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 specified 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.

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

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.

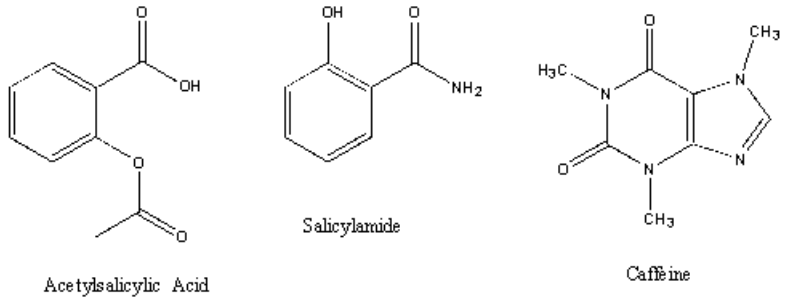

Figure 1

Separating Each Compound

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.

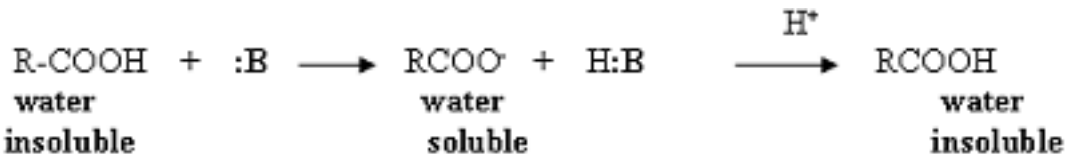

Figure 2

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.

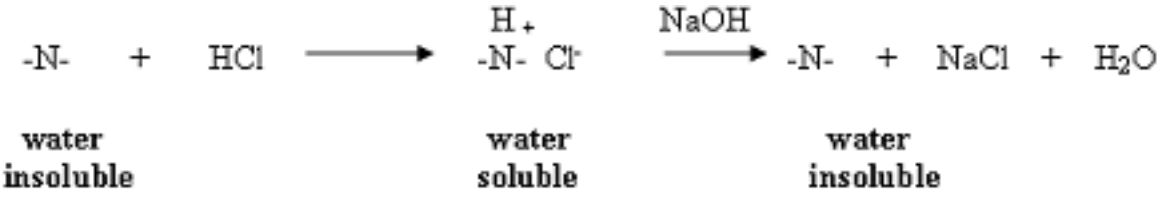

Figure 3

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

One of the most commonly used pieces of equipment in the Organic lab is the Separatory Funnel, or "Sep Funnel". Many reactions are completed by separating an aqueous layer from an organic

layer. Many reactions require that a component be removed by acid-base extraction. The isolation of useful compounds from naturally occurring materials is a common organic process. All of these can be accomplished by means of a 'Sep Funnel'.

As shown below, the Sep Funnel is a pear shaped glass device equipped with a stopcock at the bottom and a stopper to close the top opening. Sep Funnels come in all sizes from about 50 mL to 5 L or larger. **They are all very FRAGILE!**

The Sep Funnel acts like a cocktail shaker. With the stopcock closed, ingredients are added through the top. The stopper is securely placed, and the contents are shaken. While the Sep Funnel is being shaken, the stopper must be held securely in place and the stopcock must be tightly shut. **(Your TA will demonstrate the 'art' of securing the stopper in the palm of your hand while shaking the Sep Funnel.)**

Quite often, the components develop some pressure on being shaken. This pressure must be **carefully** relieved by slowly opening the stopcock while the Sep Funnel is inverted. **Of course, the Sep Funnel must be 'aimed' away from any nearby person in case the pressure is larger than expected!**

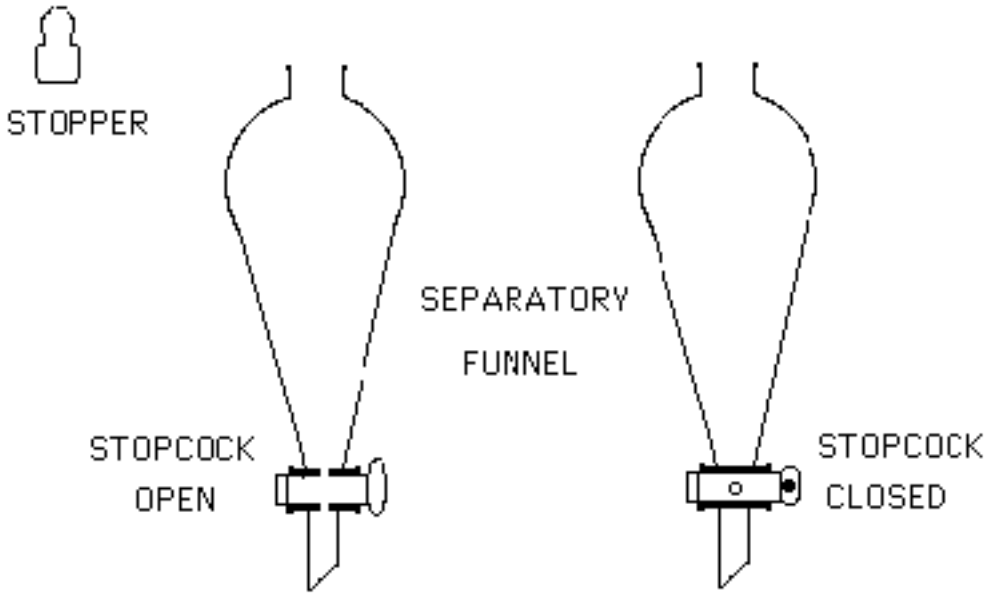

Figure 4

After the Sep Funnel has been shaken a few times and the pressure relieved once or twice, the Sep Funnel is placed upright in an iron ring, and **the stopper is removed.** When the two layers are clearly separated, the lower layer may be carefully drained into an Erlenmeyer flask by slowly opening the stopcock. **CAUTION** - allow the liquid to drain slowly so that the layers remain clearly separated and a vortex does not develop.

If a second extraction is needed, the layer to be extracted is placed in the Sep Funnel and a new portion of the extracting liquid is added, and the shaking, venting, process is repeated. This is commonly encountered during the "work up" of a chemical reaction, when the organic layer is

washed with several different aqueous solutions.

Reminder - the stopcock must be cleaned before and after each use. When not in use the stopcock is left clean and assembled, but **very loose fitting. The plastic will distort if left tightly held in the glass part.** When is use, the stopcock nut must be tightened to keep the stopcock securely held in the glass.

PRE-LAB

1. Brief outline of procedure
2. Reagent data (Aldrich/MSDS) (structure, formula weight, MP or BP, density (if applicable), Hazards) for salicylamide, caffeine, acetylsalicylic acid, diethyl ether, and ethanol
3. Answers to any assigned questions

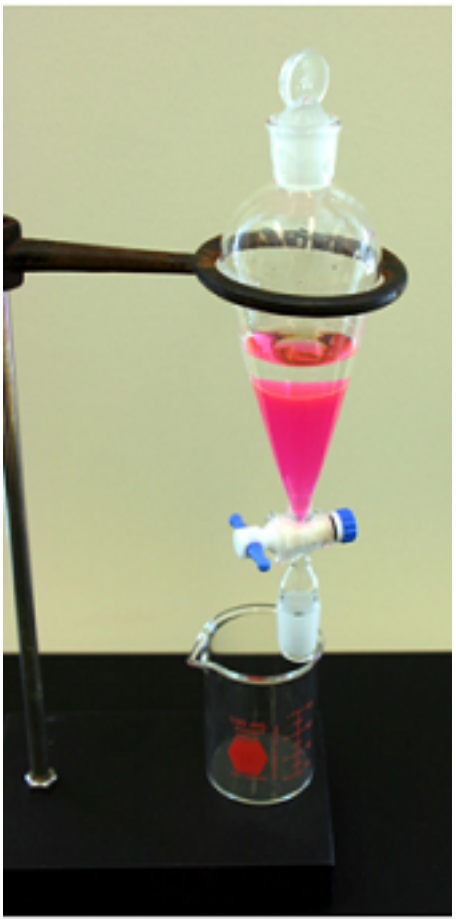

Figure 5

Questions

Question 1: Explain why diethyl ether is a superior solvent to hexane for extracting caf-

feine from an aqueous solution. The structure of caffeine may be found at the beginning of this experiment.

Question 2: When 100 mL of an aqueous solution containing 1.0 g of caffeine is extracted with 10 mL of chloroform at room temperature, 0.5 g of caffeine is transferred to the chloroform layer. Calculate the distribution coefficient of caffeine between chloroform and water at room temperature.

Question 3: At 20°C only 0.24 g of an organic acid "A" dissolves in 100 mL of water, but 2.70 g of the same acid dissolves in 100 mL of ether. Calculate the value of partition coefficient.

Question 4: Why must the stopper be removed from the separatory funnel before the lower layer is removed?

Question 5: The distribution (or partition) coefficient is:

(a) the temperature at which a compound precipitates out of a solution
(b) the ratio of the vapor pressure of a liquid and atmospheric pressure
(c) the ratio of the amount of a compound which is a liquid and a solid at a particular temperature
(d) the ratio of the concentrations of a solute in two solvents at a particular temperature

Question 6: Under neutral conditions, a carboxylic acid is soluble in:

(a) aqueous phase
(b) organic phase

Question 7: In an extraction procedure, it is advisable to:

(a) throw away all layers as soon as you have extracted them
(b) save all layers until an experiment is complete
(c) put the aqueous layer down the drain
(d) put the organic layer in the aqueous waste

Question 8: Table of physical constants

PROCEDURE

In a 50 mL Erlenmeyer flask, dissolve the contents of one packet of headache powder in 20 mL of diethyl ether. Since the binder, etc. are sometimes inert material, all of the powder may not dissolve, but this is not a problem. Pour the solution into the separatory funnel and use a fresh 5 mL of diethyl ether to transfer the remaining contents of the flask to the separatory funnel. Extract the ether solution with 20 mL of 3M HCl, then remove the aqueous layer (which is it, top or bottom???) into a beaker labeled "**HCl layer**". Remember, emulsions and the identification of the solute are common problems encountered in simple extractions. Emulsions sometimes are diminished by the addition of an ionic compound such as sodium chloride (NaCl) which changes the ionic strength of the aqueous layer and increases the solubility of some components. The determination of which layer is organic and which is aqueous is easily accomplished by knowing the densities of the solvents

used. Also, one can add a drop of water to the seperatory funnel and observe whether the droplets dissolve in the upper layer, or pass through the lower.

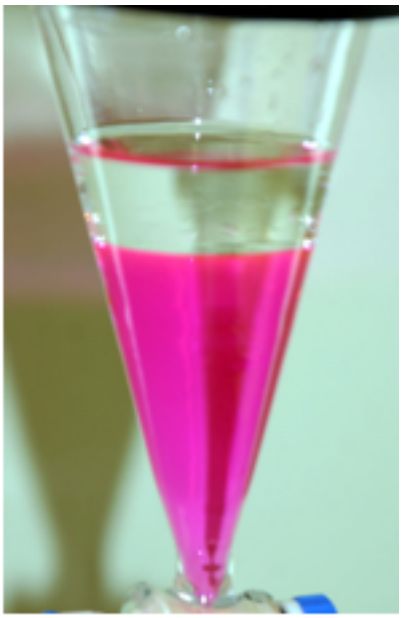

Figure 6: Close-up of the distinction between layers

Next, extract the ether layer with 20 mL of a 5% sodium bicarbonate ($NaHCO_3$) solution. **(Care must be taken in this step, since pressure buildup is possible)** Again, remove the aqueous layer into a beaker labeled "**bicarbonate extract**". (**Some members of the group should work with this solution (see below), while the others continue with the extractions**). The ether solution is finally washed with 20 mL of a saturated sodium chloride solution. Allow the layers to separate, discard the aqueous layer (make sure which is which), and transfer the ether solution to a clean, dry 50 mL Erlenmeyer flask.

Add a small amount (enough to cover the bottom of the flask) of anhydrous sodium sulfate (Na_2SO_4) to the ether solution to absorb any residual water. Allow the drying process to occur for about 5 minutes, then, pour (or filter through a funnel with a small cotton plug) the ether solution into a clean 50 mL Erlenmeyer flask. The ether is evaporated in the hood to yield crude salicylamide, and a melting point is determined.

HCl Layer:

This solution contains the conjugate acid of caffeine. Since the majority of powders contain a small portion of caffeine, isolation will not be performed. The solution should be neutralized by the gradual addition of 6 M NaOH and discarded in the appropriate waste container.

Bicarbonate Extract:

This solution contains the conjugate base of acetylsalicylic acid. Cool in an ice bath and carefully acidify this solution by the addition of 6 M HCl. Add the acid slowly since CO_2 will be produced and effervescence will occur. The acetylsalicylic acid should begin to precipitate as the acid is

added. Once the solution is acidic, collect the precipitate by vacuum filtration, dry it, weigh it, and determine a melting point.

IN-LAB QUESTIONS

Download and print the following worksheet. You will use this worksheet to record your answers to the In-Lab questions.

Questions

Question 1: Amount of Acetylsalicylic acid in powder (see box) _____

Question 2: Amount of Acetylsalicylic acid recovered _____

Question 3: Percentage Recovery _____

Question 4:

Melting Point of Acetylsalicylic Acid _____ (observed)
Melting Point of Acetylsalicylic Acid _____ (lit. reported)

Question 5: Amount of Salicylamide in powder _____

Question 6: Amount of Salicylamide recovered _____

Question 7: Percentage Recovery _____

Question 8:

Melting Point of Salicylamide _____ (observed)
Melting Point of Salicylamide _____ (lit reported)

The two solids should be shown to your instructor and then placed in the appropriate waste container.