Evidence for Newton Black Films between Adhesive Emulsion Droplets

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A soap film (made of two air/water interfaces covered by surfactant) may turn into a so-called Newton black film (NBF) which essentially consists in a surfactant bilayer. Oil-in-water emulsion droplets covered with surfactant (oil/water interfaces) may become adhesive in similar conditions. We show by analyzing the neutron scattering pattern from a collection of submicronic oil-in-water adhesive droplets that the thin film that forms between them is structurally identical to the NBF. As a consequence, the formation of NBF is a general property of ionic surfactants. [S0031-9007(96)01385-3]

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A thin soap film is easily obtained by drawing a frame from a surfactant water solution. Such a film is comprised of two air/water interfaces covered by surfactant with water in between and appears initially colored. Then, the film thins under the action of gravitational and capillary forces and ultimately becomes black when observed with reflected light [1]. Optical measurements have revealed that, in the presence of certain salts, films made of ionic surfactants may achieve two distinct equilibrium thicknesses [1]. At low salt concentration and high temperature the film is more than 10 nm thick and is called a common black film (CBF) whereas its thickness abruptly jumps to a few nanometers at high salt concentration or low temperature: the film is then known as the Newton black film (NBF). The NBF is surprisingly stable and may stand for days in the absence of mechanical disturbances or evaporation. The CBF-to-NBF transition temperature T^* systematically increases with the salt concentration [1,2]. Contact angle measurements performed on NBF's have revealed that the adhesion energy of the two surfactant monolayers increases when lowering the temperature below T^*. From optical measurements the bilayer thickness was shown to remain constant, about 40 Å in the case of sodium dodecyl sulfate (SDS), which indicates the presence of essentially no free water. X-ray reflectivity leads to a more precise representation [3]: the bilayer confines a few molecules of hydration water, the aliphatic part of the surfactant being exposed towards air; the bilayer thickness is found to be equal to 32 Å.

Air may be replaced by oil and, for these interfaces, observations may be conveniently performed on large oil-in-water droplets instead of suspended films. When covered with the same ionic surfactant these droplets have been shown to become spontaneously adhesive in very similar conditions of salt and temperature [4]. A transition temperature T^* at which the droplets start to adhere (nonzero contact angle) is identified and found linearly related to the salt concentration as for the NBF [5]. However, there is so far no structural information about these oil/water/oil interfaces. In Fig. 1, we report the variation of T^* as a function of salt concentration C for 50 μm dodecane-in-water droplets. SDS (about 0.002 mol/l) is used as the surfactant, the added salt being sodium chloride. In Fig. 2 we report the adhesion energy ϵ as a function of temperature for four distinct salt concentrations, deduced from optical microscopy measurements of the contact angle θ with the help of the Young-Dupré equation $\epsilon = 2\gamma(1 - \cos\theta)$. Here γ is the oil/water surface tension (spinning drop technique) in the presence of surfactant. The adhesion energy increases when the temperature is lowered below T^*, or when the salt concentration increases.

In order to measure the thickness of the thin film that forms between adhesive oil droplets, and to learn whether it varies with the adhesion energy, we performed small-angle neutron scattering (SANS) experiments on bulk samples. [The SANS experiments have been made on the beam line PACE at Laboratoire Léon-Brillouin (Laboratoire mixte CEA-CNRS).] As compared to single film reflectivity measurements in which one has control over the film orientation, we have here the advantage of averaging over a large number of presumably identical films, with little

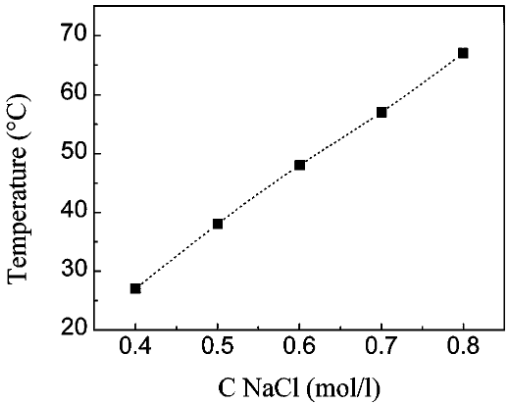

FIG. 1. Onset of adhesion (nonzero contact angle) between 50 μm dodecane-in-water droplets stabilized by SDS, as a function of the sodium chloride concentration C and temperature T.

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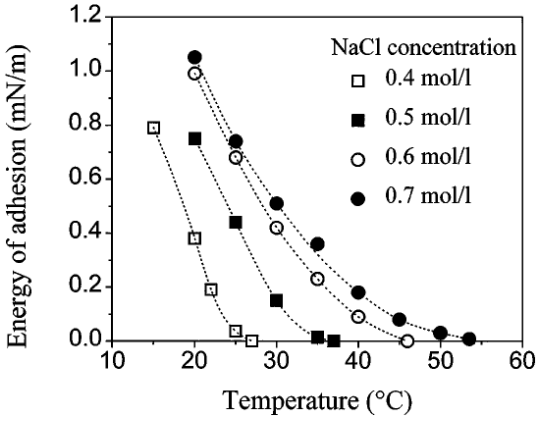

FIG. 2. Evolution of the adhesion energy as a function of temperature at four distinct sodium chloride concentrations.

trouble in sample preparation and conservation. Neutron scattering is then appropriate since one may eliminate the bulk scattering from oil and water by matching their scattering length densities.

The neutron scattering measurement is performed on a bulk sample containing a maximum amount of randomly oriented thin films originating from droplets of about 0.4 μm in diameter. By comparing the experimental neutron scattering pattern to the one expected from a simple model for randomly oriented films we believe that we accurately deduce their thickness. Moreover, we show that the thickness (29 Å) is independent of the adhesion energy. This value is almost equal to the one obtained on a NBF from x-ray reflectivity [3]: the bilayer thickness does not depend on the nature (oil/water or air/water) of the interface. We also conclude that adhesion is an intrinsic phenomenon for this ionic surfactant and thus may not originate only from the classical van der Waals forces in the presence of screened electrostatic repulsions [6].

We produce oil-in-water monodisperse emulsion droplets of about 0.4 μm in diameter by using the method of Ref. [7] and set the droplet volume fraction to about 70%. The emulsifier is hydrogenated SDS (2×10^{-3} mol/l) with as dispersed phase a mixture of deuterated and hydrogenated *n*-dodecane in respective amounts 95–5 wt. %. The continuous phase is heavy water with a varying content of sodium chloride: 0.3 and 0.7 mol/l. The oil and water scattering length densities are about the same, i.e., 6.39×10^6 m^{-2} neglecting the small contribution from the salt. The scattering length densities of, respectively, the surfactant polar heads or aliphatic tails may be estimated to be around 4.46×10^6 or -0.4×10^6 m^{-2}, meaning that most of the coherent scattering is likely to originate from the aliphatic part of the surfactant films. We have recorded the small-angle neutron scattering spectra with wave vectors in the range $7 \times 10^{-3} - 0.6$ Å^{-1}, from nonadhesive to highly adhesive conditions.

In the absence of adhesion the droplets—though slightly deformed owing to the random close-packing colloidal structure—remain essentially spherical as inferred from elasticity and osmotic pressure measurements [8]. Flat thin films between adjacent droplets develop in the presence of adhesion, i.e., below T^*: such a collection of flat films is easily observed by optical microscopy on monodisperse droplets of about 50 μm [4,5]. This shape transformation is sketched in Fig. 3(a) and 3(b) for the two extreme limits: in Fig. 3(a) the contact angle is strictly zero; in Fig. 3(b) the contact angle is large enough to allow—at least locally—a space-filling packing [9]. In Figs. 3(a) and 3(b), we also schematically draw the expected scattering length density profile perpendicular to the droplet interface, h being the film thickness and δ the surfactant tail length. In the absence of adhesion the surfactant layers around droplets may be considered as a collection of randomly distributed curved monolayers, whereas in the presence of adhesion the surfactant films partially organize themselves as randomly distributed flat bilayers. Increasing the adhesion energy induces both the lateral extension of the flat thin films and the augmentation of the contact angle, therefore increasing the amount of flat bilayers compared to the amount of curved monolayers.

We measure the scattering intensity in various conditions from nonadhesive to highly adhesive conditions. After subtraction of the incoherent background, the measured intensity is normalized by both the cell thickness and transmission. We further divide this normalized intensity by the normalized intensity scattered by a 1 mm thick water sample in order to get the absolute scale intensity. Figure 4 shows the scattering curve for nonadhesive conditions where $T = 45$ °C and $C = 0.3$ mol/l. Figure 5 shows the scattering curve for strongly adhesive conditions where $T = 18$ °C and $C = 0.7$ mol/l, leading

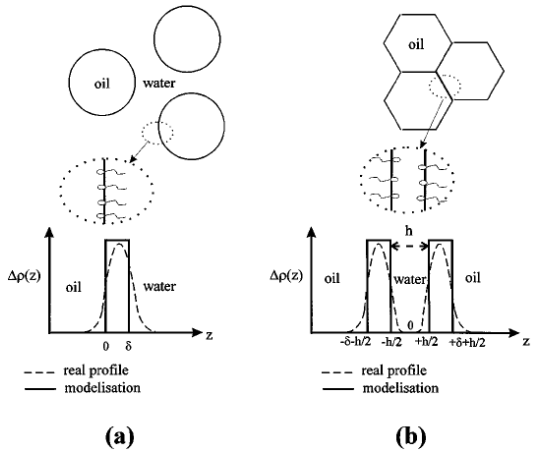

FIG. 3. Schematic representation of the shape transformation induced by adhesion: (a) Nonadhesive close-packed droplets. The scattering length density profile normally to the interface may be—schematically—viewed as a square function of range δ and height $\Delta\rho$; (b) adhesive close-packed droplets, with formation of a thin bilayer in between and nonzero contact angle. The scattering length density profile may be sketched as a double square function defined by the three parameters δ, h, and $\Delta\rho$.

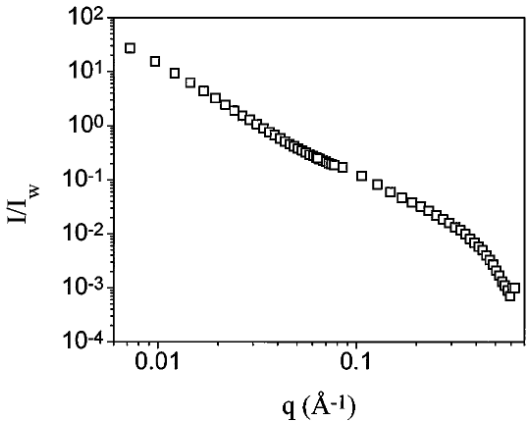

FIG. 4. Normalized data for nonadhesive conditions: $T = 45\,^{\circ}\mathrm{C}$, $C_{\mathrm{NaCl}} = 0.3$ mol/l.

to a contact angle of about 40°. As expected, the shape of the normalized intensity changes significantly. We consider that in the limit of large contact angles the adhesive emulsion may be considered in terms of its scattering pattern as a collection of randomly oriented *infinite* bilayers of total thickness $2\delta + h$ [see Fig. 3(b)]. Indeed, the range of wave vector q which is probed in our experiment is such that $qr \gg 1$ (r is the undeformed droplet radius); hence we neglect the finite lateral extension of the bilayers, of order r. Moreover, the absence of Bragg diffraction peaks in the light scattering pattern (even in the limit of large contact angles) implies the presence of a sufficient amount of defects to justify the random orientation hypothesis.

The expression for the transverse form factor of an infinite bilayer (restricted to wave vectors parallel to the normal of the bilayer plane: z direction) when parametrized by the two lengths δ and h as defined in Fig. 3(b), is

$$P(q_z) = \Delta\rho^2 \left| \int_{-\delta-h/2}^{-h/2} e^{iq_z z}\, dz + \int_{h/2}^{\delta+h/2} e^{iq_z z}\, dz \right|^2, \tag{1}$$

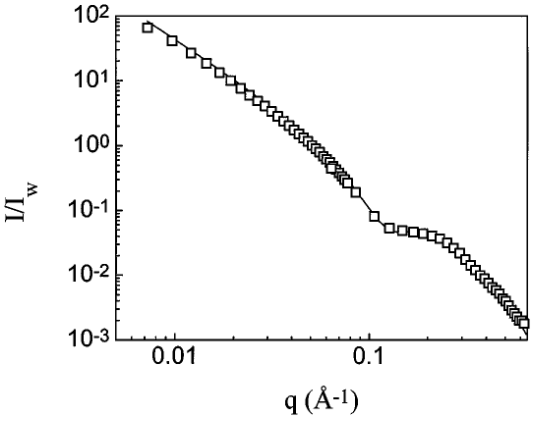

FIG. 5. Normalized data for highly adhesive conditions: $T = 18\,^{\circ}\mathrm{C}$, $C_{\mathrm{NaCl}} = 0.7$ mol/l. The full line corresponds to a fit by Eq. (3) (see text).

where $\Delta\rho$ is the scattering length density contrast. By integrating we get

$$P(q_z) = \frac{8\Delta\rho^2}{q_z^2} \sin^2\!\left(\frac{q_z\delta}{2}\right)\{1 + \cos\,[q_z(h+\delta)]\}. \tag{2}$$

In order to account for the random orientation of the bilayers we perform an orientational average of the transverse form factor. This may be done in a convenient but approximated way in replacing q_z by the modulus q of the scattering wave vector in Eq. (2) and by multiplying $P(q)$ by the Lorentz factor $2\pi/q^2$ [10]. This procedure leads to a simple, analytical expression for the scattered intensity with, in particular, the stringent prediction that $P(q) = 0$ for q an integral multiple of $\pi/(\delta + h)$. It may be argued that, since the real bilayers have a finite lateral extension, there is a small but finite scattered intensity for any wave vector lying within the bilayer plane; besides, some smearing occurs from the wave vector dispersion owing to finite experimental resolution. These corrections have modest practical consequences, however. Stronger effects may arise, for instance, from peristaltic excitations of the adhesive films. Moreover, our *a priori* choice of a square-well scattering length density profile amounts to a rather drastic simplification. Leaving this matter unsettled, we simply smooth out the oscillations, introducing an *ad hoc* Gaussian damping (with parameter σ), which allows us to keep the following analytical expression for $I(q)$:

$$I(q) = I_w \Sigma \frac{16\pi\Delta\rho^2}{q^4} \sin^2\left(\frac{q\delta}{2}\right) \times \{1 + \cos\,[q(h+\delta)]e^{-q^2\sigma^2/2}\}, \tag{3}$$

where Σ is the bilayer area per unit volume—it may be expressed as $\Sigma = 3\Phi/2r$, Φ being the droplet volume fraction—and I_w is the normalized (incoherent) scattered intensity from light water. The continuous line of Fig. 5 represents the best fit of Eq. (3) to our data. The agreement between the model and the experimental data on absolute scale is fairly good and allow us to determine precisely the four parameters r, δ, h, and σ. The droplet radius r governs the absolute scale intensity whereas δ and h set the position of the oscillations. We find for this adhesive emulsion $r = 0.19\ \mu$m, $\delta = 6$ Å, $h = 17$ Å, and $\sigma = 7.7$ Å. From these values we can therefore determine the total thickness D of the thin film expressed as $D \equiv 2\delta + h$, i.e., $D = 29$ Å. This value is almost identical to the one measured on a suspended NBF made of the same surfactant and salt by using x-ray reflectivity: 32 Å [3]. As another check of the reliability of our analysis we also find a good agreement between the fitted value for r and the independently measured hydrodynamic radius of the droplets: by using dynamic light scattering (the sample is then a very dilute suspension of the same droplets) we find $r \approx 0.22\ \mu$m.

We examine the evolution of the scattering spectra as the adhesion energy is decreased. We plot in Fig. 6 Iq^2/I_w as a function of q for various temperatures: 18, 23,

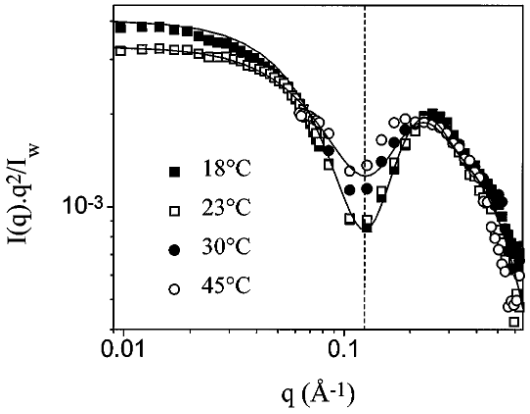

FIG. 6. Temperature dependence of scattering data (Iq^2/I_w vs q) at $C = 0.7$ mol/l. The full lines correspond to fits by Eq. (4) (see text).

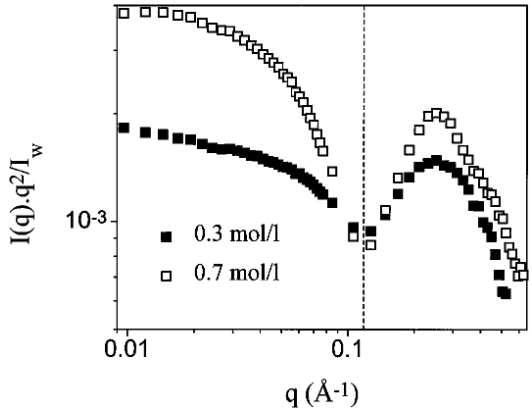

FIG. 7. Salt concentration dependence of the scattering data at $T = 18$ °C.

30, and 45 °C at a constant salt concentration (0.7 mol/l), corresponding to different conditions of adhesion (including the conditions in Fig. 5): from 18 to 45 °C the adhesion energy changes from about 1 to 10^{-2} mN/m. We find that the position of the oscillation does not change whereas its amplitude is modified. These results suggest that the total bilayer thickness is constant, irrespective of the adhesion energy, the latter quantity being nevertheless very sensitive to T and C. In the case of small adhesion energy (small contact angle), where bilayers coexist with monolayers a quantitative description of the full scattering pattern may be simply derived from the previous description. We note f the fraction of adhesive films and introduce that parameter in Eq. (3) which then becomes

$$I(q) = I_w \Sigma \frac{16\pi\Delta\rho^2}{q^4} \sin^2\left(\frac{q\delta}{2}\right) \times \{1 + f\cos[q(h + \delta)]e^{-q^2\sigma^2/2}\}, \quad (4)$$

since the transverse form factor of a *single* film is proportional to $\sin^2(q_z\delta/2)$. The expression of Σ is modified because of the coexistence of both monolayers and bilayers: $\Sigma = 3(2 - f)\Phi/2r$. By fitting our experimental data with Eq. (4), we find $f = 0.95$ for $T = 18$ °C, the other parameters remaining as in the previous model—where f was forced to be equal to 1. As expected, when the temperature is increased the parameter f decreases, following the evolution of the amount of bilayers within the sample; f reaches the value 0.6 at 45 °C. Moreover, along the temperature path the parameters h, δ, and σ remain constant. These results imply that the bilayer thickness is not changing with the adhesion energy. In Fig. 7 we show the role of the salt concentration (0.7 and 0.3 mol/l) at a constant temperature ($T = 18$ °C). As evidenced in Fig. 7 an increase of C does not change the oscillation position. However, our model fails in describing the data at $C = 0.3$ mol/l. The discrepancy is linked to an important loss in the small-angle intensity. Because the oscillation position is not changing we again conclude that the salt concentration—which changes the adhesion energy—does not affect the bilayer thickness.

Finally we emphasize the adequacy of neutron scattering in measuring film thicknesses in concentrated emulsion of various types; this information might be suitable for broadening the knowledge of surface forces between adsorbed layers of surfactants—or various surface agents—on liquid interfaces. By using this technique we have shown that the thin film that forms between adhesive droplets in the presence of ionic surfactant and salt have the same thickness that the one previously measured on the analogous NBF. Moreover, we clearly establish that this thickness is constant over all adhesive conditions. This suggests the existence of an attractive interaction between charged monolayers which does not originate from the classical van der Waals mechanism since it is governed only by the temperature and salt concentration at a constant separation.

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