Experiment 36

FV 1/5/05

DETERMINING THE SIZE OF A SINGLE MOLECULE

MATERIALS: Large watchglass (14.5 cm diameter), Pasteur pipet and bulb, 25-mL volumetric flask, graduated pipet, methanolic NaOH solution, liquid soap and brush, 10-mL graduated cylinder, stock hexane solutions of stearic acid, palmitic acid, and myristic acid, hexane, molecular model of stearic acid, small storage vials and caps, plastic pipets

PURPOSE: The purpose of this experiment is to both estimate and experimentally determine the physical dimensions (length and cross-sectional area) of a single fatty acid molecule.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Use the concept of intermolecular force to explain how a monolayer of fatty acid molecules forms on the surface of water.
2. Using trigonometry and knowledge of the geometries of bonds, estimate the length of a fatty acid molecule.
3. Using a reasonable model for the shape of the fatty acid molecules and their solid densities, estimate the cross-sectional area taken up by one molecule.
4. Calibrate the average droplet-size delivered by a Pasteur pipet.
5. Using the estimated size of the fatty acid molecule, determine how to make a solution, via dilution of a stock solution, which delivers a monolayer of molecules in a selected number of droplets, using dimensional analysis.
6. Explain how the endpoint of the monolayer "titration" is recognized.
7. Using the data from the "titration," and the estimate of the cross-sectional area of a single molecule, estimate the value of Avogadro's number.

DISCUSSION:

Intermolecular Forces involving Fatty Acids. Most molecules discussed in general chemistry courses are small enough that they are characterized by a single type of polarity, e.g., polar or non-polar. For example, water is polar and hexane is non-polar. Some molecules are large enough, however, that they are able to exhibit both polar and non-polar characteristics simultaneously. For example, stearic acid (a fatty acid with chemical formula $C_{18}H_{36}O_2$ or $CH_3(CH_2)_{16}COOH$) consists of a polar carboxylic acid region at one end of the molecule, with a long non-polar hydrocarbon tail. Computers are excellent tools for exhibiting the structures of large molecules, as demonstrated for the case of stearic acid at the following website: http://chemistry.beloit.edu/Fats/pdbfiles/stearicAcid.pdb . Symbolically, water, hexane, and stearic acid may be represented as in Figure 1.

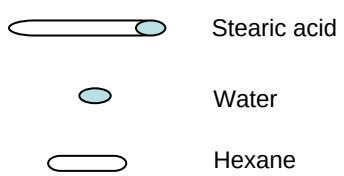

Figure 1.

The darkened areas of the molecules represent the polar regions, and the undarkened areas represent the non-polar regions.

There are many fatty acids that occur naturally in biological systems, including the three saturated fatty acids that will be studied in this experiment: stearic acid, $C_{18}H_{36}O_2$, used in making candles, soaps,

and cosmetics; palmitic acid, $C_{16}H_{32}O_2$, found in palm oil, meat, milk, butter, and cheese; myristic acid, $C_{14}H_{28}O_2$, found in nutmeg, coconut, and palm kernel oils. Fatty acids (lipids) are an essential component of the human diet, and a shortage of dietary fats can lead to cardiovascular, neurological, and dermatological problems and can diminish the body's ability to repair itself. Lipids comprise 50% of the dry weight of the brain and 5-10% of other cells.

The consequences of a molecule possessing polar and non-polar regions simultaneously are interesting and lead to many unique applications. For example, a mixture of stearic acid and water will start with a random arrangement of the molecules, as in Figure 2, and may then automatically assemble into more organized structures called micelles, as in Figure 3.

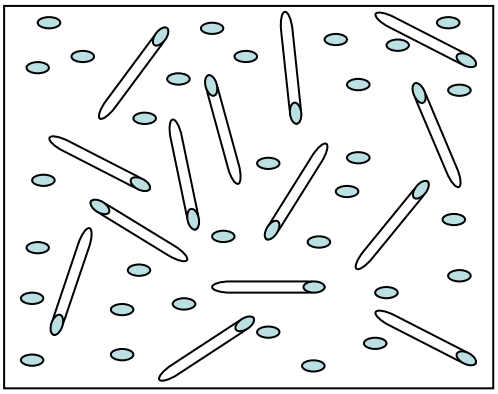

Figure 2. Initially formed mixture of stearic acid and water

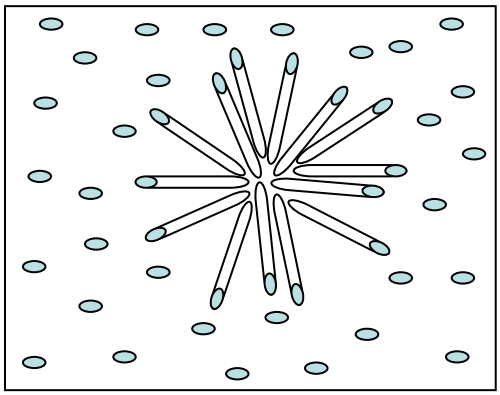

Figure 3. Micelle formation (one possible result)

There are other types of structures that can spontaneously form, including the famous bilayer structure characteristic of biological cell membranes.

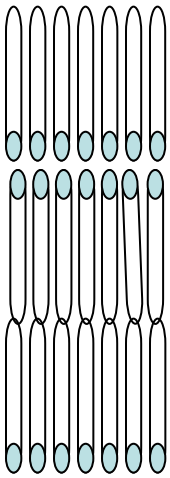

Figure 4. Stacking of stearic acid molecules in the solid

Another consequence of having both polar and non-polar regions is the unique manner in which such molecules tend to crystallize. Symbolically, stearic acid molecules stack together as in Figure 4, where the layers of stacked molecules alternate their orientation, with polar regions of neighboring stacks adjacent to one another, etc. A computer image of this, found at http://chemistry.beloit.edu/Fats/pdbfiles/stearicCrystal.pdb , helps illustrate the crystal structure of these types of molecules.

Forming a Monolayer of Fatty Acid on a Water Surface. Of particular interest to this experiment is the formation of a single layer of fatty acid molecules on the surface of water. This can be accomplished by depositing stearic acid molecules, dissolved in hexane, on the surface of the water. As the volatile hexane evaporates, the polar regions of the stearic acid molecules are attracted to the polar water, while the non-polar tails of the stearic acid molecules remain above the water. Each stearic acid

molecule occupies space on the surface of the water, similar in magnitude to the cross-sectional area of stearic acid molecules when in the solid phase (see Figure 5). The hydrocarbon tails of the stearic acid molecules are represented in this illustration (greatly exaggerated, of course) by square towers. Each molecule occupies area on the water surface equivalent to the area of the square. The circle represents the edge of the watchglass holding the water on which the single layer of stearic acid molecules (i.e., monolayer) forms. Not shown in the Figure are the polar end-groups of each stearic acid molecule which are imbedded in the water surface.

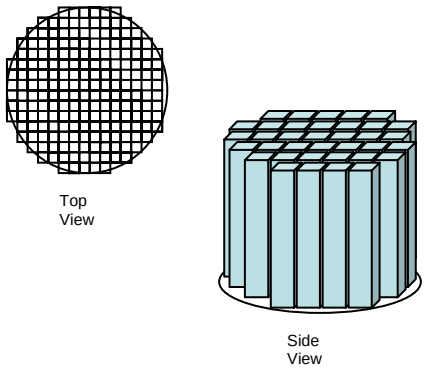

Figure 5. The non-polar regions of fatty acid molecules sticking up from the surface of the water (side view). The top view shows the area occupied by each stearic acid molecule of the monolayer.

The formation of the monolayer is similar to the endpoint of a titration. As more stearic acid molecules are added, via the placement of droplets of hexane solution on the water surface, the layer becomes more completely occupied, until finally every space on the water surface is occupied. One additional droplet of hexane solution results in an excess of stearic acid molecules, beyond those needed for the monolayer, and exhibits an observable "endpoint of the titration," which is symbolically illustrated in Figure 6.

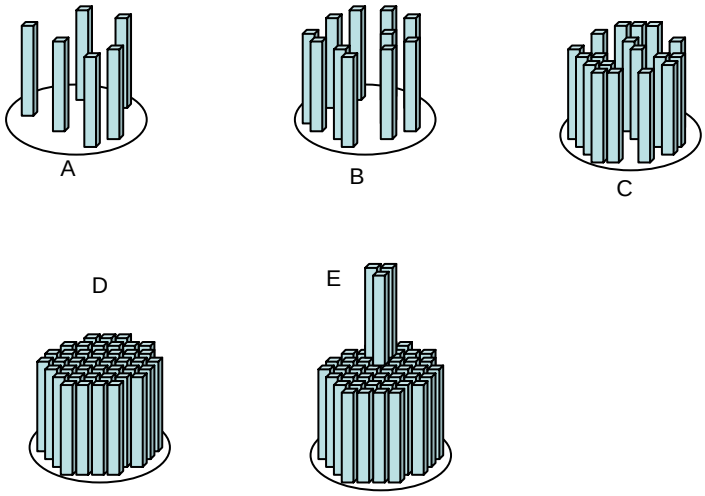

Figure 6. Progression of "titration" [A, B, C gradual buildup of monolayer, D monolayer complete, E visible residue due to molecules beyond monolayer].

PROCEDURE: (some of the steps outlined below may be assigned as pre-lab exercises)

1. After dividing the lab section into five groups (three or four midshipmen each), the instructor will assign each group one of the three fatty acids (stearic acid, palmitic acid, or myristic acid). ***In the procedure below, substitute stearic acid with either palmitic or myristic acid, as needed.***

2. Your instructor will demonstrate (1) the proper use of the Pasteur pipet, and (2) the proper procedure for cleaning and rinsing the watchglasses. Refer to the special note below.

3. Estimate the <u>length</u> of a stearic acid molecule, using the fact that typical C-C bond lengths are 0.154 nm, and the bond angle between adjacent carbon atoms is the tetrahedral angle. The length is the straight-line distance from one end of the molecule to the other, <u>not</u> the total length of all the C-C bonds. Use a model of stearic acid to help you visualize the overall shape of the molecule. Assume the non-polar tail is "stretched out."

4. Assuming that stearic acid molecules stack together in the solid phase as suggested in the Discussion section, and assuming that they effectively use up the volume of a square tower as illustrated in Figures 5 and 6, determine the square cross sectional area taken up by a single stearic acid molecule. Use the density of the solid fatty acid: stearic, 0.839 g/cm^3; palmitic, 0.841 g/cm^3; myristic, 0.858 g/cm^3. [Hint: assume that the density of the bulk solid is the same as that of a single molecule.]

5. Sketch a sequence of simple drawings showing what happens when a droplet of a hexane solution of stearic acid is added to the surface of water. Use the symbolic representations of the molecules as given in the Discussion section.

6. Using the results of Step 4, estimate the number of stearic acid molecules required to completely form a monolayer on top of the surface of water which fills the large 14.5 cm watchglass.

7. Using items available in the lab, devise a procedure and determine the average volume of one drop of hexane as delivered by the Pasteur pipet. If needed, based on your devised procedure, the density of hexane is 0.659 g/cm^3.

8. Using the provided stock solution of stearic acid in hexane, make 25-mL of a diluted stearic acid solution such that approximately 15 drops of the diluted solution will deliver enough stearic acid to form one monolayer on the water surface held by the large watchglass. Take just slightly more hexane than you will need for this dilution. Divide the prepared solution among the members of the group, using the small capped vials. Label these vials and return to your instructor if you need to save them until the next week.

9. Your instructor will demonstrate the basic procedure for setting up the watchglass as well as how to detect the endpoint of the drop-by-drop titration. Basically, the hexane from each drop must completely evaporate before adding the next drop. The endpoint is reached if a noticeable solid residue remains on the surface after the hexane evaporates.

10. Working individually, add the dilute stearic acid solution to the surface of the watchglass, drop by drop using the calibrated Pasteur pipet, until the monolayer is completed. Record all pertinent data from your procedure and combine your data with the other members of the group. Repeat this titration several times, as time permits, rinsing/washing the watchglass in between titrations as outlined in the note at the end of the procedure. After completing titrations, dispose of all hexane solutions in the labeled container in the Instructor's hood.

11. Using your titration results and the density of solid stearic acid (assumed to be about the same as found in the monolayer), determine the thickness of the monolayer (in cm). How does this compare to your earlier estimate of the length of a stearic acid molecule? Provide your results to the instructor.

12. Based on your titration results, knowing how many stearic acid molecules were incorporated into the monolayer, and using Avogadro's number, determine the square cross-sectional area taken up by a single stearic acid molecule (in cm^2). How does this compare to your earlier estimate? Provide your results to your instructor.

13. Your instructor will provide the collected results from the various groups. Do the results for the stearic, palmitic, and myristic acids show the patterns for length and cross-sectional area that you would expect? Explain.

14. Alternatively, using your earlier estimate of the number of fatty acid molecules that would occupy a monolayer on the water surface of the filled watch glass, obtain an estimate of Avogadro's number, and compare to the accepted value.

Note about watchglass cleaning: The watchglass must be very clean in order for this procedure to work properly. Watchglasses will be soaked in a solution of NaOH/methanol overnight and between use during different lab periods. While wearing a pair of Latex gloves, remove a watchglass from the NaOH/methanol solution, and rinse thoroughly (i.e., several times) with distilled water. Avoid touching the watchglass with your fingers. Fingerprints may leave an oily residue which includes molecules that will interfere with the monolayer formation process. Between individual trials, the watchglass should be cleaned with the pink liquid soap solution and a brush. After scrubbing, rinse thoroughly (i.e., several times) with distilled water. When finished using the watchglass, carefully rinse with distilled water, then replace in the NaOH/methanol solution. All rinses can be washed down the drain.

QUESTIONS FOR CONSIDERATION:

1. Explain why the average volume of droplets of hexane solutions are much smaller than those of aqueous solutions.

2. Draw a sketch of another possible self-assembled structure (besides the micelle structure discussed above) resulting from a mixture of stearic acid in water.

3. Determine the number of grams of fatty acid actually contained in your 25-mL diluted solution. Explain why this solution could not simply be prepared by weighing out solid stearic acid and dissolving in hexane to make 25 mL of solution.

4. Knowing that hexane is much more volatile than water, explain a possible source of error in determining the average hexane droplet volume, and how this might affect the calculation in Step 11 leading to the length of the fatty acid molecules (i.e., the thickness of the monolayer).

5. Why do the non-polar tails of the fatty acid molecules project into the air above the water surface? Explain in terms of intermolecular forces.

6. How is the formation of the monolayer of fatty acid molecules on a water surface similar to the filling of a mall parking lot during the holiday season? How is it different?