

# Contact Angles in Thin Liquid Films

## III. Interaction Forces in Newton Black Soap Films

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The interaction parameters of Newton black soap films stabilized by NaDS, as derived from contact angle experiments, have been interpreted in terms of the structure and the interaction forces in the films. From the film thickness and the difference between the surface excess of the salt in the film and at the bulk surface it is concluded that (a) the diffuse double-layer overlap in the film is practically complete; (b) the film only contains adsorbed DS<sup>-</sup> ions and an equal amount of Na<sup>+</sup> counterions, but no salt; and (c) the double layer at the bulk surface is still partly diffuse. A model for the structure of the NB films is proposed according to which the adsorbed DS<sup>-</sup> ions with their counterions form a two-dimensional square lattice at each film surface. It is found that the interaction free energy of the NB films can be explained by taking into account the electrostatic interactions between the discrete ions in the two opposing surface lattices. The model of the NB film is qualitatively in agreement with the experimental results of other workers.

### 1. INTRODUCTION

The interaction forces in common black (CB) films stabilized by ionic surfactants, with thicknesses ranging from ~6 to ~100 nm, are relatively well known. They consist of two types: van der Waals attraction and the diffuse double-layer repulsion. At equilibrium the two forces balance the hydrostatic suction in the film. A characteristic feature of CB films is that their equilibrium thickness,  $h_e$ , decreases with increasing electrolyte concentration, caused by the fact that the action range of the double-layer repulsion decreases with increasing electrolyte concentration (1–3).

The nature of the interaction forces in very thin Newton black (NB) films, which are formed at high electrolyte concentration, is still largely obscure. In contrast to CB films, the equilibrium thickness of NB

films (~4 nm) is practically independent of the electrolyte concentration (4–8). A systematic study of the contact angles of NB films, stabilized by sodium dodecyl sulfate (NaDS), was published by Huisman *et al.* (9). The interaction free energy,  $\Delta F(h_e)$ , of the films, as obtained from the contact angles, was found to depend strongly on the salt concentration and the type of counterion. The results could not be explained in terms of the theories of van der Waals attraction and diffuse double-layer repulsion alone.

Jones *et al.* (4) studied the effect of different counterions and temperature on the salt concentration at which the transition from CB to NB films takes place. They concluded that NB films must have a well-organized structure which can accommodate only certain counterions. A similar conclusion was arrived at by Platikanov *et al.* (10, 11) who investigated the electroconductivity of NB films. According to Ibbotson *et al.* (6) the transition from CB to NB films

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shows a close similarity with the flocculation of a hydrophobic colloid.

In a previous paper (12), referred to hereafter as paper II, we described contact angle experiments of NB films stabilized by NaDS, the indifferent electrolytes being NaCl and Na<sub>2</sub>SO<sub>4</sub>. From the contact angles we derived the interaction free energy,  $\Delta F(h_e)$ , the interaction entropy,  $\Delta S(h_e)$ , the interaction energy,  $\Delta U(h_e)$ , and the difference between the surface excess of the surfactant,  $\Delta\Gamma_2$ , and the salt,  $\Delta\Gamma_3$ , at the film surface and the bulk surface. We found that the formation of NB films is energetically a highly favorable process with  $\Delta U(h_e) \approx -20 \text{ m J/m}^2$ , but entropically very unfavorable with  $-T\Delta S(h_e) \approx +20 \text{ m J/m}^2$ , the two effects tending to compensate each other. The surface excess of surfactant at the film surface,  $\Gamma_2^f$ , was found to be practically equal to the surface excess,  $\Gamma_2^g$ , at the bulk surface, whereas the surface excess of the salt was found to be higher at the film surface than at the bulk surface ( $\Delta\Gamma_3 \equiv \Gamma_3^f - \Gamma_3^g = \text{positive}$ ).

In this paper we shall make use of the experimentally determined interaction parameters of the NB films to develop a more complete picture of the structure of the NB films and the interaction forces which act in the films.

## 2. STRUCTURE OF NEWTON BLACK FILMS

Information about the structure of the NB films can be obtained from the optical reflectivity of the films, provided additional information on the composition of the films is available. Assuming that the film is a homogeneous water layer with refractive index  $n = 1.333$ , the so-called equivalent thickness,  $h_w$ , of the film can be calculated with the Rayleigh formula (13). In paper II we found for NB films stabilized by NaDS:  $h_w = 4.4 \pm 0.1 \text{ nm}$ , practically independent of the salt concentration.

The surface excess,  $\Gamma_2^f$ , of NaDS in the NB films is equal, within 1%, to the surface

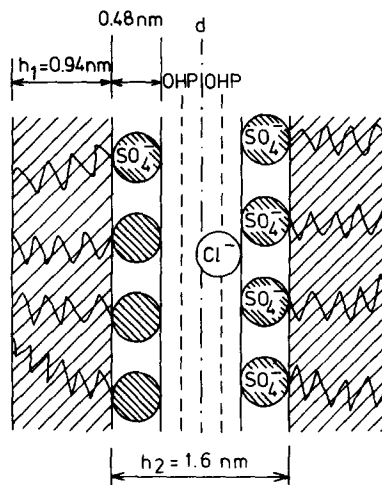


FIG. 1. Structure of the Newton black soap film stabilized by NaDS.

excess,  $\Gamma_2^g$ , at the bulk surface (see paper II and Ref. (8)). It is therefore likely that NB films consist of an aqueous core covered with two monolayers of DS<sup>-</sup> ions (sandwich structure) (Fig. 1). Assuming that the three layers are homogeneous, the thickness  $h_2$  of the aqueous core can be calculated from  $h_w$  with the correction formula derived by Duyvis (14), Frankel *et al.* (15), and Rijnbout (16), namely:

$$\begin{aligned} h_2 &= h_w - 2h_1 \frac{(n_1^2 - 1)}{(n_2^2 - 1)} \\ &= h_w - h(\text{corr}), \end{aligned} \quad [1]$$

where  $h_1$  is the thickness of the hydrocarbon layers with refractive index  $n_1$ , formed by the alkyl chains of the DS<sup>-</sup> ions at the film surface;  $n_2$  is the refractive index of the aqueous core ( $n_2 = 1.333$ ). The ionic groups of the DS<sup>-</sup> ions are assumed to belong to the aqueous core.  $h_1$  can be calculated from  $\Gamma_2^f$  with:

$$h_1 = \Gamma_2^f(M/\rho_1), \quad [2]$$

where  $\rho_1$  is the density of the hydrocarbon layer and  $M$  is the molecular weight of the hydrocarbon tail of the DS<sup>-</sup> ion. For the range of salt concentrations studied (0.19 to 0.50 mole/dm<sup>3</sup>) we have (8, 17, 18):

$\Gamma_2^f \approx \Gamma_2^g \approx 4.2 \times 10^{-6}$  mole/m<sup>2</sup> (one DS<sup>-</sup> ion per 0.40 nm<sup>2</sup>). Assuming that  $M$ ,  $\rho_1$ , and  $n_1$  have the same value as for liquid dodecane, viz.,  $M = 170$  g/mole,  $\rho_1 = 0.749$  g/cm<sup>3</sup>, and  $n_1 = 1.422$  (19), we find:  $h_1 = 0.94$  nm and  $h(\text{corr}) = 2.5$  nm. For the thickness of the aqueous core we then find:  $h_2 = 1.9$  nm for  $h_w = 4.4$  nm. The assumption of the values of  $\rho_1$  and  $n_1$  gives rise to an uncertainty in the value of  $h_1$ . However, it will hardly affect  $h_2$  as the correction factor  $h(\text{corr})$  is insensitive to this assumption. This follows from the relationship between  $\rho_1$  and  $n_1$  as given by the Lorentz-Lorenz equation (13).

The refractive index  $n_2$  of the aqueous core will certainly be larger than 1.333 as the aqueous core contains not only water molecules, but also the ionic head groups of the DS<sup>-</sup> ions, the counterions Na<sup>+</sup>, and possibly some salt. We have at least four ions per 0.40 nm<sup>2</sup> of the film; two SO<sub>4</sub><sup>-</sup> groups of the adsorbed surfactant ions and two Na<sup>+</sup> counterions. An aqueous layer of 1.9 nm in thickness contains about 25 water molecules per 0.40 nm<sup>2</sup>. Taking into account the volume of the ions this is about five water molecules per ion. The aqueous core will thus have the optical properties of a very concentrated electrolyte solution, roughly equivalent to a 3 M Na<sub>2</sub>SO<sub>4</sub> solution. A value of  $n_2 = 1.38$  would therefore seem more realistic (19). When  $h_2$  is recalculated using  $n_2 = 1.38$  we find:  $h_2 = 1.6$  nm. The film then contains about five water molecules per ion which is hardly more than the hydration water of the ions. Practically the same conclusion was arrived at by den Engelsen *et al.* (7), who investigated the optical properties of the NB films of the system NaDS + NaCl using both reflectivity and ellipsometry. They found that the optical properties of the NB films are equivalent with those of a homogeneous film with a thickness of 3.6 nm and a refractive index of 1.365. This would mean:  $h_1 = 1.1$  nm and  $h_2 = 1.4$  nm with  $n_1 = n_2 = 1.365$ . Using the Lorentz-Lorenz equation they conclude that the NB

film should contain six to seven water molecules per ion. In general it is found that, for the NB films,  $h_w$  tends to increase with increasing salt concentration  $c_3$  (4, 5, 12). This does not necessarily mean that  $h_2$  increases with increasing  $c_2$ ; a slight increase of the surface excess of the surfactant  $\Gamma_2^f$ , as observed by Jones *et al.* (8), would produce the same effect.

The aqueous layer contains the SO<sub>4</sub><sup>-</sup> groups of the adsorbed DS<sup>-</sup> ions, Na<sup>+</sup> ions, and possibly some Cl<sup>-</sup> ions or SO<sub>4</sub><sup>2-</sup> ions. The unhydrated Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions have radii of 0.18 and 0.22 nm, respectively (20). The radii of the hydrated ions are larger, but not well known. As the limiting mobilities of these ions are almost equal (20) one may use a value of 0.24 nm for both, and also for the SO<sub>4</sub><sup>-</sup> group of the adsorbed DS<sup>-</sup> ions. The distance,  $2l$ , between the inner Helmholtz planes (IHP) of the two film surfaces (i.e., the planes through the centers of the adsorbed DS<sup>-</sup> ions) is then about  $1.6 - 2 \times 0.24 \approx 1.1$  nm. If diffuse double layers were present in the NB film, the position of the outer Helmholtz planes (OHP) of the two film surfaces should be located at the centers of the co-ions at closest approach to the adsorbed SO<sub>4</sub><sup>-</sup> groups. Then the distance between the OHPs of the two surfaces,  $2d$ , will only be  $1.6 - 6 \times 0.24 \approx 0.2$  nm (see Fig. 1), implying that hardly any diffuse part can be expected for the electrical double layers in the NB films. The film parameters of the NB films, as derived from the optical reflectivity, are summarized in Table I.

### 3. SURFACE EXCESS OF SALT

In paper II, we found that the surface excess of the salt in the film over that of the bulk surface  $\Gamma_3^f - \Gamma_3^g \equiv \Delta\Gamma_3$  is positive. Although in our case one can hardly expect a diffuse double layer inside the film, it is still of interest to see what the diffuse double-layer theory tells us about  $\Delta\Gamma_3$ , because the double layer at the bulk surface may at least be partly diffuse.

TABLE I

Geometrical Parameters of NB Films of the Systems NaDS + NaCl and NaDS + Na<sub>2</sub>SO<sub>4</sub> (23.5°C) as Derived from the Optical Reflectivity of the Films

$h_w$ (nm)	$h_1$ (nm)	$h_2$ (nm)	$2l$ (nm)	$2d$ (nm)
$4.4 \pm 0.1$	$0.94^a$	$1.6 \pm 0.2$	$1.1 \pm 0.2$	$0.2 \pm 0.3$

<sup>a</sup> Based on the assumption that  $n_1 = 1.422$ .

The distribution of ions near a charged surface of an electrolyte solution is described by the Boltzmann equation (21). The counterions are attracted by and the co-ions are repelled from the surface. The surface excess of the co-ions is therefore negative. From the electroneutrality condition of the surface it follows that the surface excess,  $\Gamma_3$ , of the (neutral) salt is equal to the surface excess of the co-ion. Thus, the salt is negatively adsorbed at a charged surface ( $\Gamma_3$  is negative). When two diffuse double layers interact, as in soap films, the repulsion of the salt becomes less effective, i.e., the absolute value of the surface excess of the salt at the film surface,  $\Gamma_3^f$ , is smaller than the absolute value of the surface excess  $\Gamma_3^\alpha$  at the bulk surface. Thus, the diffuse double-layer theory predicts  $\Delta\Gamma_3$  to be positive. The  $\Delta\Gamma_3$  values of the NB films being positive (see paper II) is therefore qualitatively in accordance with the predictions made by this theory.

In the systems studied—NaDS + NaCl and NaDS + Na<sub>2</sub>SO<sub>4</sub>—the surface of the bulk solution is negatively charged by the adsorption of DS<sup>-</sup> ions. The solutions of these systems can be considered as single salt solutions as the salt concentration  $c_3$  was always at least 200 times larger than the surfactant (monomer) concentration  $c_2 \approx \text{CMC}$ . For a quantitative comparison between the experimental  $\Delta\Gamma_3$  values and those predicted by the diffuse double-layer theory we therefore need expressions for  $\Gamma_3^f$  and  $\Gamma_3^\alpha$  for systems containing a single 1-1 electrolyte (NaCl), and a single 1-2 electrolyte (Na<sub>2</sub>SO<sub>4</sub>) with the valency of the

co-ion being 2. The negative adsorption of electrolyte at a single surface (the bulk surface) has been treated by several authors (22-24). In dimensionless form the expression for a 1-1 electrolyte reads:

$$[(\beta(N)^{1/2})/N]\Gamma_3^\alpha \equiv P_{11}^\alpha = 2[\exp(z^\alpha/2) - 1], \quad [3]$$

and for a 1-2 electrolyte:

$$[(\beta(N)^{1/2})/N]\Gamma_3^\alpha \equiv P_{12}^\alpha = [2 \exp(2z^\alpha) + 4 \exp(z^\alpha)]^{1/2} - (6)^{1/2}, \quad [4]$$

where  $\Gamma_3^\alpha$  is expressed in equivalents per unit area, and the electrolyte concentration  $N$  is expressed in equivalents per unit volume, and  $\beta$  is a physical constant given by (SI units):

$$\beta = (2F^2/\epsilon RT)^{1/2}, \quad [5]$$

where  $F$  is the Faraday constant,  $R$  is the gas constant, and  $\epsilon = \epsilon_r \epsilon_0$  is the permittivity of the medium. ( $\epsilon_r$  is the relative permittivity and  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{N m}^2$  is the permittivity of vacuum.)  $\beta(N)^{1/2} = \kappa_{11}$  is the reciprocal Debye length of a 1-1 electrolyte solution. The dimensionless parameters  $P_{11}^\alpha$  and  $P_{12}^\alpha$  only depend on the reduced (negative) electrostatic potential  $z^\alpha \equiv F\Psi_0^\alpha/RT$  at the outer Helmholtz plane (OHP) of the bulk surface. They can be considered as the thickness of the surface layer [expressed in multiples of the double-layer "thickness"  $\kappa_{11}^{-1} = (\beta(N)^{1/2})^{-1}$ ] from which the salt is completely expelled.  $P_{11}^\alpha$  goes from zero for  $z^\alpha = 0$  to  $-2$  for  $z^\alpha = -\infty$ . Thus, for very high (negative) surface potentials, the 1-1 electrolyte is completely expelled from a surface layer with twice the "thickness" of the diffuse double layer ( $\Gamma_3^\alpha = -2\kappa_{11}^{-1}N$ ). For a given value of  $z^\alpha$  the absolute value of  $P_{12}^\alpha$  is always larger than  $P_{11}^\alpha$ , with the ratio of  $P_{12}^\alpha/P_{11}^\alpha$  decreasing from 1.63 to 1.225 when  $z^\alpha$  goes from zero to  $-\infty$ . Thus, expressed in equivalents per unit area, the 1-2 electrolyte is more effectively expelled from the bulk surface than a 1-1 electrolyte. The expression for the negative adsorption of two

interacting double layers is more complicated involving elliptic integrals. Here, too, the expression for the (negative) adsorption of the salt can be written in the dimensionless form (25–27):

$$[(\beta(N)^{1/2})/N]\Gamma_3^f \equiv P^f(z^f, \beta d(N)^{1/2}), \quad [6]$$

where the dimensionless parameter  $P^f$  depends on both the reduced electrostatic potential  $z^f$  at the OHP of the film surface, and the double layer interaction parameter  $\beta d(N)^{1/2}$ , where  $d$  is the distance between the OHP and the mid plane of the film. The complete expressions for  $P_{11}^f$  of a 1–1 electrolyte and  $P_{12}^f$  of a 1–2 electrolyte are given in Refs. (25)–(28). For large double layer overlap ( $\beta d(N)^{1/2} < 1$ ), the negative adsorption of the 1–1 and 1–2 electrolyte is to a good approximation given by:

$$\begin{aligned} [(\beta(N)^{1/2})/N]\Gamma_3^f &= P_{11}^f \\ &\approx [\exp(z^f) - 1]\beta d(N)^{1/2} \end{aligned} \quad [7]$$

and:

$$\begin{aligned} [(\beta(N)^{1/2})/N]\Gamma_3^f &= P_{12}^f \\ &\approx [\exp(2z^f) - 1]\beta d(N)^{1/2} \end{aligned} \quad [8]$$

For large (reduced) surface potential  $z^f$ , Eqs. [7] and [8] reduce to:

$$\begin{aligned} [(\beta(N)^{1/2})/N]\Gamma_3^f &= P_{11}^f \\ &= P_{12}^f \approx -\beta d(N)^{1/2} \end{aligned} \quad [9]$$

or (for both the 1–1 and 1–2 electrolyte):

$$\Gamma_3^f \approx -Nd \quad [10]$$

This means that, for large double-layer overlap and large surface potentials, the salt is completely expelled from the film.

The difference between the surface excess of the salt at the film surface and at the bulk surface is given by:

$$\begin{aligned} \Delta\Gamma_3 &\equiv \Gamma_3^f - \Gamma_3^g = [N/(\beta(N)^{1/2})] \\ &\times [P^f(z^f, \beta d(N)^{1/2}) - P^g(z^g)] \end{aligned} \quad [11]$$

For our NB films, the double-layer overlap is large. Using  $d \approx 0.1$  nm (see section 2), the interaction parameter  $\beta d(N)^{1/2} = \kappa_{11}d$

varies from 0.14 to 0.23 for salt concentrations between 0.2 and 0.5 Eq/dm<sup>3</sup>. Thus, when the double layer in the film would be partly diffuse, the value of  $\Delta\Gamma_3$  would be rather insensitive to the value of the electrostatic potential  $\Psi_0^f$  at the film surface. As the uncertainty in  $d$  is  $\pm 0.15$  nm, it is even possible that the double-layer overlap is complete ( $\beta d(N)^{1/2} = 0$ ). Then one has:

$$\Gamma_3^f = 0$$

and

$$\Delta\Gamma_3 = -\Gamma_3^g. \quad [12]$$

In that case  $\Delta\Gamma_3$  only depends on the electrostatic potential  $\Psi_0^g$  at the OHP of the bulk surface, i.e., the  $\Delta\Gamma_3$  values derived from the contact angles of the NB films give information about the diffuse double layer at the *single* (bulk) surface.

When the experimental values of  $\Delta\Gamma_3$  are compared with those predicted by the diffuse double layer theory it should be realized that the  $\Gamma_3^f$  and  $\Gamma_3^g$  values, as given by theory, are the surface excesses with respect to the OHP of the surface. In paper I of this series (29) it is shown that the  $\Delta\Gamma_3$  values, as derived from the contact angles, give the difference between the surface excesses at the film and the bulk surfaces with respect to the Gibbs dividing planes with  $\Gamma_1 = 0$  of the two surfaces. In general the OHP and the  $\Gamma_1 = 0$ -plane will not coincide. However, a direct comparison between the experimental and theoretical  $\Delta\Gamma_3$  values is allowed when the distance between the OHP and the  $\Gamma_1 = 0$ -plane is the same for the film and the bulk surfaces. This would imply that the  $\Delta\Gamma_3$  values of the NB films are completely determined by the distribution of the co-ions in the *diffuse* part of the ionic double layers at the film surface and the bulk surface.

By inserting the experimental  $\Delta\Gamma_3$  values into the double-layer equations, we can see what the theory predicts about the value of  $\Psi_0^g$ . If the double layer in the NB films is still partly diffuse ( $d > 0$ ) we have to make an assumption concerning the value

TABLE II  
Calculated  $\Psi_0^\alpha$  Values of the Bulk Surface, for the  
System NaDS + NaCl at 23.5°C<sup>a</sup>

$c_3(\text{NaCl})$ (M)	$d = 0$	$d = 0.1 \text{ nm}$		$\zeta$
		$\Psi_0^\alpha = -\infty$	$\Psi_0^\alpha = \Psi_0^\alpha$	
0.2	-35 <sup>b</sup>	-41 <sup>b</sup>	-40 <sup>b</sup>	-73 <sup>b</sup>
0.3	-26	-34	-32	-70
0.4	-22	-30	-28	-68
0.5	-19	-28	-25	-66

<sup>a</sup> The last column gives the  $\zeta$  potentials of the NaDS micelles.

<sup>b</sup> Values given in millivolts.

of  $\Psi_0^f$ . As for partially overlapping double layers it is likely that  $|\Psi_0^f| \geq |\Psi_0^\alpha|$ ; we made the calculation using the complete equations given in Refs. (25) and (32) for the two extreme cases  $\Psi_0^f = \Psi_0^\alpha$  and  $\Psi_0^f = -\infty$ . The results for the NB films with NaCl at 23.5°C, with  $d = 0.1 \text{ nm}$ , and  $\Delta\Gamma_3 = +1.34 \times 10^{-7} \text{ Eq/m}^2$  (see paper II) are shown in Table II. It is seen that the theory predicts  $\Psi_0^\alpha$  to vary from -40 to -25 mV when the salt concentration increases from 0.2 to 0.5 Eq/dm<sup>3</sup>. The potentials hardly depend on the (assumed) value of  $\Psi_0^f$ . Table II also shows the  $\Psi_0^\alpha$  values as calculated with  $d = 0$ . In that case  $\Psi_0^\alpha$  is independent of  $\Psi_0^f$ . Because of the uncertainty in  $d$  ( $\pm 0.15 \text{ nm}$ ), the uncertainty in  $\Psi_0^\alpha$  is of the order of 10 mV. The results for the NB films with Na<sub>2</sub>SO<sub>4</sub> at 23.5°C, with  $d = 0.1 \text{ nm}$  and  $\Delta\Gamma_3 = +1.71 \times 10^{-7} \text{ Eq/m}^2$ , are given in Table III. Here  $\Psi_0^\alpha$  is seen to range from -36 to

TABLE III

Calculated  $\Psi_0^\alpha$  Values of the Bulk Surface for the  
System NaDS + Na<sub>2</sub>SO<sub>4</sub> at 23.5°C

$c_3(\text{Na}_2\text{SO}_4)$ (Eq liter <sup>-1</sup> )	$d = 0.1 \text{ nm}$	
	$\Psi_0^\alpha = -\infty$	$\Psi_0^\alpha = \Psi_0^\alpha$
0.2	-36 <sup>a</sup>	-35 <sup>a</sup>
0.3	-28	-27
0.4	-24	-23
0.5	-22	-21

<sup>a</sup> Values given in millivolts.

-22 mV for  $c_3(\text{Na}_2\text{SO}_4)$  increasing from 0.2 to 0.5 Eq/m<sup>2</sup>. They are thus about 5 mV smaller than for the system with NaCl. In paper II we found that  $\Delta\Gamma_3$  of the NB films of the system NaDS + NaCl decreases with increasing temperature. This suggests that (the absolute value of)  $\Psi_0^\alpha$  decreases with increasing  $T$  ( $\sim 10\%$  per 5°C), whereas one would expect that the double layer becomes more diffuse with increasing  $T$ . However, this effect might also be caused by a slight increase of  $d$  with increasing  $T$  ( $\sim 0.05 \text{ nm}$  per 5°C).

The surface potentials as given in Tables I and II are considerably smaller than the maximum value that can be reached by  $\Psi_0^\alpha$  when the double layer would be completely diffuse. From the primary surface charge due to the adsorption of the DS<sup>-</sup> ions ( $\sigma_0 \approx 0.4 \text{ C/m}^2$ ) the maximum value of  $\Psi_0^\alpha$  can be calculated to range from -140 mV for  $c_3(\text{NaCl}) = 0.2 \text{ mole/dm}^3$  to -116 mV for  $c_3(\text{NaCl}) = 0.5 \text{ mole/dm}^3$ . From the  $\Psi_0^\alpha$  values as given in Tables I and II we find, using the double-layer equation for the surface charge (30), that the charge of the DS<sup>-</sup> ions adsorbed at the bulk surface is for 90% neutralized by Na<sup>+</sup> ions which penetrated behind the OHP. The remaining 10% is then compensated for by an excess positive charge in the diffuse double layer. Taking into account the high salt concentrations used, this does not seem unrealistic.

It is often assumed that the electrical potential  $\Psi_0^\alpha$  at the OHP is equal to the electrokinetic, or  $\zeta$  potential of the surface. This implies that the OHP coincides with the so-called slipping plane between the fixed and the flowing liquid (30, 31), an assumption which is open to considerable doubt. In the last column of Table II, the  $\zeta$  potentials are shown of NaDS micelles, the electrical double layer of which should be closely similar to that of the bulk surface. They were obtained from the data of Stigter and Mysels (32) and Wiersema (33) by extrapolation, as the highest NaCl concentration considered by them was 0.1 mole/dm<sup>3</sup>. They are seen

to range from  $-75$  to  $-60$  mV and are thus about twice as large as the  $\Psi_0^\alpha$  values derived from the contact angles of the NB films. However, this does not allow definitive conclusions to be drawn concerning the validity of the diffuse double-layer theory at the high salt concentrations involved: a difference of a few tenths of a nanometer between the OHP and the slipping plane could already account for the differences. As the order of magnitude of the  $\Psi_0^\alpha$  values is realistic, there is hardly any doubt that the  $\Delta\Gamma_3$  values of the NB films must be due to the (large) interaction of the diffuse double layers in the films, i.e., the films will only contain the adsorbed  $DS^-$  ions and an equal amount of  $Na^+$  counterions. The same conclusion was arrived at by Platikanov *et al.* (10, 11) who studied the electroconductivity of the NB films.

#### 4. INTERACTION FORCES IN NEWTON BLACK FILMS

In paper II we found that the interaction free energy,  $\Delta F(h_e)$ , of the NB films stabilized by NaDS ranges from  $\sim -0.01$  to  $\sim -1.1$  mJ/m<sup>2</sup> for salt concentrations,  $c_3$ , between 0.19 and 0.50 Eq/dm<sup>3</sup> and temperatures,  $T$ , between 20.5 and 29.5°C. From the variation of  $\Delta F(h_e)$  with  $T$  we found for the

interaction entropy term,  $T\Delta S(h_e)$ , of both systems:  $T\Delta S(h_e) = -20 \pm 1$  mJ/m<sup>2</sup> independent of  $c_3$  and  $T$ . The interaction energy  $\Delta U(h_e) = \Delta F(h_e) + T\Delta S(h_e)$  is then also approximately  $-20$  mJ/m<sup>2</sup>. Apparently, the formation of a NB film is energetically a highly favorable process, but entropically highly unfavorable, with the two effects tending to compensate each other. In the previous section we found that  $\Delta\Gamma_3$ , as obtained from a derivative of  $\Delta F(h_e)$ , could be semiquantitatively explained with the theory of diffuse double-layer interaction. However,  $\Delta F(h_e)$  itself cannot be explained by the classical theories of long-range interaction forces. This is illustrated in Fig. 2 which shows the double-layer interaction free energy,  $\Delta F_{el}(h_e)$ , the London-van der Waals interaction free energy,  $\Delta F_w(h_e)$ , and the sum of the two terms for the NB films of the system NaDS + NaCl at 23.5°C.  $\Delta F_{el}(h_e)$  was obtained by assuming that in the NB films, the overlap of the diffuse double layers of the two film surfaces is complete ( $d = 0$ ). Then (30):

$$\begin{aligned} \Delta F_{el}(h_e) &= -2F_{el}^\alpha \\ &= \frac{16NRT}{\beta(N)^{1/2}} \left( \cosh \frac{z^\alpha}{2} - 1 \right), \quad [13] \end{aligned}$$

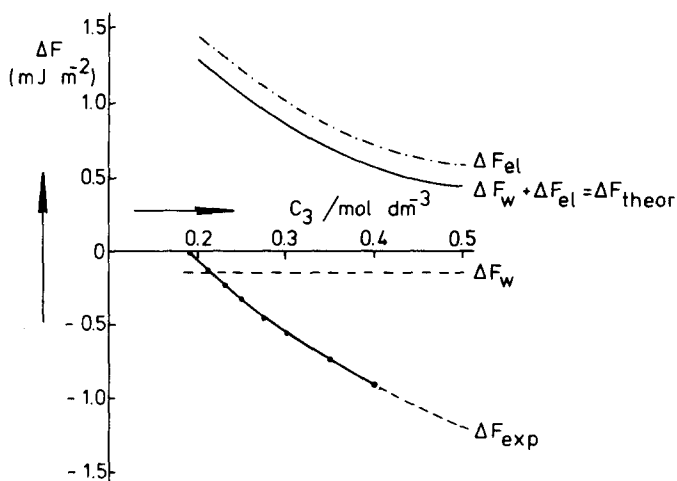


FIG. 2. Interaction free energy of a NB film as a function of the salt concentration for the system NaDS + NaCl; 23.5°C.

where  $F_{ei}^a$  is the free energy of a (single) diffuse double layer at the bulk surface. For the (reduced) surface potential  $z^\alpha = F\Psi_0^\alpha/RT$  we used the value as given in Table II ( $d = 0$ ). The value of  $\Delta F_w(h_e)$  was obtained from the data for a triple-layer film with  $h_1 = 1.0$  nm,  $n_1 = 1.42$ ,  $h_2 = 1.5$  nm, and  $n_2 = 1.33$ , as calculated by Ninham *et al.* (34) using Lifshitz theory. From Fig. 2 it is seen that according to the classical theory of long-range interaction forces, the interaction free energy

$$\Delta F(h_e) = \Delta F_{ei}(h_e) + \Delta F_w(h_e) \quad [14]$$

is positive, whereas the experimental values are negative. For salt concentrations between 0.2 and 0.4 mole/dm<sup>3</sup>, the gap between the theoretical and experimental values is of the order of 1.2 to 1.5 mJ/m<sup>2</sup>. Because of the uncertainty in the double-layer parameters and the high salt concentrations involved, the  $\Delta F_{ei}(h_e)$  values should only be looked upon as rough estimates. Nevertheless, Fig. 2 clearly illustrates the main problem encountered in the interpretation of the  $\Delta F(h_e)$  values of the NB films: according to the classical double-layer theory  $\Delta F_{ei}(h_e)$  must be positive. This implies that the total interaction free energy,  $\Delta F(h_e)$  must be larger (more positive) than the van der Waals interaction free energy,  $\Delta F_w(h_e)$ . According to Lifshitz theory,  $\Delta F_w(h_e)$  of a NB film is of the order of  $-0.14$  mJ/m<sup>2</sup> (34), whereas experimental  $\Delta F(h_e)$  values as low as  $-1.1$  mJ/m<sup>2</sup> (see paper II) and even  $-2.8$  mJ/m<sup>2</sup> have been reported (35). Because of the uncertainty in the film parameters used, the value of  $\Delta F_w(h_e)$  is also open to some doubt (36). However, it is quite unlikely that this would give rise to an error of a factor of 10 or more. Ninham *et al.* (34) suggested that, because of the high electrolyte concentration in the NB films, the absolute value of  $\Delta F_w(h_e)$  could be considerably larger. However, from their own data it can be inferred that this could affect  $\Delta F_w(h_e)$  by at most 30%. In the present context this is hardly significant. There-

fore, we must conclude that the classical theories of long-range interaction forces cannot explain the  $\Delta F(h_e)$  values of the NB films. The same conclusion was arrived at by Huisman *et al.* (9), who considered the force balance in the NB films.

The above analysis suggests that, in addition to the classical long-range interaction forces, a (possibly short range) attractive force is operating in the NB films. In the previous section we concluded that, in the NB films, the primary surface charge of the adsorbed DS<sup>-</sup> ions is practically completely compensated by (Na<sup>+</sup>) counterions penetrating into the Stern layer of the two film surfaces. The distance  $2l$  between the inner Helmholtz planes (IHP) of the two surfaces (see Table I) is of the same order of magnitude as the distance between the ions in the Stern layer of each surface. Recent theoretical work of Richmond (37, 38) indicates that under these conditions the discreteness of the surface charge may significantly affect the free energy of double-layer interaction. When the oppositely charged ions in the Stern layer of the two opposing surfaces face each other this may give rise to a strong attractive force.

An estimate of the discrete ion effect, to be expected for the NB films, can be made when we make the following simplifying assumptions: (a) The DS<sup>-</sup> ions and the Na<sup>+</sup> ions in the Stern layer of the film surface and the bulk surface form a plane, square lattice. (b) At the bulk surface about 90% of the positive lattice sites are occupied; the remaining 10% are compensated in the diffuse part of the double layer (see section 3). (c) In the film the diffuse layer overlap is complete ( $d = 0$ ); all the positive sites are occupied and the surfaces have no net charge. (d) The oppositely charged ions of the opposing film surfaces face each other. The formation of the NB film from two bulk surfaces can then be considered to consist of two successive steps: First, the diffuse double layers of the two bulk surfaces are discharged by transferring Na<sup>+</sup> ions from



the solution to the vacant sites of the surface lattice; and second, the distance between the two bulk surfaces, the net charge of which is zero, is reduced from  $h = \infty$  to the equilibrium thickness  $h = h_e$  of the NB films. Although the discharging process of a diffuse double layer with a smeared out surface charge is not completely identical with the discharging process as considered in step 1, we assume that they give rise to an equally large free energy change, i.e.,  $\Delta F_1 = -2F_{el}^{\alpha} = \Delta F_{el}(h_e)$ , where  $\Delta F_{el}(h_e)$  is given by Eq. [13]. For a non-smeared-out surface charge both the "electrical" and the "chemical" contribution (30) to this free energy [13] would need a separate treatment. We do not expect a greatly different result which would be comparable to the contribution of the second step. The free energy change in the second step,  $\Delta F_2$ , consists of two terms: the van der Waals interaction free energy,  $\Delta F_w(h_e)$ , of a NB film with thickness  $h_e$ , and the interaction free energy of the two surface lattices,  $\Delta F_d(h_e)$ . Hence, according to the above model, the total interaction free energy reads

$$\Delta F(h_e) = \Delta F_{el}(h_e) + \Delta F_w(h_e) + \Delta F_d(h_e). \quad [15]$$

The extra term,  $\Delta F_d(h_e)$ , can be calculated with the expression for the interaction free energy of two square surface lattices with a net zero charge, as derived by Richmond (37). For the conditions as met in the NB films, where the distance  $2l$  between the surface lattices is of the order of 1.1 nm and the lattice constant  $a$  is  $\sim 0.45$  nm (one  $DS^-$  ion and one  $Na^+$  ion per  $0.40$  nm<sup>2</sup>), it reduces to:

$$\Delta F_d = -(\sigma_1^2/\epsilon_2 p) \exp(-2pl), \quad [16]$$

where  $\sigma_1$  is the sum total of the positive and negative charges of each lattice per unit area (for the NB films with one ion per  $0.20$  nm<sup>2</sup>,  $\sigma_1 = 0.8$  C/m<sup>2</sup>),  $\epsilon_2 = \epsilon_2^* \epsilon_0$  is the permittivity of the medium between the lattices, and

$$p^2 \equiv (\kappa_{11}^2 + Q^2), \quad [17]$$

with:  $Q = (2\pi)^{1/2}/a$  where  $\kappa_{11}$  is the reciprocal Debye length of the (1-1) electrolyte solution.

For salt concentrations between 0.2 and 0.5 mole/dm<sup>3</sup>, the parameter  $p^{-1}$  ranges from 0.17 to 0.16 nm. Equation [16] then predicts that the absolute value of  $\Delta F_d$  decreases with a factor of  $\sim 2.7$  when the distance  $2l$  between the two lattices increases by  $\sim 0.17$  nm. Assuming that  $\epsilon_2^* = 79$  (relative permittivity of bulk water at 23.5°C) we find for the NB films with  $2l = 1.0$  nm (Table I) that  $\Delta F_d$  is of the order of  $-0.5$  mJ/m<sup>2</sup>. This indicates that in the NB films, the interaction free energy of the discrete ions in the Stern layers of the two film surfaces may considerably exceed the van der Waals interaction free energy ( $\Delta F_w \approx -0.14$  mJ/m<sup>2</sup>). For the NB films of the system NaDS + NaCl at 23.5°C, the gap between the theoretical  $\Delta F(h_e)$  values, as predicted by the classical interaction theory, and the experimental values is found to be of the order of 1.2 to 1.5 mJ/m<sup>2</sup> (see Fig. 2). This gap can be bridged by  $\Delta F_d$  when it is assumed that the permittivity of the medium between the surface lattices of the NB films is smaller than for bulk water (e.g.,  $\epsilon_2^* \approx 30$  instead of 79). Because in the NB films a significant part of the water molecules is hydration water of the ions ( $\sim 50\%$ ; see section 2) such a lower value seems not unacceptable. The water dipoles are aligned in strong electrical fields near the ions, which makes the effective  $\epsilon_r$  smaller. This is not in contradiction with a high refractive index of the layer (see section 2) because this is connected with the permittivity at optical frequencies which depends on the electronic polarizabilities of all the molecules. This would mean that the experimental  $\Delta F(h_e)$  values of the NB films can largely be explained by taking into account the discreteness of the surface charge. The electrostatic interactions between the discrete ions in the Stern layer of the two film surfaces would

then constitute the driving force for the formation of the NB films, with the van der Waals interaction being of minor importance.

It will be clear that, because of the simplifications underlying the present model, quantitative conclusions must be looked at with reservations. A quantitative test of the model is also hampered by lack of sufficiently accurate data on the structure of the NB films. The experimentally observed variation of  $\Delta F(h_e)$  with salt concentration and temperature (see paper II) could, for instance, be explained by a small decrease of  $2l$  with increasing  $c_3$  ( $\sim 0.1$  nm for  $c_3$  increasing from 0.2 to 0.5 mole/dm<sup>3</sup>) and a small increase of  $2l$  with increasing  $T$  ( $\sim 0.1$  nm per 10°C). These small variations of  $2l$  cannot be detected by the present techniques.

An analysis of the force balance in the NB film reveals that the present model is not yet complete: the strong decay of  $\Delta F_d$  with increasing distance  $2l$  between the surface lattices implies that the interaction between the surface lattices must give rise to a very strong attractive force (of the order

of 10<sup>7</sup> N/m<sup>2</sup>) which largely exceeds the (attractive) van der Waals force and the (repulsive) diffuse double-layer force. Mechanical equilibrium requires that the attractive force is balanced by an equally large repulsive force which should decay even more steeply with increasing distance than the attractive force. Repulsive forces of the same order of magnitude have been reported in Ref. (39) for lecithin bilayers with  $d_2 \approx 1.0$  nm. According to Marčelja *et al.* (40) such forces can be expected from the interaction between the oriented water layers at the two surfaces.

Qualitatively, the present model of the NB films seems to be in agreement with the experimental results of other workers. Platikanov *et al.* (10) found that the electroconductivity of NB films is independent of the salt concentration in the bulk solution. This is in agreement with our conclusion that the NB films only contain the adsorbed DS<sup>-</sup> ions and an equal amount of Na<sup>+</sup> counterions, but no salt (section 3). The highly organized crystal-like structure of the NB films, as presupposed in the present model,

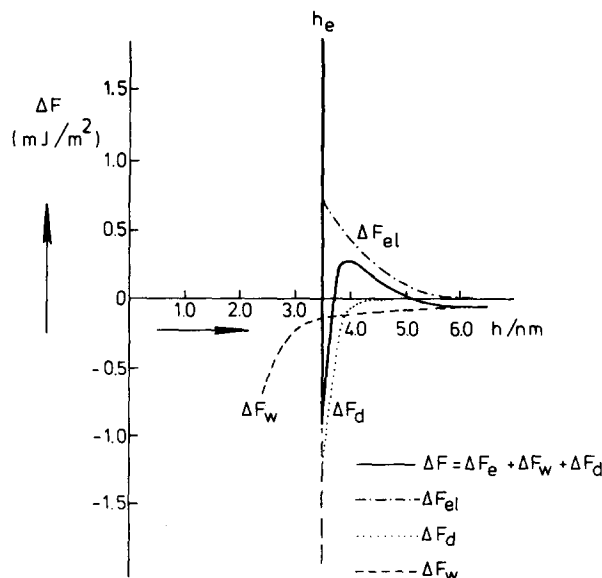


FIG. 3. Interaction free energy as a function of film thickness for soap films of the system NaDS + 0.4 mole/dm<sup>3</sup> NaCl at 23.5°C.

is in agreement with the conclusions of Jones *et al.* (4). It is also supported by the finding that the mobility of the ions in the NB films is much lower than in the CB films and the bulk solution (10, 11). The model also predicts that the (primary) minimum of the interaction free energy curve is very sharp. This is illustrated in Fig. 3 for films of the system NaDS + 0.4 mole/dm<sup>3</sup> NaCl, and is in agreement with the fact that the thickness of the NB films is rather insensitive to variations in the salt concentration and temperature (4, 5, 12). The large influence of the counterion size, as observed by Jones *et al.* (4) and Huisman *et al.* (9), can qualitatively be ascribed to the fact that the lattice can accommodate small ions only. The fact that Li<sup>+</sup> and quaternary ammonium ions impede the formation of the NB films would mean that they are too large to fit in the surface lattice.

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