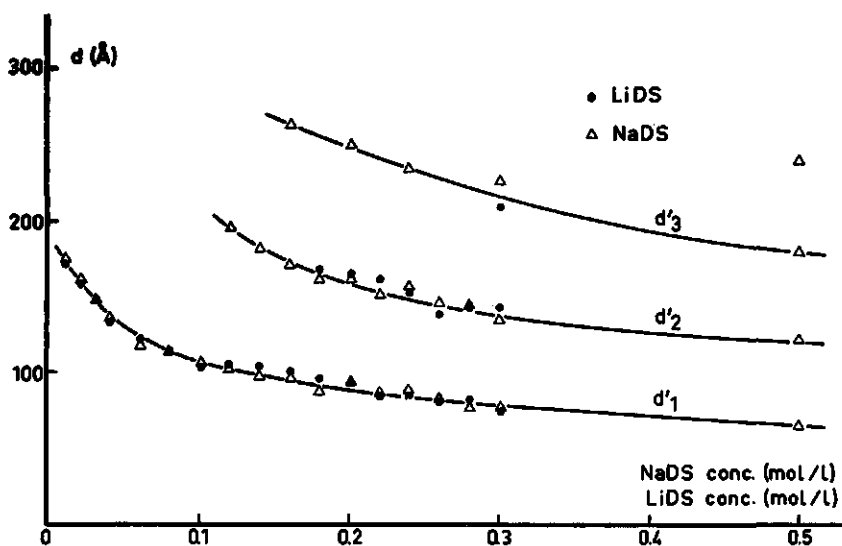
Fɪɢ. 7-2. Equilibrium thickness of stratified films.
Influence of surfactant concentration. T = 25 °C.

The reproducibility is 1 %. The equilibrium thicknesses (d_1', d_2', d_3' and d_4') were calculated from the equivalent water thicknesses (d_w', d_w'', d_w''' and d_w'''') using the theory of FRANKEL and MYSELS (1) concerning the light reflection by multilayer films. Here again the refractive index of the surfactant layers was put equal to 1.43 and that of the aqueous layers to 1.33.

7.3 DISCUSSION

With respect to the present experimental results, the following may be remarked.

1. All observed equilibrium thicknesses decrease with increasing surfactant concentration. The differences between the thicknesses of the films stabilized by LiDS or NaDS is not significant. Films stabilized by NaDS show a somewhat greater tendency to stratification than films stabilized by LiDS. In this respect there is a certain analogy with the formation of second black films, which are formed by NaDS + NaCl but not by LiDS + LiCl.

2. The thinnest films (line d_1') have thicknesses in good agreement with those of first black films stabilized by NaDS + NaCl at 25 °C. Apparently the counterion concentration in both film systems is the same at the same analytical bulk concentration.

3. In the concentration range studied ($c \leqslant 0.5$ mole/l) no second black films are formed.

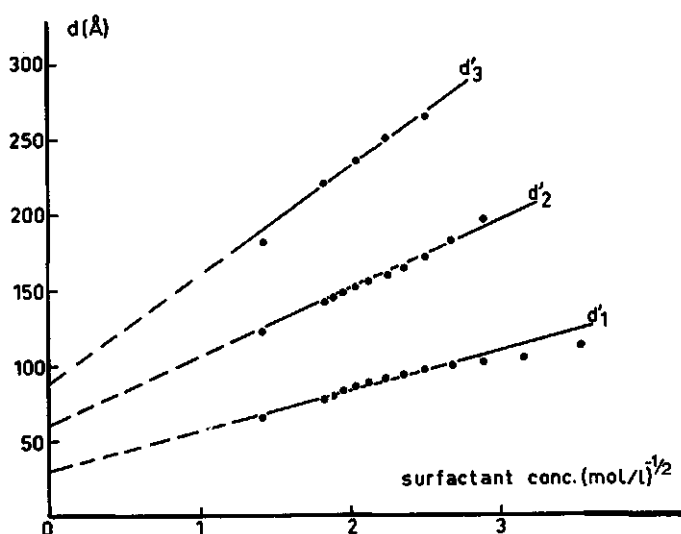One of the most important conclusions which can be drawn from the observ-

FIG. 7-3. Equilibrium thicknesses (Å) of stratified films as a function of the surfactant concentration. Region of high concentrations. T = 25 °C.

ed phenomena is that these films have a layered structure, which is called stratification.

This stratification was already observed by NEWTON (2), JOHONNOTT (3), PERRIN (4) and WELLS (5). PERRIN concluded that a soap film is composed of multiples of elementary layers of about 50 Å thickness.

Also in bulk surfactant solutions multiples of elementary units were observed by several investigators. LUZZATI et al. (6), GALLOT and SKOULIOS (7) and FRANCOIS et al. (8) studied the structure of very concentrated surfactant solutions by means of X-ray diffraction. The general trend is that lamellar micelles are present, separated by aqueous layers having a smaller thickness as surfactant concentration is increased. In more recent publications (9, 10) the existence of lamellar layers or multiples of elementary structures in surfactant solutions is mentioned also.

Returning to our stratified films it may be argued that the distance of closest approach of the surfactant layers could well be proportional to $c^{-1/2}$. This was checked with the present system. In figure 7–3 the film thicknesses are plotted against the reciprocal values of the square root of the surfactant concentrations.

It is seen that linear plots are obtained. By extrapolating to infinite concentrations where the limiting case of crystalline surfactant is attained, values for the intercepts $d_1' = 30$ Å, $d_2' = 60$ Å and $d_3' = 90$ Å are found. Obviously there is a multiplicity of about twice the length of the NaDS molecule (32 Å). On this basis the picture of the stratified films becomes as depicted by figure 7–4. Thus
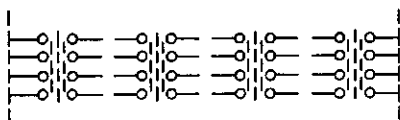
Fig. 7-4. Stratification in thin films.

the idea is that soap films stabilized by concentrated surfactant solutions ($c \gg$ c.m.c.) are built up by lamellar micelles. Moreover, as in concentrated bulk surfactant solutions, the aqueous layer thickness between the ionic headgroups of the surfactant molecules decreases with increasing surfactant concentration, which is perhaps related to the decreasing electrical double layer repulsion with increasing counterion concentration. The amounts of water in the films having thicknesses d_1', d_2' and d_3' may be expected to be in the ratios $1:2:3$. The slopes of the lines of figure 7–3 have the ratios $1:1.8:2.7$.

Extrapolation of line d_1' in figure 7–3 suggests that the gradual formation of second black films of thickness $d = 37$ Å can be realized at concentrations of about 11 mole/l. This tendency is also shown by films stabilized by LiDS–LiCl (figure 4–2).

The fact that the thinnest films stabilized by pure NaDS solutions are as thick as the first black films stabilized by NaDS + NaCl at the same total bulk concentration of counterions indicates that these thicknesses are true equilibrium thicknesses.

SUMMARY

Films stabilized by pure concentrated solutions of NaDS or LiDS are stratified. This means that films exist with more than one equilibrium thickness. The stratification is more pronounced at increasing surfactant concentrations. The films stabilized by NaDS show a somewhat greater tendency of stratification than those stabilized by LiDS. Except for this there is no specific influence of the counterions.

The thinnest films are as thick as the first black films stabilized by surfactant plus electrolyte with the same total concentration of counterions.

The formation of second black films is not observed at the concentrations studied, although the possibility is not excluded that they may be formed from very concentrated solutions.

Presumably, the stratified films consist of repeating structure units of about 30 Å, separated by layers of aqueous solution the thickness of which decreases as the surfactant concentration is increased.

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SUMMARY

The purpose of this thesis was to study specific effects of counterions on the structure of the electrical double layer in free liquid films by means of measurement of the equilibrium thickness. The underlying idea was, that on the basis of the magnitude of this counterion specificity insight might be gained into the extent of the deviations from the classical GOUY-CHAPMAN theory of the diffuse double layer and hence from the theory of DERYAGIN-LANDAU and VERWEY-OVERBEEK about the stability of lyophobic colloids. Moreover, a critical study of these deviations could be helpful in explaining the disparity between experimental and theoretical equilibrium thicknesses, observed by several investigators.

Chapter 1 deals briefly with the position of the soap film as a colloid chemical model besides that of the classical silver iodide sol and other systems. The role of specific counterion effects is also discussed.

The phenomenology of free liquid films, the forces which play a part and the light reflection are described in chapter 2.

Chapter 3 contains the experimental part: the preparation of the alkali dodecyl sulphates, the apparatus for the measurement of the equilibrium thickness of the films and the performance of the measurements. Two principally different measuring-methods were used, the static and the dynamic one. With the static method a vertical film is drawn manually from the surfactant solution. By drainage an equilibrium film is formed in the course of time. With the dynamic method the film is pulled very slowly from the solution, so that the equilibrium film is formed directly. It appeared that the thicknesses measured according to both methods are equal.

The remaining part of this thesis is devoted to the experimental results and their interpretation. Chapters 4 and 5 deal with the influence of nature and concentration of counterions, co-ions and of temperature and non-electrolytes on the equilibrium thickness of films stabilized by alkali dodecyl sulphates (0.01 mole/l). The general trend is a decreasing equilibrium thickness with increasing counterion concentration. At 25 °C, films containing sodium counterions ($c > 0.05$ eq/l) appear to be systematically a few percent thinner than those containing the counterions lithium, ammonium or phenyltrimethylammonium. This specificity is not progressive and must be mainly attributed to specific counterion effects in the STERN layer. There is no measurable influence of the co-ions sulphate, nitrate and chloride on the equilibrium thickness.

Interpretation of the equilibrium thickness of the films at 25 °C, stabilized by sodium dodecyl sulphate ($+$ NaCl) *solely* in terms of electrical double layer repulsion and VAN DER WAALS attraction is not possible. Adaptation of parameters which affect the double layer repulsion does not lead to satisfactory results, from which it is concluded that perhaps a third force acts in these films. Although precautions have been taken against evaporation and the experimental reproducibility is very good – also between the two different ways

of producing the equilibrium films – the possibility that a number of the films are too thin due to evaporation can not be fully excluded.

At 45 °C the equilibrium thickness of films stabilized by the alkali dodecyl sulphates turns out to be practically independent of the counterion concentration. The lithium-sodium specificity occurring at 25 °C, is maintained at 45 °C.

The influence of the nature of the counterions on the critical concentration at which second black films are formed (25 °C and 45 °C) was also investigated. The systems containing the counterions lithium, cesium, ammonium and phenyltrimethylammonium do not form second black films but those with the counterions sodium, potassium and rubidium do. The critical concentrations of the latter group of ions vary widely, which ultimately must be interpreted on the basis of slight differences in the physico-chemical properties of these ions. The thickness of the second black films is 37.4 ± 1.5 Å.

The equilibrium thicknesses of films stabilized by solutions of sodium dodecyl sulphate (+ NaCl) to which are added the non-electrolytes urea or sucrose were also measured at 25 °C. It turns out that these films are thicker than the corresponding ones without non-electrolytes at counterion concentrations lower than about 0.15 eq/l. The effect of these non-electrolytes can be ascribed to a desorption of counterions from the STERN layer to the diffuse part of the double layer. Also the possibility that evaporation is retarded must not be ruled out. The desorption picture can also account for the absence of the lithium-sodium specificity in film systems containing large amounts of urea. The equilibrium thickness of these films can be interpreted rather well with the DERYAGIN-LANDAU and VERWEY-OVERBEEK stability theory. The VAN DER WAALS force follows the third power law and the HAMAKER-VAN DER WAALS constant is about 1.7×10^{-13} erg.

In chapter 6 the effect of electrolytes and ionic surfactants on the equilibrium thickness of films stabilized by non-ionic surfactants at 25 °C is described. It is found that the equilibrium thickness of films stabilized by $n-C_8H_{17} -C_6H_4-O$ $(CH_2CH_2O)_{11}H$, OP–11, is not or hardly a function of the surfactant concentration, nor of the concentration of the added electrolytes NaCl, $MgCl_2$ or $La(NO_3)_3$. In this last respect these systems show great similarity with the second black films. The equilibrium thickness of films stabilized by mixtures of the ionic surfactant sodium dodecyl sulphate and the non-ionic surfactant OP-11 decreases with increasing NaCl concentration. Interpretation of these thicknesses in terms of the electrical double layer repulsion and VAN DER WAALS attraction is possible with reasonable values for the parameters.

The phenomenon of the stratification or multiplicity of soap films is the subject of chapter 7. It appears that films stabilized by concentrated solutions of LiDS or NaDS at 25 °C have more than one equilibrium thickness. The stratification is more pronounced at higher surfactant concentration. Several times three equilibrium thicknesses could be measured with good reproducibility. All thicknesses become smaller with increasing surfactant concentration. The films stabilized by NaDS show a somewhat greater tendency of stratification than those which are stabilized by LiDS. Except for this, there is no specific

influence of the lithium and sodium counterions on the equilibrium thickness. The thinnest films are as thick as the first black films stabilized at 25 °C by NaDS + NaCl of the same total counterion concentration of the bulk solution. Second black films are not formed in the system in question ($c \leqslant 0.5$ mole/l) but this does not mean that they could not be formed from very highly concentrated surfactant solutions at high temperature. Presumably the stratified films consist of repeating structure units of about 30 Å thickness, separated by aqueous layers, the thickness of which decreases with increasing surfactant concentration.

SAMENVATTING

Het doel van het in dit proefschrift beschreven onderzoek was de bestudering van specifieke effekten van tegenionen op de struktuur van de elektrische dubbellaag in vrije vloeistoffilms en wel door middel van de meting van de evenwichtsdikte. Het hieraan ten grondslag liggende idee was, dat op grond van de grootte van deze tegenionen specificiteit inzicht verkregen zou kunnen worden in de mate van de afwijkingen van de klassieke GOUY-CHAPMAN theorie van de diffuse dubbellaag en van de theorie van DERYAGIN-LANDAU en VERWEY-OVERBEEK over de stabiliteit van lyofobe kolloiden. Bovendien zou een kritische bestudering van de afwijkingen nuttig kunnen zijn ten aanzien van de verklaring van het verschil tussen experimentele en theoretische evenwichtsdikten, dat door verschillende onderzoekers is gemeten.

Hoofdstuk 1 behandelt beknopt de plaats van het zeepvlies als kolloidchemisch model naast die van het klassieke zilverjodide sol en van andere systemen. De rol van specifieke tegenionen effekten wordt eveneens besproken.

De fenomenologie van vrije vloeistoffilms, de krachten welke werkzaam zijn en de lichtreflektie worden beschreven in hoofdstuk 2.

Hoofdstuk 3 bevat het experimentele gedeelte van het onderzoek: de bereiding van de alkalidodecylsulfaten, de apparatuur waarmee de evenwichtsdikten van de films werden gemeten en de uitvoering van de metingen. Twee principieel verschillende meetmethoden werden gebruikt: de statische en de dynamische. Bij de statische methode wordt met de hand snel een vertikaal vlies uit de zeepoplossing getrokken, waarna door drainage na verloop van tijd een evenwichtsfilm ontstaat. Bij de dynamische methode wordt de film zeer langzaam uit de oplossing getrokken zodat direkt de evenwichtsfilm ontstaat. Het bleek dat de dikten, gemeten volgens beide methoden, even groot zijn.

Het resterende gedeelte van het proefschrift is gewijd aan de experimentele resultaten en de interpretatie hiervan. De hoofdstukken 4 en 5 hebben tot onderwerp de invloed van soort en koncentratie van tegenionen, co-ionen en van temperatuur en niet-elektrolyten op de evenwichtsdikte van door alkalidodecylsulfaten ($c=0.01$ molair) gestabiliseerde films. De algemene trend is dat de evenwichtsdikte afneemt met toenemende tegenionenkoncentratie. Bij 25 °C blijken films welke natrium tegenionen bevatten ($c>0.05$ eq/l) systematisch enige procenten dunner te zijn dan die welke de tegenionen lithium, ammonium of fenyltrimethylammonium bevatten. Deze specificiteit is niet progressief en moet hoofdzakelijk worden toegeschreven aan specifieke tegenioneneffekten in de STERN laag. Er bestaat geen meetbare invloed van de co-ionen sulfaat, nitraat en chloride op de evenwichtsdikte.

Interpretatie van de evenwichtsdikten van de films bij 25 °C, gestabiliseerd door natriumdodecylsulfaat (+ natriumchloride) *enkel en alleen* op basis van de elektrische dubbellaag repulsie en VAN DER WAALS attraktie is niet mogelijk. Aanpassing van parameters welke de dubbellaagrepulsie beïnvloeden leidt niet tot bevredigende resultaten, waaruit wordt geconcludeerd dat misschien een

derde kracht in deze films werkzaam is. Hoewel voorzorgsmaatregelen tegen verdamping zijn getroffen en de experimentele reproduceerbaarheid zeer goed is – ook tussen de twee verschillende manieren waarop de evenwichtsfilms tot stand worden gebracht – kan de mogelijkheid dat een aantal films te dun is ten gevolge van verdamping niet volledig uitgesloten worden.

Bij 45°C blijken de evenwichtsdikten van de door de alkalidodecylsulfaten gestabiliseerde films praktisch onafhankelijk te zijn van de tegenionenkoncentratie. De lithium-natriumspecificiteit, optredend bij 25°C, blijft bij 45°C gehandhaafd.

De invloed van de soort tegenionen op de kritische koncentratie waarbij tweede zwarte films worden gevormd (25°C en 45°C) is ook onderzocht. De systemen met de tegenionen lithium, cesium, ammonium en fenyltrimethylammonium blijken geen tweede zwarte films te vormen, wel echter die met de tegenionen natrium, kalium en rubidium. De kritische koncentraties hiervan lopen sterk uiteen, hetgeen uiteindelijk verklaard moet worden op grond van de geringe verschillen in de fysico-chemische eigenschappen van deze ionen. De tweede zwarte films hebben een dikte van 37.4 ± 1.5 Å.

De evenwichtsdikten van films, gestabiliseerd door oplossingen van natriumdodecylsulfaat ($+$NaCl) waaraan de niet-elektrolyten ureum en sucrose zijn toegevoegd werden eveneens gemeten en wel bij 25°C Het blijkt dat deze films dikker zijn dan de overeenkomstige films zonder niet-elektrolyten bij tegenionenkoncentraties kleiner dan ongeveer 0.15 eq/l. Het effect van deze niet-elektrolyten kan worden toegeschreven aan een desorptie van tegenionen van de STERN laag naar het diffuse deel van de dubbellaag. Ook moet de mogelijkheid dat verdamping wordt vertraagd niet worden uitgesloten. Het beeld van de desorptie kan ook de afwezigheid van de lithium-natrium specificiteit in film systemen met hoge ureum koncentraties verklaren. De evenwichtsdikte van deze films kan tamelijk goed geïnterpreteerd worden met de stabiliteitstheorie van DERYAGIN- LANDAU en VERWEY-OVERBEEK. De VAN DER WAALS kracht volgt de derde macht wet en de HAMAKER-VAN DER WAALS konstante is ongeveer 1.7×10^{-13} erg.

In hoofdstuk 6 wordt de invloed van elektrolyten en ionogene zeep op de evenwichtsdikte van door niet-ionogene zeep gestabiliseerde films bij 25°C beschreven. Gevonden wordt dat de evenwichtsdikte van films gestabiliseerd door n–C_8H_{17}–C_6H_4–$O(CH_2CH_2O)_{11}H$, OP-11, niet of nauwelijks een funktie is van de zeepkoncentratie, noch van de koncentratie van de toegevoegde elektrolyten NaCl, $MgCl_2$ of $La(NO_3)_3$. In dit laatste opzicht vertonen deze systemen grote gelijkenis met de tweede zwarte films. De evenwichtsdikte van films, gestabiliseerd door mengsels van de ionogene zeep natriumdodecylsulfaat en de niet-ionogene zeep OP-11 neemt af met toenemende NaCl koncentratie. Interpretatie van deze dikten in termen van de elektrische dubbellaag repulsie en VAN DER WAALS attractie is mogelijk met redelijke waarden voor de parameters.

Het fenomeen van de stratificatie of multipliciteit van zeepvliezen wordt beschreven in hoofdstuk 7. Het blijkt dat films, gestabiliseerd door gekoncentreerde oplossingen van LiDS of NaDS bij 25°C meer dan een evenwichtsdikte heb-

ben. De stratificatie is des te geprononceerder naarmate de zeepkoncentratie hoger is. Meermalen kunnen drie evenwichtsdikten reproduceerbaar worden gemeten. Alle dikten worden kleiner met toenemende zeepkoncentratie. De films, gestabiliseerd door NaDS vertonen iets meer neiging tot stratificatie dan die, welke gestabiliseerd zijn door LiDS. Behalve dit, is er geen specifieke invloed van de lithium – en natrium tegenionen op de evenwichtsdikte. De dunste films zijn even dik als de eerste zwarte films, welke bij 25 °C zijn gestabiliseerd door NaDS + NaCl met dezelfde tegenionenkoncentratie van de bulk-oplossing. Tweede zwarte films worden in het onderhavige systeem ($c \leqslant 0.5$ molair) niet gevormd, hetgeen niet betekent dat ze niet gevormd zouden kunnen worden uit zeer hoog gekoncentreerde zeepoplossingen bij hoge temperatuur. Vermoedelijk bestaan de gestratificeerde films uit repeterende struktuureenheden van ongeveer 30 Å dikte, gescheiden door waterige lagen waarvan de dikte afneemt met toenemende zeepkoncentratie.

LIST OF SYMBOLS AND ABBREVIATIONS

A	area of soap film
A	HAMAKER–VAN DER WAALS constant
A_{11}	HAMAKER–VAN DER WAALS constant of the surfactant monolayer of the soap film
A_{22}	HAMAKER–VAN DER WAALS constant of the aqueous core material of the soap film
A_{12}	composite HAMAKER–VAN DER WAALS constant, approximately equal to $(A_{11}.A_{22})^{\frac{1}{2}}$
c_i	concentration of component i
CsDS	cesium dodecyl sulphate
d	distance between two semi-infinite plates
d	equilibrium film thickness
d_1	thickness of the surfactant monolayer
d_2	thickness of the aqueous core of the soap film
d_1'	equilibrium thickness of stratified film
d_2'	equilibrium thickness of stratified film
d_3'	equilibrium thickness of stratified film
d_4'	equilibrium thickness of stratified film
d_b	equilibrium thickness of black film
d_s	film thickness at which maximum reflection occurs (silvery film)
d_w	equivalent water thickness
d^*	correction to be applied to the equivalent water thickness
e	elementary charge
G	GIBBS free energy per unit surface area
G_{vdw}	GIBBS free energy due to VAN DER WAALS attraction
G_{el}	GIBBS free energy due to electrical double layer repulsion
G_h	GIBBS free energy due to hydrostatic pressure
G_s	GIBBS free energy due to steric hindrance
g	gravitational constant
h	height difference between the part of the film under consideration and the surface of the solution
h_0	height where the meniscus becomes vertical
I_0	intensity of the incident light beam
I_r	intensity of the reflected light beam
I_b	reflected intensity from the black film
I_s	reflected intensity from the silvery film (first maximum)
k	BOLTZMANN constant
KDS	potassium dodecyl sulphate
LiDS	lithium dodecyl sulphate
n	number of counterions/cm^3 bulk solution
n	refractive index of film consisting of pure water

n_0	refractive index of air
n_1	refractive index of surfactant monolayer
n_2	refractive index of the aqueous core of the film
NaDS	sodium dodecyl sulphate
OP-11	$n\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(CH_2CH_2O)_{11}H$
p	order of interference
p	pressure of the film
q	number of molecules/cm^3
R	fraction of light reflected by a film
r	distance between the centres of two molecules
r	FRESNEL coefficient
r_b	FRESNEL coefficient for the black film
r_s	FRESNEL coefficient for the silvery film
RbDS	rubidium dodecyl sulphate
S	entropy of the film
T	absolute temperature
V	volume of the film
V	energy of attraction between two molecules
z	valency of counterions
α	angle of refraction
α'	angle of incidence
β	interaction constant for two molecules (LONDON equation)
γ_d	$\tanh\left(\dfrac{ze\psi_d}{4kT}\right)$
Δ	phase difference between the light beam reflected at the top and at the bottom of the film (horizontal) or at the front and back face (vertical)
ε	dielectric constant
κ	$= \left(\dfrac{8\pi z^2 e^2 n}{\varepsilon kT}\right)^{1/2}$ (reciprocal DEBYE length)
λ	wavelength
μ_i	thermodynamic potential of component i
Π_{vdW}	VAN DER WAALS attractive force
Π_{el}	electrical double layer repulsion
Π_h	hydrostatic pressure
Π_c	capillary force
Π_s	force due to steric hindrance
ρ	density difference between film phase and the outer phase
σ	surface tension
σ_f	surface tension of the film
σ_o	surface charge of the film
σ_d	charge of the diffuse part of the double layer
σ_m	charge of the non-diffuse part of the double layer
ψ_d	diffuse double layer potential

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Na het behalen van het diploma B aan het Stedelijk Lyceum te Zutphen in 1953 ging de schrijver chemie studeren aan de H.T.S. te Eindhoven, alwaar het eindexamen in 1957 werd afgelegd. Na vervulling van de militaire dienstplicht werd in september 1959 de studie in de scheikunde aan de Rijksuniversiteit te Utrecht aangevangen. Het candidaatsexamen, letter g, werd afgelegd op 22 october 1962, het doctoraal examen scheikunde met als specialisatie fysische chemie en als bijvak natuurkunde op 10 mei 1965.

Gedurende de periode mei 1965 tot en met december 1969 was hij werkzaam als wetenschappelijk medewerker in het laboratorium voor fysische en kolloid-chemie van de Landbouwhogeschool te Wageningen, alwaar dit proefschrift werd bewerkt.

Sedert januari 1970 is hij verbonden aan het Centraal Laboratorium van de Koninklijke Industriëele Maatschappij Noury & Van der Lande te Deventer.