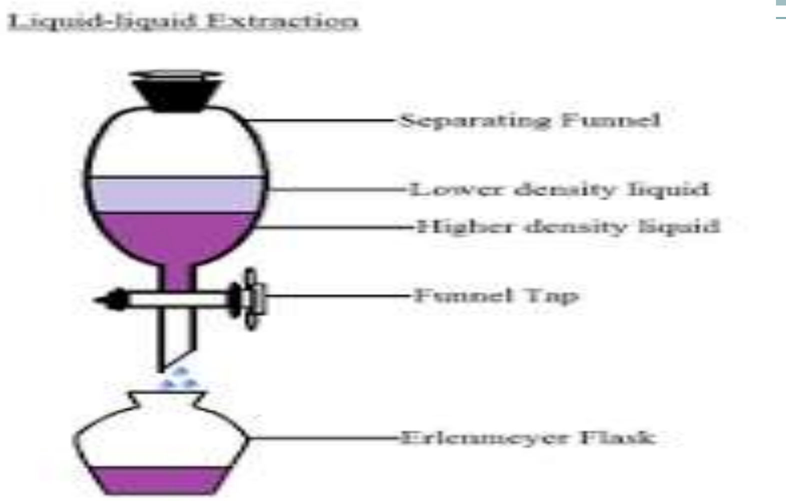
SOLVENT EXTRACTION



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- Solvent extraction, also called liquid-liquid extraction (LLE) and partitioning

- **Immiscible liquids** are ones that cannot get mixed up together and separate into layers when shaken together. These liquids are usually water and an organic solvent.

- Solvent extraction is the process in which a compound transfers from one solvent to another owing to the difference in solubility or distribution coefficient between these two immiscible (or slightly soluble) solvents.

- It is a method of quantitative separation of compounds.

- 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 now it contains solute of interest.

- Compared with other separation methods, it gives a better separation effect than chemical precipitation, and a higher degree of selectivity and faster mass transfer than the ion exchange method.
- Compared with distillation, solvent extraction has advantages such as low energy consumption, large production capacity, fast action, easy continuous operation and ease of automation.

Commonly used solvents

- **ethyl acetate** (8.1 %),
- diethyl ether (6.9 %),
- dichloromethane (1.3 %) and
- **chloroform** (0.8 %) dissolved up to 10 % in water.

Water also dissolves in organic solvents:
- **ethyl acetate** (3 %),
- diethyl ether (1.4 %),
- dichloromethane (0.25 %)
- **chloroform** (0.056 %).

Uses of solvent extraction process

- **Solvent extraction** is **used** in the processing of perfumes, vegetable oil, or biodiesel.
- It is also **used** to recover plutonium from irradiated nuclear fuel, a process which is usually called nuclear reprocessing.
- The recovered plutonium can then be re-**used** as nuclear fuel.

The properties of the solvent used for solvent extraction

1. The solvent should be well miscible with the liquid to be extracted.
2. The solvent should not be miscible with the other components of the mixture or react with the solute.
3. The boiling point of the solvent should be low enough (well below the melting point of the solute) such that it can be evaporated easily after collection.
4. It should have a favourable temperature coefficient.

Points to be considered

- The solvent should be able to dissolve at least one component to a large extent than the rest of the components in the mixture.
- The reaction taking place should be stable and irreversible. Reversible reactions can bring back the dissolved components in their previous form and the extraction will not be completed successfully.
- The compound formed after the reaction should be easily separated from the extracted compound so that it can be reused.
- The density of the compound should be different from the required component to help the separation readily.
- It should be inexpensive and cost-effective.
- The solvent should not be toxic or corrosive as it can harm the extraction instruments.
- Other factors important during solvent selection are viscosity, boiling point, flammability, etc.

Distribution coefficient

- When a solution is placed in a separatory funnel and shaken with an immiscible solvent, solutes often dissolve in *part* into both layers.
- The components are said to "partition" between the two layers, or "distribute themselves" between the two layers.
- When equilibrium has established, the ratio of concentration of solute in each layer is constant for each system, and this can be represented by a value K
- K is called the **partition coefficient** or **distribution coefficient**.
- K_D=Molarity in organic phase / Molarity in aqueous phase

Distribution coefficient

- When a compound is placed in contact with two immiscible liquids then the compound itself get distributed in these two liquids.
- This is an equilibrium process (dissolution equilibrium) governed by temperature of the system.
- Suppose compound A is to be extracted from aqueous solution into organic liquid, then for compound A, dissolution equilibrium can be represented by the equation –
- $A_{(aq)} \rightleftharpoons A_{(org)}$

Distribution coefficient

- Under dissolution equilibrium concentration of compound A in aqueous phase and in organic phase is definite.

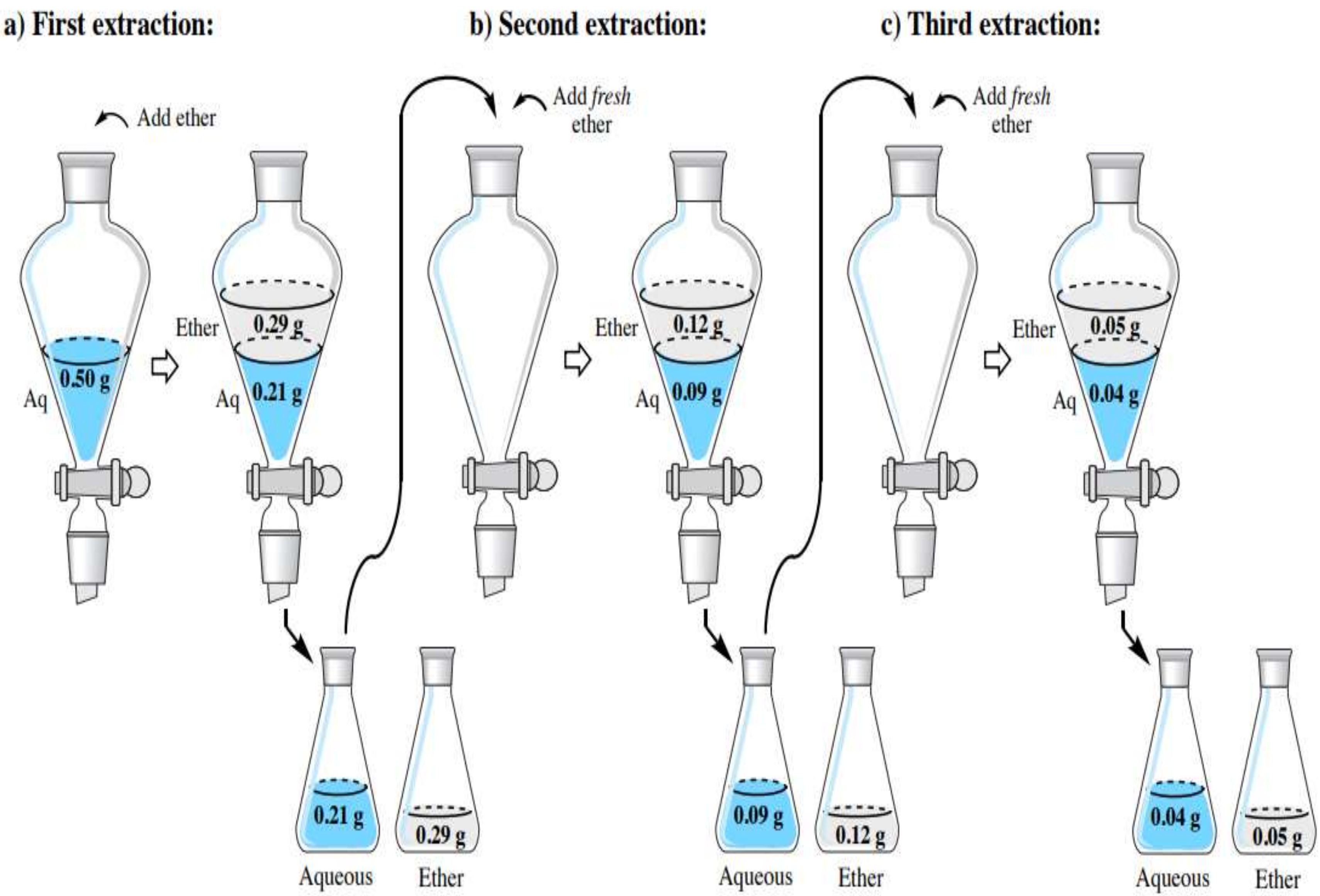
- **K_D=Concentration in organic phase / Concentration in aqueous phase**

Amount remain extracted

- From equilibrium coefficient it is clear that some quantity of a compound will remain unextracted in aqueous phase.

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

- Thus for quantitative extraction of a compound from aqueous phase into organic phase, aqueous phase must be extracted again or number of times.


a) First extraction:
b) Second extraction:
c) Third extraction:
Add ether
Add fresh ether
Add fresh ether
Ether
Aq
0.50 g
0.29 g
0.21 g
0.12 g
0.09 g
0.05 g
0.04 g
0.21 g
0.29 g
0.09 g
0.12 g
0.04 g
0.05 g
Aqueous
Ether
Aqueous
Ether
Aqueous
Ether

Equation

$$X_n = X_a \left[\frac{V_{aq}}{K_D V_o + V_{aq}} \right]$$

Where,

n- no. of times solute is extracted from aqueous phase

X_n - quantity of solute remained in aqueous phase after n extractions

X_a - millimoles of solute taken in aqueous phase

K_D - distribution coefficient

V_{aq} – volume of aqueous phase taken for extraction

V_o – Volume of organic phase used for extraction at a time in multiple extraction

Efficiency of extraction

- Percent extraction is another term used in solvent extraction to express efficiency of extraction.
- Percent extraction or efficiency of extraction (%E) can be calculated as –

$$\%E = \frac{\boxed{\mathbf{100 \ x \ m \ mol \ extracted}}}{\boxed{\mathbf{Total \ m \ mol \ in \ aqueous \ phase}}}$$

Separation factor

- If the solution to be extracted consists of two solutes A and B, and we have to separate A from B, then we will use extracting solvent which will dissolve more quantity of A and very less quantity of B.
- Under this condition, effectiveness of separation is expressed in terms of separation coefficient or separation factor.
- It is the ratio of distribution coefficients of two solutes A and B and denoted by -

β

$$\beta = \frac{K_{DA}}{K_{DB}}$$

β should be very high to separate two solutes by solvent extraction, otherwise clear separation will be very difficult.

Distribution ratio

- Many substances undergo dissociation in aqueous phase like weak carboxylic acid such as benzoic acid, phenol, etc.
- Now consider the weak acid HA which will dissociate in aqueous phase as follows –

$$HA \rightleftharpoons A^- + H^+$$

- The substances which undergo by accounting dissociation in aqueous layer the distribution coefficient in modified form can be defined as **distribution ratio (D)**

- $$D = \frac{[HA]_{org}}{[A-]_{aq} + [HA]_{aq}}$$

Factors affecting solvent extraction

- *Masking agent* – these are chemical species which do not allow to extract unwanted metal ion with metal ion of interest.

- *Modifiers* – these are the substances when added into aqueous phase, they increase the solubility of solute to be extracted into organic solvent. Usually high molecular weight alcohols are used as modifiers in solvent extraction

- *Oxidation state* – by carrying out redox reaction with suitable reagent, oxidation state of metal ion can be changed.

Factors affecting solvent extraction

- ***pH*** – pH affects stability and charge on the metal complex. The pH at which metal ion complex is most stable and neutral is the best pH for extraction of metal ions.

- ***Salting effect*** – the high concentration of salt sometimes help to extract metal ions from aqueous phase to organic phase. Salt increases ionic strength of aqueous phase and thereby increases the solubility of metal complex into organic phase.

- ***Synergic agents*** – these are 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.

Solvent extraction methods of Metal ions

- Chelate formation
- Ion- Association method
- Solvation
- Synergic extraction

Solvent extraction techniques

Chelate formation –

- Metal forms stable and neutral complexes with chelating agents.
- Such chelates are usually water soluble
- The chelating agents are usually bidentate or multidentate organic ligands which provide hydrophobic pocket to the metal ion.
- The organic part of such ligands strongly interact with organic solvent and thereby meta-chelate become soluble into organic phase.

Ion association method

- Metal ions form ionic complexes with certain ions. In turn these ionic complexes get associated with oppositely charged ions called as ion association complex.

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

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.

Solvent extraction techniques

- Batch extraction
- Continuous extraction
- Countercurrent extraction

Batch extraction

- Batch extraction, the simplest and most commonly used method, consists of extracting the solute from one immiscible layer in to other by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle before sampling.
- This is commonly used on the small scale in chemical laboratories.
- The most commonly employed apparatus for performing a batch extraction is a separatory funnel.
- The batch extractions may also be used with advantage when the distribution ratio is large

Countercurrent extraction

- Extraction by continuous countercurrent distribution is the third general type and is used primarily for fractionation purposes.

- The separation through continuous countercurrent method is achieved by virtue of the density difference between the fluids in contact.

- In vertical columns, the denser phase enters at the top and flows downwards while the less dense phase enters from the bottom and flows upwards.

- The choice of method to be employed will depend primarily upon the value of the distribution ratio of the solute of interest, as well as on the separation factors of the interfering materials.

Features essential for an extractant

1) To be selective for the required metal.
2) The ability to extract the metal at the desired acidity or pH.
3) Ease of formation of complex with metal of interest and high solubility of metal organic species in the organic phase.
4) Ease of recovery of the metal from the organic phase.
5) It must be stable throughout the principle stages of solvent extraction.
6) It is to be prepared in laboratory in large scale.
7) To have acceptable rates of extraction and stripping.
8) Regeneration of extractant for recycling in economical large scale processes.
9) There is no emulsion formation

Applications of solvent extraction

- Determination of iron
- Determination of lead in the blood
- Determination of copper in the alloys such as steel
- Determination of uranium
- Separation and Purification of organic compounds by organic chemists
- Used in drug industry by analytical chemists, bio-chemists, pharma chemists.

- https://study.com/academy/lesson/solvent-extraction-definition-process.html
- https://youtu.be/N96JaRnE7n0