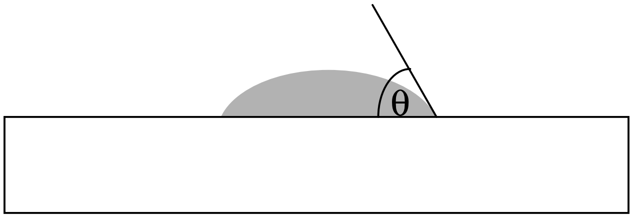
Laboratories 2 & 3

Contact Angles and Surface Energies

In this laboratory, you will use contact angle measurements in an effort to determine surface energies. Surface energies are important in understanding wetting of materials and adhesion properties. As you will see below, determining surface energies is not trivial. Measuring contact angles is, however, a simple matter. You are simply looking for the angle between the surface and a line that is tangent to a drop of liquid on the surface at the point where it intersects the surface (see the figure below).



Schematic diagram of a contact angle.

We discussed the physics of contact angles in class. The governing equation is Young's equation (eq 1) where γ_{sv} is the surface free energy of the solid in contact with vapor, γ_{sl} is the surface free energy of the solid covered with liquid, γ_{lv} is the surface free energy of the liquid-vapor interface, and θ is the contact angle. We can measure θ and γ_{lv} relatively easily, but that still leaves us with two unknowns. For this reason, it is very difficult to measure the surface free energy of a solid. In order to determine surface free energy, we need to be able to relate γ_{sv} and γ_{sl}. A recent article describes two approaches to this (*Langmuir* **1998**, *14*, 5907).

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta$$

The first method involves developing an equation of state that relates γ_{sl} to γ_{sv} and γ_{lv}. The approach is rather empirical and doesn't appear to be generally applicable. The second approach involves dividing surface free energies into different components (dispersive, acid-base, hydrogen bonding, etc.). The approach seems to work well only when primarily dispersive actions are present. This is in fact the only situation that is well-developed. Thus we are limited to utilizing dispersive interactions so we will measure the contact angles of hydrocarbons on a self-assembled monolayer.

When only a dispersive interaction is involved, a geometric mean combining rule is used for determining γ_{sl} from γ_{sv} and γ_{lv} (equation 2). The value of Φ is often close to one so we will neglect it. Combining equations 1 and 2 along with some algebraic rearrangement yields equation 3. Equation 3 suggests that we should plot cos θ versus $1/(\gamma_{lv})^{1/2}$. The intercept should be negative 1 and the slope should be equal to $2\,(\gamma_{sv})^{1/2}$. This is the approach that we will use to estimate the surface free energy of a self-assembled monolayer. Note that this technique actually assumes that adsorption of vapor on the solid surface is negligible.

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\Phi(\gamma_{lv}\gamma_{sv})^{1/2} \qquad (2)$$

$$\cos\theta = 2\Phi\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} - 1 \qquad (3)$$

Historically, the approach to comparing surfaces has been even more empirical than that given above. Zisman noticed that a plot of cos θ versus γ_{lv} is often linear. The value of γ_{lv} for which cos θ would extrapolate to 1 is termed the critical surface tension, γ_c. The relative inertness of surfaces can be evaluated by comparing the value of γ_c of the surface. After the previous paragraph, you may ask why a plot of cos θ versus γ_{lv} is linear. First, if nonpolar liquids are used the theory becomes complex. Second there can be scatter in the data. Neglect of adsorption on a surface and the assumption that $\Phi = 1$ are not always valid. Given these variations, it is not surprising that a plot of cos θ versus γ_{lv} could seem to be as linear as a plot of cos θ versue $1/(\gamma_{lv})^{1/2}$. As you plot your data, see if you can convince yourself that you could get a Zisman plot.

Surface free energy varies widely with the types of functional groups at the surface. For hydrophobic surfaces, free energy decreases in the order $-CH_2 > -CH_3 > -CF_2 > -CF_2H > -CF_3$ (*Langmuir* **1999**, *15*, 4321). Hence the inertness of teflon. In the case of a self-assembled monolayer, if the surface is well-ordered, it will expose $-CH_3$ and have a different surface energy than if it exposes $-CH_2$ groups. Hopefully you will prove this in the laboratory.

Advancing and Receding Contact Angles

The above treatment of contact angles assumes that everything is in equilibrium. In principle, this requires letting the drop sit on the surface for a long period of time. Often one measures advancing and receding contact angles. In this case, we can measure the contact angle as the drop is expanding (advancing contact angle) or contracting (receding contact angle). In every case of which I am aware, the advancing contact angle is larger than the receding angle.

There are at least three possible reasons for contact angle hysteresis.

1. Contamination. The drop may become contaminated as it moves across the surface. This will change the surface tension of the liquid. This may also clean or contaminate the surface.
2. Surface roughness. On a rough surface, the drop may spread over different portions of the surface. The less polar portions may affect advancing angles while the receding angle may be affected by polar regions (*Langmuir* **1999**, *15*, 3395).
3. Surface reconstruction. The surface itself may change in the presence of the liquid. For example, the hydrophobic group of a monolayer may become slightly buried when using water to measure contact angles.

Given the above reasons, a small difference (<5 degrees) between advancing and receding angles suggests that the surface is free of contamination, well organized, and smooth.

Measuring advancing and receding contact angles is done in several ways. In the most legitimate method, a drop would be advanced quasistatically (very slowly) over the surface and the contact angle would be measured during the advance. A similar method is applicable for the receding angle, but the drop is quasistatically contracted. In this case, the needle must be in contact with the drop.

Whitesides employs another procedure (*J. Am. Chem. Soc.* **1989**, *111*, 321). It this case a drop is formed at the end of a hydrophobic needle. The drop is placed on the surface and the needle is retracted. This causes the drop to advance and the contact angle is measured within a few seconds. This seems to yield water contact angles a few degrees lower than the method of keeping the needle in the drop and advancing the drop. For receding contact angles, the needles must be in the drop and the drop contracted. There seems to be no other way.

Laboratory 3

1. Remove the monolayers from solution and rinse them with hexane and water. Dry them with nitrogen.

2. Measure the thicknesses of these films using the procedures that you learned in laboratory 2. Are they different from the prior thicknesses? If so, explain your observation.

3. Take the sample that was cleaned in piranha solution and immerse it in pure hexane. We will look at this sample next time.

4. Using the freshly evaporated slide that you coated with a monolayer, we are going to determine critical surface tension. To do this, we will use the following liquids (the value in parentheses is the surface tension of the liquid in mN/m): *n*-heptane (20.2), *n*-octane (21.7), *n*-nonane (22.9), *n*-undecane (24.8), *n*-hexadecane (27.6), bicyclohexyl (32.8). Measure the contact angle on the film using each of these liquids. Between liquids, rinse the surface with EtOH and dry with nitrogen. (Find out if the cleaning process changes the contact angle. You can figure out how to do that.) The surface tension of the liquid is crucial in these experiments. You must clean the syringe thoroughly with acetone and dry it in the oven between measurements. In addition, flush the syringe with the solvent of interest once or twice before measurements. Take three measurements with each liquid to determine how reproducible the angles are.

5. Notice that I didn’t give you many details on the measurement of contact angles. This is because we have two different goniometers. Your TA will explain the operation of your particular system.

6. After collecting your data, make a Zisman plot as discussed in class. Are your data linear or does a quadratic fit better. Make an estimate of critical surface tension. Explain why or why not you think that the critical surface tension can be considered as a surface tension of the solid.

7. Put your slide back in thiol solution and save it for next time.