Chapter 11: Extraction

Extraction is the physical process by which a compound is transferred from one phase to another. It has been used since ancient times to prepare tea, a process in which compounds in tea are extracted or "pulled out" of the solid leaves into water. This is an example of solid-liquid extraction. Another type of extraction is liquid-liquid extraction. This type of extraction employs two liquids that do not mix, or are immiscible. Think of "oil and vinegar" salad dressing: you can shake the container of dressing, but when you set it down, it will settle into two layers.

Liquid-liquid extraction, or for simplicity, extraction, is the extraction technique used most frequently in the organic laboratory. It is used to separate organic compounds, either from inorganic chemicals or from each other. Usually one of the liquids is water and the other is an organic solvent. Extraction of a particular compound from a mixture of compounds is possible when the desired product is more soluble in one liquid (e.g., the organic solvent) than in the other liquid (e.g., the water), while the reverse is true for the undesired compounds. Extraction is usually one of the early steps in a purification scheme or the work-up of a reaction.

Extractions are carried out by dissolving the mixture of compounds in one of the solvents, adding the second solvent, and then by shaking them in a separatory funnel (Figure 11-1), commonly abbreviated as "sep funnel". When the separatory funnel is allowed to stand undisturbed, the liquids settle into two layers, commonly referred to as the "organic" layer and the "aqueous" layer.
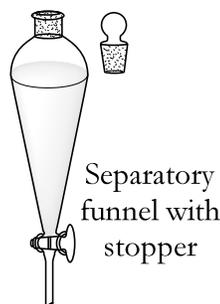

Separatory funnel with stopper

Figure 11-1: A separatory funnel is used to perform extractions.

11.1 Simple Liquid-Liquid Extraction

Two things must be satisfied for a successful extraction of a compound from one liquid to another. First, the two liquids must be immiscible. Second, the compound must be more soluble in one solvent than in the other.

A. Immiscibility

Solvents that are not soluble in each other are called "immiscible." Water is immiscible with most organic solvents: butanol, chloroform, cyclohexane, dichloromethane, ethyl acetate, hexanes, toluene, diethyl ether, and pentane. This information is summarized in Table 11-1. Note that water is miscible with methanol, ethanol, isopropyl alcohol, and acetone. Therefore, these solvents cannot be used to extract a compound from an aqueous solution. Acetone and ethanol are miscible with every solvent listed in the chart, therefore they are not used as extraction solvents.

Table 11-1: Miscibility of some common solvents. (Shading in a square indicates immiscibility.)

	Acetone	Butanol	Chloroform	Cyclohexane	Dichloromethane	Ethanol	Ethyl acetate	Diethyl ether	Hexanes	Methanol	Pentane	Isopropyl alcohol	Toluene	Water
Acetone														
Butanol														■
Chloroform														■
Cyclohexane										■				■
Dichloromethane														■
Ethanol														
Ethyl acetate														■
Diethyl ether														■
Hexanes										■				■
Methanol				■					■		■			
Pentane										■				■
Isopropyl alcohol														
Toluene														■
Water		■	■	■	■		■	■	■		■		■	

The designation "immiscible" is somewhat subjective. Some solvent-pairs designated immiscible in the above chart are miscible to a small degree, as shown in Table 11-2.

Table 11-2: Solubility of common solvents in water and vice versa.

Solvent	Solubility of water in solvent (g/100 mL solution)	Solubility of solvent in water (g/100 mL solution)
Diethyl ether	1.24	5.6
Ethyl acetate	2.92	8.20
Hexanes	0.007	0.001
Dichloromethane	0.32	1.6

Note that water is somewhat soluble in diethyl ether and in ethyl acetate. Although these solvents can be used in an extraction of a compound from water, a small amount of the solvent and therefore a small amount of the compound being extracted will remain in the water. If the organic compound will be isolated from the organic layer, it will likely be necessary to dry the organic layer first (see the chapter "Drying Organic Solutions" in this Handbook.)

When choosing a pair of solvents for extraction, choose the least toxic, flammable, and volatile solvents possible, applying the same rules as in the chapter of this Handbook about recrystallization.

If two immiscible solvents are mixed together and allowed to separate into layers, which solvent will be on top, and which on the bottom? The answer lies in the densities of the two solvents: the solvents always separate so that the densest solvent is on the bottom. Density values are physical properties of compounds and are listed in physical data tables along with the melting points, boiling points, refractive index, molecular weight, etc. Density values are reported in units of "g/mL." Since the density of water at 3.98°C is 1.00 g/mL, the density of a solvent is often reported as specific gravity, or how many times more dense it is than water. For instance, a solvent that weighs 0.68 g/mL has a specific gravity of 0.68.

When an organic solvent is mixed with water, after settling the organic solvent will be on top if it has a density less than 1.00, and on the bottom if it has a density greater than 1.00. The four most common solvents used in the teaching labs are listed in Table 11-3. In a mixture of water and hexanes or water and diethyl ether, the water will be the bottom layer. If water and dichloromethane are mixed, the water will be the top layer.

Table 11-3: Densities of commonly used extraction solvents.

Solvent	Density (g/mL at room temp.)
Hexanes	0.68
Diethyl ether	0.71
Water	0.997
Dichloromethane	1.33

Although pure water has a density of 1.00, if it contains dissolved salt, acid, or base, the density will increase. A saturated aqueous solution of sodium chloride has a density of 1.20; concentrated sulfuric acid has a density of 1.84. In laboratory situations, the composition and therefore the density of an aqueous reaction mixture is often not known. When extracting a solution of unknown density, the relative densities of the two solutions must be tested in the laboratory, as described in the procedure for extraction.

11.2 Distribution of a Compound Between Two Solvents

If a compound is given a choice between two different solvents, the majority of it will dissolve in the solvent in which it is more soluble. Consider common table salt dropped into a vessel containing water and oil. If the vessel is shaken to mix the immiscible liquids and the salt, most of the salt will dissolve in the water because it is more soluble in water than it is in oil.

The distribution of a compound between two solvents in an extraction depends on the solubility of the compound in each of the pure solvents. At equilibrium, the ratio of these solubilities is a constant known as the distribution or partition coefficient, *K*:

$$K = \frac{C_2}{C_1}$$

where C_2 is the concentration of the compound in solvent 2

C_1 is the concentration of the compound in solvent 1.

By convention, solvent 2 is the solvent in which the compound is more soluble; it is the solvent into which it is being extracted. The values for concentration can be expressed either as g/mL, moles/liter (M), or percent. The units do not matter, but it is critical that both C2 and C1 are expressed in the same units.

The larger the value of K, the more efficient is a solvent for extracting a particular compound from another solvent. This concept is illustrated in the example problems below.

Example Problem 1

Suppose you have 1 g of caffeine dissolved in 100 mL of water, and want to extract it into 100 mL of dichloromethane. The distribution coefficient for caffeine between these two solvents is 10:

$$K_{caffeine(dichloromethane/water)} = 10$$

After one extraction, how much caffeine will be in the dichloromethane?

Let x equal the amount of caffeine remaining in the water after the extraction. Therefore, the amount that has been extracted into the dichloromethane will be 1–x. Plug these values into the equation:

$$K = 10 = \frac{C_{dichloromethane}}{C_{water}}$$

$$10 = \frac{(1-x)/100}{x/100}$$

$$10 = \frac{(1-x)}{x}$$

$$10x = 1-x$$

$$11x = 1$$

$$x = 0.091$$

Thus, 0.909 g of caffeine will be dissolved in the 100 mL of dichloromethane at the end of the extraction, and 0.091 g will remain in the water.

Example Problem 2

Again begin with 1 g of caffeine dissolved in 100 mL of water. This time, extract with hexanes. The distribution coefficient for caffeine with this solvent pair is 3.

After one extraction, how much caffeine will be in the hexanes?

$$K = 3 = \frac{C_{hexanes}}{C_{water}}$$

$$3 = \frac{(1-x)/100}{x/100}$$

$$3 = \frac{(1-x)}{x}$$

$$3x = 1 - x$$

$$4x = 1$$

$$x = 0.25$$

At the end of the extraction of caffeine from water with hexanes, there is 0.25 g of caffeine remaining in the water, and 0.75 g of caffeine in the 100 mL of hexanes, as compared with 0.91 g in Example 1. This illustrates mathematically how the efficiency of an extraction depends on the distribution coefficient, and thus on the solubilities of the compound in each of the two solvents.

Example Problem 3

Often, a second extraction of the water layer is performed to obtain a larger yield of product. In example 2, at the end of one extraction with 100 mL of hexanes, there is 0.25 g of caffeine remaining in the water. Let's see what would happen if the 100 mL of water were re-extracted with another 100 mL of hexanes:

$$K = 3 = \frac{C_{hexanes}}{C_{water}}$$

$$3 = \frac{(.25 - x)/100}{x/100}$$

$$3 = \frac{(.25 - x)}{x}$$

$$3x = .25 - x$$

$$4x = .25$$

$$x = 0.0625$$

$$K = 3 = \frac{C_{hexanes}}{C_{water}}$$

$$K = 3 = \frac{x/100}{(0.25 - x)/100}$$

$$3 = \frac{x}{0.25 - x}$$

$$0.75 - 3x = x$$

$$x = 0.19$$

Thus, the total yield of caffeine from the two extractions is 0.75 + 0.19 g, or 0.94 g.

A way to improve the yield in an extraction without increasing the total amount of solvent used is to perform multiple extractions as in Example 3, but to use a smaller amount of solvent in each extraction. For instance, the yield in Example 2 would be increased if the volume of extraction solvent, hexanes, is again 100 mL, but it is split into two 50 mL portions, and two extractions using 50 mLs each time are performed. This is illustrated in Example 4.

Example Problem 4

Dissolve the 1 g of caffeine in water and extract with 100 mL of hexanes, but instead of one extraction, perform two sequential extractions, using 50 mL of hexanes each time. Let y equal the amount of caffeine in the hexanes after extraction.

$$K = 3 = \frac{y/50}{(1-y)/100}$$

$$3 = \frac{2y/100}{1-y/100}$$

$$3 = \frac{2y}{1-y}$$

$$3 - 3y = 2y$$

$$y = 0.60$$

Thus, after one extraction, 0.60 g of caffeine is in the hexanes, and 0.40 g is in the water. Now extract the water with another 50 mL portion of hexanes:

$$K = 3 = \frac{y/50}{(0.40 - y)/100}$$

$$3 = \frac{2y/100}{0.40 - y/100}$$

$$3 = \frac{2y}{0.40 - y}$$

$$1.20 - 3y = 2y$$

$$y = 0.24$$

Therefore, the total yield from two 50 mL extractions is 0.60 + 0.24 = 0.84 g. This is a larger yield than the result of 0.75 from the one extraction with 100 mL hexanes in Example 2.

Example 4 illustrates the following rule: it is more efficient to perform several small extractions than one large extraction. How many and what size of extractions to perform will depend on the experiment. If the compound you are isolating is very precious, several extractions are advised. If the solvent used is expensive, you should take the time to do several small extractions rather than one large extraction.

11.3 Chemically Active Liquid-Liquid Extraction

Separation by the simple extraction method illustrated above is possible only if the compounds to be separated have very different solubility properties in the two solvents. If the purpose of an extraction is to separate an organic compound from inorganic salts and acids or bases in an aqueous mixture, a simple extraction with an organic solvent will usually pull the desired organic compound into the solvent. The polar inorganic compounds are soluble in water while the organic product is soluble in an organic solvent. This is often the case in the work-up of an organic reaction.

However, separation by extraction of two or more organic compounds is often more difficult, and a procedure called chemically active extraction is used. In this type of liquid-liquid extraction, an organic compound is altered chemically to change its solubility properties. Usually this is accomplished by treating it with an acid or a base, and is sometimes referred to as acid-base extraction. Acid-base extraction is used to separate organic compounds that undergo acid-base reactions from organic compounds that do not.

Almost all organic compounds with six or more carbon atoms are freely soluble in organic solvents but have only a limited solubility in neutral water. (Ionic and very polar organic compounds such as amino acids and sugars are exceptions to this rule.) If you mixed benzoic acid and naphthalene (Figure 11-2) in water and added dichloromethane, shook, and allowed the layers to separate, most of both of these compounds would be in the dichloromethane.

Benzoic Acid   Naphthalene

Figure 11-2: Benzoic acid and naphthalene.

In chemically active extraction, the compounds are treated with an acid or a base to alter their chemical structure and thus their solubility in water. The following groups of compounds can undergo this process:

- Carboxylic acids
- Phenols
- Amines

Any of the above compounds can be separated from either each other or from other types of organic compounds by treatment with aqueous acid or base. The mixture of organic compounds is dissolved in an organic solvent and then extracted with one of three aqueous solvents:

- Strong aqueous base, NaOH
- Weak aqueous base, $NaHCO_3$
- Aqueous acid, HCl

If an organic compound reacts with the acid or with the base, it will become soluble in the aqueous layer, leaving unreacted organic compounds behind in the organic layer. Thus, separation is achieved.

Carboxylic acids are weak organic acids (pK_a 3–4) that will undergo reaction with a strong base (NaOH) or with a weak base ($NaHCO_3$) to form water-soluble salts (Figure 11-3).
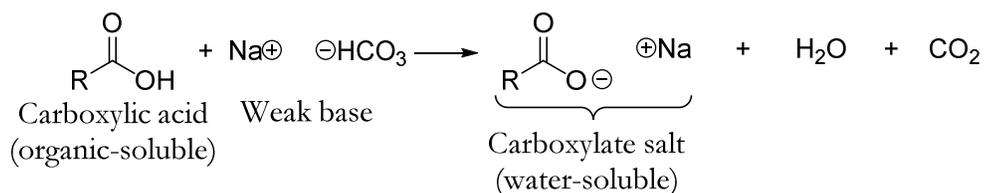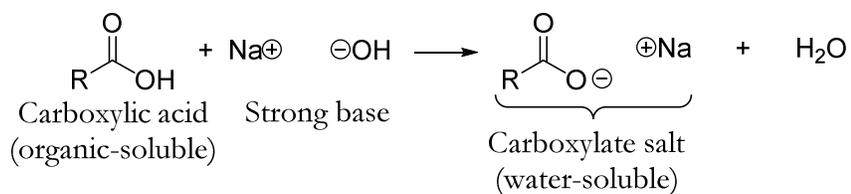
Figure 11-3: Chemically active extraction of a carboxylic acid can be done by strong bases or weak bases.

Phenols are weaker acids (pK_a 7–10) than carboxylic acids and will undergo reaction with a strong base (NaOH) but not with a weak base ($NaHCO_3$) to form water-soluble salts (Figure 11-4).
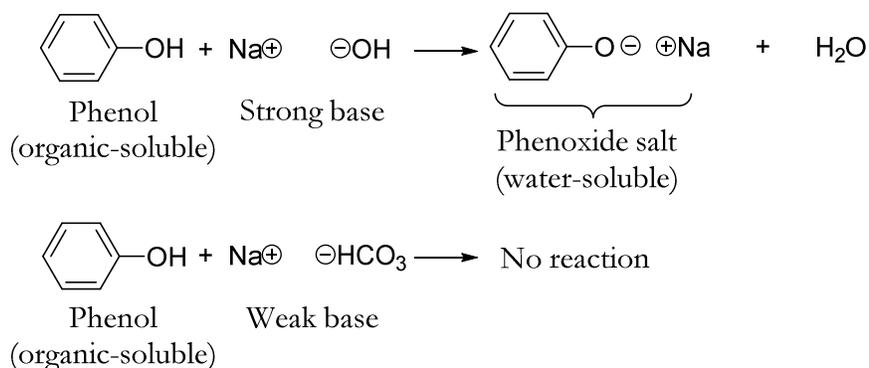
Figure 11-4: Chemically active extraction of a phenol can be done by strong bases only.

Amines are bases that will undergo reaction with an acid (HCl) to form water-soluble salts (Figure 11-5).
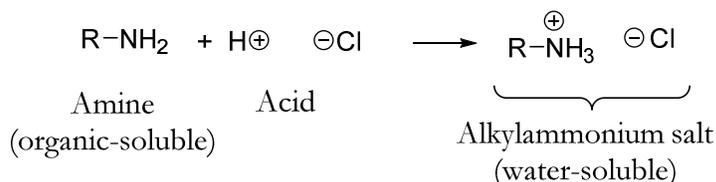

Figure 11-5: Chemically active extraction of an amine can be done by acids.

These results are summarized in Figure 11-6. Study this image and convince yourself that you could separate an organic solvent mixture of:

- A carboxylic acid and an amine by extracting with weak aqueous base
- An amine and a carboxylic acid by extracting with aqueous acid
- A carboxylic acid and a phenol by extracting with weak aqueous base
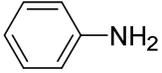- An amine and a phenol by extracting with aqueous acid

Functional Group	Example	In Weak Base (sat. $NaHCO_3$)	In Strong Base (1 M NaOH)	In Acid (1 M HCl)
Carboxylic acid				
Phenol				
Amine				
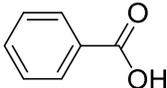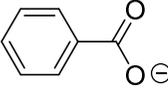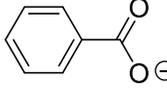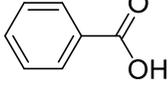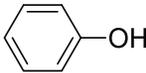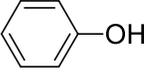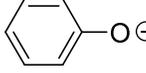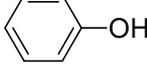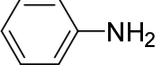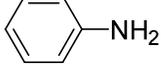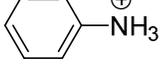
Figure 11-6: Summary of changes that occur during chemically active extractions.

After a compound has been extracted into an aqueous layer, the acid or base is neutralized, and the compound precipitates out of solution because it is no longer soluble in water in its neutral form. The compound is then isolated by vacuum filtration. (Or if it does not precipitate out, it is extracted into an organic solvent.) The compound that is in the organic layer is isolated by evaporating off the volatile solvent and recovering the compound as a residue.

The extraction schemes for the separation of mixtures of organic compounds can involve many steps. The mixture of the compounds in an organic solvent may be extracted by different aqueous solutions sequentially in a complex procedure. For convenience, the steps are outlined as flowcharts. Flowcharts for the separation of benzoic acid and naphthalene (Figure 11-7) and benzoic acid, benzophenone and aniline (Figure 11-8) are given as examples.
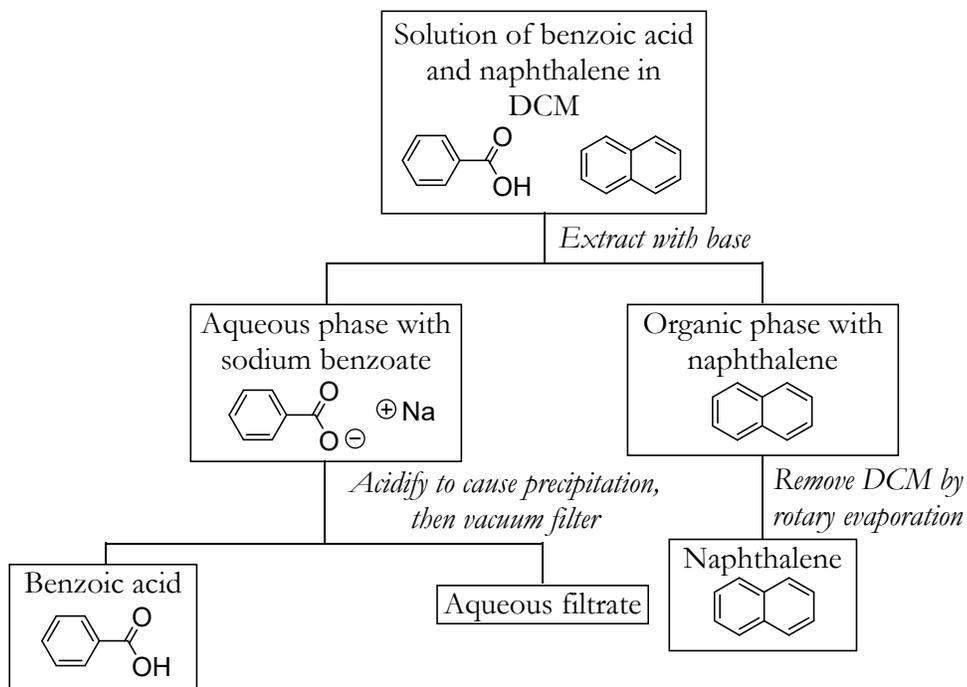
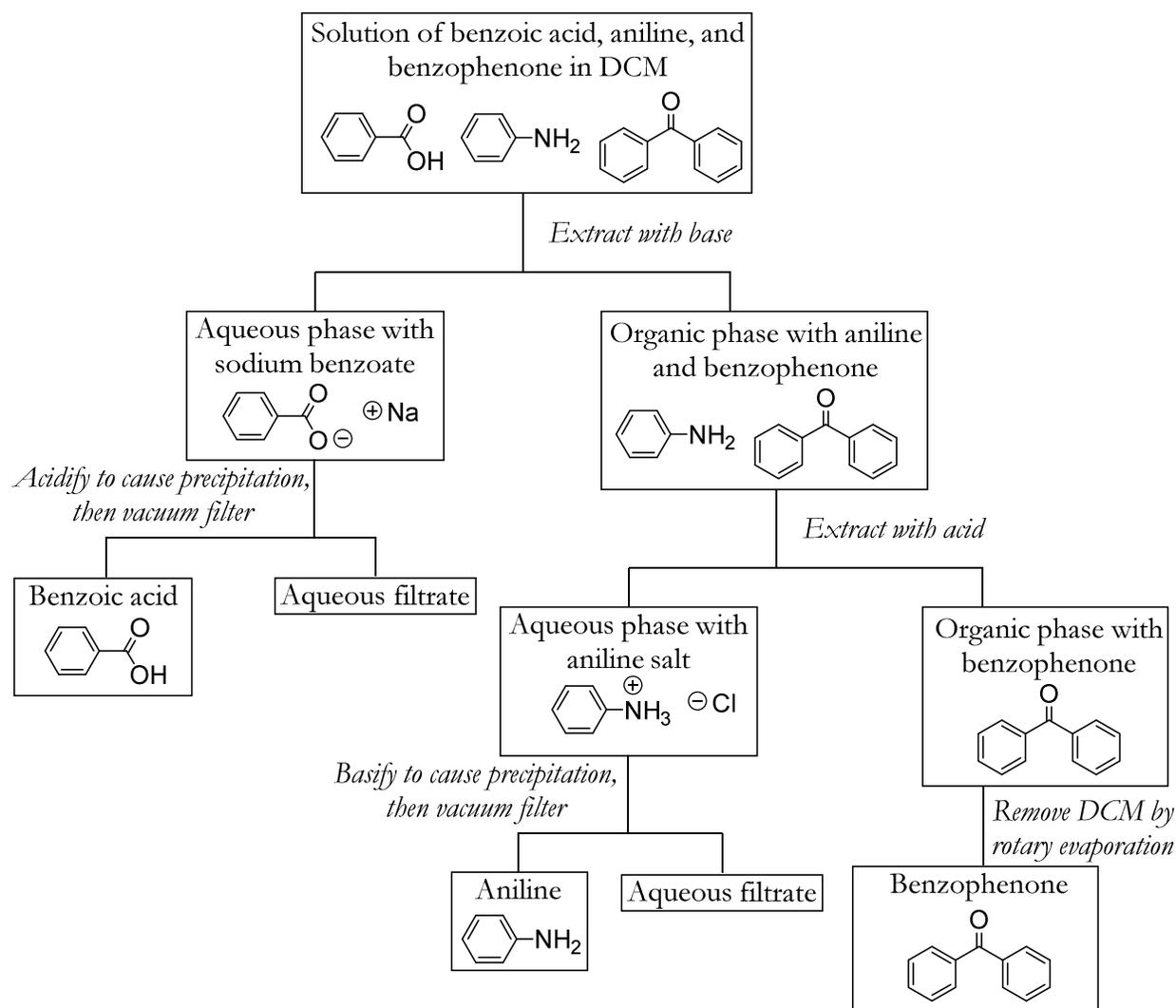Figure 11-7: Flowchart for the separation of benzoic acid and naphthalene.

Figure 11-8: Flowchart for the separation of benzoic acid, aniline, and benzophenone.

11.4 Aqueous Workups for Product Purification

In most of the synthetic experiments in the organic chemistry teaching labs, a series of operations involving extractions is used after the synthesis reaction is completed. These operations are called part of the *work-up* of the reaction mixture. The purpose of a work-up scheme is to separate unwanted starting material and side-products (such as inorganic salts) from the desired product. The extraction operations are usually followed by chromatography, crystallization, or distillation to further purify the product.

Chemically active extractions serve to separate the desired organic product from undesired organic starting materials and side-products; these extractions are often part of a work-up scheme. These extractions are discussed in detail above.

A. Washes

Simple extractions employing neutral water, dilute acid or base, or salt water as the extraction agent are often called *washes*. If a procedure calls for a "wash with water," this means that you extract the organic

solution with water. Generally, a wash solution is discarded and the organic layer is saved. Strictly speaking, the purpose of a wash is to remove impurities (Figure 11-9), although many chemists use the terms "wash" and "extract" interchangeably.

○ Product

● Impurity

Extract →

Wash →

Extraction occurs when the product changes layers, leaving the impurities behind

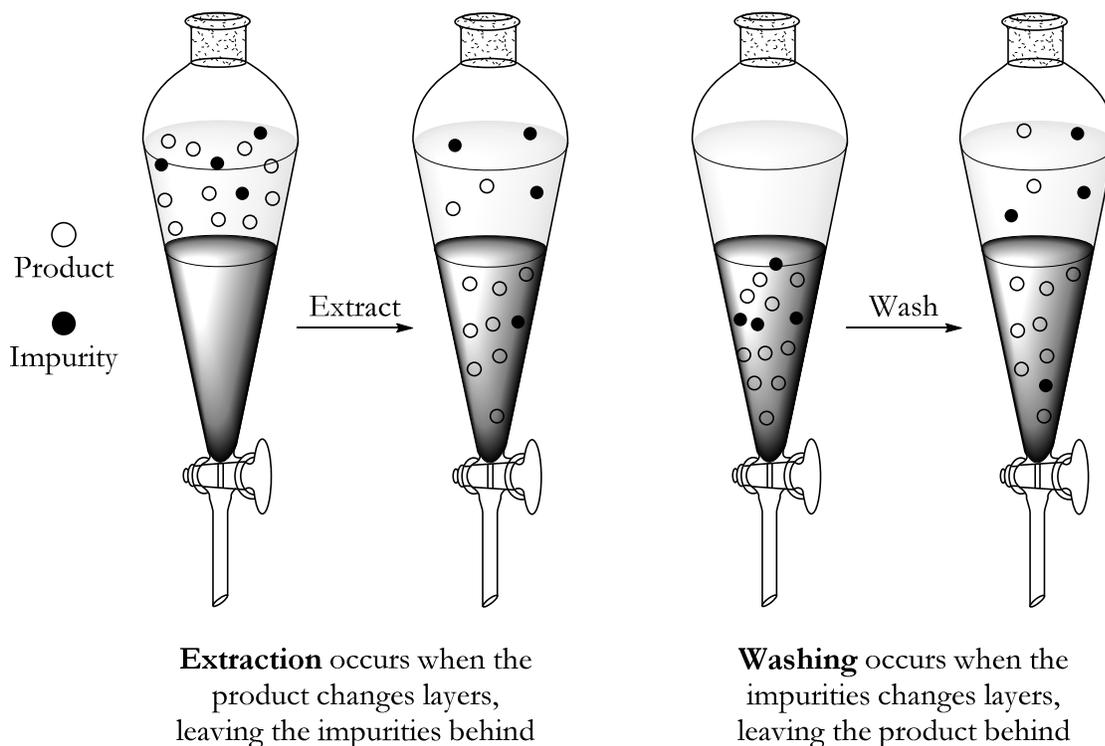**Washing** occurs when the impurities changes layers, leaving the product behind

Figure 11-9: The difference between an extraction and a wash.

Water washes serve to remove highly polar materials such as inorganic salts, acids, and bases, and low molecular weight, water-soluble carbon compounds. Often a water wash is the first step in a work-up, designed to remove the bulk of the impurities. A water wash also often follows an extraction of an organic reaction mixture with an acid or base in order to remove traces of these substances from the mixture.

Another "wash" is the extraction of an acidic reaction mixture with a dilute aqueous base. This wash serves both to neutralize the acid and to remove water-soluble polar compounds. Similarly, a basic reaction mixture is often washed with a dilute aqueous acid.

A saturated aqueous sodium chloride wash is frequently part of a work-up scheme. Oddly enough, washing with this water solution actually removes water from an organic reaction mixture, since the water in the mixture is pulled into the brine by osmotic pressure. Thus, the purpose of a sodium chloride wash is to dry the organic layer. This is discussed in the section on drying agents.

B. Salting Out

In an extraction procedure designed to extract the product into an organic solvent from an aqueous medium, the efficiency of the process is improved if salt is added to the water. The purpose of the salt is to make organic compounds less soluble in the water, and is especially important when the organic compound is partly soluble in water. The water molecules prefer to be nearer to the salt than to the organic compound, thus the organic compound is forced into the organic layer.

Often a saturated aqueous sodium chloride wash can serve a dual purpose, both to remove water from the organic layer and to force the organic product into the organic layer.

11.5 Procedure for Extraction

Liquid-liquid extractions are usually performed in a separatory funnel (Figure 11-10). These vessels are designed to allow for a secure seal when shaking liquids, a means for venting built-up pressure between successive shakings, sloping sides to help the layers form a clean and visible interface after shaking, and a drain spout in the bottom to allow for clean removal of the layers, even with small volumes. (Microscale extractions can also be carried out in test tubes or small vials. When using test tubes or vials, the container is stoppered during shaking, the layers allowed to separate, and the desired layer is removed with a pipet.
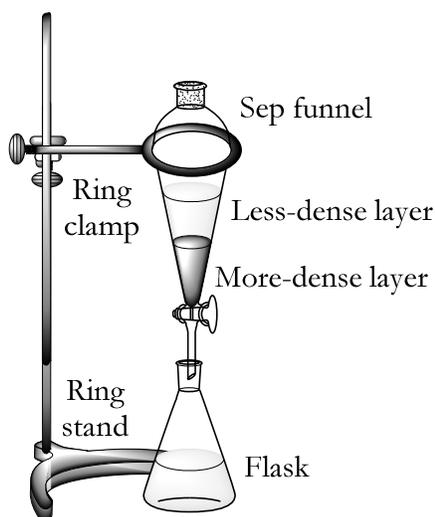

Figure 11-10: The setup for an extraction.

Before you begin performing the extraction, you should inspect your separatory funnel. Make sure that the stopper fits snugly in the top of the flask. Use a proper separatory funnel stopper; they can be either glass or plastic. Do not use a black rubber stopper or a cork instead of a proper separatory funnel stopper. Black rubber stoppers can expand and become stuck in the separatory funnel; corks will leak.

Check the stopcock for a proper fit and make sure the plastic nut holding it in place is tight. Most of the separatory funnels in the teaching labs have Teflon stopcocks; these do not require grease. If you have a glass stopcock, grease it lightly with stopcock grease.

Attach a ring clamp to a ring stand, then gently set the separatory funnel in it. If the ring clamp is too large to hold the funnel, you can pad out the ring by adding pieces of cut tygon tubing to the ring.

The general steps you should follow for an extraction are shown in Figure 11-11.
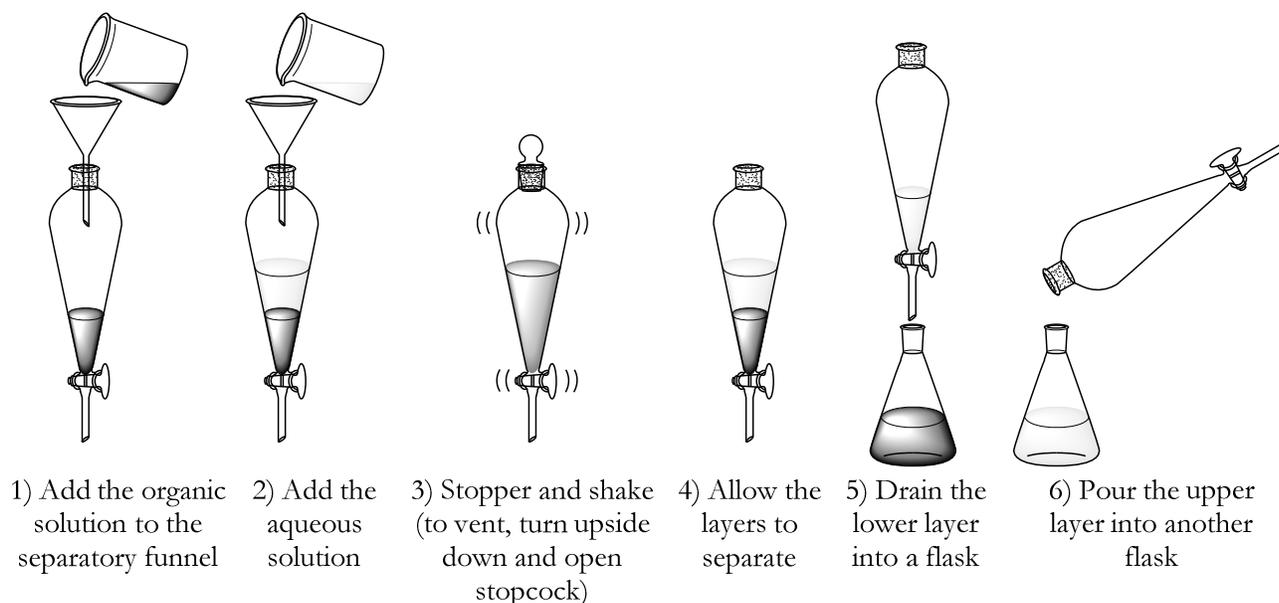
1) Add the organic solution to the separatory funnel

2) Add the aqueous solution

3) Stopper and shake (to vent, turn upside down and open stopcock)

4) Allow the layers to separate

5) Drain the lower layer into a flask

6) Pour the upper layer into another flask

Figure 11-11: Steps in a separatory funnel liquid-liquid extraction.

1. Add the organic solution to the separatory funnel.

Make sure the stopcock of the separatory funnel is closed! Then, place a stemmed funnel in the neck of the separatory funnel. Add the organic solvent in which your product has been dissolved. To avoid dangerous pressure buildup in the funnel, the solution to be extracted must be cool.

2. Add the aqueous solution to the separatory funnel.

Add the aqueous solution with which you will be extracting or washing your organic solution. The total volume in the separatory funnel should not be greater than three-quarters of the funnel volume. Wet the stopper with water (this keeps it from sticking tightly and prevents solvent leakage) and insert it in the neck of the separatory funnel.

3. Shake the separatory funnel.

Pick up the separatory funnel and hold it in both hands, with one hand on the stopcock and one hand securing the stopper. Rock the funnel once gently, then point the stem up and slowly open the stopcock to release excess pressure. Close the stopcock. Repeat this procedure until only a small amount of pressure is released. Now, shake the funnel vigorously for a few seconds. Release the pressure, then shake vigorously some more. About 30 seconds total vigorous shaking is usually sufficient to allow solutes to come to equilibrium between the two solvents.

Note: **Vent frequently** to prevent pressure buildup, which can cause the stopcock and perhaps hazardous chemicals to blow out. Take special care when washing acidic solutions with bicarbonate or carbonate since this produces a large volume of CO_2 gas. Always point the tip of the separatory funnel away from yourself and others during venting.

4. Allow the layers to separate.

Return the separatory funnel to the ring clamp and wait several minutes until the layers have separated. This is the stage where problems are most commonly encountered. See section 11.6 for instructions on what to do if the layers do not separate.

5. Drain the lower layer.

Place an Erlenmeyer flask under the stem of the funnel. When the layers have clearly separated, **remove the stopper**. Carefully open the stopcock and allow the lower layer to drain into the flask. Drain just to the point that the upper liquid barely reaches the stopcock.

6. Pour out the upper layer.

If the upper layer is to be removed from the funnel, remove it by pouring it out of the top of the funnel. This minimized the amount of lower layer that it picks up on its way out of the funnel.

7. Perform multiple extractions as necessary.

Often you will need to do repeated extractions with fresh solvent. You can leave the upper layer in the separatory funnel if this layer contains the compound of interest. If the compound of interest is in the lower layer, the upper layer must be removed from the separatory funnel and replaced with the drained-off lower layer, to which fresh solvent is then added.

Yes, it can be confusing! Plus, the beginning student often does not know in which layer contains the compound of interest. The best advice: **Always save all layers until the experiment is completely finished!**

8. Clean your separatory funnel and store it without the stopper in place.

Glass stoppers can become frozen to the separatory funnels. In some cases, they cannot be separated and the separatory funnel—an expensive item—has to be thrown away. Please, take the stopper out before you store the separatory funnel.

11.6 Common Problems Encountered in Extractions

1. The wrong layer is discarded.

The most common mistake by beginning students is that they keep the wrong phase and discard the one with the desired product. As a matter of precaution, all phases should be saved, well-labelled, until the end of the experiment.

2. You do not know which layer is organic and which is aqueous.

First, find the density of the solvents in Table 11-3 or in a suitable reference table. Remember, the solvent with the lower density will be on top in the separatory funnel.

You can also use a more empirical method to determine which layer is aqueous and which is organic. The best way to be certain is to get a Pasteur pipet and inject a few drops of water into the upper layer. If the droplets disappear, the upper layer is aqueous; if they sink to the layer interface, the upper layer is organic.

If this does not work, remove a small amount of the upper layer from the separatory funnel and place it in a test tube. Add a small amount of water to the test tube, mix it and allow it to settle. If you now see two layers, the upper layer in the separatory funnel is the organic layer. If you see only one layer, the upper layer in the separatory funnel is the aqueous layer.

3. You see a cloudy mixture instead of well-defined layers.

This is because an emulsion has formed in the separatory funnel, preventing separation of the liquids. If you have an emulsion, try the following:

- Allow the funnel to stand for a few minutes, periodically swirling it gently.
- Add some saturated sodium chloride solution to the mixture. (This increases the ionic strength of the aqueous layer and decreases the miscibility of the two liquids.)
- Add a few drops of ethanol to the funnel.
- Filter the entire mixture by vacuum filtration.

Sometimes an emulsion-like solution forms when both solvents, while immiscible, have the same densities. This often happens when the water layer contains large amounts of inorganics and the organic solvent is heavier than water (i.e., chloroform or dichloromethane). If you suspect this has happened, try diluting the aqueous layer with water by adding water to the separatory funnel and shaking again.

Often, the best solution for emulsions is prevention. If you know or are told that a mixture is apt to form an emulsion, swirl it rather than shake it vigorously during the extraction process. Sometimes the addition of salt before extraction prevents emulsions.

4. The interface is hard to see.

Sometimes the mixture is very dark and it is not possible to see the interface between the two liquids. Try adding more organic solvent. Also, hold the funnel up to the light or place a small lamp behind it. If this doesn't work, try draining the funnel slowly and carefully observing the flow of solvents. Usually, as they flow it is possible to determine when a solvent of different viscosity properties reaches the stem of the funnel.

5. You only see one layer when you should see two.

If the original reaction mixture contains large amounts of water- and organic solvent-miscible solvents such as ethanol, only one layer will form. Try adding more extraction solvent or saturated NaCl solution to the separatory funnel and shaking it again.

Otherwise you might have made a mistake in your extraction scheme. Hopefully, you have saved all of your layers!

6. There is insoluble material or a tiny emulsion at the interface.

This is quite common. Try to leave this insoluble material in the layer that you are not planning to save. However, this is nothing to worry about, since the required liquid will always be processed further, and the insoluble impurity can be removed by filtration at a later stage.

7. The funnel is very slow to drain.

Perhaps you forgot to remove the stopper and the air pressure can't equalize. Alternatively, perhaps there is particulate matter clogging the stopcock. In this case, try stoppering the funnel, taping the stopper in place firmly, and holding the funnel upside-down. Then open the stopcock and poke a piece of wire into it to clear the clog.

11.7 Study Problems

1. Consider the following solvent pairs. If mixed together, which pairs would form two layers? If they form two layers, which solvent would be on top?

 a. Hexanes and water

 b. Water and dichloromethane

 c. Hexanes and dichloromethane

 d. Methanol and hexanes

 e. Ethanol and water

 f. Acetone and toluene

2. You have 100 mL of water and add 4 mL of ether to it. You notice only one layer. Then, you add 6 mL more and see a small layer of a clear liquid on top of the water. Explain what is happening.

3. You want to extract a compound from water, and have determined that the compound is equally soluble in both hexanes and diethyl ether. Which solvent would be the better choice for the extraction?

4. The distribution coefficients for a compound are as follows:

 $K_{cyclohexane/water} = 1.5$

 $K_{pentane/water} = 11.2$

 $K_{diethyl\ ether/water} = 5.1$

You have an aqueous mixture of the compound. Which solvent system, cyclohexane/water, pentane/water, or diethyl ether/water, would give the most efficient extraction into the organic solvent?

5. One gram of a compound requires the following quantities of solvent to dissolve: 47 mL of water, 8.1 mL of chloroform, 370 mL of diethyl ether, or 86 mL of benzene. Calculate the solubility of the compound in these four solvents (as g/100 mL). Estimate the partition coefficient of the compound between chloroform and water, ethyl ether and water, and benzene and water. Which solvent would you choose to extract the compound from an aqueous solution?
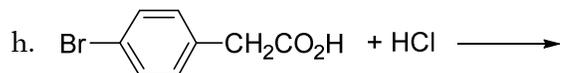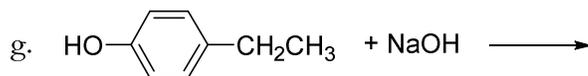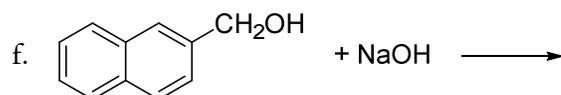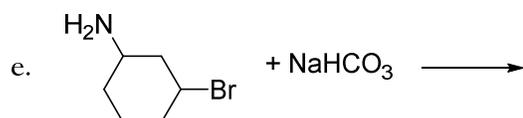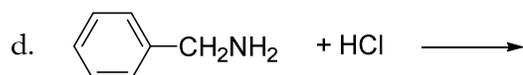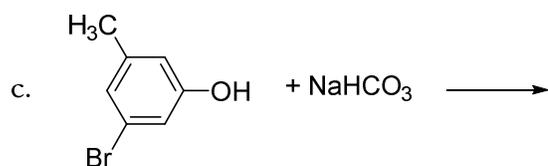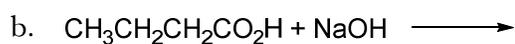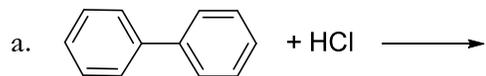
6. Five grams of Compound A is dissolved in 90 mL of water. The distribution coefficient for Compound A between hexanes and water is 5:

 $K_{Compound\ A(hexanes/water)} = 5$

 a. How much of Compound A will be in the hexanes if you extract it from the water one time with 90 mL of hexanes?

 b. How much of Compound A will be in the hexanes if you extract it from the water with three sequential extractions using 30 mL of hexanes each time, and then combine the hexanes extracts?

7. You carefully purified phenanthrene from a very long, complicated procedure. It took days. It is very important for you to hand the purified phenanthrene in to your TA in one hour to get a good grade. Oops! You accidentally put the phenanthrene into a vial that you thought was clean, but instead had a lot of NaCl clinging to the sides. What can you do to quickly purify the phenanthrene again?

8. Show the product of the following reactions. If there is no reaction, write "NR".

a. + HCl $\longrightarrow$

b. $CH_3CH_2CH_2CO_2H$ + NaOH $\longrightarrow$

c. —OH + NaHCO$_3$ $\longrightarrow$

d. —CH_2NH_2 + HCl $\longrightarrow$

e. + NaHCO$_3$ $\longrightarrow$

f. + NaOH $\longrightarrow$

g. HO——CH_2CH_3 + NaOH $\longrightarrow$

h. Br——CH_2CO_2H + HCl $\longrightarrow$

9. Which of the following compounds could be separated by acid-base extraction?

a. —CH$_2$NH$_2$ HO——CH$_2$CH$_3$

b. Br——CH$_2$CO$_2$H

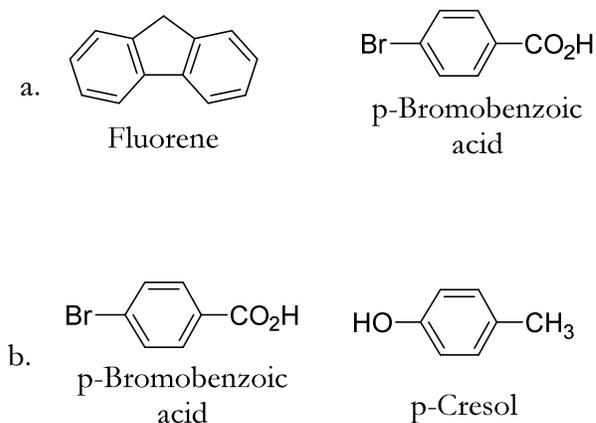c. CH$_3$CH$_2$CH$_2$CO$_2$H   Br——CH$_2$CO$_2$H

d.

e.
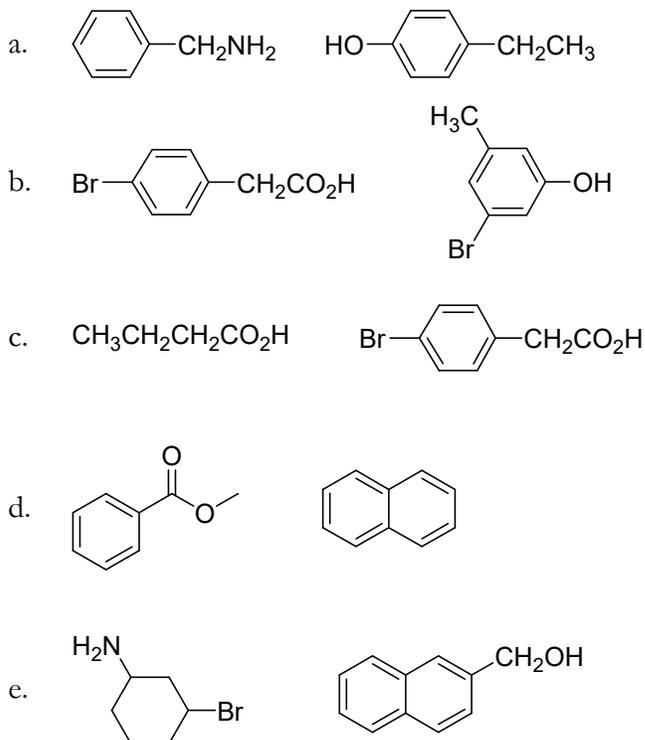
10. If you test an unknown organic compound and find it to be soluble in 5% aqueous NaHCO$_3$, what functional group does it probably contain?

11. You are going to extract a compound into diethyl ether from water, using two successive extractions. Make a detailed step-wise summary of all operations in the procedure, paying attention to the location of the solute at each step and the position of each layer in the separatory funnel. Start with step 1 as: "Put the separatory funnel in the ring on the ring stand."

12. Repeat the above problem using dichloromethane as the extraction solvent.

13. Outline in a flowchart how you would separate the following compounds:

a.
Fluorene
   Br——CO$_2$H
   p-Bromobenzoic
   acid

b. Br——CO$_2$H   HO——CH$_3$
   p-Bromobenzoic
   acid
   p-Cresol

14. A reaction work-up for an aqueous reaction mixture calls for extraction first with diethyl ether and then a wash with saturated aqueous sodium chloride. What is the purpose of the saturated sodium chloride wash?

15. You have prepared an organic compound by reacting it with strong aqueous acid. The work-up calls for extraction into dichloromethane, then a wash with 5% $NaHCO_3$. What is the purpose of the $NaHCO_3$ wash?

16. What can you do if you do not know which layer is which in an extraction procedure?