Introduction
Introduction

Solvent extraction is becoming more and more important in inorganic and analytical chemistry, and the number of chemists who are employing this simple but excellent experimental technique in their work today is enormous. Since a variety of liquid-liquid systems have been developed, it should be possible to find, among the solvent extraction methods that have been reported, one which meets the requirements of almost any chemical problem; and the extraction can be carried out successfully if the operations are properly conducted according to the recommended procedure in the literature.

Transport of materials from one phase to another is the most fundamental procedure for the separation of a chemical species from the medium or from other coexisting components. Thus distillation and condensation (liquid phase to gas phase and vice versa), dissolution and crystallization or precipitation (solid phase to liquid phase and vice versa), and sublimation (solid phase to gas phase and vice versa) have been employed in various experiments since the early days of chemistry. Solvent extraction is also a kind of interphase transport process; and from this point of view, it should be regarded as essentially the same kind of experimental technique as these classical methods. Solvent extraction, however, usually permits much simpler and cleaner separation of materials at both macro and tracer concentrations. The procedure can be carried out by using only a simple apparatus and merely shaking the sample for a few minutes by hand, and yet the contamination from other components is less than that in these other methods.

The difference in the liquid-liquid distribution behaviour among various organic substances was recognized by many early chemists, and solvent
extraction has been a fundamental technique of organic chemistry for a very long time [1]. Actually, a separatory funnel has always been a basic tool in every organic chemistry laboratory, just like distillation apparatus and many other common items of glassware. The solvent extraction of some inorganic compounds was known in the nineteenth century. The first of such examples was the extraction of uranyl nitrate into diethylether reported in 1842 by Peligot [2]. The second example worthy of note was the extraction of iron in hydrochloric acid with diethylether reported in 1892 by Rothe [3] and by Hanroit [4]. This method was then applied to the separation of this element from many other ions [5]. A quantitative understanding of liquid-liquid distribution equilibria was first introduced empirically in 1872 by Berthelot and Jungfleisch [6], and elucidated thermodynamically in 1891 by Nernst [7]. The distribution law, “when a material is distributed between two mutually immiscible liquid phases, the concentration ratio in the two phases at a given temperature is independent of the total amount,” was applied to the determination of chemical equilibria of various solutes in solutions as early as about 1900 [8-14].

A period of extremely rapid progress in solvent extraction began during World War II. Chemists engaged in atomic energy research encountered the problem of separating and purifying almost all the elements in amounts ranging from very low traces up to the usual macro levels. Among the solutions to these difficult problems were the precipitation method and the ion-exchange method. The former was found to be suitable for the treatment of materials in solution at high electrolyte concentrations and the latter for the treatment of ions in dilute solution or for the separation of very similar elements such as lanthanides and transplutonium elements. However, the method that proved most attractive to these chemists was that of solvent extraction, because separation was cleaner than by the precipitation method and operation time
was shorter than that of the ion-exchange method. In addition, its variety of extractants made possible an easy selection of the most suitable system for any given problem.

Since then, many solvent extraction systems have been studied and various useful extractants have been effectively employed. The theoretical background of extraction has been widely developed and statistical treatment of the chemical equilibria involved fairly well systematized [15].

Solvent extraction studies have been reviewed by a number of authors. After early publications [16-18], Morrison and Freiser wrote a comprehensive monograph on solvent extraction in analytical chemistry [19]. The solvent extraction of metal chelate complexes was reviewed from the standpoint of analytical chemistry by Stray [20] and from a more fundamental standpoint by Zolotov [21]. The ion exchange of metal complexes and their solvent extraction were discussed by Marcus and Kertes [22], and the analytical uses of solvent extraction of metals was published in book form by De et al. [23]. Two other reviews of note are also concerned with the solvent extraction of inorganic substances; one was written by Diamond and Tuck [24], the other by Marcus [25]. Various reports of up-to-date research on the fundamentals and application of solvent extraction chemistry presented to the International Conference on Solvent Extraction Chemistry have been compiled and published [26-29]. The application of solvent extraction methods has been reviewed by some authors; for example, applications to solution chemistry were described by Rossotti and Rossotti [30] and to analytical chemistry by Sandell [31], Ringbom [32], and Korkisch [33]. Furthermore, a series of reviews on solvent extraction in various fields has been published [34]. The applications to analytical chemistry are comprehensively reviewed by the journal Analytical Chemistry [35-46].
Principles of solvent extraction

Distribution Coefficient

The distribution equilibrium between two liquid phases is governed by the Gibbs phase rule, which is stated mathematically as,

\[ P + V = C + 2 \]

where \( P \) = number of phases, \( V \) = variance or degree of freedom, and \( C \) = number of components.

In case of solvent extraction there are two phases namely aqueous and organic, while solute is the only component in solvent and water phases and at constant temperature and pressure.

i.e. \( P = 2 \), \( C = 1 \) and \( V = 1 \).

At constant temperature and pressure, the rule predicts a variance of unity. This means if we choose the concentration of solute in one phase, the solute concentration in the other phase is fixed. Hence there will be definite relation between the concentration of solute in each of the solvent phase. Phase rule predicts that a system composed of two immiscible solvents and one distributing solute has one degree of freedom. The ratio of solute concentrations is shown to be invariant i.e. independent of total concentration. The relation between solute concentration in both the phases is described by distribution law.

Distribution law

The relation between concentration of solute in two immiscible liquids can be given by distribution law. The distribution law was first stated in 1872 by Berthelot and Jungfleish [6] and was later elaborated by Nernst in 1891 [7] and is known as Nernst's distribution law. It states that when solute is distributed between two immiscible solvents in such a manner that, at equilibrium the ratio of the concentration of solute in two phases at same
temperature and pressure will be constant, provided the solute has the same molecular form in both the phases.

At equilibrium if \( [X_1] \) is the concentration of solute in phase 1 and if \([X_2]\) is the concentration of solute in phase 2, then

\[
K_D = \frac{[X_1]}{[X_2]}
\]

where \( K_D \) is the distribution coefficient. It is constant and independent of total concentration of solute. However in above expression for \( K_D \), activity coefficient of the species in organic as well as in the aqueous phase are not considered.

**Distribution ratio \((D)\)**

The above law is valid only if the solute exists in the same molecular state in both solvents. In many cases solute may undergo dissociation, association in one or both the phases. In such cases distribution law has to be modified. It can be represented as

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

where \( D \) is called distribution ratio.

Now assuming that there is no dissociation, association or polymerization in both the phases, then under idealized conditions, \( K_D \) is equal to \( D \).

**Percentage extraction**

The efficiency of extraction is expressed in terms of percentage extraction. The percentage extraction is nothing but fraction of solute extracted \((E)\) multiplied by 100 and is related to distribution ratio by following equation:

\[
\% E = \frac{100D}{D + \frac{V_w}{V_o}}
\]
where \( V_0 \) and \( V_w \) represent the volumes of the organic and aqueous phases respectively.

The above equation demonstrates that increase in the phase volume ratio increases the extraction. Similarly instead of single batch extraction, if multiple ‘n’ extractions are carried out from the same aqueous solution by successive portion of the organic solvent keeping volume ratio constant, the percentage extraction is given by,

\[
\% E = 100 \cdot \left\{ \frac{1}{\left( \frac{1 + D \cdot V_w/V_0}{1+D \cdot V_w/V_0} \right)^n} \right\}
\]

Relation between distribution ratio (D) and percentage extraction (%E)

\[
D = \frac{E}{(100-E)}
\]

where \( V_w \) is volume of aqueous phase
\( V_0 \) is volume of organic phase

When volumes of organic and aqueous phases are equal i.e. \( V_0 = V_w \)\n
\( D \) reduces to

\[
D = \left\{ \frac{E}{100-E} \right\}
\]

Further the extraction is considered to be quantitative when \( E = 100 \), under these circumstances.

\[
D = \left\{ \frac{100}{100-100} \right\} = \frac{100}{0} = \infty \text{ infinity (if } V_0 = V_w)\]
Extraction equilibria

The extraction equilibria gives information regarding experimental parameters which play a major role in the selectivity of extraction.

Consider the extraction of metal ion M by chelating ligand HR. The chelating ligand distributes between two phases according to the Nernst distribution law as

$$HR_{aq} \leftrightarrow HR_{org} \quad K_{DR} = \frac{[HR]_{org}}{[HR]}$$

The chelating ligand dissociated as

$$HR_{aq} \leftrightarrow H^+ + R^- \quad K_a = \frac{[H^+][R^-]}{[HR]}$$

The chelating anion combines with metal ion $M^{n+}$ to form extractable neutral chelate

$$M^{n+} + nR^- \leftrightarrow MR_n \quad K_f = \frac{[MR_n]}{[M^{n+}][R^-]^n}$$

This chelate distributes in two phases, hence

$$MR_n(aq) \leftrightarrow MR_n(org) \quad K_{Dx} = \frac{[MR_n]_{org}}{[MR_n]_{aq}}$$

However, distribution ratio ($D$) can be evaluated if metal chelate $MR_n$ is in organic phase and $M^{n+}$ is in aqueous phase

$$D = \frac{|MR_n|_{org}}{|M|} = \frac{|MR_n|_{org}}{|M^{n+}|}$$

By combining above all equations

$$D = \frac{[MR_n]_{org}}{[M^{n+}]} = \frac{K_fK_aK_{Dx}}{K_{DR}^n} \times \frac{[HR]_{org}^n}{[H^+]^n}$$

In above expression
\[ K_j = \text{formation constant of metal complex}, \]
\[ K_a = \text{acid dissociation constant}. \]
\[ K_{dx} = \text{distribution coefficient of metal complex}, \]
\[ K_{DR} = \text{distribution coefficient of chelating ligand}. \]

The above equation was verified by Kolthoff and Sandell. The equation shows that distribution ratio depends upon the chelate stability \( (K_i) \) and solubility of chelate \( (K_{dx}) \) in the organic phase.

Acidic reagents with high \( K_a \) value and low \( K_{DR} \) favour good extraction. Increase in reagent concentration increases distribution ratio as much as would a rise of one unit in pH. The nature of solvent is not a critical factor. The selectivity of extraction is evaluated in terms of the separation factor \( (\alpha) \) given as

\[ \alpha = \frac{D_1}{D_2} = \frac{K_{f1} K_{dx1}}{K_{f2} K_{dx2}} \]

There will be no separation if \( \alpha = 1 \) as \( D_1 = D_2 \). Separation is maximum if \( (\alpha) \) has large value. Thus separation of two ions depends on difference in chelate formation constant \( (K_i) \) values and on relative solubilities \( (K_{dx}) \) of chelates in organic phase.

**Classification of extraction systems**

The process of metal extraction is based on the formation of neutral metal chelates. All types of chelating agents find useful applications in metal extraction procedures.

Various extraction systems can be classified in several ways. The classical one is based on the nature of the extracted species. The present day classification is based upon the process of extraction. Thus based upon the process of extraction, extraction systems can be classified into four major classes viz.,

A) Chelate extraction,
B) Extraction by solvation.
C) Extraction involving ion pair formation
D) Synergic extraction.

All the above extractions are based on the fact that the neutral or uncharged species are extracted easily in organic solvents. These are described here briefly.

A] Chelate extraction - In this class extraction proceeds by the process of formation of chelate or by the formation of closed ring structure between the chelating agent and the metal ion to be extracted.

e.g. a) The extraction of uranium with 8-hydroxyquinoline in chloroform.
    b) The extraction of iron with cupferron in carbon tetrachloride.

B] Extraction by solvation - In this class the extraction proceeds by the process of solvation of the species which is extracted into organic phase.

e.g. a) The extraction of iron(III) from hydrochloric acid with diethyl ether,
    b) The extraction of uranium from nitric acid with tributyl phosphate.

C] Extraction involving ion pair formation - This class involves the process of ion pair formation in order to form neutral uncharged species which is extractable into organic phase.

e.g. The extractions of scandium and uranium with trioctylamine from mineral acids.

In this case an ion pair is formed between complex of metal ion with high molecular weight amine and anionic species of mineral acids.

D) Synergic extraction - In this class there is an enhancement in the extraction on account of use of two extractants.

e.g. The extraction of uranium with tributylphosphate (TBP) as well as 2-thenoyltrifluoroacetone (TTA).
Mechanism of extraction

Solvent extraction proceeds in three stages viz.,
1) The formation of uncharged extractable complex,
2) The distribution of the extractable complex and
3) Interaction in the organic phase.

1) The formation of uncharged extractable complex

It is absolutely essential to have the extractable complex without any charge, hence the formation of uncharged complex is the most important step in the extraction. Such uncharged complex can be formed by the process of chelation, solvation or ion pair formation.

Thus, if M is metal ion with positive valency ‘n’ and if R is anion of the ligand (HR) then through coordination we have

\[ M^{n+} + nR^- \rightarrow MR_n \]

If the basic group of chelating agents is uncharged, a positively charged metal chelate is formed, which in turn gets associated to anionic species of the acid media to form neutral ion pair or uncharged complex as

\[ M^{n+} + bB \rightarrow MB_{b}^{b+} \]

\[ MB_{b}^{b+} + nX^- \rightarrow (MB_{b}^{b+}, nX^-)^0 \text{ cationic complex} \]

\[ B = \text{neutral ligand}, \quad X = \text{anion}, \quad M = \text{metal} \]

\[ M^{n+} + (n+a)X^- \rightarrow MX^{(n+a)} \]

\[ MX^{(n+a)} + aY^+ \rightarrow (aY^+ M X^{(n+a)})^0 \text{ anionic complex} \]

The formation of complex by a metal ion depends upon its tendency to fill up vacant atomic orbitals to accomplish stable electronic configuration. Metal chelates represent a type of coordination compounds in which a metal ion combines with polyfunctional base capable of occupying two or more positions in the coordination sphere of the metal ion to form a cyclic compound. The functional group of the chelating agent must be so situated in
the molecule that it permits the formation of stable ring. The general characteristics of metal chelate are governed by the basic nature of the chelating ligand, the acidic nature of metal ion, size and number of chelate rings formed. Five or six membered chelate rings are more stable as they have minimum steric hindrance and no strain. Chelate stability rises with number of rings. They are formed as increasing number of water molecules are displaced from the metal coordination sphere by the molecule of the polyfunctional ligand.

In extractions involving ion pair formation, the value of ion pair formation constant is related to dielectric constant (\(\varepsilon\)) and temperature (\(T\)) by expression

\[
K = \frac{4\pi Ne^2}{1000\varepsilon kT} \text{ if } b = \frac{e^2}{a\varepsilon kT}
\]

Where \(N\) = Avogadro’s number, \(e\) = Charge, \(Q(b)\) = Calculable function, \(k\) = Boltzmann constant, \(T\) = absolute temperature, \(a\) = empirical parameter dependent upon the distance between charge center of the paired ions when in contact.

Above expression suggests that low value of dielectric constant favours extensive association and distribution of the extractable complex depends upon the organophilic characters of distribuents. Thus there are two main factors which cause the distribuent to favour the organic phase, (a) low affinity of distribuend to aqueous phase and (b) high affinity of distribuend to the organic phase. The low affinity of species for the aqueous phase is because of following factors –

1) Large size,
2) Zero or low charge
3) Non-polar nature
4) Absence of electronegative atom at the surface
5) Low water activity and highly ordered water structure.

Salting out agent decrease the availability of water for interaction with distribuend. In addition to the parameters of the aqueous phase, ion association extraction systems are especially sensitive to organic phase parameters. These variables are nature, structure, size and concentration of the extractant and type of the diluents used. Each of these factors affect the degree of extraction of the metal complex.

Almost as important as the selectivity of the extractant is recovery of the solute from the organic extract. Recovery can be achieved by distillation or evaporation of the solvent provided that the solute is nonvolatile and thermally stable. However, this technique is less frequently used than the principle of back-extraction (stripping) which involves the treatment of the organic extract with an aqueous solution containing a reagent which causes the extracted solute to pass quantitatively into the aqueous layer.

(2) The distribution of extractable complex

The species extracted is invariably neutral and is least soluble in aqueous phase. Thus the theory of like dissolves like is largely applicable. The substitution of hydrocarbon group in chelate structures results in an increase in solubility of chelate in organic solvents due to structural resemblance.

In case of extraction by solvation, the solvent itself participates in extraction of complex. The basic character of the oxygen atom enables the incorporation of the solvent molecule in coordination sphere of the metal ion to form solvated complex which is extractable. Thus the oxygenated solvents like alcohols, ketones or neutral organophosphorus compounds compete with water molecule for the acidic metal ion. The competitive strength of water may be reduced by adding salting out agent.
(3) Interaction in the organic phase

For covalent metal chelates such problem never arises. But in extraction by solvation, there is a possibility of polymerization, which results in reduced activity of the extractable species, but overall equilibrium is shifted in favour of higher distribution ratios.

Technique in extraction

Choice of solvent

Perhaps the most important consideration in the selection of a solvent for use in a particular extraction procedure is the extractability of the element of interest. For subsequent analytical processing a consideration of the solubility of the solute in particular solvent, the ease of recovery of the solvent or the ease of recovery of the solute from the solvent is very important. Thus the boiling point of the solvent or the ease of stripping by chemical reagents enters into selection of a solvent when the possibility of a choice exists. Similarly, the degree of miscibility of the two phases, the relative specific gravities, viscosities and tendency to form emulsion should be considered.

From the point of view of safety, the toxicity and the flammability of the solvent should also be considered.

Stripping

It is back extraction of the extracted solute from the organic phase so that it becomes easier for the estimation. In many colorimetric procedures and even radioactive techniques the concentration of the solute is determined directly in the organic phase. However, where other conventional methods of estimation are to be employed, or where further separation steps are required, it is necessary to remove the solute from the organic phase to more suitable medium. When organic solvent is volatile the simplest procedure is to evaporate the volatile solvent on the steam bath, care should be taken, however
to avoid loss of volatile solute during evaporation. Addition of acid to water before evaporation helps to break the chelate complexes, thereby causing the metal ion to enter the aqueous phase. In the process of destroying the residual organic matter nitric acid, perchloric acid or *aqua regia* is used.

When the extracting solvent is non-volatile it is necessary to strip the solute from the solvent by chemical means. The usual procedure is to shake the solvent with a volume of water containing acids or other reagents under conditions whereby the extracted complex is dissociated or destroyed and the metal ion is quantitatively back-extracted.

### Variation of oxidation state

The selectivity of an extraction is increased by changing the oxidation state of the metal ions in order to prevent the formation of the extractable complex e.g. reduction of cerium(IV) to cerium(III) prevents extraction of this element from nitrate media, conversely for complete extraction of the element proper adjustment of the valence state is required. Also the variation of valence state of certain elements in the organic phase after extraction serves as a method of stripping by destroying the extracted complex.

### Use of masking agents

Masking agents are themselves metal-complexing agents, which serve to prevent a particular metal from taking part in their usual reaction, and thus remove their interference without the necessity of actual separation. In solvent extraction, masking agents are used to prevent certain metals from forming extractable complexes and increasing the selectivity of the method. In extraction of metals normally cyanide, tetratate, citrate, fluoride, and EDTA are used as masking agents. The selection of a particular masking agent largely depends on the acidity of the system and the complex formation constants of the metal with both the masking agent and the extraction agent.
Use of salting-out agents

The term salting-out agent is applied to those electrolytes whose addition greatly enhances the extractability of complexes. The function of salting-out agent would be primarily of providing a higher concentration of complexing anion which, by mass action, would increase the concentration of complex and thus improve the extraction. Water is probably bound as a shell of oriented water dipoles around the ion and thus becoming unavailable as "free solvent". Addition of salting-out agents decreases the dielectric constant of the aqueous phase, which favours the formation of the ion association complexes.

Salting-out agents have been used with great success in separation involving the halide and thiocyanate systems.

Now a days solvent extraction has been recognized as a powerful separation technique having applications to various broad areas such as metallurgy, nuclear, chemical, petrochemical, food, pharmaceutical and environment waste management. Some very important applications have been mentioned below. Super critical fluid extraction and liquid membrane extraction are the latest developments in this field.

Applications

Petroleum and petrochemicals

1. High purity benzene, toluene, xylene which are essential raw material for the petrochemical industry are obtained by N-methyl pyrrolidone (NMP) process [47], Udex process [48], Duo-Sol process [49], DMSO process [50] and sulfolane process [51].

2. Solvent such as phenol and furfural [52] are used for removing sulphur containing compounds and cyclic compounds from diesel oil and lubricating oil production.
3. Another widely used application of solvent extraction in the petroleum industry is in dewaxing lubricating oils using liquid propane [53].

**Pharmaceutical manufacturing process**

The separation and purification of pharmaceutical and natural products have been possible by using solvent extraction techniques.

1. Solvents such as butyl acetate and amyl acetate [54] are used for extracting penicillin from the fermentation broth.
2. Butanol is used for extraction of bacitracin and tetracycline [55].
3. Vitamin A, B12 and C, prednisolone steroid, daacinomycin anticancer drug are some more examples of application of solvent extraction in pharmaceutical process.

**Food industry**

1. Deacidification of edible oils by removal of fatty acids in the process of refining of oils are done by extraction using acetone containing 10-15% water as an extractant [56].
2. The removal of caffeine (trimethylxanthine) from coffee by using trichloroethylene [57].
3. Methanol and pentane as a solvent pair in extraction of citral from citrus oils containing high proportions of hydrocarbons of terpene [58].

**Industrial effluent treatment**

Solvent extraction appears to have great potential in the field of effluent treatment both for the economic recovery of valuable chemicals and for their removal to comply with environmental requirements.

1. Phenols from catalytic petroleum cracking plant effluent streams are recovered using light catalytic cyclic oil by the process known as phenex process [59].
2. Valuable acetic and formic acids are recovered from pulp milk black liquor using methylethyl ketone.

3. Solvent benzene is used for extraction of thiazole based chemicals from a rubber processing effluent.

**Inorganic industries**

Solvent extraction is a well established process within the inorganic chemical and hydrometallurgical industries.

1. Spent fuel from a nuclear reactor contains $^{238}$U, $^{235}$U, $^{239}$Pu, $^{232}$Th and a large number of other radioactive isotopes. Spent fuel is reprocessed in order to separate the isotopes from fission product for reuse as fuel by extraction with tributylphosphate from nitric acid media.

2. Selective extraction and separation of transition metals by thiophosphorus extractants like Cyanex-302 [60] and Cyanex-301 [61].

3. Extractants such as triphenylphosphine oxide, tris (2-ethylhexyl) phosphate and aliquat 336 have been applied for extraction and separation of Ga-In-Tl [62,63], V-Nb-Ta [64, 65], Ti-Zr-Hf [66,67], Zn-Cd-Hg [68], Sb-Bi [69], Mo-W [70,71] and U-Th [72] from a variety of real samples.

4. Production of phosphoric acid by extraction with C$_4$–C$_5$ alcohols [73] from rock phosphate.

5. Recovery of Bromine from bromide salts by extraction with tetrabromomethane [73] after treatment with chlorine.

6. Organophosphorus extractants like HDEHP and Cyanex-921 (TOPO) have been used for separation of Be(II) from Al(III) [74,75] while PC-88A has been used for extraction of main group elements such as Bi(III) [76], Sn(IV) [77] and Ga(III) [78].
References


CHAPTER - 1

Synthesis and characterization of

N-n-octylaniline
1.1 Solvent extraction with basic extractants

High molecular weight primary, secondary and tertiary amines that are organophilic weak bases are used for solvent extraction of anionic species in acidic aqueous solutions. The interaction of these extractants with the anionic species is due mainly to electrostatic forces and in this sense they are similar to the ion-pair-forming cationic extractants such as tetraalkyl- or tetraphenyl-ammonium ions. However, the effectiveness of the extractants treated here in the extraction of anions is dependent on the hydrogen ion concentration and as they show a great tendency to polymerize, the extraction equilibria are much more complicated.

These high molecular weight amines can be regarded as “liquid anion-exchangers” in the same way as the alkylphosphoric acids can be regarded as “liquid cation-exchangers”. This is because the extraction equilibria can at least formally, be expressed by an ion-exchange reaction of anionic metal complexes in the aqueous phase with ligand anions combined with the extractant in the organic phase. However it should be pointed out that, although these extractants are liquid anion exchangers, it is not necessary to consider that only those chemical species in the aqueous phases that have a negative charge are extractable. It has often been found that an extraction of metal ions with these extractants is possible even when anionic complexes of the metal in the aqueous phase are negligible.

Since the extraction is due mainly to the formation of ion-pairs, it is dependent on the charge and the ionic size, and no specificity can be expected among anions of the same charge and similar size. However these extractions
can be used specifically for the separation of many metal ions because they form a variety of complexes with nitrate, halide, thiocyanate, sulfate and a number of other organic and inorganic anions. The ease of formation of anionic complexes of different metal ions with these ligands varies greatly, and since only the anionic metal complexes are extractable with protonated amines, the distribution behaviour of different metal ions in this type of solvent extraction system is quite different. For this reason a very high specificity of extraction is obtained by using these extractants, provided that a suitable extractant and a suitable anionic ligand are employed and that proper experimental conditions are adopted for the given problem.

There are three kinds of amines, namely, primary RNH₂, secondary RR'NH and tertiary RR'R''N amines, in addition to quaternary ammonium ions, RR'R''R'''N⁺. All these organic derivatives of ammonia can be used for solvent extraction of metal ions and other anions (some or all of the R, R' and R'' may be the same). However, since the lower molecular weight amines are very soluble in water, high molecular weight ones have been used for solvent extraction.

These three types of amines in the aqueous phase are weak bases; they can accept one further proton and form amine salts. The amine salts, RₐHₐN⁺X⁻, dissociate in aqueous solution, but they are present essentially as ion pairs in nonpolar organic solvents. Thus when an amine in a nonpolar solvent is equilibrated with a basic or neutral aqueous solution, the amine in the organic phase remains unchanged; but when the aqueous solution is acidic, the amine in the organic phase becomes the salt of the amine and the acid. The extraction capacity of many amines of these three classes has been extensively studied [1,2], and several of them have been used for the extraction of metal complexes.
The basicity of primary or secondary amines in aqueous solutions is not greatly affected by the chain length. However, that of tertiary amines increases as the molecular weight increases [3,4]. The basicity of secondary amines in aqueous solution is somewhat higher than primary or tertiary amines [3,4]. The basicity of these three classes of amines in organic solvents is different from that in aqueous solutions [5].

Due to the action of the hydrogen combined with the nitrogen atom, primary and secondary amines polymerize by forming hydrogen bonds with each other or with water and thus their solubility in the organic solvent is somewhat lower than tertiary amines, which are completely miscible with nonpolar organic solvents if the molecular weight is not very high [6-8]. Their solubility in water or polar solvents often shows the opposite tendency. However, since the solubility of amines is dependent not only on the basicity but also on the branching of the aliphatic chain and total molecular volume, a simple comparison of the solubilities of primary, secondary and tertiary amines having the same alkyl group or similar molecular weight may not have any special meaning.

In most studies, basic extractants have been used for the extraction of metal ions in acid solutions, and thus the amines are in the salt form in the organic phase. Extraction with these basic extractants are quite different from those with free amines.

1.2 Solvent extraction with high molecular weight amines

The ion exchange resin in solid form packed in column have been employed in various separations on continuing basis. However, these separations suffer from several limitations. In a short cycle, back wash requirement of fixed bed is a problem. So also the dilution phenomena and loss of reagent is common. The void volume in the interstices of bed of solid ion exchanger also create difficulty. On the contrary, in the solvent extraction with
high molecular weight amines all difficulties associated with the use of ion exchange are mitigated. The solvent extraction with high molecular weight amines facilitates selective transfer of solute between the organic and aqueous phase. The organic phase containing the high molecular weight amine is completely anhydrous in contrast to the usual ion exchange resin. The latter are normally highly hydrated during the process.

1.3 Solvent extraction from organic acid media

High molecular weight amines i.e. liquid anion exchangers have found very wide applications in the separation chemistry. The separation of metals were carried out from both mineral acids as well as organic acids by taking the advantage of the difference in the $K_D$ values of the anionic complexes of metals. The basis for the separation devised was by exploiting the inability of some elements to form any anionic complex in comparison with others which formed the complexes. The parameters which govern the formation of anionic complex are the effect of acidity, effect of salting out agents and stability of the complex.

Amongst the organic acids, dicarboxylic acids such as oxalic, malonic, citric and tartaric acids and monocarboxylic acids such as salicylic, succinic, acetic acids have been extensively used as complexing ligand. The extraction depends upon the pH, nature and concentration of the amine as well as that of the ligand. The extractions involving organic acids are more selective and specific. These complexing acids have advantages over other mineral acid media.

1.4 Common liquid – anion exchangers

The most common liquid-anion exchangers used for the solvent extraction studies of metals are listed in Table 1.1.
Table 1.1 The structures of various high molecular weight amines.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Structure</th>
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<tbody>
<tr>
<td>n-octylaniline</td>
<td><img src="image" alt="n-octylaniline structure" /></td>
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<tr>
<td>N-n-octylaniline</td>
<td><img src="image" alt="N-n-octylaniline structure" /></td>
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<tr>
<td>Primene JMT (Trialkylmethyl amine)</td>
<td>( \text{H}_2\text{N} - C (R) (R') R'' )</td>
</tr>
<tr>
<td>Amberlite LA-1 [N-Dodecyl (trialkylmethyl)amine]</td>
<td><img src="image" alt="Amberlite LA-1 structure" /></td>
</tr>
<tr>
<td>Amberlite LA-2 [N-lauryl (trialkyl-methylamine)]</td>
<td><img src="image" alt="Amberlite LA-2 structure" /></td>
</tr>
<tr>
<td>TLA (tri-n-lauryl amine)</td>
<td>( \text{N-} [\text{CH}_3(\text{CH}<em>2)</em>{10} \text{CH}_3]_3 )</td>
</tr>
<tr>
<td>TOA Trioctylamine</td>
<td>( \text{N-}[\text{(CH}_2)_7 \text{CH}_3]_3 )</td>
</tr>
<tr>
<td>TIOA (tri-iso-octylamine)</td>
<td>( \text{N-} [\text{C}<em>8\text{H}</em>{17}]_3 )</td>
</tr>
<tr>
<td>TBA (tri-benzylamine)</td>
<td>( \text{N-} [\text{C}_6\text{H}_5\text{CH}_2]_3 )</td>
</tr>
<tr>
<td>Aliquat – 336S (trialkylmethyl ammonium chloride)</td>
<td>( \text{[CH}_3 - \text{N-} (-\text{CH}<em>2)</em>{7-11} (\text{CH}_3)_3]\text{Cl} )</td>
</tr>
</tbody>
</table>

1.5 Synthesis and characterization of N-n-octylaniline

High molecular weight amines (HMWA) popularly known as liquid anion exchangers, uniquely combine some of the advantages of liquid-liquid
extraction and ion exchange. There are several general features which are essential for an extraction, if it has to achieve the selective extraction of a metal. These are as follows:

(i) The ability to extract the metal at the desired acidity or pH.

(ii) To be selective for the required metal.

(iii) Ease of formation of complex with metal of interest and high solubility of metal organic species in the organic phase.

(iv) Ease of recovery of the metal from the organic phase.

(v) It must be stable throughout the principal phases of solvent extraction.

(vi) It is to be prepared in laboratory in large scale.

(vii) To have acceptable rates of extraction and stripping.

(viii) Regeneration of extractant for recycling in economical large scale process.

Due to greater solubility in water, primary amines are used less frequently as compared to secondary amines. In addition, in N-n-octylaniline, the presence of octyl group attached to amino group in aniline renders this amine less soluble in water. There is no emulsion formation.

N-n-octylaniline was prepared by the Gardlund’s method [9]. A solution of distilled aniline and n-octylbromide (3:1 molar ratio) was refluxed overnight. After cooling to room temperature, the reaction mixture was made basic with dilute aqueous ammonia. The aqueous layer was repeatedly washed with pentane. The pentane washings were combined with organic layer and treated with 50% aqueous zinc chloride solution. Extraction of resulting solid with pentane, followed by drying with anhydrous potassium carbonate and flash evaporation of pentane yield crude N-n-octylaniline. A pure compound was obtained by fractional distillation on a spinning band column. The yield
and boiling range was as follows: 98.5%, 177-178°C at 25 mm pressure (found C, 82.1; H. 11.4; \( \text{C}_{14}\text{H}_{23}\text{N} \) requires C, 81.9; H, 11.3%). N-n-octylaniline was found to be 0.89 g/cm³. The \( p \)-toluensulphonyl derivative crystallized from alcohol in fan-shaped clusters of needles, M.P. 42-43°C (found: N, 4.1; \( \text{C}_{21}\text{H}_{29}\text{O}_{2}\text{NS} \) requires N, 3.8%).

Proton resonance assignment for the pure product were made using TMS as an internal standard and chemical shift expressed in δ values. PMR (\( \text{CCl}_4, 90 \text{ MHz, Fig. 1.1} \) : 0.9 (3H, t, \( \text{CH}_3 \)), 1.3 (12H, br, s, \(-\text{(CH}_2\text{)}_6\text{-}\)), 3.0 (2H, t, \(-\text{NH – CH}_2\)), 3.38 (3H, s, \(-\text{NH-}\)), 6.5 (5H, m, \text{Ar-H}). Purity of the product checked by thin layer chromatographic technique.
FIG. 1-1 — PROTON MAGNETIC RESONANCE SPECTRA OF N-n-OCTYLANILINE.
References


