

### Experiment 3: Extraction: Separation of an Acidic, a Basic and a Neutral Substance

Read pp 113-125, 131-132, Technique 11 and pp 132-141, Technique 12, in *TOC*.  
View the videos: 4.2 Extraction (Macroscale); 4.6 Drying Organic Liquids; 4.7 Separation of Drying Agents (Macroscale).

When separating mixtures of organic compounds that have acidic or basic functional groups, such as carboxylic acids, phenols (acidic) and amines (basic), one can exploit the different solubility properties of their protonated and non-protonated forms. For instance, an organic acid is often insoluble in water but soluble in a less polar organic solvent such as ether. In a separatory funnel containing ether and water, it would reside in the ether layer. When a basic solution is added to the funnel, the acidic compound is deprotonated and becomes an ionic salt. It is now soluble in water but insoluble in ether. At this point, the de-protonated organic salt would reside in the aqueous layer. A similar "solubility switch" exists for basic organic compounds. A water insoluble organic base can be protonated by reaction with an acidic solution and can thus move from the ether layer into the aqueous layer in a separatory funnel.

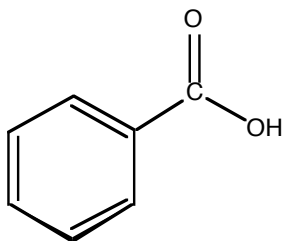
Many of the carboxylic acids are strong enough that they can be deprotonated by a saturated solution of sodium bicarbonate, a relatively weak base. Phenols, on the other hand, require a stronger basic solution, such as aqueous sodium hydroxide, to be deprotonated. Hydrochloric acid is generally used to protonate amines.

The ionic forms of the acidic and basic organic compounds can be recovered from the aqueous solution using the same solubility switch principles. When acid is added to an aqueous solution that contains the salt of a deprotonated organic acid, the organic acid is re-protonated. In this form, it is now water insoluble and precipitates from the aqueous solution as a solid, which can be collected by vacuum filtration. Similarly, the salt of a protonated amine can be deprotonated by addition of base, at which point it will precipitate from the aqueous solution and can be collected in its solid form by filtration.

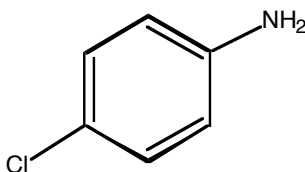
In some cases, a neutral organic compound, one which has neither an acidic nor a basic functional group, is present in the mixture. Such a compound would remain soluble in the non-polar organic solvent throughout any extractions with acid and base solutions. At the end of a procedure to separate the components of a mixture, the neutral compound can be recovered in its solid form by evaporation of the organic solvent.

The flow chart on the next page outlines a general procedure for separating acidic, basic and neutral organic compounds using the principles of the solubility switch.

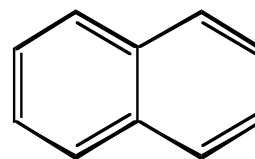
You will separate a mixture that contains benzoic acid, 4-chloroaniline and naphthalene. The 4-chloroaniline is separated first by extraction with hydrochloric acid. Since no phenolic compound is present in this mixture, two extractions with base solution are not required; thus, the benzoic acid could be separated from the neutral compound by



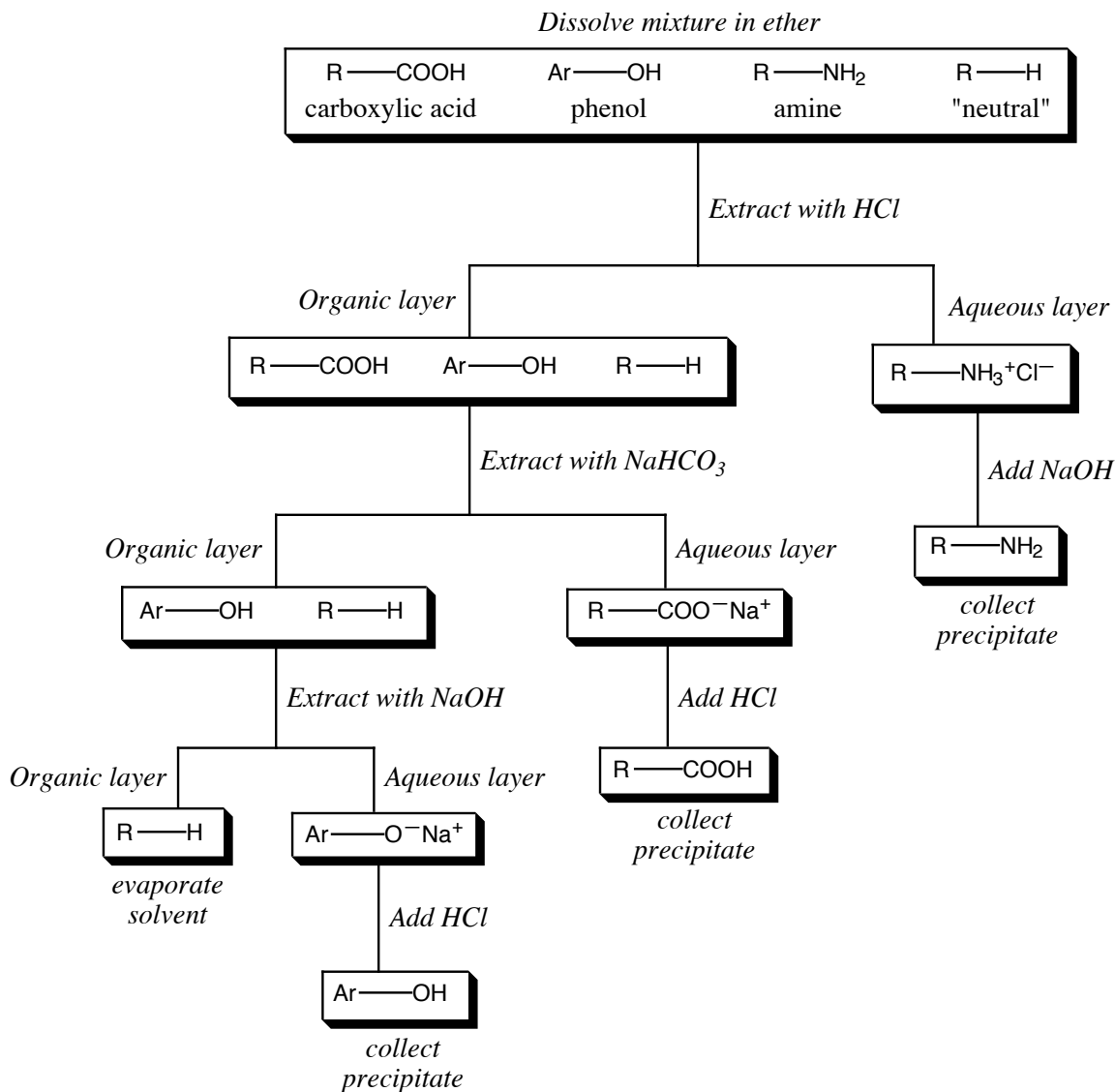
Benzoic acid  
mp 122-123°



4-Chloroaniline  
mp 68-71°



Naphthalene  
mp 80-82°



extraction with *either* aqueous sodium bicarbonate *or* aqueous sodium hydroxide solution. We have chosen to extract the acidic compound into the aqueous layer using sodium hydroxide.

**Outline** the steps of the following procedure:

Place 3 g of the mixture in a 50 mL Erlenmeyer flask and add 30 mL of diethyl ether. **Note: Diethyl ether is highly flammable! Care should be taken when handling this solvent. Keep away from flames and direct heat.** You will need to swirl and stir the solution with a stirring rod to get everything to dissolve completely. Transfer the solution to a separatory funnel using a little ether to complete the transfer. Pour 10 mL of water into the "sep" funnel and note which layer is organic and which is aqueous. Next, add 10 mL of 3 M HCl. Stopper the funnel, invert it and open the stopcock to vent the vapors. Alternate between gently shaking the funnel and venting the vapors by opening the stopcock. Toward the end of the extraction, you may shake more vigorously to be sure the extraction is complete. Place the funnel in a ring clamp, allow the layers to separate completely, then drain the lower layer into a 50 mL Erlenmeyer

flask labeled Flask A. Add another 5 mL of water to the sep funnel, shake the mixture as before and add this lower layer to Flask A. Make a note of the contents of Flask A in your notebook.

Add 10 mL of 1.5 M aqueous NaOH to the sep funnel, shake the mixture thoroughly with venting as above, allow the layers to separate, and drain the lower layer into a 25 mL Erlenmeyer flask, labeled Flask B. Add another 5 mL of water to the sep funnel, shake the mixture as before and add this lower layer to Flask B. Make a note of the contents of Flask B in your notebook.

At this point, a significant amount of water is present in the ether layer. It can be removed by performing an extraction with a saturated solution of sodium chloride. Add 15 mL of saturated aqueous NaCl to the sep funnel, shake the mixture thoroughly, allow the layers to separate and drain the lower layer (this aqueous layer can eventually be discarded down the drain). Pour the ether layer from the *top* of the separatory funnel into a 50 mL Erlenmeyer flask labeled Flask C. Add anhydrous sodium sulfate to the ether layer until some of it swirls freely, and set aside.

When doing extractions, it is a good idea not to discard *any* solutions until the very end of the experiment in order to avoid inadvertently discarding one of the products. As you proceed, think about which compound each flask contains and make a note of it in your notebook.

Pour approximately 5 mL of 8 M sodium hydroxide solution into a small beaker. **Use care when handling concentrated bases. Wear gloves!** Make the contents of Flask A basic by adding drops of NaOH solution to it. Test the pH of the solution with alkacid indicator paper until a pH of 10 or higher is reached. Cool the flask in an ice bath.

Pour approximately 3 mL of concentrated hydrochloric acid solution into a beaker. Acidify the contents of Flask B by adding drops of HCl solution to it. **Use care when handling concentrated acids. Wear gloves!** Test the pH of the solution with alkacid indicator paper until a pH of 2 or lower is reached. Cool the flask in an ice bath. **Note:** Do *not* pour concentrated acid into an organic byproducts jar! If it is not contaminated with organic material, *carefully* neutralize it with some sodium hydroxide, and pour it down the sink with running water. If it contains organic material, neutralize it before pouring it into a **Laboratory Byproducts** jar.

Clean and dry a 125 mL side-arm filter flask. Push a small plug of cotton into a short stem, glass filtering funnel. Decant the ether solution in Flask C through the cotton and collect the filtrate in the side-arm filter flask. Wash the drying agent with additional ether to ensure complete transfer of the product. Evaporate the ether under vacuum by connecting the side-arm to the house vacuum with pressure tubing and placing a # 5 (*not* #3) stopper in the mouth of the flask (see [Figure Page, Expt. 3](#)). Turn on the vacuum **slowly**. The ether will begin to bubble vigorously as it evaporates. A steam bath can be used to heat the flask to speed up the evaporation. When the liquid in the flask has evaporated, turn off the steam, and release the vacuum by removing the tubing from the side-arm of the flask.

Naphthalene is soluble in methanol and insoluble in water. It will dissolve in a hot mixture of 3:1 methanol:water, but is less soluble when this mixture is cold. To recrystallize the naphthalene, heat about 50 mL of a mixture of 3:1 methanol:water almost to the boiling point on a steam bath. *Slowly*, add *just enough* of the hot mixture to the compound in the side-arm flask until it just dissolves. The side-arm flask should be

heated on the steam bath during this addition of the solvent mixture. Once all of the compound has dissolved, allow the flask to cool to room temperature then on ice, and collect the solid by vacuum filtration on a Buchner funnel (see p. 192 in *TOC*, and [Figure Page, Expt. 1](#)). Wash the crystals with water. Dispose of the filtrate, which contains methanol, in the **Laboratory Byproducts** jar.

Collect the basic and acidic products in Flasks A and B by vacuum filtration on a Buchner funnel. Wash with small amounts of ice water. There will not be enough time to recrystallize the basic and acidic compounds.

The naphthalene will sublime (change directly from the solid phase to the vapor phase) at room temperature; therefore, you should obtain the melting point and weight of this compound before leaving the lab. Allow all three products to dry in your drawer. Next week you will obtain the weights and melting points of the acidic and basic compounds, and you can re-take the melting point of the neutral compound, if any is left.

Name \_\_\_\_\_ Date \_\_\_\_\_

T. A. \_\_\_\_\_ Lab period \_\_\_\_\_

**Results and Calculations** (to be handed in two days after the next lab period)

Calculate the percent recovery of 4-chloroaniline from the mixture.

Melting range for 4-chloroaniline \_\_\_\_\_

Calculate the percent recovery of benzoic acid from the mixture.

Melting range for benzoic acid \_\_\_\_\_

Calculate the percent recovery of (recrystallized) naphthalene from the mixture.

Melting range for naphthalene \_\_\_\_\_

Comment on your percent recoveries, citing possible reasons for either high or low percent recoveries (remember that the original mixture was a 1:1:1 combination of the three compounds by weight). Comment on your melting points, citing possible reasons if the data indicate low purity.

Write balanced chemical equations for all transferals of the compounds from organic to aqueous phases and for all the precipitation reactions. [Note: If a compound does not move from one layer to another, no reaction has occurred and no equation can be written.] In the equations that you write, indicate the state, solid (s), liquid (l), gas (g) or aqueous (aq), of each *product* formed in the reaction. You must write out the entire structural formula for each compound. Do not abbreviate an alkyl or aryl group with the letter "R".