Solvent Extraction

Part1

For 5^{th} sem students (DSE-2)

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Solvent extraction……

- Solvent extraction technique is a part of analytical chemistry and has been recognized as an excellent separation technique because of its ease, simplicity, speed and wide scope
- Solvent extraction is a process in which compounds are separated based on their relative solubility.
- Solvent extraction, also called liquid – liquid extraction, can be used to separate a substance from a solution by extraction into another solvent. It can be used either to recover a valuable substance from the original solution, or to purify the original solvent by removing an unwanted component.
- The extraction can be applied to liquids (liquid–liquid extraction, LLE), to solid samples (liquid–solid extraction, LSE), to gas samples, and to semi solid samples

Classification extraction processes:

- **Periodical extraction -** is the process in which separatory funnel (which contain substance which extragent) is shaked
- **Continuous extraction**
- **Countercurrent extraction**

1. Periodical or batch extraction:

- It consists of extracting the solute from one immiscible layer in to other by shaking the two layers until the equilibrium reached.
- It is commonly carried out in chemical laboratories using separating funnel

2. Continuous extraction:

- Continuous flow of immiscible solvent through the solution or a continuous countercurrent flow of both phases
- It consists of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution being extracted

3. **Countercurrent extraction:**

- It is used for the fractionation purposes.
- The separation is based on the density difference between the fluids in contact

The choice of method to be employed will depend upon the value of distribution ratio of the solute of interest.

Uses:

Industries	
Chemical	• Washing of acids/bases, polar compounds from organics
Pharmaceuticals	• Recovery of active materials from fermentation broths • Purification of vitamin products
Effluent Treatment	• Recovery of phenol, DMF, DMAC • Recovery of acetic acid from dilute solutions
Polymer Processing	• Recovery of caprolactam for nylon manufacture • Separation of catalyst from reaction products
Petroleum	• Lube oil quality improvement • Separation of aromatics/aliphatics (BTX)
Petrochemicals	• Separation of olefins/parafins • Separation of structural isomers
Food Industry	• Decaffeination of coffee and tea • Separation of essential oils (flavors and fragrances)
Metals Industry	• Copper production • Recovery of rare earth elements
Inorganic Chemicals	• Purification of phosphoric acid
Nuclear Industry	• Purification of uranium

Application of Extraction

- Extraction processes are well suited to the petroleum industry because of the need to separate heat-sensitive liquid feeds according to chemical type (e.g. aliphatic, aromatic, naphthenic) rather than by molecular weight or vapour pressure.

- Other major applications exist in the biochemical or pharmaceutical industry, where emphasis is on the separation of antibiotics and protein recovery.

- In the inorganic chemical industry, they are used to recover high-boiling components such as phosphoric acid, boric acid, and sodium hydroxide from aqueous solutions.

Types of extraction

- Liquid–liquid extraction.
- Solid-phase extraction.
- Acid-base extraction.
- Supercritical fluid extraction.
- Ultrasound-assisted extraction.
- Heat reflux extraction.
- Mechanochemical-assisted extraction.
- Microwave-assisted extraction.

Liquid–liquid extraction.

- The basic procedure for performing a liquid-liquid extraction is to take two immiscible phases, one of which is usually water and the other of which is usually an organic solvent. The two phases are put into a device called a separatory funnel, and compounds in the system will distribute between the two phases.

- There are two terms used for describing this distribution, one of which is called the distribution coefficient K_d, the other of which is called the partition coefficient.
- The distribution coefficient is the ratio of the concentration of solute in the organic phase over the concentration of solute in the aqueous phase (the V-terms are the volume of the phases). This is essentially an equilibration process whereby we start with the solute in the aqueous phase and allow it to distribute into the organic phase.
- The distribution coefficient represents the equilibrium constant for this process

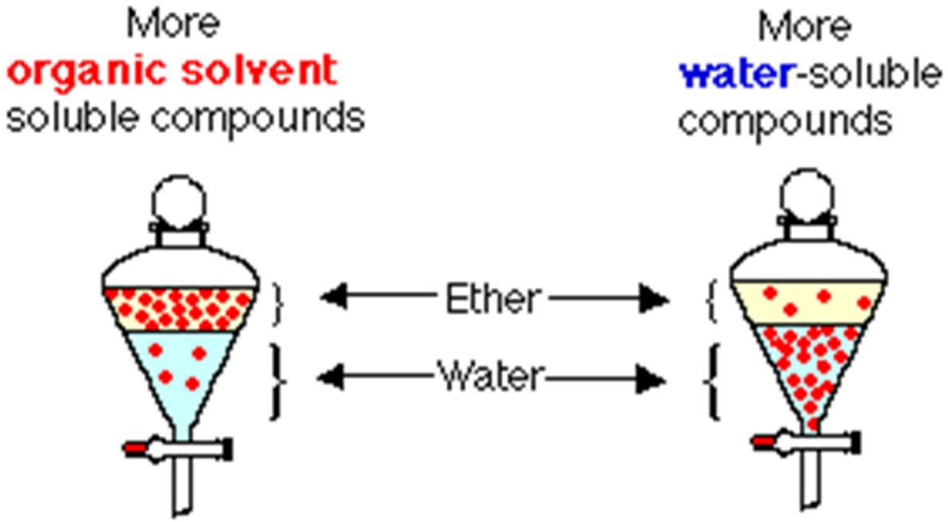
Distribution coefficient "K"

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

- This ratio is the distribution coefficient, K_D or partition coefficient. (solvent1 and solvent2 are immiscible liquids), Solvent 2=Organic layer and Solvent 1= Aq layer

- When shaken, 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 solvents, while some organic compounds are more soluble in water.
- At a certain temperature, the ratio of concentrations of a solute in each solvent is always constant.



Introduction to Extraction

- Liquid-liquid extraction (also known as solvent extraction) involves the separation of the constituents (solutes) of a liquid solution by contact with another insoluble liquid.

- Solutes are separated based on their different solubilities in different liquids.

- Separation is achieved when the substances constituting the original solution is transferred from the original solution to the other liquid solution

- The simplest liquid-liquid extraction involves only a ternary (i.e.3 components) system.

- The solution which is to be extracted is called the feed, and the liquid with which the feed is contacted is the solvent.

- The feed can be considered as comprising the solute A and the "carrier" liquid C. Solvent S is a pure liquid.

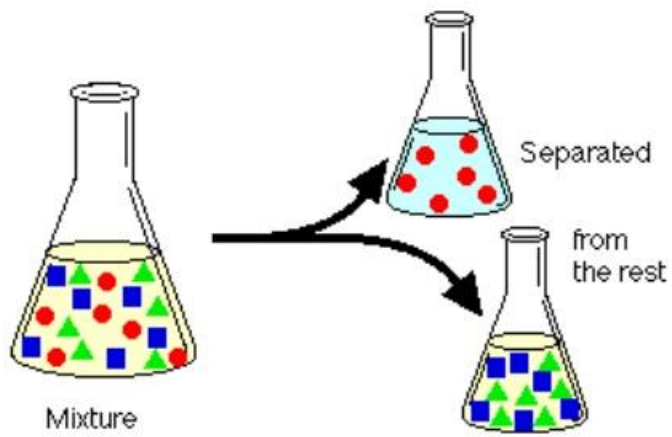
- During contact, mass transfer of A from the feed to the solvent S occurs, with little transfer of C to S.

- The solvent (with the solute) is then permitted to separate from the carrier liquid.

•The solvent-rich product of the operation is called the **extract**, and the residual liquid from which solutes has been removed is the **raffinate**

•In some operations, the solutes are the desired product, hence the extract stream is the desirable stream.

•In other applications, the solutes may be the contaminants that need to be removed, and in this instance the raffinate is the desirable product stream.



LLE Extraction

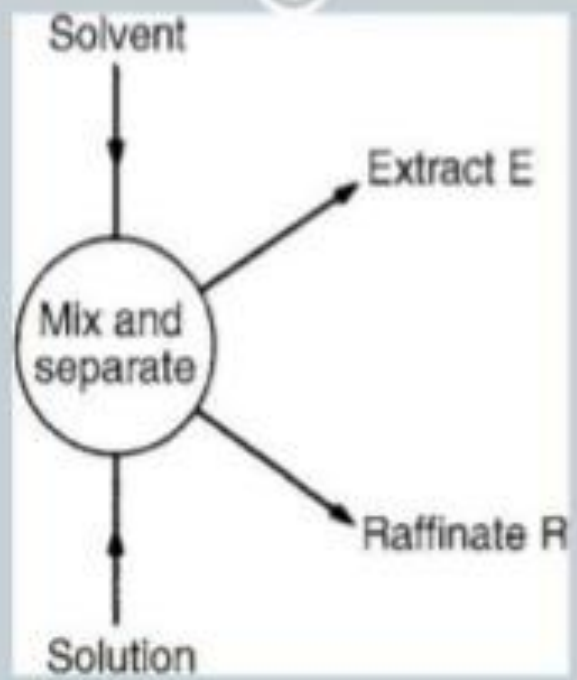
The separation of the components of a liquid mixture by treatment with a solvent in which one or more of the desired components is preferentially soluble is known as liquid-liquid extraction.

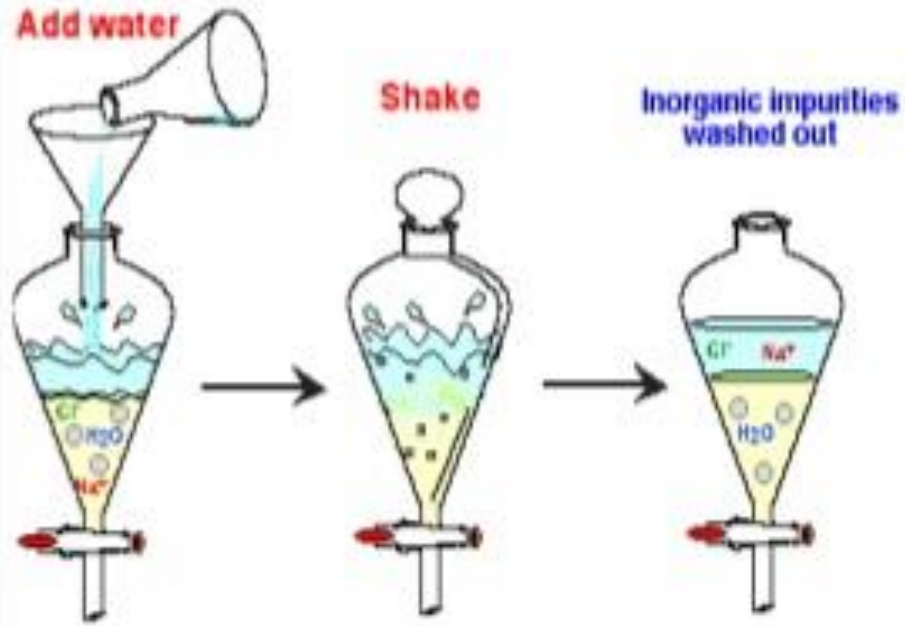
LLE extraction Principle

- The Solute present in the aqueous phase gets partitioned or distributed in both the phases
- If the solute has solubility in the organic solvent, more of the solute would be present in the organic phase at equilibrium and extraction is said to be more efficient

(a) Bringing the feed mixture and the solvent into intimate contact,
(b) Separation of the resulting two phases, and
(c) Removal and recovery of the solvent from each phase.

Single stage Batch Extraction





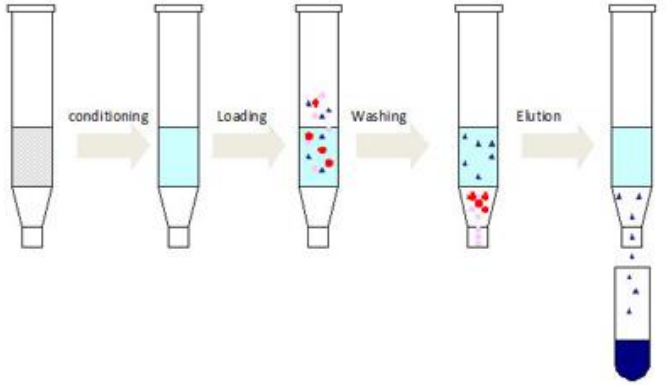
Points need to be considered

1. Higher the partition coefficient greater will be the extraction efficiency
2. Large density differences between the extractant and raffinate = better separation if the separation is by gravity alone
3. High viscosity of solvent affect the phase separation.
4. Should have negligible miscibility/ solubility in the aqueous feed to minimize solvent loss
5. Easily recovered and purified for recycling after extraction.
6. Should be easily available and cost effective
7. Low interfacial tension between the phases facilitates the dispersion of phases and improves mass transfer
8. Physio-chemical properties such as boiling point, density, interfacial tension, viscosity, corrosiveness, flammability, stability compatibility with product, availability should be satisfactory

Choice of solvent

- Factors to be considered:
- Selectivity
- Distribution coefficient
- Insolubility of solvent
- Recoverability of solute from solvent
- Density difference between liquid phases
- Interfacial tension
- Chemical reactivity
- Cost
- Viscosity, vapour pressure
- Flammability, toxicity

Solid-Phase extraction……



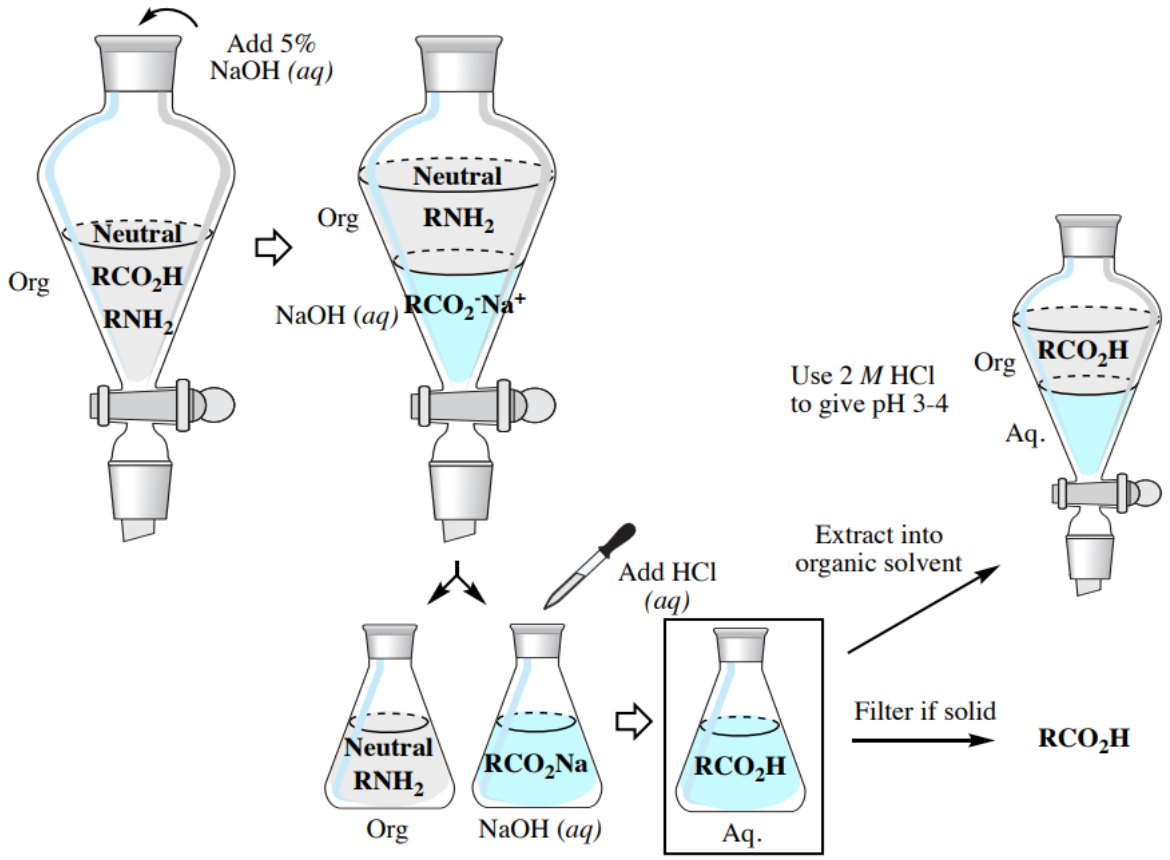
- Solid phase extraction (SPE) is a more rapid, modern alternative to liquid-liquid extraction.
- SPE is the process by which compounds that are dissolved or suspended in a liquid mixture are separated from other compounds in the mixture according to their physical and chemical properties.
- SPE is based on the principle that the components of interest are retained on a special sorbent
- Solid-phase extraction (SPE) is a sample preparation technique routinely used in analytical laboratories for the extraction of analytes from a complex matrix.
- The advantage of solid-phase synthesis is that the products can be isolated easily since all the intermediates are immobilized on polystyrene. Thus, the products can be purified by filtration and washing.

Acid Base Extraction…..

- Acid/base extraction is a process that allows the separation of organic acids, organic bases, and organic neutral compounds (not an acid or base) from each other based on the solubility differences of the organic acid (or base) and its conjugate base (or conjugate acid).
- Extraction is a particularly useful means of separating organic compounds if one compound in the mixture can be chemically converted to an ionic form.
- The ionic form is soluble in an aqueous layer and can be extracted into it. Other, non-ionic organic compounds in the mixture will remain dissolved in the organic solvent layer.
- Separation of the two layers results in the separation of the two compounds.
- The objective of this exercise is to separate a two-component mixture using extraction techniques and then to identify the isolated components by determining their melting points.

Examples……..

1. **a) Extract the Acidic Component**



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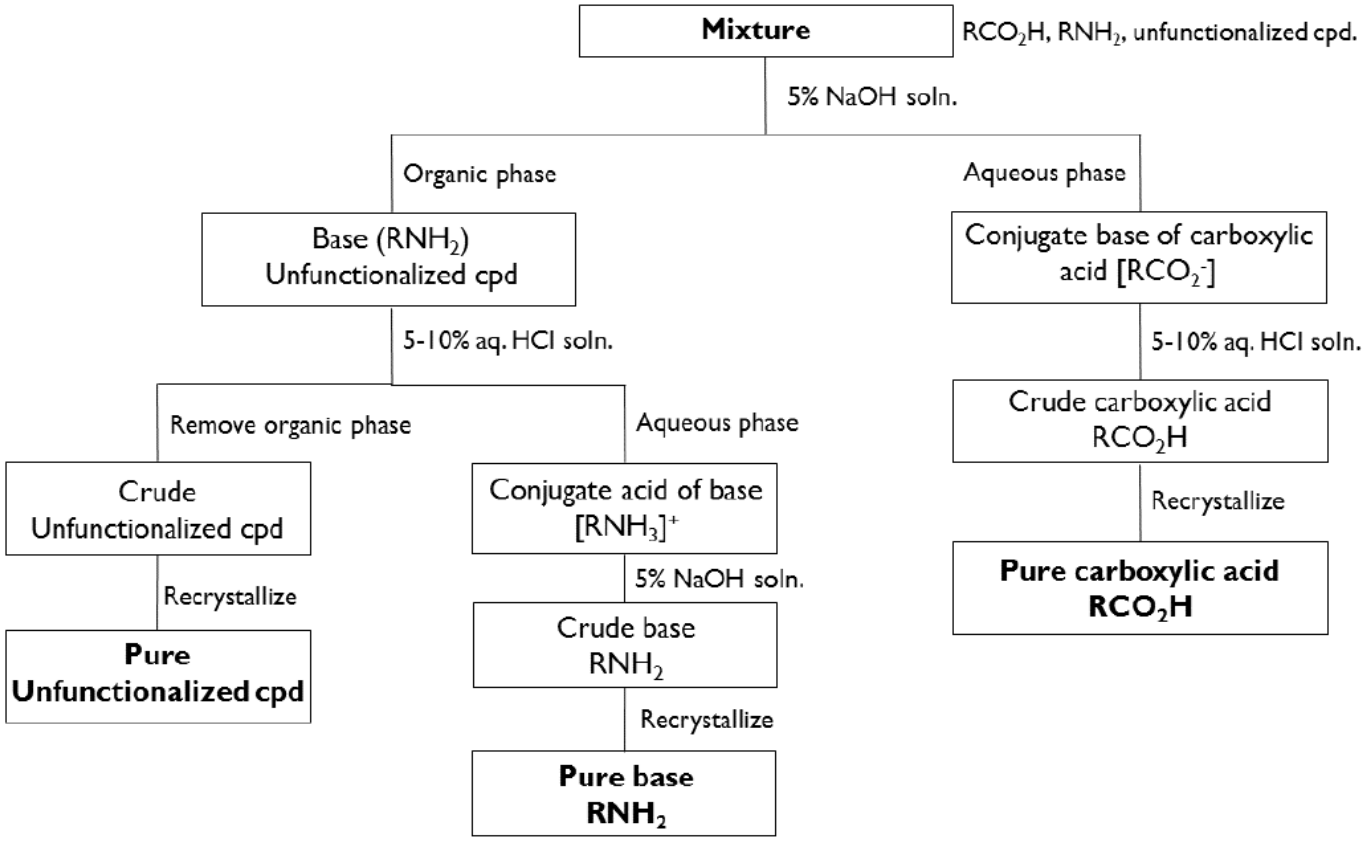
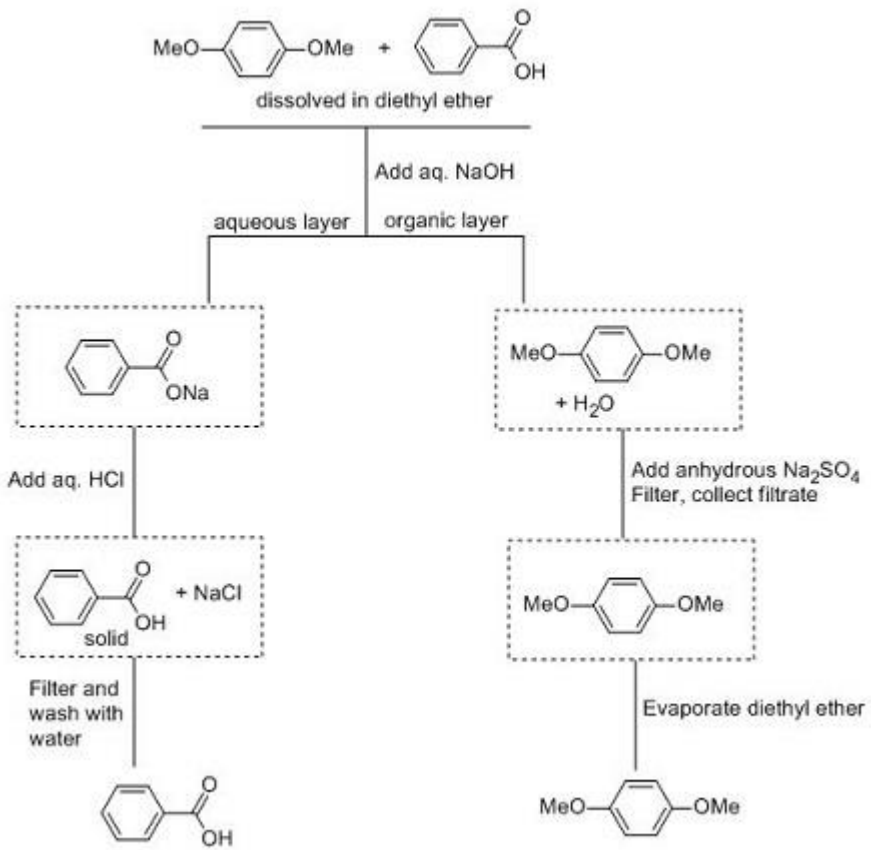
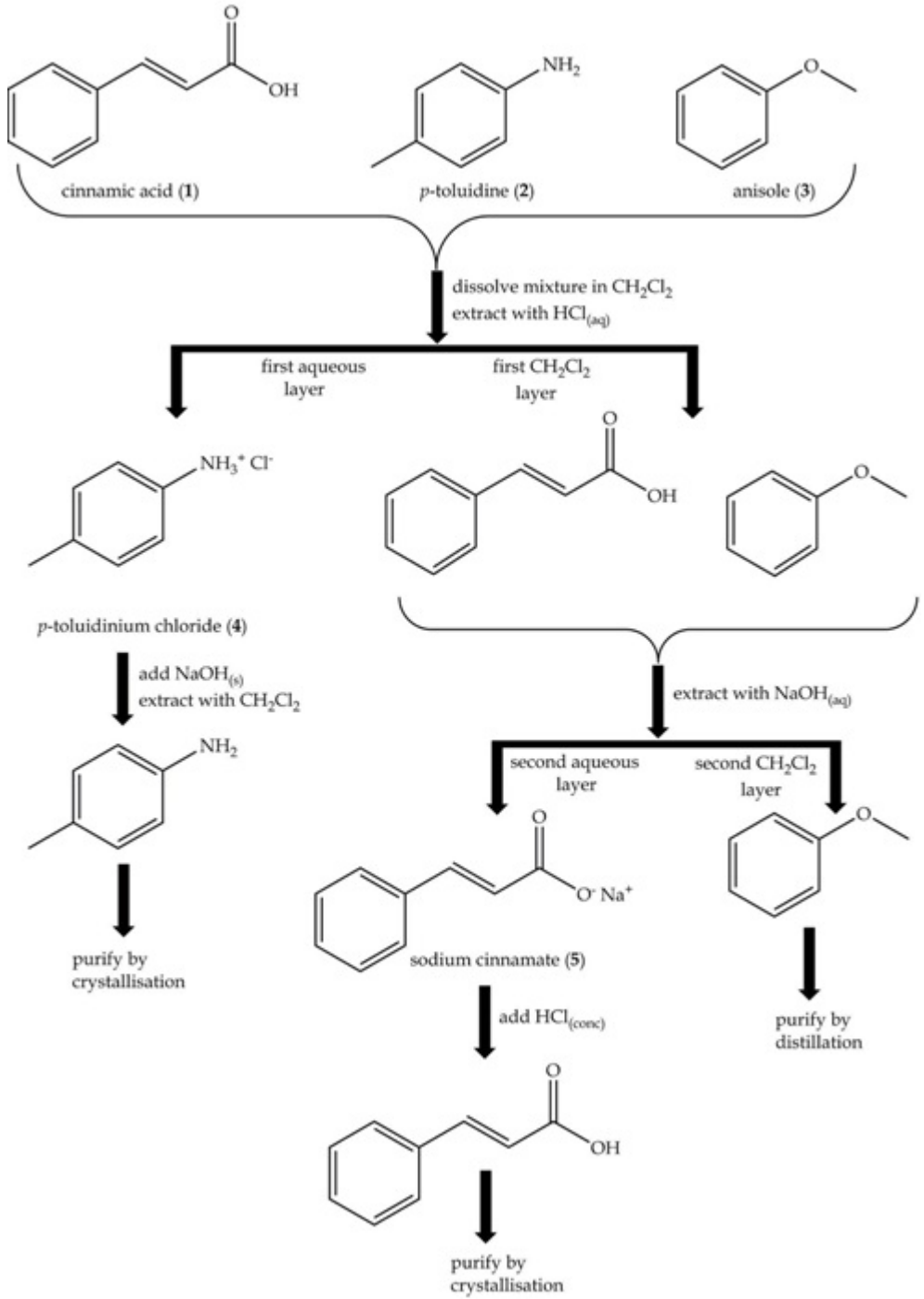
2.


Mixture
RCO_2H, RNH_2, unfunctionalized cpd.
5% NaOH soln.
Organic phase
Aqueous phase
Base (RNH_2)
Unfunctionalized cpd
Conjugate base of carboxylic acid [RCO_2^-]
5-10% aq. HCl soln.
5-10% aq. HCl soln.
Remove organic phase
Aqueous phase
Crude carboxylic acid
RCO_2H
Crude
Unfunctionalized cpd
Conjugate acid of base
$[RNH_3]^+$
Recrystallize
5% NaOH soln.
Recrystallize
Pure carboxylic acid
RCO_2H
Crude base
RNH_2
Recrystallize
Pure
Unfunctionalized cpd
Pure base
RNH_2

3.


MeO
OMe
+
OH
dissolved in diethyl ether
Add aq. NaOH
aqueous layer
organic layer
ONa
Add aq. HCl
+ NaCl
solid
OH
Filter and wash with water
OH
MeO
OMe
+ H_2O
Add anhydrous Na_2SO_4
Filter, collect filtrate
MeO
OMe
Evaporate diethyl ether
MeO
OMe

4.


OH
cinnamic acid (1)
NH_2
p-toluidine (2)
O
anisole (3)
dissolve mixture in CH_2Cl_2
extract with $HCl_{(aq)}$
first aqueous layer
first CH_2Cl_2 layer
NH_3^+ Cl^-
p-toluidinium chloride (4)
add $NaOH_{(s)}$
extract with CH_2Cl_2
NH_2
purify by crystallisation
OH
O
extract with $NaOH_{(aq)}$
second aqueous layer
second CH_2Cl_2 layer
O^- Na^+
sodium cinnamate (5)
add $HCl_{(conc)}$
purify by distillation
OH
purify by crystallisation