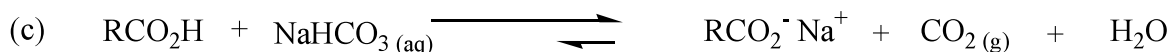
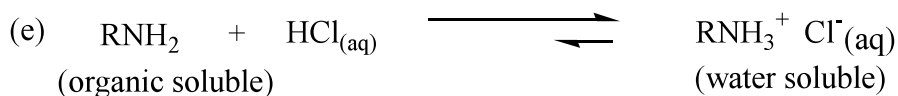




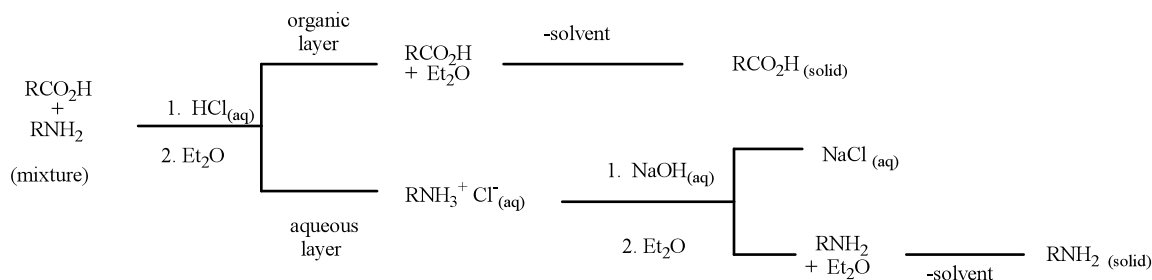
Noteworthy is that an aqueous solution of  $\text{NaHCO}_3$  converts carboxylic acids to their sodium carboxylates equation (c), but  $\text{NaHCO}_3(\text{aq})$  is not a strong enough base to form sodium salts of phenolic compounds equation (d). Thus two weak organic acids can be partitioned or separated providing their  $\text{pK}_a$  values differ by five or so  $\text{pK}_a$  units and the aqueous base used in the deprotonation is not basic enough to remove the hydrogen from the weaker organic acid. Note, if aqueous  $\text{NaOH}$  were used instead of  $\text{NaHCO}_3(\text{aq})$  in the extraction of a mixture containing a carboxylic acid and a phenol, aqueous  $\text{NaOH}$  would deprotonate both the carboxylic acid and the phenol (eq a and b) and subsequently, both the carboxylate and phenolate would reside in the aqueous base layer and the separation would not be feasible using  $\text{NaOH}(\text{aq})$  as a base.



The water solubility of organic compounds having basic groups e.g., amino, can be increased by the addition aqueous acid. The less water soluble organic amine in the presence of acid is converted to the more water soluble organo ammonium ion. Dilute hydrochloric acid is often used for extraction of basic organic substances or for removal of basic impurities from an organic phase.



Liquid-liquid extraction can be used to separate a weak organic acid from a weak organic base. The extraction can be performed using aqueous acid or aqueous base as described above along with an immiscible organic solvent such as ether. The process of extraction and separation can be best understood if a flow chart is used as an "outline" to detail the process. The flow chart will allow you to "know where you are in the process" and as well, keep track of the reagents, solvent layers and products.



Likewise, an organic compound that is not a weak acid nor weak base (alkanes, alkenes, ketones etc.) can be separated from weak organic acids or bases. In short, weak organic acids, bases or neutral organic compounds whether they be the desired compound or impurities with in a mixture can be separated by extraction using the appropriate aqueous acid, aqueous base and a suitable organic solvent. To assure yourself that you understand these principals, you are required to **generate a flow chart as part of the prelab preparation for experiment IIB.**

## Part A: Determination of the partition coefficient of benzoic acid between MTBA and H<sub>2</sub>O.

### Equipment and supplies

You need a centrifuge tube fitted with a cap and a couple Pasteur filter pipettes. Syringe pipettes will be provided for each solvent used in this part of the experiment. **Your TA will instruct you on how to use the syringe pipettes.** The chemicals needed for experiment IIA are benzoic acid, MTBE, water and anhydrous sodium sulfate.

### Procedure

Add 50 mg of benzoic acid followed by the addition of 1 ml of water and 1 ml of MTBE to a centrifuge tube. A syringe is supplied for each transfer (a syringe is attached to each solvent bottle). Cap the centrifuge tube and carefully shake the tube for 30 seconds by hand or a Vortex mixer. Remove the cap and allow the two layers to separate. Which solvent is the top layer? Which solvent is the bottom layer? What is a quick and simple technique/way to identify either layer?

Carefully remove the aqueous phase using a Pasteur pipette. Transfer the MTBE layer to a dry tube and add about 50 mg of anhydrous sodium sulfate. Sodium sulfate is a drying agent (absorbs water) and removes only trace of moist. You might need to add some extra anhydrous sodium sulfate in order to dry the organic phase completely. Recap the tube and let the sodium sulfate dry the organic phase for 5 minutes.

Transfer the dried organic phase (the MTBE layer which was treated with the drying agent) via a dry Pasteur pipette to a tared and dry conical vial containing a boiling chip. Rinse the sodium sulfate that was left in the tube by adding ~600  $\mu$ l of MTBE. Transfer the MTBE to the conical vial (combine with the first extraction). Evaporate the organic solvent in the fume hood using a warm sand bath until a constant weight of the solid is obtained. Turn in your dried product in a properly labeled plastic bag. Determine the amount of benzoic acid recovered and calculate a value for the distribution coefficient ( $K_D$ ).

## **Part B: Separation of a sample mixture; a carboxylic acid, an amine and a neutral organic compound by liquid-liquid extraction and identification by melting point.**

You will be provided an unknown solid that is a mixture of three compounds. Using liquid-liquid extractions you will be able to separate the mixture to its pure components.

### **Procedure**

***Remember to label each tube!***

Weigh 150 mg of the unknown and transfer the solid into a centrifuge tube labeled “unknown mixture”. Add 3 mL of MTBE and then cap the test tube and gently shake the solution until the solid dissolves.

### **Part 1: Isolation of the amine**

**Extraction with acid :** Add 1.5 mL of 5% HCl and then cap the tube and shake it for 30 sec. This will allow effective mixing of the layers and therefore efficient extraction. Allow the layers to separate and then remove the bottom layer (aq) to a new tube. Repeat this step with two additional portions of 5% HCl, (2x1.5 mL). At the end of the three extractions you should have two tubes: the original tube containing the mixture and a tube with 4.5 mL HCl

**Back-extraction:** Add 1.5 mL of fresh MTBE to the tube containing the combined HCl solutions. Cap the tube and shake it for 30 seconds. Allow the layers to separate and then transfer the organic layer to the original tube containing the mixture. The back-extraction removes the neutral and carboxylic acid molecules that are dissolved in the aqueous solution during the extractions. This step carries back the lost compounds to the original container.

**Treatment with base:** Neutralize the combined HCl extracts with 10% NaOH. Add the base dropwise with continuous stirring and frequently check the pH of the mixture with a litmus paper. A precipitate of the free amine should form. Be careful not to add too much base since this will prevent the formation of a precipitate. Cool down the solution and then filter the precipitate using a Hirsch funnel. Your TA will demonstrate the correct use of a Hirsch funnel.

***If a precipitate didn't form:*** Extract the aqueous solution with three portions of 1.5 mL MTBE. Combine the MTBE fractions and dry the solution by adding a small amount of sodium sulfate. Transfer the solution to a tared and clean conical vial and then evaporate the solution to dryness in the fumehood.

### **Part 2: Isolation of the carboxylic acid**

**Extraction with base:** Extract the “unknown mixture” three times with 5% NaOH as you did before with the HCl, (3 portions of 1.5mL each). At the end of the three extractions you should have two tubes: the original tube containing the mixture and a tube with 4.5 mL NaOH.

**Back-extraction:** Extract the combined NaOH solutions with 1.5 mL of fresh MTBE. Transfer the organic layer to the original tube containing the mixture. The back-extraction removes any neutral compound that was dissolved in the aqueous solution and otherwise will be lost.

**Treatment with acid:** Neutralizing the combined NaOH extracts with 10% HCl. Add the acid dropwise with continuous stirring and frequently check the pH of the mixture with a litmus paper. . A precipitate of the free carboxylic acid should form. Cool down the solution and then filter the precipitate using a Hirsch funnel.

### Part 3: Isolation of the neutral

Add 1.5 mL of water to the MTBE solution (“unknown mixture” tube). Shake and separate the organic layer from the water. This step is known as a “wash”, since you remove from the organic layers any water soluble impurities. Dry the MTBE with sodium sulfate and then transfer the solution to a tared and clean conical vial. Evaporate the solution to dryness in the fumehood.

Once you have separated and isolated the components of the mixture, you need to dry the compound thoroughly (usually in a desiccator) before you determine the amount recovered and the melting point of the compound. Why is dry compound desirable? Use the melting point of the compounds to identify the components of the unknown mixture. If your melting point is questionable you should go ahead and perform a recrystallization or perform a mixed melting point. The possible unknowns are provided in Table 2.1 below.

**Table 2.1 list of unknowns**

Unknown acid	MP °C	Unknown base	MP °C	Unknown neutral	MP °C
o-Toluic acid	104	p-Chloroaniline	72	Benzil	95
Benzoic acid	122	Ethyl p-aminobenzoate	89	Fluorene	114
trans-Cinnamic acid	133	2-aminobenzophenone	106	9-Fluorenone	84
m-Nitrobenzoic acid	140	p-Phenylenediamine	140		
m-Bromobenzoic acid	155	4-Aminoacetanilide	162		
p-Toluic acid	180				

\*) Ratio 1:1:1 among the unknowns (50mg each).

\*\*\*) See previous experiment, IB, "microscale recrystallization using a Craig tube".