Solvent Extraction

Course Teacher: Dr. Binita Dutta

Department of Chemistry, B.B. College, Asansol

- The Analyte: Substance(s) to be analysed
- The Matrix: Rest of the material

Separation Techniques

Bulk Separation process

- Filtration
- Distillation, evaporation, drying
- Solvent extraction, crystallization, precipitation
- Ion exchange, dialysis, lyophilisation

Instrumental Separation

- Chromatography
  - GC
  - HPLC
  - TLC
  - SFC)
- Capillary electrophoresis (CE)

How to select Separation method

Chemical species with Difference in…	Separation method
Solubility of compounds formed	Precipitation and filtration
Volatility	Distillation
Solubility in two immiscible phases	Extraction
Interaction of reactants with ion exchange resin	Ion exchange
Rate of movement through stationary phase	Chromatography
Migration rate of charged species in electronic field	Electrophoresis

Depending on physical state

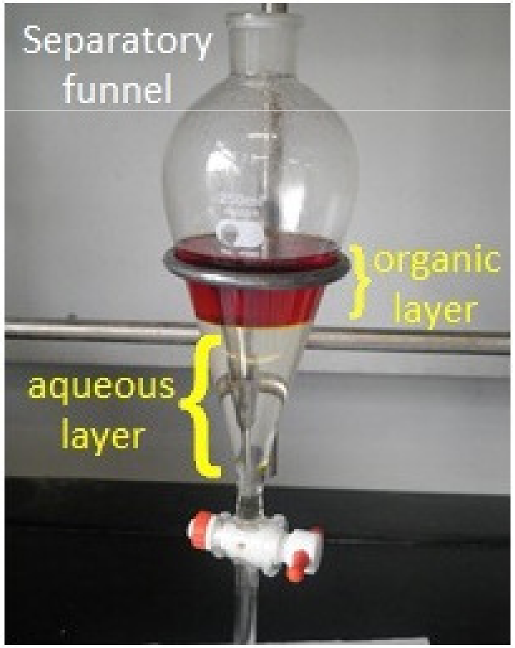
- Gas-liquid contact e.g. absorption, evaporation, distillation etc
- Liquid-liquid contact e.g. extraction
- Liquid-solid contact e.g. crystallisation, adsorption
- Gas-solid contact e.g. adsorption, drying etc

Choice of separation process

- Feasibility
- Product value
- Cost
- Product quality
- Selectivity

Solvent Extraction

The extraction of an analyte or group of analytes from one liquid phase into another, liquid-liquid extraction, is still probably <u>the most widely employed technique for bulk separations</u> where appreciable quantities of analye are involved.



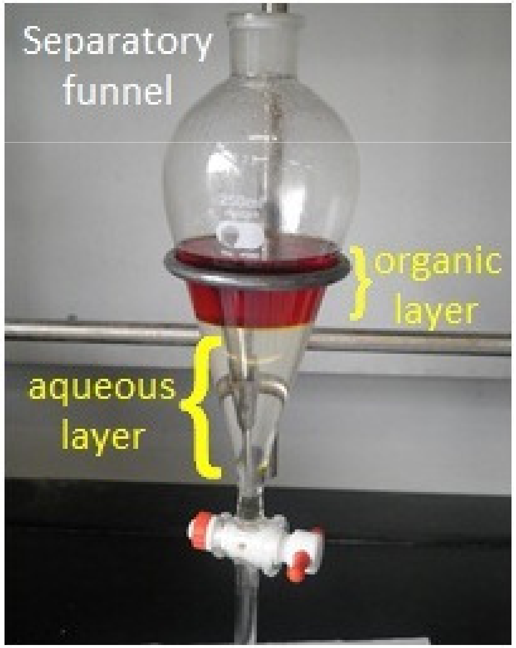
Liquid liquid extraction involves the partitioning of the analyte between two immiscible liquid phases, normally by shaking them in a simple separatory funnel. In most cases

Phase 1: Pure water, acidic/basic/buffered solution

Phase 2: Organic solvent, Solution of organic extracting species in suitable organic solvent

Examples of aqueous and organic phases

Choice of Aqueous phase
Pure water
Acidic solution (pH 0-6)
Basic solution (pH 8-14)
High ionic strength (salting out)
Complexing agents
Ion-pair reagents
Chiral complexing agents



Choice of Organic Phase
Chlorinated solvents like dichloromethane, chloroform
Aliphatic hydrocarbon C5 or above
Aromatic hydrocarbon like toluene
Alcohols above C6
Ketones above C6
Ethers like diethyl and above

Nernst Distribution Law

When a solute is distributed into two immiscible solvents remaining in contact, the activity ratio (loosely speaking, the concentration ratio of the solute in these two solvents, is constant at a constant temperature. This constant is called Partition Coefficient (K) or for very dilute solution, Distribution Constant (K_D).

$$K_D = [A]_{org} / [A]_{aq} \quad \text{at constant temperature}$$

Note:

- The law takes no account of the activities of the various species.
- Thus it is applicable for very dilute solutions only where the ratio of the activities approaches unity.
- This Law is not applicable if any of the distributing species undergo dissociation or association in either phase.

Distribution Ratio

- The fraction of the total solute in each phase, regardless of association, dissociation or the other interactions with dissolved species.

$$D = [A]_{org} / [A]_{aq}$$

at constant temperature

$$D_M = \frac{[M^{n+}]_{org} + [MX_n]_{org} + [MX_{n-1}]_{org} + \cdots}{[M^{n+}]_{aq} + [MX_n]_{aq} + [MX_{n-1}]_{aq} + \cdots} = \frac{[MX_n]_{org}}{[M^{n+}]_{aq}}$$

D is dimensionless. Value of D depends only upon the nature of each solvent, the solute and the temperature.

Separation Factor

If there are two species for partitioning A and B

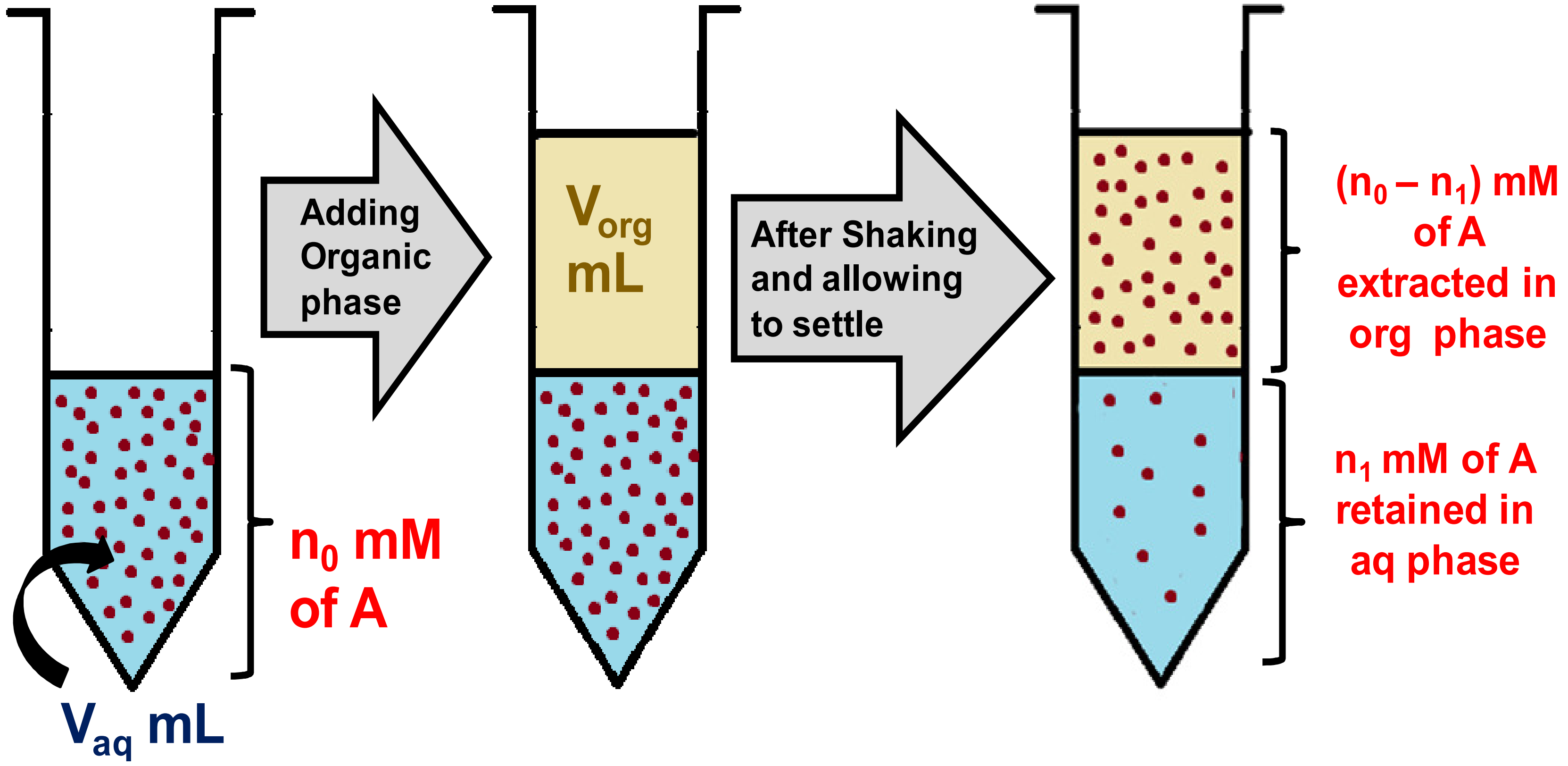
$$D_A = [A]_{org} / [A]_{aq} \quad \text{and} \quad D_B = [B]_{org} / [B]_{aq}$$

- Then separation of the two species

$$= \text{Separation Factor} = S_{A/B} = \alpha = D_A / D_B$$

Percent Extraction(%E)

Let us think of a practical situation for extraction of A depicted pictorially below

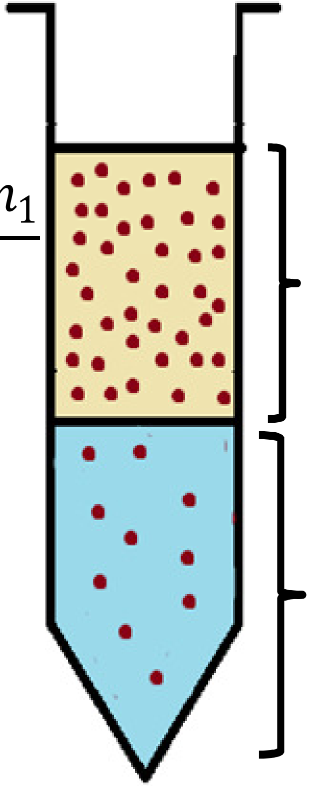


Percent Extraction(%E)

$$[A]_{org} = \frac{n_0 - n_1}{V_{org}}$$

$$[A]_{aq} = \frac{n_1}{V_{aq}}$$

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



($n_0 - n_1$) mM of A extracted in V_{org} mL of organic phase

n_1 mM of A retained in V_{aq} mL of aqueous phase

%E is the more commonly used term than D for expressing the extraction efficiency by analytical chemists

$$\%E = \frac{extracted\ A\,[(n_0 - n_1)\ mM] \times 100}{total\ amount\ of\ A\,(n_0\ mM)}\ \%$$

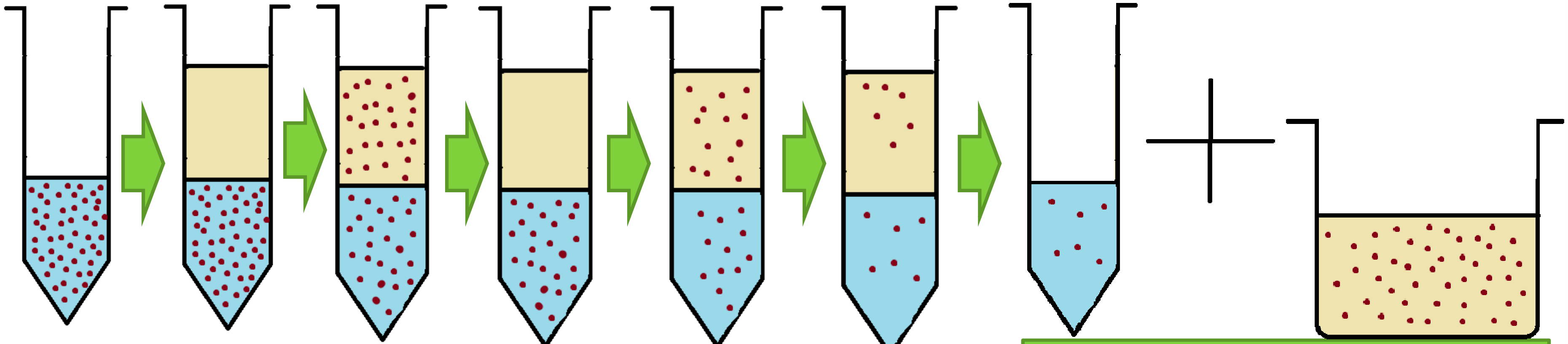
$$\boxed{\%E = \frac{(n_0 - n_1) \times 100}{(n_0 - n_1) + (n_1)}\ \%}$$

$$\%E = \frac{[A]_{org} \times V_{org} \times 100}{([A]_{org} \times V_{org}) + ([A]_{aq} \times V_{aq})}\ \%$$

$$\%E = \frac{\frac{[A]_{org}}{[A]_{aq}} \times 100}{\left(\frac{[A]_{org}}{[A]_{aq}}\right) + \left(\frac{V_{aq}}{V_{org}}\right)}\ \%$$

$$\boxed{\%E = \frac{D \times 100}{D + \left(\frac{V_{aq}}{V_{org}}\right)}\ \%}$$

Multiple Step Extraction



unextracted A in aqueous phase $\mathbf{V_{aq}}$

add $\mathbf{V_{org}}$

collect used $\mathbf{V_{org}}$

add fresh $\mathbf{V_{org}}$

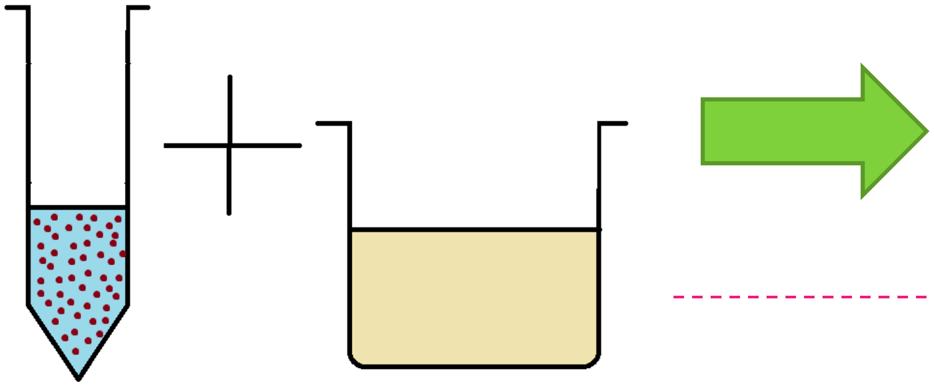
collect used $\mathbf{V_{org}}$

add fresh $\mathbf{V_{org}}$

retained A in aqueous phase $\mathbf{V_{aq}}$

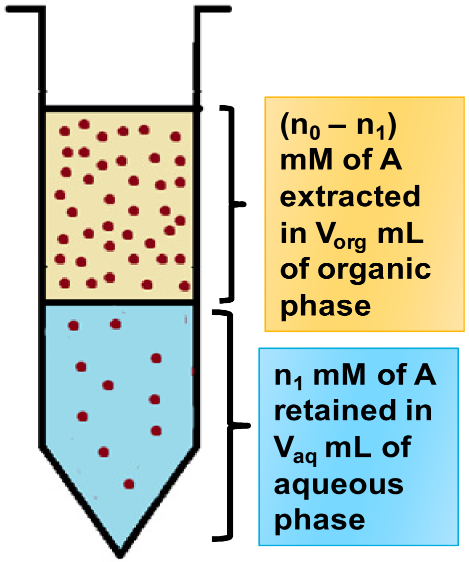
Extracted/ separated A collected in org phases $\mathbf{n \times V_{org}}$

What happens if we do-



Single stage extraction of A?

Let n_0 mM of A in V_{aq} mL of aqueous phase is extracted each time with V_{org} mL of an immiscible organic layer. Let n_1 mM of A remains in aqueous phase after I^{st} extraction.



$(n_0 - n_1)$ mM of A extracted in V_{org} mL of organic phase

n_1 mM of A retained in V_{aq} mL of aqueous phase

$$[A]_{org} = \frac{n_0 - n_1}{V_{org}}$$

$$[A]_{aq} = \frac{n_1}{V_{aq}}$$

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

$$Hence, \quad D = \frac{[A]_{org}}{[A]_{aq}} = \frac{(n_0 - n_1)}{V_{org}} \times \frac{V_{aq}}{n_1}$$

$$n_1 \times D \times V_{org} = (n_0 \times V_{aq}) + (n_1 \times V_{aq})$$

$$n_1 [(D \times V_{org} + V_{aq}) = n_0 \times V_{aq}$$

$$Or, \quad n_1 = \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right] \times n_0$$

Similarly, after second extraction with equal amount of fresh organic layer, n_2 mM of A remains in aqueous phase

$$Hence, \quad n_2 = \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right] \times n_1$$

$$Or, \quad n_2 = \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right] \times \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right] \times n_0$$

$$Or, \quad n_2 = \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right]^2 \times n_0$$

$$Or, \quad \boxed{n_i = \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right]^i \times n_0}$$

General formula, where i = number of extractions

Multiple Step Extraction vs Single Step Extraction

We have 100 mg analyte in 50 mL aqueous solution. Distribution ratio D =85

$$n_i = \left[\frac{V_{aq}}{\{(D \times V_{org}) + V_{aq}\}}\right]^i \times n_0$$

- Single stage extraction by
- 50 mL organic phase

- After extraction, analyte remaining in aqueous phase
- =(50*100)/{(85*50)+50}
- =5000/8550

= 1.163 mg

- Two times extraction by
- 25mL fresh organic later each

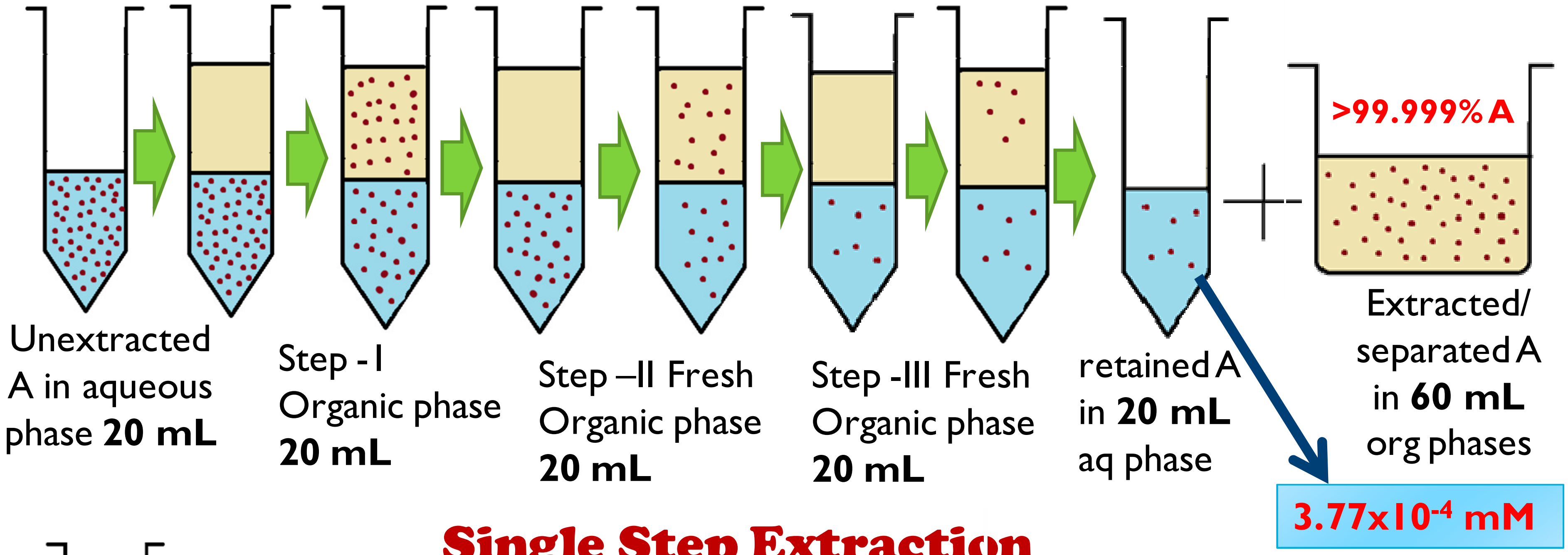
- After two times extractions, analyte remaining in aqueous phase
- $=100^* (50)^2 /\{(85^*25)+50\}^2$

= 0.053 mg

Thus multiple extraction with a solvent is more efficient than a single step extraction.

If D = 50, Vaq = 20 mL, Vorg = 20 mL, Total amount of A =50 mM

Multiple Step Extraction



Unextracted A in aqueous phase **20 mL**

Step - I Organic phase **20 mL**

Step –II Fresh Organic phase **20 mL**

Step -III Fresh Organic phase **20 mL**

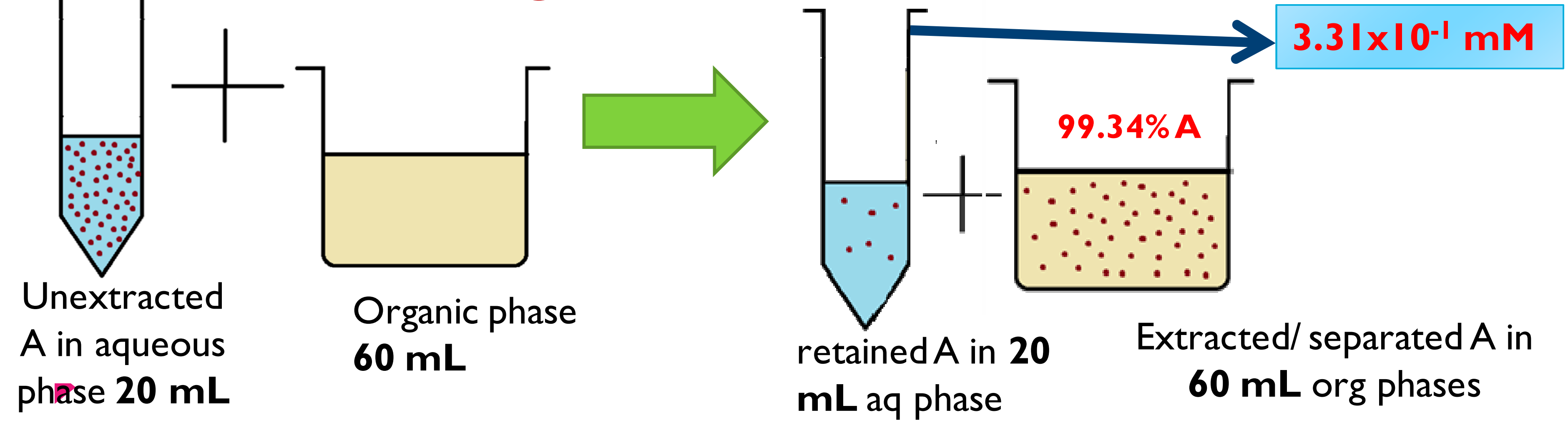
retained A in **20 mL** aq phase

>99.999% A

Extracted/ separated A in **60 mL** org phases

3.77×10^{-4} mM

Single Step Extraction



Unextracted A in aqueous phase **20 mL**

Organic phase **60 mL**

retained A in **20 mL** aq phase

99.34% A

Extracted/ separated A in **60 mL** org phases

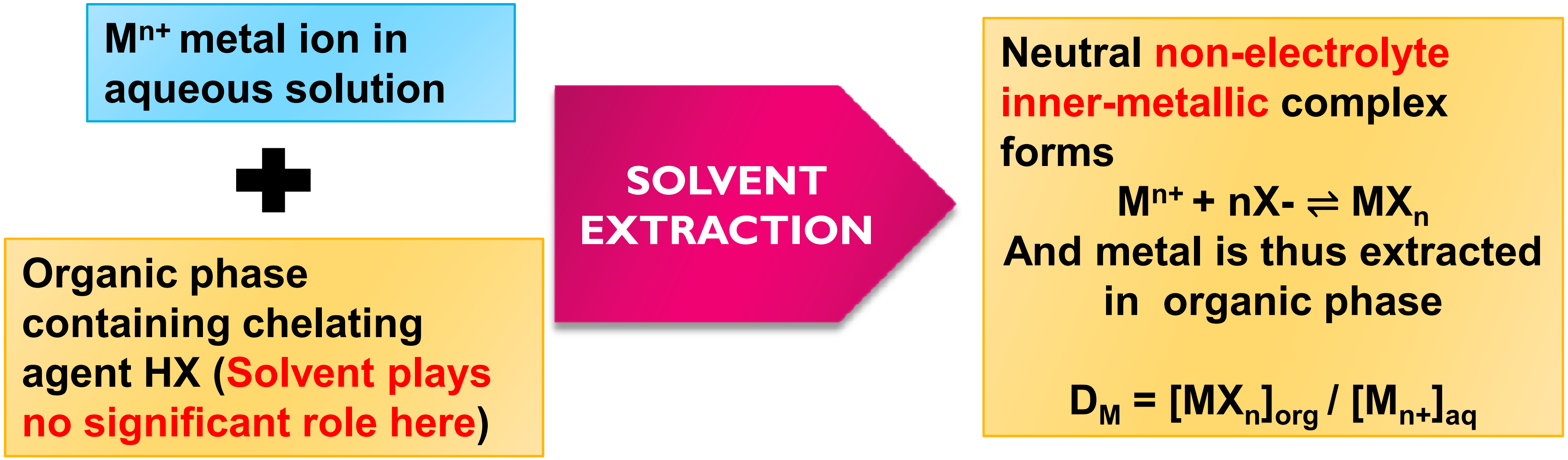
3.31×10^{-1} mM

Extraction equilibrium

The inorganic analytes tend to be more soluble in water rather than organic solvents. Also, there occurs a large loss of electrostatic solvation energy, if inorganic solutes are directly expected to be extracted by organic solvents. In order to enable efficient extraction into an organic phase, we have to modify the species, most preferably by

-(a) formation of chelated complexes using suitable organic ligands

-(b) formation of ion-associated complex



M^{n+} metal ion in aqueous solution

+

Organic phase containing chelating agent HX (Solvent plays no significant role here)

SOLVENT EXTRACTION

Neutral non-electrolyte inner-metallic complex forms

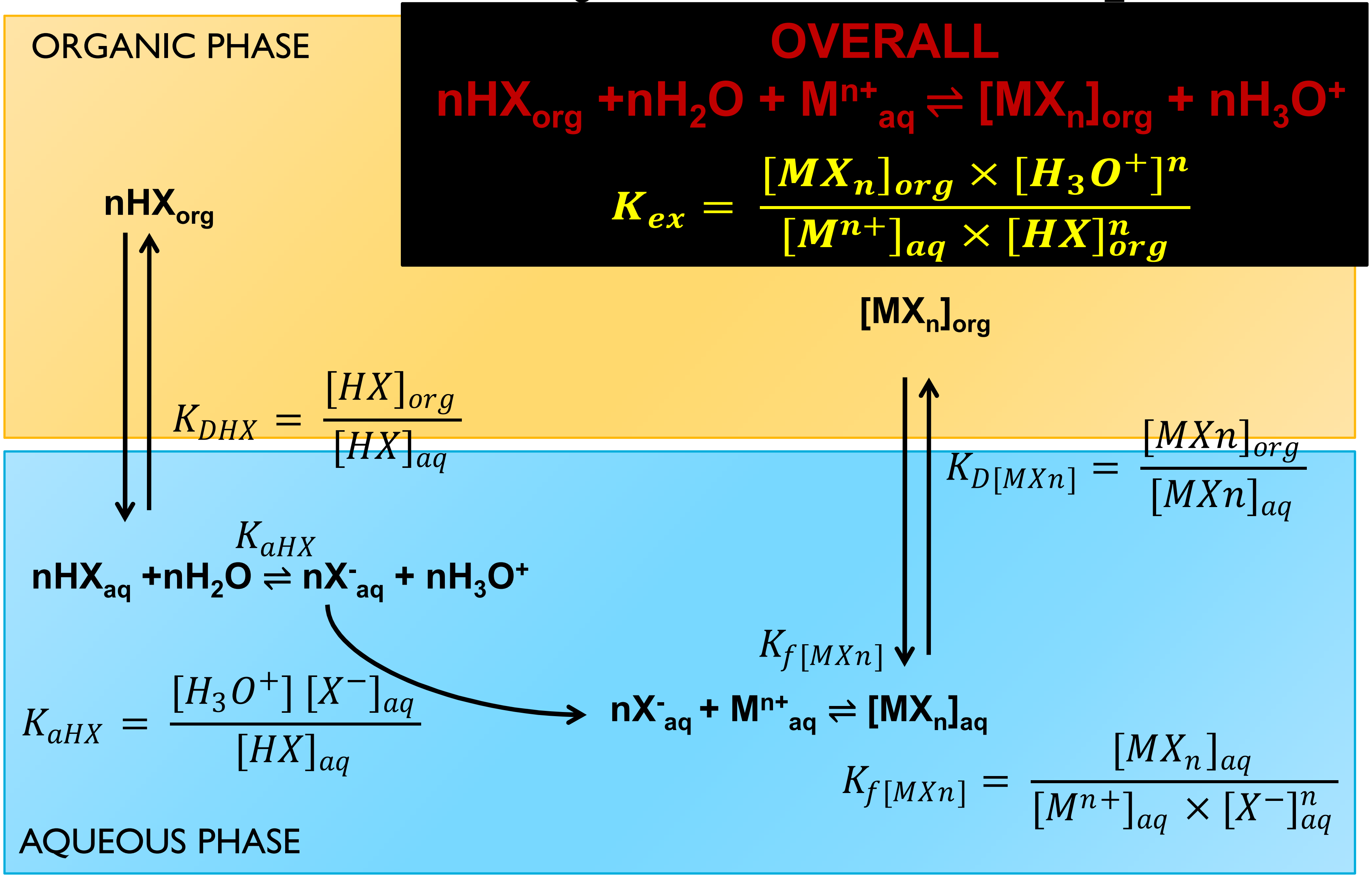
$$M^{n+} + nX^- \rightleftharpoons MX_n$$

And metal is thus extracted in organic phase

$$D_M = [MX_n]_{org} / [M_{n+}]_{aq}$$

Possibility of forming $[MX_{n-1}]^{+,}$ $[MX_{n-2}]^{2+}$, etc., complexes are well expected, but we generally ignore them for simplicity.

A Summary of Relevant Equilibria



ORGANIC PHASE

OVERALL

$nHX_{org} + nH_2O + M^{n+}_{aq} \rightleftharpoons [MX_n]_{org} + nH_3O^+$

$$K_{ex} = \frac{[MX_n]_{org} \times [H_3O^+]^n}{[M^{n+}]_{aq} \times [HX]^n_{org}}$$

nHX_{org}

$[MX_n]_{org}$

$$K_{DHX} = \frac{[HX]_{org}}{[HX]_{aq}}$$

$$K_{D[MXn]} = \frac{[MXn]_{org}}{[MXn]_{aq}}$$

$nHX_{aq} + nH_2O \overset{K_{aHX}}{\rightleftharpoons} nX^-_{aq} + nH_3O^+$

$K_{f[MXn]}$

$nX^-_{aq} + M^{n+}_{aq} \rightleftharpoons [MX_n]_{aq}$

$$K_{aHX} = \frac{[H_3O^+]\,[X^-]_{aq}}{[HX]_{aq}}$$

$$K_{f[MXn]} = \frac{[MX_n]_{aq}}{[M^{n+}]_{aq} \times [X^-]^n_{aq}}$$

AQUEOUS PHASE

OVERALL REACTION

$$nHX_{org} + nH_2O + M^{n+}_{aq} \rightleftharpoons [MX_n]_{org} + nH_3O^+$$

$$K_{D[MXn]} = \frac{[MXn]_{org}}{[MXn]_{aq}}$$

$$K_{aHX} = \frac{[H_3O^+]\,[X^-]_{aq}}{[HX]_{aq}}$$

$$K_{ex} = \frac{[MX_n]_{org} \times [H_3O^+]^n}{[M^{n+}]_{aq} \times [HX]^n_{org}}$$

$$K_{f[MXn]} = \frac{[MX_n]_{aq}}{[M^{n+}]_{aq} \times [X^-]^n_{aq}}$$

$$K_{DHX} = \frac{[HX]_{org}}{[HX]_{aq}}$$

$$K_{ex} = \frac{K_{D[MX_n]} \times [K_{aHX}]^n \times K_{f[MXn]}}{[K_{DHX}]^n}$$

Images from Day & Underwood

Effect of pH on equilibrium

$nHX_{org} + nH_2O + M^{n+}_{aq} \rightleftharpoons [MX_n]_{org} + nH_3O^+$

$$K_{ex} = \frac{[MX_n]_{org} \times [H_3O^+]^n}{[M^{n+}]_{aq} \times [HX]^n_{org}}$$

$$D_M = \frac{[MX_n]_{org}}{[M^{n+}]_{aq}}$$

$$Or, \quad K_{ex} = \frac{D_M \times [H_3O^+]^n}{[HX]^n_{org}}$$

$$Or, \quad D_M = \frac{K_{ex} \times [HX]^n_{org}}{[H_3O^+]^n}$$

$$logD_M = logK_{ex} + n\,log[HX]_{org} - n\,log[H_3O^+$$

$$\boxed{logD_M = logK_{ex} + n\,log[HX]_{org} - n\,pH}$$

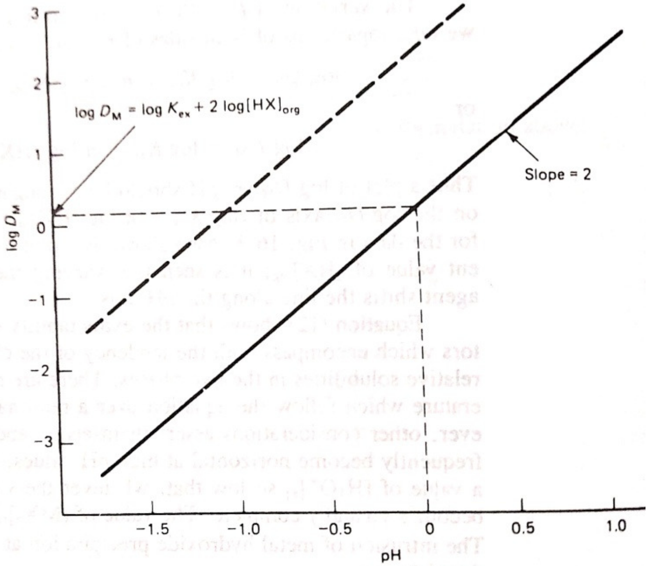


Figure 16.4 Plot of Eq. (13) for the extraction of Cu^{2+} from aqueous solution into CCl_4 as the dithizone chelate. Solid line: conditions are the same as for the curve in Fig. 16.3. Dashed line: calculated for $[HX]_{org} = 1.0 \times 10^{-4}$ *M*.

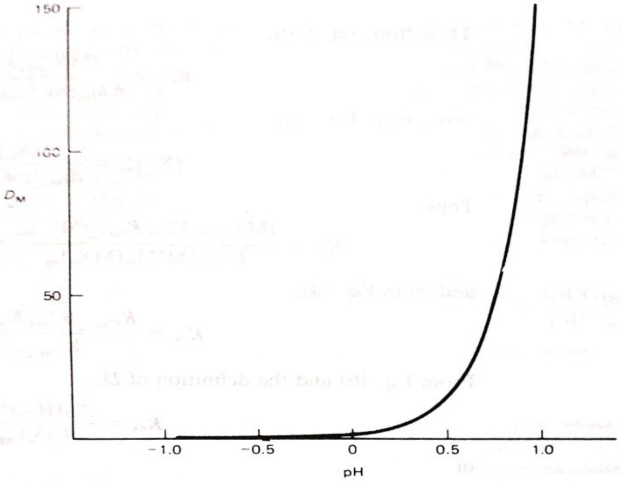


Figure 16.3 D_M vs pH_{aq} for extraction of a metal ion from aqueous solution into an organic solvent as a chelate compound. The curve is calculated, using Eq. (12), for the extraction of Cu^{2+} into CCl_4 with dithizone, where $K_{ex} = 1.5 \times 10^{10}$ and $[HX]_{org}$ is assumed to be constant at 1.0×10^{-5} *M*.

Effect of pH on %E of metal ion

As the distribution ratio D_M for the metal is a concentration ratio, the extent of extraction depends upon the volume ratio of organic solvent to water .

Let **f** be the fraction of the total metal ion in the organic solvent at equilibrium, then **(1-f)** is the fraction remaining in aqueous phase.

Also, let $\mathbf{V_{org}}$ and $\mathbf{V_{aq}}$ be the volumes of the two phases respectively.

$$D_M = \frac{[MX_n]_{org}}{[M^{n+}]_{aq}} = \frac{f\ /V_{org}}{(1-f)/V_{aq}} = \frac{f \times V_{aq}}{(1-f) \times V_{org}}$$

Rearraning,

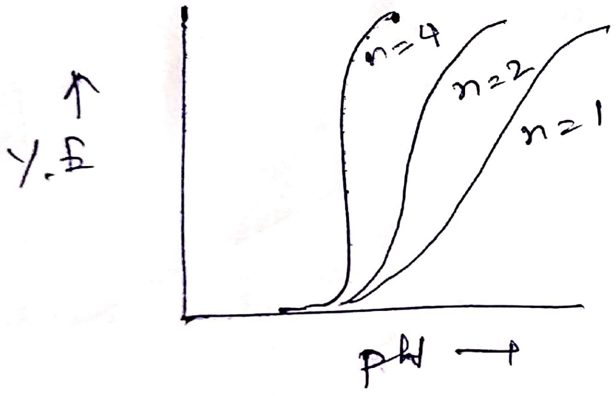
$$f = \frac{D_M \times V_{org}}{V_{aq} + (D_M \times V_{org})} = \frac{D_M}{D_M + (V_{aq}/V_{org})}$$

$$Or, \qquad \%E = \frac{D_M \times 100}{D_M + (V_{aq}/V_{org})}$$

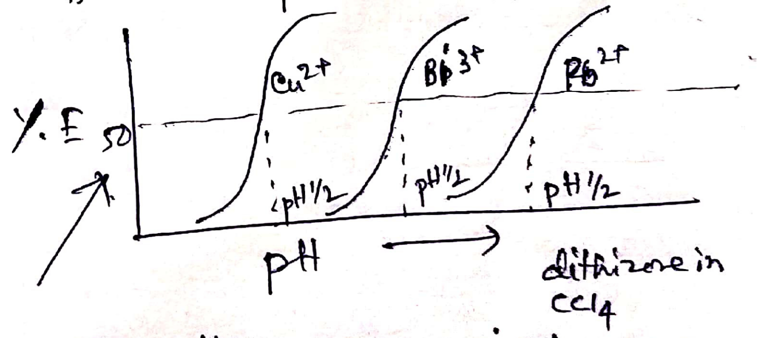
$$logD_M = logK_{ex} + n\ log[HX]_{org} - n\ pH$$

The term $[HX]_{org}$ is constant if V_{org} and V_{aq} are constant. Thus, percentage of chelated complex extracted into the organic layer will vary with the pH.

%E vs pH gives a sigmoidal curve.



position of curve along pH axis depends on diff. K_{ex} for diff metals.



pH½ = pH value at 50% extraction.

$Cu^{2+} \rightarrow$ pH 1

$Pb^{2+} \rightarrow$ pH~10

$$\boxed{logD_M = \ logK_{ex} + n\ log[HX]_{org} \ - n\ pH}$$

$$Now, \qquad D = \frac{Extracted}{Unextracted} = \frac{E}{100 - E}$$

$$\log(E) - \log(100 - E) = \ logD_M$$
$$= logK_{ex} + nlog[HX]_{org} + npH$$

$$logD_M = \log\left(K_{ex} \times [HX]^n_{org}\right) + n\,pH$$

$$logD_M = \log K^* + n\,pH \qquad (say)$$

Hence,

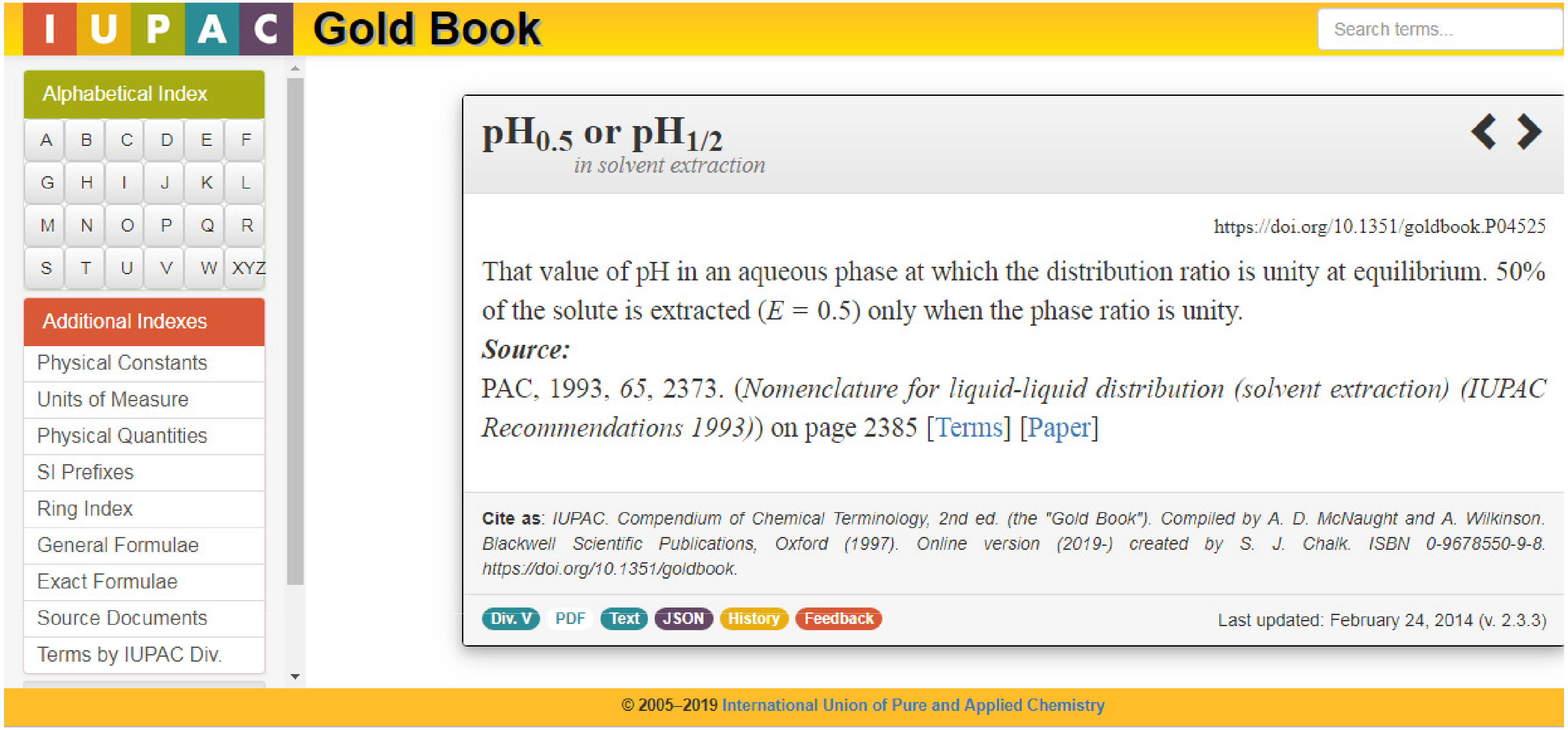
$$\log(E) - \log(100 - E) = logD_M = \log K^* + n\,pH$$

at $pH_{1/2}$, $E = 50$, thus,

$$\log(E) - \log(100 - E) = 0$$

Thus the equation becomes $\log K^* + n\,pH_{1/2} = 0$

$$Or, \mathbf{pH_{1/2}} = -\frac{\mathbf{1}}{\mathbf{n}}\mathbf{logK^*}$$



$pH_{0.5}$ or $pH_{1/2}$

in solvent extraction

https://doi.org/10.1351/goldbook.P04525

That value of pH in an aqueous phase at which the distribution ratio is unity at equilibrium. 50% of the solute is extracted ($E = 0.5$) only when the phase ratio is unity.

Source:

PAC, 1993, *65*, 2373. (*Nomenclature for liquid-liquid distribution (solvent extraction) (IUPAC Recommendations 1993)*) on page 2385 [Terms] [Paper]

Cite as: *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.*

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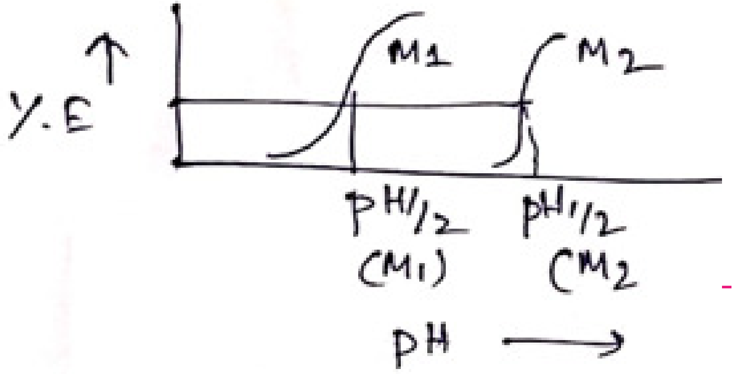
$$\boxed{pH_{1/2} = -\frac{1}{n}\log K^*}$$

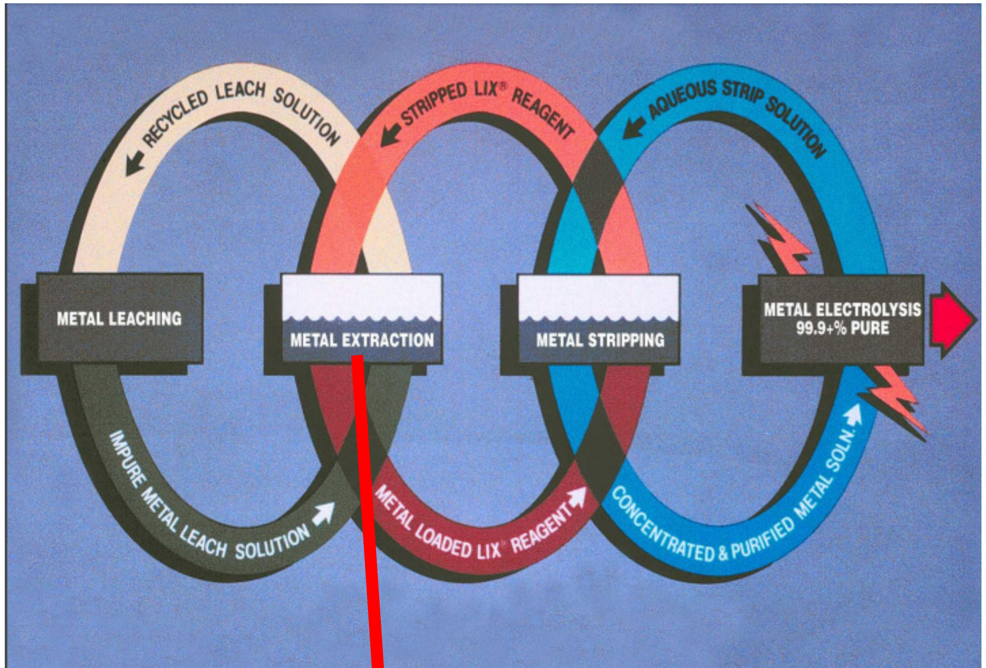


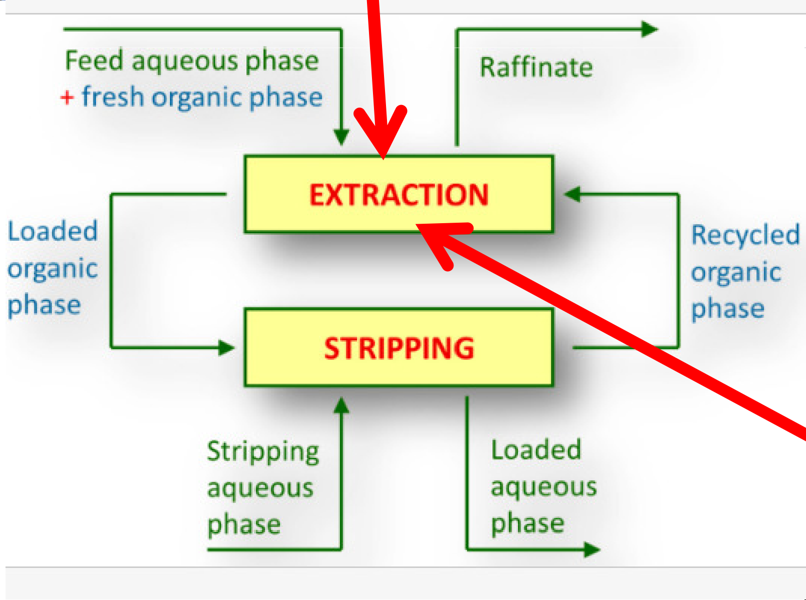
Thus if the $pH_{1/2}$ values are sufficiently far apart, then excellent separation can be achieved by controlling the pH of extraction.

Controlling $pH_{1/2}$ value

- $pH_{1/2}$ values may be altered using competitive complexing agents or masking agents.
- e.g. Cyanides rises $pH_{1/2}$ values for Hg, Cu, Zn, Cd in dithizone in CCl_4.
- e.g. Separation of Hg and Cu – adding EDTA can trap C in aqueous phase by complex formation whereas Hg will be extracted by dithizone in CCl_4.

A typical example of application of Solvent Extraction in Industry




Feed aqueous phase
+ fresh organic phase

Raffinate

EXTRACTION

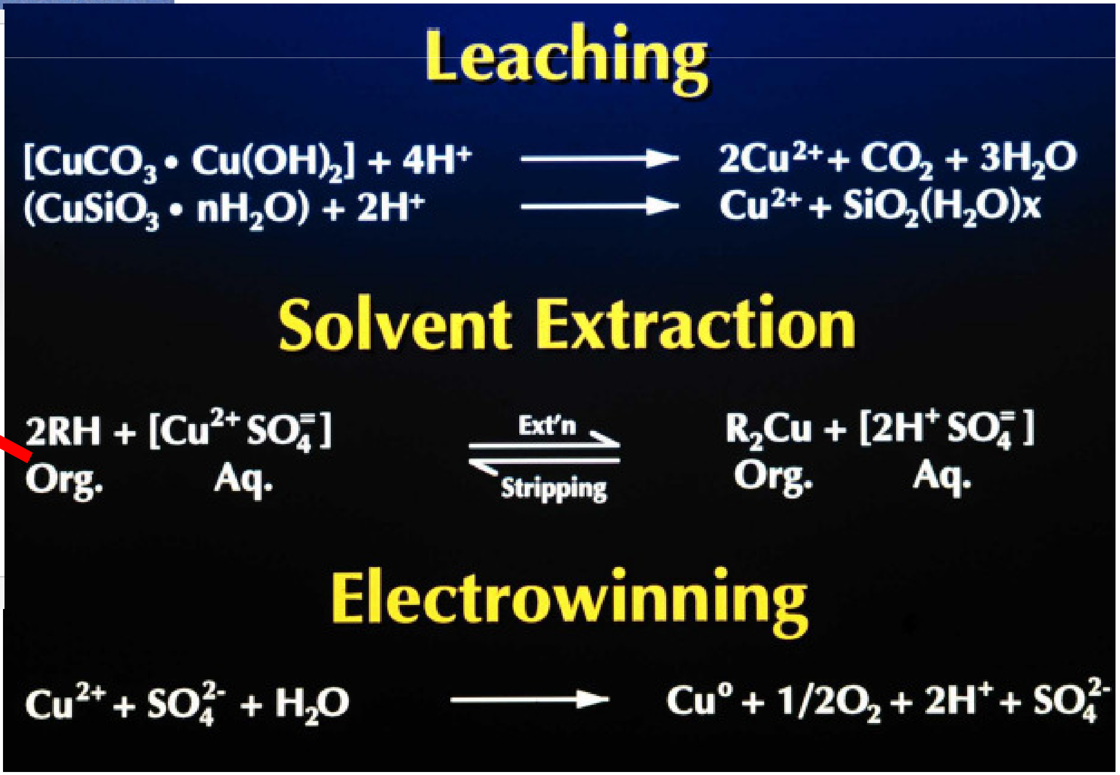
Loaded organic phase

Recycled organic phase

STRIPPING

Stripping aqueous phase

Loaded aqueous phase


Leaching

$$[CuCO_3 \bullet Cu(OH)_2] + 4H^+ \longrightarrow 2Cu^{2+} + CO_2 + 3H_2O$$

$$(CuSiO_3 \bullet nH_2O) + 2H^+ \longrightarrow Cu^{2+} + SiO_2(H_2O)x$$

Solvent Extraction

$$\underset{Org.}{2RH} + \underset{Aq.}{[Cu^{2+}SO_4^{=}]} \underset{Stripping}{\overset{Ext'n}{\rightleftharpoons}} \underset{Org.}{R_2Cu} + \underset{Aq.}{[2H^{+}SO_4^{=}]}$$

Electrowinning

$$Cu^{2+} + SO_4^{2-} + H_2O \longrightarrow Cu^{o} + 1/2O_2 + 2H^{+} + SO_4^{2-}$$

Ref Link And Link 2

Cation extraction

Metal cations like Cu^{2+}, Zn^{2+}, Fe^{3+}, etc. are extracted. Typical extractants used are carboxylic acids, phosphoric acid compounds or hydroxyoximes .

e.g. Different types of hydroxyoximes are used in commercial copper extraction from heap leaching of low grade copper ores. The extraction is pH-dependent and copper is usually extracted at pH values of 1.5-2 and stripping is usually achieved with ~2M sulphuric acid.

Anion extraction

Extraction of negative metal ion complexes like $CoCl_4^{2-}$, $CuCl_4^{2-}$, $FeCl_4^{-}$, etc.. is done by extractants which are long chain amines with primary, secondary, tertiary or quaternary amine groups.

e.g. An example of Co^{2+} extraction

$2R_3NH{+}Cl^{-}(o) + CoCl_4^{2-}(aq) \rightarrow$

$(R_3NH{+})_2CuCl_4^{2-}(o) + 2Cl^{-}(aq)$

Extraction requires high chloride concentration so that the negatively charged cobalt chloride complex can form and stripping can be done with water.

Solvating extraction

Non-charged metal ion complexes are extracted. A typical extractant is tributylphosphate (TBP).

Choice of suitable extractants

USING CHELATING AGENTS

- The acids forming chelates are usually weak and more soluble in organic than in aqueous phase.
- The composition of the chelates is usually unaffected by the nature of the diluents. However, an increased extraction of these chelates is observed by oxygen containing polar diluents, such as ketones, esters and alcohols. (synergistic extraction).
- It is possible to achieve selectivity by factors other than pH control. One of the most popular approaches is by use of masking agents which form water soluble complexes of higher stability than those formed by the chelating agents.
- Generally, introduction of a hydrophobic group in the chelating molecule favours the transfer of its metal chelate in the organic phase.
- The well-known reagents under the head of chelating agents are dithizone, 8-hydroxyquinoline, nitrosophenols, hydroxyoximes, etc.

Choice of suitable extractants

USING ACIDIC ORGANOPHOSPHORUS COMPOUNDS

- Alkylphosphoric, phosphonic and phosphinic acids fall under this category. The organophosphorus acids have pronounced tendency of association into dimers and larger aggregates.

$$M^{m+}_{(a)} + m(HX)_{2(o)} \rightleftharpoons M(HX)m_{(o)} + mH^{+}_{(a)}$$

- As the charge on the metal ion increases, then so does its extractability. For metals having the same charge, extraction varies inversely as the ionic radius. Thus, at a fixed pH, Ce^{4+} and Th^{4+} exhibit much higher extractability when sodium or ammonium salt of DEHPA (di-2-ethylhexyl phosphoric acid) can be used for the extraction.
- The nature of organic diluent can affect the extraction depending on the dielectric constant, dipole moment and polarizability of the diluent and the complex and the hydrogen bond donor and acceptor abilities.
- Among this class of extractants, the mono esters, mono-2-ethylhexyl phosphoric acid is the most commonly used extractant and among the dialkylphosphates, di-2-ethylhexyl phosphoric acid (DEHPA) has by far received the maximum attention.

Choice of suitable extractants

USING CARBOXYLIC AND SULPHONIC ACIDS

- Different carboxylic, alkyl or aryl-alkyl sulphonic and sulphuric acids form salts with a number of metal ions including alkali and alkaline earths. These salts are generally less soluble in aqueous solutions but more in some organic solvents. For carboxylic acids of normal or branched chain (with seven or more carbon atoms) and aliphatic sulphuric acids (with at least 15 carbon atoms), have been shown to be potentially useful extractants. Carboxylic acids have a tendency to higher polymerization with increase in concentration of extracted metal. In the extraction of Ni(II) by naphthenic acid, the extracted species have been reported as $Ni_2.A_4.4HA$.

EXTRACTION BY ION PAIR FORMATION

- This involves the extraction of a ion pair formed between an anionic metal species with cation furnished by an organic base. The strongly basic high molecular weight amines (HMWA), by quaternary phosphonium, arsonium, phenylonium bases are able to extract the metals by forming such ion pairs.
- E.g. $R_3NH^+FeCl_4^-$, $(C_6H_5)_4As^+.MnO_4^-$, etc.

Selection of suitable solvents

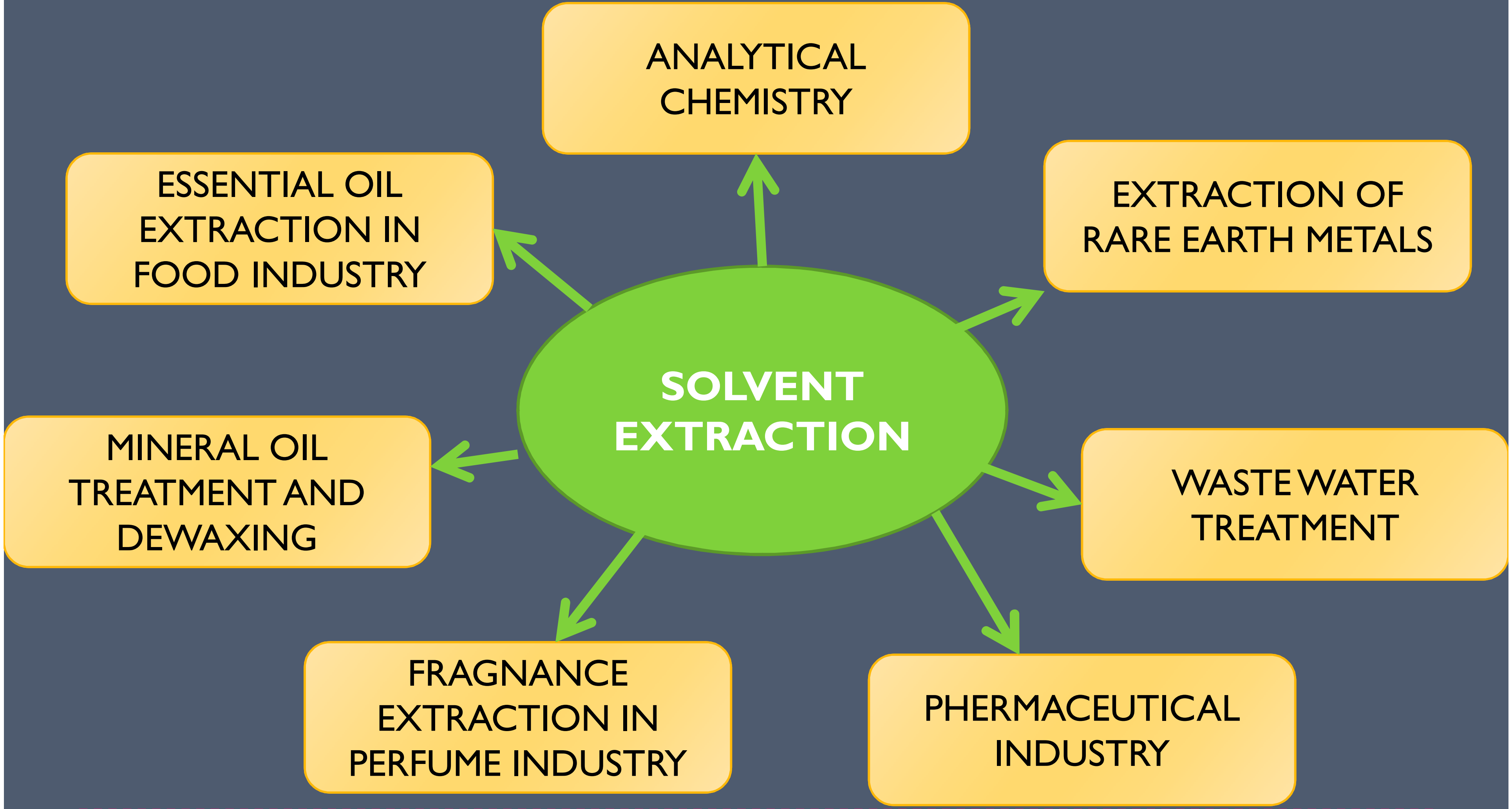
- Selectivity –High separation factor (s)
- Extraction Capacity- High value of K or D
- Insolubility- Must be immiscible in aqu
- Solvent recovery- Desired to be easily recoverable
- Density- Sufficiently large density difference between the two phases is required
- Interfacial Tension-Interfacial tension is desired to be large for easier coalescence of the dispersed organic phase after shaking
- Other desirable criteria- Stable, Inert, non-toxic, non-flammable, low viscosity, low vapour pressure, low freezing point, less expensive.

Diluents

- Diluents are often required for dissolving or diluting the organic extractant so that its physical properties like density and viscosity become more favourable for better mixing of two phases and consequent separation.
- Aliphatic or aromatic hydrocarbons or a combination of both are used as diluents.
- The presence of diluent affects the extraction, scrubbing, stripping and phase separation process significantly.
- Examples of diluents

Kerosene, Benzene, Chloroform, Cyclohexane, Xylene, Toluene, etc.

APPLICATIONS



SOLVENT EXTRACTION

ANALYTICAL CHEMISTRY

EXTRACTION OF RARE EARTH METALS

WASTE WATER TREATMENT

PHERMACEUTICAL INDUSTRY

FRAGNANCE EXTRACTION IN PERFUME INDUSTRY

MINERAL OIL TREATMENT AND DEWAXING

ESSENTIAL OIL EXTRACTION IN FOOD INDUSTRY

Thank You