(b) Solvent Extraction :-

Solvent extraction is a common technique utilized for both industrial applications and in the laboratory. The technique is successfully applied as a sample preparation procedure for chromatography. it can be used for separation purposes by using selective extractions, or for concentration purposes. The extraction can be applied to liquids (liquid - liquid extraction, LLE), to solid samples (liquid - solid extraction LSE), to gas samples, and to semisolid samples. The chapter starts with a description of parameters describing the liquid-liquid equilibrium; and with a discussion on various parameters used for for the characterization of solvents. it continues with the presentation of common LLE procedures, and then with that of special LLE s such as single drop microextraction, membrane-assisted solvent extraction (MASE), microporous membrane liquid-liquid extraction, hollow fiber liquid-phase microextraction, liquid-liquid-liquid microextraction, dispersive liquid-liquid microextraction, salting-out-assisted LLE, cloud point extraction, etc. conventional LSE, as well as accelerated solvent extraction, microwave-assisted solvent extraction (MWASE), and supercritical solvent extraction are also presented including some theoretical aspects and practice of these procedures.

* Principles :-

Solvent extraction is based on the transfer of solutes from one solvent to another immisible solvent. when they are brought into contact with each other during the period of contact the solutes in the mixture are distributed between the two solvents. The distribution is equilibrium process.

Account of nernest distribution law the ratio of the concentration of solutes of equilibrium will be can at a given temperature provided its molecular sta is same in both phases. it is given by Kd.

$$Kd = \frac{\text{concentration of solute in solvent - I}}{\text{concentration of solute in solvent - II}}$$

when Kd is a con knows as distribution coeffici ent or partition coefficient.

* Distribution ratio (D) :-

The distribution law in its sample form does not apply. when the distributing species undergoes dissociation / Association in either phase.

In the actual practice the distribution of

solute in all its chemical forms between the a Phases is expressed in terms of distribution ratio, D.

$$D = \frac{\text{Total concentration of solute in all its form in solvent -I}}{\text{Total concentration of solute in all its form , solvent- II}}$$

when the solute is in the same chemical species in both the phases that means its there is no association, dissociation / polymerization in the phases.

$$\therefore D = K_d$$

Ex:- consider the distribution of benzoic acid between 2 liquid phases benzene & H_2O.

In the Aq phase benzoic acid is partly ionised

$$HBz + H_2O \rightleftharpoons H_3O^+ + \underset{\text{Benzoate}}{Bz^-}$$

In Benzene Phase benzoic acid is partialy dimerized through. H- bonding.

$$2\,HBz \rightleftharpoons (HBz)_2$$

The species HBz, Bz^- and $(HBz)_2$ will have their own particular Kd values. The distribution coefficient of these species the given by

$$K_d(HBz) = \frac{[HBz]_{org}}{[HBz]_{Aq}}$$

$$K_d(Bz^-) = \frac{[Bz^-]_{org}}{[Bz^-]_{Aq}}$$

$$K_d(HBz)_2 = \frac{[(HBz)_2]_{org}}{[(HBz)_2]_{Aq}}$$

The benzoate ion (Bz^-) remain totally in Aq Phase the benzoic acid dimer exists only in org Phase.

The distribution of benzoic acid in all its terms in 2 Phases is given by 'D'.

$$D = \frac{\text{Total benzoic acid in solvent - I}}{\text{Total HBz in solvent - II}}$$

$$= \frac{[HBz]_{org} + [(HBz)_2]_{org}}{[HBz]_{Aq} + [Bz^-]_{Aq}}$$

$$\left[\begin{array}{l} \rightarrow A_{Aq} \longrightarrow A_{org} \quad K_d = \dfrac{[A]_{org}}{[A]_{Aq}} \\ \rightarrow \text{Petrolium purification} \end{array}\right]$$

* Percentage of extraction (% E) :-

The distribution is also expressed in percentage of extraction, E This is related to distribution ratio D, by the eqn

$$\%E = \frac{100\,D}{(D + V_1/V_2)}$$

where V_1 & V_2 are the volumes of solvent 1 & 2 in quantitative extractions one solvent is usually water and the other is organic solvent.

$$\%E = \frac{100\,D}{D + (V_w/V_o)}$$

when $V_w = V_o$

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

$$\Rightarrow DE + E = 100D$$

$$\Rightarrow 100D - DE = E$$

$$\Rightarrow D[100 - E] = E$$

$$\therefore D = \frac{E}{100 - E}$$

If $E = 100$

then $D = \frac{100}{100 - 100} = \frac{100}{0} = \infty$

When E approaches 100, D tends, towards infinity.

* completeness of extraction :-

The completeness of extraction depends upon two factors, they are

① Distribution ratio

② No. of extractions.

Best results are obtained with large no. of extractions with small amount of solvents. This can be prooved mathematically in the following way.

Let us consider that V_w ml of an aqueous solution contain x gm of solute is extracted with V_o ml of an immiscible organic solvent. After equilibrium in the first extraction, x_w' gm of solute is left in Aq solution, Then.

concentration of solute in organic layer $= \frac{x - x_w'}{V_o}$

concentration of solute in Aqueous layer $= \frac{x_w'}{V_w}$

$\therefore$ Distribution ratio

$$= (x - x_w'/V_o) / (x_w'/V_w)$$

$$= \frac{x - x_w'}{V_o} \times \frac{V_w}{x_w'}$$

$$\therefore D V_o x_w' = x V_w - x_w' V_w$$

$$\Rightarrow D V_o x_w' + x_w' + V_w = x V_w$$

$$\Rightarrow x_w' [D V_o + V_w] = x V_w$$

$$\Rightarrow x_w' = \frac{x V_w}{D V_o + V_w} \longrightarrow ①$$

In another extraction of the Aqueous layer is made with V_o ml of solvent, will be the weight of solute remaining in the Aqueous layer therefore after 2nd extraction

$$x_w'' = x_w' \frac{V_w}{D V_o + V_w} \longrightarrow ②$$

By substituting eqn ① in eqn ②

we get $x_w'' = x \left[\frac{V_w}{D V_o + V_w}\right]^2$

Similarly the weight of solute in aqueous layer after in extraction is given by.

$$x_w^n = x \left[\frac{V_w}{D V_o + V_w}\right]^n$$

$\therefore$ Complete extraction is Acompinated by keeping V_o small, pesteming Propeated extractions. In other words extraction with small volumes of solvent provide

more complete extraction with a large volume of solvent

(P.) 50 ml of water containing 0.1 g of I_2 is shaken with 25 ml of CCl_4. The distribution ratio of I_2 between CCl_4 & water is 85 calculate the weight of I_2 remaining Aq. Layer After 1 extraction with 25 ml and also after extraction with 8.33 ml of solvent.

$V_w = 50$ ml $\quad V_o = 25$ ml $\quad\quad 0.02299$

$x = 0.1$ g $\quad D = 85$ $\quad\quad \frac{0.0023}{0.000001}$

Amount left after one extraction

$$x_w' = x\left[\frac{V_w}{DV_o + V_w}\right]$$

$$= 0.1\left[\frac{50}{85\times25+50}\right]$$

$$= 2.3\times10^{-3}\,g$$

Amount left after 3 extraction

$$= 0.1\left[\frac{50}{85\times8.33+50}\right]^3$$

$$= 2.79\times10^{-5}\,g$$

* Processes of solvent extraction :-

Essentially, solvent extraction consists of two circuits of non-miscible liquids put in contact, where a valuable metal in an aqueous solution is captured by an extractant in the organic phase.

Solvent extraction (SX) is a mass transfer operation and the technique used in metallurgical industry for selective extraction of metal ions from an aqueous solution. During the process, the desired metal ion is both purified and concentrated. An extractant capable of binding metal ions is dissolved in an organic Kerosene type diluent. The extractant has an active hydrophilic group bound to along chain hydrocarbon molecule in order to reduce solubility in the organic phase. The organic phase is then intensively mixed with the metal-bearing aqueous solution (feed) allowing the metal ions to bind to the extractant. The aqueous and organic phases are then allowed to separate and the wanted metal ion is now transferred to the organic phase. The extracted metal ion is then back-extracted (stripped) into a new aqueous phase in a pure and concentrated form. ideally, only the desired metal transfers selectively from the aqueous phase to the organic phase.

* Distribution law :-

When a solute distributes it self between two non-miscible phase in contact and in again with each other ratio of the concentrations of the sub in the two phases & constant at constant temperature provided molecular state of the distributed solute & same in both phase

$$A_{aq} \rightleftharpoons A_{org}$$

* Partition Coefficient :-

For ideal solutions, the partition coefficient of a substance 'A' between two phases is related to the free energy required to transport one mole of 'A' from one phase to another.

If an ideal pairs of solutions is considered, the chemical potential of the partioning solute in the two phase are represented by,

$$S.P \longrightarrow \mu_S = \mu_S^\circ + RT \ln N_S \quad \text{——(1)}$$

$$M.P \longrightarrow \mu_m = \mu_m^\circ + RT \ln N_m \quad \text{——(2)}$$

at equilibrium

$$\mu_S = \mu_m$$

$$\mu_S^\circ + RT \ln N_S = \mu_m^\circ + RT \ln N_m$$

$$\ln\left(\frac{N_m}{N_S}\right) = \frac{(\mu_S^\circ - \mu_m^\circ)}{RT} = \frac{\Delta\mu^\circ}{RT}$$

$$\boxed{\frac{N_m}{N_S} = K_d = e^{-\frac{\Delta\mu^\circ}{RT}}}$$

→ The difference in standard chemical potential express, the concent required to transport a mole of solute from one phase to the other phase.

→ In case of dilute solutions, the mole fractions of the solute may be replaced by the concentration in relative phase.

→ Kd is partition coefficient.

* Distribution Ratio :-

The distribution of the solute between two phases for equal phase volume is given by the distribution ratio 'D'.

$$D = \frac{[A_{org}]}{[A_{aq}]} = \frac{[A_o]}{[A]}$$

$A_o \rightarrow$ Total concentration of solute 'A' in all chemical forms in the organic phase.

$[A] \rightarrow$ Total concentration of solute 'A' in all chemical forms in the aqueous phase.

* Nature of partition forces :-

The physical interaction that are present in the partition are.

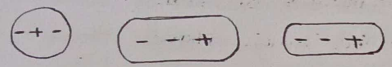
① Dispersion interaction.
② Dipole - Dipole interaction.
③ Induced dipole interaction.
④ Hydrogen bond interaction.

* Dispersion interaction :-

These are inter molecular forces which hold neutral molecules together a liquid in liquid or solid. These forces are purely physical in nature. They donate involve the formation of any chemical bonds They are very weak forces.

The electrons of a neutral molecules oscillate w.r.t. the nuclei of the atoms because of this at a

given instant, the charge may fre concentrated in one region and -ve charge in another region of the same volume. Hence, a non polar molecule may be self polarized. This polarized molecule may induce a dipole-moment in a neighbouring molecule.



original molecule | original dipole due to e⁻ oscillation | Induced dipole.

When similar type of molecules approach each other closely, their e⁻ shells begin to overlap then weak attractions changes to repulsion. Then the molecules exist in a disordered manner. Then a 2nd non polar solvent mixes in all proportions with organic solvent.

* Dipole - Dipole interaction :-

Although polar molecules are neutral, yet they have parment dipoles. The forces are mainly due to electrical interaction between the +ve pole of the one molecule and -ve pole of the other molecule. This type of interaction is known as dipole dipole interaction. The magnitude of interaction is dependent upon the dipole moment of the molecule of the attraction between the solvent molecule and solute molecule is more than the attraction between two solvent molecules then the solute mixtures in all proportions with the solvent.

* Induced dipole interaction :-

Some times a polar molecule may polarize a neutral neighbouring molecule. It induces dipolarity in that molecule then the induced dipole undergoes interaction with the dipole moment of polar molecule and there by the molecules are attracted together. The magnitude of this interaction depends upon the magnitude of the dipole moment of the polar molecule and polarisability of the neutral molecule.

$$\overset{\delta+}{A}-\overset{\delta-}{B} + C::D \longrightarrow \overset{\delta-}{C}::\overset{\delta+}{D} \quad (\delta+A \cdots B\delta-)$$

* Hydrogen bond interactions :-

Although hydrogen conform only one covalent bond, the very small size of the hydrogen atom and its lak of inner closed e⁻ shells makes it possible to form an additional bond with e⁻ rich atoms outside [Inter molecules] or inside [Intra molecular] the molecule, hydrogen bond is formed between a molecule with hydrogen attached to F, O_2, or N_2 or In certain cases carbon on a molecule with an shared e⁻s.

$$R_3N \longrightarrow H-\underset{\underset{R}{|}}{O} \quad : \quad H_3C-H \longleftarrow O=C\begin{matrix}-R\\ \backslash R\end{matrix}$$

Flurine forms very strong H bonds oxygen weaker and nitrogen still weaker.

The compounds participating H-bonding can be classified as follows.

① compounds containing active hydrogen but no donar atom

Ex:- $CHCl_3$.

② compounds which contain adonar-atom but no active hydrogen.

Ex:- ethers, Ketones, Aldehydes, esters etc.

③ compounds containing both the donar atom and an active hydrogen atom.

Ex:- Alcohols, fatty acids, Phenols, 1^0 & 2^0 amines etc.

④ compounds capable of forming multiple H-bonds.

Ex:- water, glycol, Amino alcohols.

* different types of solvent extraction systems:

on the basis of methods of conducting extractions, the solvent extraction systems can be classified into 3 types. They are

① Batch extraction

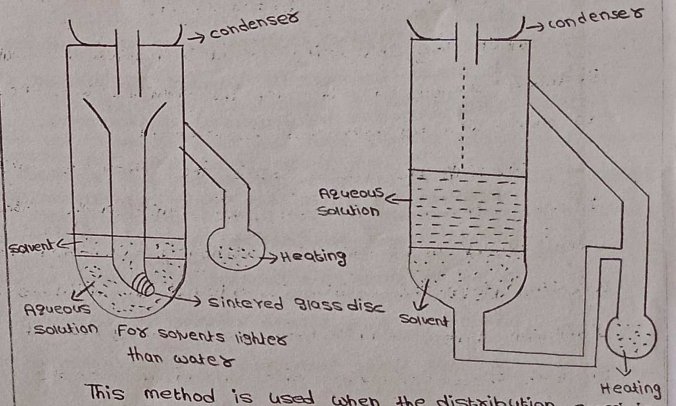
② continuous extraction

③ counter current extraction.

* Batch extraction :-

This method is used when the distribution coefficient, Kd of the compound to be isolated is very large. In this process, the solvent is added to the solution containing the compound in a separating funnel. It is shaken thoughly and allowed to equilibrate the two phases are allowed to separate and the lower layer is drained off through a stop cock. This process may be repeated 2 or 3 times with fresh solvent, since the extraction is done in 2 or 3 batches of attraction operations. it is called batch attraction.

* continuous extraction :-



This method is used when the distribution coefficient, K_d of the compound is very small. A small volume of the extracting agent is needed. In continous extraction, the extraction is passed continously through the stationary

liquid containing the sample until all the desired components is used for subsequent operations. In course of time, extracting solvents becomes rich in the compound even though its Kd value is less.

In continous extraction it is not necessary to reach equillibrium. Two types of extraction apparatus are used depending on weather the extracting solvent is lighter or heavier than the solution.

When the extracting solvent is lighter then it moves upwards through the solution, then this technique is called upward displacement.

When the extracting solvent is heavier the solution, it moves downwards through the solution. It is known as extraction by downward displacement.

In both these techniques. The extracting solvent dissolves extracts the solute. The solution of the extracting solvent and solute is continously separated into a boiling flask. The solution is subjected to continous distillation. Thus solvent returns as extracting solvent. In both these techniques the concentration of the solute in boiling flask increases.

* Counter current extraction (CCE):-

The C.C.E is a very useful technique in the separation of complex mixtures, particular biological molecules such as peptides and other natural producer. In case of mixtures containing substance with close distribution ratios, a single separation stage does not give clean separation.

In such cases the separation is carried out by performing more than a single separation step.

This multi stage separation process is called C.C.E. In this technique, The Immiscible liquids move in opposite directions in contact with each other. The device used for this purpose was developped by "craig". It consists of the series of glas tubes mounted on a rack. In such a manner that a whole of extractions can be carried out of the same time. When solvent layers are separated the rack can be so that the upper layer of each tube is transferred to the next tube in next series.

consider 1000 mg of solute dissolved in 100ml of water this is taken in a separating funnel designated with a number zero to this 100 ml of an immiscible organic solvent lighter than water is added. Assume that the Kd distribution coefficient of the solute is unity. Then the contents of the flask are shaken and allowed to settle, After equilibrium, there will be 500 mg of the solute in Aqueous layer and 500 mg in the organic phase.

Funnel '0'

500 mg org
500 mg Aq

no. of transfers = 0

Next take a 2nd separating funnel designated as number-1, transfer the upper organic layer from first funnel into the 2nd funnel then add fresh organic solvent into first funnel & fresh Aqueous layer into the 2nd funnel Now shake funnels until equilibrium is obtained. There will be 250 mg of the solute in each layer in each funnel. This operation is designated as first transfer.

Funnel '0'	Funnel '1'
250 mg org	250 mg org
250 mg Aq	250 mg Aq

No. of transfers n = 1

Funnel '0'	Funnel '1'	Funnel '2'
125 mg org	250 mg org	125 mg org
125 mg Aq	250 mg Aq	125 mg Aq

No. of transfers, n = 2

Now take a 3rd separating funnel designated as 'no-2' then transfer upper organic layer from 2nd funnel into 3rd funnel and from first funnel into the 2nd funnel then add fresh organic layer into the first funnel and fresh Aqueous layer into the 3rd funnel, Now shake the 3 funnels to equilibrium this operation is designated as the 2nd transfer and the amount of the solvent in the 3 separating funnels is shown below.

It may be noted that, the no. of funnels is 'one' more than the no. of transfers. For this reason the first funnel is labeled as 'zero'.

i/g for the fourth step n = 3

Funnel '0'	1	2	3
62.5 mg org	187.5 mg org	187.5 mg org	62.5 mg org
62.5 mg Aq	187.5 mg Aq	187.5 mg Aq	62.5 mg Aq

i/g for the 5th step n = 4.

Funnel '0'	1	2	3	4
31.25 org	125 mg org	187.5 mg org	125 mg org	31.25 org
31.25 Aq	125 mg Aq	187.5 mg Aq	125 mg Aq	31.25 Aq

As the no. of transfers increases the solute spreads out through more and more funnels but it reaches up towards the centre. The fractional solute in the extreme funnels decreases. Thus for an Aqueous solution containing several compounds with close Kd values, after several transfers, the compounds are concentrated [left, middle & right] depending upon their Kd values.

* Solvent extraction systems :- [depending upon nature of species].

Hydrated inorganic salts are more soluble in water than in organic solvents. where as organic substances are

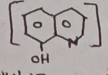
more soluble in organic solvents than in water.

on the basis of nature of extractable species, solvent extraction systems can be classified into two types they are.

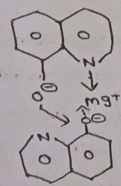
① chelate systems

② Ion Association systems.

* chelate systems :-

In the chelate systems, chelates soluble in organic solvents are formed between metal ions and ligands that are neutral in charge. 8-hydroxy quinoine.  forms neutral, water insoluble of chloso form soluble complex with a no. of metal ions.

For ex, Extraction of 'mg' with hydroxy quinoline



$Mg^{+2} + 2\,HOX \rightleftharpoons Mg(OH)_2 + 2H^+$

Mg-8 hydroxy quinolate.

* Ion Association System (IAS) :-

In the IAS_2, the inorganic ion associates with oppositely charged ions to form a neutral extractable species. These are classified into 3 types

① These are formed from a reagent yielding a large organic ion.

For ex Phenyl Arsonium ion while forms large ion with suitable opposit charged ions shel as MnO_4^-, ReO_4^- The species which passes into the organic Phase is an ion pair.

$(C_6H_5)_4 As^+ MnO_4^-$ (or) $(C_6H_5)_4 As^+ ReO_4^-$

② Those involving an Arsenic or cationic complex of a chelate complex of metal ion.

For ex, Formation and extraction of a blue complex Ag(I) - 1,10 Phen.

It involves a cationic complex of a metal in $[Ag^+]$ Associated with an anionic counter ion derived from Bromopyrogallol red.

③ Ion association systems in which there solvent molecules are directly involved in the formation of ion Association complex.

most of the solvents [ethers, esters, ketones, Alcohols] which participate in this way contain donar oxygen atoms and the co-ordinating ability of the solvent is significance contain donar oxygen atoms and the co-ordinating ability of the solvent is significance.

For ex, ether extraction of Iron (III) from strong HCl solution. The AQ Phase chloride ions replace water molecules co-ordinated to the Fe^{3+} ion to give tetrahedral $FeCl_4^-$. The hydrated H_3O^+ ion, $H_3O^+(H_2O)_3$ combined with the complex anion. But in presence of organic solvent, the solvent molecules enter the AQ Phase and