

Teoria da Extração



QFL314- Química Orgânica Experimental

SEPARAÇÕES

→ Sistemas heterogêneos

- filtração
- centrifugação
- decantação

→ Isolamento de produtos

- extração
 - ❖ a. extração por solvente
 - ❖ b. extração por micela reversa
 - ❖ c. extração por fluido supercrítico

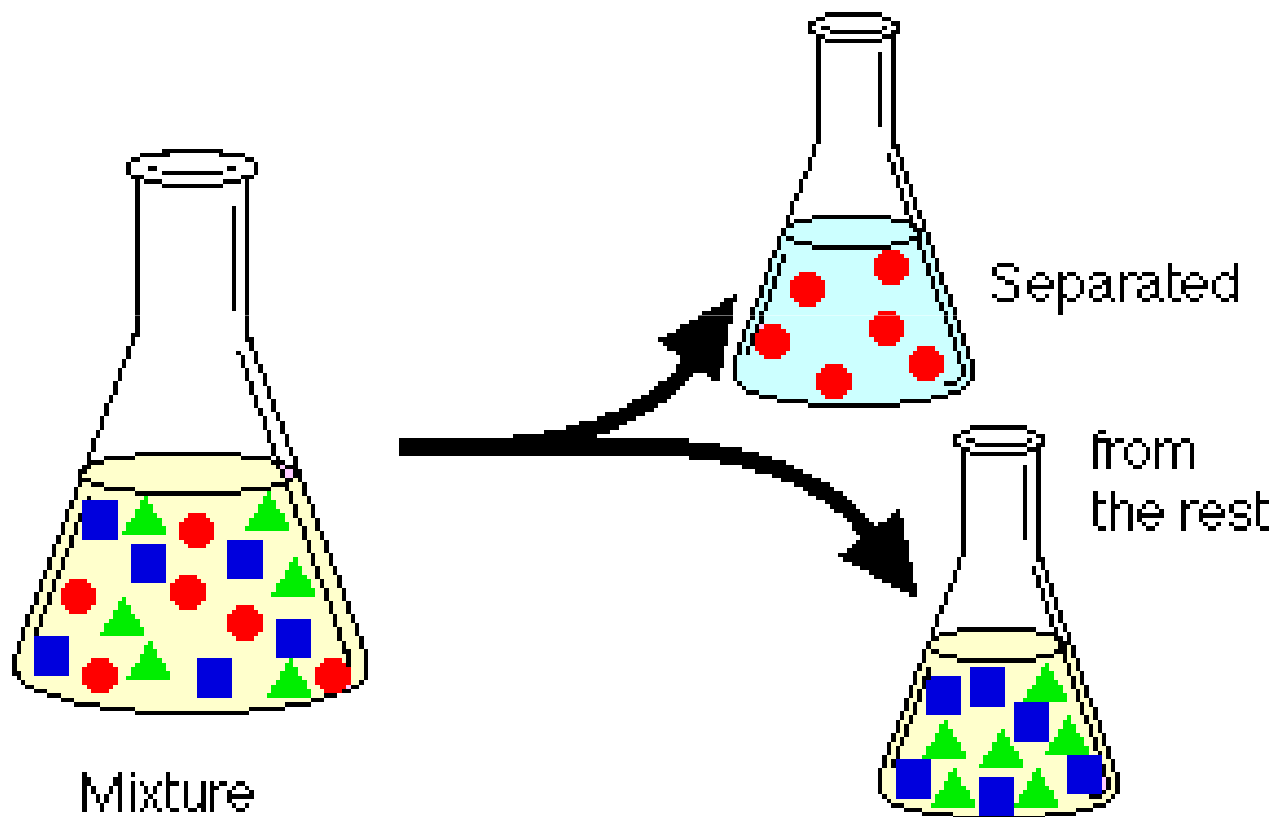
EXTRAÇÃO

transferência de solutos de uma fase **líqüida** ou **sólida** para um solvente líquido

♦ Extrações

- ♦ líquido- líquido
- ♦ sólido- líquido
- ♦ supercrítica: um proceso de extração líquida no qual se empregam fluídos comprimidos ao invés de solventes usuais

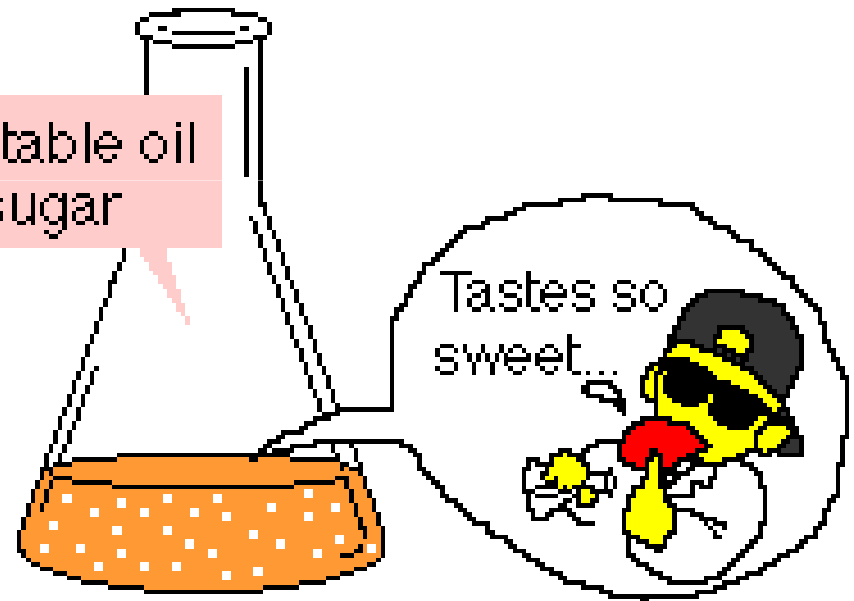
A **extração líquido-líquido** é um método útil na separação de componentes (substâncias) de uma mistura

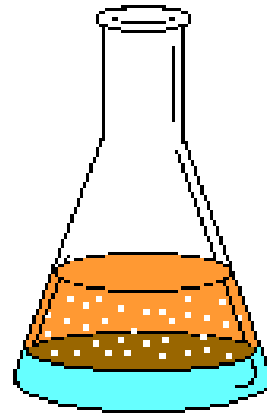
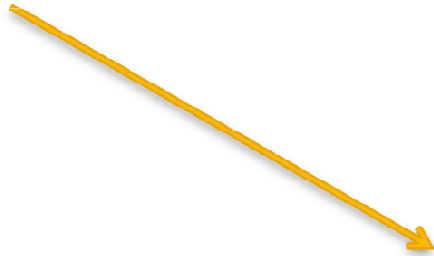
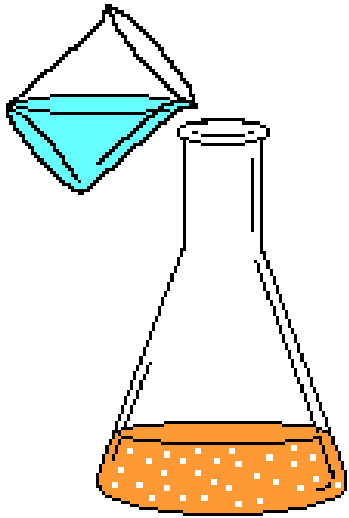
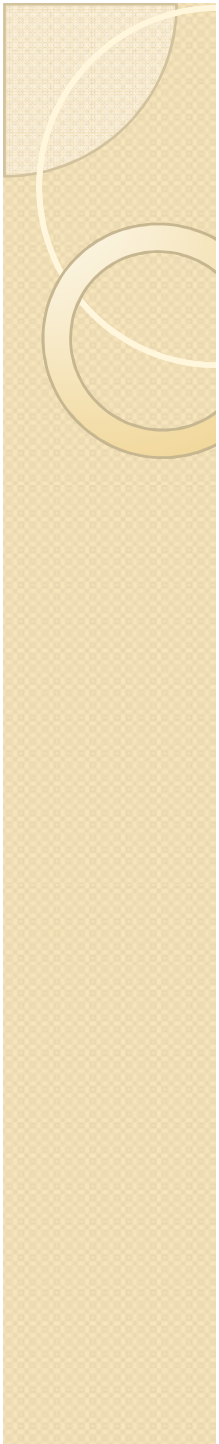


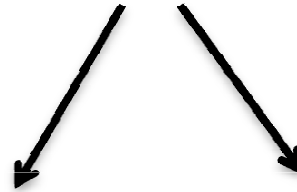
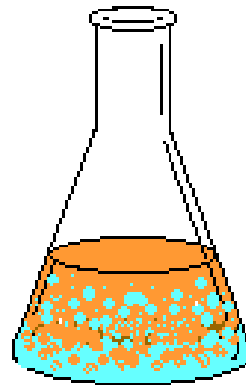
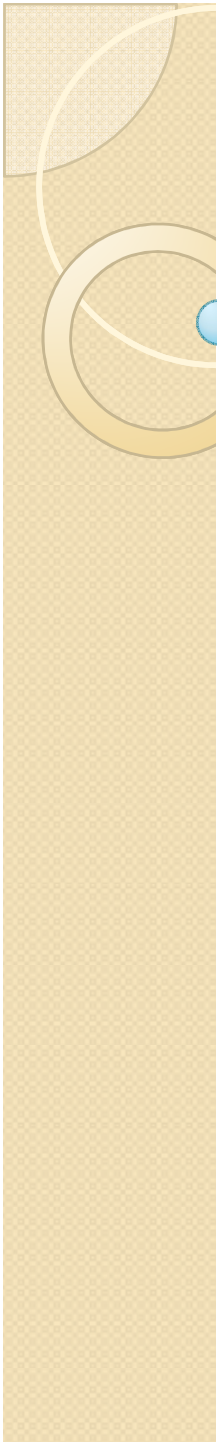
Vamos ver um exemplo:

- Imagine uma mistura de açúcar em óleo vegetal (tem sabor doce) e você quer separar o açúcar do óleo. Você observa que as partículas de açúcar são muito pequenas para filtrar e você suspeita que o açúcar se encontra parcialmente dissolvido no óleo vegetal.

Vegetable oil
and sugar

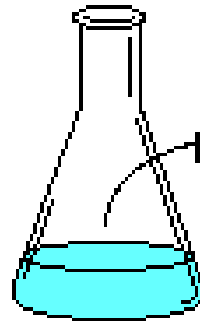
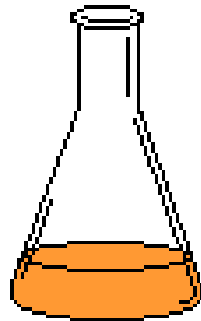




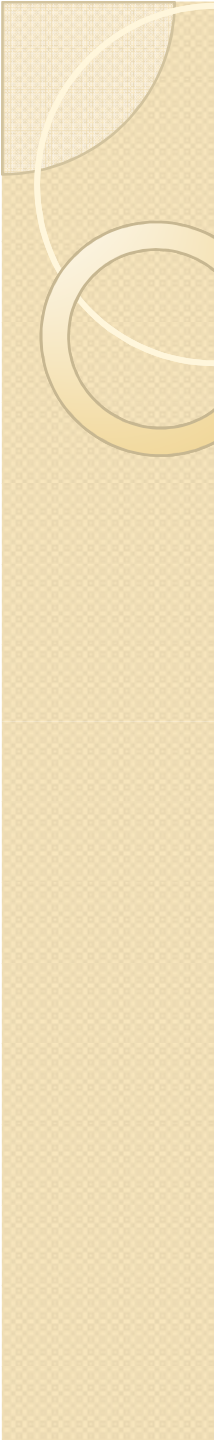


Oil Phase

Water phase



Now the water layer tastes sweet...



A extração Líquido-líquido se baseia na transferência de um soluto de uma fase líquida para outra de acordo com a sua solubilidade.

A extração se torna uma ferramenta útil na separação de compostos orgânicos se forem escolhidos os solventes de extração adequados. Assim, essa técnica pode ser usada para separar seletivamente uma substância de uma mistura ou para remover impurezas de uma solução. Na prática, normalmente **uma das fases é a água ou uma solução aquosa e a outra um solvente orgânico que é imiscível com a água.**

Para um composto determinado, as diferenças de solubilidade entre os solventes podem ser quantificadas sendo denominadas de **“Coeficiente de distribuição”**.

Coeficiente de Partição K_p (Coeficiente de Distribuição K_d)

Quando um composto é misturado em um funil de separação com dois solventes imiscíveis, o composto irá se distribuir entre os dois solventes.

Solventes

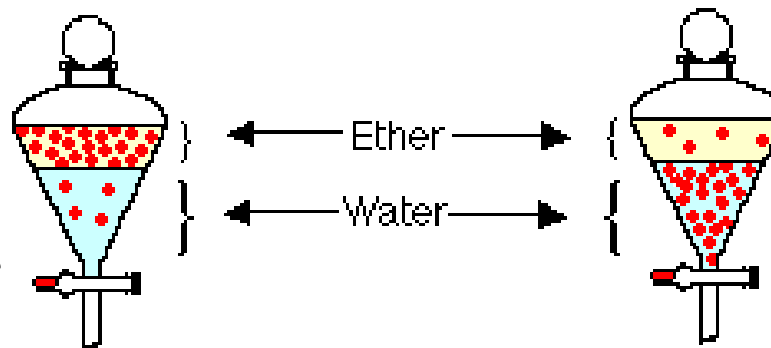
Água

Um solvente orgânico
imiscível em água

A maioria dos compostos orgânicos é mais solúvel nos solventes orgânicos.

More
organic solvent
soluble compounds

More
water-soluble
compounds



A uma determinada temperatura, a razão de concentrações de um soluto em cada solvente é uma constante. Essa razão é chamada de Coeficiente de distribuição, K.

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

(quando solvente₁ e solvente₂ são líquidos imiscíveis.
Por convenção o solvente orgânico é o [1] e a água é o [2])

Suponhamos que um composto possui um coeficiente de distribuição $K = 2$ entre solvente₁ and solvente₂

$$K = \frac{[\bullet]_{\text{solv}_2}}{[\bullet]_{\text{solv}_1}} = 2$$

Figure 1

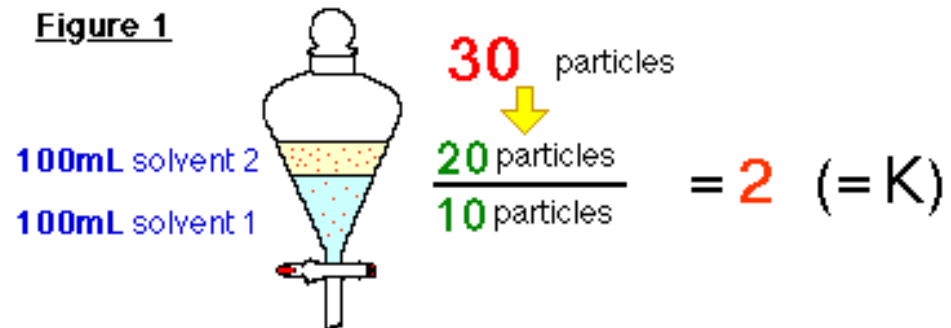


Figure 2

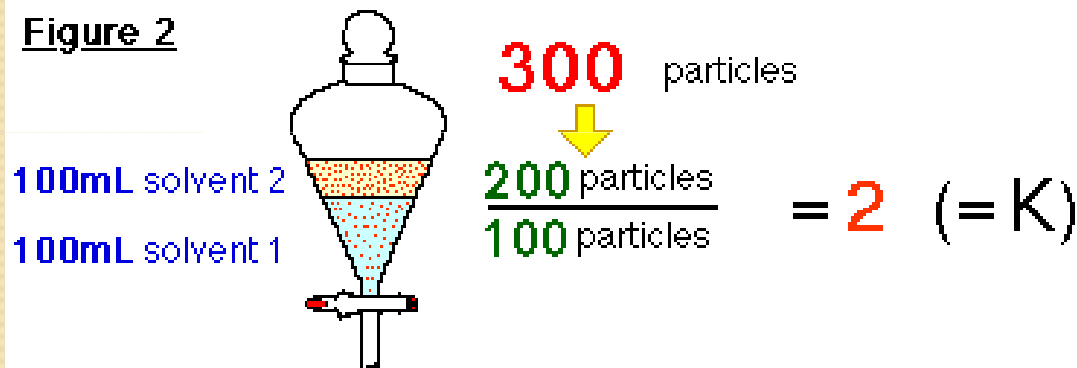
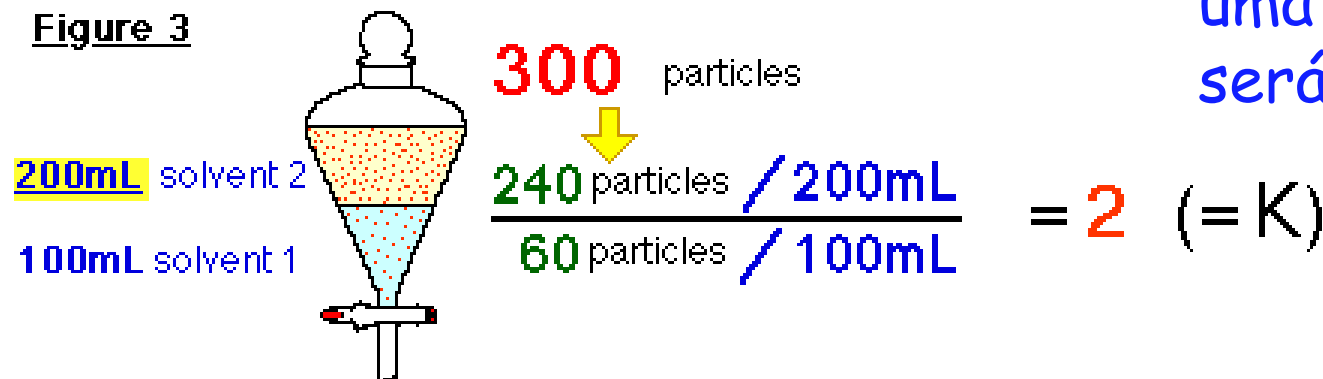


Figure 3



Se você usar uma quantidade maior do solvente de extração, uma maior quantidade será extraída.

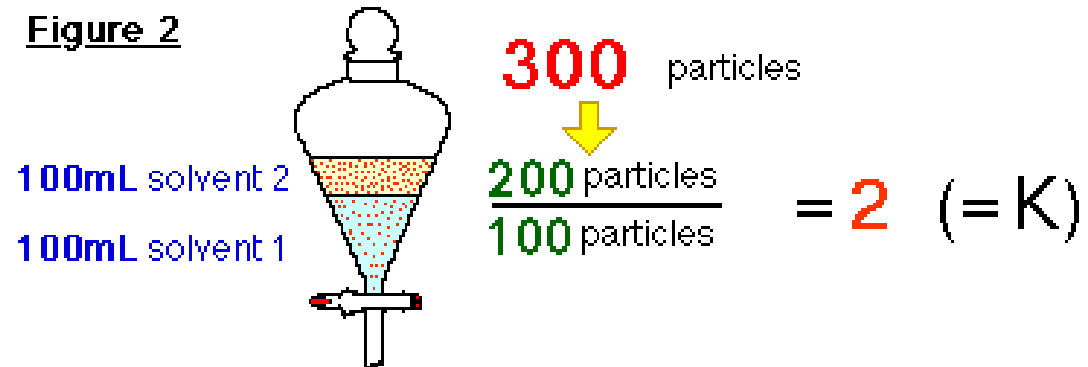
O que aconteceria se vc extraísse 2 vezes com 100 mL de solvente?

Você ainda tem 100 mL do solvente₁, contendo 100 partículas.

Adicione uma segunda porção de 100 mL de solvente₂ puro.

200 mL de solvente₂ : 240 partículas do composto. Uma extração com 200 mL fornece um TOTAL de 240 partículas, contra 267 em duas etapas

Figure 2



Suppose x particles are extracted out of 100 dissolved in solvent 1

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

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

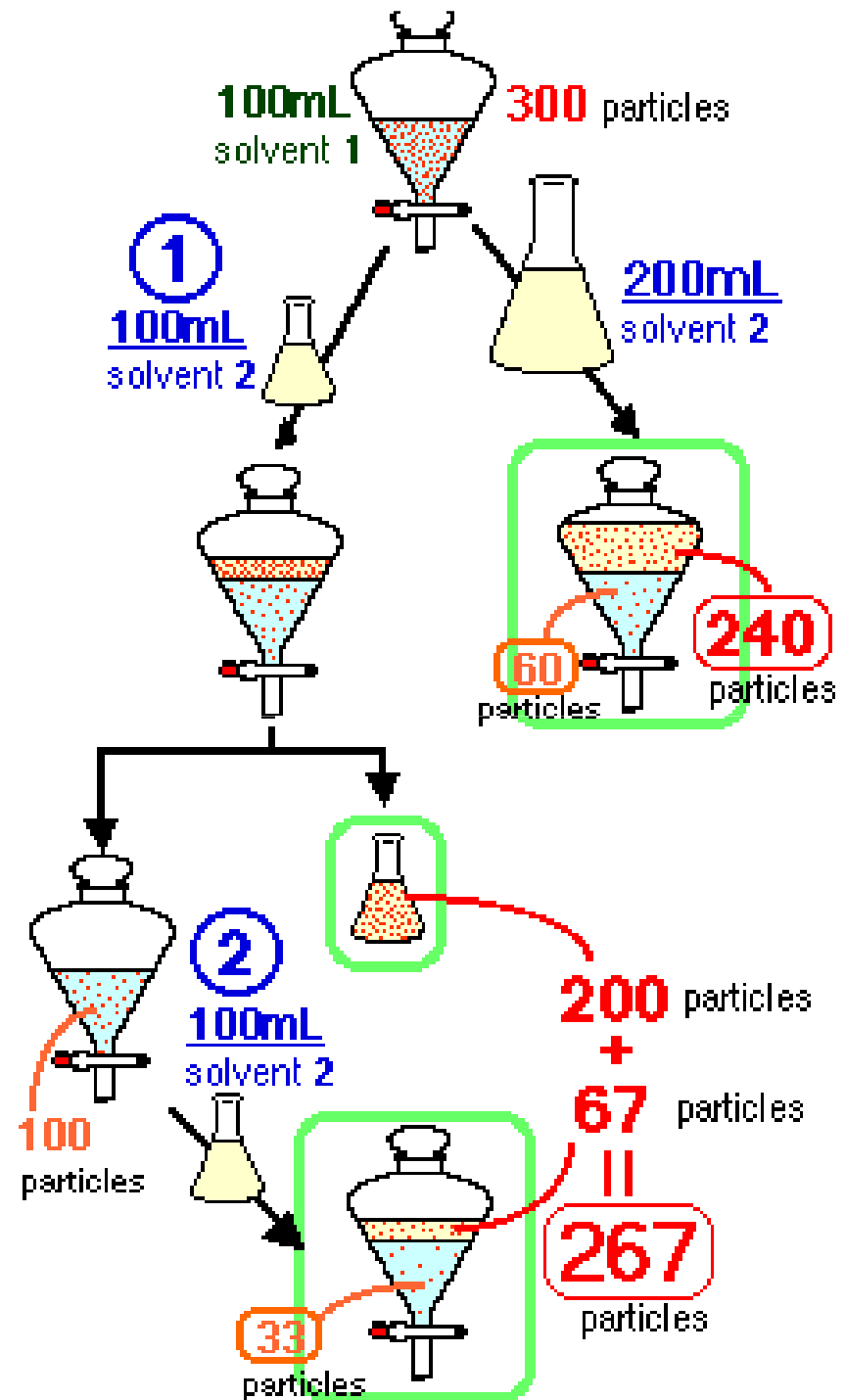
$$x = 200 - 2x$$

$$3x = 200$$

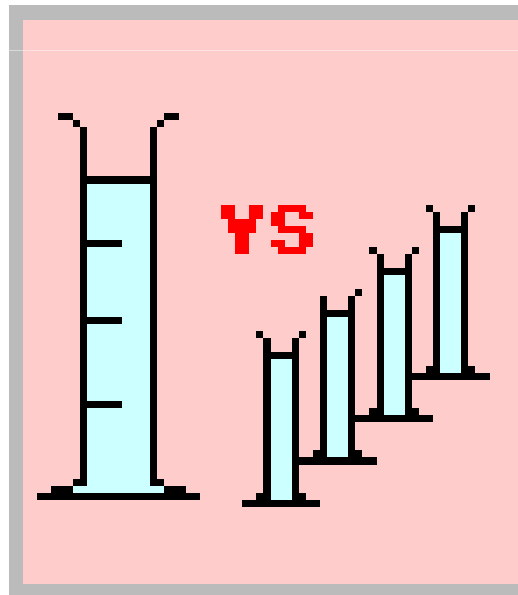
$$x = 66.6... \cong 67$$

∴ 67 particles are extracted with the second portion of solvent 2

É mais eficiente
fazer duas
extrações com $1/2$
do volume do
solvente de
extração do que
uma com um grande
volume!



Quanto maior o número de pequenas extrações, maior será a quantidade de soluto removida. Entretanto, para otimizar a eficiência a regra geral é extrair três vezes com com $1/3$ do volume.

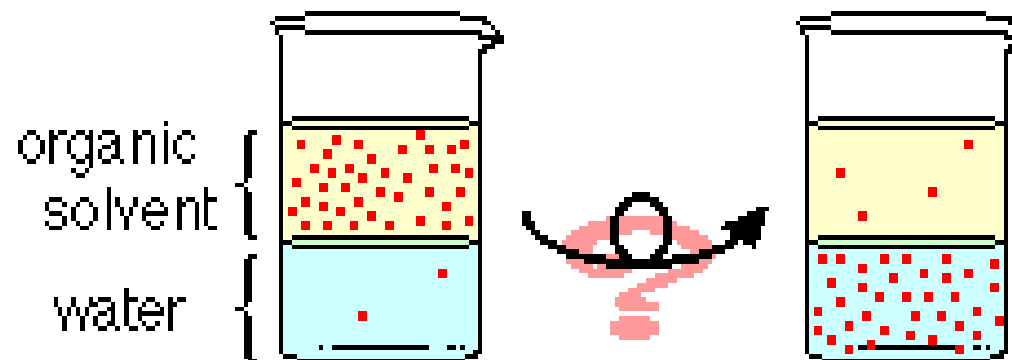


Extração Quimicamente Ativa (ácido-base)

É possível mudar as características de solubilidade de um composto? Como?

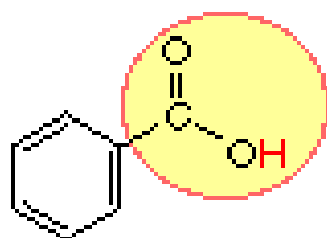
A maioria dos compostos orgânicos é mais solúvel em solventes orgânicos do que em água, normalmente o coeficiente de partição $K > 1$

Contudo, algumas classes específicas de compostos orgânicos podem ser **alteradas quimicamente** para se tornarem **mais solúveis em água**.

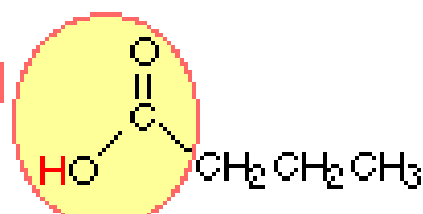


Que tipos de compostos orgânicos podem ser feitos solúveis em água? Os ácidos e as bases orgânicas

Examples of **Carboxylic acids**

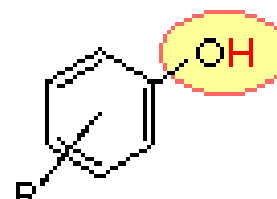


Benzoic acid

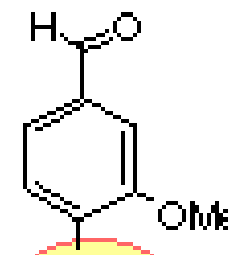


Butyric acid

Examples of **Phenols**

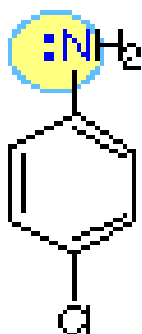


Phenol



Vanillin

Examples of **Amines**



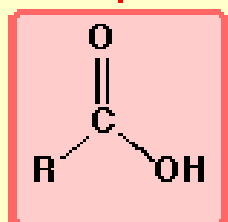
p-Chloroaniline



Tributylamine

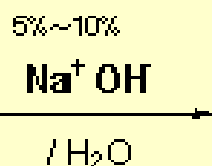
Como podem ácidos ou bases orgânicos serem convertidos em uma forma solúvel em água?

Carboxylic acid

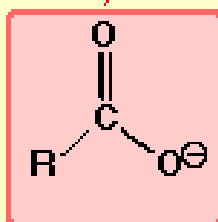


Protonated form:
NOT IONIC

soluble in ether
not soluble in water

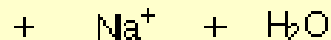


Carboxylate ion



De-protonated form:
IONIC

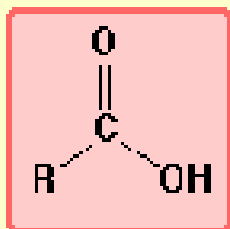
not soluble in ether
soluble in water



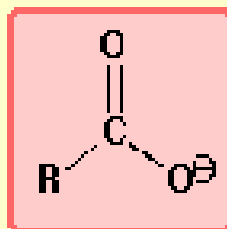
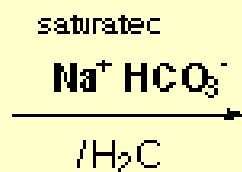
Ácidos carboxílicos (pKa = 3 a 4)

5% de solução aquosa de NaOH. O NaOH é uma base inorgânica forte.

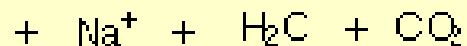
também pode reagir com fracas bases inorgânicas (solução aquosa de NaHCO_3)



not soluble in water



soluble n water



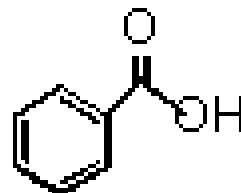
Vamos tentar um exemplo de problema.
Aqui temos uma mistura de ácido benzóico e naftaleno dissolvidos em diclorometano.

Naphthalene



a neutral compound

Benzoic acid



a carboxylic acid

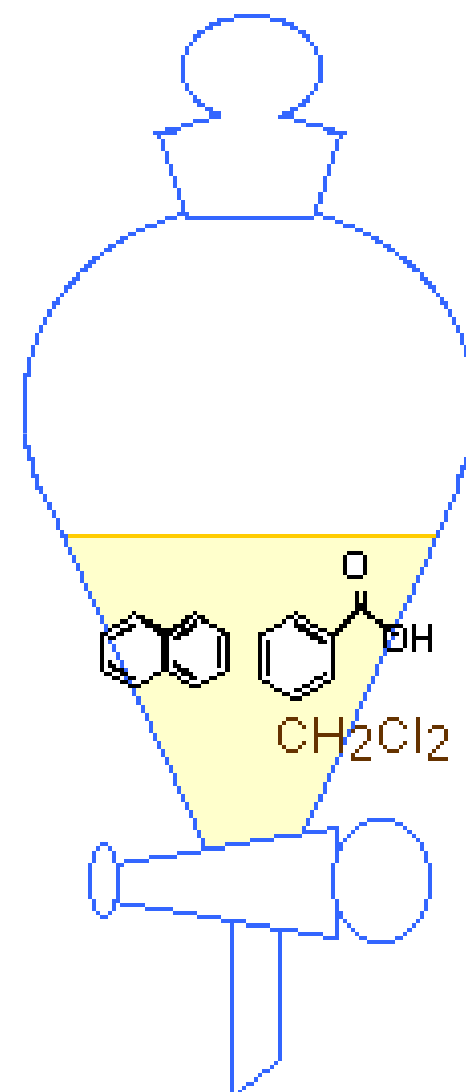
Dichloromethane

CH_2Cl_2

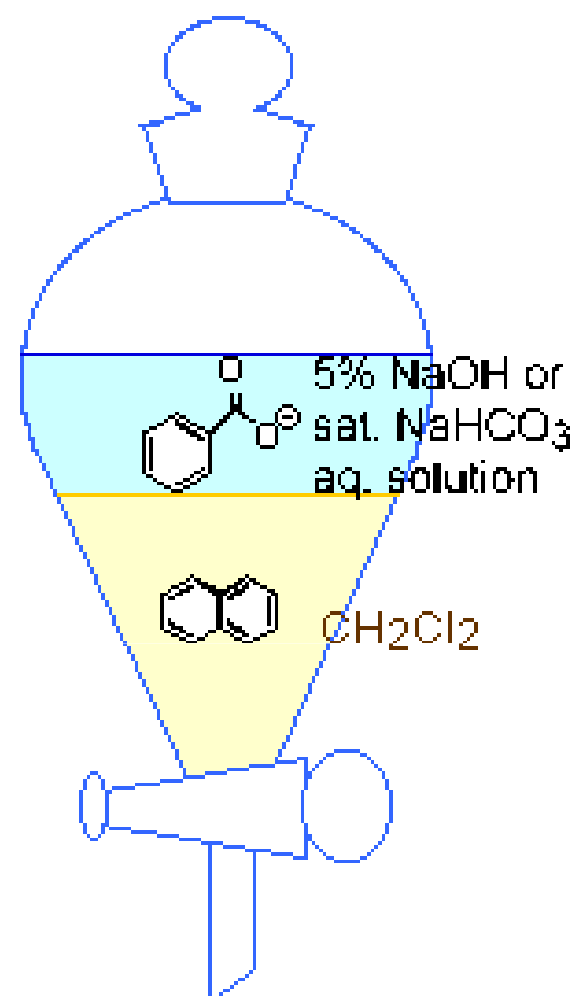
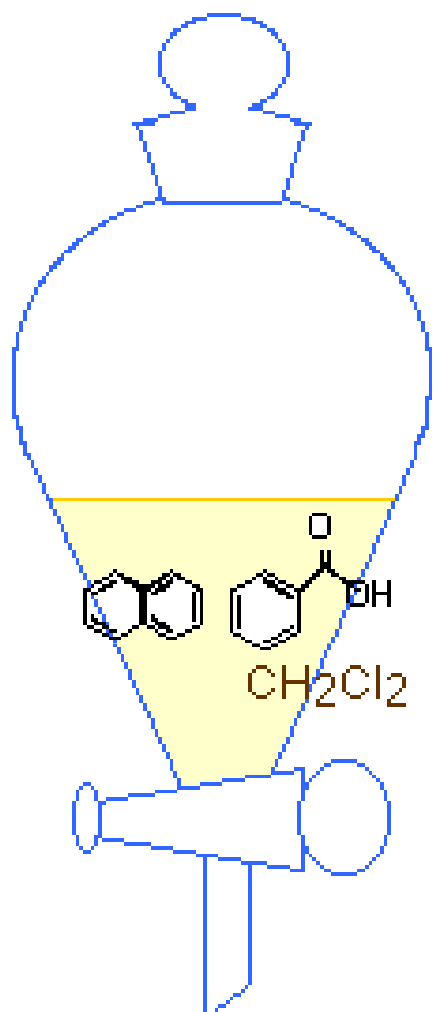
an organic solvent

$d = 1.325$

(denser than water)

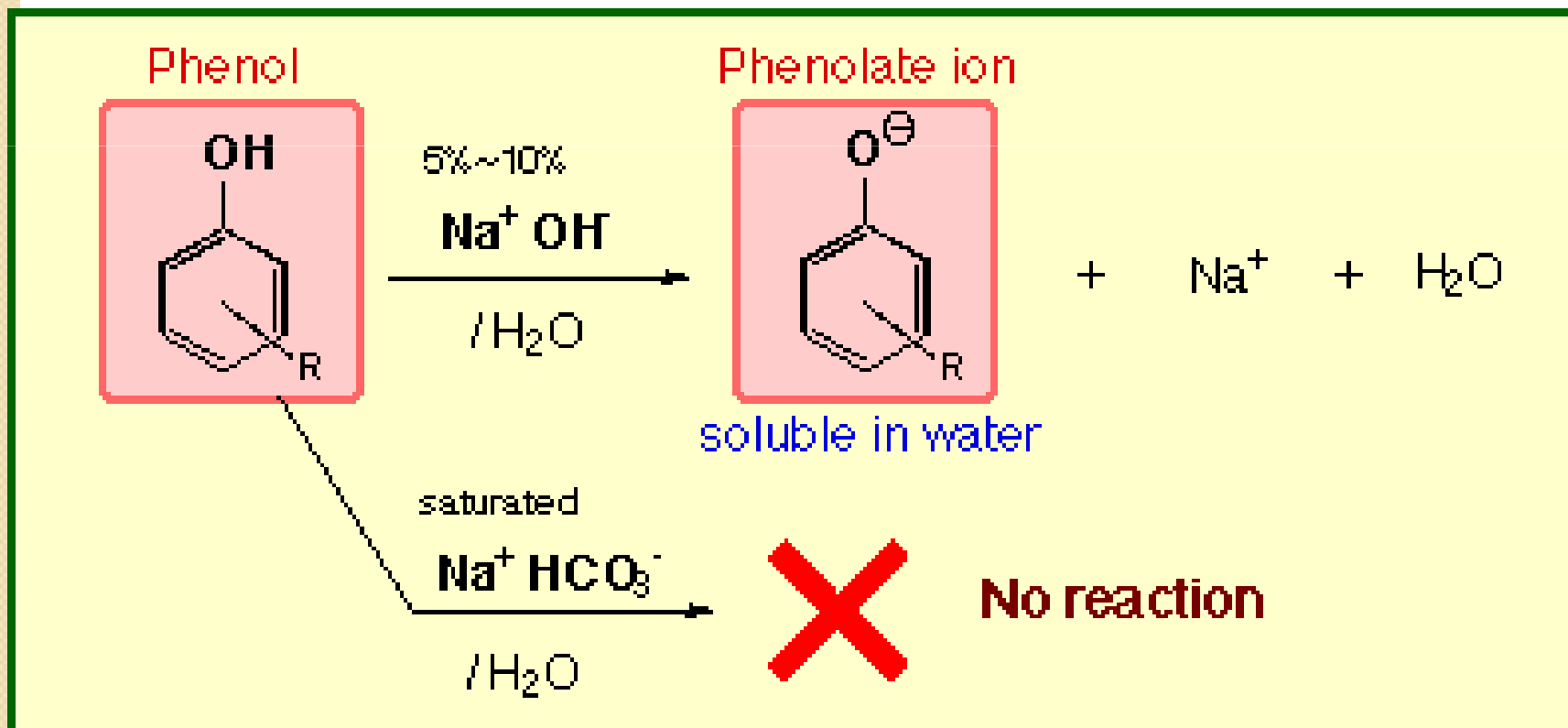


Você quer separar esses dois compostos. O que você pode fazer?



Pode usar uma solução aquosa de NaOH 5% ou uma solução saturada de NaHCO_3 , para extrair o ácido benzóico como uma forma de sal.

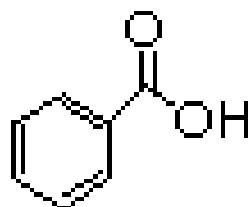
Fenóis são considerados ácidos orgânicos fracos. Fenol, o composto base da série, é parcialmente solúvel em água (1 g irá dissolver em 15 mL de água), enquanto que fenóis substituídos não o são. Uma solução aquosa de bicarbonato de sódio (NaHCO_3), uma base fraca, não irá desprotonar fenóis para torná-los iônicos, porque não é suficientemente forte. No entanto, o tratamento com NaOH , uma base forte, pode mudar a sua forma de fenol (sal) iônica.



Vamos tentar um outro exemplo de problema.

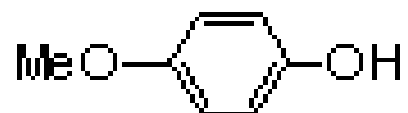
Aqui temos uma mistura de ácido benzóico e *p*-metoxifenol, **dissolvidos em diclorometano**.

Benzoic acid



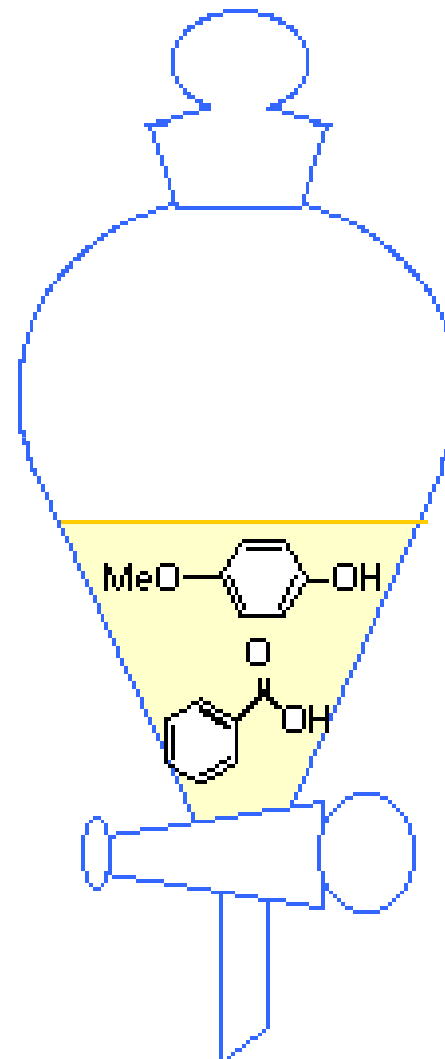
pKa = 4.2

p-Methoxyphenol

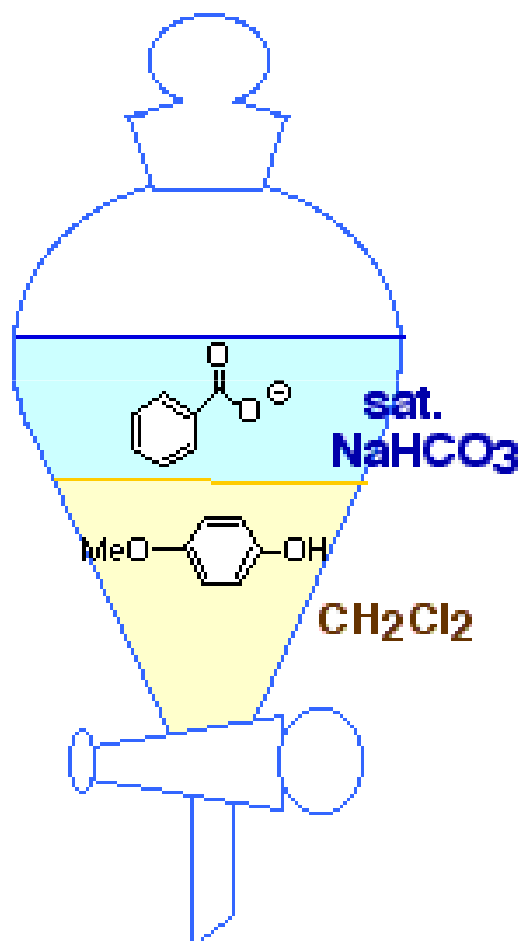
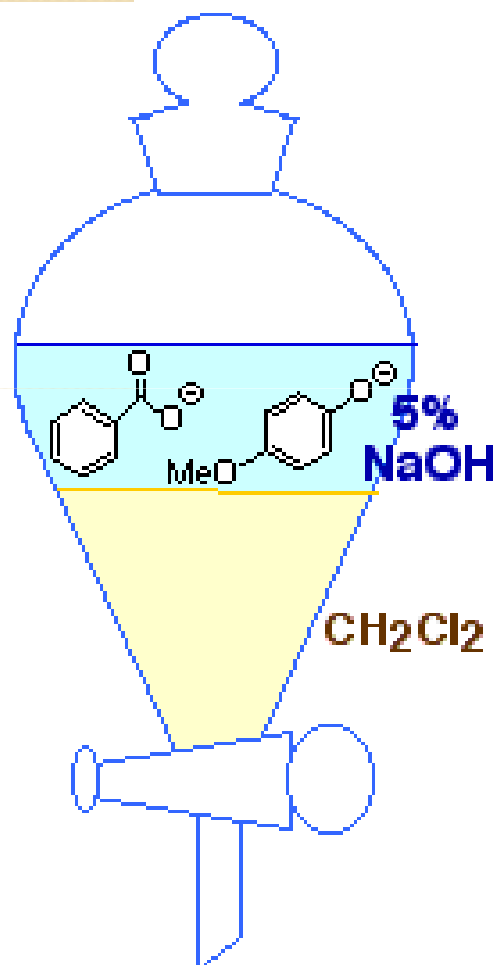


pKa = ~10

Você quer separar esses dois compostos. O que você pode fazer?



NaOH era muito forte a base, portanto, não diferencia os ácidos orgânicos fortes e fracos. A utilização de uma base inorgânica fraca tal como NaHCO_3 irá diferenciar entre os compostos



Ácidos orgânicos fortes, tais como ácido benzóico, seriam desprotonados e ionizados, enquanto ácidos orgânicos fracos, tais como fenóis, NÃO seriam desprotonados.

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).

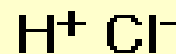
Recall that salts are ionic and generally soluble in water but not soluble in water-immiscible organic solvents.

Amine (or aniline)



NOT IONIC

soluble in ether
not soluble in water



Ammonium (or anilinium) ion



De-protonated form:

IONIC

not soluble in ether
soluble in water

Let's try a third sample problem.

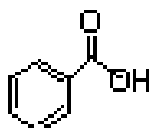
Here is a mixture of benzoic acid and p-chloroaniline, dissolved in dichloromethane.

p-Chloroaniline



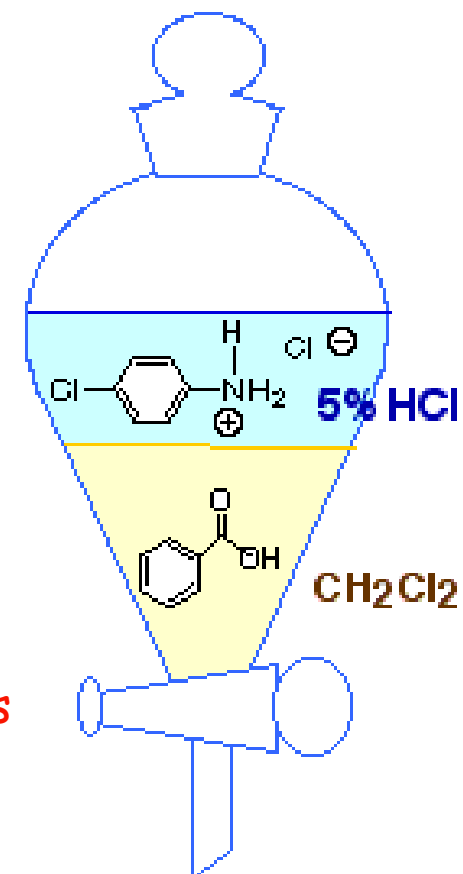
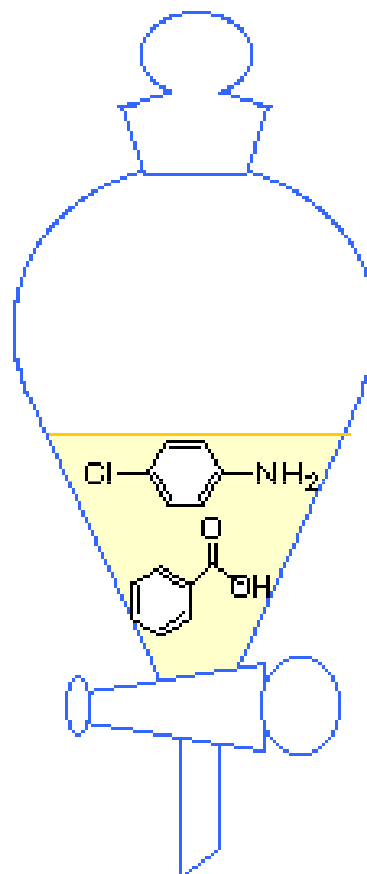
an amine

Benzoic acid



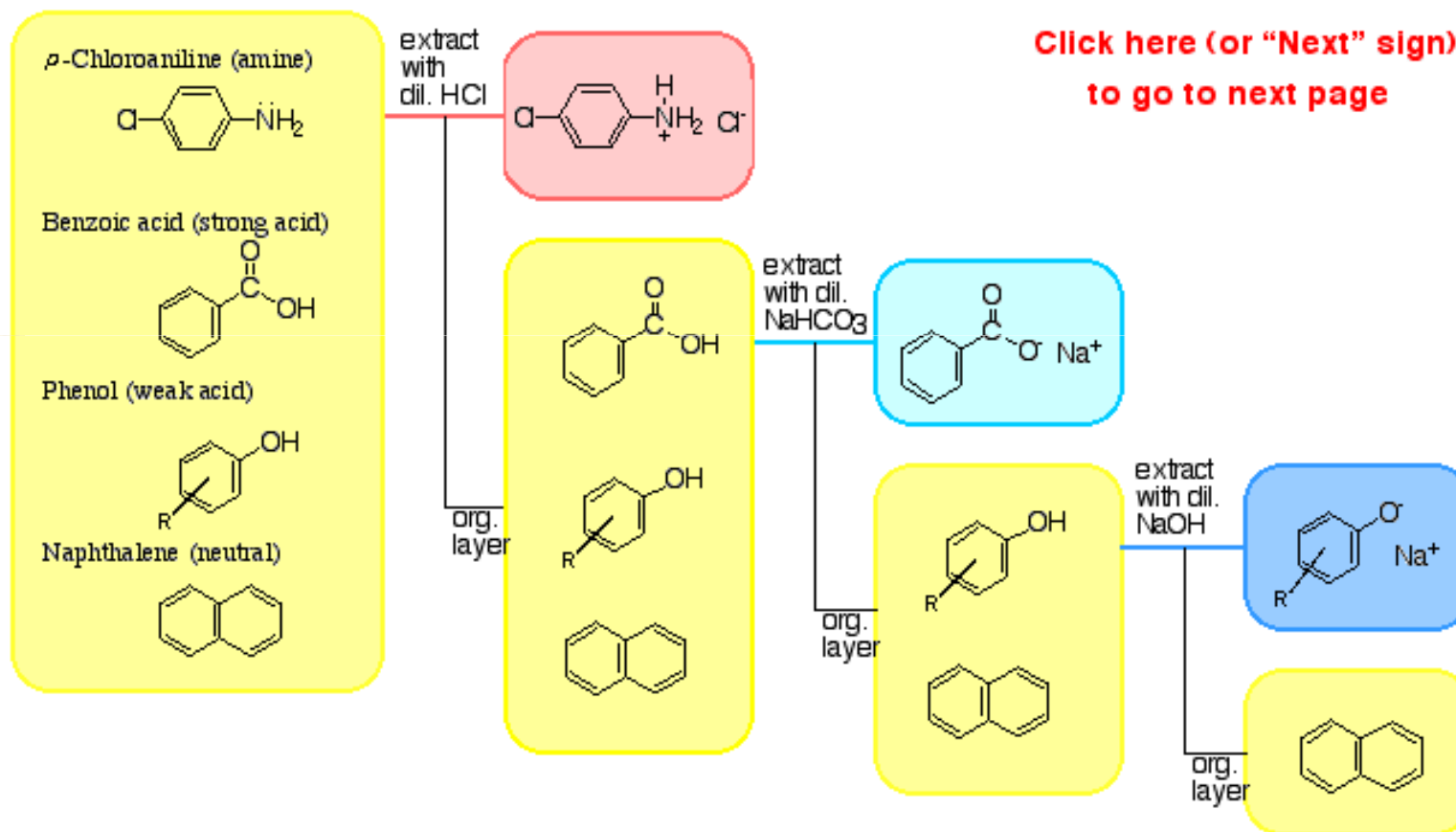
a carboxylic acid

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

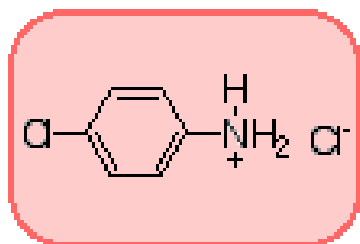


You may use an aqueous solution of either 5% HCl, to extract the amine as a salt form and benzoic acid has remained in the organic layer

Pode-se separar quatro classes de compostos diferentes de uma mistura com base nas suas diferenças de solubilidade específicas. As quatro classes são: **1. Aminas** (base orgânica) **2. Ácidos Carboxílicos** (ácidos fortes) **3. Fenóis** (ácidos fracos) **4. Compostos Neutros**.

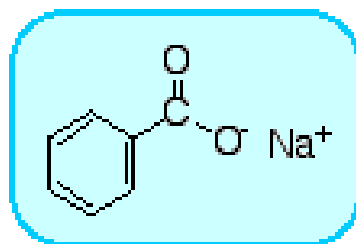


After the separation of the mixture of four components, we will have four solutions: each solution contains one component.



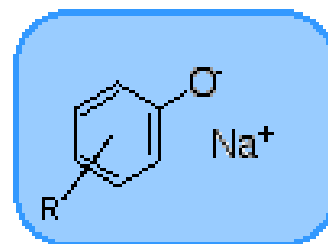
Salt of
Amine

dissolved in
dil. HCl (aq)



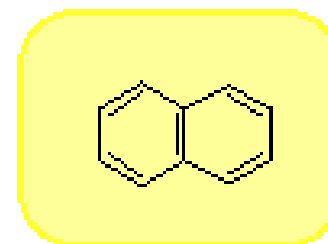
Salt of
carboxylic acid

dissolved in
dil. NaHCO₃ (aq)



Salt of
phenol

dissolved in
dil. NaOH (aq)



Neutral compound
(NOT chemically
altered)

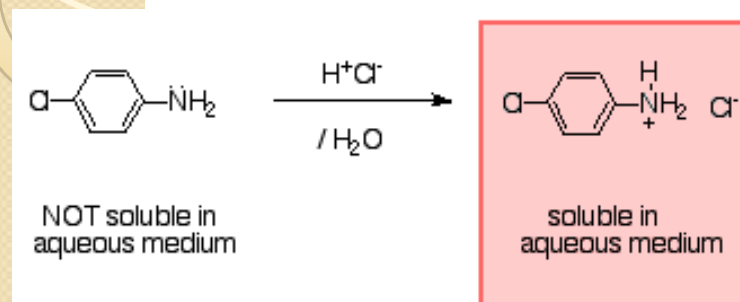
dissolved in
organic layer

The first three compounds are chemically altered, existing in their salt form dissolved in aqueous solution. The fourth 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

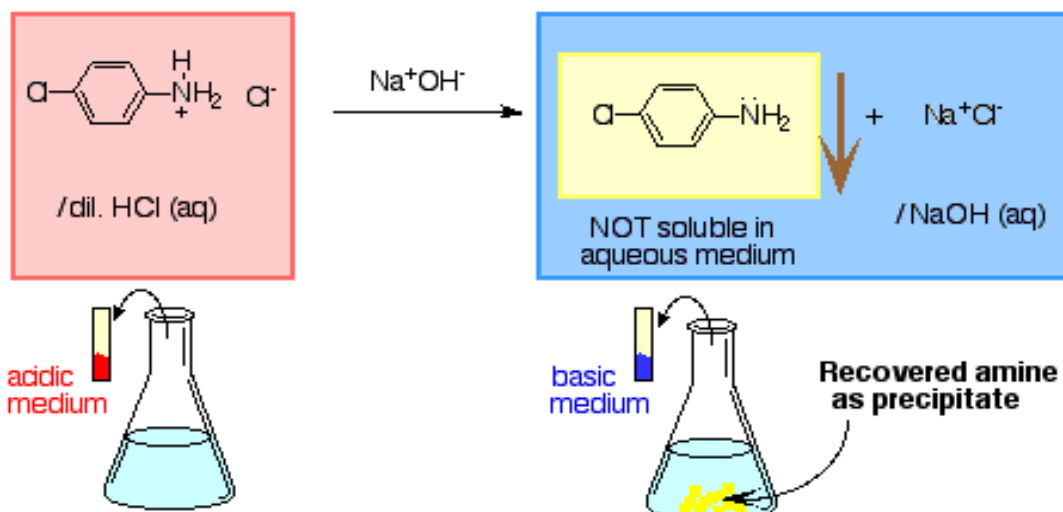
An amine is a basic compound. It is protonated in the presence of excess HCl forming a salt that is soluble in aqueous solution. This is how you separated the amine from the original mixture containing it.



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**.

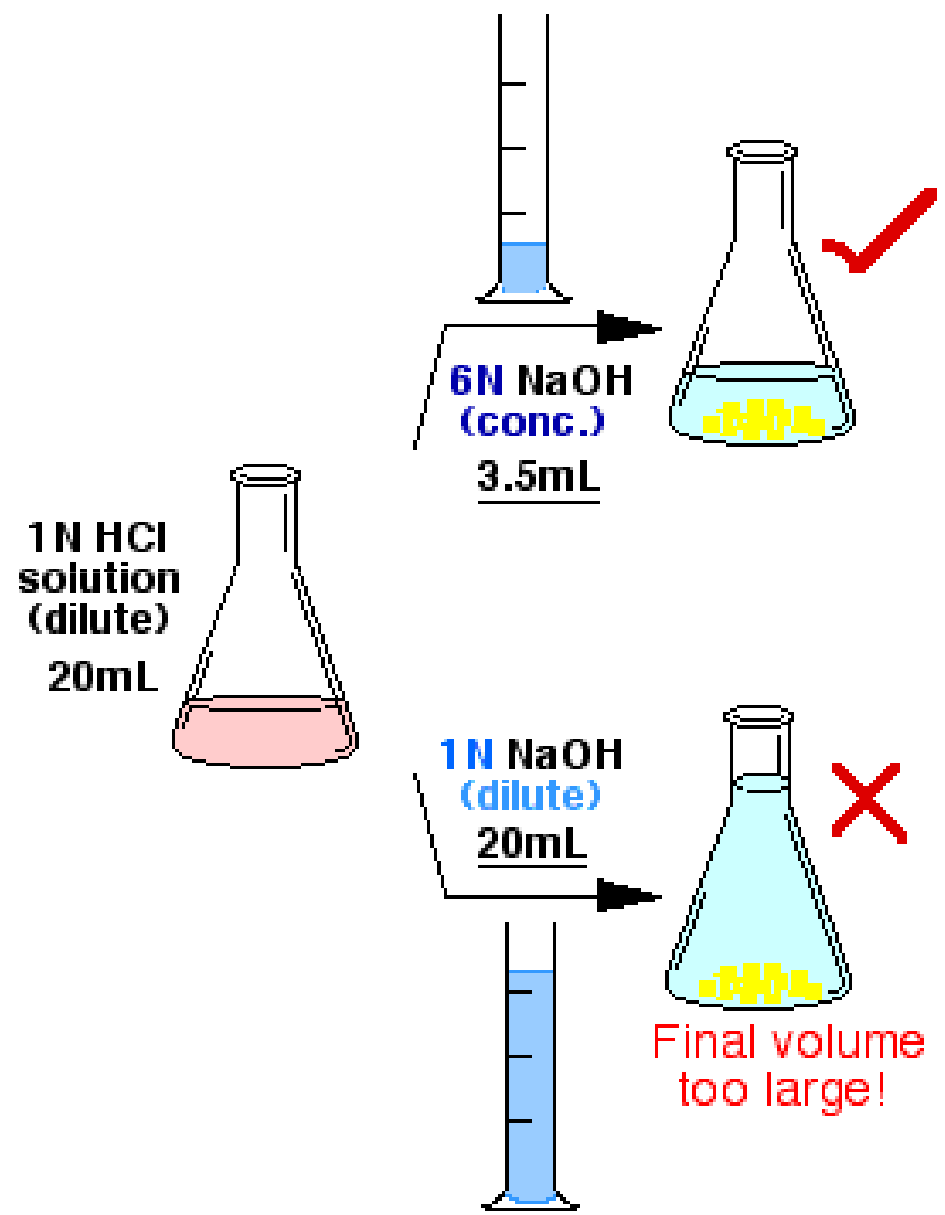
Basification is done by carefully adding concentrated NaOH solution to the solution containing the amine salt until it becomes basic.



▪ 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).

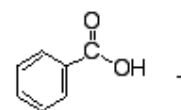
▪ Basification must be done carefully, portion by portion, with swirling each time because the acid-base neutralization reaction is exothermic.

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

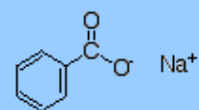
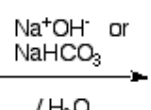


Isolation (Recovery) of Acids

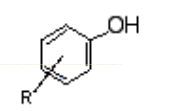
There are two different groups of organic acids: **carboxylic acids** (strong acids) and **phenols** (weak acids). In the separation procedure, acids were extracted using (weak or strong) basic aqueous solutions



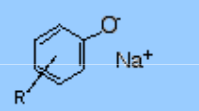
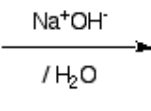
NOT soluble in aqueous medium



soluble in aqueous medium

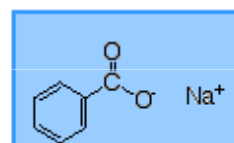


NOT soluble in aqueous medium

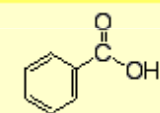
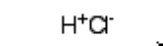


soluble in aqueous medium

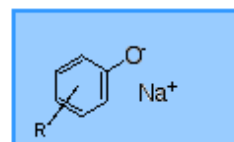
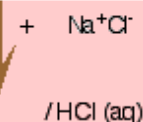
Both acids can be returned to the original form in the same manner! Organic acids are currently dissolved in a **basic aqueous solution**, because the acid forms a salt, an ionic form. When you make the aqueous solution **acidic**, the organic acids no longer remain dissolved because they are no longer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



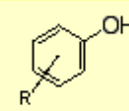
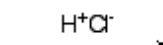
/dil. NaOH or NaHCO₃ (aq)



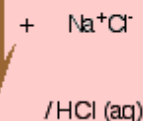
NOT soluble in aqueous medium



/dil. NaOH (aq)

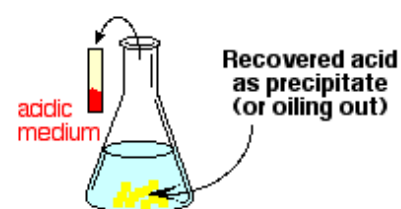
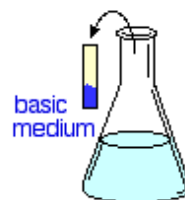


NOT soluble in aqueous medium



Acidification is done by carefully adding concentrated HCl solution until the mixture becomes **acidic**,

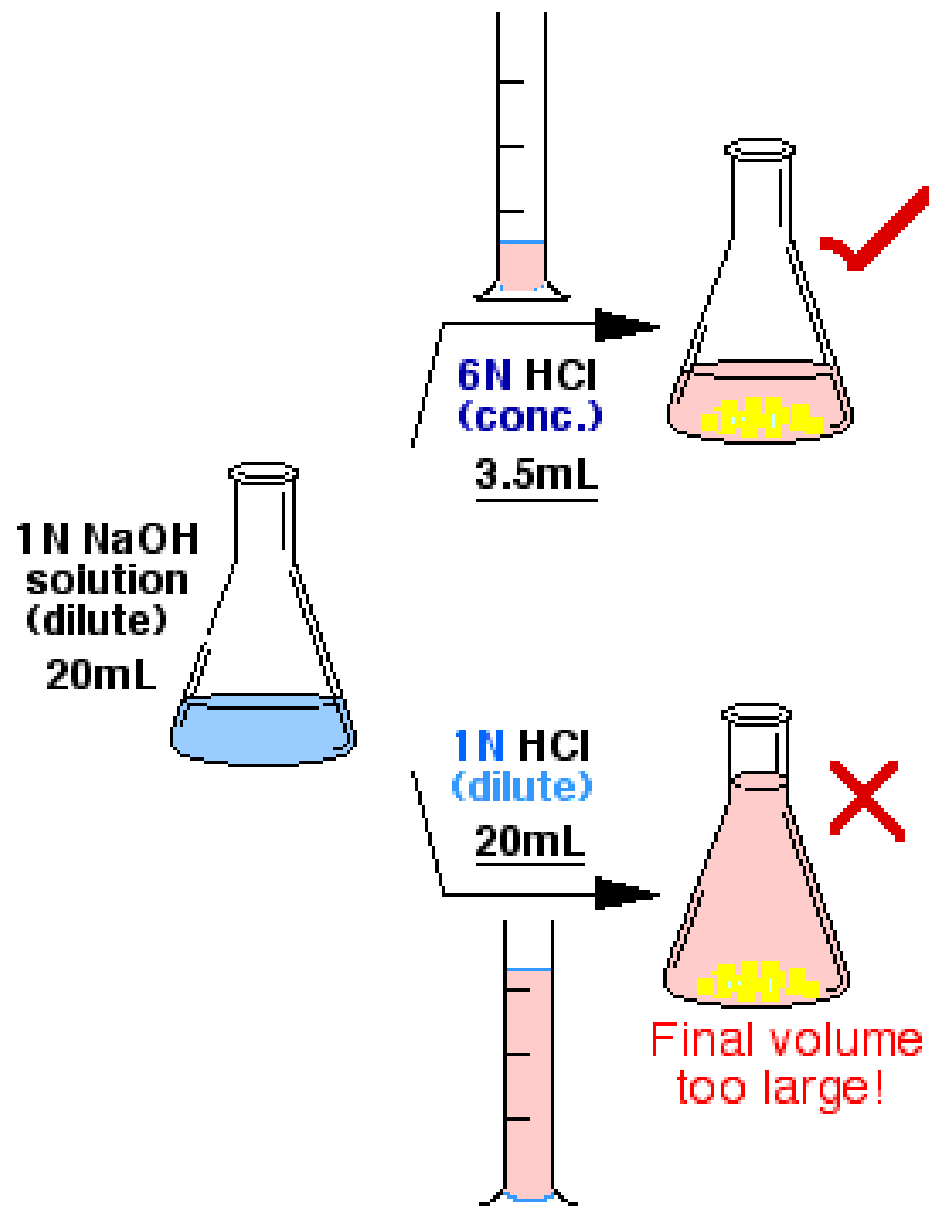
When the weak base, NaHCO₃, was the extracting solution, CO₂ gas will evolve during acidification.



▪ 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

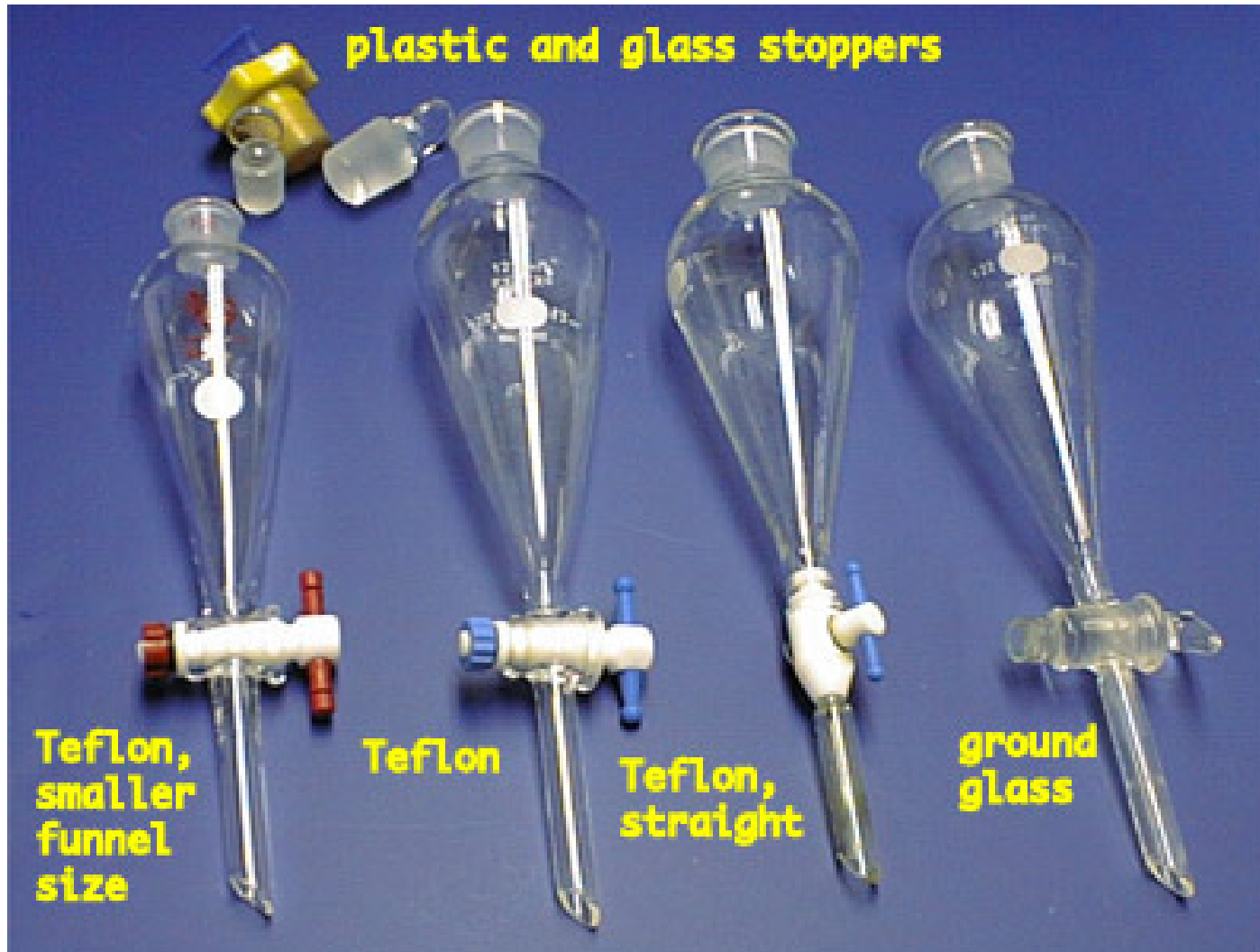
▪ Acidification must be done carefully, portion by portion, with swirling each time because the acid-base neutralization reaction is exothermic.

▪ 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



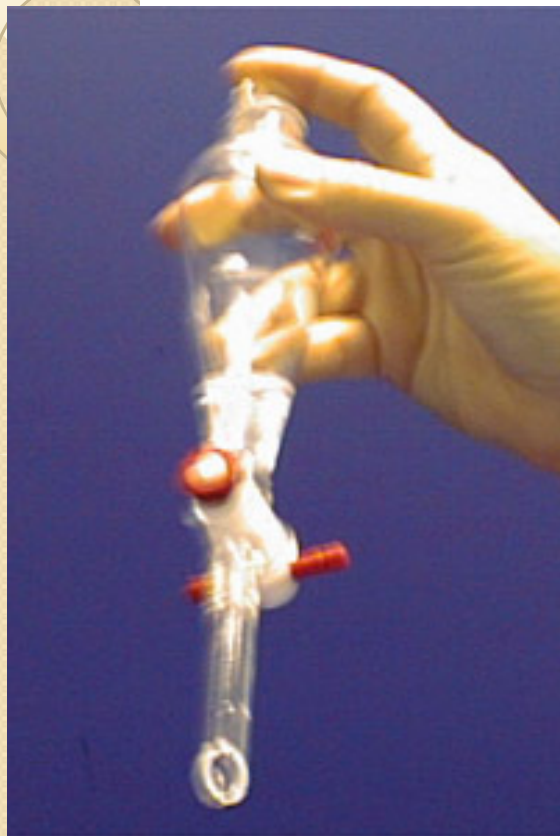
3. Add extraction solvent



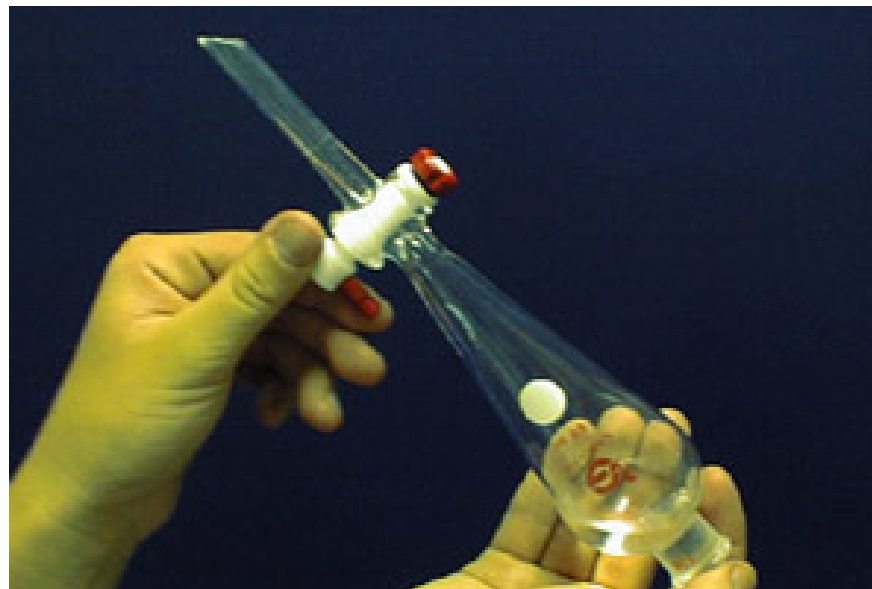
4. Add ground glass Stopper (well greased)

Separatory Funnel Extraction Procedure

Shake the separatory funnel.



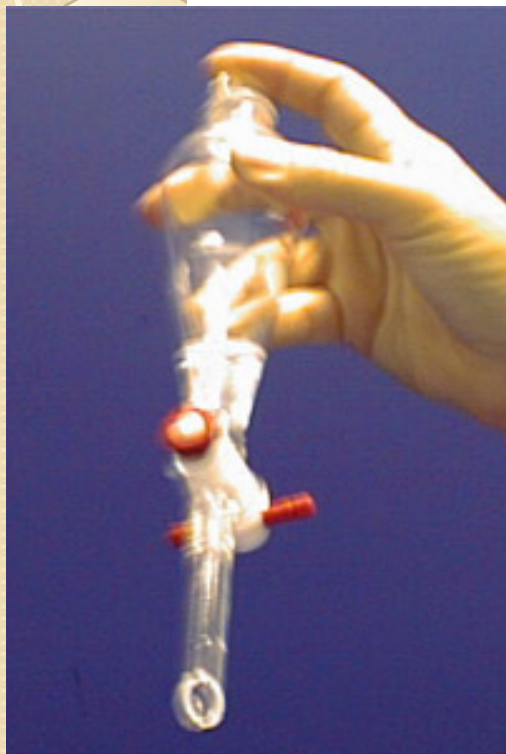
Pick up the separatory funnel with the stopper in palce and the stopcock closed, and rock it once gently.



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

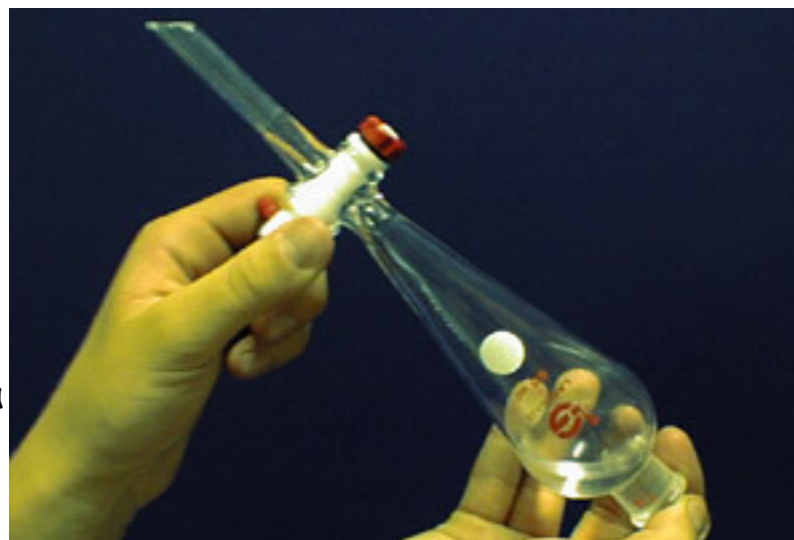
Separatory Funnel Extraction Procedure

Shake the separatory funnel vigorously.



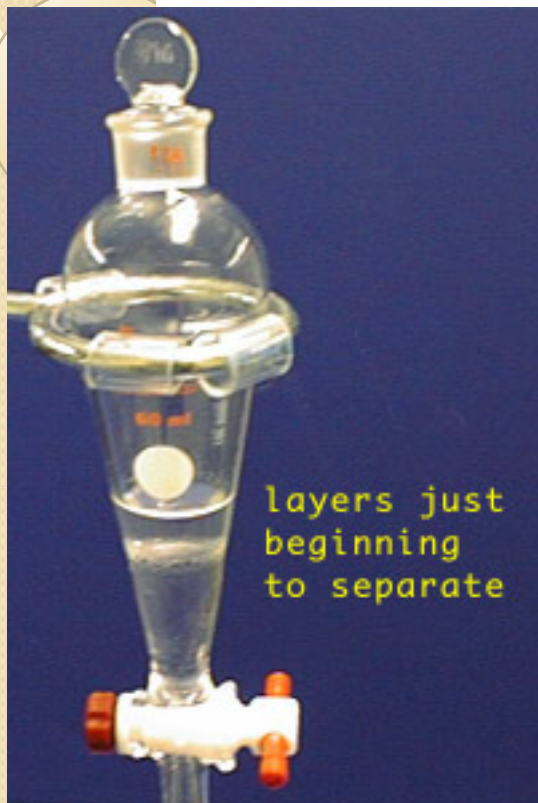
Now, shake the funnel vigorously for a few seconds. Release the pressure, then again shake vigorously. About 30 sec total vigorous shaking is usually sufficient to allow solutes to come to equilibrium between the two solvents.

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

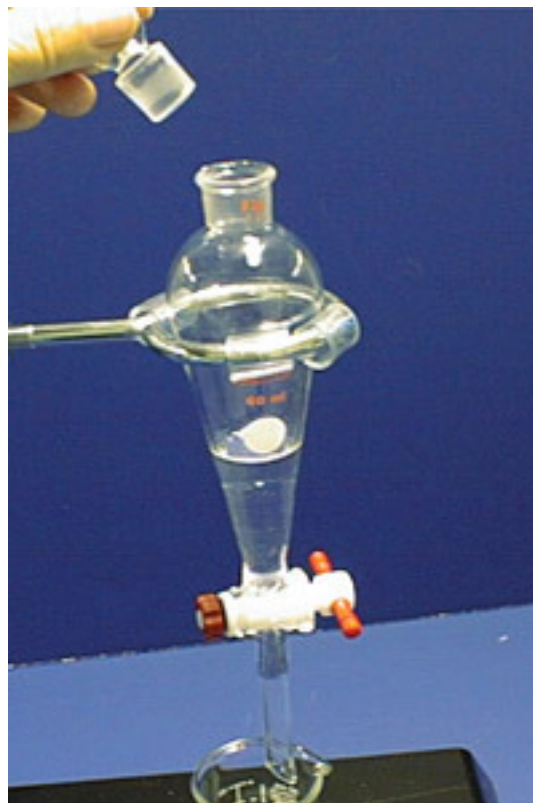


Separatory Funnel Extraction Procedure

Separate the layers.



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