1.1 Introduction and historical aspects of solvent Extraction

Solvent or liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an organic solvent such as benzene, carbon tetrachloride or chloroform. In certain cases the solute can be more or less completely transferred into the organic phase. The technique can be used for purposes of preparation, purification, enrichment, separation and analysis, on all scales of working, from microanalysis to production processes.

In analytical chemistry, solvent extraction has come to the forefront in recent years as a popular separation technique because of its elegance, simplicity, speed and applicability to both tracer and macro amounts of metal ions. The aspects and basic principals of solvent extraction are very well explained [1, 2].

The solvent extraction method has made great strides in last four decades. A number of monographs have been published [2-6] dealing with various aspects of solvent extraction. Some of them put emphasis on the theory of chelaets extraction [3-6] while others have dwelt on rigorous treatment of extraction equilibria [5-7] or on the mechanism of extraction. Few of them have ramification with aspects of solvent extraction [2, 3]. The chemical engineering aspects pertaining to design and development have been covered by worthwhile monographs [8-10]. The handbook [11] of solvent extraction is an excellent source of information on all aspects of the extraction. The modern chemistry of supramolecules in solvent extraction is very well covered in recent research monographs [12] by the author. An account of various separation methods [13-17] like chromatography, reversed osmosis, electrophoresis, and dialysis are available in the monographs [18-25]. They indicate how an excellent instrumental method of analysis can be used if supplemented by an efficient separation technique.

1.2 Theory of spectrophotometry and colorimetry:

Theory of spectrophotometry which is helpful in the quantitative analysis of sample is very well explained [26]. When light (monochromatic or heterogeneous) is incident upon a homogeneous medium, a part of the incident light is reflected, a part is absorbed within the medium, and the remainder is transmitted. If the intensity of the incident light is expressed by I_o, that of the absorbed light by I_a, that of the transmitted light by I_t, and that of the reflected light by I_r, then:

$$I_o = I_a + I_t + I_r \qquad (1)$$

For air-glass interfaces consequent upon the use of glass cells, it may be stated that about 4 per cent of the incident light is reflected. I_r is usually eliminated by the use of a control, such as a comparison cell, hence:

$$I_o = I_a + I_t \qquad (2)$$

Lambert (1760) investigated the relation between I_o and I_t. Beer (1852) extended the experiments to solutions. Spectrophotometry and colorimetry are based upon Lambert's and Beer's laws.

1.3 Lambert's laws:

This law states that when monochromatic light passes through a transparent medium, the rate of decrease of intensity with the thickness of the medium is directly proportional to the intensity of the light. Mathematically the Lambert's law may be stated as follows:

$$kI = -\frac{dI}{dt} \qquad (3)$$

Where I is the intensity of the incident light of wavelength λ, t is the thickness of the medium, and k is the proportionality factor. Integrating (3) and putting $I = I_o$ when t = o, we obtain,

$$\ln \frac{I_0}{I_t} = kt \qquad (4)$$

Or stated in other terms,

$$I_t = I_o . e^{-kt}$$

Where I_o is the intensity of the incident light falling upon an absorbing medium of thickness t, I_t is the intensity of the transmitted light, and k is a constant called the absorption coefficient for the wavelength and the absorbing medium used. On changing the equation (4) from natural to common logarithms, we get

$$I_t = I_o . 10^{-0.4343\,kt} = I_o 10^{-Kt} \qquad (5)$$

Where K = k / 2.3026 and is usually termed the absorption coefficient.

1.4 Beer's law:

The light absorption and the light transmission for monochromatic light as a function of the thickness of the absorbing layer only. In quantitative analysis, however, it is concerned with solutions. Beer (1852) studied the effect of concentration of the coloured constituent in solution upon the light transmission or absorption. He found the same relation between transmission and concentration as Lambert had discovered between transmission and thickness of the layer {equation (4)}, i.e. the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written in the form:

$$I_t = I_o . e^{-K'c}$$

$$= I_o . 10^{-0.4343k'c} = I_o . 10^{-K'c} \qquad (6)$$

where c is the concentration of the absorbing substance, and k' and K' are constants. Combining (5) and (6), we get

$$I_t = I_o . 10^{-\epsilon ct} \qquad (7)$$

or

$$\log I_o / I_t = \epsilon ct$$

This is the fundamental equation of colorimetry and spectrophotometry, and is often spoken of as the Beer-Lambert Law. The value of ϵ will clearly depend upon the method of expression of the concentration. If c is expressed in gram

moles per litre and t in centimeters then ϵ is the molar extinction coefficient (also termed molar absorbtivity or molar absorbency index). The latter is equal to the reciprocal value of the thickness in centimeters of a 1 molar solution (c = 1) at which:

$I_t = 0.1\ I_o$, since $I_t = I_o \cdot 10^{-\epsilon}$ when t = 1 and c = 1.

1.5 Deviation from Beer's law:

From Beer's law it follows that if we plot absorbance A against concentration, a straight line passing through the origin should be obtained. But there is usually a deviation from a linear relationship between concentration and absorbance and an apparent failure of Beer's law may ensure. Deviations from the law are reported as positive or negative according to whether the resultant curve is concave upwards or concave downwards.

Deviations from law can arise due to following factors:

1. Beer's law will hold over a wide range of concentration provided the structure of the coloured ion or of the coloured non-electrolyte in the dissolved state does not change with concentration. If a coloured solution is having a foreign substance whose ions do not react chemically with the coloured components, its small concentration does not affect the light absorption whereas its large concentration may affect light absorption and may also alter the value of the extinction coefficient.
2. Deviation may also occur if the coloure4d solute ionizes, dissociates or associates in solution.
3. Deviation may also occur due to the presence of impurities that fluoresce or absorb at the absorption wavelength. This interference introduces an error in the measurement of absorbance of radiation penetrating the sample.
4. Deviations may occur if monochromatic light is not used.
5. Deviations may occur if the width of slit is not proper and, therefore, it allows undesirable radiations to fall on the detector. These undesirable

radiations might be absorbed by impurities present in the sample which would cause an apparent change in the absorbance of the sample. The magnitude of this deviation becomes appreciable at higher concentrations.

6. Deviation may occur if the solution species undergoes polymerization.
7. Beer's law can not be applied to suspensions but the latter can be estimated colorimetrically after preparing a reference curve of known concentration.

1.6 Basic Principals of Solvent Extraction

The solvent extraction methods are based on the four basic principals

(a) Gibb's phase rule

(b) Distribution ratio or extraction coefficient

(c) Partition coefficient, P

(d) Percentage extraction

(a) Gibb's phase rule

For all phase distribution the classical Gibb's phase rule is

$$P+V = C+2$$

Where, P = number of phases

C = number of components

V = degrees of freedom

In solvent extraction we have two phase aqueous and organic phases.

Component is (c = 1) solute in solvent and water phases.

At constant pressure and temperature the value of v = 1

i.e. $P+V = C+2$

$2+1 = 1+2$

(b) Distribution ratio (D) or Extraction coefficient

Distribution ratio can be defined as it is the ratio of concentration of metal in the organic phase to the concentration of metal in the aqueous phase.

For a given metal, M, present as various species M1, M2, -----Mi, and partitioned between an organic and aqueous phase, the extraction can be defined in the following terms.

Distribution ratio or extraction coefficient, D

$$D = \frac{\text{Total concentration of metal in the organic phase}}{\text{Total concentration of metal in the aqueous phase}}$$

$$D = \frac{[\mathrm{M}]_{org.}}{[\mathrm{M}]_{aqu.}}$$

(c) Partition coefficient, P

The partition coefficient is a true constant and is independent of the total amount of partitioned solute in the two phases. The Nernst partition isotherm is valid for a single species over the range for which the activity coefficients in the two phases are equal. In other words under identical conditions where the solute exists in the same form in both phases, the phase are completely immiscible, there are no interactions between solute and solvent, and association or dissociation reactions do not occur, the terms 'extraction coefficient' and 'partition coefficient' becomes equal.

(d) Percentage extraction

The percentage extraction is related to distribution ratio (D) by an expression

$$D = \frac{\left(V_W / V_O \right) \% E}{100 - \% E}$$

Where, V_w = Volume of aqueous phase
V_o = Volume of organic phase
% E = Percentage extraction

When volume of organic and aqueous phases is equal then the relation between percentage extraction and distribution ratio becomes as

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

If the extraction is 100 % then the distribution ratio becomes infinity.

1.7 Classification of solvent extraction systems

Extraction can be classified on the basis of

I] Nature of extracted species

II] Process of extraction

I] On the basis of nature of extracted species there are two types

1. Chelate extraction
2. Ion association

II] Classification based on the basis of process of extraction

(a) Extraction by chelation or Chelate formation

(b) Extraction by Ion pair formation

(c) Extraction by salvation

(d) Synergistic extraction

Now a day's extraction based on the process of extraction is widely used and is explained as follows:

(a) Extraction by chelation or chelate formation

Chelating ligand may play an important role in extraction of metal. The substance which brings about chelation is called as chelating agent.

Metal ion + chelating agent $\longrightarrow$ Metal chelate

The chelates are classified according to the type of basic group present. If both the basic groups are uncharged it results into a positively charged metal chelate. However, if the reagent has one anionic group, a neutral chelate is formed while multiple negative charge on chelating agent results in negative charged chelates. Neutral chelates are easily extracted in organic solvent.

(b) Extraction by Ion pair formation

The extraction will proceed with formation of a neutral uncharged

Species which interns is extracted into organic phase. Most of the high molecular weight amines or so called liquid ion exchanger comes under this group. The mechanism of extraction by ion pair formation can be described as follows

$$R_3N_{org} + H^+_{aq.} + A^-_{aq.} \rightleftharpoons R_3NH^+A^-_{org} \text{ (Extraction)}$$

$$R_3NH^+A^-_{org} + B^-_{aq.} \rightleftharpoons R_3NH^+B^-_{org} + A^-_{aq.}$$

Best separations are possible with good diluents. The control of temperature and activity is most important in accomplishing quantitative separations. In ion pair extraction the metal may be incorporated with by co-ordination in either the cation or anion of the extractable ion pair.

(c) Extraction by solvation

Solute molecules are associated with the solvent molecules this is known as salvation. In extraction by salvation solvent molecules are directly involved in formation of the ion association complex. The value of ion pair formation constant, K is related to dielectric constant, and temperature.

$$D = \frac{4\pi \, Ne^2 Q(b)}{1000 \, \varepsilon K_T}$$

$$b = \frac{e^2}{a \, \varepsilon K_T}$$

Where, N = Avogadro's number

K_T = Boltzmann's constant

Q(b) = Calculable function

a = emperical parameter

ε = dielectric constant

In case of solvent extraction, the solvent itself participates in extraction of complex.

E.g. Extraction of Fe^{3+} from 5.5 M HCl by diethyl ester

$$FeCl_3 + HCl \longrightarrow H^+ + FeCl_4^- \longrightarrow H_3O^+ - FeCl_4^-$$

In case of extraction by salvation the extracted species is solvated with a definite number of solvent molecules and provided that the solvent must be inert.

(d) Synergistic extraction

This extraction involves two extractants i.e. chelating ligand and solvating solvent.

Conditions for Extractions

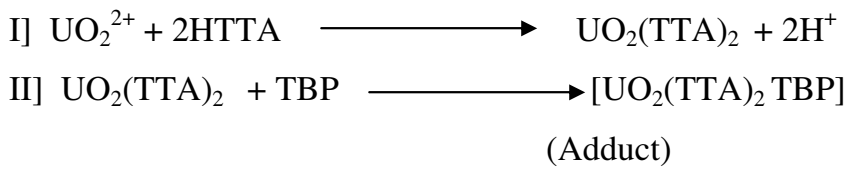
(c) The chelating ligand HX should neutralize the metal charge by chelation.

(d) The solvent should co-ordinates less strongly than chelating ligand.

(e) The solvent should displace any residual co-ordinated water from the neutral metal complex, rendering it less hydrophilic.

(f) The maximum co-ordination number of the metal and geometry of the ligand should be favourable.

E.g. extraction of uranyl ion by tributyl phosphate(TBP) and thinyl trifluoroacetate (HTTA).



$$\text{I]}\ UO_2^{2+} + 2HTTA \longrightarrow UO_2(TTA)_2 + 2H^+$$

$$\text{II]}\ UO_2(TTA)_2 + TBP \longrightarrow [UO_2(TTA)_2\,TBP]$$

(Adduct)

Due to adduct formation the extraction efficiency of uranyl ion by HTTA in presence of TBP increases this is called as synergism.

1.8 Experimental setup and instruments

Separating funnels for batch extraction, special glass apparatus for continuous extraction, automatic shakers used for discontinuous countercurrent distribution. The instruments required for the whole solvent extraction and determination process are very simple like, separating funnels, digital flame photometer, pH meter, spectrophotometer etc. which are shown in figure 1.8.

Figure1.8 Experimental Setup and Instruments

Digital pH meter

Separating Funnel

Digital Flame photometer

Spectrophotometer

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