Recrystallization of Benzoic Acid and Acetanilide

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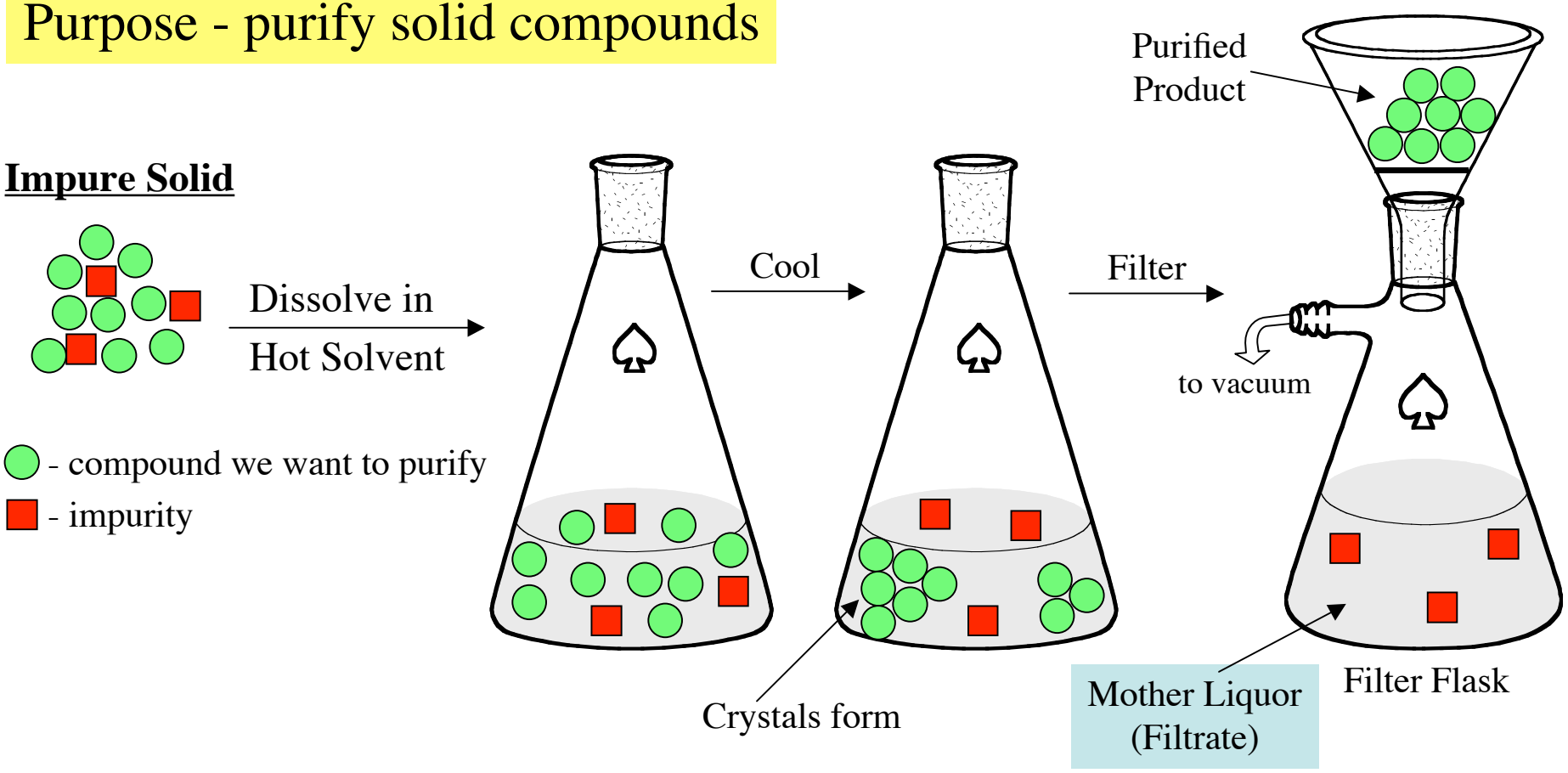
Part B - 5: Mixed solvent recrystallization of benzoic acid, p. 106

Important Concepts

- Purification technique for solids
- Solvent polarity "like dissolves like"
- Mixed solvent recrystallization
- Hot filtration technique
- Crystallization techniques
- m.p. determination

Theory of Recrystallization

Purpose - purify solid compounds



- Use minimum amount of hot solvent to dissolve crude solid.
- Cool slowly to avoid trapping impurities.

Choosing a Solvent for Recrystallization

1. Compound should be insoluble at room temperature or when cold.

2. Use a minimal amount of solvent so the solution is concentrated.

3. Compounds are soluble in solvents with similar polarity,
   (i.e. like-dissolves-like):

   - use a polar solvent to remove polar impurities and solubilize polar compounds.

   - use a nonpolar solvent to remove nonpolar impurities and solubilize nonpolar compounds.

Polar → large dipole moment, typically contains a heteroatom (e.g. N, O).

NonPolar → small dipole moment, typically a hydrocarbon
(e.g. hexane, benzene, toluene, petroleum ether).

Safety Issues

- Organic solvents are usually highly flammable

- ***Flash point*** is the temperature at which a solvent may spontaneously ignite (e.g. Diethyl ether = -40 °C, ethanol = 16 °C, water = none)

- Avoid spilling organic solvents onto hot surfaces, such as a hotplate since they may ignite.

- ***Materials Safety Data Sheets*** (MSDS) are forms that describe available safety information (e.g. mp, bp, Fp, toxicity).

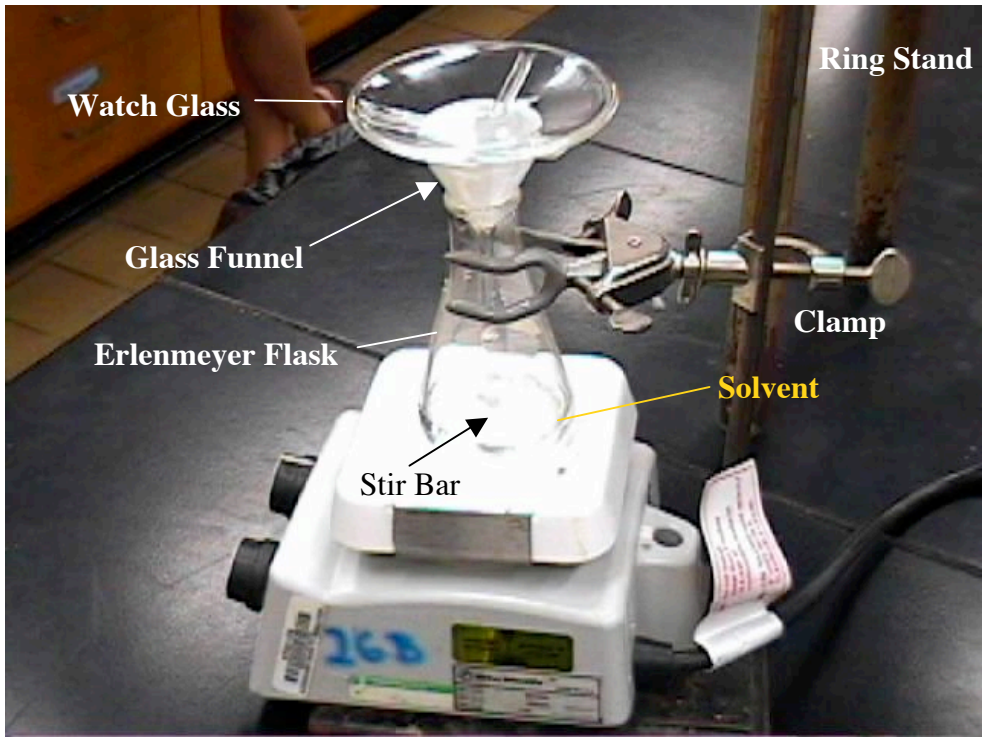
  - MSDS forms can be found at a variety of sources including:
    [http://www.cehs.siu.edu/Chemical/msds.htm]
    [www.brookscole.com/chemistry/gilbert4]

or a google search: ex. [msds benzoic acid]

Recrystallization Procedure

1. Dissolve crude solid in a minimal amount of hot solvent:
   - typically this means bringing the solution to a boil;
   - add decolorizing carbon if you have colored impurities;
   - perform a hot filtration if you have insoluble impurities (e.g. sand or dirt)

Hot Filtration Apparatus



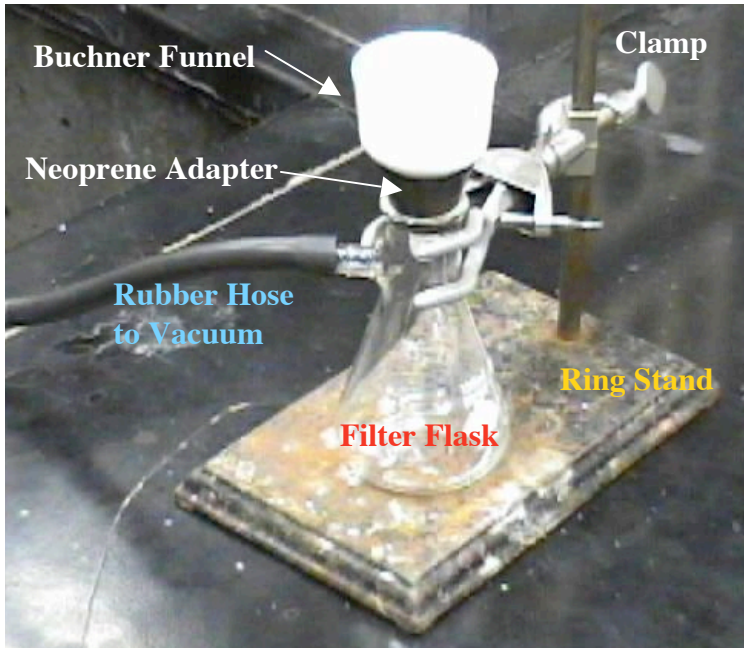
Hot Filtration Procedure

- Add clean solvent to flask and bring to a boil until solvent condenses on glass funnel.
- Touch filter paper to make sure it is moist and hot before filtering.
- Filter quickly and rinse with a small amount of hot solvent.
- If excess compound remains on filter paper, then allow system to boil (reflux) for 10-20 minutes in order to dissolve all of your compound. [Note: you may have insoluble impurities]
- **Safety** - remember that hot glass looks identical to cold glass!

Recrystallization Procedure - Cont.

2. Let the solution cool slowly after hot filtration:
   - slow cooling ensures that impurities are not trapped in the crystal lattice
3. Cool in an ice bath after crystals begin to form and the solution has reached room temperature:
   - if you place the flask in the ice before it has reached room temperature, then you will likely get small crystals with entrapped impurities
4. After cooling in the ice bath, perform a vacuum filtration to recover your product.

Vacuum Filtration Apparatus



Vacuum Filtration Procedure

- Assemble apparatus making sure that the filter flask is securely clamped over the base of the ring-stand.
- Turn vacuum on and wet the filter paper with clean solvent.
- Pour crystals from Erlenmeyer flask onto filter paper as rapidly as possible. [Note: swirl the flask while pouring to maximize delivery of the solid]
- Rinse crystals with cold solvent to wash away any of the mother liquor that remains. [recall that the mother liquor contains the soluble impurities]
- Suck air through the Buchner funnel to dry the crystals. [Note: crystals are dry when the Buchner funnel is no longer cold and the filter paper is dry]

What should I do if I do not get crystals?

(a) Make sure that the solvent has reached room temperature since crystals may not form if the solution is too hot.

(b) Scratch the inside of the flask with a glass rod. [Note: crystallization is a kinetic event, so scratching may provide a new surface that induces crystal formation]

(c) “Seed” the solution with some pure crystals from another student. [Note: seeding provides surface area for more crystals to form]

(d) Remove excess solvent by evaporation (i.e. boil some off).

(e) As a last resort cool in an ice bath. [Note: rapid crystallization may entrap impurities in the crystal lattice]

What should I do if I get an oil that separates out from solution?

(a) Stir the solution vigorously while heating.

(b) Add more solvent.

(c) Add a different solvent that the product is more soluble in (e.g. mixed solvent recrystallization).

What should I do if I have colored impurities?

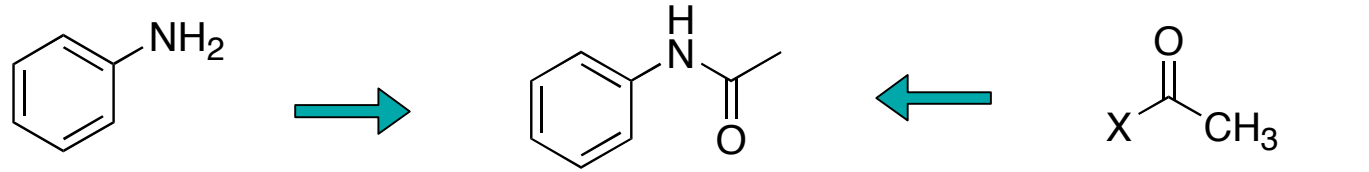
(a) Add a small amount of activated carbon, also known as charcoal or Norite. [**Safety Note:** Be careful when adding charcoal as the solution may boil over. To prevent this, remove the flask from the heat source and place on counter for 30 seconds before adding charcoal]

(b) Remove black carbon by regular filtration or hot filtration.

(c) Allow solution to slowly cool in order to form crystals.

Procedural Details

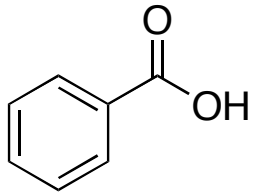
Part B - 2. Recrystallization of Acetanilide



Aniline Acetanilide Acetyl Group

- use water as the recrystallization solvent

Part B - 5. Mixed recrystallization of Benzoic Acid



Benzoic Acid

- perform a mixed solvent recrystallization with ethanol and water.
- use ~ 8 ml ethanol to start with

Mixed Solvent Recrystallizations

(a) Perform when you cannot find a single solvent system. For example, the compound is too soluble in ethanol but too insoluble in water.

(b) Dissolve in minimal amount of hot ethanol with stirring.

(c) Add water slowly (e.g. dropwise) until solution remains cloudy for a few seconds before returning to a clear solution.

(d) Turn off stirring and allow solution to slowly cool.

(e) Be careful not to let the first solvent evaporate off while adding second solvent.

Melting Point Determinations

The purity of our compounds will be measured by melting point.

Compare your m.p. to the literature value, which can be found in MSDS forms or in Aldrich or Acros catalogs.

Always record a range of temperatures, where it starts melting and where it is completely melted.

Impurities lower the m.p. because they disrupt the crystal packing and require less energy to break up (i.e melt) the crystals.

The TA's will demonstrate the use of the m.p. apparatus in the labs.