CHAPTER – 1

INTRODUCTION

Recent advances in analytical chemistry are characterized by great progress toward more powerful methods of separation, equaling in significance the great forward stride made in instrumental methods of determination. Problems of chemical analysis almost always involve two steps: separation of the desired constituent and measurement of the amount or concentration of this constituent. Much worthy research has been dedicated to the development of more discriminatory methods of estimation, such as spectrographic, spectrophotometric, and polarographic methods, which minimize the need for separating steps preceding the measurement step. However, with the rapid growth of chemical technology, the analytical chemist called upon to deal with mixtures of increasing complexity. In recent years, many elements previously considered laboratory curiosities have assumed industrial significance. The use of titanium, tantalum, niobium and zirconium, for example, either as pure metals or as important high temperature alloy constituents; germanium in the rapidly expanding transistor field; uranium, thorium, lanthanides, and actinides in the nuclear energy programme has forced the analytical chemist to take cognizance of these and other elements in this analytical schemes. Despite the availability of modern, more discriminating methods of measurement, successful solutions to many analytical problems depend heavily on separation processes [1].

The separation science plays a significant role in analytical chemistry. In the past many methods have been developed using large number of sophisticated instruments. It facilitated quantitative analysis of metals from milligram ($10^{-3}$) to ato gram($10^{-18}$). The methods are rapid and sensitive. They includes absorption spectroscopy, fluorescence technique, plasma spectrometry including atomic absorption method and numerous electroanalytical and radiochemical methods. However, in spite of these methods being so sensitive and selective, for the purpose of quantitative analysis the demand grew for
analysis of extra pure materials specially those free from interfering components. Some methods could not furnish reliable results if in case of nanogram \(10^{-9}\) impurities were present. This led to search for reliable methods for the purpose of isolation and purification of compounds before one could undertake the task of instrumental quantitative analysis. Many separation methods are described in authoritative monographs. Each of them is important in a true sense. The account of various separation methods like chromatography, reversed osmosis, electrophoresis, dialysis are available in the monographs. They indicate how an excellent instrumental method of analysis can be used if supplemented by an efficient separation technique. All colorimetric methods need preliminary separation of impurities. In the presence of such impurities it would influence the process of analysis. Some books present information on the specialized methods for the isolation and determination of rare metals or the radioactive isotopes. Only few methods were an exception to this rule of pre-separation as are atomic absorption spectroscopies or inductively coupled plasma atomic emission spectroscopy which generally do not need preliminary treatment of sample solution for separation. Amongst separation methods so far utilized, solvent extraction occupies the most favoured position.

Solvent extraction enjoys a favored position because of its ease, simplicity, speed, and wide scope [2-4], utilising apparatus no more complicated than a separatory funnel, requiring several minutes at the most to perform, applicable both to trace and macro levels of metals, extraction procedures offer much to the analytical chemist. A further advantage of the extraction method over the widely used precipitation method lies in the cleaner separations that can be achieved by the former. With the latter, contamination of the precipitate by coprecipitation phenomenon is a decided limitation which is minimized only with difficulty, whereas the analog of coprecipitation, i.e., coextraction, is almost unknown in solvent extraction.
1.1 Solvent extraction technique

The separation of constituents of a homogeneous liquid mixture is a problem frequently encountered in the chemicals processing industry. Liquid-liquid extraction has been emerging very important method for separating such liquid mixtures. The addition of a solvent in this process corresponds to the addition of heat in the case of separation by distillation. The solvent used in the extraction process should be immiscible or partially miscible to facilitate the separation of the liquid phases. The liquid-liquid extraction operation consists of the following steps:

(a) Intimate contacting of the solvent with the solution containing the component to be extracted (extractant or solute) so that the solute will be transferred from the solution to the solvent and
(b) Separation of the two immiscible phases.

The phase containing greater concentration of the solvent and smaller concentration of the original liquid is normally called an ‘extract’ and other phase containing greater concentration of the solvent is referred to as “raffinate”. The complete liquid-liquid extraction process may involve other operations such as distillation to recover the solvent from the extract and the distillation may be performed easily.

The case for the use of liquid-liquid extraction will depend upon its either accomplishing a separation that cannot be achieved by other operations such as distillation, evaporation and crystallization, or effecting the separation more economically. Liquid-liquid extraction is now being adopted as a more economic alternative to other separation processes and has found immense applications in the separation of:

1) Solutions of components having low relative volatility, especially when vacuum distillation is expensive.
2) Solutions of close boiling and azeotrope-forming components
3) Dissolved solute when evaporation may be impractical
4) Solutions of heat-sensitive components such as antibiotics
5) Components of differing chemical type whose boiling points may overlap as in the case of petroleum hydrocarbons.

1.2 Basic principles of solvent extraction [5]

As per the phase rule of Gibb’s et. al.

\[ P + V = C + 2 \]

where, \( P \) = number of phases, \( C \) = components, \( V \) = degree of freedom

In solvent extraction, we have \( P = 2 \), i.e. two phases namely aqueous and organic phase, the component is \( C = 1 \), viz., solute, thus we therefore have,

\[ 2 + 1 = 1 + 2 \]

According to the Nerst distribution law,

If \([X_1]\) is concentration of solute in phase 1 and if \([X_2]\) is concentration of solute in phase 2 at equilibrium,  \( K_D = \frac{[X_2]}{[X_1]} \)
where \( K_D \) is called as the partition coefficient. This partition or distribution coefficient is independent of the total solute concentration in either of the phases. In the above expression for \( K_D \), the activity coefficient of the species in the organic as well as in the aqueous phase not considered.

Therefore the term distribution ratio (\( D \)) could be used to account for the total concentration of species in two phases. In these circumstances we have distribution ratio (\( D \)) as,

\[ D = \frac{\text{Total concentration of species in the organic phase}}{\text{Total concentration of species in the aqueous phase}} \]

Now, assuming, if there is no association, dissociation or polymerization in the phases then under the idealized condition \( K_D \) would be equal to \( D \). now in practical work, instead of using term \( K_D \) or \( D \) one prefers to use term percentage extraction (\( % \) E). This is related to distribution ratio (\( D \)) by an expression as,
\[
D = \frac{(V_w / V_o) \times \% E}{(100 - \% E)}
\]

where \(V_w\) = volume of the aqueous phase
\(V_o\) = volume of the organic phase

When volumes of organic and aqueous phases are equal i.e. \(V_o = V_w\)
\(D\) reduces to,
\[
D = \frac{\% E}{(100 - \% E)}
\]

Further the extraction could be considered to be quantitative when \(E = 100\), under these circumstances,
\[
D = \frac{100}{(100 - 100)} = \infty \text{ (infinity) (if } V_o = V_w)\]

### 1.3 Classification of extractions [5]

The present day classification is based upon more scientific base, and upon the process of extraction and can be classified as,

**a) Chelate extraction**

If the extraction proceeds by formation of chelate or close ring structure, then it is called as chelate extraction.

e.g. a) The extraction of uranium with 8-hydroxyquinoline in chloroform.

b) Extraction of iron with cupferron with carbon tetrachloride as the solvent.

**b) Extraction by solvation**

This class of extraction can be termed as the extraction by solvation because the extracted species gets solvated into the organic phase.

e.g. a) Extraction of iron from hydrochloric acid with diethylether
b) Extraction of uranium from nitric acid media with tributyl phosphate.

c) **Extraction due to the ion-pair formation**

This category of extractions involves the process of ion-pair formation. The extraction proceeds with the formation of neutral uncharged species which in turn get extracted into the organic phase.

e.g. a) Extraction of scandium with trioctylamine

b) Extraction of uranium with trioctylamine.

In both the cases an ion-pair is formed between Sc and U in mineral acid along with high molecular weight amine.

d) **Synergic extraction**

The last category of extraction can be termed as the synergic extraction. As the name implies, there is an enhancement in extraction on account of use of two extractants.

e.g. Extraction of uranium with tributylphosphate(TBP) as well as 2-thienoyltrifluoroacetone (TTA).

Although either TBP or TTA are individually capable of extracting uranium, if one uses mixture of these two extractants, one finds enhanced extraction.

1.4 **Factors affecting extraction**

a) **Salting out agents**

The extraction of metals may be enhanced by adding high concentrations of inorganic salts to the aqueous phase. This process is known as salting out effect and this is due to the pronounced effect of the added salt on the activity of the disturbing species by the common ion effect and also due to strong ability of these ions to bind water around them (depleting the aqueous phase of water molecules for use as a solvent)
b) pH value

The process of liquid-liquid extraction is largely influenced by pH. Two metals may be extracted at different pH values by keeping same extraction conditions. In some cases, effective stripping of the loaded organic phase may be achieved by simply bringing in contact with another aqueous phase at a different pH values.

C) Oxidation state

The selectivity of extraction may sometimes be increased by modifying the oxidation state or metal or the impurity. For example, extraction of Fe from chloride solutions can be prevented by reducing Fe(III) to Fe(II), which does not extract. Variation of the valence states of some element in the organic extract is also useful as a method of stripping.

d) Masking agents

These agents, which are metal complexing agents, prevent particular metals from taking part in their usual reactions and in this way they remove their interference without requiring an actual separation. These agents, also known as sequestering agents, are used to prevent certain metals from forming extractable complexes in solvent extraction and thus greatly increase the selectivity of the extraction methods. For example, aluminium can be extracted in presence of iron with 8-quinolinol by masking iron with an alkali cyanide to form stable ferrocyanide ion. Cyanide, tartrate, citrate, fluoride and EDTA are commonly used as masking agents.

e) Modifiers

Modifiers are the additives to the organic phase to increase the solubility of the extractant in diluent. High molecular weight alcohols (e.g. capryl alcohol) are commonly used as modifiers.
f) Synergistic agents

Synergistic agents are added to the organic phase to increase the solubility of the extraction. They form complexes which are taken by the extractant, even if the extractant does not form suitable complexes directly with the desired metallic species. Neutral organophosphorus compounds exert synergistic effects.

1.5 Basic criteria’s for selection of extractants

1) Easily available at reasonable cost.
2) Having low aqueous solubility and high solubility in organic solvents.
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 and good regeneration of extractant after recycling.
5) Reasonable selectivity for the extraction of the desired metal.

1.6 Organic solvents and organic solutions [6]

The essential character of an organic solvent that can be used for ordinary solvent extraction is low mutual solubility and low reactivity with water. It is also usually desirable that the melting point should be too high, the boiling point not too low, the vapor pressure not too high, the viscosity rather low, slight emulsion formation, the density sufficiently different from the aqueous solution to allow an easy phase separation, high chemical stability, and the substance be nonpoisonous.

Both single solvent and mixed solvents have been used as the organic phase, and the terms diluent and extractant are used to denote the role of the component in the mixed solvents, when necessary.
1.6.1. General properties of organic solvents

Water is an ordinary liquid, due to its polarity and dielectric constant, it has high tendency for solvation, somewhat regular arrangement of molecules by the hydrogen bonds.

Amongst the different properties, following are very often referred to in order to describe a solvent.

a) Solubility

The distribution of a liquid material into another liquid is somewhat different from the dissolution of a solid into a liquid. When a solid is dissolved, only the molecules (or ions) in the solid will be dissolved into the liquid. However, when the solute is a liquid, the solute also act as solvent for the solvent. Thus, in order to describe the equilibrium in a binary liquid system, their mutual solubility, should be considered [6].

b) Vapour pressure and boiling point

With regard to solvent extraction at room temperature, the boiling point of diethylether (bp = 34°C) may be one example of lower limit. A solvent of high vapour pressure at room temperature is not practical because of fire hazard and possible leak of the liquids from the vessel causing poisoning or trouble due to a loss of materials and a volume change during the operation.

c) Melting point

When the melting point of a solvent is too high, special apparatus for heating is necessary. However, there may be some merit in the use of high melting point substances, such as naphthalene (mp 80.05 °C) or biphenyl (mp 70.5°C) in some cases [7]. In such systems, the solvent extraction is carried out at temperature above the melting point of the organic compound, and the phase separation is made after the two liquid phases have cooled down and the organic phase has solidified.
d) Density

The density of almost all the solvents used for the solvent extraction in the ordinary laboratory lies between 0.63 g/cm$^3$ ($n$-heptane, $20^\circ$C) and 1.59 g/cm$^3$ (carbon tetra chloride, $20^\circ$C). Some heavier organic solvents are known (for example, o-dibromobenzene, $d_4^{20} 1.96$ and di-iodomethane $d_4^{20} 3.3345$) but they are seldom used. When the difference in the densities of the two phases is very small, the two-phase agitation is incomplete [8].

e) Viscosity and surface tension

Use of too viscous solvent is not favorable due to difficulty in the phase agitation and the phase separation. When the viscosity is too high or too low, the transference of the liquid from one vessel to another becomes difficult. Cyclohexanol (49.8 cp, $25^\circ$C) is an example of a very high viscosity solvent, and diethyl ether (0.233 cp, $20^\circ$C) of a low viscosity solvent [8].

f) Optical properties

When the refractive indices of the two phases are similar, the interface between them is not clear. Most of the solvents used for solvent extraction have no notable absorption in the visible region but they do absorb in the ultraviolet (UV) region. When the UV absorption of the solute in an organic phase is measured, the solvent should not have overlapping absorption with the solute. Hexane is one of the most transparent solvents but some other solvents, for example, ketones, are unfavourable for spectrometry in the UV region.

1.7 Techniques for solvent extraction [9]

Solvent extraction may be made use analytically for concentrating or rejecting a particular substance, or for the separation of mixtures. The extraction may be accomplished by the following processes,
1) Batch extraction

This is the simplest and most widely used method. This method is used where a large distribution ratio for the desired separation is readily available. In this method, the solute is extracted from one layer by distributing it with a second immiscible layer until partition equilibrium has been attained. The two layers may be shaken in a separatory funnel. The layers are then allowed to settle out and the layer containing the desired constituent is removed.

2) Continuous extraction

This method of extraction is applicable when the distribution ratio is low. This method makes use of continuous flow of immiscible solvent through the solution to be extracted. Although partition equilibrium may not be achieved during the time of contact, solute is being removed continuously with the spent extracting solvent. If the extracting solvent is volatile, it is recycled by distillation and condensation and is dispersed in the aqueous phase with the help of a sintered glass disc or any other suitable device.

3) Continuous countercurrent extraction

The method of extraction involves a process whereby the two liquid phases are caused to flow counter to each another. It is used for separating materials for isolation or purification purposes. The continuous counter current extraction method is especially applicable for the extraction of organic compounds and less to inorganic compounds.

In general choice of the method depend upon the value of the distribution ratio of the solute and separation factor of interfering ions. Generally counter current extraction methods are used for fractionation purposes.

1.8 Applications

The industrial applications of liquid-liquid extraction are too extensive to be discussed here in detail. An attempt is, however, made to indicate some of
the important processes. The chemical industries in which liquid-liquid extraction processes are adopted may be broadly classified under organic and inorganic chemical industries.

A) Organic chemical industries

The liquid - liquid extraction technique has been used for separating and purifying organic compounds of commercial importance on a large scale. However, it was used in the petroleum industry as one of the first large scale applications of liquid-liquid extraction especially in the was made viz., the separation of aromatic compounds from aliphatic compounds. Important applications in various organic chemical industries are summarized in following table 1.1

Table: 1.1 Important applications of liquid-liquid extraction in organic chemical industries

<table>
<thead>
<tr>
<th>Feed</th>
<th>Solvents</th>
<th>Extractant</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>Petroleum fractions in the boiling range from kerosene to lubricating oil.</td>
<td>Liquid sulphur dioxide</td>
<td>Aromatic and sulphur containing compounds</td>
<td>Edeleanu Process</td>
</tr>
<tr>
<td>Petroleum stocks of wide boiling range</td>
<td>A mixture of diethylene glycol and glycol</td>
<td>High purity aromatics</td>
<td>Udex process</td>
</tr>
<tr>
<td>Diesel oil, heating oil and lubricating oil fractions</td>
<td>Furfural</td>
<td>Sulphur containing and cyclic compounds</td>
<td>Treatment improves octane number and burning qualities</td>
</tr>
<tr>
<td>Wax containing heavy crude residues</td>
<td>Propane</td>
<td>Wax and aliphatic materials</td>
<td>Asphaltic and resinous materials are insoluble in propane</td>
</tr>
<tr>
<td>Crude distillate</td>
<td>Propane and cresylic acid phenol mixture</td>
<td>Paraffin and naphthenes wax</td>
<td>Duo-sol process</td>
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### Coal tar industry

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<tr>
<td>Coke oven oil</td>
<td>Diethylene glycol –</td>
<td>Aromatics</td>
<td>Udex process</td>
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<td></td>
<td>water</td>
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<tr>
<td>Crude tar distillate</td>
<td>Aqueous methanol and</td>
<td>Tar acids</td>
<td>Fractional</td>
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<td></td>
<td>hexane</td>
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<td>extraction</td>
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<tr>
<td>Commercial tar acid</td>
<td>Aqueous sodium</td>
<td>2,4 and 2,5</td>
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<td>fraction</td>
<td>hydroxide fraction</td>
<td>xylenol</td>
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<td>and toluene</td>
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### Oils and fats

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<tbody>
<tr>
<td>Vegetable oil and animal</td>
<td>Propane</td>
<td>Unsaturated</td>
<td>Solexol</td>
</tr>
<tr>
<td>fats</td>
<td></td>
<td>glycerides</td>
<td>process</td>
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<tr>
<td>Vegetable oils</td>
<td>Furfural</td>
<td>Unsaturated</td>
<td>For production</td>
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<td></td>
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<td>glycerides</td>
<td>of drying oil</td>
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### Pharmaceuticals

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<tr>
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<th>Butyl and amyl</th>
<th>Penicillin</th>
<th>Multiple rapid</th>
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<tr>
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<td>acetate</td>
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<td>extraction</td>
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<tr>
<td>Soyabean meal fermented</td>
<td>Butanol</td>
<td>Bacitracin</td>
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<td>beer</td>
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### Miscellaneous

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<th>Phenex</th>
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<tr>
<td>Pulp mill black liquor</td>
<td>ketone</td>
<td>and formic</td>
<td>process</td>
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<tr>
<td>Catalytic cracking</td>
<td>Light catalytic</td>
<td>acid</td>
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<td>petroleum plant effluent</td>
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<tr>
<td>water industry</td>
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<td>Phenol</td>
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### B) Inorganic Industries

Solvent extraction has been widely used in metallurgy now a days. The method is based on the preferential solubility principles. We know that ionic compounds are usually insoluble in organic solvents but soluble in inorganic solvents such as water. Similarly covalent compounds are insoluble in water. An immiscible organic solvent can therefore separate an uncharged species from an aqueous solution.
Analytical liquid-liquid extraction procedures have been developed for separating practically all the metals that have been recovered by hydrometallurgical processing. In metallurgy, liquid-liquid extraction can be applied for the following operations.

(a) Extraction of metal from leach liquors obtained from low grade or complex ores.
(b) Separation of metals that are either chemically similar or occur in combined state in ore deposits and are difficult to be separated by pyro and hydro-metallurgical techniques.
(c) Purification in order to obtain a very pure starting material for further metallurgical processing.
References


