Extraction

OBJECTIVE

In this experiment, you will separate the components of a commercial headache powder via an extractive process. This separation will be accomplished by taking advantage of the fact that each component contains different functional groups which will react differently when treated with a specific reagent.

INTRODUCTION

Extraction is a widely used method for the separation of a substance from a mixture. It involves the removal of a component of a mixture by contact with a second phase. Solid-liquid and liquid-liquid extractions are commonly performed by batch and continuous processes. The removal of caffeine from coffee beans with dichloromethane is an example of a solid liquid extraction. Crystal violet may be removed from a water solution by liquid-liquid extraction with n-amyl alcohol (1-pentanol). Other common applications of liquid-liquid extractions involve:

1 Isolation of organic reaction products

2 Removal of acid, base, and salt impurities

3 Removal of organic acids and bases from other organic compounds

Liquid-liquid extractions involve partitioning of a solute, **A**, between two immiscible solvents, **S** and **S'**. This distribution between the two layers may be described by the following relationship.

$$K_p = \frac{\text{concentration of A in S (g/mL)}}{\text{concentration of A in S' (g/mL)}} \tag{1}$$

The KD value is generally > 1; therefore, **S** is the solvent in which **A** has the greatest solubility. The KD may be used to evaluate the effectiveness of an extracting solvent and to plan an extraction. An extracting solvent should be immiscible, have a favorable KD, be nonreactive (with the exception of aqueous solutions of acids and bases) and be easily separated from solute. Some commercial headache remedies contain aspirin as well as caffeine, salicylamide and/or acetaminophen.

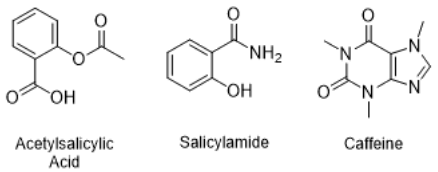

Figure 1

BC Powder has recently changed its formula, but the old formulation contained acetylsalicylic acid, salicylamide, and caffeine. You will be separating one of these three components in this experiment. Look up the structures of the three components.

Acetylsalicylic acid, Aspirin, is an organic acid; therefore, it is soluble in an organic solvent (diethyl ether), but will react with a basic reagent (**:B**) such as sodium hydroxide or sodium bicarbonate to produce the conjugate base of the acid. The conjugate base is a salt and is water soluble; therefore, it is removed from the organic solvent layer. Reacidification of this basic aqueous layer will regenerate the organic acid, which will precipitate from the aqueous solution due to the acid's limited solubility in water.

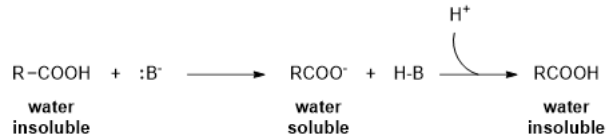

Figure 2

Caffeine is an amine; therefore, it has a basic nitrogen that will react with a proton source such as hydrochloric acid. Reaction with the acid produces the conjugate acid of the amine (an ammonium ion) which is a salt and is water soluble (recall the ammonium ion from General Chemistry). Adding base to the acidic aqueous layer will regenerate the water insoluble amine.

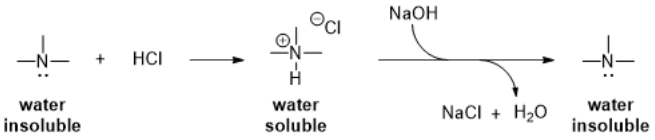

Figure 3

The amide, **salicylamide**, is neither acidic nor basic enough to react; therefore, it will remain soluble in the organic solvent throughout the extraction process.

PROCEDURE

1 Before you start, watch the liquid-liquid extraction video[1].

2 In a 50 mL Erlenmeyer flask, dissolve 1 g of headache powder (the contents of one packet) in 20 mL of diethyl ether. The headache powder contains some binders which are insoluble in ether. All of the powder may not dissolve, but this is not a problem.

3 Make sure the stopcock on the separatory funnel is closed.

4 Pour the solution into the separatory funnel.

5 Use a fresh 5 mL of diethyl ether to transfer the remaining contents of the Erlenmeyer flask to the separatory funnel.

6 Measure approximately 20 mL of a 5% sodium bicarbonate ($NaHCO_3$) solution.

7 Transfer the bicarbonate solution to the separatory funnel.

[1] https://www.youtube.com/watch?v=1YEAB_qHK4Q

8 Stopper the funnel, invert the funnel, and release the pressure by opening the stopcock.

9 Continue extraction by shaking, inverting, and venting until no audible or visible gas emerges (i.e. nothing comes out of the stopcock when releasing pressure).

10 Place the separatory funnel in an iron ring on a ring stand and remove the stopper immediately.

11 Remove the aqueous layer (which is it, top or bottom?) into a labeled beaker. Be careful and slow to dropwise flow as the level of the layers lowers in the funnel. Be sure to leave a drop of the bottom layer in the separatory funnel. This solution contains the conjugate base of acetylsalicylic acid.

12 Obtain 1-2 mL of 6 *M* HCl in a small test tube and a Pasteur pipet.

13 Cool the Sodium Bicarbonate Layer that you just extracted in an ice bath.

14 While still in an ice bath, carefully acidify this solution by slowly adding the 6 *M* HCl dropwise until no additional acetylsaliylic acid solid is produced. Add the acid slowly since CO_2 will be produced and effervescence will occur.

15 Once the solution is acidic, collect the precipitate by vacuum filtration. You can watch a short video that describes the vacuum filtration set up.

- **a** Clamp the filter flask to a ring stand.
- **b** Connect filtration assembly to vacuum.
- **c** Put neoprene seal on the mouth of the flask.
- **d** Put Buchner funnel in the seal.
- **e** Put the filter paper in the funnel.
- **f** With vacuum running, squirt water on the entire surface of the filter paper to seat paper.
- **g** Slowly, pour the solution into the center of the funnel.
- **h** If necessary, transfer the remaining solid from beaker with a spatula.
- **i** For best yield, refilter the filtrate (i.e. the liquid in the filter flask) if it is cloudy.

16 Dry your filtered acetylsalicylic acid.

- **a** Separate paper from funnel with spatula.
- **b** Scrape solid off of paper into a small beaker.
- **c** Dry in oven for ten minutes.

17 Once you have isolated the acetylsalicylic acid, make sure to dispose of the ether layer in the waste container provided. Ask your TA if you have any questions.

Determining the Melting Point

1 You can watch a short video[2] that describes how to determine a melting point using a DigiMelt apparatus.

[2] https://www.youtube.com/watch?v=oKPqXAT0bG8

2 Loading the melting point capillary:

- **a** Place the open end of the capillary tube gently into the substance several times to achieve a sample height of 2 to 3 mm inside the capillary tube.
- **b** The sample is pushed to the bottom of the capillary tube by tapping the bottom against a hard surface via a drop tube.
- **c** Place the capillary tube in the DigiMelt **sealed end down.**
- **d** Load samples from three groups before running the DigiMelt in order to minimize time spent running Melting Points.

3 Following the steps on the front of the instrument (read them carefully), set the starting temp 30°C below the theoretical melting point, the ramp rate at 5°C/min, and the end temp 10°C above the theoretical melting point.

4 To record the start of the melt temperature and the end of melt temperature press the number of the sample as you reach each temperature.

5 Instructions are on the DigiMelt for recalling these values.

IN-LAB QUESTIONS

Please print the worksheet for this lab. You will need this sheet to record your data.

Questions

1 Amount of Acetylsalicylic acid in powder (see box or bulk container) _____

2 Amount of Acetylsalicylic acid recovered _____

3 Percentage Recovery _____

4 Melting Point of Acetylsalicylic Acid _____ (observed)

Melting Point of Acetylsalicylic Acid _____ (lit. reported)

5 A. Which of the compounds in the BC powder is the most acidic? The most basic?

B. Draw the compounds obtained for each step of the extraction in the boxes provided in the experiment in the following flowchart.

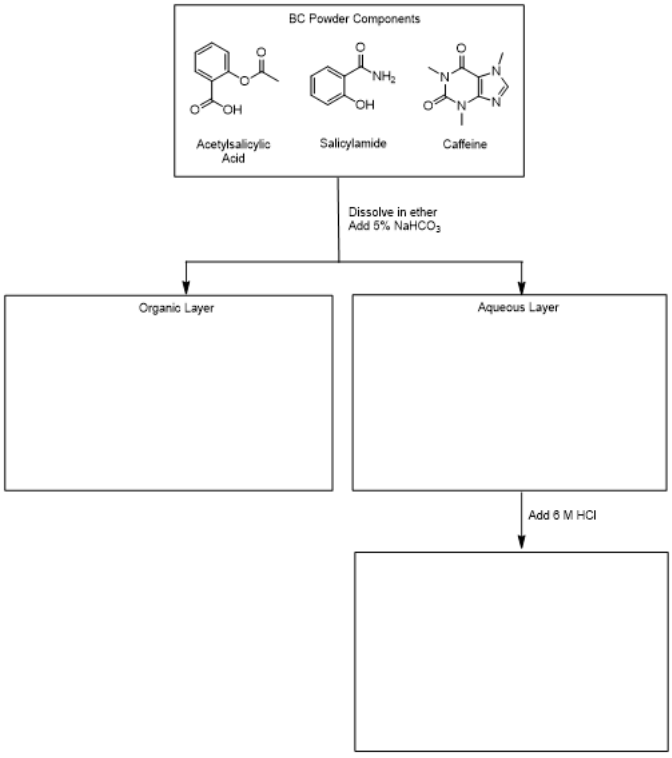

Figure 6

