Experiment 4 – Physical Properties of Organic Compounds

The determination of the physical properties of organic compounds is very important. If you know the melting point, boiling point, density, and solubility properties of a substance, this information can help to identify the compound and can also give an indication of how pure the compound is.

The **melting point** of a substance is the temperature at which the substance changes from a solid to a liquid. You can determine the melting point of a substance by melting a small amount of the substance in a melting-point apparatus. The sample is packed in a small capillary tube and then heated slowly while the temperature is monitored. At the first sign of liquification, the temperature is measured. When the sample has completely melted, the temperature is noted again. The melting point is expressed as a temperature range: the first temperature is the temperature it starts to melt and the second temperature is the temperature at which it is completely melted.

If the sample is impure, there will be two effects on the melting point. An impure sample will melt at a lower temperature than the corresponding pure sample. Also, impure samples have a wider temperature range. Pure samples should melt within a temperature range of 1-2°C.

The **boiling point** of a liquid is the temperature at which it boils (boiling is observed as bubbles that form within the liquid). When you measure a boiling point, it is important to put a "boiling stone" in the liquid before you start heating it. This will insure even boiling and will minimize or eliminate boiling over or "bumping" of the liquid. The boiling point can be measured by clamping a thermometer just over a sample in a test tube and gradually heating the sample. The temperature will rise and then remain steady when the substance starts boiling. The vapor rising from the liquid will condense when it hits the bulb of the thermometer. The temperature of any phase change should be constant, so the reading will stabilize.

Density is defined as the mass of a substance per unit volume. The density of a liquid is usually expressed in units of grams per milliliter. To determine the density of a liquid substance, you can weigh a measured volume of the substance. (The volume can be measured with a pipet or a graduated cylinder.) The density is calculated by dividing the mass of the sample by its volume. The density of organic liquids can range from about 0.6 g/mL to 1.5 g/mL.

Solubility may be described either qualitatively or quantitatively. Qualitatively, a substance may either dissolve in a particular solvent or not. For example, nonpolar substances are not soluble in water (a polar solvent). Nonpolar substances (like hydrocarbons) are soluble in other nonpolar solvents. If you were to mix a polar and a nonpolar liquid (such as hexane and water), they would always separate into two layers. The more dense of the two liquids will be on the bottom layer. The quantitative solubility of a substance is defined by the mass of the substance that will dissolve in a specified amount of a particular solvent at a specified temperature. The temperature must be specified because the solubility of most substances is temperature dependent.

Some substances are not very soluble in a particular solvent at low temperatures, but are significantly more soluble at higher temperatures. This idea is exploited in a

purification technique called recrystallization. In order to recrystallize a substance, it is first dissolved in a small amount (the minimum amount) of the solvent at a high temperature. One assumption is that some of the impurities present at this point will not dissolve under these conditions, and so these impurities can be filtered out at this point. (If you do filter at this point, it is important to keep the mixture hot and to use hot solvent to rinse the solid on the filter paper. This is important because as the solution cools, the solubility of the compound you're trying to purify will decrease. If it cools too much, some of it will crystallize out and you will lose some of it.)

After this first filtration, the solution is allowed to cool slowly to room temperature. It is then placed in an ice bath so that it can reach the lowest possible temperature. As it cools, the solute will crystallize out, because its solubility is lowered at a lower temperature. After the sample has reached the temperature of the ice bath, it is assumed that the maximum amount of solid has crystallized out. It is also assumed that other impurities will not crystallize under these conditions and will remain in solution. At this point, the mixture is filtered (usually using vacuum filtration) and rinsed with a small amount of cold solvent. (It is important that the solvent be cold, because you are trying to collect the maximum amount of solid. Some will dissolve in warm or room-temperature solvent, and the amount that dissolves will just run through the filter paper and will be impossible to then recover. It is also important to use a small amount of the solvent. The more solvent present, the more solid can dissolve in it. Again, this makes it more likely that you will lose some of the solid.) The impurities that stay in solution will thus be separated from the purified solid. The solid is then dried. To verify that it is more pure, a melting point determination is made. If the melting point is higher and if it has a smaller range, then the solid is more pure than it was before the recrystallization.

Safety Precautions:

- Organic compounds are extremely flammable. Do not use Bunsen burners in the organic chemistry laboratory.
- Keep the organic solvents (hexane and toluene) under the fume hood.
- Wear your safety goggles.

Waste Disposal:

- Any waste that contains hexane or toluene (or any other organic solvents) must be placed in the **organic** waste containers (pink label) in one of the fume hoods.

Procedure

Part 1: Melting Point Determination

1. Put a small amount of impure aspirin on a watch glass and pack a capillary tube (which is closed on one end) with aspirin. To do this, press the open end of the capillary tube into a mound of the sample and then invert the tube and tap gently. You will need a height of about 2-3 mm of aspirin in the tube. The instructor will

demonstrate how to use a long glass tube to pack the aspirin into the bottom of the tube.

2. Determine the melting point of the impure aspirin sample using a melting point apparatus (See below).

Melting Point Apparatus

The rate of heating can be faster at first (5-10°C per minute) but then should be slowed (to about 2-3°C per minute) as the approximate melting point is approached. The rate of heating should be slowed at around 100 °C. When you see the first signs of liquid formation, record the initial melting temperature. When the sample is completely melted, record the final melting temperature. Your melting point will thus not really be a point but will be a range. (If you use the melting point apparatus after another student, let it cool to 90°C or lower before you put your sample in it.)

Part 2: Recrystallization of Impure Aspirin

3. Measure about 3 mL of ethanol and put it in an ice bath to cool. This chilled ethanol will be used in a later step to rinse the solid that is collected on the filter paper.
4. Transfer 1.5 g of impure aspirin to a medium test tube. Add 4 mL of ethanol and heat this mixture in a water bath on a hot plate. Periodically mix the contents of the test tube by shaking it or tapping the bottom of the tube as you gently hold the top of the tube in place. You may also use a stirring rod to mix the contents of the

tube. Heat this mixture until all of the solid dissolves. If necessary, filter out any undissolved solid using vacuum filtration. (If you need to filter at this step, make sure that the flask you will be filtering into is clean and dry.)

5. Take the test tube out of the water bath and let the solution cool to room temperature. If there are no crystals in the solution once it reaches room temperature, carefully scratch the inner wall of the test tube to initiate the crystallization. When no more crystals appear to be forming, place the test tube in an ice bath for 10 minutes.
6. Filter the crystals using vacuum filtration. (See the equipment set-up on the next page.) You will need a flask with a side arm, a porcelain Büchner funnel with a rubber adapter, a piece of rubber tubing, a ring stand with a clamp, and a piece of filter paper. Clamp the side-arm flask to the ring stand (this is important because these flasks fall over and break easily once the rubber hose is connected). Connect one end of the rubber tubing to the side-arm and the other end to an aspirator at one of the sinks in the lab. Put the Büchner funnel on the flask, and put a piece of filter paper flat in the Büchner funnel. Turn on the water full blast (this running water acts as a vacuum – it sucks air out of the flask), and wet the filter paper with a small amount of the solvent. Push down on the funnel to make sure there is a good seal between the rubber adapter and the flask. Then swirl your sample in the test tube and dump it on the filter paper. After the solvent runs through the filter paper, wash the crystals with the chilled ethanol and let the aspirator keep running until the crystals are dry. Carefully lift out the filter paper with the aspirin crystals on it and place it on a clean, dry watch glass. Keep this purified aspirin sample in your laboratory locker until the next laboratory period – it will dry in your drawer.

Vacuum Filtration Setup

7. After the sample is completely dry, determine the melting point of the purified aspirin. Use the same procedure that you did in steps 1 and 2.

Part 3: Boiling Point Determination

8. In the hood, measure out 4 mL of 1-butanol and pour it into a small test tube. Clamp this test tube to a ring stand in the hood.
9. Put one small boiling stone in the test tube.
10. Fill a glass dish with sand (if it is not already done for you) and place it on a hot plate in the hood. Carefully lower the test tube into this "sand bath". (The tube should still be clamped to the ring stand.) Clamp a thermometer in place so that the tip of the thermometer is in the test tube about 2 cm <u>above</u> the surface of the liquid.
11. Carefully heat the liquid. The temperature will rise, but at some point the liquid will start boiling and the temperature reading will become constant. This happens when there is an equilibrium established between the liquid and its vapors. This constant temperature is the boiling point of the liquid. (Be careful when you are heating the sample – make sure that the liquid does not all evaporate! If it does, you will not be able to measure an accurate boiling point, and you will need to start over.) Record the boiling point on the report sheet. When it cools, discard the remaining liquid in the organic waste container (which has a pink label).
12. Determine the boiling point of 2-butanone, following the same procedure (Steps 8-11). Use a clean test tube.

Part 4: Density Determination

13. Using an electronic balance, weigh a clean, dry vial and cap.
14. Measure out 2.0 mL of an unknown liquid using a graduated cylinder or a pipet, and place the liquid into the vial. Make this measurement as accurately as possible. Record the actual volume used to the nearest ± 0.01 mL. Also record the unknown number of your sample.
15. Cap the vial, and weigh the vial with the liquid inside. Calculate the density of the liquid. (Density = mass/volume.)
16. Your unknown is one of the following substances. Based on your value of density, determine the identity of your unknown.

Substance	**Density, g/mL**
Allyl alcohol	0.8540
Benzyl alcohol	1.0413
1-butanol	0.8097
6-chloro-1-hexanol	1.204

17. Pour the unknown in the organic waste (which has a pink label).

<u>Questions</u>

1. What are two ways that impurities affect the melting point of a solid substance?
2. What is the purpose of a boiling stone?
3. Explain how the process of recrystallization works to purify substances.

4. In part 3 of this lab (the boiling point determination), which substance had the higher boiling point? Explain the reason behind the differing boiling points, based on the intermolecular forces present in each substance.
5. In the recrystallization process that you performed in this lab, explain what would happen if you used 40 mL of ethanol instead of 4 mL of ethanol to dissolve the aspirin. Would your results be different?
6. Why should the ethanol used for washing the crystals be chilled? What would happen if this ethanol was not chilled?
7. The following data was obtained for an unknown liquid:
   mass of vial 3.543 g
   mass of vial and liquid 4.869 g
   volume of liquid 1.55 mL
   Calculate the density of the unknown liquid.
8. Often, different substances have similar densities. In order to help identify the substance, you would need additional information, such as the boiling point or melting point. The following compounds have very similar densities. Using a chemistry handbook, look up the boiling points of these substances to see if you could distinguish between the compounds on the basis of their boiling points.

Substance	**Density, g/mL**	**Boiling Point**
1-Pentyne	0.6901	
1,2-Pentadiene	0.6926	
3,3-Dimethylpentane	0.6933	
2,2-Dimethylhexane	0.6953	