

## Separation techniques: Solvent extraction

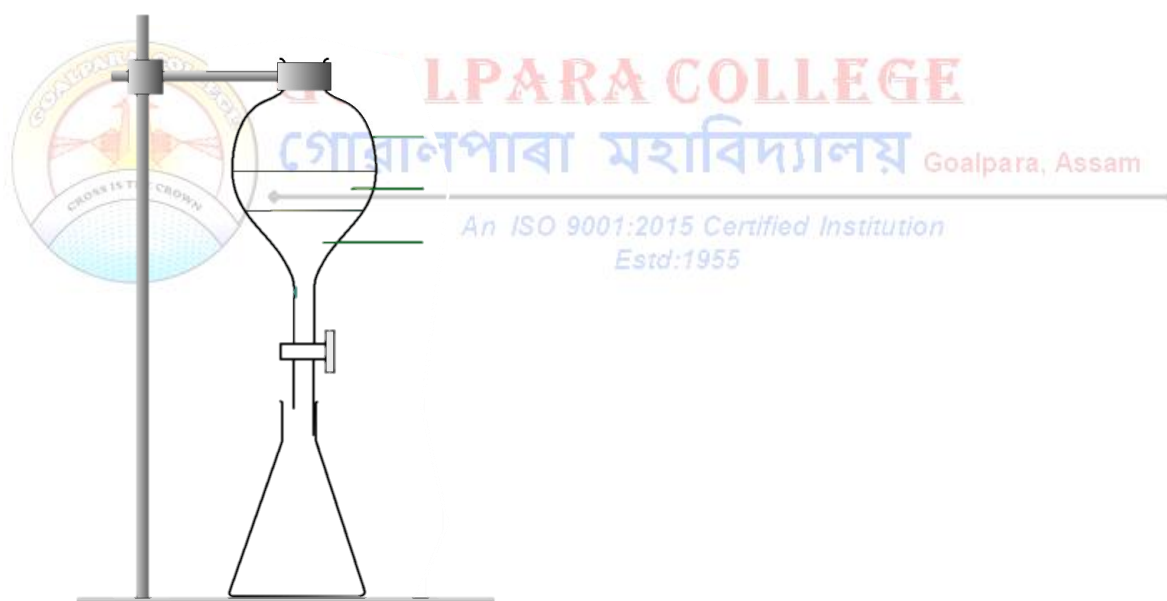
### Principles:

#### Nernst Distribution law and Distribution Coefficient:

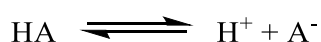
Let us consider a solute S, which is soluble in two immiscible solvents 1 and 2. The concentrations of the solute in the two solvents are  $[S]_1$  and  $[S]_2$ , respectively. Now the ratio of the concentrations will be a constant at constant temperature, and this ratio is known as **distribution coefficient** or **partition coefficient** and denoted by  $K_D$ .

$$K_D = \frac{[S]_1}{[S]_2}$$

**Solvent extraction:** Let us consider a solution of ethanol in benzene. Now the mixture is taken in a separation funnel and water is added. The top of the funnel is then closed with a stopper and the contents inside are shaken vigorously. The contents are then allowed to settle into two distinct layers. The top layer contains (benzene + ethanol) and the bottom layer contains (water + ethanol). The bottom layer is then taken out in a conical flask or beaker. This process is repeated until most of the ethanol are removed from the benzene layer.



Some solute ionizes partially in aqueous solution at pH = 7 (Weak acids). E.g. Benzoic acid.



Ionisation constant,  $K_a = \frac{[H^+]_a[A^-]_a}{[HA]_a}$  in aqueous solvent

When we use two immiscible solvents such as ether and water

The distribution coefficient,  $K_D = \frac{[HA]_o}{[HA]_a}$  o = ether/organic; a = water/aqueous

**Distribution ratio:** The partition coefficient does not account for any equilibrium that may present in either of the two phases.

Hence a new term called distribution ratio is introduced and defined as "It is the ratio of the concentrations of all the species of solute in each phase. The concentration in the two phases are expressed as total concentrations rather equilibrium concentration."

$$\text{Distribution ratio, } D = \frac{[S]_o}{[S]_a}$$

$[S]_o$  = total concentration of all the species in organic solvent

$[S]_a$  = total concentration of all the species in aqueous solvent

$$\text{For weak acids, } D = \frac{[HA]_o}{[H^+]_a + [A^-]_a}$$

$$K_a = \frac{[H^+]_a [A^-]_a}{[HA]_a}$$

$$\Rightarrow [A^-]_a = \frac{K_a [HA]_a}{[H^+]_a}$$

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

This final expression shows that the distribution ratio is dependent of pH or  $[H^+]$ .

*In acidic condition,*

$[H^+] \gg K_a$ ,  $D \approx K_D$ ; which means extent of ionization is very small.

When  $K_D$  is large,  $D$  will be large and the weak acid can be extracted into organic layer.

*In basic condition,*

$$[H^+] \ll K_a, D \approx \frac{K_D [H^+]_a}{K_a}$$

$D$  will be small in this case and the weak acid will remain in the aqueous solution.

$D$  is independent of initial concentration of the acid and the volume ratio of the solvents.

#### Percent extracted:

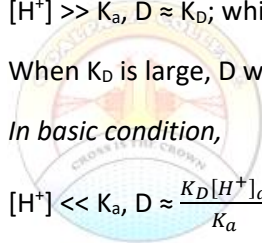
Fraction of the solute extracted is given by the following formula,

$$\begin{aligned} \% E &= \frac{\text{Millimoles of solute in the organic layer}}{\text{Total number of millimoles of solute}} \\ &= \frac{[S]_o V_o}{[S]_o V_o + [S]_a V_a}; V_o = \text{volume of the organic solvent, } V_a = \text{volume of the aqueous solvent} \\ &= \frac{\frac{[S]_o V_o}{[S]_a V_o}}{\frac{[S]_o V_o}{[S]_a V_o} + 1} \\ &= \frac{100D}{D + \frac{V_a}{V_o}} \end{aligned}$$

$$\text{Therefore } \% E \propto \frac{V_o}{V_a}$$

So, the extraction efficiency can be improved by increasing the volume of the organic solvent.

$$\text{When } V_a = V_o, \% E = \frac{100D}{D+1}$$



$D \gg 1000$ ; solute is quantitatively extracted.

$D \ll 1000$ ; solute is quantitatively retained.

### Multiple extraction:

For one-time extraction;  $V_o$  = volume of the organic solvent and  $V_a$  = volume of the aqueous solvent

If we repeat the process for  $n$  times; total volume used is  $nV_o$ .

$W_0$  = initial weight in aqueous layer

$w$  = weight remained after extraction

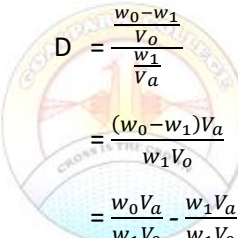
Weight of the extracted solute =  $w_0 - w$

### First extraction

$V_o$  mL of solvent used for extraction; after extraction  $w_1$  g solute left in the aqueous layer.

Concentration of the organic phase =  $\frac{w_0 - w_1}{V_o}$

Concentration of the aqueous phase =  $\frac{w_1}{V_a}$


$$D = \frac{\frac{w_0 - w_1}{V_o}}{\frac{w_1}{V_a}}$$
$$= \frac{(w_0 - w_1)V_a}{w_1 V_o}$$
$$= \frac{w_0 V_a}{w_1 V_o} - \frac{w_1 V_a}{w_1 V_o}$$

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$$\Rightarrow D + \frac{V_a}{V_o} = \frac{w_0 V_a}{w_1 V_o}$$

$$\Rightarrow \frac{DV_o + V_a}{V_o} = \frac{w_0 V_a}{w_1 V_o}$$

$$\Rightarrow \frac{w_1}{w_0} = \frac{V_a}{DV_o + V_a}$$

$$\Rightarrow w_1 = w_0 \frac{V_a}{DV_o + V_a}$$

Fraction extracted =  $\frac{w_0 - w_1}{w_0} = \frac{(w_0 - w_1)V_a}{w_1 V_o} \times \frac{V_o w_1}{V_a w_0} = \frac{DV_o w_1}{V_a w_0}$

### Second extraction

$V_o$  mL of solvent used for extraction; after extraction  $w_2$  g solute left in the aqueous layer.

Concentration of the organic phase =  $\frac{w_1 - w_2}{V_o}$

Concentration of the aqueous phase =  $\frac{w_2}{V_a}$

$$D = \frac{\frac{w_1 - w_2}{V_o}}{\frac{w_2}{V_a}}$$
$$= \frac{(w_1 - w_2)V_a}{w_2 V_o}$$

$$= \frac{w_1 V_a}{w_2 V_o} - \frac{w_2 V_a}{w_2 V_o}$$

$$\Rightarrow D + \frac{V_a}{V_o} = \frac{w_1 V_a}{w_2 V_o}$$

$$\Rightarrow \frac{DV_o + V_a}{V_o} = \frac{w_1 V_a}{w_2 V_o}$$

$$\Rightarrow \frac{w_2}{w_1} = \frac{V_a}{DV_o + V_a}$$

$$\Rightarrow w_2 = w_1 \frac{V_a}{DV_o + V_a} = w_0 \left( \frac{V_a}{DV_o + V_a} \right)^2$$

$$\text{Fraction extracted} = \frac{w_1 - w_2}{w_0} = \frac{(w_1 - w_2)V_a}{w_2 V_o} \times \frac{V_o w_2}{V_a w_0} = \frac{DV_o w_2}{V_a w_0}$$

### ***nth extraction***

$V_o$  mL of solvent used for extraction; after extraction  $w_n$  g solute left in the aqueous layer.

$$w_n = w_0 \left( \frac{V_a}{DV_o + V_a} \right)^n$$

$$\text{Fraction extracted} = \frac{DV_o w_n}{V_a w_0}$$

$$\text{So, total fraction extracted} = \frac{DV_o w_1}{V_a w_0} + \frac{DV_o w_2}{V_a w_0} + \dots + \frac{DV_o w_n}{V_a w_0}$$



$$= \frac{DV_o}{V_a} \left( \frac{w_1}{w_0} + \frac{w_2}{w_0} + \dots + \frac{w_n}{w_0} \right)$$

$$= \frac{DV_o}{V_a} \left( \frac{V_a}{DV_o + V_a} + \left( \frac{V_a}{DV_o + V_a} \right)^2 + \dots + \left( \frac{V_a}{DV_o + V_a} \right)^n \right)$$

$$= DV_o \left( \frac{1}{DV_o - V_a} + \frac{V_a}{(DV_o - V_a)^2} + \dots + \frac{V_a^{n-1}}{(DV_o - V_a)^n} \right)$$