

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

Read pp 142-155, 161-162, Chapter 10 and pp 163-173, Chapter 11, in *LTOC*.
View the videos: 10.1 Liquid/Liquid Extraction; 11.2 Tips for Separatory Funnel Handling and 11.1 Drying of Organic Liquids at:
<http://www.macmillanlearning.com/Catalog/studentresources/mohrig4e>

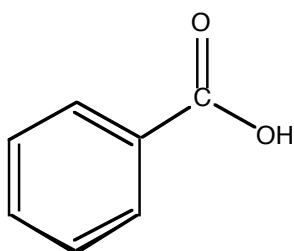
When separating mixtures of organic compounds that have acidic or basic functional groups, such as carboxylic acids, phenols (acidic) and amines (basic), one can exploit the different solubility properties of their protonated and non-protonated forms. For instance, an organic acid is often insoluble 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.

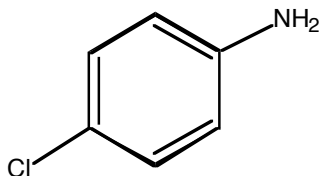
The solid forms of the acidic and basic organic compounds can be recovered from the aqueous solution using the same solubility switch principles. When acid is added to an aqueous solution that contains the salt of a deprotonated organic acid, the organic acid is re-protonated. In this form, it is now 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.

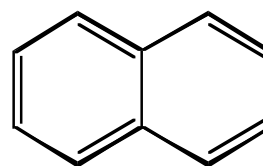
The flow chart on the next page outlines a general procedure for separating acidic, basic and neutral organic compounds using the principles of the solubility switch. You will separate a mixture that contains benzoic acid, 4-chloroaniline and naphthalene.



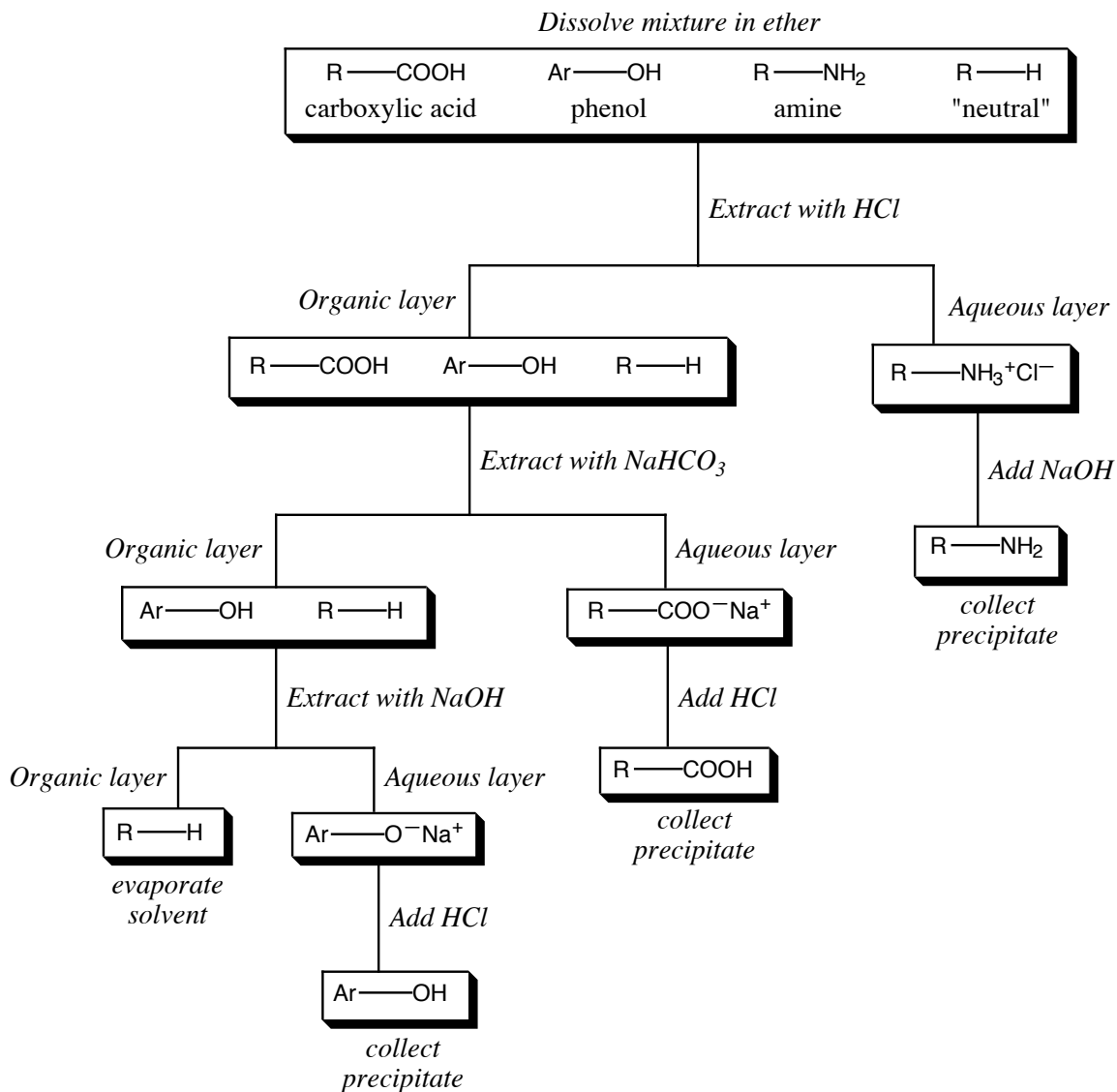
Benzoic acid
mp 122-123°



4-Chloroaniline
mp 68-71°



Naphthalene
mp 80-82°



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 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 sep 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 (read about “salting out” on p. 151 in *LTOC*). 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.

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.

Push a small plug of cotton into a short stem, glass filtering funnel and rest the funnel in a ring clamp. Place a large (40 mL) vial under the funnel. Decant the ether solution in Flask C through the cotton and collect the filtrate in the vial. Wash the drying agent with additional ether to ensure complete transfer of the product. Place the vial in a Centrifan. Be sure there is another vial that contains an equivalent volume of ether in the pocket across from your vial in the rotor. The TA will attach the plastic “splitter disk” so that the tabs are inserted into each vial (there must be four vials in the rotor). When the lid is closed and latched, the evaporation process will begin. It will take about fifteen minutes for the ether to evaporate.

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.

Check your vial in the Centrifan. At this point, all of the ether should have evaporated, leaving behind the dry naphthalene. If this is the case, remove your vial from the Centrifan.

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 the 3:1 methanol:water mixture almost to the boiling point on a steam bath (see p. 78 in *LTOC*). Add some of this hot solvent to the vial that contains your naphthalene. Stir the mixture to create a suspension and transfer the liquid and solid to a 125 Erlenmeyer flask. Use another portion of hot solvent to be sure all the solid has been transferred to the flask. Continue to add *just enough* of the hot solvent to the compound in the flask until it just dissolves. The flask should be heated on the steam bath during this addition. 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. 230 in *LTOC*, 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 benzoic acid and 4-chloroaniline, and you can re-take the melting point naphthalene, 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".