12AL Experiment 2: Identifying the Unknown Component of a Medicinal Mixture & Checking Purity of Aspirin & Unknown via Recrystallization & Melting Point

Safety: Proper lab goggles/glasses must be worn (even over prescription glasses). Even a lab as simple as recrystallization has hazards – heating of organic solvents releases irritating and sometimes toxic vapors, and often times, volatile solvents splatter vigorously out of their containers! As always, ask where organic waste containers are located in the lab.

Background:

Recrystallization

Recrystallization is a technique that chemists use to purify solid compounds. It is one of the fundamental procedures each chemist must master to become proficient in the laboratory. Crystallization is based on the principles of solubility: compounds (solutes) tend to be more soluble in hot liquids (solvents) than they are in cold liquids. If a saturated hot solution is allowed to cool, the solute is no longer soluble in the solvent and forms crystals of pure compound. Impurities are excluded from the growing crystals and the pure solid crystals can be separated from the dissolved impurities by filtration.

This simplified scientific description of crystallization does not give a realistic picture of how the process is accomplished in the laboratory. Rather, successful crystallization relies on a blend of science and art; its success depends more on experimentation, observation, imagination, and skill than on mathematical and physical predictions. Understanding the process of crystallization in itself will not make a student a master crystallizer; this understanding must be combined with laboratory practice to gain proficiency in this technique.

What Happens During a Crystallization

To crystallize an impure, solid compound, add just enough hot solvent to it to completely dissolve it. The flask then contains a hot solution, in which solute molecules - both the desired compound and impurities - move freely among the hot solvent molecules. As the solution cools, the solvent can no longer hold all of the solute molecules, and they begin to leave the solution and form solid crystals. During this cooling, each solute molecule in turn approaches a growing crystal and rests on the crystal surface. If the geometry of the molecule fits that of the crystal, it will be more likely to remain on the crystal than it is to go back into the solution. Therefore, each growing crystal consists of only one type of molecule, the solute. After the solution has come to room temperature, it is carefully set in an ice bath to complete the crystallization process. The chilled solution is then filtered to isolate the pure crystals and the crystals are rinsed with chilled solvent.

Additional notes by Michelle Hagerman. The information is available for academic use without restriction.)

***Please Review "How to Perform a Recrystallization" on our class website!**

The Melting Point

Physical Properties of a compound are those properties that are intrinsic to a given compound when it is pure. A compound may often be identified by determining a number of its physical properties. The most commonly recognized physical properties of a compound include its color, melting point, boiling point, density, refractive index, molecular weight, and optical rotation. Modern organic chemists also use various types of spectra: IR (infrared) spectra, NMR (nuclear magnetic resonance), and mass spectrometry. We will learn to how to use and understand equipment associated with melting points, IR, NMR, and Mass Spec this year in organic chemistry.

The melting point of a compound is used by organic chemists to identify the compound and establish its purity. A small amount of material is heated <u>slowly</u> in a special apparatus equipped with a thermometer. <u>Two temperatures</u> are always recorded which will be called the <u>melting point range</u>. The first is the point at which the first drop of liquid forms among the crystals; the second is the point at which the whole mass of crystals turns to a clear liquid. For example, the melting point of a substance may be recorded as 51 – 54°C.
The melting point indicates purity in two ways. First, the more pure the substance, the higher its melting point <u>and</u> the <u>more narrow</u> its range. The presence of a *minimal* amount of impurity (ie: unreacted substrate, incomplete rxn, contamination, *wet* sample) causes the melting point of the sample to <u>decrease</u>. Melting Point Lowering is also known as Freezing Point Depression. (If your melting point increases, this can indicate that your sample is mainly comprised of the impurity (ie: unreacted substrate) and this impurity has a higher melting point that the product desired).

Recall, the melting point of a substance is the exact same temperature as its freezing point. Melting and freezing, both physical processes, occur between the solid and liquid phases. Melting simply requires the addition of heat to break up many of the intermolecular forces between the rigidly packed molecules in the solid phase – this allows for a more fluid formation found in the liquid phase. Freezing requires the removal of heat energy so that the molecules may move closer together in order to form more intermolecular attractions.
The presence of an impurity interferes with the formation of intermolecular forces during freezing as well as disrupting the intermolecular forces more quickly during melting. As such, the freezing process must release more energy in order to freeze and the melting process is quicker since the attractive forces are already disrupted. Thus, freezing point depression &/or melting point lowering occurs.

Packing a Melting Point Capillary Tube
A melting point capillary tube looks like a miniature test tube – a small thin-walled piece of glass tubing that has been sealed at one end (~1mm x 100mm). To pack the tube, press the open end gently into a pulverized (powdered) sample of your crystalline solid material. Crystals will stick in the open end of the tube. The amount in the tube should be about 1-2mm high. To transfer the crystals to the closed end of the tube, drop the capillary, closed end first, down a long piece of glass tubing, which is held upright on the desktop. When the capillary hits the desktop it will bounce and the crystals will pack down in to the bottom of the tube. Repeat this procedure if necessary.

Determining the Melting Point
Place the capillary into a COOL melting point apparatus. Turn the apparatus ON, and adjust the control dial for a desired rate of heating (this should be LOW), and observe the sample through the magnifying eyepiece. Two temperatures are always recorded which will be called the melting point range. The first is the point at which the first drop of liquid forms among the crystals; the second is the point at which the whole mass of crystals turns to a clear liquid. Once you have determined your melting point range, turn the apparatus OFF so that it may cool down for another student to use. Dispose of your capillary in the Organic Solid Waste Jar in hood, not in the trash.

Objective: 1. To determine the purity of your aspirin & unknown isolated from the medicinal mixture in Experiment 1. 2. To determine the identity of the unknown. 3. To learn the method of recrystallization, which will be used to purify all subsequent organic compounds isolated, extracted, and/or synthesized in 12AL and 12BL. 4. To learn the method of melting point determination, which will be used to determine purity for many future labs.

Procedure/Data:
1. Perform a Recrystallization of your impure aspirin isolated in Experiment 1. Use hot ethanol as your recrystallization solvent.

2. Take a melting point range of your dry pure aspirin ________________________˚C.

3. Perform a Recrystallization of your impure unknown isolated in Experiment 1. Use hot water as your recrystallization solvent.

4. Take a melting point range of your dry pure unknown ______________________˚C.

5. Look up the literature melting points of…

Acetanilide ___________________˚C.

Phenacetin ___________________˚C.

5. What is the identity of your unknown? _________________________________.

6. Take a melting point range of the following provided for you:

Pure Aspirin ______________________˚C.

80:20 Aspirin:Sucrose ______________________˚C.

60:40 Aspirin:Sucrose ______________________˚C.

40:60 Aspirin:Sucrose ______________________˚C.

20:80 Aspirin:Sucrose ______________________˚C.

Pure Sucrose ______________________˚C.

7. Explain your results in #6 thoroughly & clearly.

12AL Prelab 2: Identifying the Unknown Component of a Medicinal Mixture & Checking Purity of Aspirin & Unknown via Recrystallization & Melting Point

1. Read & constantly review "How to Perform a Recrystallization" on our class website: www.venturacollegeorganicchemistry.weebly.com

*Instructors: Please include questions on Quiz about performing a recrystallization, in addition to the normal questions about the previous lab experiment.

2. How many temperatures are always recorded when taking a melting point? When do you take these temperatures?

3. What does a narrow range of a melting point indicate? A broad range?

4. Why does melting point depression of a pure solvent/solid (also called freezing point depression) occur when an impurity is added to the pure solid? *Explain your answer in terms of Intermolecular Forces! Be brief and specific.

5. Give an example of a substance…

   a. That has only dispersion attractions

   b. Dipole-Dipole attractions

   c. H-Bonding

6. What two factors affect the strength of Dispersion attractions?

7. What will affect the strength of Dipole-Dipole attractions?

8. Why do we perform recrystallizations of all products that are isolated or synthesized in the lab?

12AL Postlab 2: Identifying the Unknown Component of a Medicinal Mixture & Checking Purity of Aspirin & Unknown via Recrystallization & Melting Point

1. All calculations must be shown neatly with UNITS & using Dimensional Analysis.

   Important Information: Solubility of Phenacetin in cold water is 1.0 gram per 1310mL water, and in boiling water is 1.0 gram per 82mL water

   a. What is the minimum volume of boiling water needed to dissolve 0.200 grams of phenacetin?

   b. Calculate the mass of phenacetin that will *remain dissolved* when the water is cooled?

   c. Calculate the mass of phenacetin that will recrystallize (*undissolved*)?

2.

a. What is the strongest intermolecular force ortho-toluic acid has? Draw two molecules of o-toluic acid to show their intermolecular attraction (use --- to indicate which atoms are attracting A--------B)

b. How will the melting point of o-toluic acid change if it has benzoic acid impurities in it? Explain clearly.

3. For each set of molecules…. Draw the structure of each compound, Label <u>only the strongest</u> type of intermolecular force each compound contains, AND indicate which compound in the set will have the lowest melting AND WHY? (in terms of intermolecular force strength!)

   a. Butane, Isobutane, Pentane

   b. Ethanol, Acetic Acid

   c. 1-chloroebutane, 1,4-dichlorobutane