Flow of a surfactant across a thin liquid film wetting a solid substrate

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Transfer of a monolayer (valinomycin) between two Langmuir troughs via an interconnecting glass "bridge" has been observed when there is a difference between the monolayer pressures in the two troughs. Assuming that the transfer occurs over the surface of the thin film of water that wets the "bridge," the transfer rate can be used to estimate the thickness of the liquid film. The thickness thus determined may be used to determine the retarded van der Waals (Hamaker) constant associated with the interaction of the film with the underlying substrate.

Studies of wetting phenomena continue to be of both scientific and technological value. Although much attention has lately been focused on the critical properties associated with the wetting transition, the static and dynamic properties of adsorbed liquid films (with thicknesses larger than molecular dimensions) are of equal interest.[1] Although resistivity[2] (for conducting films) and ellipsometry[3] (for transparent films) have provided valuable information, the number of techniques available to probe such films is unfortunately rather limited; thus the development of a new probe (as described here) should be of particular value.

The technique makes use of an organic monolayer on the surface of water (a Langmuir film). In an earlier paper,[4] we described a curious phenomenon: When a flint-glass microscope slide was lowered until it touched the surface of water on which a monolayer of the surfactant valinomycin had been spread, the monolayer slowly transferred to the glass surface. At higher surface pressures (Π), the amount of material transferred to the slide (calculated from the change in the area at constant pressure of the Langmuir film on the trough) implied that the film had climbed a distance of order 10 cm. It was thus natural to ask whether the glass strip might function as a "bridge" if the other end were in contact with a second Langmuir trough; i.e., whether we could continuously transfer surfactant molecules from one trough to the other over the thin film of water wetting the glass slide by maintaining a differential surface pressure, $\Delta\Pi$. This surface pressure difference will maintain a surface-tension gradient and, via the Marangoni effect, drive the motion of the liquid.[5]

Carrying out the proposed experiment required the construction of a "double" Langmuir trough.[6] The new instrument sits in a stainless-steel enclosure; the double walls of the enclosure allow a thermostatting fluid to be circulated, and (when the lid is closed) the system is hermetically sealed. Both features are vital if we are to be certain that the water in the two troughs, the glass bridge, and the surrounding atmosphere are in thermodynamic equilibrium (involving both a constant temperature and a saturated vapor pressure). Although the instrument may be equipped with two separate troughs, we used a single long trough; a fixed Mylar barrier at its center divided the water surface into two, and moving barriers on each side allowed the two monolayers to be independently maintained at the desired surface pressures.

Two types of glass bridges were fashioned from microscope slides; single-glass sides were bent to form either an inverted, flat-topped, U-like structure (with two bends) or a V-like structure (with one bend). The radius of the bends is of order 3 mm and is not thought to perturb the film flow properties. The bridges were positioned to span the Mylar partition and could be raised or lowered by a vertically translating arm (originally intended for the deposition of Langmuir-Blodgett multilayer films). A Teflon clamp was used to hold the bridge at its edges; it is not wetted by water and thus results in no loss of surfactant. For this experiment we operated the barriers in a constant pressure mode (via feedback from two Wilhelmy filter-paper balances).

When the monolayers in the two troughs were maintained at different surfaces pressures Π and $\Pi + \Delta\Pi$, respectively, we observed a loss of monolayer material in the higher-pressure side and an equal gain on the lower-pressure side. The average monolayer velocity can be calculated from the translation rate of the constant-pressure barriers, the trough width, and the slide perimeter. Figure 1 shows the average velocity V_s across the U bridge as a function of the differential surface pressure (the curve through the points will be discussed shortly). Note that the transfer is completely reversible (i.e., changing the sign of $\Delta\Pi$ causes the material to flow in the opposite direction) and that the flow velocity is approximately linear in the applied pressure differential (see below). The data shown resulted from several independent runs involving replacing the water subphase and respreading the valinomycin. After spreading the film (and prior to lowering the bridge into the water) the interior of the trough enclosure was allowed to equilibrate for about 10 h. After the bridge touched the water, a sufficient time (~ 1 h) is allowed to elapse so that the transfer takes on its steady-state behavior; the interval immediately following contact involves the dynamics of a spreading, surfactant-covered film—a complicated hydrodynamic problem which has recently been examined by Joanny.[7]

We now present the theory for determining the film thickness from the transfer rate. We choose a coordinate system with the x and y axis parallel to the direction of film motion and the substrate normal, respectively. Ex-

Solid Curve: Theoretical curve with $\dfrac{\ell_{vw}}{\ell_c} = 7 \times 10^{-4}$

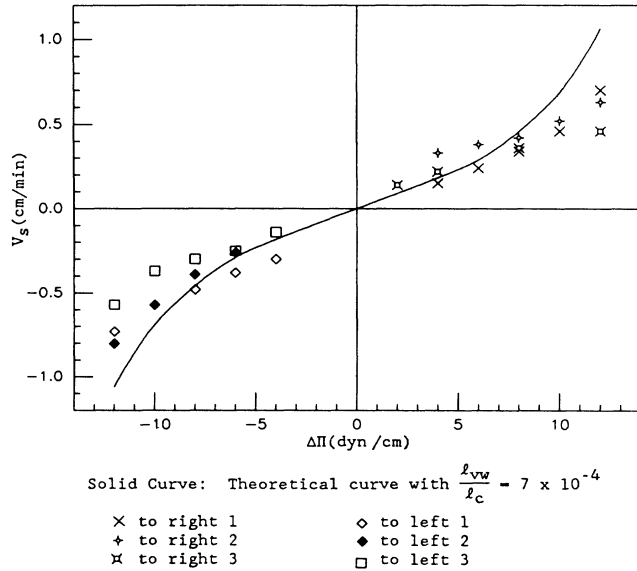| × to right 1	◇ to left 1
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FIG. 1. The surfactant flow velocity V_s as a function of the driving pressure $\Delta\Pi$. The different symbols mark different runs involving both directions of surfactant transport. The curve is a fit to the full numerical version of the theory (Ref. 9).

cept in the region where the bridge contacts the bulk water surface the flow is quasi-one-dimensional and, a solution of the form $\mathbf{v} = v_x(y)\hat{\mathbf{x}}$ is appropriate. The relevant component of the linearized, steady-state Navier-Stokes equation[8] (for an incompressible fluid) is

$$-\frac{\partial p}{\partial x} \mp \rho g \cos\theta + \eta \frac{\partial^2 v_x}{\partial y^2} = 0, \tag{1}$$

where θ is the angle of the substrate with the vertical, and the upper (lower) sign refers to the rising (falling) segment of the bridge.

Since the fluid motion is driven by a Marangoni force, the effect of capillarity and hydrostatic pressure may be neglected; thus $\partial p/\partial x = 0$. Equation (1) may then be integrated to obtain

$$v_x(y) = \pm \frac{\rho g \cos\theta}{2\eta} y^2 + ay + b.$$

Requiring $v_x = 0$ and $v_x = V_s$ for $y = 0$ and $y = h$, respectively, yields

$$v_x(y) = \pm \frac{\rho g \cos\theta}{2\eta}(y - h)y + \frac{V_s}{h}y. \tag{2}$$

Integrating from 0 to h where h is the film thickness (which is yet to be determined) we obtain the volume of liquid transported per unit time per unit width,

$$\dot{\mathcal{V}} = \frac{V_s h}{2} \mp \frac{\rho g h^3}{12\eta} \cos\theta.$$

A positive volume transport clearly requires

$$V_s > \pm \frac{\rho g h^2 \cos\theta}{6\eta},$$

which can only be satisfied above some critical V_s for the rising segment of the bridge.

For the particular form of the solution of the equations of motion that we have selected, we cannot simultaneously conserve the quantities V_s, $\mathcal{V}$, and h on the rising, flat, and falling segments of the bridge. We will assume that no evaporation (or condensation) occurs and that the film is incompressible (although the treatment can be generalized to include the effect of film compressibility). Conservation of the liquid and the surfactant then require that $\mathcal{V}$ and V_s be constant; hence h must change as θ varies for a rising, flat, or falling segment of the bridge. The surface-pressure drop follows from equating the tangential stress at the liquid surface to the surface-tension gradient

$$\frac{\partial\Pi}{\partial z} = \eta \frac{\partial v_x}{\partial y}\bigg|_{y=h}. \tag{3}$$

The overall pressure drop for the rising and falling segments of a V bridge (having thicknesses h and h', respectively, and total length L) is

$$\frac{\Delta\Pi}{L} = \frac{\eta V_s}{2}\left[\frac{1}{h} + \frac{1}{h'}\right] + \frac{\rho g}{4}\cos\theta(h - h'). \tag{4}$$

If we assume conservation of bulk liquid transported, h' follows from the condition

$$V_s h - \frac{\rho g \cos\theta h^3}{6} = V_s h' + \frac{\rho g \cos\theta}{6}h'^3. \tag{5}$$

In practice, h and h' are nearly equal for our case, and we will take them as identical in what follows. In particular, when gravity is neglected Eq. (4) may be replaced by

$$\frac{\Delta\Pi}{L} = \frac{\eta V_s}{h}; \tag{6}$$

the same expression will be used for the U bridge where L then includes the rising, falling, and flat segments.

Up to this point we have not addressed the question of what determines the film thickness h. A detailed analysis[9] shows that it is fixed by the flow conditions in the immediate vicinity of the classical contact line. A generalization of the "lubrication approximation" of Landau and Levich,[10] to include not only the pressure due to capillarity, but also the pressure associated with the retarded van der Waals interaction

$$p_{vdW} = -\frac{B}{y^4} \tag{7}$$

(where B is the Hamaker constant), can be used to treat the problem. The results of detailed numerical calculations[9] are well represented by the expression

$$V_s = \left\{\left[\left[\frac{\gamma}{\mu}\left(\frac{l_{vdW}}{l_c}\right)^{5/4}\frac{\Delta\Pi/L}{\gamma/l_c}\right]^n + \left[1.20\frac{\gamma}{\mu}\left(\frac{\Delta\Pi/L}{\gamma/l_c}\right)^3\right]^n\right]\right\}^{1/n}, \tag{8}$$

which accurately interpolates between the limiting $V_s \propto \Delta\Pi$ (van der Waals–dominated thin film) and $V_s \propto (\Delta\Pi)^3$ (classical thick film) regimes. A value of $n = 2$ represents the numerical calculations with a maximum error of 10% (which is presently better than the experimental error). Here $l_c = (2\gamma/\rho g)^{1/2}$ is the capillary length and $l_{vdW} = (B/\rho g)^{1/5}$ is the van der Waals length.

The smooth curve in Fig. 1 is a fit of the data to the full numerical version of the theory. The value of the retarded Hamaker constant which best fits the data is $B = 2.6 \times 10^{-15}$ cm^{3}g/s^2. Although water is, strictly speaking, not a van der Waals liquid, the value is nonetheless reasonable. The thickness of the film, in the low-velocity limit, obtained using the formula in Ref. 9, is

$$h_0 = l_c \left(\frac{l_{vdW}}{l_c} \right)^{5/4} = 0.5 \ \mu\text{m} .$$

Although we have tried this experiment only with valinomycin, our previous studies of capillary rise on a vertical substrate[4] showed that other materials (such as stearate salts) did not spontaneously transfer to the substrate to the same extent. The film forming properties of valinomycin, including the Π-A diagrams,[11] contact-angle studies,[12] and the deposition of Langmuir-Blodgett multilayer films[11] have all been explored previously. Valinomycin has the rather symmetric torus or ringlike structure depicted in Fig. 2(a). As drawn it appears to have mirror symmetry in the plane of the molecule, but examination of a molecular model [Fig. 2(b)] shows that steric hindrance effects require rotations of the subgroups of the molecule (about an axis running around the ring) and the favored orientations are presumably those which bring the more hydrophilic groups in better contact with the water surface. This structure is radically different from the more common film-forming molecules which typically have long chains on one end of which a hydrophilic group is attached. In particular, valinomycin has a rather delicate balance between the hydrophobic and hydrophilic sections; this is probably why the collapse mechanism of Langmuir films of valinomycin is not the usual one (in which the monolayer irreversibly transforms into a three-dimensional phase and floats as a scum on the surface) but rather a reversible escape into the water in the immediate vicinity of the surface. We think that the unusual nature of valinomycin is what makes it an ideal surfactant for the experiment reported here. The spreading of a thin water film covered with a more conventional surfactant may "roll it under" causing the hydrophilic end to attach to the substrate surface and render it hydrophobic, thus pinning the water film and effectively halting the spreading process. Valinomycin is presumably (for reasons given above) more immune to this process.

In conclusion, we have observed a new effect which is useful as a probe of liquid-solid interactions in wetting
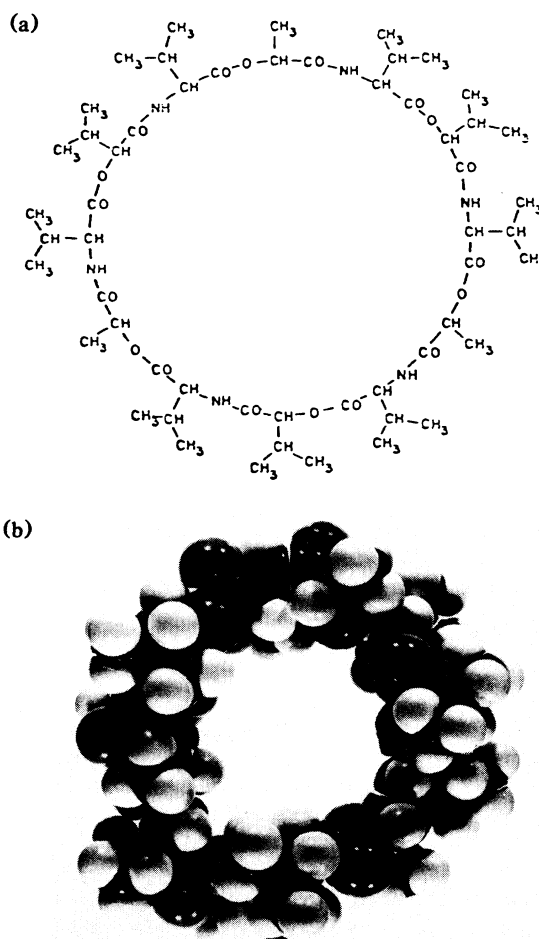

(a)

(b)

FIG. 2. (a) Chemical structure of valinomycin; (b) molecular model.

liquid films. It is hoped that our observations will stimulate both a search for other surfactants which display the effect and a study of such surfactants on other substrates.

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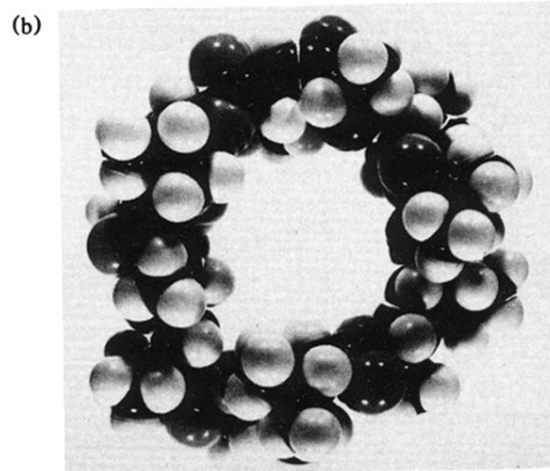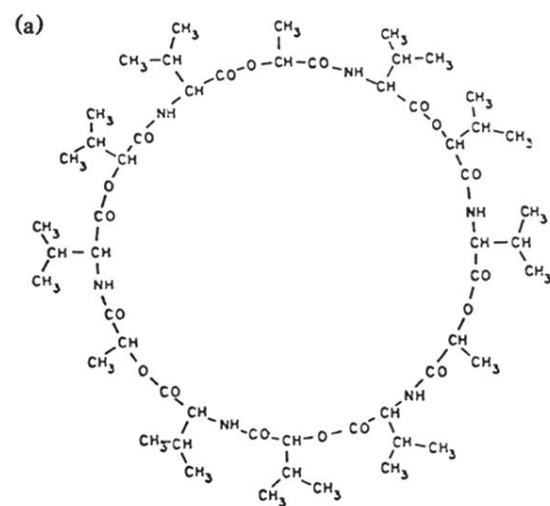
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