INVESTIGATING INTERMOLECULAR FORCES

INTRODUCTION

There are two different experiments performed during the laboratory session that will investigate intermolecular forces. Each experiment has a separate background section followed by a procedure. In Part 1, we will exploit the interesting dual polarity of stearic acid molecules to estimate the length of one molecule. In Part 2, we will seek to answer the question - Should there be a Law of Conservation of Volume? - by observing the results of mixing equal volumes of water and ethanol.

This experiment is to be worked out in pairs. The lab instructor will indicate which experiment, Part 1 or 2, each pair should start with first to minimize the lines at the balance/reagents.

SAFETY AND WASTE DISPOSAL

1. **No open flames in lab since we will be using organic solvents** (hexane and denatured alcohol). Both substances are ingestion hazards. Do NOT ingest the alcohol!
2. Please follow proper waste disposal procedures. All ethanol/water mixtures are disposed of in the proper waste container.
3. Always wear your safety glasses!

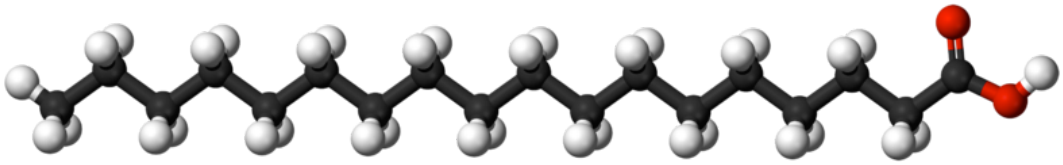
ITEMS TO CHECK OUT FROM THE STOCKROOM (FOR EACH PAIR OF STUDENTS)

- 15 cm watch glass
- 50 mL graduated cylinder **(TC)**
- **Automatic pipet with tip**
- two 25 mL volumetric pipets labeled water and ethanol
- one pipet pump
- You will need a rubber stopper to fit your 50 mL Erlenmeyer flask. If you do not have one in your drawer, you can get one from the stockroom.

PART 1: DETERMINING THE LENGTH OF A STEARIC ACID MOLECULE

BACKGROUND

We are all very familiar with the fact that oil and water do not mix. The reason for this is that water molecules are polar and oil molecules are nonpolar. Some molecules can possess both a polar end and a nonpolar end. These types of molecules can exhibit some very interesting behavior. Stearic acid is an example of a molecule exhibiting this dual polarity.

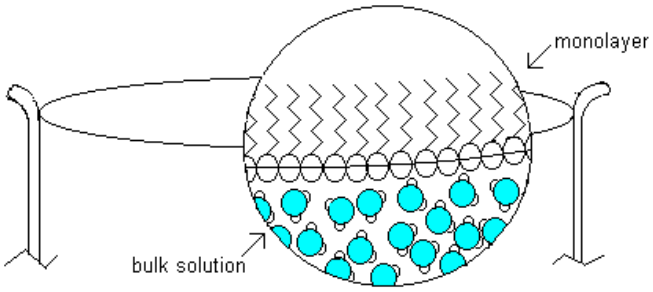


Stearic Acid ($C_{18}H_{36}O_2$, MW 284.49 g/mol)

As depicted above, the long hydrocarbon chain is the nonpolar portion of the molecule. This nonpolar "tail" is **hydrophobic** or water-hating. The difference in electronegativity between the C and H atoms is small and thus the bonding electrons are equally shared between the two atoms. The remaining portion of the stearic acid molecule contains the carboxylic acid functional group (-COOH), which is the polar portion of the molecule. In contrast to the tail, this polar "head" is **hydrophilic** or water-loving. The two O atoms are more electronegative than the C atom and thus they pull the bonding electrons closer creating a partial negative charge towards the O atoms. In addition, the O–H group allows for hydrogen bonding with other molecules that possess O–H or N–H type bonds.

When one carefully places molecules of stearic acid on top of water, the stearic acid arranges itself in a very elegant pattern. The polar portion of the molecule interacts with the water and the nonpolar portion of the molecule does its best to stay away from the water. Once a few molecules of stearic acid are present, the molecules self assemble into something

called a monolayer. They line up parallel to one another but perpendicular to the water. One can actually produce a full monolayer of these molecules across a large area of water.



Magnified view of stearic acid monolayer formation on water surface.
(http://wwwchem.csustan.edu/chem1102/surfc2.gif)

The length of a stearic acid molecule can be approximated to be equivalent to 18 times the diameter of a carbon atom. This length can be obtained with a simple experiment we are going to perform in lab. We will form a monolayer of known area and volume. By dividing the volume by the area we obtain a value for the height of the monolayer. This height corresponds to the length of the molecule. The area of the monolayer will be equivalent to the surface area of the water beneath it. So we can use a watch glass filled with water and measure its diameter. Using the equation for the area of a circle we can obtain a value for the area of water. The volume of stearic acid can be obtained by knowing the mass of stearic acid in the monolayer and the density of stearic acid.

Unfortunately, stearic acid is a solid at room temperature. Thus we cannot just sprinkle the solid over the water and expect it to disperse itself throughout the surface of the water. We need to determine a good way of delivering the stearic acid to the water surface so that the molecules can move to arrange themselves in a monolayer. It would seem that a solution of stearic acid would work best. We are interested in creating a layer of stearic acid molecules so the solution must be prepared with a solvent that has two properties; it must dissolve stearic acid, and it must evaporate rapidly so that what remains on the surface of the water is stearic acid and not a mixture of stearic acid with the solvent. These two properties strongly suggest we should use a low molar mass, nonpolar solvent (Why?). The solvent selected is hexane. Since we need to know what mass of stearic acid is delivered to the surface we will need to know the concentration of stearic acid in hexane.

PROCEDURE Stearic Acid Monolayer

1. Holding the watch glass by the edges, clean the 15 cm watch glass thoroughly with water and detergent. **Rinse it well with tap water followed by distilled water, then an acetone rinse and once again with distilled water**. The acetone rinse should be collected and disposed of properly. Carefully dry the edge of the watch glass with a paper towel, making sure you only touch the bottom of the watch glass. Place the watch glass on the lab bench making sure it is level.

2. **Slowly and carefully** fill the watch glass on the table with distilled water making very sure none of the water spills over the edge of the watch glass. If it does spill, you will need to remove all the water from the watch glass, dry the edge again and attempt to fill it again with water. The watch glass needs to be full without any overflow. Carefully measure the diameter of the water surface on the watch glass to within 1 mm. (Let the water sit for a while so that the air bubbles escape.) **Record the diameter in your notebook.**

3. Review the usage of an automatic pipet. See the instructions at the end of this lab. **SET the VOLUME to 20 µL**. Rinse the tip of the automatic pipet once with the stearic acid solution and discard. Draw a fresh stearic acid sample into the pipet. **Dispense the whole sample onto the surface of the water.** This sample will disperse rapidly so it might be difficult to detect the motion of the stearic acid over the water surface. Draw a second sample into the pipet and dispense onto the surface of the water. Repeat this procedure of dispensing 20 µL samples over random surface positions until the monolayer is complete. When is the monolayer complete? After the third or fourth sample of stearic acid you should observe the sample on the surface of the liquid (it looks like a contact lens floating) and you can watch it spread out. Wait until it disperses and you can't see the "contact lens" before adding the next sample. When a sample does not disperse after 20-30 seconds, you are done adding samples. **Record the number of 20 µL samples used to prepare the monolayer in your notebook.**

4. The solution in the watch glass can go down the drain. You might want to use a disposable pipet to remove some of the solution prior to trying to lift the watch glass. **Repeat the monolayer procedure a second time for consistency.**

PART 2: SHOULD THERE BE A LAW OF CONSERVATION OF VOLUME?

BACKGROUND

One of many fundamental laws of nature is the Law of Conservation of Matter. It states that the amount of matter must remain the same even after a chemical or physical change. We all feel very confident in stating that when we combine 100 g of water with 100 g of ethanol we will obtain 200 g of a water-ethanol solution. Does the same "conservation" occur with volume? When we combine 100 mL of water with 100 mL of water at constant temperature we do obtain 200 mL of water. This would suggest that volume is also conserved. Let's see whether the same conservation applies when we combine volumes of different liquids. For our experiment we will combine 25 mL of water with 25 mL of ethanol. If there truly were a "Law of Conservation of Volume" then we would expect to obtain a volume of 50 mL. If we don't obtain a volume of 50 mL then we will need to explain why a Law of Conservation of Volume is not possible.

PROCEDURE Conservation of Volume

1. Using a 50 or 100-mL **clean, dry** beaker, obtain 30 mL of distilled water. Using a **clean, dry** 50 ml Erlenmeyer flask, obtain 30 ml of ethanol. Stopper the flask. Please note the ethanol is denatured. A small amount of a toxic alcohol (ingestion poison) is added to it, so this is not "drinkable" ethanol but rather a poisonous solution. The "drinkable" ethanol is controlled by the ATF (Alcohol, Tobacco and Firearms) and cannot be easily used in a freshman chemistry lab. Let the distilled water sit for a while so as to allow most of the dissolved air to escape. The bubbles will give an incorrect volume reading.

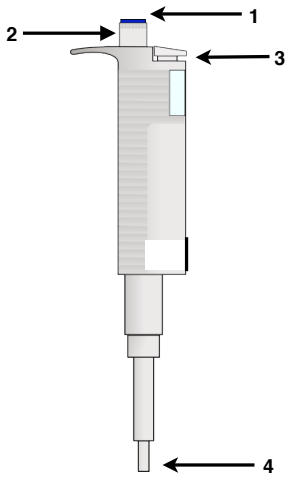
2. Check your 50 mL (TC) graduated cylinder. If it is dry, do not wet it with any solution. If it is wet inside, you will need to dry it to the best of your abilities using a paper towel and/or compressed air.

3. Fill the pipet labeled ETHANOL with 25 mL of ethanol. Once the pipet is filled, discharge the ethanol into the 50 mL graduated cylinder. Remember the pipet is calibrated to deliver, so you should not attempt to remove the last drop by blowing or shaking the pipet. You need only to touch the tip of the pipet to the inner wall of the cylinder.

4. Fill the other pipet with 25 mL of distilled water and discharge its contents into the 50 mL graduated cylinder that contains the ethanol. Swirl or agitate to mix the water and ethanol. Touch the cylinder and see if you can **determine whether the mixing of the two solutions caused a temperature change, record this observation in your notebook**. What else do you observe? Does the cylinder indicate that you have 50 mL of solution? **Record the combined volume in your notebook AFTER most of the bubbles have disappeared, about a 10-minute time period.**

5. **WASTE**: **Dispose of all ethanol containing waste in the proper waste bottle.**

DIAGRAM OF AN AUTOMATIC PIPETTE



1. **Control Button:** Use to aspirate and dispense the liquid. As you slowly push down on the button, there is a "first stop" and a "second stop".
2. **Setting Ring:** Turn to set the volume.
3. **Ejection Button:** Use to eject the tip.
4. **Tip:** Attach a suitable tip here.

INSTRUCTIONS FOR USE OF AUTOMATIC PIPETTES

Volume Setting

The volume can be changed continuously over a specific range by rotating the **setting ring**. The range and units will be stated on the pipette; look carefully at the pipette to determine the units and range. Typical units are milliliters or microliters. The digits in the display are read from top to bottom. If the display has a horizontal line, the line represents a decimal point. For the best accuracy and precision in the measured volume, it is advisable to adjust the volume setting from a higher value down to a lower value. In other words, first ensure that the instrument is set to a volume above the desired volume and then turn the setting ring to bring the value down to the desired volume.

Pipette tips

The pipette must be fitted with a suitable tip for the volume being measured. Students can obtain suitable tips from the chemistry stockroom. **DO NOT attempt to use the pipette without a suitable tip.**
To guarantee precision and accuracy, tips should be pre-wetted with the liquid to be measured. To do this, aspirate and dispense the liquid two to three times before pipetting. The liquid that is aspirated to pre-wet the tip should be dispensed into a waste container.

Aspirating (pulling up) the liquid

1. The liquid that is to be aspirated must be in a suitable vessel, one that will allow the pipette tip to be immersed 3-5 mm into the liquid.
2. Attach a suitable tip onto the pipette.
3. Press down the **control button** to the "first stop", where resistance to being pressed further is first felt. (You can practice finding this "first stop" as well as the "second stop" before aspirating any liquid into the tip.)
4. For microliter amounts, immerse the pipette tip approximately 3 mm into the liquid to be measured. When measuring 1-10 mL amounts, immerse the tip approximately 5 mm into the liquid.
5. Allow the control button to slide up **SLOWLY.** While doing this, **be careful to keep the tip immersed in the liquid**. If the tip is removed from the liquid while the button slides up, air will be aspirated into the tip and liquid may be suctioned up out of the tip into the pump itself, causing damage to the pump.
6. Wait approximately three seconds before removing the tip from the liquid.
7. **SLOWLY** pull the tip out of the liquid.
8. Remove any remaining droplets of liquid on the outside surface of the tip by gently dabbing the tip with a paper towel. When doing this, DO NOT touch the paper towel to the opening in the bottom of the tip since doing so may cause liquid to be drawn from the tip onto the paper towel.

Dispensing the liquid

NOTE: NEVER lay the pipet down on the lab bench when it contains liquid in the tip. Doing so may result in liquid flowing into the pump itself, causing damage. ALWAYS hold the pipette upright when liquid is in the tip.

1. Hold the tip at an angle against the inside wall of the container you are dispensing the liquid into.
2. Press down the control button to the "first stop" and wait until the liquid stops flowing out of the tip.
3. Press down the control button to the "second stop". The tip should now be completely empty of liquid.
4. While still holding down the control button, pull the tip up the inner wall of the container.
5. After pulling the tip out of the container, allow the control button to slide up **SLOWLY**.

Eject the tip

1. When finished pipetting eject the tip by pressing the **ejection button**.

RAW DATA

Part 1 –Monolayer Data

Concentration of stearic acid solution: _____

Automatic pipet sample volume _____

Diameter and samples of stearic acid to form monolayer (two trials).

Trial	Diameter of water surface (cm)	Samples of stearic acid dispensed
1		
2		

Part 2 – Water/ethanol Mixture Data

Observation(s) after mixing:

Observed combined volume of mixture: _____

PART 1: MONOLAYER CALCULATIONS

Our goal is to obtain an approximate length of one stearic acid molecule in the monolayer.

Using your data from Part 1 for the monolayer, calculate the following for each trial. Show your work below.
Some useful information:

The density of ***solid stearic acid*** is 0.85 g/cm^3.
Area of monolayer = πr^2.
Thickness of monolayer = volume/area.

1. Total volume of stearic acid SOLUTION dispensed to make monolayer (µL):
   Trial 1 Trial 2

2. Grams of stearic acid dispensed to make the monolayer. Use the CONCENTRATION of stearic acid in hexane and the volume dispensed.
   Trial 1 Trial 2

3. Volume of stearic acid forming the monolayer. Use the mass of stearic acid and the density of solid stearic acid to find this volume. Here, we are assuming the monolayer is made from solid stearic acid with a density of 0.85 g/cm^3.
   Trial 1 Trial 2

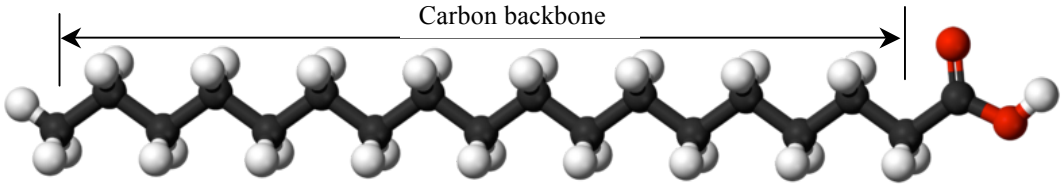
4. Area of stearic acid monolayer. Use your diameter measurement. (cm^2)
   Trial 1 Trial 2

5. Thickness of stearic acid monolayer. Use thickness = volume/area. (cm)
   Trial 1 Trial 2

6. Calculate an average EXPERIMENTAL monolayer thickness in cm and then convert to Angstroms. The thickness of the monolayer is the experimental length of one stearic acid molecule. (10 Å = 1 nm)

Calculation of the Length of a Stearic Acid Molecule based on its formula and shape.

1. This is a geometry question and you may want to use the drawing below of stearic acid to help you. In the ball and stick model the angle bewtween carbons is 109.5 ° and the C-C bond length is 1.54 Å.



   Calculate the length of the **carbon backbone** in stearic acid.
   This is a good approximation to the length of a stearic acid molecule that would be resting on top of the water in the monolayer.

2. How does this length compare to your experimental value of the monolayer height? Comment on any differences.

PART 2: IS VOLUME CONSERVED?

1. When mixing 25 mL each of water and ethanol was the volume conserved? _____

   If no, calculate the % change in the volume relative to the expected volume of 50 mL. (Note: if your volume was less than 50 mL, your percent change should be negative.)

   a) Based on your observations of the volume of the water/ethanol mixture, does the average intermolecular distance between molecules increase or decrease upon mixing?

   b) Coulomb's Law of Electrostatic Force: $|F| = k_c \frac{|q_1||q_2|}{d^2}$, where F is the force, k_c is a constant, q_1 and q_2 are the partial charges of the interacting molecules and **d is the distance of interaction**. Using your answer to 1a) did the average intermolecular force between molecules increase or decrease upon mixing?

2. For water and ethanol is the mixing process endo- or exothermic? (What did you feel?)

   a) Is this an increase or decrease in **potential energy of the system** as mixing occurs?

3. Based on your answers to 1 and 2, how is a change in intermolecular force strength related to a potential energy change for a system?

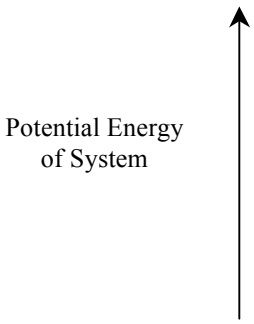
4. During the mixing of ethanol and water you should have observed the formation of tiny bubbles. These bubbles are O_2, N_2, and some CO_2 gas that are dissolved in the ethanol and water prior to mixing. One possibility of why the gas is released upon mixing is the observed change in temperature. Gasses tend to be less soluble in warmer liquids. However, this is not the primary reason. Give another more likely reason why the mixed solution would release some of the dissolved gases. Hint: think volume change and average intermolecular distance!

5. You should now have learned that as IM forces are formed, the potential energy of the system decreases and thermal energy is released to the surroundings. In another words, as IM forces are formed, the system moves to a lower potential energy state. The overall change in strength of the IM forces determines the change in potential energy. The greater the change in strength of the IM forces in the system, the greater the change in potential energy of the system.

   We are studying four types of intermolecular forces, each depends upon the polarity of the molecules interacting:
   1) London dispersion 2) dipole-induced dipole 3) dipole-dipole 4) hydrogen bonding

   a) Rank these four IM forces from strongest to weakest assuming EQUAL molar masses of SMALL molecules interacting.

   b) Now rank each IM force as to the final potential energy state of the system on the diagram below:



6. Realistically, should there be a "Law of Conservation of Volume"? If not, explain why such a law should not exist.

Molarity determination of the ethanol/water mixture

1. Using the density of ethanol (0.7892 g/mL) at 20° C, calculate the mass and moles of ethanol transferred in the 25.00 mL sample. Use proper significant figures.

2. Using the **experimental volume** you measured for this mixture, calculate the molarity of ethanol in this solution. Use proper significant figures.

Reference: Singmaster, Karen. "Chemistry 1A Laboratory Manual for Fall 2002", 2002, 1st ed., Department of Chemistry San Jose State University.