Contact Angle Experiment

Please note that this experiment is NOT in the P. Chem lab in Mergenthaler. Students doing this experiment should go directly to NCB 228.

Objective

- To explore the concepts of surface free energy, adhesion and wetting by measuring the contact angle of a series of liquids on a polytetrafluoroethylene (teflon) substrate.
- To create a Zisman Plot from a series of contact angle measurements to determine the surface tension of polytetrafluoroethylene (teflon).

Introduction

The interaction between a liquid and a solid involves three interfaces; the solid-liquid interface, the liquid-vapor interface and the solid-vapor interface. Each of these interfaces has an associated **surface tension**, γ, which represents the energy required to create a unit area of that particular interface.

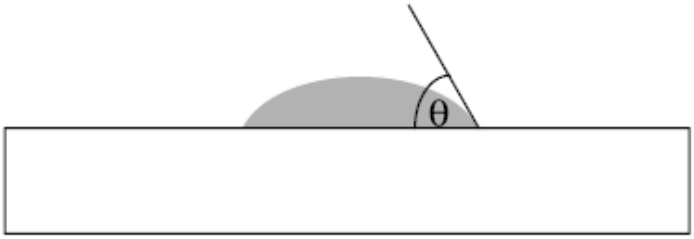

Figure 1. Diagram of the contact angle

The angle between a liquid drop and a solid surface, Young's contact angle, is related to the surface tensions of the three interfaces according to the relationship:

$$\cos\theta_Y = (\gamma_{\text{Solid-Vapor}} - \gamma_{\text{Solid-Liquid}}) / \gamma_{\text{Liquid-Vapor}} \quad (1)$$

The magnitude of Young's contact angle is a result of energy minimization. If the liquid-vapor surface tension is smaller than the solid-vapor surface tension ($\gamma_{LV} < \gamma_{SV}$), the liquid-solid interface will increase to minimize energy. As the drop wets the surface, the contact angle approaches zero.

The **critical surface tension** of a material, γ_c, is a measure of the surface's wettability and it is proportional to the surface free energy of the material. A liquid with a surface tension less than or equal to the critical surface tension of a particular material will "wet" that surface, i.e. the contact angle will be less than or equal to 90^o. A material's critical

surface tension can be determined from a **Zisman Plot**, which measures variation in Young's contact angle as a function of the surface tension of a series of liquids. Zisman noticed empirically that a plot of cos(θ) versus γ_{LV} is often linear. The value for which cos(θ) extrapolates to 1 is termed the critical surface tension.

Materials

n-heptane	cyclooctane
n-octane	bicyclohexyl
n-undecane	acetone
n-tetradecane	hexanes
n-hexadecane	ethanol
1-mL syringe	flat piece of teflon (~3cm x 3cm)
clean cotton swabs	

Procedure

Prepare software

Open contact angle folder on the desktop. Double click on the CAM100 camera image. In the right margin, make the ***Number of Frames*** "1" and ***Wait after Rec Click*** "0." Make sure that the boxes next to ***Allow Tilt*** and ***Auto Calculate*** are checked.

Prepare solid

Clean the teflon surface with hexanes and ethanol using a cotton swab. Dry with clean cotton swab. Place teflon on the sample stage.

Prepare liquid

1. Clean syringe by filling it with acetone past 0.1 mL mark and emptying three times. Depress plunger multiple times to get out any residual acetone. (Do not turn the top too far – it will make the glass crack!)
2. Pre-rinse syringe with the testing liquid by filling with ~0.05 mL, turning syringe upside down and depressing the plunger past 0.1 mL, then turning it upside down a few times to rinse the sides of the syringe. Empty pre-rinse liquid into waste.
3. Fill syringe with ~0.1mL of testing liquid and secure in the syringe holder above the sample stage.

Set Up Instrument

1. Turn on the light switch at the left of the sample stage.
2. Adjust the height of the syringe so that the tip can be seen at the top of the screen. Center the tip of the syringe on the screen by using the knob to the left of the syringe holder.
3. Adjust the height of the solid sample by turning the three knobs at the base of the sample stage. The solid surface should be visible at the bottom of the screen and there should be distance between the tip of the syringe needle and the solid surface. Pay particular attention to ensuring that the sample is flat.

4. Adjust lighting by turning the knob on the camera lens farthest from the sample stage and focus using the silver knob at the base of the camera. The background should be white and the needle tip should appear sharply. If the image needs more focusing, click on ***Show Camera Settings*** in the right margin of the screen and adjust the brightness, gain etc.

Measurement

1. Move the teflon so that the syringe is over an un-wetted part of the surface. Adjust the position of the teflon so that there are no other drops on the screen that would obstruct the camera's view.
2. Slowly turn the syringe plunger until a drop falls from the syringe onto the surface. Adjust the focus using the silver knob at the base of the camera. Be sure that you can see where the drop meets its reflection on the solid surface (the baseline). You may need to adjust the camera angle to do this (knob at the back of the camera). Allow the drop to equilibrate on the sample stage for a total of 10-30 seconds.
3. Press ***Rec***. The screen now shows an image of the picture the camera took. It should automatically calculate the contact angle. The angle measurements for the left, right and mean contact angle appear at the bottom right of the screen.
4. If the baseline (red line) appears to lie along the line of intersection between the drop and its reflection and the red tangent lines appear to be tangent to the drop, click ***Test Auto Baseline*** to be certain it is accurate. If the drop outline and baseline look accurate, click next and go to step 6.
5. If the contact angle was not automatically calculated or the automatic baseline looks inaccurate, click the box next to ***Use Auto Baseline*** so it is not checked and manually adjust the baseline using the position and tilt arrows. Drag the blue outlined box so that it frames the drop and click ***Fit*** in the top right corner of the screen. Adjust the baseline until the tangent lines look accurate. Then click ***Next***. If the software is still unable to measure the contact angle, click ***Back*** and create a new drop on an un-wetted part of the surface.
6. Do not worry about naming the measurement. Click ***Copy to Clipboard***. ***Open Excel*** and ***paste*** data. Make sure 3 sets of numbers appear in the excel file. Label each column (trial number, left contact angle, right contact angle, average contact angle) and ***save*** file. Email the file to you and your partner.
7. Click ***Next*** and repeat the process for a total of six measurements per liquid. (6 drops of each liquid total).
8. After six measurements, empty the syringe into the waste and begin the procedure again for the remaining liquids.

Additional notes:

-No contact angle may be obtained for n-heptane; try a few times and skip if necessary.
-Between liquids, rinse the syringe with ~0.05mL of the next liquid, depressing plunger past the 0.1mL mark as done previously. Clean the teflon with excess ethanol and wipe dry with cotton swab.
-Make sure to empty syringe thoroughly by depressing multiple times

Data and Zisman Plot

The software records the time of the measurement (in seconds from the time of pressing the Record button), the left contact angle, the right contact angle and the mean contact angle. Find the mean cos θ_Y for each liquid and the standard deviation of cos θ_Y. Plot the mean cosine value for each liquid against its surface tension. Find the best linear fit and extrapolate this line to find the surface tension value that gives a cosine value of 1.

Questions

Pre-Lab Questions:

1. What is the contact angle a measurement of and where can it be found?
2. What do low values of θ suggest about a liquid and it's interaction with a surface?
3. Predict the trend you might expect to find in the contact angles measured in this lab and explain.
4. What do you expect to see if the liquid surface tension is less than or equal to the critical surface tension of a surface?
5. What is the "work of adhesion" and how is it determined?
6. What is hydrophobicity and hydrophilicity? Give an example of a hydrophobic and hydrophilic surface encountered in day-to-day life.

Lab Questions:

1. Explain the differences you observed in the θ's for the different liquids.
2. Compare your calculated value of the surface tension of teflon to a literature value. Explain any discrepancy between your value and the one you find.
3. Why is it difficult to measure the surface free energy of a solid? How can the Zisman plot be used to estimate this value? What assumptions are made in estimating this value?
4. Describe a real-world example of a readily observable liquid-solid interaction and explain the underlying molecular level rationale.
5. Self-assembled monolayers (SAMs) play an increasingly important role in research studies of interfacial phenomena. What is a SAM?
6. Why are contact angle measurements useful in determining quality of SAMs?
7. Draw a picture of a water drop on $-CF_3$, -COOH, $-OH^-$ and $-CH_3$ -terminated SAMs. Indicate how you expect the contact angle to vary on these SAMs. Explain your diagram.