Structural Properties of Soap Black Films Investigated by X-Ray Reflectivity

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Common and Newton black films, which are the ultimate stage of thinning of soap films, are investigated by absolute x-ray reflectivity. The challenging and open problem concerning these two systems is the determination of the equilibrium thickness of the aqueous core. X-ray reflectivity provides very detailed and new information about their sandwich structure: The Newton black film appears much thinner than expected. As opposed to the common black film, it does not contain any aqueous core but only a hydration layer. In both cases the amphiphilic structure is the same.

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Thin soap films are simple and well-defined chemical systems which involve the basic physical interactions existing in more complex structures, for example, biological membranes. The first observations of the thinning of soap films due to Hooke[1] and Newton[2] are historical. Black films [common or first (CBF) and Newton or second (NBF)], the final stages of the thinning of soap films due to the draining of water in the absence of evaporation, are generally formed from solutions of an ionic surfactant in the presence of a salt. Depending on the salt concentration and the temperature,[3] two different types of black films can be observed. For the CBF, the equilibrium thickness is known to be determined by a balance between van der Waals attraction and the double-layer repulsion forces.[4] This state is stable or at least metastable. The theory of lyophobic colloid stability of Deryaguin, Landau, Verwey, and Overbeek[5] (DLVO) has been successfully employed to explain the dependence of the equilibrium thickness of soap films upon the hydrostatic pressure.[6] For the NBF, more subtle and complex, strongly repulsive short-range forces associated with the local structure of water (hydration, steric, undulation, and "protusion" forces[7]) are expected to play a role in the stability. In the absence of or with a very small concentration of salt ($<0.1M$), and if drawn rapidly, soap films are relatively thick and show interference colors; they thin gradually at first and then turn to a CBF whose thickness remains unchanged. This thickness is small compared to the wavelength of light; thus the film appears black due to a diminished reflected intensity. This results from the approximate phase opposition of the reflected beams at the front and back film interfaces. For higher salt concentrations, the NBF can be observed. In spite of the great number of important and pioneering investigations of the CBF and NBF by many different techniques (mainly optical reflectance, infrared absorption, electrical, and contact-angle measurements),[8,9] their structures as well as the nature of the forces determining these structures remained obscure.

In the present work, we describe x-ray reflectivity at grazing incidence studies of the NBF and the CBF formed from sodium dodecylsulphate (SDS) solutions in the presence of salt (NaCl). The object of this investigation has been to determine the complete black-film structures along the layer normal (i.e., the exact amount of water between the amphiphilic layers, the interfacial roughnesses, and the different densities). A first attempt to measure the total film thickness of the NBF of decyltrimethylammoniumdecylsulphate by x-ray scattering[10] was made using a standard diffractometer and a steel frame to draw vertical films. However, these measurements were not very sensitive (because of the lack of measurement of absolute intensities and background subtraction and a much too simplified treatment of the experimental curve) and led to a very overestimated value of the total thickness of the film (ranging from 50 to 70 Å), and thus an incorrect interpretation of the water-layer thickness (20 Å). The only reported neutron-reflectivity experiment[11] relates only to relatively thick soap films (decyltrimethylammonium bromide mixed with decanoic acid) since the authors were unable to maintain the CBF long enough to produce reliable reflectivity profiles.

All the present reflectivity experiments of the free soap films were performed using an original four-circle diffractometer for vertical surfaces which is described further in Ref. 12 (as well as a basis for reflectivity formalism). A conventional, fine-focus copper tube is used as an x-ray source. The monochromator is LiF(200) which selects the Cu $K\alpha_1$ line ($\lambda = 1.5405$ Å). A low divergence ($\approx 0.7\times10^{-3}$ rad) is obtained by means of small slits (S_D, 50-μm width) placed at a distance of 40 cm from the source. A slit S_H (1.25 mm) is used to limit the height of the illuminated area on the sample. The scattered beam is detected by a scintillation counter placed behind an analysis slit S_A (700 μm) at a distance of 40 cm from the center. The incident and reflected beams pass through vacuum flight paths. A goniometric head and a perpendicular translation are used to accurately position the surface of the film at the center of the diffractometer (within a few μm), parallel to the beam sheet at $\theta=0$.

The stability diagram for the two black films formed by solutions of SDS as a function of temperature and NaCl concentration is reported in Ref. 3. We have chosen to explore two paths on this diagram: one to determine the thickness dependence with NaCl concentration at a constant temperature of (22 ± 0.5) °C, and another to observe the NBF-CBF transition as a function of temperature at a given salt concentration (0.1*M*). The soap solutions contained sodium dodecylsulphate (Fluka Chemie, *AG*, Switzerland, ≥ 99%), 1 g/l in aqueous solutions of 0.4*M*, 0.25*M*, 0.15*M*, and 0.1*M* of NaCl. The surfactant concentration in these solutions is above the critical micelle concentration. The films were drawn on a rectangular glass frame whose width (6 cm) is sufficiently large to allow reflectivity measurements at extreme grazing incidence (from 5 to 10 mrad); see Fig. 1. The minimum incident angle is thus only related to the size of the lateral meniscus (≈ 200 μm) and that of the beam. The height of the film (1 cm) is large enough that the x-ray beam does not penetrate the horizontal meniscus. The soap solution is contained in a cylindrical glass beaker (diameter, 8 cm). The frame and the beaker are placed in a Perspex cell with two sealed Kapton windows in order to maintain a saturated vapor atmosphere. The temperature is regulated within ± 0.5 °C. The two most delicate problems of the experiment are the accessibility of the film at grazing incidence and the alignment of the plane of the film. The first of these problems requires that the path of the x-ray beam not be obstructed by the suspending frame. This frame was thus constructed by bending a round glass rod (diameter, 3 mm); the rod cross section is milled flat to the center where the film forms (Fig. 1). The question of alignment (placing the film surface parallel to and centered within the width of the beam sheet) was critical for accurate reflectivity measurements. The vertical alignment is obtained by means of an optical level, adjusting the meniscus parallel to the reticule. The horizontal, and the more important, alignment is obtained by an iterative procedure: The quality of the alignment is checked by scanning the reflected beam around the specular position. After aligning the frame, new films are drawn by raising and lowering the beaker containing the soap solution, the glass frame remaining fixed in order to preserve its delicate alignment.

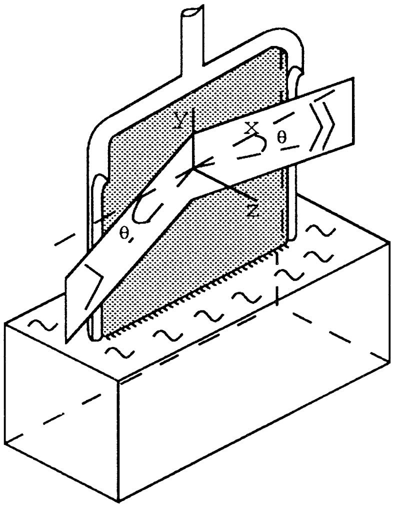

FIG. 1. Schematic diagram of the sample assembly.

The experimental reflectivity profile of the NBF at a NaCl concentration of 0.4*M* is reported in Fig. 2. This results from a series of approximately 500 experiments, each requiring a new film whose mean lifetime was about 45 min under our conditions. The film can only be seen by its meniscus on the water surface. The absolute reflectivity is obtained by a careful subtraction of the background at each angle of incidence. Each point of the reported experimental curve consists, in fact, of a scan of the reflected beam which is then modeled by a Gaussian. It should be pointed out that the reproducibility of the experiment has been checked by recording the profiles of the reflected beam around a given angle θ on different films. Somewhat surprisingly, the observed reflectivity profile shown in Fig. 2 exhibits three well-defined interference fringes and relatively high values of the reflectivity. Moreover, reflectivity values close to 10^{-8} have been measured; the signal-to-noise ratio appears large due to the fact that the water scattering is weak. These observations are consistent with the presence of a very small amount of water.

The rigorous way to compute and to fit the reflectivity profile is through the use of the optical matrix formalism, valid at all angles.[13,14] As in many similar cases, the system can be described as composed of slabs of different densities. Several possibilities were explored.

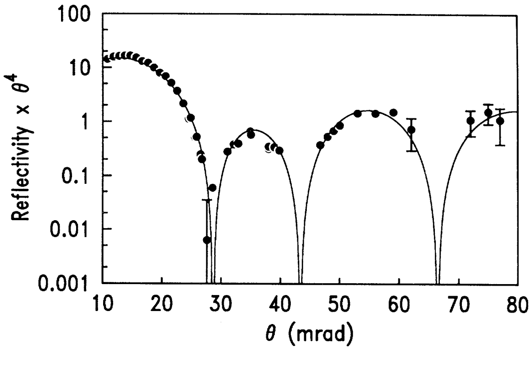

FIG. 2. Experimental reflectivity curve of the Newton black film from the SDS solution in presence of 0.4*M* of NaCl. The solid line passing through the experimental points is the theoretical profile using the parameters given in the text.

The reflectivity calculated from a single-slab model absolutely cannot give an account of the experimental data, especially after 35 mrad, and yields $\chi^2 \approx 3.5$. A "three-laminae" model, which must respect the symmetry of the film, only involves two independent slabs (the aliphatic medium and the aqueous core). The fit is acceptable and $\chi^2 \approx 1.6$. A model broken down into an aliphatic medium, the polar heads, and the water layer slightly improves the fit: $\chi^2 \approx 1.3$. We do not take it as unambiguous proof of the validity of this model, but, together with chemical grounds, it provides an indication of the ionic part of the film. In both cases, the total thickness, the chain density, and the roughness, which are accurately determined by the fit, are practically equal. The determined experimental roughness of 2.7 ± 0.1 Å is almost completely due to thermal fluctuations; a value of ≈ 2.4 Å is calculated using the theory given in Refs. 15 and 16, assuming that the surface tension is 76 mN/m (twice that of the corresponding monolayer, ≈ 38 mN/m) and the bending rigidity is $k_B T$. The diffractometer δ_x resolution was $\approx 3.25 \times 10^6$ m^{-1} FWHM (Ref. 16) at 30 mrad. The disagreement with the estimated roughness proves that the film has a small intrinsic disorder. The aliphatic medium appears to be rather well organized and can therefore be viewed as composed of tilted and probably rather stretched chains. The measured total thickness of the NBF is 32.9 ± 0.5 Å (the uncertainty is calculated as follows: 0.15 Å comes from the statistical analysis of the fit, and the width of the analysis slit through the alignment procedure yields an error in the angular calibration of the order of 0.4 Å). This is the most important result since it means that this film is so thin that it cannot contain any water in a liquid state, as opposed to the previous optical measurements[3] in which the total thickness was found to be 45 ± 2 Å ("stray light is a likely culprit" according to Mysels[17]). The water-layer thickness obtained by the fit (3.7 ± 0.5 Å) corresponds to a hydration layer of the polar heads, or more exactly to sodium ions with hydration shells in order to preserve electroneutrality. Our results are in qualitative agreement with those estimated from optical reflectometry.[18] Another interesting feature concerns the aliphatic medium whose density appears low [$\delta_{\text{ch}} \approx (2.85 \pm 0.1) \times 10^{-6}$] and can be correlated with a large area per molecule. We have calculated the area per molecule from the measured values of the real part of the index ($\delta = \lambda^2 r_e \rho / 2\pi$, where ρ is the mean electron density) and the thickness of the aliphatic medium (10.85 ± 0.5 Å), finding 33 Å^2 per chain, consistent with other measurements[19] but not in agreement with certain assumptions[3] of 52 Å^2. Let us remark that this area per molecule corresponds to the value measured in the liquid state in the case of monolayers of fatty acids on water.[15] This feature suggests that the in-plane order of the surfactant may be similar. A schematic drawing of the structure is shown in Fig. 3(a), with the corresponding electron density profile along the layer-normal axis in Fig. 3(b). It may be viewed as a kind of "smectic bilayer."

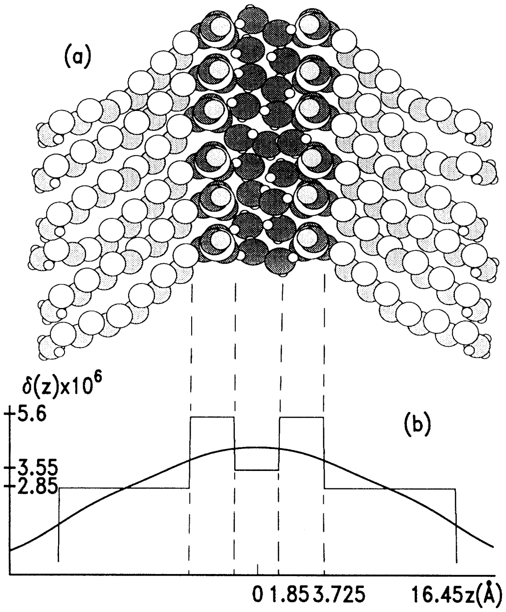

FIG. 3. (a) Schematic view of the structure of the Newton black film; (b) profile of the electron density along the normal of the film.

When we change the ionic strength[3] at constant temperature ($C_{\text{NaCl}} = 0.4M, 0.25M, 0.15M$ at $T = 22\,^\circ\text{C}$), no significant structural changes can be observed since the reflectivity profiles remain identical (except perhaps for a slightly increasing roughness for lower concentrations). In particular, the total thickness is constant as well as that of the hydration layer. The ionic-strength independence of the thickness of the second black film indicates, as first mentioned,[3] that the role of the electric repulsive forces is negligible. One can expect that, in fact, the high in-plane order in the absence of water is such that the counterions do not form a diffuse layer. The thickness of the equilibrium state which appears to be thermodynamically stable (or metastable) could only be determined by a balance between van der Waals attractive forces and short-range forces whose origin remains to be understood.

The question of the nature of transition between NBF and CBF has not yet been elucidated. Nevertheless, it has been previously observed[20] that it is possible to have the two black films coexisting within the same film. We observe that, at given concentrations and temperatures, the film drawn under the same conditions will form either the NBF or the CBF. In Fig. 4, we report the low-angle part of the reflectivity curve recorded in the CBF: $C_{\text{NaCl}} = 0.1M$ and $T = (30 \pm 0.5)\,^\circ\text{C}$. It should be mentioned that, at such a low salt concentration, the film is clearly unstable, and the mean lifetime becomes shorter (≈ 1-5 min). Moreover, as the film contains water, the

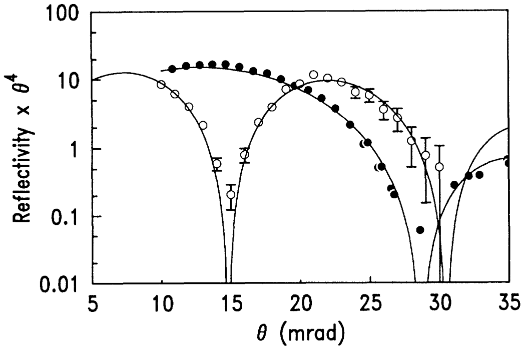

FIG. 4. Comparison at small angles of experimental reflectivity profiles of the Newton black film (at $C_{\mathrm{NaCl}}=0.15M$ and $T=22\,°\mathrm{C}$, solid circles) and the first black film (at $C_{\mathrm{NaCl}}=0.1M$ and $T=30\,°\mathrm{C}$, open circles).

corresponding "noise" is increased. Thus reflectivity profiles cannot be accurately measured at higher angles. Nevertheless, the position of the first interference fringe allows an accurate determination of the overall thickness of the CBF which varies slightly with temperature. We found $d=54.4\pm0.5$ Å. This value is significantly smaller than the thickness of the CBF reported in Ref. 3 (≈ 90 Å). However, it is in agreement with the previous investigations which describe the general features previously observed by many workers, in particular, the sandwich structure of the film. The thickness of the aqueous core is $\approx 27\pm0.5$ Å, obviously not a hydration layer of the polar heads but clearly a liquid layer. Concerning the surfactant layers, we find approximately the same values of roughness, densities, and chain length [respectively, $\sigma=2.75\pm0.15$ Å, $\delta_{\mathrm{ch}}=(2.94\pm0.1)\times10^{-6}$, and $l_c=10.3\pm0.5$ Å] and, consequently, almost the same area per molecule (≈ 34 Å^2). This new result clearly demonstrates that the surfactant organization is identical to that found in the NBF; we have proven that the transition between NBF and CBF consists only in a strong and abrupt increase of the aqueous-core thickness, whereas the aliphatic-medium structure remains unchanged.

In summary, x-ray reflectivity experiments using a conventional source have given very detailed and unambiguous structural pictures of the black films of SDS in the presence of salt: The NBF consists of a well-defined (probably in a liquidlike order) bilayer and a hydration layer ≈ 3.7 Å, whereas the CBF, with an identical external structure, contains a liquid layer of ≈ 27 Å.

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