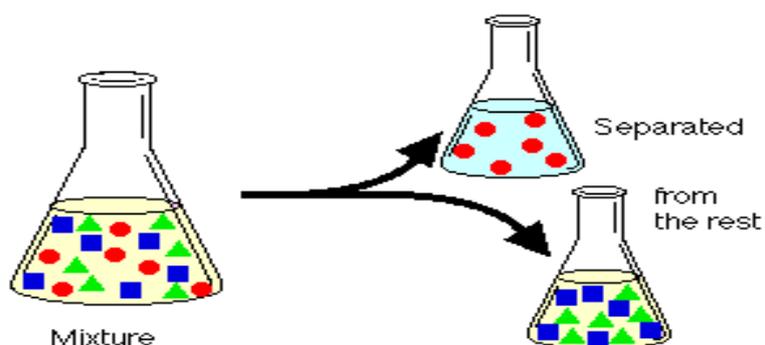# Extraction Theory

Org I Lab
W. J. Kelly

Liquid-liquid extraction is a useful method to separate components (compounds) of a mixture


Let's see an example.

Suppose that you have a mixture of **sugar** in **vegetable oil** (it tastes sweet!) and you want to **separate the sugar from the oil**. You observe that the sugar particles are too tiny to filter and you suspect that the sugar is partially dissolved in the vegetable oil.


What will you
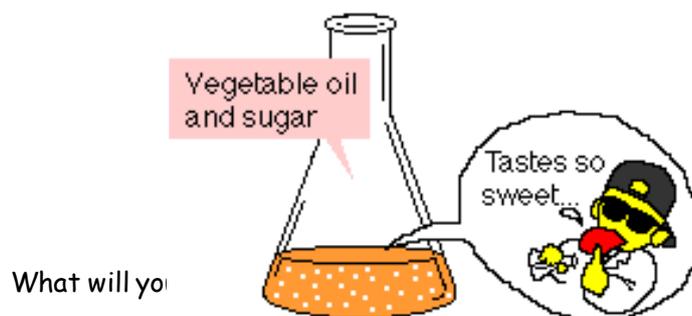
How about **shaking the mixture with water**

Will it separate the sugar from the oil? **Sugar is much more soluble in water than in vegetable oil**, and, as you know, water is *immiscible* (=not soluble) with oil.
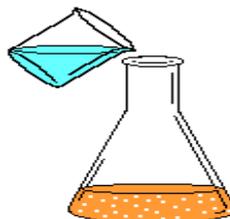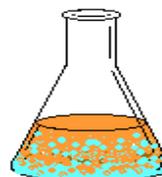
Did you see the result? The **water phase is the bottom layer** and the **oil phase is the top layer**, because **water is** *denser* than oil.

*You have not shaken the mixture yet, so sugar is still in the oil phase.
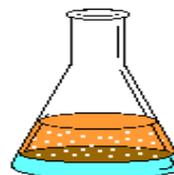
By shaking the layers (phases) well, you increase the contact area between the two phases.**The sugar will move to the phase in which it is most soluble: the water layer**

Now the water phase tastes sweet, because the sugar is moved to the water phase upon shaking. **You extracted sugar from the oil with water.** In this example, water was the extraction solvent ; the original oil-sugar mixture was the solution to be extracted; and sugar was the compound extracted from one phase to another. Separating the two layers accomplishes the separation of the sugar from the vegetable oil

Oil Phase   Water phase

Now the water layer tastes sweet...
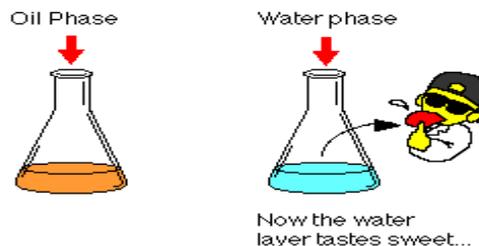
Did you get it? .....the concept of liquid-liquid extraction?

Liquid-liquid extraction is based on the transfer of a solute substance from one liquid phase into another liquid phase according to the solubility. Extraction becomes a very useful tool if you choose a suitable extraction solvent. You can use extraction to separate a substance selectively from a mixture, or to remove unwanted impurities from a solution. In the practical use, usually one phase is a water or water-based (aqueous) solution and the other an organic solvent which is immiscible with water.

The success of this method depends upon the difference in solubility of a compound in various solvents. For a given compound, solubility differences between solvents is quantified as the **"distribution coefficient"**

Partition Coefficient Kp (Distribution Coefficient Kd)

When a compound is shaken in a separatory funnel with two immiscible solvents, the compound will distribute itself between the two solvents.

Normally one solvent is **water** and the other solvent is **a water-immiscible organic solvent**.

Most organic compounds are more soluble in organic solvent while some organic compounds are more soluble in water.
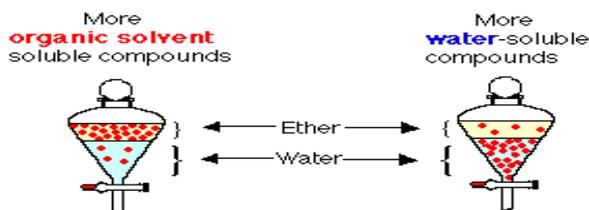
Here is the universal rule:

At a certain temperature, the ratio of concentrations of a solute in each solvent is always constant. And this ratio is called the **distribution coefficient, K.**

$$K = \frac{\text{concentration in solvent}_2}{\text{concentration in solvent}_1}$$
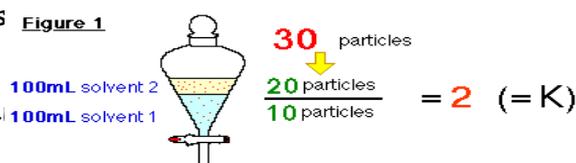
(when solvent

For example, Suppose the compound has a distribution coefficient **K = 2** between **solvent$_1$** and **solvent$_2$**

By convention the organic solvent is (1) and waater is (2)

$$K = \frac{[\bullet]solv2}{[\bullet]solv1} = 2$$

(1) If there are **30** particles of compound , these are distributed between **equal volumes** of solvent$_1$ and solvent

Figure 1

30 particles
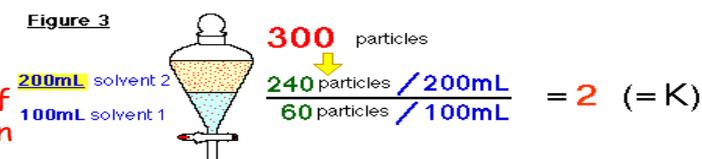
$$\frac{20 \text{ particles}}{10 \text{ particles}} = 2 \ (=K)$$

100mL solvent 2
100mL solvent 1

(2) If there are **300** particles of compound , the same distribution ratio is observed in solvents 1 and 2

Figure 2

300 particles

$$\frac{200 \text{ particles}}{100 \text{ particles}} = 2 \ (=K)$$

100mL solvent 2
100mL solvent 1
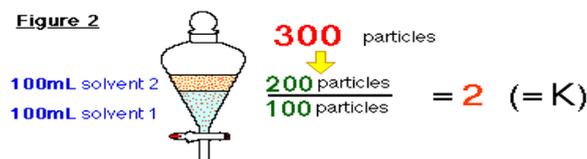
(3) When you **double** the volume of solvent$_2$ (*i.e.,* **200 mL** of solvent$_2$ and **100 mL** of solvent$_1$), the **300** particles of compound distribute as shown

Figure 3

300 particles

$$\frac{240 \text{ particles} / 200\text{mL}}{60 \text{ particles} / 100\text{mL}} = 2 \ (=K)$$

200mL solvent 2
100mL solvent 1

If you use a **larger amount of extraction solvent, more solute** is extracted

What happens if you extract **twice** with **100 mL** of solvent$_2$?
In this case, the amount of extraction solvent is the same volume as was used in Figure 3, but the total volume is divided into two portions and you extract with each.

As seen previously, with 200 mL of solvent$_2$ you extracted **240 particles of compound . One extraction with 200 mL gave a TOTAL of 240 particles**

You still have 100 mL of solvent$_1$, containing **100** particles. Now you add a **second 100 mL volume of fresh solvent$_2$**. According to the distribution coefficient K=2, you can extract **67 more particles from the remaining solution**

Suppose **x** particles are extracted out of **100** dissolved in solvent1

$$K = \frac{x \quad /100mL\,solv2}{(100-x)\,/100mL\,solv1} = 2$$

$$x = 2(100-x)\frac{100mL\,solv1}{100mL\,solv2}$$

$$x = 200 - 2x$$

$$3x = 200$$

$$x = 66.6... \cong \boxed{67}$$

∴ **67** particles are extracted with the second portion of solvent2

An additional 67 particles are extracted with the second porti of extraction solvent (solvent$_2$). The total number of particles extracted from the fir (200 particles) and second (67 particles) volumes of extraction solvent is 267. This is a greater number of particles than the single extraction (240 particles) using one 200 mL portion of solvent$_2$!

It is more efficient to carry o two extractions with 1/2 volum of extraction solvent than one large volume!
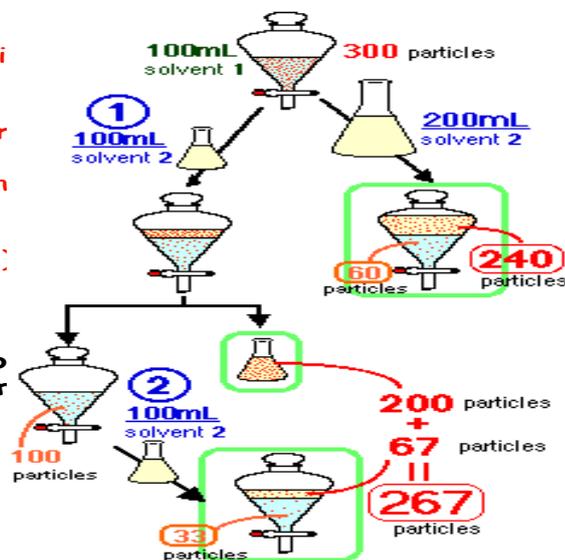
If you extract twice with 1/2 the volume, the extraction is more efficient than if you extract once with a full volume. Likewise, extraction three times with 1/3 the volume is even more efficient…. four times with 1/4 the volume is more efficient….five times with 1/5 the volume is more efficient…*ad infinitum*

The greater the number of small extractions, the greater the quantity of solute removed. However for maximum efficiency the rule of thumb is to extract three times with 1/3 volume
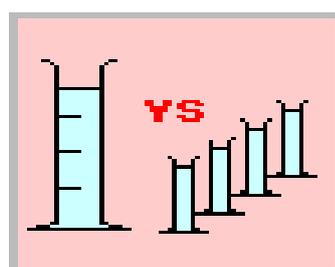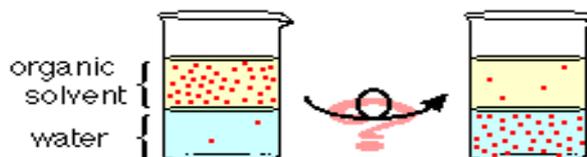
Chemically active (acid-base) extraction

Can you change the solubility property of a compound? How?

Most organic compounds are more soluble in **organic solvents** than in **water**, usually by the **distribution coefficient K > 4**

However, specific classes of organic compounds can be **reversibly altered** chemically to become **more water-soluble**.


This is a powerful technique and allows you to separate organic compounds from a mixture -- if they belong to different solubility classes
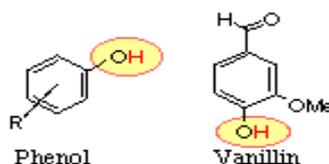
What type of organic compounds can be made water-soluble?
Compounds belonging to the following solubility classes can be converted to their **water-soluble salt form**

(1) **Organic acids** include **carboxylic acids (strong organic acids)** and **phenols (weak organic acids).**
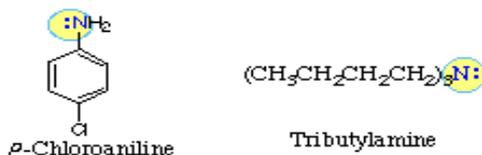
Examples of **Carboxylic acids**

Benzoic acid   Butyric acid
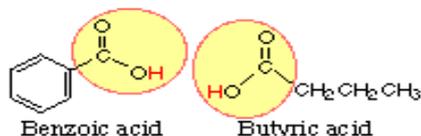
Examples of **Phenols**

Phenol   Vanillin

(2) **Organic**

Examples of **Amines**

*p*-Chloroaniline   Tributylamine

How can organic acids or bases be converted to a water-soluble form?

1. **Organic Acids** can be converted to their **salt** form when treated with an aqueous solution of inorganic base (*e.g.,* **NaOH** (sodium hydroxide) and **NaHCO₃** (sodium bicarbonate)). Salts are **ionic**, and in general, ions are **soluble in water** but **not soluble in water-immiscible organic solvents**. Remember: water is a very *polar* solvent thus salts (*i.e.,* ionic species) are well dissolved in it.

A. **Carboxylic Acids** are converted to the salt form with **5% NaOH** aqueous solution. NaOH is a **strong inorganic base**.

Carboxylic acids are **strong** organic acids (pKa = 3 to 4), so they can also be ionized with **weak** inorganic bases (*e.g.,* **NaHCO₃ (sodium bicarbonate)**) aqueous solution.
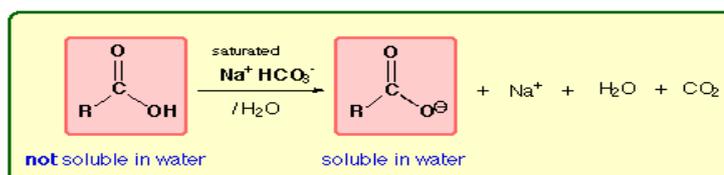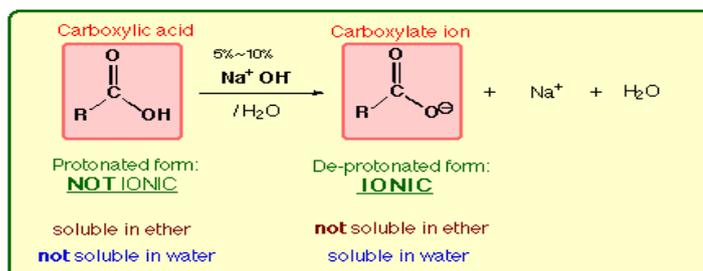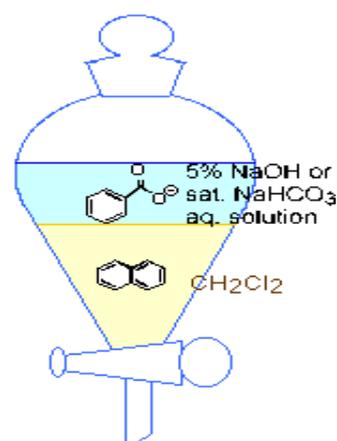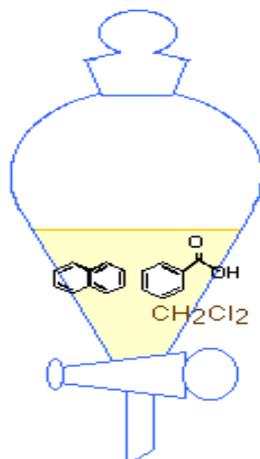

Let's try a sample problem.
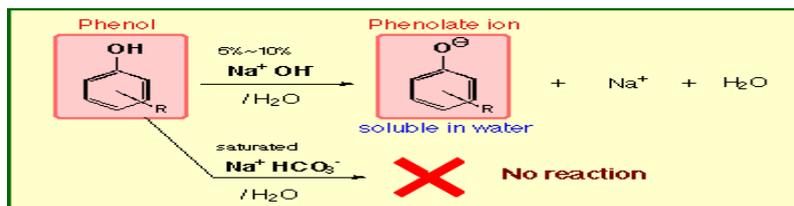Here is a mixture of **naphthalene** and **benzoic acid**, dissolved in **dichloromethane**.
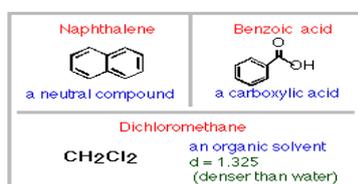
You want to separate these two compounds. What will you do?

You may use an aqueous solution of either 5% NaOH or sat. NaHCO₃, to extract **benzoic acid** as a **salt** form

B. Phenols are considered to be **weak** organic acids. Phenol, the parent compound, is partially water-soluble (1 g will dissolve in 15 mL of water), whereas substituted phenols are not. Sodium bicarbonate ($NaHCO_3$) aqueous solution, a **weak** inorganic base, **will not deprotonate phenols to make it ionic**, because it is not strong enough. However, treatment with NaOH, a **strong** inorganic base, can change phenol to its ionic (salt) form.
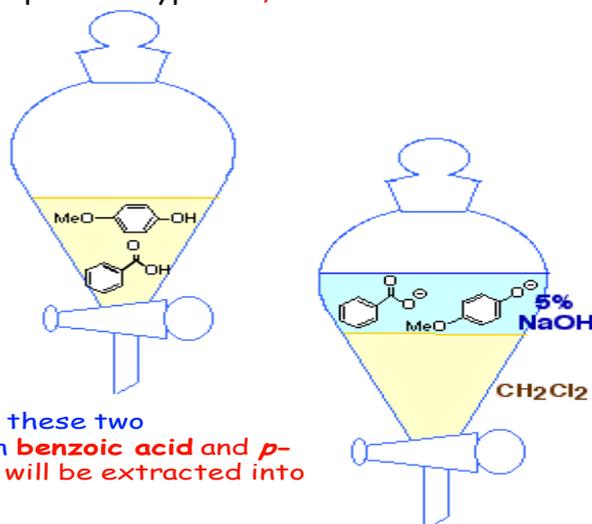

Let's try a another sample problem.
Here is a mixture of benzoic acid and p-methoxyphenol, dissolved in dichloromethane.

Benzoic acid	p-Methoxyphenol
pKa = 4.2	pKa = ~10

You want to separate these two compounds. What will you do?

You cannot use 5% NaOH to separate these two compounds. NaOH will react with both **benzoic acid** and **p-methoxyphenol**, thus both compounds will be extracted into aqueous layer.

Let's try this problem again.
Here is another mixture of benzoic acid and p-methoxyphenol, dissolved in dichloromethane.

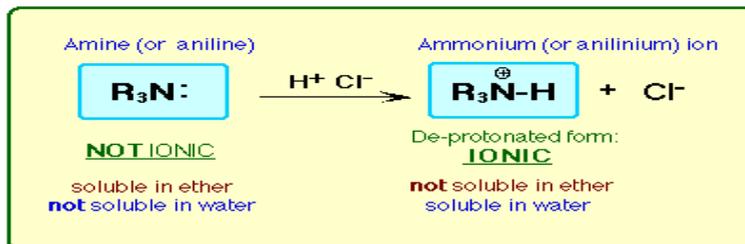| Benzoic acid	p-Methoxyphenol
pKa = 4.2	pKa = ~10

NaOH was too strong a base, thus it does not differentiate the strong and weak organic acids. Use of weak inorganic base such as $NaHCO_3$ will differentiate between the compounds
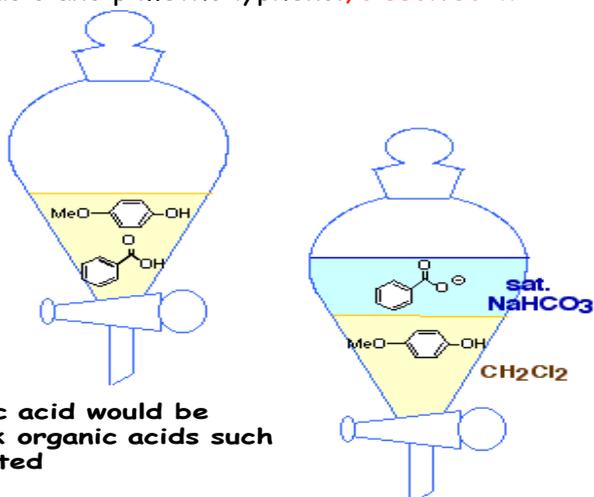
Strong organic acids such as benzoic acid would be deprotonated and ionized, while **weak organic acids such as phenols would NOT be deprotonated**

2. Organic Bases (amines) can be converted to their **salt** form when treated with an aqueous solution of an inorganic acid such as **HCl** (hydrochloric acid).

Recall that salts are **ionic** and generally **soluble in water** but **not soluble in water-immiscible organic solvents**.


Amine (or aniline)   Ammonium (or anilinium) ion

$R_3N:$ $\xrightarrow{H^+ \ Cl^-}$ $R_3\overset{\oplus}{N}\text{-}H$ + Cl^-

NOT IONIC   De-protonated form:
                                    IONIC

soluble in ether   **not** soluble in ether
not soluble in water   soluble in water

Let's try a third sample problem.

Here is a mixture of benzoic acid and p-chloroaniline, dissolved in dichloromethane.

p-Chloroaniline   Benzoic acid

Cl—⟨ ⟩—NH₂   ⟨ ⟩—COOH

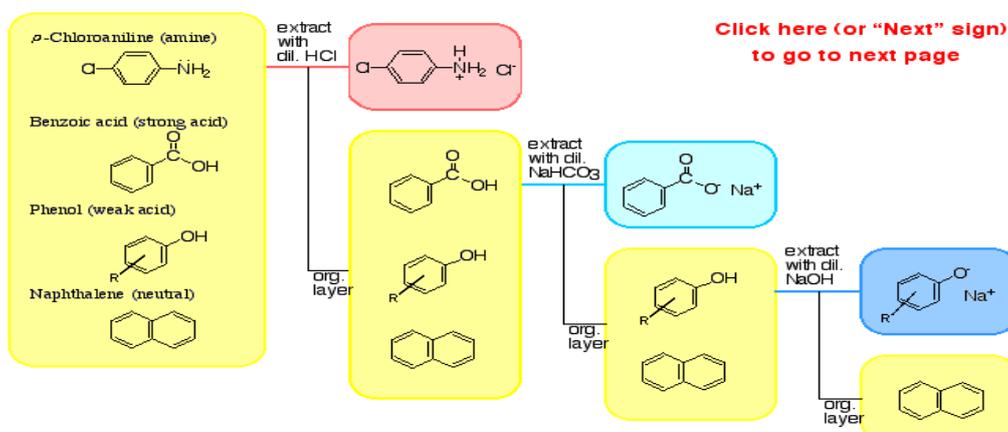an amine   a caboxylic acid

You want to separate these two compounds. What will you do?
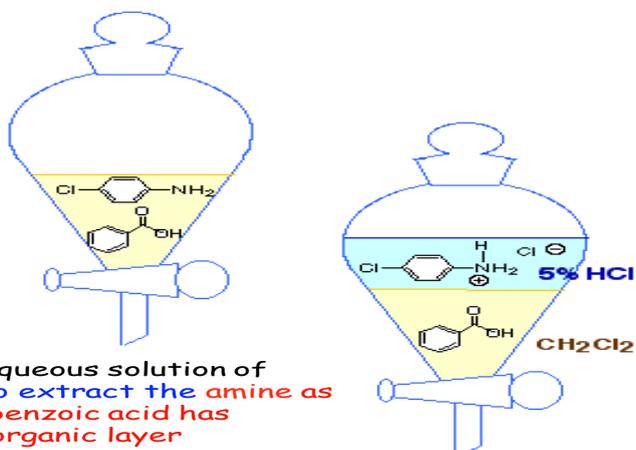
You may use an aqueous solution of either 5% HCl, to extract the amine as a **salt** form and benzoic acid has remained in the organic layer

5% HCl
CH2Cl2

You can separate four different classes of compounds from a mixture based on differing solubility properties. The four classes are:**1.Amines** (organic base)**2.Carboxylic acids** (strong acid)**3.Phenols** (weak acid)**4.Neutral compounds.**

p-Chloroaniline (amine)

Benzoic acid (strong acid)

Phenol (weak acid)

Naphthalene (neutral)

extract with dil. HCl

extract with dil. NaHCO₃

extract with dil. NaOH

org. layer

org. layer

org. layer

Click here (or "Next" sign) to go to next page

After the separation of the mixture of four components, we will have four solutions: each solution contains one component.
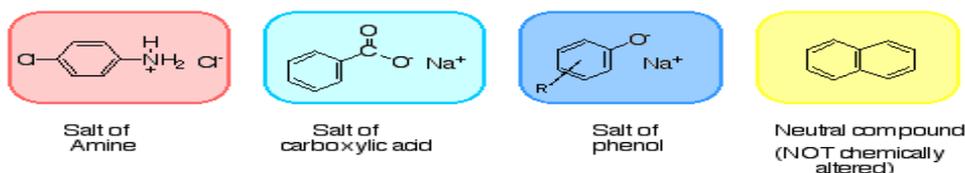
| Salt of Amine	Salt of carboxylic acid	Salt of phenol	Neutral compound (NOT chemically altered)
dissolved in dil. HCl (aq)	dissolved in dil. NaHCO$_3$ (aq)	dissolved in dil. NaOH (aq)	dissolved in organic layer

The ~~first three compounds~~ dissolved in aqueous solution. The four th compound is not chemically altered, but it is dissolved in an organic solvent. We now want to **recover** each compound in its original state (*i.e.,* in the non-ionic form) to complete the experiment. We call this step **isolation** or **recovery**.

Let's see, one by one, how to recover each compound obtained from the separation process

Isolation (Recovery) of amines
An amine is a basic compound. It is protonated in the presence of excess HCl forming a salt that is soluble in aqueous solution. This is how you separated the amine from the original mixture containing it.
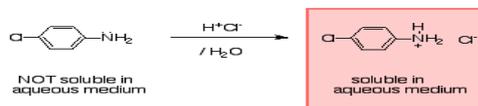
An amine is soluble in **acidic** aqueous solution because it forms a salt, an ionic form.

However, if you change the pH of the solution to **basic** the amine can no longer stay dissolved because it is no longer ionic! This process is called **basification**.
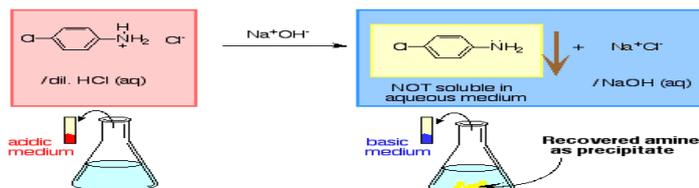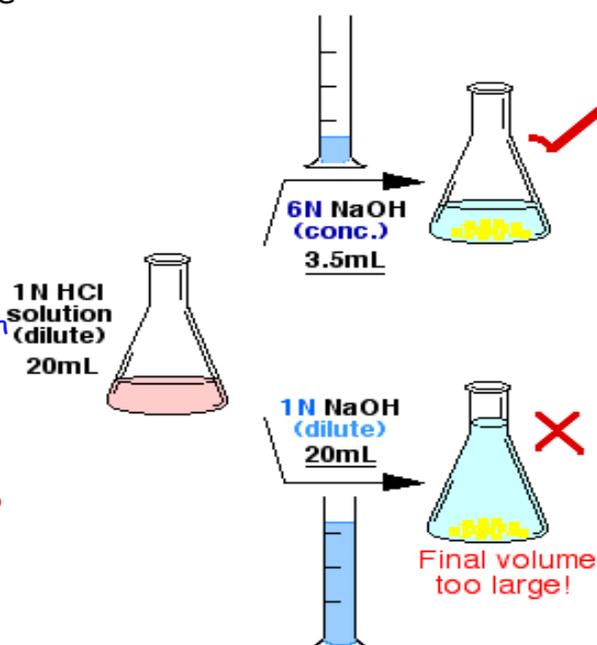
Basification is done by carefully adding concentrated NaOH solution to the solution containing the amine salt until it becomes basic.

■ In the basification step, you use **concentrated** NaOH solution to minimize the volume of the final solution. Recall that a dilute solution of HCl was used to extract the amine as its water-soluble salt (see the picture on the right side).

■ Basification must be done carefully, portion by portion, with swirling each time because the acid-base neutralization reaction is exothermic.

■ Check the pH of the solution to ensure that it is basic. (~pH 10)

1N HCl solution (dilute) 20mL

6N NaOH (conc.) 3.5mL ✓

1N NaOH (dilute) 20mL ✗

Final volume too large!

Isolation (Recovery) of Acids

There are two different groups of organic acids: **carboxylic acids** (strong acids) and **phenols** (weak acids). In the separation procedure, acids were extracted using (weak or strong) basic aqueous solutions
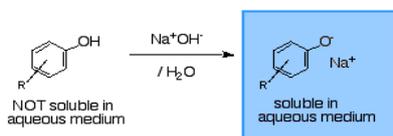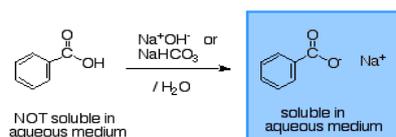

Both acids can be returned to the original form in the same manner! *Organic acids are currently dissolved in a* **basic** *aqueous solution, because the acid forms a salt, an ionic form. When you make the aqueous solution* **acidic**, *the organic acids no longer remain dissolved because they are no longer ionic and usually precipitate out of solution. This process is called* **acidification**.
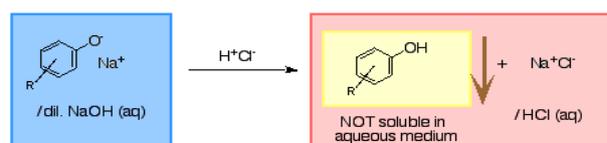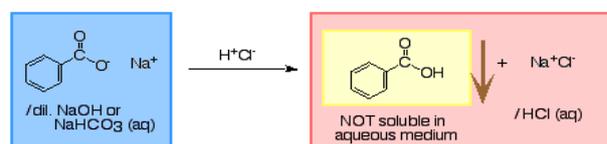
Acidification is done by carefully adding concentrated HCl solution until the mixture becomes **acidic,**

When the weak base, $NaHCO_3$, was the extracting solution, CO_2 gas will evolve during acidification.
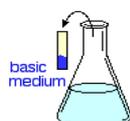
▪ The recovery of organic acids requires acidification with **concentrated** HCl solution. Recall that in the extraction step for the separation of an organic acid either dilute $NaHCO_3$ or NaOH was used. Concentrated HCl will now help minimize the volume of the final aqueous solution

▪ Acidification must be done carefully, portion by portion, with swirling each time because the acid-base neutralization reaction is exothermic.

▪ Check the pH of the solution to ensure that it is acidic. (~pH 3)

Separatory Funnel Extraction Procedure

Separatory funnels are designed to facilitate the mixing of immiscible liquids
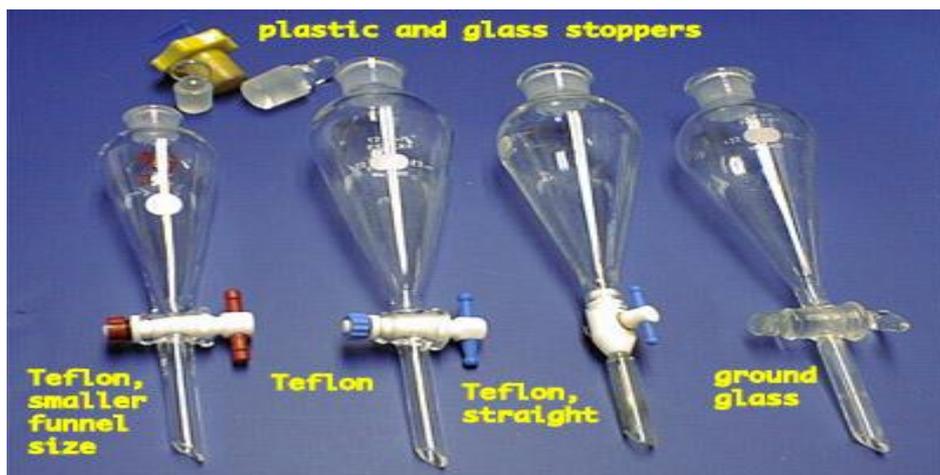
Separatory Funnel Extraction Procedure

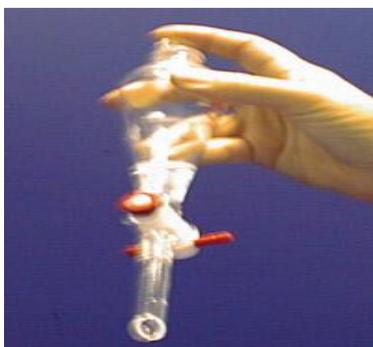1. Support the separatory funnel in a ring on a ringstand. Make sure stopcock is closed

2. Pour in liquid to be extracted

3. Add extraction solvent

4. Add ground glass Stopper (well greased)

Separatory Funnel Extraction Procedure

Shake the separatory funnel.

Pick up the separatory funnel with the stopper in palce and the stopcock closed, and rock it 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 when it is vented
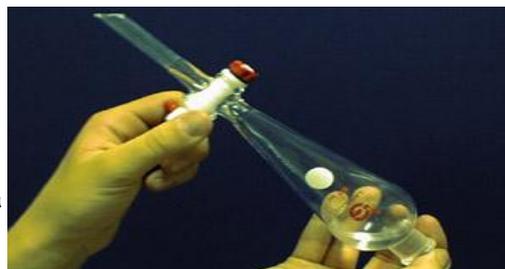
Separatory Funnel Extraction Procedure

**Shake the separatory funnel vigorously**.

Now, shake the funnel vigorously for a few seconds. Release the pressure, then again shake vigorously. About 30 sec total vigorous shaking is usually sufficient to allow solutes to come to equilibrium between the two solvents.

Vent frequently to prevent pressure buildup, which can cause the stopcock and perhaps hazardous chemicals from blowing out. Take special care when washing acidic solutions with bicarbonate or carbonate since this produces a large volume of CO_2 gas

Separatory Funnel Extraction Procedure

Separate the layers.

layers just beginning to separate
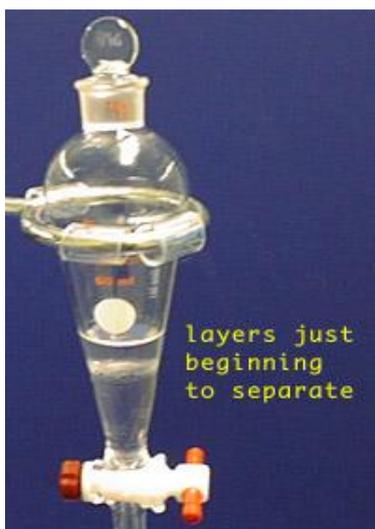
Let the funnel rest undisturbed until the layers are clearly separated

While waiting, remove the stopper and place a beaker or flask under the sep funnel.

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