CHAPTER 2
THEORETICAL
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2.1 PRINCIPLE OF SOLVENT EXTRACTION

2.1.1 Phase Rule

Nernst’s Distribution law explains solvent extraction as a partition process where selective distribution of substances takes place in two immiscible phases. A third component added to system, will distribute itself in two phases in different manner. For all distributions, the classical phase rule of Gibb’s is as follows –

\[ P + V = C + 2 \]

Where \( P \) is the number of phase, \( V \) is the variance or degree of freedom, and \( C \) is the number of components is most useful. In the particular case of solvent extraction, we are dealing basically with two essentially immiscible solvents and one solute distributed between them so that \( P = 2, C = 3 \). At constant temperature and pressure the Gibb’s rule predicts a variance of unity. We can see that there will definite relations between the solute concentrations in each of the solvent phases.

2.1.2 Distribution Coefficient

Liquid-liquid extraction is a technique in which a solution (usually aqueous) is brought in contact with second solvent usually organic and essentially immiscible with first, in order to bring about a transfer of one or more solute into the second solvent.

The Nernst distribution (or partition) law states that a solute distributes itself between two immiscible liquids in such a way that the ratio of concentrations of the solute in the two phases at equilibrium remains constant at a particular temperature. Thus
\[ K_D = \frac{\text{Concentration of species in organic phase}}{\text{Concentration of species in aqueous phase}} \]

\[ = \frac{[X]_{\text{org}}}{[X]_{\text{aq}}} \]

Where the bracketed terms are molar concentrations of X. \( K_D \) refers to equilibrium constant or distribution constant. The law is valid only when the species is same in both the phases. The Distribution Coefficient has following limitations –

1. The temperature remains constant
2. The solutions are dilute
3. The two solvents are immiscible
4. The molecular state of the solute remains the same in the two solvents i.e. the solute does not undergo dissociation, association and polymerization or interact with other dissolved species. With all its limitations, still, it is a useful term.

2.1.3 Distribution Ratio

In a two phase system a metal ion \( M^{n+} \), can exist in several chemical forms such as \( M, MR_1, \ldots, MR_n \), where \( R \) is a ligand. In most of the analytical problems the total effective concentration of metal ion in each phase can be determined experimentally. The Distribution Ratio \( D \) or extraction coefficient \( E \), which is defined as the ratio of concentration of metal in a different species in the respective phases is more meaningful.
Total concentration of M in all chemical forms in the organic phase

\[
D \text{ or } E = \frac{\text{Total concentration of M in all chemical forms in the aqueous phase}}{[M]_0 + [MR_1]_0 + \ldots + [MR_n]_0}
\]

\[
D \text{ or } E = \frac{[M]_w + [MR_1]_w + \ldots + [MR_n]_w}{100 \times [M]_0 V_0}
\]

\[
\% E = \frac{[M]_0 V_0}{V_0 [M]_0 + [M]_w V_w}
\]

\[
\text{But } D = \frac{[M]_0 V_0}{[M]_w V_w}
\]

\[
\% E = \frac{100 D}{D + V_w/V_0}
\]

Where \( V_w \) and \( V_0 \) are the volumes of aqueous and organic phases respectively.
2.1.5 Selectivity of Extraction

The ability to separate two solutes depends on the relative magnitude of their distribution ratios. For solute A and B, whose distribution ratios are $D_A$ and $D_B$, the separation factor ($\beta$) is defined as the ratio –

$$\beta = \frac{D_A}{D_B}$$

where $D_A > D_B$

A separation can be made more efficient by adjustment of the proportion of organic and aqueous phase. The optimum ratio for the best separation is given by the Bush – Densen Equation

$$\frac{V_0}{V_w} = \left[ \frac{1}{D_A D_B} \right]^{1/2}$$

Successive extraction helps to increase the efficiency of extraction of both solute but simultaneously it may lead to poor separation. It is possible to enhance or suppress the extraction of a particular solute by adjustment of pH or by complexation or any other suitable mechanism.

2.2 Techniques of Solvent Extraction

There are three basic methods used in liquid-liquid extraction,

1) Batch Extraction
2) Continuous Extraction
3) Countercurrent Extraction
2.2.1 Batch Extraction

This is most common extraction technique used for the analytical separation. The batch extraction is carried in a simple apparatus such as a separating funnel. In batch extraction, the aqueous solution containing the solute to be extracted is taken in a separating funnel and it is shaken with the known volume of the organic solvent. The two phases can be brought in contact so that the solute can pass from one liquid phase to another.

After sufficient shaking, the system is left undisturbed for the separation of two layers. Depending upon the density of organic solvent it either occupies a lower layer or upper layer. The liquid layers are then withdrawn by opening the stopcock. When the distribution ratio is low, three or four extraction are required. This method is generally used for extraction when the distribution ratio is high, which requires a single step for complete extraction.

2.2.2 Continuous Extraction

This method is used for extraction of solute having small distribution ratios. In this technique, multiple extractions are carried for the quantitative separation. The apparatus used is a continuous extractor like Soxphlet apparatus. The solution containing the solute and the extracting liquid are brought in contact continuously and hence the solute is continuously extracted by the solvent and accumulates in a reservoir.

2.2.3 Countercurrent Extraction

A solvent extraction technique in which two immiscible liquids move in opposite directions in continuous contact with each other, resulting in separation of solute is
called countercurrent extraction or countercurrent distribution. It is generally used when the solutes to be separated have small differences in their distribution ratios. Countercurrent Extraction is a multiple distribution process with a large number of glass tubes arranged in series. These tubes are called Craig countercurrent tubes. This technique is mainly used for separating complex mixtures.

2.3 ROLE OF EXTRACTION PARAMETERS

2.3.1 Extraction
The choice of solvent is based on consideration of solubility of the solute in the particular solvent, ease of recovery of solvent of solute from the solvent, toxicity and inflammability of an organic solvent. Sometimes a mixed solvent system is very useful. Thus, mixture of alcohol and ethers are commonly used in thiocynate extraction of cobalt, iron etc. Also a mixture of dibutoxytetraethylene glycol and ether is used to extract thorium from nitrate solutions. Sometimes organic diluents are used to vary the composition of the extracting solvent for extraction purpose. Thus kerosene and other hydrocarbons are generally used to dilute tributyl phosphate and many other type of extraction.

2.3.2 Stripping
For analysis the solute is generally stripped i.e. removed from the organic phase for subsequent analysis. When the organic phase becomes coloured after extraction, it may be used directly for spectrophotometric determination of the solute. Again, when radioactive materials are extracted, direct determination is possible for the phase containing the extracted radioisotope by counting the radioactivity. These are the two cases where stripping is not necessary. In general procedure of stripping, a small volume of water is added to the organic layer and evaporates the solvent on
steam bath. This is carried out in case of volatile solvents like ether. When chelate complexes are involved, they are decomposed and the metal ions bought to the aqueous phase by addition of acid to the organic layer, before evaporation of the volatile solvent. The residual organic matter in the aqueous solution, after the organic solvent is evaporated, is destroyed by nitric acid followed by sulfuric and perchloric acids. When the organic solvent is non-volatile, it is shaken with later containing acids or bases or suitable stripping agents, where by the extractable complex is decomposed. The cations are quantitatively back-extracted into the aqueous phase.

2.3.3 Diluents and Modifiers

Sometimes better solvent properties can be obtained with a solvent mixture than with a single-component solvent. In such case the solvent constituent that principally interacts with the solute of interest is often termed as extractant, particularly if the interaction is strong. Other major components are known as diluents and are added –

1) To control the density of the solvent mixture
2) To reduce the viscosity of the solvent phase
3) To put a solid extractant into liquid solution
4) To enable vapourization when solvent regenerated by distillation

Kerosene related hydrocarbon substances are often used as inexpensive diluents. The choice of diluents can strongly affect the phase-equilibrium behaviours for the extraction. In these cases the exact chemical nature of the diluents is more important. Another frequent practice is to add still another component to improve the emulsification and setting properties of the dispersion, or
to keep the organic phase from spitting apart into two phases. Such components are commonly called Modifiers. Higher alcohols such as dodecanol are commonly used for this purpose in the process of hydrometallurgy and can be useful in the extraction of organic phase from water phase.

2.3.4 Specific Gravity

The use of diluents having higher density could have considerable effect on the rate of phase separation, especially at the higher extractant concentration and high metal ion loading.

2.3.5 Viscosity

It becomes necessary to operate the solvent extraction system at elevated temperature or to use diluents having a low density and surface tension, both to reduce viscosity effect and to overcome the rate of separation of phase.

2.3.6 Polar Nature

The diluents affect the solvation of extractant and hence its extractive properties. Diluents such as benzene, hexane having low dielectric constant and diluents such as chloroform, dichloromethane reduce the extraction. In addition to these, other parameters such as impurities, degree of aromaticity, solubility of water in diluents etc. are also considered. In many cases, extraction coefficients can not be correlated with one particular physical property of the diluents.

2.3.7 Treatment of emulsion

While shaking certain combinations of immiscible liquids emulsion may form where by one liquid is dispersed in a certain amount of the other. From the
extraction point of view, breaking of an emulsion is an important step. Since it is necessary to separate the phases for further analytical procedure, addition of neutral salt, probably increases the surface tension or the density that may help in reducing the tendency of emulsification. Another way of avoiding emulsion is to allow only a small volume of aqueous solution to come contact with a relatively large volume of the organic solvent or addition of few drops of higher alcohol (e.g. dodecanol) before shaking the two phases which may prevent the formulation of emulsion.

### 2.3.8 Use of Masking Agent

Masking agents are themselves metal complexing agent which serve to prevent particular metals from taking part in their usual reaction and thus prevent their interference without actual removal. Since the masked metal must remain in solution, the complex obviously must be water soluble. In solvent extraction, masking agents are used to increase the selectivity of extraction e.g. extraction of Aluminium in the presence of iron with 8-quinolinol into chloroform. Iron is prevented by the addition of an alkali cyanide prior to extraction, so that it forms ferrocyanide complex ion \([\text{Fe} \,(\text{CN})_6]^{4-}\)

### 2.3.9 Variation of oxidation state

A useful method of increasing the selectivity of extraction involves modification of the oxidation state of some of the ions present in solution in order to prevent the formation of a metal complex necessary for extraction. Thus, the extraction of iron from chloride media can be prevented by reduction of iron(III) to iron(II), which does not extracted. Similarly, reductions of cerium(IV) to cerium(III) prevent its extraction from nitrate solution. Conversely, it is important in the preparation of the solution for extraction to adjust an ion to the particular valence state required for
formation of complex in order to ensure complete extraction of that element. These variations in oxidation states are accomplished by the addition of an appropriate oxidizing or reducing agent depending on the chemistry of the particular element of interest and the nature of the extraction system.

2.3.10 Salting out Agents

The term salting out Agents is applied to those inorganic salts whose addition greatly enhances the extractability of complexes. Though Salting out Agents may very well enhance the extraction, it may at the same time increase the extraction of impurities. Therefore, it is quite necessary to choose an agent which produces a favourable separation factor. Salting out Agents has been used with great success in separations involving the nitrate, halide and thiocyanate systems.

**Use of Salting out Agents:**

1. Added to aqueous layer to increase the solubility of complex in organic layer.
2. Increases concentration of complexing anions which in turn by mass action would increase concentration of complex and thus improves the extraction.
3. Binds water molecules in the co-ordination sphere of the metal.

2.4 Process of Extraction

The extraction process proceeds in three stages viz.

2.4.1 The Formation of Uncharged Complex

It is most important step in the extraction. It is obvious that if the complex is charged, it will not be extracted into the organic phase. The uncharged Complex can be formed by the process of chelation, solvation or ion pair formation. Thus if $M^{n+}$ is metal ion with valency ‘n’ and if ‘R’ is the anion of the ligand (nR) then
Here MR\textsubscript{n} is the neutral complex. Now in solvation phenomenon or in ion pair formation process, the complex formed may be anionic or cationic which in turn gets associated with anion or cation respectively to give uncharged complex which consequently gets extracted into organic phase.

2.4.2 The distribution of Extracted Species

Any metal species will distribute itself between two immiscible solvents. However, such distribution depends upon various factors like basicity of ligand, the dielectric constant, solvating ability of organic solvent, the number of carbon atoms in homologous series of metal complexes and pH of the solution, stereochemical factors, presence of salting out agent in extraction system and the type of bond formed. The solubility of substances in water or alcohol is governed by the ability of the substances to form a hydrogen bond rather than its polarity is measured by dipole moment.

2.4.3 Chemical Interaction in the Organic Phase

When the neutral complex gets extracted into the organic phase, it undergoes various reactions in the organic phase. Polymerization of the complex in the organic phase or dissociation of the complex is the typical reaction of extracted species in the organic phase. At higher concentration polymerization is fast. This polymerization tends to reduce the activity of the extractable species in the organic phase but the over all equilibrium is shifted in favor of higher distribution ratios. The dissociation of ion pair complex may also occur in diluted solutions. For covalent metal chelates such problems never arise. Some times extraction of buffer
compounds affect overall stability of metal ion with chelating agent but such cases are very rare.

2.5 Spectrophotometry

Spectrophotometry facilitates the determination of the concentration of the colored substances in a solution and has been employed for the analysis of metals at trace and ultra trace levels. Spectrophotometry is based on the quantitative study of absorbance or radiation by the light absorbing species is given by,

\[
I_0 = I_a + I_t + I_r
\]  \hspace{1cm} (a)

Where \( I_a \) = Intensity of absorbed light

\( I_t \) = Intensity of transmitted light

\( I_r \) = Intensity of reflected light

Since the intensity of the reflected light can be neglected by control, the incident light can be given as,

\[
I_0 = I_a + I_t
\]  \hspace{1cm} (b)

The two laws governing the absorption of light by the molecules are the Lambert’s Law and the Beer’s Law. A combination of both these laws is known as the Beer-Lambert’s law which states that, “When monochromatic light passes through a transparent medium, the rate of decrease of intensity of light with respect to the thickness and concentration of the absorbing species is proportional to the intensity of light”.

Mathematically, it can be given as,
\[ \frac{\log_{10} \text{Io}}{\text{It}} = \varepsilon \cdot b \cdot c \]  
(c)

Where, \( \text{Io} \) = Intensity of the incident light

\( \varepsilon \) = Molar absorptivity

\( C \) = Molar concentration of the solution

The fraction of the incident light transmitted by the solution is called Transmittance \( (T) \) and given by,

\[ T = \frac{\text{It}}{\text{Io}} \]  
(d)

Therefore

\[ \log_{10} T = \log_{10} \frac{\text{It}}{\text{Io}} \]  
(e)

\[ -\log_{10} T = \log_{10} \frac{\text{Io}}{\text{It}} \]  
(f)

It follows from equation (c) that,

\[ -\log_{10} T = \varepsilon \cdot b \cdot c \]  
(g)

- \( \log T \) is called absorbance \( (A) \) or optical density

Therefore, substituting \( A = -\log T \) in equation (g), we get

\[ A = \varepsilon \cdot b \cdot c \]

Thus, from Beer - Lambert’s law the relation between the absorbance of light and the thickness and concentration of the absorbing species is obtained.
2.6 Composition of the complex

A number of methods can be used to study the composition of the metal ligand complex in the solution. But in the present study Job’s Continuous variation Method, Mole ratio and Slope ratio the \((\text{LogD} - \text{LogR})\) methods. Using these methods composition of metal-ligand complex has been determined. The details are given below.

2.6.1 Job’s Continuous Variation Method

A number of methods can be used to study the composition of the metal ligand complex in the solution. However, Job’s Continuous Variation Method is one of the most suitable conventional methods for investigating the formation of complex in the solution.

Originally the method was developed to study the composition and stability of the complex in aqueous solution. Vosburgh and Cooper extended it to the system where two or more complexes are formed in the solution. Later Irving and Pierce have shown that it could be employed in two-phase systems. In this method, the total molar concentrations of the metal ion and ligand is kept constant, but the ratio of the moles of the components is varied in series of solutions i.e. total Conc. = \(C_M + C_L = \text{Constant}\). The absorbance of each solution is plotted as a function of the moles fraction of one of the components. The absorbances are measured at a wavelength where the complex shows maximum absorption. The curve starts from zero absorbance when only components one is present in the solution. The absorbance rises as second component is added and the absorbing complex is formed. Maximum absorbance is attained when the one component is totally chemically reacted with the equivalent amount of other to form complex and
no either of the two left unconsumed. After the maxima, the absorbance drops down as the concentration of component on decreases.

In this method, mixture solutions are prepared by mixing two reacting solutions i.e. (Reagent and metal) in different proportions keeping the total volume of the mixture constant, and the variation of one physical property of the mixture is measured. When mixing two equimolar solutions forms only one complex, a suitably chosen properly attains a maximum or minimum value for mixture of a particular composition. It can be shown that the ratio of the volume of the two reacting solutions at this particular composition denotes the ratio in which the two substances are reacting to form the complex in the solution. Let us consider the reaction of the type:

\[
M + Rn \rightarrow MRn
\]

Equimolar solutions of the metal ion M and the neutral or ionic ligand R mixed in varying proportions in such a way that the sum (C) of the concentrations of the ligand (C_R) and the metal (C_m) is constant i.e (C_m + C_R = C) and only their ratio is varied. A suitable colligative property of the mixture is measured and the difference (t) in the value of the property observed after interaction and no interaction of the components for each composition is plotted against the mole fraction of the metal (R = C_m / C). The composition of the solution corresponds to maximum value of (t) bears a simple ratio to ‘n’.

If the absorbance measurement of the resulting mixture is carried out in a region where only the complex species MRn absorbs and the absorbance due to M and R being negligible then a plot of the absorbance due to M and R in the mixture versus absorbance gives a curve with a maximum for equimolar solutions. The ratio
of the value \((I - R)\) and \(R\) corresponding to the maximum point of the curve gives the formation of the complex. Thus,

\[
n = \frac{C_R}{C_m} = \frac{(I - R)}{R}
\]

2.6.2 Mole Ratio Method

Mole Ratio method is also applicable for studying the nature of the complex in the solution. In this method the concentration of either of the reactant is kept constant while the other is varied keeping the total volume of the mixture constant. The property of the mixture is measured and plotted against the ratio of the concentrations of the two reactants. The sharp break in the curve indicates the ratio in which the reactants react. This method was developed by the Yoe and Jones. Consider the formation of a coloured complex by the reaction of two reactants of the type

\[
M + Rn \rightarrow MRn
\]

If the concentration of the metal ion and the total volume of the mixture solutions are kept constant then the absorbance of the mixture solutions will increase with the increase in the concentration of the ligand till the equivalence point is reached. After this point the absorbance of the solution will either remain constant or will increase with a different slope with a further rise in the concentration of the ligand, depending upon the stability of the complex.

2.6.3 Log D - Log R Method (Slope Ratio Method)

A.E. Harvey, D.X. Manning first introduced this in 1950 for the determination of nature of complex in the solution. In order to ascertain the nature of the extracted species it is necessary to evaluate the distribution ratio \((D)\) while varying the
extractants concentration. The probable composition of the extracted species is confirmed from the plot of log D Vs log [R].

\[ \text{xM} + \text{yL} \leftrightarrow \text{MxLy} \]

Where ‘x’ moles of cation M reacts with ‘y’ moles of ligand L to form a complex. If the concentration of the metal M is kept constant and the concentration of ligand is sufficient and in excess to make dissociation negligible, the equilibrium concentration of the complex MxLy will be essentially proportional to the analytical concentration of ligand L added in the reaction.

\[ [\text{MxLy}] = \frac{\text{Cm}}{x} \]

Cm is the molar analytical concentration

From Beer’s Lambert’s law

\[ A_1 = \varepsilon \cdot b \cdot [\text{MxLy}] \]

\[ A_1 = \varepsilon \cdot b \cdot \text{Cm} / x \]

A plot of absorbance as a function of Cm becomes linear whenever sufficient L is present and is also proportional to extraction coefficient.

The slope of this plot is \( \varepsilon b / x \)

If the concentration of the metal ion varied and the concentration of ligand kept constant we get the reverse condition then

\[ A_2 = \varepsilon \cdot b \cdot [\text{MxLy}] \]
\[ A_2 = \varepsilon \cdot b \cdot C_L / y \]

Again a linear plot of \( A_2 \) Vs \( C_L \) is observed at very high concentration of \( M \) having a slope of \( \varepsilon \cdot b / y \)

The ratio of two straight lines gives the combining ratio between \( M \) and \( L \)

\[ A = \frac{\varepsilon b}{x} / \frac{\varepsilon b}{y} = \frac{y}{x} \]

When log \( D \) is plotted against different analytical concentration of reagent log \( R \) keeping concentration of metal ion constant, a straight line is obtained having slope ‘\( n \)’.

From the value of slope ‘\( n \)’ the empirical formula can be calculated.
2.7 SCOPE AND METHODOLOGY OF THE PRESENT WORK

Today, separation of the desired component from the complex sample is an avoidable step. In the modern days analysis methods that are faster, easily reproducible relatively cheaper and which are applicable to tracer concentration is one of the method that satisfies all the requirements and hence is one of the most applied method today.

In the present study, solvent extraction methods are proposed for the metals like Ni(II), Fe(II), Co(II), Cu(II), Mn(II). These metals have proved to be of immense importance in various chemicals, biochemical, pharmaceuticals and industrial applications. It provides good separation and determination methods. Optimum extraction conditions are evaluated to study several experimental parameters like effect of reagent concentration, different diluents, effect of temperature etc. Diverse ion studies are carried out to study the selectivity for the method. This method is used for the analysis of real sample like various alloys, pharmaceutical samples. In this way, it is a very useful method and therefore, it is studied in the present work.
2.8 REFERENCES


