Experiment V-D: Extraction

Background Reading

Zanger, M. and McKee, J.R. Small Scale Syntheses.
pp 26 (see C1) and 28-30 (extraction and drying agents).
Zubrick, J.W. The Organic Chem Lab Survival Manual.
Chapter 15 (extraction and washing).

Key Words

extraction, immiscible, phase, emulsion, solubility

Experimental Data

- For your procedure section, make a flow diagram of the experiment showing each phase involved and the compound(s) that the phases contain. Show separate branches for each phase, that is, split diagram into two lines whenever a separation is made. Incorporate the procedure steps into the diagram. (This is similar to qualitative analysis flowcharts in your general chem text and lab manual.)
- For the reactions section, show how the organic acid is converted into its aqueous conjugate base anion with NaOH. Then, show how the dissolved ion is converted back into a solid with HCl. Include full skeletal structures and phase subscripts for each reaction.
- Determine mass/mass recovery % for each of the solids by dividing each isolated mass by its initial mass.
- Record the experimental melting or sublimation ranges for both of the solids, and compare with tabulated values as well.

Substances

2 g mixture (benzoic acid and naphthalene)
20 mL CH_2Cl_2 (dichloromethane)
45 mL 3 M $NaOH_{(aq)}$
15 mL concentrated (18 M) $HCl_{(aq)}$
2 g anhydrous $Na_2SO_{4(s)}$

Apparatus

Items in kit
125-mL separatory funnel with glass stopper
50-mL round-bottom flask

Items not in kit
50-mL and 125-ml Erlenmeyer flasks (one each)
size #1 rubber stopper
55-mm filter paper and Büchner funnel
250-mL vacuum flask
watch glass
capillary tubes
Rotovap

Procedure

1. Weigh 1 g each of benzoic acid and naphthalene. Record the exact masses. Combine in a 125-mL Erlenmeyer flask.

2. Add 20 mL CH_2Cl_2 to the mixture, and stir until the solid is completely dissolved.

3. Place a 125-mL separatory funnel in a ring on a stand. Pour the organic solution into the funnel. Ensure stopcock on bottom of funnel is completely closed before filling or liquid will drain out of the funnel.

4. Add 15 mL of 3 M NaOH to the organic solution in the separatory funnel. Be sure that you use the 3 M NaOH solution, and not the 20% NaOH solution, as concentrated base will cause a precipitate to form in the separatory funnel.

5. Shake the separatory funnel for 15 to 30 seconds with frequent venting per the instructor's demonstration. Vent the separatory funnel by slowly and carefully opening the stopcock while holding the funnel upside-down. Be sure to close the stopcock before shaking the funnel again. The shaking process maximizes the contact between the two solutions, which optimizes the basification and aqueous extraction of the dissolved acid.

   Caution - Pressure typically builds inside separatory funnel when shaken! Be sure to vent the separatory funnel frequently while shaking! Do not point the vent towards yourself or any other individual!

6. Place the separatory funnel onto the ring stand, and allow the two liquid layers to separate. An emulsified boundary layer between the two liquids may be visible. If this emulsion is present, discard it in the organic waste container during the separation in the next step.

7. Look up the density of dichloromethane and compare it with that of water. The solution with the higher density is normally the bottom layer inside the funnel. Add up to 1 ml of DI water to the layer that you expect to be aqueous (and basic). It should dissolve fully.

   Drain the bottom layer form the separatory funnel into a 50-mL Erlenmeyer flask. Be sure to remove the stopper from the top of the separatory funnel before opening the stopcock on the bottom to prevent a vapor lock (vacuum) from being created. Label the flask containing the organic solution. Always be sure that you know what your solutions are while you are working.

   Drain the aqueous layer into a 125-mL Erlenmeyer flask labeled as Aqueous. Return the organic layer to the separatory funnel.

   Do not discard any fluid yet. Once discarded with the waste, it cannot be retrieved.

8. Wash the organic solution in the separatory funnel with an additional 15 mL of 3 M NaOH, then separate the layers. Add that aqueous layer to the Aqueous flask, while the organic phase remains in the separatory funnel again. Repeat with a third 15 mL portion of 3 M NaOH, and add the aqueous layer to the Aqueous flask again.

   Refer to **Caution** notes in step 5.

9. Place the Aqueous flask in an ice-water bath. Slowly and carefully add 10 to 15 mL of concentrated HCl with constant stirring until the mixture is acidic to pH paper. Be sure that you use concentrated HCl, not the 3 M HCl solution, or precipitation may not occur.

   Continue to cool the flask to crystallize the benzoic acid. Collect product crystals by vacuum filtration using a weighed 55-mm filter paper in a Büchner funnel with a 250-mL vacuum flask. Rinse the flask with the filtrate and use a spatula to recover as much of the solid from the flask as possible.

   Dry the crystals on a weighed watch glass in the oven at 100 ^{o}C for 5 minutes. Weigh the dried benzoic acid product. Then, obtain the melting point/range.

   Caution – Concentrated HCl solutions and vapors are corrosive and cause acid burns.
   Use gloves and avoid all contact with skin, eyes, and nose.
   Do not remove the source bottle of concentrated acid from the fume hood.

10. Drain the organic phase from the separatory funnel into its labeled flask. If water is visible and floating on top of the solution, then remove it with a pipette and discard it in the waste container.

11. Add 2 to 3 g of anhydrous $Na_2SO_{4(s)}$ to the organic phase in the flask. Place a #1 stopper on the flask and let the flask stand for 15 minutes to remove water. Add another 1 g of drying agent and let flask stand for 5 more minutes if the hydrated solid appears slimy or forms clumps.

12. Weigh a 50-mL round-bottom flask. You may place the flask on a cork ring to weigh it after the cork ring has been tared. Decant the organic liquid phase without the solid into the round-bottom flask. Use a rotovap with the instructor's assistance to remove the solvent.

    If water remains in the flask after removing the organic liquid with the rotovap, then place the flask in an oven at 100 ^{o}C for 5 minutes.

    If rotovap is unavailable, transfer solution to a weighed watch glass in a fume hood. Allow the solvent to evaporate completely to obtain the naphthalene crystals. Do not leave naphthalene on watch glass overnight. It can sublime.

    Weigh the dried naphthalene product in flask, and then obtain melting point/range.

Waste Disposal

Place all solutions, crystals, and used drying agents in the appropriately-labeled waste container(s). Place used filter paper in a trash receptacle after all of the crystals have been scraped off of it. Place used capillary tubes in the broken glass container. Lab techs will place collected solvent from the rotovap in a separate waste container.

Post-Lab Q's

1. Describe the chemical process that happens to the organic acid molecules when they are extracted in the aqueous phase with NaOH. Then, describe the chemical process that happens to that basic aqueous solution when HCl is added.

2. Describe two physical properties that make water a good choice as an extraction solvent, and the property that determines whether its layer is above or below the organic layer.

3. What is the difference between isolation and purification of compounds? Which describes extraction and which describes recrystallization?

4. What happens if the layers are not separated effectively when draining the separatory funnel? How are the products' melting points affected?

5. What physical processes could occur to product crystals that are dried in an oven? Refer to the drying steps in the procedure.