CH 361/CH 361H Lecture

Melting Points,
Recrystallization,
Yields

Sept 29/30, 2015
Identify unknown carboxylic acid

mp, MW, pK\textsubscript{a}, derivative mp

recrystallize

“pure” unk. carboxylic acid
mass: ? g

crude unk. carboxylic acid
mass: ? g

melting point (“mp”)

conc. HCl; filter

decolorize, filter

aq. sol’n of unk. sodium salt + sol. impurities

colored dye(s)
mass: ~ 20 mg

water-soluble imp.

aq. sol’n of unk. sodium salt + sol. impurities

dissolve in water, filter

insoluble impurities
mass: ? g

sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities
total mass: ? g

account for all masses; calculate %recovery
Melting Point Determination

**melting point**: temperature at which solid and liquid are in equilibrium

**melting range**: range of temps. over which a solid sample becomes liquid

**melting point determination serves two purposes:**
1) identity
2) purity

Alq3, tris(8-hydroxyquinolinato)aluminum
Two-component (A & B) phase diagram

**eutectic point**: point on phase diagram that represents particular ratio of 2-component mixture with the lowest melting point

Figure from “Laboratory Techniques in Organic Chemistry, 4th Edition” by Mohrig, Alberg, Hofmeister, Schatz, Hammond
Melting Point Determination – *practical considerations*

**Preparation of sample tube**
- 1 - 2 mm compound
- tightly packed
- never re-use sample tubes

**Rate of temperature increase**
- *first time: fast increase*
- thereafter: 1 - 2 °C/minute
- consult chart for voltage settings

**Melting point standards**
- choose standard with mp +/- 10 °C your sample
- heat standard sample alongside your sample
Melting Point Determination – *practical considerations*

Images downloaded from: http://www.csi.edu/ip/physsci/faculty/rex/MPTips.htm
Recrystallization

Why??

need pure compound to conduct analytical tests
very common lab technique

How?

exploit temperature-dependence of solubility

solid, crude sample
(unk. Ar-CO₂H + imp.)

dissolve in minimum vol.
of appropriate solvent

minimal solubility
at room temp.

heat to ~boiling point of solvent

all solids dissolve at high temp.

slowly cool

imp. stay dissolved;
unk. Ar-CO₂H crystallizes

filter

pure crystals of unk. Ar-CO₂H

impurities dissolved in filtrate
(“mother liquor”)
What makes an “appropriate” solvent for recrystallization?

- very low solubility at low temp; very high solubility at high temp
- impurities are soluble at all temps
- gives good recovery (>70%) and significant purification
- does not co-crystallize with compound of interest
- chemically inert

Figure from “Laboratory Techniques in Organic Chemistry, 4th Edition” by Mohrig, Alberg, Hofmeister, Schatz, Hammond
Recrystallization – *practical considerations*

**Progressive approach:**
1) solvent selection on micro-scale (~20 mg)
2) medium batch (~100 – 200 mg)
3) large batch (~3 – 5 g) – also involves hot filtration

**Solvent selection**
- *sample must be completely dry!*
- *careful, detailed observations are crucial!*
- *begin with 20 mg in ~0.1 mL solvent; incrementally add more solvent*
- *if > 1.0 mL solvent required, solvent is not suitable*

**Solvent choices**
- *water*
- *ethanol (CH\(_3\)CH\(_2\)OH)*
- *hexane (CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\))*
- *toluene (methylbenzene)*

**Mixed solvent systems**
- *water/ethanol*
- *hexane/toluene*
Common “pitfalls”:

1) crystals do not form
   - seed crystal
   - “scratching”
   - too much solvent?

2) crystals are of insufficient purity
   - was solution cooled slowly?
   - inappropriate solvent
   - sample “melting” at boiling point of recrystallization solvent

3) low recovery
   - filtrate (mother liquor) contains compound of interest
   - too much solvent?
   - insufficient cooling
Recrystallization

Crystallization that occurs with slow cooling:

1. Initial solution
2. Nucleation begins
3. Crystal growth proceeds
4. Crystal growth stabilizes
5. Crystal growth continues
6. Crystal growth completes

Crystallization that occurs with fast cooling:

1. Initial solution
2. Nucleation occurs rapidly
3. Crystal growth accelerates
4. Crystal growth completes

Images downloaded from:
http://orgchem.colorado.edu/Technique/Procedures/Crystallization/Crystallization.html
Recall the overall scheme:

10.00 g

sodium salt of unknown aromatic carboxylic acid + soluble imp. + insoluble imp.

remove insolubles 3.50 g

decolorize ~ 20 mg

acidify ("crude" acid) 6.00 g

recrystallize ("pure" acid) 4.80 g