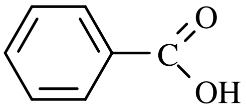
Extraction

Concept goals: Correlation of structure, polarity, acid and base characteristics and separation efficiency, role of extraction in separation rather than purification of compounds.

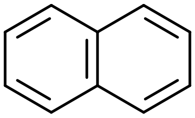
Operational goal: Develop the skills to perform an extraction effectively, including the use of appropriate solvents, ability to prevent the formation of an emulsion layer, removing residual water from the organic layer and evaporating the organic solvent.

Introduction

It is often necessary to separate an organic compound from a mixture of compounds. These mixtures are often derived from natural sources or are the result of synthetic reactions. Extraction is a technique that selectively dissolves one or more of a mixture of compounds into an appropriate solvent. In this experiment you will use the common technique of *liquid-liquid extraction* to separate and purify benzoic acid and naphthalene from a mixture to the two.



Benzoic Acid



Naphthalene

A typical liquid-liquid extraction involves partitioning a mixture of compounds between two immiscible solvents. Dissolving the mixture in the first solvent and then adding a second immiscible solvent that will selectively dissolve one of the components of the mixture does this. Since the solvents used are immiscible, the two layers are then vigorously mixed to allow the transfer of a dissolved compound from one layer to another. Once the transfer is complete, the two layers are again allowed to form. Separating the two layers then completes the extraction of one compound from the mixture.

A useful variation of liquid-liquid extraction is acid-base extraction. In this technique, a mixture of compounds with different acidities can be separated if an appropriately basic or acidic aqueous solution is used. In the case of a mixture of two acidic components (with largely different pK_a values), a basic solution will interact preferentially with the strongly acidic component to deprotonate it, so it becomes an anion. In general, anionic compounds are more soluble in water than in organic solvents, so the conjugate base of the strongly acidic component is extracted into the aqueous layer. In order to recover crystals for the strongly acidic component, the aqueous anionic conjugate base must be re-protonated to allow it to crystallize from cold acidic water in its neutral form. The weakly acidic component remains behind in the organic layer. In order to recover crystals from an organic solution, the solvent must be removed by evaporation.

The purpose of this laboratory is to separate a binary solid mixture by extraction, washing, solvent removal via evaporation, and crystallization into its pure components. Purity will be tested by thin layer chromatography and/or melting point determination.

Reading and Pre-Lab Assignments

Read the following sections in *The Organic Chem Lab Survival Manual: A Student's Guide to Techniques* by James W. Zubrick, John Wiley & Sons, Inc.

Topics and Concepts to consider:

- Drying Agents
  - What does this do to the organic layer?
  - Can you "dry" the aqueous layer?
- Extraction and Washing
  - What is the difference?
- Theory of Extraction
  - Why do some compounds dissolve better in water and others in organic solvents?
  - How can we use acid-base extraction to separate the components of a mixture with different pKa's? Why do you need to know the densities of your solvents?

Using the handbooks (see Zubrick), look up the data you will need for this experiment. This includes the melting point and solubilities (in water and ether) of benzoic acid and naphthalene as well as the boiling point, solubility in water, and density of diethyl ether or *tert*-butyl methyl ether.

Before you come to the laboratory, do the Pre-Lab assignments for this laboratory as assigned by your instructor.

Prepare your laboratory notebook as required by your instructor.

Procedure

Weigh out 2.0 g of a 50:50 mixture of benzoic acid and naphthalene (record the exact mass in your notebook) into a 50 mL Erlenmeyer flask. Add 20 mL of *tert*-butyl methyl ether and swirl to dissolve. Save a small portion (about 0.5 mL) of this dissolved mixture for TLC analysis (Plate B, spot 1). Transfer the solution to a separatory funnel using a little ether to rinse the flask. Add 10 mL of a 1 M sodium hydroxide solution to the funnel.

Why did you do this? What chemistry is occurring?

Stopper the funnel and carefully mix the contents. Vent the funnel and then shake the mixture thoroughly, venting often. Allow the layers to separate completely, remove the stopper from the funnel, and then draw off the lower layer into a labeled 50 mL Erlenmeyer flask. At this point, identify the layers in the flask and the in the funnel as the "aqueous layer" and "ether layer." (See "Dutch Uncle Advice", Zubrick.) Reserve a small portion of the ether layer for TLC analysis.

At this point, what compounds are in each layer?

Extract the ether layer twice more with 5 mL portions of fresh 1M sodium hydroxide solution. The rationale behind extracting three times with smaller volumes, rather than using the full 20 mL in a single extraction, is that a larger fraction of the compound being extracted will move into the aqueous phase over multiple extractions. Your instructor may demonstrate this principle as part of the pre-lab discussion. Add these aqueous extracts to the original aqueous extract and set aside.

Why can you combine all the aqueous extracts?

Wash the ether layer with 10 mL of a saturated aqueous sodium chloride solution. Combine this aqueous wash layer with the previous aqueous extraction layers.

What does sodium chloride solution do to the aqueous layer?

Acidify the aqueous extracts by addition of 3*M* hydrochloric acid while stirring with a glass stirring rod (add the acid dropwise towards the end of the addition). It should take 6-7 mL of hydrochloric acid (if you have 20 mL of 1M base!) Periodically test the pH by transferring a drop of the solution onto a small piece of litmus paper on a watch glass. Benzoic acid is only sparingly soluble in cold acidic water.

How acidic is too acidic? Does it matter? Why are you acidifying in the first place?

Once the solution is acidic, place the flask in an ice-water bath for 5 minutes to complete the crystallization. Collect the crystals of benzoic acid by vacuum filtration using a small Hirsch funnel. Let the crystals dry in air. When your sample is dry, measure the mass and calculate your percent recovery. Take a melting point and assess its purity by comparing the measured melting point with the literature value. Reserve a small sample of your benzoic acid product crystals for TLC analysis.

Transfer the ether layer into a 50 mL Erlenmeyer flask, taking care not to transfer any residual water. Add 2 g of anhydrous calcium chloride to the flask and set it aside. (Note: If you have excess water mixed with the ether solution you may need to add additional anhydrous calcium chloride.)

Why do you use a drying agent here?

Decant (pour off) the ether solution into a tared (previously weighed) 50 mL Erlenmeyer flask, taking care to leave all of the drying agent behind. Wash the flask and drying agent with a little ether and add this ether wash to the ether in the tared flask. Save a small sample of the ether liquid mixture for TLC analysis.

You have two options to retrieve the product from your ether (organic) layer by evaporative methods.

Option 1:

Place a boiling stick in the flask and evaporate the ether by placing the flask on a hot plate in your fume hood. Keep your hot plate just warm enough to boil the ether. If your hot plate is too hot you may evaporate or char the naphthalene. When the ether has completely evaporated, a small amount of oil will remain. Remove the flask from the hot plate (too much heat causes naphthalene to sublime) and allow it to cool to room temperature and crystallize. The naphthalene should be nearly colorless.

Option 2:
A superior procedure for recovering the naphthalene from the ether layer uses a rotary evaporator**.** This device is often used in research laboratories to quickly remove low boiling solvents from reaction mixtures by heating the mixture under a vacuum in a rapidly rotating round-bottomed flask. As the flask rotates, a thin layer of volatile solvent evaporates and is collected in a condenser. If your instructor chooses to use this device, Decant your ether solution into a tared (previously weighed) 100 mL round-bottomed flask and follow your instructors specific directions for using the rotary evaporator.

If necessary, you can recrystallize the naphthalene from methanol and water. Measure the mass and calculate your percent recovery. Take a melting point and assess its purity by comparing the measured melting point with the literature value. Save a small sample of the naphthalene crystals for TLC analysis.

Determining the purity of the separated components: TLC

You need 4 mL of developing solvent to run a TLC. Prepare the developing solvent using 9 parts hexane: 1 part ethyl acetate. Two TLCs should be run as done previously. Visualize the spots using the short-wave UV lamp. The first plate will provide information on the identity and purity of your product. In the second plate, you will be able to see the purity of the naphthalene fraction changes over the course of the extraction.

Plate A:
Spot 1: A sample of the impure mixture on first being dissolved in ether
Spot 2: The sample of liquid mixture taken before the rotary evaporation/or re-crystallization.
Spot 3: A few crystals, ~0.001g/mL, benzoic acid product in 1 mL ethyl acetate.
Spot 4: A few crystals of naphthalene product in 1 mL ethyl acetate.

Plate B:
Spot 1: A sample of the impure mixture on first being dissolved in ether.
Spot 2: The ether layer after a single extraction.
Spot 3: The ether layer just prior to evaporation.
Spot 4: A few crystals of naphthalene product in 1 mL ethyl acetate.

Plate A will provide information on the effectiveness of your extraction overall. Plate B demonstrates the impact of multiple extractions. Show the developed chromatograms to your instructor. Discuss the results of the TLC and/or the melting point and the percent recovery of each component in your lab report.

Results, Discussion and Conclusion

Write your results, discussion of results and your conclusion. Complete any post-lab questions.

Abstract

This part should be filled in after the completion of the experiment and analysis of all data. <u>When submitting the report, the abstract should appear at the beginning of the report.</u>

Report

Adhere to the format required by your instructor and submit the report on time.

Summary

1. Extraction is a separation technique used to separate two or more solids or liquids by utilizing the difference in their solubility properties.
2. Solid compounds must first be dissolved in a suitable solvent in order to perform an extraction.
3. Given an impure sample and the solubility properties of each component in the mixture, you should be able to figure out how to separate the mixture using extraction techniques.
4. You should be able to assess the effectiveness of the separation using melting points and TLC.

Questions

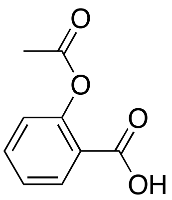
Your instructor may assign these questions as pre- or post-laboratory assignments.

1. It is often useful to prepare a flow chart to be better able to understand all the steps of an extraction. One example is included in the introductory chapter on keeping a notebook. Prepare a similar flow chart for this experiment. Be sure to include appropriate structures of the compounds and explicitly state what chemicals are present at each step.
2. Write balanced chemical equations for the reactions of a) sodium hydroxide with benzoic acid, b) hydrochloric acid with sodium hydroxide and c) hydrochloric acid with sodium benzoate.
3. What is the difference between extraction and washing?
4. What visible evidence of reaction will you see when you acidify the aqueous layer?
5. What is the significance of polarity in separating naphthalene and benzoic acid? Give one example.
6. Explain what would happen to the percent recovery of naphthalene if the calcium chloride step was omitted.
7. When doing TLC, if you only saw one spot for naphthalene and one spot for benzoic acid, would you be sure that your products are pure? Why or why not?
8. Why was melting point determination performed? What advantage does melting point determination have over TLC?
9. Explain how each of the following experimental errors would have affected your results.
   A. During the sodium hydroxide extraction, you failed to mix the organic and aqueous layers thoroughly.
   B. Instead of adding NaOH to the methyl tert-butyl ether solution, you added HCl and did the extraction.
   C. Instead of checking for acidity using pH paper, you neutralized the solution to pH= 7.0 using litmus paper.

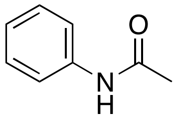
D. Instead of acidifying the aqueous extract with 3M HCl, you added 1M NaOH to the aqueous extract.

10. You are given a mixture of sugar, aspirin and Acetanilide. All three are white powders. These substances have the following solubility characteristics.

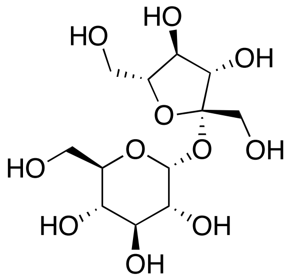
I. Sugar is not soluble in the organic solvent MTBE (methyl tert-butyl ether) but is soluble in water.
II. Aspirin is soluble in MTBE but relatively insoluble in water.
III. Acetanilide is soluble in MTBE but insoluble in water.
IV. Between acetanilide and aspirin, one reacts with NaOH to form a water-soluble compound. The other compound is unreactive towards NaOH.



Aspirin



Acetanilide



Sugar

Using the above information and what you learnt from the extraction lab, draw a flow chart or explain clearly showing how to separate these three components from the given mixture. You have to clearly show how you can isolate each component for otherwise you will not get full credit for this question.