Experiment 2: Recrystallization & Melting Point

Part A: Choosing a Solvent
Part B: Purification of Phenacetin

Reading: Mohrig, Hammond & Schatz
Ch. 15 pgs 183-197
Ch. 10 pgs 104-113
Ch. 14 pgs 174-182
Recrystallization

- Most important method for the purification of organic solids

- Separation of compounds based on differences in solubility between the compound of interest and its contaminants

- Basic technique:
  1. dissolve impure sample in an "appropriate" hot solvent
  2. cool solution slowly to induce crystal growth
  3. filter resulting mixture to isolate crystals

- Scale: 5-10 mg
  discovery based research - a new material prepared in a lab
  1,000 kg +
  commercial applications - sugar refining, synthesis of pharmaceutical agents, etc.
Recrystallization

- Molecular selection - based on size, shape, & functionality

Solution

Growing Crystal

molecules deposit on growing surface in orderly manner, excluding those of different size of shape
Recrystallization

- Molecular selection - based on size, shape, & functionality

If deposition occurs too quickly, an impure substance can result.
**Recrystallization Steps**

1. Choose an appropriate solvent
   - compound (solid) should be soluble when solvent is hot
   - compound should be insoluble when solvent is cold
   - may require some trial & error

2. Dissolve impure compound in the **minimum** amount of hot solvent
   - too much solvent & compound may not come out when cool

3. Decolorize solution **if needed** with activated charcoal (Norit)
   - skip this step if no/few colored impurities are present
   - be sure your compound is not supposed to be colored!

4. Filter off any insoluble materials
   - insoluble impurities and/or activated charcoal
   - done while solution is hot
**Recrystallization Steps**

5. **Slowly** cool the resulting solution to induce crystallization
   - first cool to room temperature, then in an ice bath
   - if no crystals form: scratch flask with glass rod or add a seed crystal to the solution
   - these methods provide a nucleation point for crystallization

6. Collect and wash the crystals
   - collection typically by filtration (large quantities)
   - for small quantities can remove solvent with a pipet
   - wash crystals with a small amount of ice cold solvent
   - filtrate ("mother liquor") can be concentrated to get "2nd crop"

7. Dry the crystals thoroughly
   - apply vacuum & continue suction until crystals are dry
   - dry crystals further under vacuum in a side arm test tube
   - can also press solids between two pieces of filter paper
Melting Point

- Melting Point: point of equilibrium between crystalline & liquid states
  point at which a crystal goes from solid to liquid

- Temperature at which a compound melts is typically a range
  
  start: temperature at which first drop of liquid forms  
  end: temperature at which all solid has turned to liquid 
  
  e.g. 82-83°C

- Why do we care about melting point?
  1. Can be used to help identify substances  
     compare mp of unknown substance with that of known substance  
     take a "mixed" melting point  
  2. Is an indicator of purity  
     pure samples have narrow mp ranges (0.5 - 2 °C)  
     impure samples melt over a broader range (>2°C) & are depressed
Factors that Influence Melting Point

Factors that influence melting point temperatures:

1. Intermolecular forces
   a. Van der Waals interactions
      very weak
   b. dipole-dipole interactions
      result from polarization of bonds
   c. hydrogen bonding
      compounds having O-H or N-H bonds
   d. ionic forces
      very strong

2. Shape
Factors that Influence Melting Point

- strength & nature of intermolecular interactions impact melting point temperature
  
  For melting to occur, surface molecules must have enough energy to break free. Stronger intermolecular interactions = more energy required for molecules to "escape". Translates to a higher mp.

- structural features that influence how molecules pack together impact melting point temperature

  symmetrical compounds typically have higher melting points
  features that disrupt crystal lattice lower melting point
Melting Point as an Indicator of Purity

• In a pure sample, all surface molecules need the same energy to escape. leads to a narrow melting point range.

![Diagram: Pure sample melting at a single temperature]

• In an impure sample, intermolecular forces are disrupted in the region of the impurity. Less energy thus required for surface molecules to break free. crystal begins to liquefy at a lower temperature

![Diagram: Impure sample melting at a range of temperatures]

• Still some regions without impurities. Additional energy required for surface molecules in these regions to break free. end result is that melting point range is broadened
Next Week

Experiment 2: Recrystallization & Melting Point

A. Choosing a Solvent
   identify an appropriate solvent for the recrystallization of phenacetin

B. Purification of Phenacetin
   purify the impure solid
   evaluate success by melting point & TLC

   Come prepared. You will get only one sample of phenacetin

DUE: Thin Layer Chromatography Lab Report (exp 1)

Lab Reports are due at the beginning of your regular lab session
Experimental Details - Part A

A. Choosing a Solvent

- prepare a hot water bath
  begin heating as soon as you arrive in lab

- put a spatual tip of the impure compound into a small test tube
  no need to get an accurate mass

- to the 1st tube, add 0.5-1mL of one of the solvents to be tested
  10-20 drops (1 drop = ca. 0.05mL)

- evaluate behavior: upon addition of solvent, when hot, when cold
  if compound dissolves upon addition, no need to go further
  if solids remain, heat in hot water bath to near boiling
  Do NOT boil all your solvent away!
  if solids dissolve upon warming, cool in an ice bath (= ice/water bath)

- repeat using other solvents

- identify the best solvent for recrystallization
Finding a Recrystallization Solvent

"Good" recrystallization solvent

"Poor" recrystallization solvent

or
Experimental Details - Part B

B. Purification of Phenacetin

- dissolve impure compound in hot solvent
  get an exact mass (not necessarily 1.00g)
  always use an Erlenmeyer flask
  use a boiling stick (prevents "bumping")
  be sure the solvent is hot before adding more
  use the minimum hot solvent (+ ca. 1mL)

- no decolorization is needed this week

- once solids dissolve, cool slowly to room temperature; then in an ice bath
  may need to tap/scratch flask w/glass rod to initiate crystal formation

- collect crystals by vacuum filtration; wash with ice cold solvent; dry

- analyze purity by mp and TLC
  can do in any order, BUT:
  be sure your compound is dry before taking a melting point

- submit recrystallized product to your TA
Some **Pointers**: Recrystallization

- Don't get impatient; cool your solution SLOWLY!
  - crystals will be bigger (and thus easier to isolate)
  - crystals will be more pure

- Don't throw anything away!
  - if it's in there, we can get it back

- Have you added too much solvent?
  - how do you know?
    - no crystals form on cooling, even after the flask is scratched
  - what should you do?
    - concentrate the solution slightly then cool again
    - no need to evaporate to dryness
**Technique: Vacuum Filtration**

method of choice for collecting organic solids

- Set up as shown at right
  - clamp the flask securely!
- Turn on vacuum (or water aspirator)
- Swirl flask containing crystals
- Quickly pour mixture into funnel
- Wash crystals with *ice cold* solvent
- Scrape crystal until "dry"
- Disconnect vacuum line
- Turn off vacuum
- Dry crystals further as needed

order is important!!
Technique: Drying the Crystals Further

- Assemble as shown at right
  clamp the test tube securely!
- Attach vacuum
- Continue until sample is dry
- Ideally, dry the entire sample
to get an accurate % recovery/% yield
- If time is at a premium, REMEMBER:
dry a small amount of sample(e.g. for mp)

[Diagram of a side arm test tube with a stopper at the top, connected to a vacuum source, and a sample at the bottom]
Technique: Melting Point

- Prepare sample
- Place loaded capillary in Mel-Temp apparatus (closed end down!)
- Turn on the unit ("3" is a good starting point)
- Heat slowly through the melting point range (~ 1°C per minute)
- Observe carefully - record temp at first sign of moisture; then again as soon as all solid has melted this is your mp range
- Turn off Mel-Temp to cool
- Discard your sample (glass waste)
- Repeat if time permits
Melting Point Sample Preparation

• Obtain a melting point capillary tube
• Place press open end of capillary into sample
  - sample on watch glass, filter paper, or in vial
  - forces sample into the capillary
  - not too much! 1-3 mm is fine
• Invert capillary & tap closed end gently on benchtop to compact sample
  - can also drop through glass or plastic tube
• Proceed with melting point
Some Pointers: Melting Point

- Dry your sample thoroughly
  residual water/solvent is an impurity!

- Don't heat the sample too quickly
  likely to overshoot true mp range

- Don't overfill the capillary
  results in uneven heating

- Pack sample well in capillary tube
  loose sample will also heat unevenly

- Never remelt a sample
  heating may cause a chemical change!

- If the mp of your sample is unknown, first do a rapid, preliminary run
  gets you in the ball park; cool MelTemp ca. 20°C below prelim mp
  take 2nd reading (slow) to get an accurate mp value
Writing the Lab Report: General

Parts of the Report (see pg 9 of the lab manual!)

A. Title Page
B. Purpose
C. Results & Discussion
D. Conclusion
E. Appendices
   Appendix A: Calculations
   Appendix B: Spectra
   Appendix C: Answers to Questions
   Appendix D: Notebook Pages (attached by TA)
Writing the Lab Report: General

Parts of the Report

A. Title Page
   • title
   • experiment #
   • identifying information (at lower right) - your name, TA, section, date

B. Purpose
   • what is the experiment about? what will you learn?
     technique vs. synthesis
   • can be the same as that written for your notebook
   • be sure to cover all aspects of the experiment
   • include a balanced chemical reaction for synthesis experiments
   • don't go overboard (1-2 sentences)
   • A purpose is not a statement of what you did, rather it explains why you are doing the experiment (e.g. to learn ...; to prepare ...).
Writing the Lab Report: General

C. Results & Discussion

• present ➔ interpret ➔ draw conclusions
• be organized! present your data in Tables divide the discussion into parts
• address all areas identified in "Writing the Report" (at end of each Expt)
• explain yourself clearly

• briefly explain what you did; do not include experimental detail!
• briefly state relevant theoretical principles (what do you expect to see?)
• summarize your results; DO: use tables; DON'T: include raw data no drawings, no measurements, no calculations, etc.
• draw specific conclusions based on the results you obtained use all the information at your disposal
do your results agree or disagree with your expectations?
  what do you expect?
  if your results do not agree, offer an explanation
"human error" is not an appropriate explanation
Writing the Lab Report: General

D. Conclusions
   • briefly summarize conclusions reached in Results & Discussion
   • DO: relate your results back to your purpose
   • DO NOT: repeat all the discussion talking points

E. Appendices - You may not have material for each appendix every time
   • Appendix A: Calculations
     - show one example of every calculation that you did
     - include the equation used as well as the actual numbers
     - don't forget the units!
     - additional info needed for synthetic experiments (see lab manual)
   • Appendix B: Spectra (IR spectra, GC trace, etc.)
   • Appendix C: Answers to assigned questions
   • Appendix D: Experimental (your notebook pages)
     - attached by your TA after your report is submitted
Writing the Lab Report: General

Format

• Follow the instructions carefully!
  see the "Lab Report" section (pg. 9)
  see instructions found at end of each experiment

• Reports must be typed and double spaced with 1" margins
  use 12 pt font ➔ Times or Arial

• Schemes & Figures may be neatly hand drawn

• Five page limit
  does not include title page or appendices
  pages in excess of 5 will not be graded

• A general template is available on the course website
Writing the Lab Report: General

→ Results

• Experimental results will be graded as part of your report
  a small component of your grade

• It's more important to accurately report & discuss the results you obtain
  than to get the "right" answer

• Be sure the data you report reflects your actual experimental findings

• Be sure your conclusions reflect your data.
Writing the Lab Report: Thin Layer Chromatography

➤ **Purpose**

*poor:* to learn about TLC

*better:* to understand the factors that influence Rf values (list?) and to use TLC to identify the components of commercial food dyes

➤ **Results & Discussion**

- divide the discussion into 4 parts (one for each section)
- for each part: report your $R_f$ values in a Table
  
  *DO NOT:* discuss the procedure or include raw data!
  
  *DO NOT:* show calculations or draw your tlc plate here!
  
- discuss your results, for example:

  **Part A:**

  discuss relationship between $R_f$ and length of TLC plate
  
  what do you expect to see? should the $R_f$ change?
  
  must answer this question before you analyze your data
  
  what did you actually observe? report you actual findings
  
  do your results agree with your expectations? yes or no
  
  why or why not? be specific
  
  if needed, identify possible sources of error
Writing the Lab Report: Thin Layer Chromatography

Results & Discussion (cont.)

Part C:

discuss how the presence of different functional groups impact \( R_f \)
(why do some compounds move further up the plate than others?)

look up the compound structures

consider what factors influence movement on a TLC plate

solvent polarity

intermolecular forces

(H-bonding, dipole-dipole, coordination, Van der Waals)

correlate compound structure with these influences to explain differences in \( R_f \) values

identify any results that do not meet your expectations (explain)

identify possible sources of error, if needed


**Writing the Lab Report: Thin Layer Chromatography**

→ **Conclusion**
- based on what you actually found, rather than on what you think you should have found
- should be brief (2-3 sentences)
- relate back to purpose

→ **Appendices**
- Appendix A: Calculations
  
  only need to show one Rf calculation
  complete with the equation & appropriate units

- Appendix C: Answers to Questions
  
  post-lab questions from the website (Course Materials/Questions)

- Appendix D: Experimental
  
  notebook pages appended by your TA