Wetting Properties of *n*-Alkanes on AOT Monolayers at the Brine-Air Interface

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On the surface of a brine-surfactant (AOT) mixture, the long-chain alkanes ($N > 11$) do not spread while the shorter ones ($N < 11$) spread leaving a very thin oil film at the surface. The interactions between the oil-water and oil-air interfaces stabilizing the height of this film are a van der Waals attractive potential, a short-range repulsive potential due to the alkane-surfactant interactions, and a repulsive potential due to the fluctuations of the oil-brine interface constrained by the oil-air surface. This is related to the phase behavior of mixtures of brine, AOT, and *n*-alkanes.

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Mixtures of water or brine, oil, and AOT (sodium diethylhexylsulfosuccinate, a pure surfactant) at $T = 20\,^\circ\mathrm{C}$ display a variety of phase equilibria as the salinity is varied. For low AOT concentrations (but above the critical micellar concentration denoted c.m.c.) and at high salt concentrations, a water-in-oil microemulsion coexists with an excess aqueous phase (Winsor II). At low salt concentrations, the oil phase coexists with a phase rich in AOT (Winsor I). At intermediate salt concentrations, a third, surfactant-rich phase coexists with both excess oil and water (Winsor III) [1].

An earlier investigation of phase equilibria of mixtures of AOT, brine, and *n*-alkanes (denoted C_N), where the chain length N of the oil was varied, revealed a close relationship between the oil chain length and the nature and structure of the third phase in the Winsor III region. This third phase is composed of AOT, brine, and oil. For the short-chain oils ($N < 11$), it is birefringent and is probably lamellar. For $N = 10$, the birefringent AOT-rich phase in the middle of the Winsor III region increases in volume incorporating the brine phase which disappears even for low AOT concentrations. For the longer-chain alkanes ($N \geq 11$) the third phase is not birefringent and becomes more and more concentrated in AOT as the brine salinity increases; it is a succession of two or three phases of different structure made of water domains separated by flexible AOT bilayers incorporating only a very small amount of oil (about one oil molecule for three AOT molecules). It is the lower phase because it is more dense than the brine. For the higher salinities, very close to the Winsor-III–Winsor-II transition, the ratio oil/water in this third phase increases abruptly and it becomes the middle phase. The two last phases which appear close to this transition for $N \geq 11$ are viscous phases rich in AOT.

In addition to these differences in the phase structure in the Winsor III interval, we had found that the bending elasticity constant K of AOT monolayers at the oil-water interface decreases steeply for $N > 10$ [2]. K is of the order of $1k_BT$ for $N < 11$ and is of the order of $0.1k_BT$ for $N > 11$ (k_B is the Boltzmann constant). This dependence of K on N was attributed to a larger extent of penetration of the short-chain oils into the monolayer making it thicker and more rigid.

In this Letter we report on the wetting properties of these alkanes on free surfaces of mixtures of brine and AOT above the c.m.c. These surfaces are covered by a saturated monolayer of the surfactant. Under these conditions, when a drop of a short-chain alkane ($N < 11$) is deposited on the surface, it spreads very rapidly. A drop of the longer-chain ones ($N > 11$) does not spread but forms a lens on the surface. This behavior has already been observed for various surfactants [3], and in our case is clearly related to the differences observed in the AOT monolayer rigidity and the phase structure in the Winsor III, depending on whether N is large or small.

We have carried out an investigation of the state of the interface before and after the deposition of a drop of oil. This is done by ellipsometry, an optical technique very sensitive to the interfacial thickness. Before the deposition of the drop, the ellipticity measured, $\bar{\rho}_{\mathrm{AOT}}$, is that of the water-air surface in the presence of an adsorbed monolayer of AOT. After deposition of a drop of a long-chain alkane which does not spread at the surface, the ellipticity remains that of the monolayer. For the shorter alkanes, however, this is no longer the case. The ellipticity changes as soon as the drop is added. It is at first unstable, but after a few seconds or a few minutes, the ellipticity settles on a constant value corresponding to an oil film a few nm thick on the surface. This value is stable with time for periods of many hours and does not depend on the number of oil drops added. This film coexists with a residual drop that resists spreading which usually just adheres to the walls of the cell used for the ellipticity measurements. However, if a very large amount of oil is added, the residual drop increases in volume and occupies the whole surface; the ellipticity measurements are performed before this happens. Our measurement cell is not fully tight. The oil vapor escapes slowly and when the drop reservoir has evaporated the ellipticity decreases steeply to reach a value close to the ellipticity of the AOT film at the water-air surface without oil (Fig. 1). The plateau value of the ellipticity is independent of the AOT concentration above the c.m.c. (it has been tested by changing the AOT concentration from 3 to 30 mM) but is dependent on the salt concentration and the oil chain length. We have carried out measurements for both C_8 and C_{10} and different salt concentrations in the brine. The plateau ellipticity $\bar{\rho}$, for each alkane, increases with the salt concentration, reaches a maximum, and decreases as more salt is added to the water. The results for both C_8 and C_{10} are similar as far as the dependence on the salt concentration is concerned [Fig. 2(b)].

For ionic surfactants like AOT at a concentration above the c.m.c., the oil-water interfacial tension γ_{ow} (measured in presence of a macroscopic oil phase so that the oil-water and the oil-air interfaces are independent) is independent of the AOT concentration but depends on the salinity; this tension decreases with salt concentration, reaches a deep minimum, and increases as more salt is added [Fig. 2(a)]. The salinity at which the interfacial tension is minimum is the salinity at which $\bar{\rho}$ (or the thickness of the wetting film) is maximum.

The ellipticity measured at the Brewster angle is related to the different refractive indices of the media involved and to the height of the layer through Drude's formula [4]:

$$\bar{\rho}=\frac{\pi}{\lambda}\frac{(n_1^2+n_2^2)^{1/2}}{n_1^2-n_2^2}\eta\,,$$
$$\eta=\int_{-\infty}^{+\infty}\frac{[n_1^2-n(z)^2][n_2^2-n(z)^2]}{n(z)^2}dz\,, \tag{1}$$

where n_1 and n_2 are the refractive indices of air and of the aqueous solution, i.e., that of the water (the salt and AOT concentrations are too small to significantly change the refractive index of the water), and $n(z)$ is the refractive index through the surfactant monolayer and the oil film. In the presence of oil, the AOT monolayer is covered by the oil film which has a constant refractive index; the thickness l of the oil film depends linearly on $\bar{\rho}$, $l=a(\bar{\rho}-\bar{\rho}_{\text{AOT}})$, where a can be deduced from (1) and $\bar{\rho}_{\text{AOT}}$ is the measured value of the AOT monolayer at the water-air surface. This formula is valid for plane interfacial films. In the following it will be used for rough films but it can be shown that in our problem the thickness deduced from the experiments by this formula is close to the mean thickness.

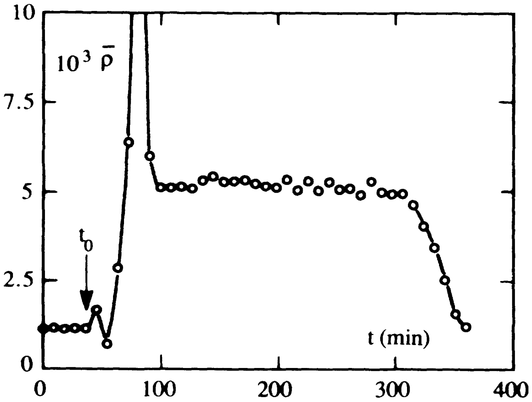

FIG. 1. Typical evolution of the ellipticity obtained in a wetting experiment at the free surface of a brine-AOT mixture at 20 °C. At the time $t=t_0$, a small drop of oil is deposited on the surface. After a few minutes the ellipticity reaches a plateau value and stays at this value for many hours. After evaporation of the oil drop, the ellipticity decreases to its initial value. (Octane on 3 mM of AOT in 0.04*M* NaCl.)

In order to understand what stabilizes the height l of the oil film, this being the thickness of the oil film between the AOT monolayer (or water-oil interface) and the oil-air surface, we have to determine the interaction potentials between these two interfaces. It must be remarked that a drop coexisting with a thin film is sometimes observed in the wetting of a solid by a liquid. It has been referred to as pseudopartial wetting and was studied theoretically and independently by Hirasaki and by Brochard-Wyart *et al.* [5]: It can result from a competition between an attractive van der Waals potential and a short-range repulsive potential. The total interaction po-

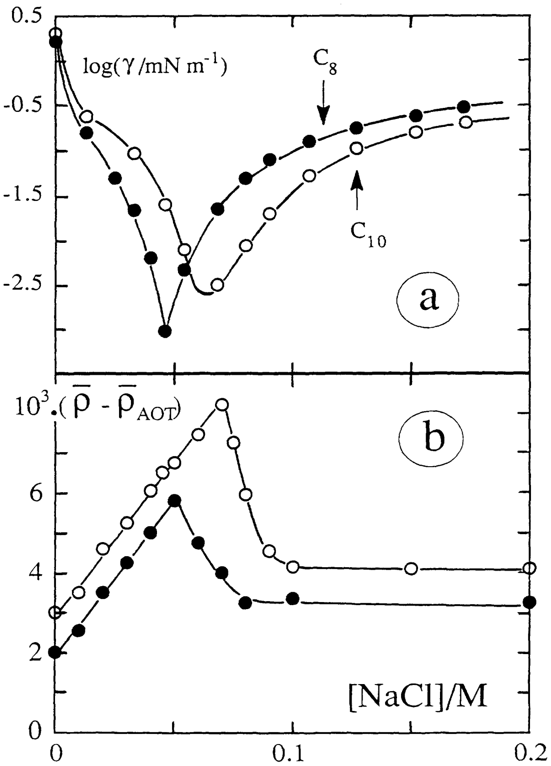

FIG. 2. (a) Variation of post c.m.c. oil-brine interfacial tension with salinity for AOT monolayers at the oil-water interface using octane and decane, and (b) that of the ellipticity $(\bar{\rho}-\bar{\rho}_{\text{AOT}})$ for the oil wetting films at the surface of a mixture of brine and AOT, at 20 °C.

tential for the two interfaces has a minimum at a small but finite separation. This case favors a surface coated by a very thin film coexisting with a residual drop that resists spreading and explains the stability of the height of the film. In our case, a van der Waals potential favors no wetting; n-alkanes, at least for $N \geq 6$, do not wet the water-air surface [6] but probably at equilibrium a thin oil layer covers the water surface [7] at least for short alkanes. The Hamaker constant is negative and is denoted by $-A$, this was confirmed by calculations [8]. We also note that, at least initially, the spreading coefficient $S = \gamma_{\mathrm{AOT}} - \gamma_{\mathrm{ow}} - \gamma_{\mathrm{o}}$ (γ_{AOT} is the surface tension of a mixture of brine and AOT, γ_{o} that of the oil surface) is positive for C_8 and C_{10} alkanes on AOT-covered brine-air surfaces. A repulsive short-ranged potential V_{sr} has to be introduced to take the positivity of S into account. *A priori*, we do not know this potential, but as we will show below, its shape can be deduced from the experiments.

The van der Waals potential is due to the different polarizabilities of the media involved and is usually written as

$$V_{\mathrm{vdW}}(l) = -A/12\pi l^2 , \tag{2}$$

where $-A$ is the water-oil-air Hamaker constant. Introducing the above-mentioned potentials is not enough as seen from the variation of the height l of the layer with the salt concentration. In order to explain the maximum of l at the minimum of γ_{ow}, we have to invoke a repulsive potential due to the fluctuations of the oil-water interface of very low tension constrained by the oil-air surface. This is the only contribution that can explain the change of the height of the layer with salt concentration, in other words, with the change in interfacial tension, which changes the amplitude of the fluctuations of the water-oil interface.

The repulsive contribution due to the fluctuations has already been derived by Helfrich [9] in the case of a tensionless membrane confined by two walls. We have used the same idea but have left the interfacial tension in the expression. The wall which constrains the thermal fluctuations of the oil-water interface is the oil-air surface. It is close to a perfect plane because its surface tension is large. When the oil-water interface is constrained by the oil-air surface at a distance l from its mean plane, it is taken as a collection of patches of area $L \times L$, the undulations of which just fill the space between l and $-l$. Following Helfrich [9], the mean-square amplitude of the fluctuations is $\langle \zeta^2 \rangle = \mu l^2$ with $\mu \approx \frac{1}{6}$. Equating this expression to the mean-square amplitude of the undulations of a patch $L \times L$ at the oil-water interface calculated as the sum of the amplitudes of the different modes of fluctuations,

$$\langle \zeta^2 \rangle = \frac{k_B T}{4\pi \gamma_{\mathrm{ow}}} \ln \left(1 + \frac{\gamma_{\mathrm{ow}}}{K q_{\min}^2} \right) \text{ with } q_{\min} = \frac{\pi}{L} , \tag{3}$$

leads to

$$L^2 = \pi^2 \frac{K}{\gamma_{\mathrm{ow}}} \left(\exp \frac{4\pi \mu l^2 \gamma_{\mathrm{ow}}}{k_B T} - 1 \right) . \tag{4}$$

The lower cutoff $q_{\min}$ is modified by the presence of the wall. In order to derive the pressure exerted by the fluctuating interface on the air-oil surface, and following Helfrich, we consider each patch of area $L \times L$ as a free particle of a one-dimensional gas and write this pressure as

$$P(l) = \frac{k_B T}{2L^2 l} = -\frac{\partial V_F}{\partial l} . \tag{5}$$

Integration of this pressure over l yields the repulsive potential V_F due to the fluctuations. The total potential is now the sum of three terms: $V_{\mathrm{total}}(l) = V_{\mathrm{vdW}}(l) + V_F(l) + V_{\mathrm{sr}}(l)$. The derivative of the total potential of the two interacting interfaces vanishes for the equilibrium height of the layer. Knowing the interfacial tension, the rigidity constant, and the height of this layer, we can get an estimate of the Hamaker constant at high l and very low tension, for which the effects of the fluctuations are most pronounced. Assuming that the vdW potential is mostly stabilized by the fluctuation potential at these heights, this constant can be calculated from

$$\frac{\partial V_{\mathrm{vdW}}}{\partial l} = P(l)$$

giving

$$A = 6\pi l^3 P(l) . \tag{6}$$

A is taken as the limiting value of the above expression at high l obtained for low γ_{ow} when the entropic repulsion is at its maximum and the short-range pressure can be neglected. It is of the order of $0.5 k_B T$ for both C_8 and C_{10} ($\sim 0.6 k_B T$ and $\sim 0.47 k_B T$, respectively) which is of the correct magnitude in these systems [10].

In order to arrive at the form of the repulsive short-range pressure $-\partial V_{\mathrm{sr}}/\partial l$ that stabilizes the film at lower l values, we have to evaluate the sum of the pressure of the vdW attractive contribution (with A as calculated above) and that of the fluctuation-induced repulsive potential which is balanced by this additional pressure. We have plotted the value of this pressure versus l in Fig. 3. The larger the thermal fluctuations, the larger is the distance l at which the potential is probed. So, the different points in the graph are obtained by varying γ_{ow}, i.e., by varying the salinity in the brine, supposing that the Hamaker constant is independent of this salinity (a reasonable approximation for the low amount of salt in these systems). There is no theoretical prediction on the variation of the short-range pressure with salinity. However, each l value for large l ($l \gtrsim 25$ Å) is obtained for two different salinities (γ_{ow} is the same at these two salinities) giving the same pressure within the experimental accuracy. V_{sr} does not depend very strongly on the salinity. At low l we cannot use the same argument because

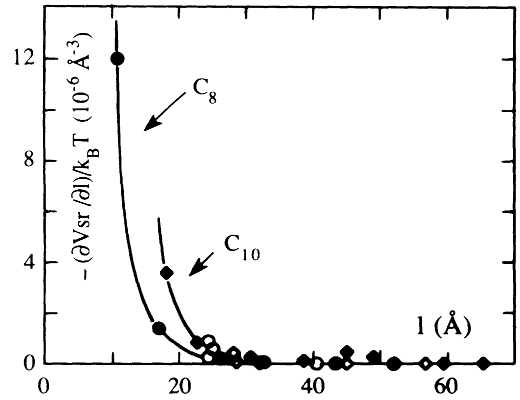

FIG. 3. The short-range repulsive pressure $(-\partial V_{sr}/\partial l)/k_BT$ between the brine-oil and the oil-air interfaces vs the oil film thickness l for octane (circles) and decane (diamonds). The experimental points obtained at low salinities are solid; the ones obtained at high salinities (i.e., larger than that of the minimum interfacial tension) are open.

the larger interfacial tensions are only obtained at low salinities: This is evident from the unsymmetrical nature of the tension curves [Fig. 2(a)]. V_{sr} for low l is only deduced at low salinity. This hard-wall-like potential is visibly short ranged (approximately 10 and 15 Å, respectively, for C_8 and C_{10}) and becomes the dominant stabilizing potential for the film height at low l. This potential is probably due to a direct attractive interaction between the alkane chain and the hydrocarbon part of the monolayer giving rise to a repulsive interaction between the two interfaces as the presence of these adsorbed oil molecules prevents their approach. This overcomes, at short distance, the attractive vdW potential between these two interfaces.

This short-ranged potential is probably the final link in the relationship between the rigidity of the monolayer, the nature and structure of the third phase, and the wetting behavior of n-alkanes, as the length of the oil chain is varied. This direct interaction between the alkane chain and the AOT chains is consistent with the penetration of the short-chain oils into the monolayer making it more rigid and thereby favoring lamellar phases. For the longer alkanes where this attraction vanishes, the surfactant forms bilayers of low k, favoring isotropic phases.

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