INTRODUCTION

General discussion : Solvent or liquid-liquid extraction is a technique in which a solution (usually aqueous) is brought into contact with a second solvent (usually organic), essentially immiscible with the first, inorder to bring about a transfer of one or more solutes into the second solvent. To understand the fundamental principles of extraction, the various terms used for expressing the effectiveness of a separation must first be considered.

Partition coefficient :

For an inorganic chemist, the aqueous-organic solvent pair is of special interest since he is concerned with the analysis of the element present in the aqueous phase. If a substance is allowed to dissolve within two immiscible or slightly miscible solvents, the species is shared between the two layers in such a way that the ratio of the concentration of the solute in the two phases at equilibrium at a particular temperature remains constant, provided that the species will have the same molecular weight in both the phases. This ratio is usually called as the distribution or partition coefficient (K_D). Thus for aqueous and organic systems,

$$K_D = \frac{[M]\text{ organic phase}}{[M]\text{ aqueous phase}} \quad \ldots \quad \ldots \quad (1)$$

where $[M]$ = matal ion concentration.

The law, as stated, is not thermodynamically rigorous (e.g., it takes no account of the activities of the various species, and for this reason would be expected to apply in very dilute solutions, where the ratio of the activities approaches unity), but is a useful approximation.

If the case is ideal, the species shares itself between the two phases in the ratio of its solubilities. Of course, it also depends upon other factors like acid concentration and extraction of molecular species.

Distribution ratio or Extraction Coefficient, D

For a given metal, M, present as various species M_1, M_2, ..., M_i, and partitioned between an organic and aqueous phase, we are more concerned with the overall or stoicheiometric distribution of the component of interest between the two phases and a more practical quantity to describe the extration is D, distribution ratio :

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

$$= [M]_{org} / [M]_{aq}$$

$$= \frac{[M_1]_{org} + [M_2]_{org} + \ldots\ldots + [M_i]_{org}}{[M_1]_{aq} + [M_2]_{aq} + \ldots\ldots + [M_i]_{aq}}$$

If polynuclear species are formed, their concentrations are multiplied by the appropriate stoicheiometric coefficient. In the ideal condition i.e., where there is no reaction between the species and other components in each phase, D, the distribution ratio and K_D partition coefficient are equal.

Percentage extraction :

For chemists, percentage extraction (% E) is more important than the distribution ratio. These two factors are related as follows :

$$\% E = \frac{100\ D}{D + \left[Vaq\ /\ Vorg \right]} \quad \cdots\cdots \quad \cdots\cdots \quad (3)$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases respectively. This equation on simplification,

$$D = \frac{V_{aq}}{V_{org}} \left[\frac{E}{100 - E} \right] \quad \cdots\cdots \quad \cdots\cdots \quad (4)$$

where E is percentage extraction, and V_{aq} and V_{org} are the volumes of aqueous phase and organic phase. When the volume of the aqueous phase is equal to the volume of the organic phase

$$D = \frac{E}{100 - E} \quad \cdots\cdots \quad \cdots\cdots \quad (5)$$

For practical purpose, the distribution ratios (D) are calculated from the percentage extraction for systems of extraction applying equation (5). So long the volumes of two phases are equal, the distribution ratio varies from 99 up to infinity as the limit as the percentage extraction increases from 99 to 100.

Multiple extraction :

The chemist's main object in the process of extraction is to separated the metal component quantitatively by a single extraction from a mixture of solution. When hundred per cent extraction is not possible by one step single extraction, multiple extraction is applied.

Thus if a fraction L_A of a substance A left after extraction of volume V_{aq} of aqueous phase with n successive portions of organic solvent having each of volume V_o, then

$$L_A = \left[\frac{V_{aq}}{V_{aq} + V_o D} \right]^n \quad \cdots\cdots \quad \cdots\cdots \quad (6)$$

For rapid and complete extraction, the above equation shows that D, the distribution ratio must be of very high value. In the above system, the partition isotherm is assumed to be linear i.e., $[A_o] / [A_{aq}] = D$ which remains constant for any value of $[A]$. For good speparation V_o should be considered as low as possible and n should be of high value as possible.

Separation Factor :

When a solution contains two species A and B, another term separation factor (β) is introduced in the process of extraction system. The separation factor (β) is also related to their corresponding distribution ratios. Thus [redacted] $\cancel{A}$ $\not{o}$,

$$\beta = \frac{[A]_o / [B]_o}{[A]_{aq} / [B]_{aq}} = \frac{[A]_o / [A]_{aq}}{[\bar{B}]_o / [B]_{aq}} = \frac{D_A}{D_B} \quad .... (7)$$

where $[A]_o$, $[B]_o$ are the concentrations of A and B in the organic phase and $[A]_{aq}$, $[B]_{aq}$. are the concentrations of A and B in the aqueous phase.

Quantitative separation is possible only when the separation factor is large. That will be only possible when one distribution ratio is too small as compared to other. Again when separation factor will be unity, it is very difficult to separate as the two distribution ratios are equal. In these cases to carry out separation counter current extractions (fractional extraction) are generally used. That is, the distribution, transfer and recombination of various fractions are repeatedly done.

Distribution ratio and concentration :

Practical considerations : Several factors have to be taken into account in choosing an extraction system, and the factors may differ~~e~~ according to the scale and purpose of the work. A system that is excellent for microanalysis may be of no value in the macro systems.

In production work, health and fire hazards, cheapness of reagents and solvents, loss of solvent by volatilization and solubility, prevention of emulsification etc, are all factors and must be balanced to arrive at the most economic method.

For analytical or laboratory purposes, other considetions may apply, such as completeness of separation, loss of material in handling operations, speed of equilibration and complexity of the method.

In analytical work, it is most efficient to use a single extraction with accurately measured volumes of the two phases, provided there is no significant change in phase volumes on equilibration; standards are treated in the same way for calibration purposes. In that case E need not be 100% and if the metal can be determined by measurement of some property of the extract, complete separation of the phases is not necessary, making the operation much simpler.

The solvent used should not be too volatile, especially if equilibration takes some time and the room is worm (the difficulties of using diethyl ether are well known). It is best if it is as immiscible as possible with water. Organic solvents often have an appriciable temperature coefficient of expansion and this must be taken into account in accurate work.

Reagents must be carefully checked for impurities when trace analysis is undertaken, and sometime extreme care must be taken to ensure cleanliness of the air and the surroundings.

Classification of Extraction Systems :

Various classifications of extraction systems have been made but are admittedly arbitrary, since a particular system under certain conditions may be grouped under more than one class. The best compromise might be to classify the systems in terms of the types of chemical compound involved. Such a classification might be :

Uncharged covalent species

- Simple molecules, e.g., I_2, $HgCl_2$, C_6H_5-COOH, RuO_4
- Chelate complexes, e.g., aluminium oxinate.

Uncharged electrovalent species (ion-association complexes)

Halometallic acids, e.g., $HFeCl_4$

Amine-anionic complex compounds, e.g., $R_3NH^+. FeCl_4{}^-$

Metal-acid ester complexes, e.g., $La(DEHP)_3$

Solvated acids and salts, e.g., $HNO_3.TBP; UO_2(NO_3)_2(TBP)_2$

Non solvated salts, e.g., $(C_6H_5)_4 As^+.FeCl_4{}^-$.

(DEHP = di-2-ethylhexylphosphate; TBP = tributyl phosphate)

Such classifications are most convenient from the view point of theoretical discussion. For practical purposes, how - ever, it is much more useful to classify according to the type of reagent used, so that the possibilities for separation, etc., can be more easily seen. There are thus various ways of displaying the information, ranging from simple tabulation of extraction characteristics of elements arranged in alphabetical order of element or symbol (1,2), through diagrams based on the periodic table and indicating which elements are wholly, partially or not at all extracted (3), and sometimes including graphs of E against pH for each element (4) to diagrams showing distri - bution -pH courves either all on one plot (5) or arranged vertically one above another, one for each element, so that the possibilities of separation can be seen at a glance (6). For descriptions of individual systems, the last named method is undoubtedly the most useful.

Uncharged Covalent Species :

Simple molecules : There are a few covalent molecules such as iodine, mercury (II) halides and ruthenium tetroxide, which are extractable from aqueous solutions into solvents such as carbon tetrachloride or aliphatic and aromatic hydrocarbons.

The extractability of mercury (II) halides is in the order $HgI_2 > HgBr_2 > HgCl_2$. The halides of germanium, arsenic (III) and antimony (III) are also members of this class. The extracted species are $GeCl_4$ (7,8,9), $AsCl_3$ (7), $AsBr_3$ (10), $AsBr_5$ (11), AsI_3 and SbI_3 (12).

The so-called polymerization of osmium tetroxide in the organic phase has not been confirmed from recent studies (13,14). The extraction coefficient of OsO_4 decrease in both alkaline and acid solutions.

Chelate complexes : The matal ion forms chelates with appropriate reagents. If the charge on the ion is neutralized by the number of ligand anions needed to satisfy the co-ordination number of the ion, and there are no hydrophilic or ionogenic groups on the periphery of the resulting complex, the chelate will be much more soluble in non-polar organic solvents than in water. The presence of hydrophilic or ionogenic groups may cause the chelate to remain in the aqueous phase depending on the conditions used. If the charge neutralization and co-ordination number requirements are not simultaneously satisfied in the chelation reaction, and some residual co-ordination sites are occupied by water molecules, there may be sufficient interaction between the water ligands and the bulk solvent water to prevent extraction, e.g., Sr $(C_9H_6NO)_2 \cdot 2H_2O$. In that case the ligand water must be displaced by another ligand which has less interaction e.g., Sr $(C_9H_6NO)_2 \cdot 2C_9H_7$ NO or Sr $(C_9H_6 NO)_2 \cdot$ 2 Bu NH_2. On the other hand, chelating agends such as EDTA, which may satisfy co-ordination number but over compensate the charge on the metal ion, will produce charged chelates which are not extractable. Many solvent extraction systems belong to this class; thus β-diketones such as acetylacetone, thenoyltrifluoroacetone, dibenzoyl methane, etc., oximes and their derivatives, diethyldithiocarbamate, pyridylazonaphthol, etc., are important examples of chelating extractants.

These chelates generally do not require further solvation. However, in some cases, such as with theonoyltrifluoroacetone (HTTA), solvation can lead to much higher extraction coefficients (synergism). Typical examples are the Uranyl (VI) complex with excess of HTTA [UO_2 $(TTA)_2$ HTTA, K = 2.7 in benzene (15)], the hydrolytic species OH $(UO_2)_2$ $(TTA)_3$ formed at low concentrations in alcohol-water solutions (16), and the thorium species such as $Th(TTA)_4\ CH_3\ COOH$ and $Th(TTA)_4(CH_3 \cdot COOH)_2$ obtained in excess of acetic acid and extracted into carbon tetrachloride (17).

Uncharged electrovalent species :

Halometallic acids : These are complexes of metals with halide ions and protons and are extracted as acids, the protons being solvated mainly by oxygenated solvents. The extraction of iron(III) chloride by ether, indium bromide by ether or protactinium chloride by isobutyl methyl ketone (IBMK) are typical examples (18).

During the past few years much work has been done on the extraction of halometallic acids. Diamond and Tuck (13) have given an excellent treatment of these systems.

Recent paramagnetic resonance studies (19) prove that in the extraction of iron(III) by ethers, the organic species is solvated $HFeCl_4$, and reject the earlier notion that there is primary solvation of iron. The latter is tetrahedrally surrounded by chloride ions and apparently saturated. The hydration and solvation are hence limited to the proton and to secondary solvation. The primary species, on extraction by dibutyl ether, is apparently $H(OBu_2)_3^+ \cdot FeCl_4^-$ which may be further solvated by water and ether (20). In solvents of low dielectric constant the primary species tend to aggregate by dipole interactions of the ion-pairs and to associate with ion-paired hydrochloric acid, whereas in high dielectric constant solvents, dissociation of both hydrochloric acid and hydrogen tetrachloroferrate (III) occures and common ion effects are possible. In a halide-deficient medium, as in a solution of anhydrous iron (III) chloride in ether, the monosolvate $FeCl_3 . Et_2O$ is obtained.

Other interesting systems include : iron (III) bromide, indium chloride, thallium chloride, gold chloride and gold bromide (21, 22, 23). In all cases the extracted species is HMX_4, the proton being solvated and probably hydrated in the organic phase. This gives rise to ion-pairs which dissociate in solvents of high dielectric constant but aggregate in solvents of low dielectric constant.

Amine-anionic complex compounds : The strongly basic, high molecular-weight amines such as tri-iso-octylamine (TIOA) extract metals by forming ion-pairs with anionic metal complexes. A typical example is the extraction of uranyl sulfate by tri-iso-octylamine ($i\text{-}Oc_3N$) as $(i\text{-}Oc_3NH)_2 UO_2 (SO_4)_2$ from sulfuric acid. The name liquid anion exchanger is often used for this type of extraction system.

Metal-acid-ester complexes: This class of reaction is often called liquid cation-exchange. The liquid cation-exchangers are mainly acidic phosphorous esters dissolved in diluents. Examples are mono - and dibutyl phosphoric acids, di(2-ethylhexyl) phosphoric acid, dinonylnaphthalene sulfonic acid, etc. They usually facilitate extraction of metals by forming complexes with them, which may be further solvated by additional molecules of esters, e.g., $La(Bu_2PO_4.HBu_2PO_4)_3$. The acid dissociation of the esters is checked by the presence of strong acids, and they may then serve as solvating solvents like TBP. In most cases the acid phosphorous esters behave as chelating agents when a metal displaces the acid hydrogen and gives rise to a chelate ring with two oxygen atoms connected to phosphorous.

Solvated acids and salts : The earlier popular extractants, diethyl ether and IBMK, contain oxygen, which is basic and can directly solvate protons and metal atoms. Thus extraction of both acids and salts is feasible. The extraction of nitrates by ethers was very common a few years ago. McKay (24) has reviewed the work on the extraction of uranyl nitrate. The extraction of cerium (IV) by butyl acetate (25), diethyl ether (26), diisopropyl ether (27) and nitromethane (28) has been reported.

The extraction of neptunium (29), uranium, plutonium and various fission products (30)by IBMK from nitric acid and calcium nitrate solutions follows the same pattern. Although there is a lot of informations on extraction from nitrate solution, there is little on extraction from sulfate solution.

Some solvents extract the metallic ion by direct solvation of it. Secondary solvation frequently occurs. Important examples of such solvents are the organophosphorous esters such as tri-n-butyl phosphate (TBP), trialkyl phosphine oxides, etc., which are more strongly basic than ethers and ketones. The more basic extractants, the trialkyl phosphine oxides, resemble the strongly basic liquid anion-exchangers. The phosphorous esters such as phosphate, phosphonate and phosphinate esters have been extensively used as extractants in recent years. The review articles by Fletcher (31), Ishimoric (32), De (33) and Marcus (34) cover the literature on tributyl phosphate, while the article by White and Ross (35) surveys the literature on phosphine oxides.

Considerable information is available on the extraction of uranium by tributyl phosphate (TBP), particularly the system uranyl nitrate-nitric acid-TBP because of its importance in the nuclear-energy industry. Marcus (34,36) has reviewed the theoreticaltreatment and offered an~~d~~ excellent thermodynamic analysis.

From nitric acid medium, uranium is extracted as the considerably polar $UO_2(NO_3)_2 \cdot (TBP)_2$. With some diluents, mixed solvates are formed, e.g., $UO_2(NO_3)_2 \cdot TBP \cdot BuOH$ with butanol (37). On the other hand, the species extracted from moderately concentrated hydrochloric acid is $UO_2Cl_2 \cdot (TBP)_2$, both by pure TBP and TBP in carbon tetrachloride or benzene. Rhenium is extracted as $H(TBP)_4-ReO_4$ from nitric acid or as $H(TBP)_3 \cdot ReO_4$ at lower TBP concentrations (38,39). Depending on the conditions, ruthenium is extracted as $RuNO(NO_3)_3 \cdot (TBP)_2$(40) or $[H(TBP)_n]_2 \cdot RuNO(NO_3)_5$(41). Compounds with a more basic phosphoryl group, P=O, than that in TBP, are better extractants than TBP. Thus the extractability increases in the order : phosphine oxide $>$ phosphinate $>$ phosphonate $>$ phosphate. The most widely used phosphine oxide is tri-n-octyl phosphine oxide (TOPO). This has been used for the extraction and determinatiom of titanium, throrium, uranium iron and molybdenum. Broadly speaking, TOPO yields more definite solvates than TBP and binds acid more strongly than TBP; so it is intermidiate in properties between the oxygenated, alightly basic solvents and the strongly basic amines.

Non-solvated salts : These include ion-pairs formed by large unsolvated cations and unsolvated anions which behave in inert solvents as covalent molecules. Examples are found in the extraction of caesium with tetraphenyl borate into nitrobenzene (42), alkali ~~f~~metal ions by poly iodides (43) fluoride by tetraphenylstibonium ions into carbon tetrachloride (44), chlora~~a~~urate with tetraphenylphosphonium ions (45), and perrhenate with tetraphenylarsonium ions (46).

~~raphenylarsonium ions (46)~~.

Extraction process :

The extraction process consists of three stages :

(1) Uncharged complex formation.

(2) Sha~~i~~ring of such complex between the two liquid phases.

(3) Interaction of the complex in the organic phase.

(1) Uncharged complex formation depends upon several factors.

The complex may be of different types, as (i) simple co-ordinattion complex, chelate complex or (ii) an ion association complex

(i) $M^{+n} + nR^{-} \rightleftharpoons MR_n$ (co-ordination) ...... (8)

where M^{+n} = n-valent cation and R^{-} = anion of the suitable chelating or co-ordinating agent.

Examples : Germanium tetrachloride (simple co-ordination complex), nickel dimethylglyoximate (chelate)

(ii) An ion association complex is formed by co-ordination of the metal with the cation or anion of the extractrable ion pair.

$$M^{n+} + \underset{\text{ligand}}{bB} \rightleftharpoons MB_b^{n+} \text{ (Ion association)}$$

$$MB_b^{n+} + \underset{\text{ion}}{nX^-} \rightleftharpoons (MB_b^{n+}, nX^-) \quad \text{..........(9)}$$

Example : $\left[(C_6H_5)_4As^+, Cl^-\right]$

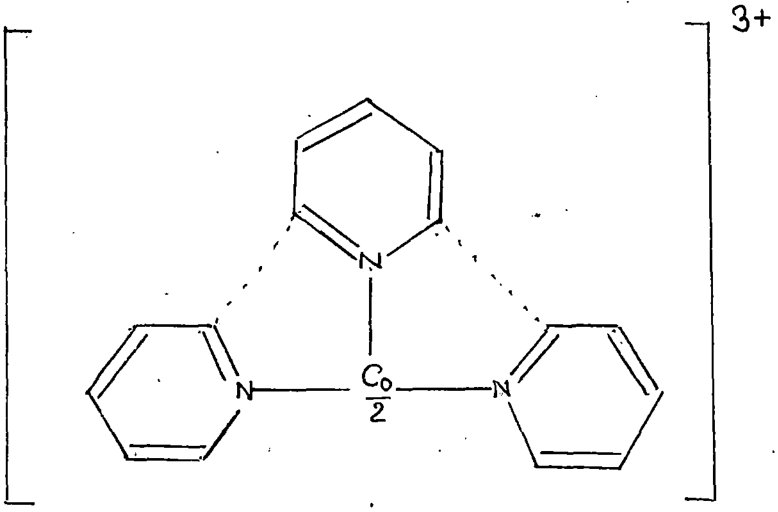
$$M^{n+} + (n + a)\ X^- \rightleftharpoons MX_{n+a}^{a-}$$

$$MX_{n+a}^{a-} + aY^+ \rightleftharpoons (aY^+, MX_{n+a}^{a-}) \text{ (ion association)} \quad \text{..........(10)}$$

Example : $\left[H^+, FeCl_4^-\right]$

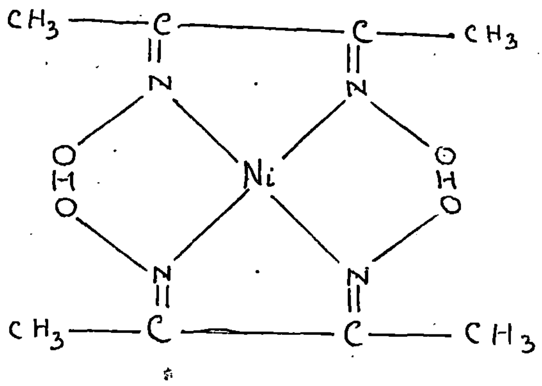
The stability of the co-ordination complex depends on two factors (a) the acidity of the metal, (b) the basicity of the ligand taking part in the complex formation. In the simple co-ordination complex the mono functional ligand takes part and in the chelate complex polyfunctional ligands are acting which occupy more than one position in the co-ordination sphere. The chelate complexes are mostly soluble in organic solvents and hence used in the process of extraction. These chelates are of either five or six - membered rings. They may be classified as follows.

(i) Positively charged chelates having requisite number of uncharged basic groups of the ligand e.g. chelates of cobalt with terpyridyl.



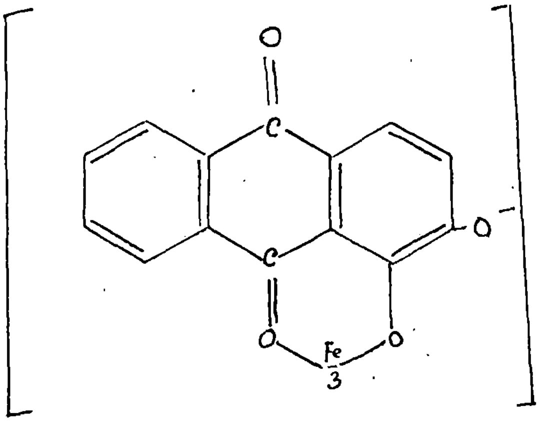
Bis (terpyridyl) - Cobalt (III)

(ii) Chelates having one anionic and one uncharged basic group of the ligand i.e., neutral chelates, e.g., chelate of nickel with dimethylglyoxime.



Nickel dimethyl glyoxime

(iii) Negatively charged chelates having negatively charged basic groups of the ligand e.g.,



Alizarine devivative of iron (III)

Ion association complexes e.g., $\left[(C_6H_5)_4As^+, ReO_4^-\right]_2$ are easily extractable in organic solvents like chloroform, benzene etc. The extent of ion association depends on ionic size of the salt involved and also on other structural factors.

(2) In the second stage of extraction either the chelate complex or ion association complex is distributed uniformly in the solvent. The distribution depends on the solubility of the complex.

(3) The third stage is the interaction of the complex in the organic phase. The chelates are not generally interacting. In case of ion association complexes polymerisation becomes an important factor as the concentration increases and higher distribution ratio is feasible. Another factor i.e., dissociation of ion association complex should be considered in case of only dilute solution.

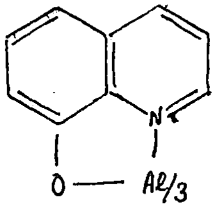
Extraction equlibria :

Mainly there are two types of metal extraction systems:

(a) Extraction of chelate complexes

(b) Extraction of ion association complexes.

(a) Mostly chelates are the extracable species here. These are generally five or six-membured ring compounds e.g.,



Aluninium-8-quinolinate.

Cupferron, dithizone, acetyl acetone, thenoyl trifluoroacetone etc., are commonly used as extractants in an organic solvent. In general the extraction equilibria may be studied by the following way. If HR is the chelating agent

(1) Ionisation of the reagent,

$$HR \rightleftharpoons H^{+} + R^{-}$$

$$K_i = \frac{[H^{+}]\ [R^{-}]}{[HR]} \qquad \ldots\ldots \qquad \ldots\ldots \qquad (11))$$

(2) Formation of the complex

$$\begin{array}{lll} M^{+n} + R^{-} \rightleftharpoons MR^{n-1} & \qquad & K_1 = \dfrac{[MR^{n-1}]}{[M^{n+}][R^{-}]} \\ \vdots \qquad \vdots \qquad\quad \vdots & & \vdots \\ MR^{+}_{n-1} + R^{-} \rightleftharpoons MR_n & & K_n = [MR_n] / [MR^{+}_{n-1}][R^{-}] \end{array}$$

$$\ldots\ldots \qquad \ldots\ldots \qquad (12)$$

The overall formation constant

$$K_f = K_1 . K_2 \ \ldots\ldots\ldots\ K_n$$

(3) Hydrolysis and metal anion co-ordination

$$M^{+n} + OH^{-} \rightleftharpoons M(OH)^{n-1}$$

$$M^{+n} + X^{-} \rightleftharpoons MX^{n-1} \qquad \ldots\ldots \qquad \ldots\ldots \qquad (13)$$

where X = anion, e.g., Cl^{-} or NO_3^{-} etc.

(4) Reagent distribution

$$K_{D_R} = \frac{[HR]_o}{[HR]_a} \quad \cdots\cdots \quad \cdots\cdots \quad (14)$$

o = Organic phase

a = aqueous phase.

(5) Chelate distribution

$$K_D = \frac{[MR_n]_o}{[MR_n]_a} \quad \cdots\cdots \quad \cdots\cdots \quad (15)$$

When chelate concentration in aqueous phase is neglected and hydrolysis in stage (3) is insignificant, the distribution ratio can be derived as a useful approximation from the above equations,

$$D = \frac{[M]_o}{[M]_a} = K\left[\frac{(MR)_o}{H^+}\right]^n \quad \cdots\cdots \quad (16)$$

when K is constant. If the reagent concentration in the organic phase is maintained constant,

$$D = K'\left[H^+\right]^{-n}$$

$$\text{i.e., } \log D = \log K' + npH \qquad (17)$$

equation (17) shows that extraction depends upon hydrogen ion concentration in the aqueous phase. The PH value at 50% extraction is called $PH_{1/2}$

(b) Ion association system - complexes are formed by the ion association or by the process of oxygen bonding and solvation with the organic solvent. Commonly esters, ethers, tributyl phosphate etc, are used as an extracting agent. The equilibria in ion association system are far more complicated than those in chelate extraction. The extraction of ferric chloride by ether serves as an example. The probable equilibria may be expressed as follows :

(i) Formation of $FeCl_4^-$ anion.

$$\begin{array}{cccccc} Fe\,(H_2O)_6^{3+} & + \; Cl^- & \underset{}{\overset{k_1}{\rightleftharpoons}} & Fe\,(H_2O)_5Cl^{2+} & + & H_2O \\ \vdots & \vdots & & \vdots & & \vdots \\ Fe\,(H_2O)_3Cl_3 & + \; Cl^- & \overset{k_4}{\rightleftharpoons} & Fe\,(H_2O)_2Cl_4^- & + & H_2O \end{array}$$

The overall reaction is

$$Fe\,(H_2O)_6^{3+} + 4Cl^- \overset{k_1'}{\rightleftharpoons} Fe\,(H_2O)_2Cl_4^- + 4\,H_2O$$

$$K_1' = \frac{[Fe(H_2O)_2Cl_4^-]\,[H_2O]^4}{[Fe(H_2O)_6^{3+}]\,[Cl_{\cancel{4}}^-]^4}$$

(ii) Solvate formation

$$Fe(H_2O)_2Cl_4^- + 2R_2O \overset{K_5}{\rightleftharpoons} Fe(R_2O)_2Cl_4^- + 2H_2O$$

$$R_2O + H_3O^+ \overset{K_6}{\rightleftharpoons} R_2OH^+ + H_2O$$ [R_2O= Ether molecule]

(iii) Formation of extractable complex

$$H_3O^+ + Fe(H_2O)_2Cl_4^- \overset{K_7}{\rightleftharpoons} (H_3O^+, Fe(H_2O)_2Cl_4^-)$$

$$R_2OH^+ + Fe(R_2O)_2Cl_4^- \overset{K_8}{\rightleftharpoons} (R_2OH^+, Fe(R_2O)_2Cl_4^-)$$

or more generally $HS^+, Cl^- + Fe(S)_2Cl_4^- \overset{K_9}{\rightleftharpoons} (HS^+, Fe(S)_2Cl_4^-)$

($S = H_2O$ or R_2O)

iv) Distribution of reagent and of extractable complex

$$[(HS^+, Fe(S)_2Cl_4^-] \overset{K_D'}{\rightleftharpoons} [(HS^+, Fe(S)_2Cl_4^-]_0$$

$$(HS^+, Cl^-) \overset{K_D}{\rightleftharpoons} [HS^+Cl^-]_0$$

(v) Polymerisation of ion-pair in ether phase

$$n\left[HS^+,\ Fe(S)_2Cl_4^-\right]_o \overset{K_{10}}{\rightleftharpoons} \left[(HS^+,\ FeS_2Cl_4^-)\right]_o$$

where n = 2 to 4

(vi) Dissociation of the extractable complex and of the reagent in ether phase.

$$(HS^+,\ Fe(S)_2Cl_4^-)_o \overset{K_{11}}{\rightleftharpoons} (HS^+)_o + (Fe(S)_2Cl_4^-)_o$$

$$(HS^+, Cl^-)_o \overset{K_{12}}{\rightleftharpoons} (HS^+)_o + (Cl^-)_o$$

The overall distribution ratio, $D = \dfrac{[Fe]_o}{[Fe]_a}$ is calculated from the above reactions and is given by, as an approximation,

$$D = K_D'K_7\left[HS^+\right]\left\{1 + K_{12}K_D\left[H^+\right]\left[Cl^-\right]\right\}^{-\frac{1}{2}} \quad \ldots\ldots \quad (18)$$

Thus equation (18) shows that with increasing acidity iron extraction is enhanced.

Computer calculations of extraction equilibria :

With the advancement of science it has become possible to extract much more information from experimental results than was possible in the days when simplifying assumptions had to be made inorder to make the mathematical operations amenable to solution by the individual working by hand or with a calculating machine. Several computer programmes have been written and used for extraction equilibrium calculations (46 a-g). The raw data from an instrument such as AKUFVE can be fed straight into a computer, and the implications for continuous controll of extraction plant are obvious.

Methods of extraction :

The methods are

(a) Batch extraction

(b) Continuous extraction

(c) Discontinuous extraction.

(a) Batch extraction is the simplest method of extraction and useful where the distribution ratio is large. In this method a metal salt from the aqueous phase is extracted into the organic phase in a separating funnel by mechanical shaking till equilibrium is reached. Then it is allowed to settle and the two layers are separated. After separation the metal in each phase is estimated.

(b) This method of extraction is applied when distribution ratio is small. Here an immiscible solvent flows continuously or both phases are allowed to pass through the solution in counter-current direction.

(c) Craig (47) has used this technique for rapid separation and applied in fractionation of organic compounds having similar distribution ratios.

Techniques in extractions :

(i) Organic solvent : The selection of an organic solvent depends on many factors, mainly the solubility of the particular complex to be extracted.

(ii) Analysis : After extraction of solute at equilibrium, the amount of solute in both the phases can be determined in various ways. One important method is back extraction of solute from organic phase with water or acid followed by analysis. A second method is the direct evaporation of organic solvent if the solvent is volatile and then the solute is estimated. If the organic solvent is not so volatile, it may be removed by heating with concentrated nitric and perchloric acid followed by estimation. Most recently the organic phase may be directly estimated by radiometric method (47a).

(iii) Selectivity : The selectivity of an extraction is frequently increased with the help of oxidising agents or reducing agents as the case may be. Thus chromium (III) is not extracted with diphenyl carbazide but chromium (iv) can be extracted from its solution. Sometimes suitable masking agents are also used to prevent extractions of the undesired element, Cyanide, citrate, tartrate, EDTA etc., are used as masking agents.

(iv) Salting-out agent : The extent of extraction may also be increased with the help of salting-out agents, specially in case of ion associaton complexes. Chlorides and nitrates of ammonium, sodium, magnesium and aluminium etc., are frequently used as salting-out agents. This is probably due to high concentration of the complexing ion supplied by the salting-out agent.

Some Practical Considerations :

Solvent extraction is generally employed in analysis to separate a solute (or solutes) of interest from substances which interfare in the ultimate quantitative analysis of the material; sometimes the interfering solutes are extracted selectively.

Perhaps the most important consideration in the selection of a solvent for use in a particular extraction procedure is the extractibility of the element of interest. The choice of solvent for extraction is governed by the following considerations.

(i) A high distribution ratio for the solute and a low distribution ratio for undesirable impurities.

(ii) Low solubility in the aqueous phase.

(iii) Sufficiently low viscosity and sufficient density difference from the aqueous phase to avoid the formation of emulsions.

(iv) Low toxicity and inflammability

(v) Ease of recovery of solute from the solvent for subsequent analytical processing. Thus the b.p. of the solvent and the ease of stripping by chemical reagents merits attention when a choice is possible. some times mixed solvents may be used to improve the above properties. Salting-out agents may also improve extractability.

Stripping : Stripping is the removal of the extracted solute from the organic phase for further preparation for the detailed analysis. In many colorimetric procedures involving an extraction the concentration of the desired solute is determined directly in the organic phase after extraction by measuring the optical density of a known volume of the solution of the coloured complex.

Where other methods of analysis are to be employed, or where further separation steps are necessary, the solute must be removed from the organic phase to a more suitable medium. If the organic solvent is volatile (e.g., ether) the simplest procedure is to add a small volume of water and evaporate the solvent on a water bath; care should be taken to avoid loss of a volatile solute during the evaporation. Sometimes adjustment of a pH of a solution, change in valance state, or the use of competitive water - soluble complexing reagents may be employed to prevent loss of the solute. When the extracting solvent is nonvolatile the solute is removed from the solvent by chemical means, e.g., by shaking the solvent with a volume of water containing acids or other reagents, whereby the extractable complex is decomposed. The metal ions are then quantitatively back-extracted into the aqueous phase.

Back-Washing : Impurities present in the aqueous phase may sometimes be removed by back-washing. The organic extract when shaken with one or more small portions of a fresh aqueous phase containing the optimum reagent concentration and of correct pH will result in the redistribution of the impurities in favour of the aqueous phase, since their distribution ratios are low : most of the desired element will ramin in the organic layer.

Completion of the analysis : Having separated a particular element or substance by solvent extraction, the final step involves the quantitative determination of the element or substance of interest. Simple colorimetric or, better, spectrophotometric methods may be applied directly to the solvent extract utilizing the absorption bands of the complex in the ultra-violet or visible region. A typical example is the determination of nickel as dimethyl glyoximate in chloroform by measuring the absorption of the complex at 366 nm.

With ion-association complexes, improved results can often be obtained by developing a chelate complex after extraction. An example is the extraction of uranyl nitrate from nitric acid into tributyl phosphate and the subsequent addition of dibenzoylmethane to the solvent to form a soluble coloured chelate or extraction of platinum (iv) with 2-thenoyl trifluoroacetone in n-butanol-acetophenone mixture and subsequent shaking the extract with Sncl$_2$ where by the newly formed orange coloured solution was measured at 410 nm to read the platinam concentration (49).

A further technique is the application of flame spectrophotometry to the solvent extract. An example is the determination of copper as the salicylaldoxime complex in chloform; the organic extract is sprayed directly into an oxyacetylene flame and the special emission of copper at 324.7nm is measured.

If the direct analysis of the solvent extract is impracticable the element is usually back-~~washed~~ extracted into an aqueous phase which can be analysed by standard methods.

Recent Developments :

1. Synergism : The term synergism was first coined by Blake et. al (48) in 1958 in their report that when a dialkyl hydrogen phosphate, $(RO)_2PO,OH$, is used in conjunction with certain neutral organophosphorus reagents e.g., TBP, the extracting power of the mixture exceeds the sum of the extracting powers of its components. This phenomenen of greatly enhanced extraction or synergism due to a mixture of extractants has attracted considerable attention in recent years. The review articles by Marcus (49) and De (50) are of interest in this connection.

Synergic systems : The most intensively studied synergic systems are of the following types : (1) a chelating agent such as HTTA or IPT (β-isopropyl tropolones) and a solvating solvent such as TBP, IBMK (isobutyl methyl ketone), DBSO (dibutyl sulfoxide), and (ii) a dialkyl phosphoric acid and a neutral organosphosphorous ester (S).

Chelating agent-solvating solvent system :

Considerable work has been done in this area. Irving and Edgington (51-56) postulated that the conditions for synergic extraction are :

(a) One of the active reagents (HX) should be able to neutralize the charge or the metal ion, preferably by forming a chelate,

(b) the solvent (S) displaces any residual co-ordinated water from the neutral metal complex, rendering it less hydrophilic;

(c) the solvent (S) should not itself be hydrophilic and co-ordinated less strongly than (HX);

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

The postulates were valid for the U(vi)-HTTA-TBP(TBTO) system but not for the tetravalent lanthanides and actinides, which are apparently co-ordinatively saturated.

With U(vi)-HTTA-TBP and U(vi)-HTTA-TBPO (tributylphosphine oxide) mixtures, synergic enhancement factors of the order of 10^3 and 10^4 respectively were observed. The extracted species were assigned the compositions UO_2X_2. TBP and UO_2X_2. $(TBPO)_3$ respectively (51,56,52), from isopiestic and infrared measurements. The studies were extended to plutonium (vi), americium (iii), europium (iii) and thorium and the species identified were $PuX_3.(TBP)_2$, $AmX_3.(TBP)_2$, $AmX_3.TBPO$, $ThX_3(NO_3).TBP$ and $ThX(NO_3)_3.TBPO$.

Healy (57) reported on synergic extraction of uranium (vi), thorium, lanthanides (iii), actinides (iii) and alkaline earth metals with HTTA-TBP, HTTA-TBPO and HTTA-TPP, TPP being triphenyl phosphate.

Healy (58) further sugested that the reaction for the system uranium (vi) - HTTA-S can be expressed as :

$$UO_2^{2+} + 2HTTA + xS = UO_2(TTA)_2S_x + 2H^+ \quad .... \quad .... \quad (19)$$

S = solvent

Sekine and Dyrssen (59-64) have reported extensive investigations on solvent extraction of metal ions with mixed ligands. They have described the adduct formation of Cu(II), Zn, Eu(iii) and Th with HTTA and TBP or IBMK and with β-isopropyltropolone, IPT and TBP or IBMK in chloroform and carbontetracholoride.

•<u>Dialkylphosphoric acid (HX)-neutral phosphorous ester (S) system</u> : Important cases in this catigory are : di(2-ethyl hexyl) phosphoric acid (HDEHP)-TBP, which was the first reported case of synergic extraction (65-67); mono (2-ethylhexyl) phosphoric acid (H_2MEHP)-TBP (68); dibutyl phosphoric acid (HDBP)-TBP (69) and HDBP-TOPO (70).

Peppard et al (68) investigated the systems lanthanide (iii), Y (iii), Am (iii), Cm (iii), Th, U(vi)-H_2MEHP-S-diluent, where the synergic agent S was n-decanol, TBP or TOPO and the diluent was tolune, cyclohexane or n-decanol.

(2) Substoicheiometric Extraction :

Ruzicka and stary (71-72) first proposed this new technique of substoicheiometric extraction and determination of metals, which is applicable to activation analysis and isotope dilution analysis.

In all conventional extractive separation procedures, an excess of the organic reagent is usually used to ensure quantitative separation of the desired metal. In the substoicheiometric method the organic reagent is added in less than the stoicheiometric ammount required for the metal to be determined. By using the same amounts of the organic reagent everytime, it is possible to isolate always the same amount of the element in question irrespective of the amount of it actually present (subject to the condition that this must be an excess relative to the amount of extractant).

This permits highly selective separations. The treatment is essentially that developed by Ruzicka and Stary (71,72).

(3) Liquid Ion-Exhargers.

The use of liquid ion exchange dates back to 1948 when Smith and Page (73) reported that high molecular-weight amines (HMWA) can be used for extraction of acids because their acid salts are insolube in Water but readily soluble in organic solvents such as chloroform, benzene or Kerosene.

$$R_3N_{org} + H^+_{aq} + A^-_{aq} \rightleftharpoons R_3NH^+A^-_{org} \text{ (extraction) .... (20)}$$

where A^- = anion of a simple acid or complex metal acid, e.g., $FeCl_4^-$ and

$$R_3NH^+ A^-_{org} + B^-_{aq} \rightleftharpoons R_3NH^+B^-_{org} + A^-_{aq} \text{ (anion exchange)}$$

The amine salt (eq-20) can undergo anion exchange with an anion (B^-) in the aqueous phase. The order of preference in the organic amine solution is similar to that in anion-exchange resins (74).

$$ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$$

The earlier work for liquid anion-exchangers (HMWA) has been reviewed by Moore, Green and Prabhu (75-78).

(4) Reversed-Phase Partition-Chromatography.

In conventional paper chromatography the organic phase is the mobile phase. In reversed-phase partition chromatography the organic extractant is immobilized on some stationary inert support such as kieselguhr, styrine-divinylbenzene copolymer or simply filter paper . The technique was introduced by Fidelis and Siekierski (79) for the separation of the lighter rare earths on columns of kieselguhr impregnated with TBP, 15M nitric acid being used as the mobile phase. In a subsequent paper (80) they extended the work to the heavier rare earths, which are usually difficult to separate. Fair separations were achieved with 11.5M, 12.3M and 13M nitric acid and concentrated hydrochoric acid as the mobile phases.

(5) Combined ion-exchange-solvent extraction (CIESE).

Korkisch (81) has presented a novel separation technique, viz., combined ion-exchange-solvent extraction (CIESE). This is based on simultanious operation of ion-exchange and solvent extraction. The concept is illustrated with two examples : The separation of Fe(iii), Co(ii) and Ni(ii) on Dowex-50 and Dowex-1 with acetone or tetrahydrofuran-hydrochloric acid, and the separation of U(vi) from numerous metal ions on Dowex-50 with tetrahydrofuran-nitric acid as eluent. The organic solvent acts as extractant for one element or a group of elements, whereas for other metal ions it leads to an increase of ion-exchange so that selective separations can be achieved.

The mechanism of CIESE for U(vi) is suggested as follows:

$$THF + HNO_3 \rightleftharpoons (THFH)^+NO_3^- \quad \ldots. \quad \ldots. \qquad (21)$$

Tetrahydrofuran Tetrahydrofuran nitrate

$$(THFH^+)NO_3^- + UO_2(NO_3)_3^- \rightleftharpoons (THFH)^+ UO_2(NO_3)_3^- + NO_3^-,$$

$$\text{or } (THFH^+)NO_3^- + UO_2(NO_3)_2 \rightleftharpoons (THFH)^+ UO_2(NO_3)_3^-$$

Ion-association complex

$$\ldots. \quad \ldots. \qquad (22)$$

At high concentration of tetrahydrofuran (90%) the ion-association complex or liquid anion exchanger is formed to a large extent. This can effectively compete with the solid cation-exchanger, Dowex-50, for UO_2(II) :

$$2R_sSO_3^- H^+ + UO_2^{2+} \rightleftharpoons (R_sSO_3)_2UO_2+2H^+ \ldots. \qquad (23)$$

where $R_sSO_3^-H^+$ represents the exchange resin.

(6) Ternary Complexes : Betteridge and West (82) described the selective extraction of microgram amounts of dibutylamine silver (I) with an ion association complex (or ternary complex) with salicylic acid. More recently Dagnall and west (83) described the extraction of a blue ternary complex - Ag (1)-1, 10-phenanthroline-Bromopyrogallol Red - as the basis of an extremely sensitive spectrophotometric procedure for traces of silver. Silver forms a blue complex on treatment with an aqueous solution of 1,10 phenanthroline and Bromopyrogallol Red, buffered to pH 7 with ammonium acetate. This complex can be extracted into nitrobenzene. The extraction system is highly selective in the presence of EDTA, Hg(II) and Br^- as masking agents. The colour reaction is very sensitive and suitable for measuring Ag(I) in the range 10-50 μg. Ternary complexes have been reviewed by Babko (84).

(7) Extraction from molten salts :

The oldest examples of extractions of solutes from molten salts are the removal of impurities by slag formation in metallurgy, the fire-assay method for separation of gold. None of these is particularly useful in solvent extraction chemistry, although a process akin to slagging was used to remove fisson products from reactor fuel by extraction with molten magnesium chloride (85,86) according to the reaction (for a tetravelent metal such as a lanthanide)

$$2M_{(m)} + 3\ MgCl_{2(s)} \rightleftharpoons 2MCl_{3(s)} + 3Mg_{(m)} \quad \ldots\ldots \quad (24)$$

where the subscripts (m) and (s) denote the metal and salt phases, respectively.

The use of organic solvents in conjunction with molten salts was reported by Green and co-workers (87) at the 1958 Geneva Conference. Marcus (88) has given an excellent review of the extraction from molten salts.

There is a marked resemblance between the molten salt-organic solvent systems and the usual aqueous phase-organic phase systems, and all classes of organic solvent have been used.

Compared with extractions from aqueous solutions, extractions from molten salts behave much more ideally in the thermodynamic sense, and equating the ligand activity with its concentration is a better approximation for salt melts than for aqueous solutions.

(8) Extractive titrations and indicators.

Solvent extraction can be used in titrations either simply to provide indication of the endpoint, or for doing the titration itself. The classic example of endpoint detection is the use of carbon tetrachloride in the Andrews titration to indicate the complete oxidation of iodine to iodine (I).

Programme of work with nickel and some platinum metals:

Different methods on separation of nickel and platinum-metals are reported in the literature. These procedures are either very complicated and lengthy or yield results which are not always unambiguous. On the other hand liquid-liquid extraction methods have been claimed by different workers to give excellent results in the case of a large number of metallic cations. Our informations about the application of this versatile method for the aforesaid elements is still poor. In consideration of this an attempt has been made to apply this technique for extraction and separations of Ni(II), Pd(II), Pt(IV) and Rh(III).

The basic points of the scheme are enumerated below :

(1) Review of the existing literature on liquid-liquid extractions of these metals and on their separation from mixtures.

(2) Selection of appropriate reagents for obtaining suitable complexes and also of solvents.

(3) Studies on the behaviour of these complexes towards different solvents and an attempt to devise a suitable technique for extraction and separation.

(4) Actual experiments on Extraction and separation.

(5) Choice of convenient and easier method for estimation.

Throughout the investigation attempt has been made to minimise the wastage of Chemicals, time and power and to prevent the loss of the precious metals.

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