

ANALYTICAL CHEMISTRY

- Syllabus

- 1) Solvent Extraction
- 2) Chromatography
- 3) Gas Chromatography
- 4) High performance liquid Chromatography
- 5) Electrophoresis
- 6) Nephelometry and Turbidimetry

Solvent Extraction

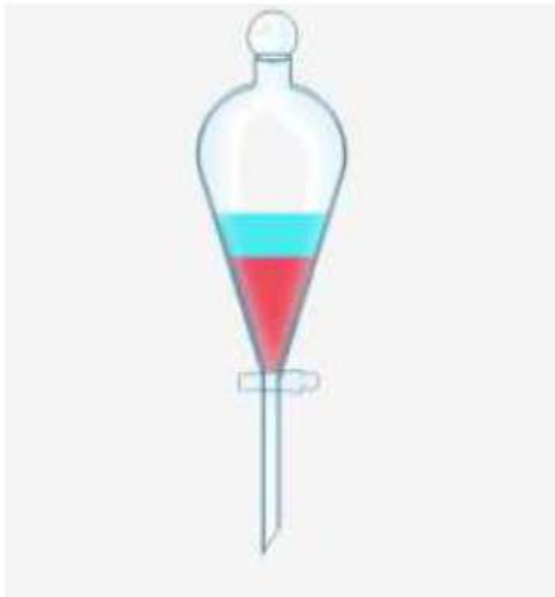
Solvent extraction:

It is the process of separation, in which a compound transfers from one solvent to another due to its different solubility in two immiscible solvents.

Solvent extraction, is also called liquid-liquid extraction (LLE)

Immiscible liquids are the liquids, that cannot get mixed up with each other and separate into layers when shaken together.

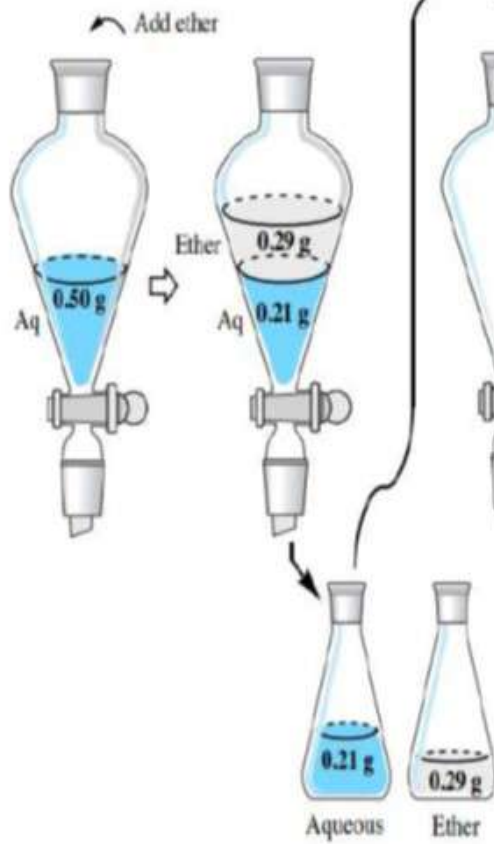
It is a method of quantitative separation of compounds.



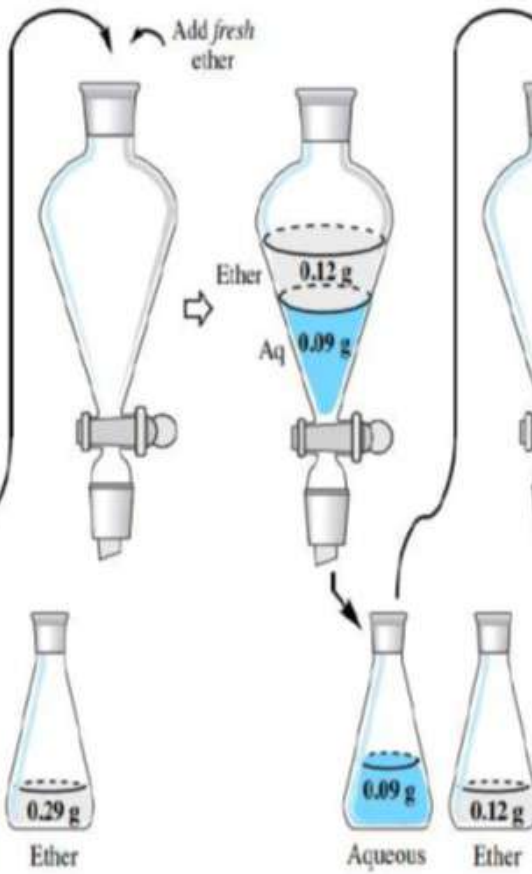
Separating Funnel

Solvent Extraction

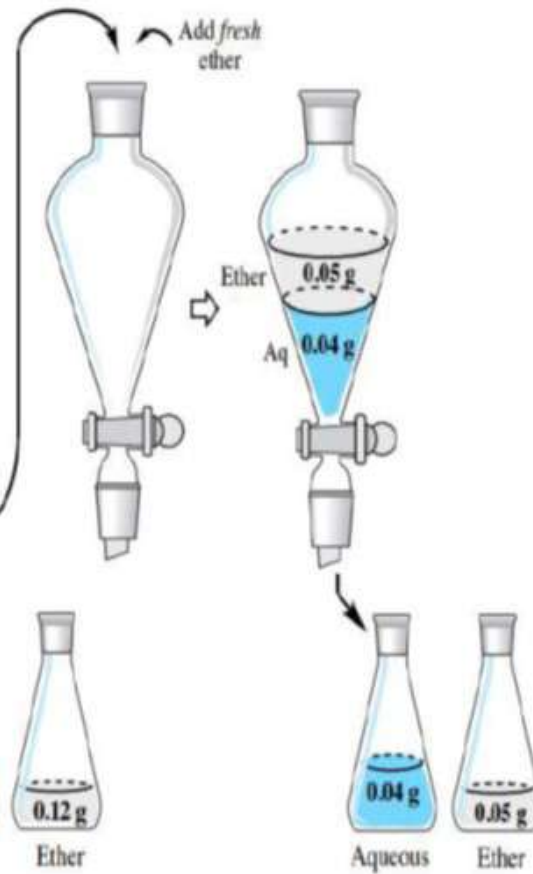
a) First extraction:



b) Second extraction:



c) Third extraction:



Solvent Extraction

Purification and separation

In purification one component is present in large quantity and other components are present in smaller quantities.

In separation all components are present in large quantities.

Solvent Extraction

Principle

On shaking, solute get distributed itself in certain ratio between two immiscible solvents.

When extracting solvent is stirred with solution containing solute, then solute from original solvent gets transferred into an extracting solvent.

When stirring is stopped extracting solvent form separate layer and contains solute to be separated.

Ionic compounds are soluble in polar solvents and insoluble in non polar solvents. Covalent compounds are soluble in non polar solvents.

Solvent Extraction

Features of Solvent extraction / Advantages

1. Simple in operation
2. It is based on simple principle that solute can distribute itself in a certain ratio between two immiscible solvents
3. No need of sophisticated instrument /equipment
4. Can be used at micro as well as macro level
5. Can separate minor constituents from major constituents
6. It is speedy technique

Solvent Extraction

Distribution coefficient / partition coefficient

When a solute distribute itself between two immiscible phases in contact and in equilibrium with each other, the ratio of concentration of the substance in two phases is constant at constant temperature provided that molecular state of solute remain same.

$$K_D = \frac{[S_1]}{[S_2]}$$

$[S_1]$ = Concentration of solute in solvent 1

$[S_2]$ = Concentration of solute in solvent 2

Limitations:

- 1) Temperature should remain constant
- 2) Solution must be dilute.
- 3) Two solvent must be immiscible
- 4) Molecular state should remain same (No association /dissociation / complex formation etc.)

Solvent Extraction

Distribution Ratio (D)

$$D = \frac{[\text{Total concentration of species in organic phase}]}{[\text{Total concentration of species in aqueous phase}]}$$

Distribution ratio is the ratio of concentration of all species in two phases (i.e. organic and aqueous)

Consider the example of benzoic acid [HBz]

Distribution coefficient is given as

$$K_D = \frac{[\text{HBz}]_e}{[\text{HBz}]_a}$$

HBz dissociate as



Solvent Extraction

Distribution Ratio (D)

Dissociation constant of HBz is

$$K_a = \frac{[H^+]_a [Bz^-]_a}{[HBz]_a}$$

Distribution ratio of benzoic acid in two immiscible liquid is given as,

$$D = \frac{[HBz]_e}{[HBz]_a + [Bz^-]_a}$$

H⁺ can move
to both layer

Relation between K_D and D

Relation between distribution coefficient (K_D) and Distribution Ratio (D)

Under ideal condition (when there is no association/dissociation/ complex formation)

$$K_D = D$$

But it hardly possible,

Distribution ratio and distribution coefficient for benzoic acid are given as

$$D = \frac{[\text{HBz}]_e}{[\text{HBz}]_a + [\text{Bz}^-]_a} \quad \text{--- (1)}$$

$$K_D = \frac{[\text{HBz}]_e}{[\text{HBz}]_a}$$

$$\therefore [\text{HBz}]_e = K_D \cdot [\text{HBz}]_a$$

We know that, $K_a = \frac{[\text{H}^+]_a [\text{Bz}^-]_a}{[\text{HBz}]_a}$

$$\therefore [\text{Bz}^-]_a = K_a \cdot \frac{[\text{HBz}]_a}{[\text{H}^+]_a}$$

Relation between K_D and D

Relation between distribution coefficient (K_D) and Distribution Ratio (D)

Substituting the value of $[Bz^-]_a$ and $[HBz]_c$ in the expression for D , we get

$$D = \frac{K_D \cdot [HBz]_a}{[HBz]_a + \frac{K_a \cdot [HBz]_a}{[H^+]_a}}$$

$$\therefore D = \frac{K_D}{1 + \frac{K_a}{[H^+]_a}}$$

Thus

when $[H^+]_a \gg \gg K_a$ the D nearly equal to K_D and benzoic acid is extracted in organic layer (ether)

when $[H^+]_a \ll \ll K_a$ the D small and benzoic acid remain in aqueous layer (water)

Solvent Extraction

The percent Extracted (i.e., Efficiency of Extraction)

It is depend upon value of distribution ratio (D) and volume ratio of aqueous and volume of organic solvent (V_a / V_o)

$$\%E = \frac{100 \times D}{D + \frac{V_a}{V_o}}$$

When, $V_a = V_o$ then,

$$\%E = \frac{100 \times D}{D + 1}$$

Solvent Extraction

The percent Extracted (i.e., Efficiency of Extraction)

Effect of Distribution ratio (D)

Consider $V_a / V_o = 1$

$$\%E = \frac{100 \times D}{D + 1}$$

If $D = 0.001$, then

$$\%E = \frac{100 \times 0.001}{0.001 + 1}$$

$$\therefore \%E = 0.099 \%$$

(ii) If $D = 100$, then

$$\%E = \frac{100 \times 100}{100 + 1}$$

$$\%E = 99 \%$$

Solvent Extraction

The percent Extracted (i.e., Efficiency of Extraction)

Effect of Distribution ratio (D)

Consider $V_a / V_o = 1$

$$\%E = \frac{100 \times D}{D + 1}$$

(iii) If $D = 500$, then

$$\%E = \frac{100 \times 500}{500 + 1}$$

$$\%E = 99.8 \%$$

(iv) If $D = 1000$, then

$$\%E = \frac{100 \times 1000}{1000 + 1}$$

$$\%E = 99.9 \%$$

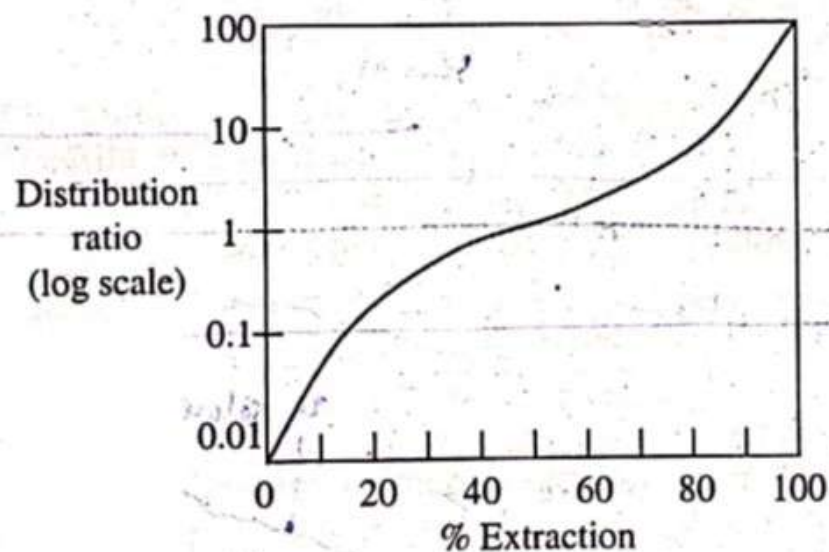
As value of D increases ,
percent extracted also
increases

Solvent Extraction

The percent Extracted (i.e., Efficiency of Extraction)

Effect of $\frac{V_a}{V_o}$,

Consider the constant D value (D=10)



percent extracted increases with decreasing value of V_a/V_o

(i) If $\frac{V_a}{V_o} = 1$, then

$$\%E = \frac{100 \times 10}{10 + 1} = 90.90 \%$$

(ii) If $\frac{V_a}{V_o} = 0.5$, then

$$\%E = \frac{100 \times 10}{10 + 0.5} = 95.2 \%$$

(iii) If $\frac{V_a}{V_o} = 0.1$, then $\%E = \frac{100 \times 10}{10 + 0.1} = 99 \%$

Separation Factor/ separation efficiency

When solution to be extracted consists of two solutes A and B, and we have to separate A from B.

In such case extracting solvent is selected in such a way that it dissolve maximum quantity of A and very less quantity of B.

Under this condition extraction of small amount of B is also possible.

Effectiveness of separation is expressed in terms of separation coefficient or separation factor (β).

It is the ratio of distribution coefficients of two solutes A and B and given by

$$\beta = \frac{K_D A}{K_D B}$$

For separation two solutes by solvent extraction, β must be high, otherwise clear separation is very difficult.

Multiple Extraction

In single extraction, quantitative separation of a compound from aqueous phase into organic phase is not possible.

Thus for maximum extraction of a compound from aqueous phase into organic phase, multiple extractions are required.

Solute remain unextracted is given by

$$W_n = W_a \left[\frac{V_a}{DV_o + V_a} \right]^n$$

Where,

W_a = quantity/concentration of solute remain unextracted

W_a = Initial quantity/concentration of solute

V_a = Volume of the aqueous phase

V_o = Volume of organic phase

D = Distribution ratio

n = number of extractions

Extraction efficiency increase as value of n increases.

Factors Affecting Solvent Extraction

1) Salting out agents:

Extraction of metal is increases by adding high concentration of inorganic salts to aqueous phase.

2) pH

pH affects the stability and charge on the metal complex. The pH at which metal ion complex is most stable is used for extraction

(neutral pH is the best pH for extraction of metal ions.)

3) Oxidation state

By carrying out redox reaction with suitable reagent, oxidation state of metal ion can be changed.

Extraction of iron from chloride solution can be prevented by reducing Fe^{3+} to Fe^{2+}

Factors Affecting Solvent Extraction

4) Masking agent

These are the complexing agents which prevent a particular metal from taking part in chemical reaction.

Example

Al can be extracted in presence of Fe by using 8-hydroxy quinoline

5) Modifiers

Modifiers increase the solubility of solute to be extracted into organic solvent. Usually high molecular weight alcohols are used as modifiers

6) Synergic agents

These are added to organic phase to increase the efficiency of extraction. They get associated with metal complex, make it more soluble into organic phase

Solvent extraction methods

- 1) Chelate formation
- 2) Solvation
- 3) Synergic extraction
- 4) Ion- Association method

Chelate formation

The chelating agents are usually bidentate or multidentate organic ligands which forms stable and neutral complex with metal ion.

Chelating agents like 8 hydroxy quinoline, Dimethylglyoxime are common chelating agents.

Solvent extraction methods

2) Solvation

It is the process in which metal ion gets solvated by solvent molecule and trapped inside the solvent cage.

The solvent used for solvation is soluble in organic phase, hence metal ion gets extracted from aqueous phase into organic phase.

Carboxylic acids, ternary amines, alkyl substituted phosphoric acids. etc. can be used as extractants

3) Synergic extraction

These are the reagents which when added to organic phase increase the efficiency of extraction

They get associated with metal complex, make it more soluble into organic phase.

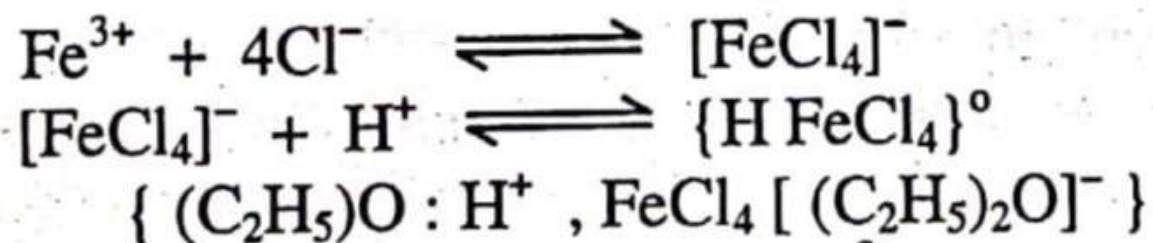
Addition of neutral organophosphorus compound to acidic organophosphorus compound

Solvent extraction methods

4) Ion association method

Metal ions form ionic complexes with certain ions.

These ionic complexes get associated with oppositely charged ions called ion association complex.



Extraction of ferric ion in diethyl ether can be carried out by using HCl. Complex form association with oxygen atom of diethyl ether.

Techniques of solvent extraction

1) Batch extraction

It is most common technique of solvent extraction.

It is carried out by using separating funnel.

Aqueous solution containing solute to be extracted is taken in separating funnel and shaken with known volume of organic solvent.

Due to shaking solute come in contact with both solvent and passed in to organic layer.

After shaking funnel is kept undisturbed for some time for separation of two layer.

When distribution ratio is small, multiple extractions are required.



Separating Funnel

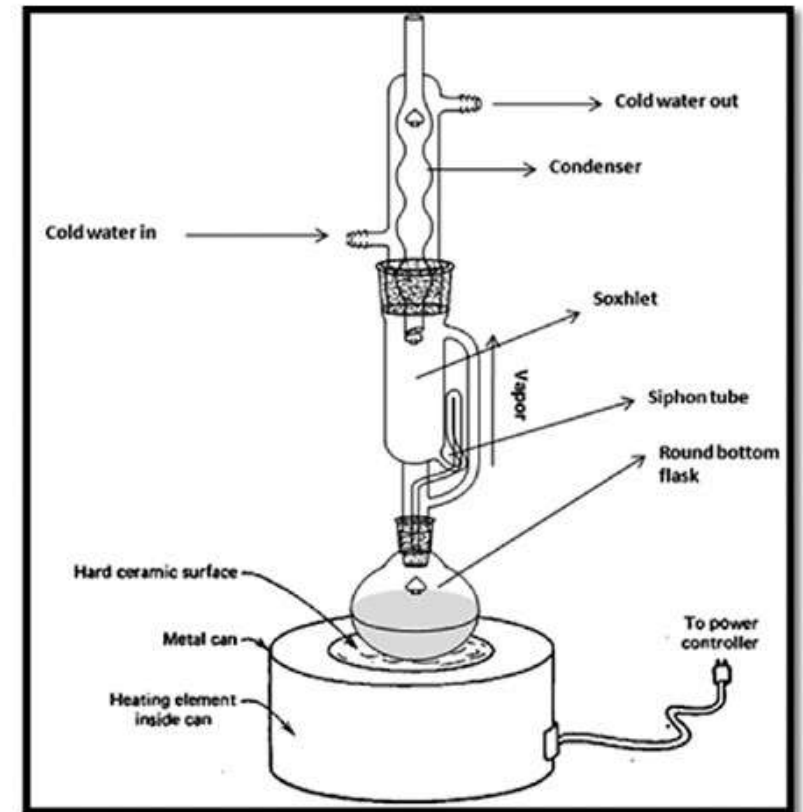
Techniques of solvent extraction

2) Continuous extraction

This technique is used for the solute having **low distribution ratio (D)**

Continuous flow of immiscible solvent through the solution to be extracted

Apparatus like **Soxhlet apparatus** is used for this extraction



Techniques of solvent extraction

3) Counter current Extraction

This technique is used for separation of two liquids having nearly same distribution ratio (D)

A Solvent extraction technique in which two immiscible liquids flow in opposite direction is called counter current extraction

Apparatus consist of large number of tubes joined together. These tubes are called as Craig counter current tubes.

A simple types of apparatus scale is a **Craig apparatus**. Craig apparatus consists of a series of glass tubes (r: 0, 1, 2..) that are designed and arranged such that the lighter liquid phase is transferred from one tube to the next.

START OF CYCLE



TRANSFER



Applications of solvent extraction

1) Determination of Iron as the 8-hydroxyquinoline

Extraction of ferric ion from aqueous medium can be done by using 1% solution of 8-hydroxyquinoline in chloroform.(pH 2 to 10)

2) Determination of Uranium as the 8 hydroxyquinoline

Uranium (VI) may be extracted by adding 8-hydroxyquinoline at pH 8.8 in presence of small amount of EDTA.

3) Determination of lead in blood

Blood sample is treated with dithizone (chelating agent). Metal chelate formed is extracted in to methylene chloride at pH 8 to 10. Amount of lead in blood is determined by using spectroscopic method.

Applications of solvent extraction

- 4) Determination of copper in cast iron, steel, solder etc.

Copper from solder or steel alloy or cast iron is first obtained in aqueous medium and then complexed with neo-cuproin and extracted with chloroform. The amount of copper can be determined by using spectrophotometric method.

- 5) Separation and Purification of organic compounds.

- 6) Used in drug industry, pharmaceutical chemistry, biochemistry for purification.

Solvent Extraction

1) Calculate Distribution ratio when concentration of solute in organic layer is 0.720 M and in aq. layer is 0.03 M.

$$D = \frac{\text{concentration of solute in organic layer}}{\text{concentration of solute in aq. layer.}}$$

$$D = \frac{0.720}{0.03}$$

$$D = 24$$

Solvent Extraction

In the extraction of Cerium (IV) with 2-Thienoyl trifluoroacetone in benzene, the distribution ratio was 999. If $V_a = 10$ ml and $V_o = 25$ ml what is percent extraction?

Ans →

Given

$$D = 999$$

$$V_a = 10 \text{ ml}$$

$$V_o = 25 \text{ ml}$$

$$\%E = \frac{100D}{D + \frac{V_a}{V_o}}$$

$$= \frac{100 \times 999}{999 + \left[\frac{10}{25}\right]}$$

$$= \frac{99900}{999.4}$$

$$\%E = 99.959\%$$