

1.1 Introduction to solvent extraction

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions: what is it ? (qualitative) and how much is it ? (quantitative). Chemicals make up everything we use or consume, and knowledge of chemical composition of many substances is important in our daily lives. Analytical chemistry plays an important role in nearly all aspects of chemistry, for example agricultural, clinical, environmental, forensic, manufacturing, metallurgical and pharmaceutical chemistry. The nitrogen content of a fertilizer determines its value. Foods must be analyzed for contaminants. The air in cities must be analyzed for carbon monoxide. Blood sugar must be monitored in diabetics (and, in fact most diseases are diagnosed by chemical analysis). The quality of manufactured products often depends on proper chemical proportions, and measurement of the constituents is a necessary part of quality control [1].

Solvent extraction technique is a part of analytical chemistry and has been recognized as an excellent separation method because of its ease, simplicity, speed, and wide scope [2-4]. Utilizing apparatus no more complicated than a separatory funnel, requiring just several minutes, at the most to perform, applicable both to trace and macrolevels of metals, extraction procedures offers much to the analytical chemist. A further advantage of the extraction method over the widely used precipitation method lies in the cleaner separations that can be achieved by the former. With the later method contamination of precipitates by coprecipitation phenomena is a decided limitation which is minimized only with difficulty, whereas the analog of coprecipitation, i.e., coextraction, is almost unknown in solvent extraction.

After world war second, chemists were 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 micro levels. Among the solution 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 later for the treatment of the ions in dilute solution or for the separation of chemically similar elements such as lanthanides and transplutonium elements.

However, the solvent extraction method proved to be most effective and

attractive to separate these metals, because in this method, the separation is almost complete than precipitation method and operation time is very less as compared to ion exchange method. With proper choice of extracting agents, this technique can achieve group separation or selective separation of trace elements with high efficiencies. In analytical applications, solvent extraction may serve the following three purposes:

- i) Preconcentration of trace elements
- ii) Elimination of matrix interference
- iii) Differentiation of chemical species.

Solvent extraction or liquid-liquid extraction by high molecular weight organic amines has become increasingly popular in recent years in studying metal complexes. Extraction by these organic amines combine many of the advantages of both solvent extraction and ion exchange. The main interest of metal extraction by the high molecular weight amines lies in their selectivity towards anionic metal complexes, reversibly formed in an aqueous solution. Hence they are generally referred to as “liquid anion exchangers”. The extent of extraction by the organic bases depends on their nature, structure, size, concentration and the nature of the organic solvent used as diluent.

- 1) The solubility of primary long chain amines in non-polar solvents increases with increasing chain length, secondary amines are generally highly soluble in non-polar solvents and sparingly soluble in highly polar solvents. Tertiary amines are completely miscible with non-polar solvents at room temperature and sparingly soluble in polar solvents.
- 2) Extractive power of the alkylamines generally increases from primary to secondary to tertiary to quaternary amines. The trend may be exceptionally changed if there is extraction by bulky amines, where steric factor play an important role.
- 3) Third phase formation :
 - a) The third phase formation, a second organic one, is more common in systems where the diluent is an aliphatic hydrocarbon. Aromatic and some derivatives of aliphatic hydrocarbons show the phenomenon usually at high organic phase loading.

- b) The splitting of organic phase is less common, when straight chain alkylamines are used.
- c) Formation of third phase is most common, characteristic of amine sulphate systems. The compatibility increases in the order: sulphate > bisulphate > chloride > nitrate.
- d) The formation of the third phase is temperature dependent.

Literature in solvent extraction is reviewed by Freiser every two years in 'Analytical Chemistry'. Morrison and Freiser wrote a comprehensive monograph on solvent extraction in analytical chemistry [5]. The solvent extraction of metal chelate complexes was reviewed by Starry [6] and Zoltov [7]. Marcus and Kertes [8] and De et al [9], the applications were compiled by Sakine and Hasegawa [10]. The extraction of many metal ions from various aqueous solutions by high molecular weight amines have been reviewed by Khopkar [11] and Green [12-13].

High molecular weight amine systems used for liquid-liquid extraction of many metals from different aqueous solutions are listed as :

Adogen 364, Alamine 336 (tricapryl amine), Aliquat 336 (tricapryl methyl ammonium chloride), Amerlite LA-1 (N-dodecyl trialkyl methyl amine), LA-2 (N-lauryl trialkyl methyl amine), n-octyl aniline, TBA (tribenzyl amine), TOA (tri-n-octyl amine), TIOA (tri-iso-octyl amine), TLA (tri-n-lauryl amine).

1.1.1 Basic Principles of Solvent Extraction Method :

An extractant, is a substance primarily responsible for the transfer of a solute (here metal) from one phase to the other. The extractant is dissolved in a suitable diluent and together act as a solvent. The diluent is immiscible with other phase which is usually water. The extractant reacts with the solute by solvation/chelation/ion pair formation etc to extract from the aqueous phase. The distribution equilibrium between two phases is governed by Gibbs phase rule, given by

$$P+V=C+2 \quad (1)$$

Where,

P = is the number of phases,

V = is the variance or degree of freedom and

C = is the number of components.

In solvent extraction, we have $P=2$ two phases namely aqueous and organic phase, the component $C=1$, viz. solute, in solvent and water phase and at constant temperature and pressure $P=1$, thus, we therefore have

$$2+1=1+2 \quad \text{i.e. } P+V=C+2 \quad (2)$$

According to Nernst distribution law,

If $[X]_1$ is concentration of solute in phase 1 and $[X]_2$ is the concentration of solute in phase 2 at equilibrium:

$$K_D = \frac{[X]_1}{[X]_2} \quad (3)$$

Where K_D is called as the partition coefficient, this partition or distribution coefficient is independent of the total solute concentration in either of the phases. In the above expression for K_D , we have not considered the activity coefficient of the species in the organic as well as in the aqueous phase. We, therefore, use the term distribution ratio (D) to account for the total concentration of species in the two phases.

Distribution Ratio (D)

The distribution of a solute between two immiscible solvents in contact to each other can be described by the distribution ratio "D".

$$D = \frac{[X]_1}{[X]_2} \quad (4)$$

Where $[X]$ represents the stoichiometric or formal concentration of a substance X and the subscripts 1 and 2 refer to the two phases. Since in most cases, two-phase system is of analytical interest, an organic solvent and aqueous are involved, D will be understood to be;

$$D = \frac{[X]_{\text{org}}}{[X]_{\text{aq}}} \quad (5)$$

The subscript org and aq refer to the organic and aqueous phases respectively. Distribution ratio 'D' is dimensionless quantity, separation of two solutes by solvent extraction is expressed by the term, separation factor (α), which is related to individual distribution ratios,

$$\alpha = \frac{D_A}{D_B} \quad (6)$$

D_A and D_B are the respective distribution ratios of solute A and B.

In the simplest extraction case, the distribution ratio is constant in accordance with the classical Nernst distribution law, a solute will distribute itself between two essentially immiscible solvents so that at equilibrium, the ratio of the concentrations of the solute in the two phases at a particular temperature will be constant, provided the solute is not involved in chemical interactions in either phases. For such a solute, then $K_D=D$. Now in practical work, instead of using term K_D or D one prefers to use term percentage extraction (E).

Percent Extraction (%E)

The more commonly used term for expressing the extraction efficiency by analytical chemist is the percent extraction "E", which is related to "D" as

$$\% \text{Extraction}(E) = \frac{100D}{D + V_{\text{aq}}/V_{\text{org}}}$$

Where, V represent solvent volume and the other quantities remain as previously defined. The percent extraction may be seen to vary with the volume ratio of the two phases as well as with D .

1.1.2 Classification of Extraction Systems

The process of metal extraction is based on the formation of neutral metal chelate. 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 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 closed ring structure between the chelating agent and the metal ion to be extracted.

- e.g. i) The extraction of Uranium with 8-hydroxyquinoline in chloroform.
ii) 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. Oxygenated organic solvents such as alcohols (C-OH), ketones, ethers and esters show some basicity because of the lone pair of electron on the oxygen atom and can therefore directly solvate protons and metal ions and bring about their extraction.

- e.g. i) The extraction of Uranium with tributyl phosphate from nitric acid
ii) The extraction of Iron(III) with diethyl ether from hydrochloric acid.

c) Extraction involving ion pair formation

The extraction proceeds with the formation of neutral uncharged species which in turn gets extracted in to the organic phase. The best example of this is the extraction of Scandium and Uranium with trioctyl amine 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 case, there is enhancement in the extraction on account of use of two extractants.

- e.g. the extraction of Uranium with tributylphosphate (TBP) as well as 2-thionyltrifluoroacetone (TTA).
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1.1.3 Methods of Extraction

Three basic methods of liquid-liquid extraction are generally utilized in the analytical laboratory.

A) Batch extraction

Batch extraction, the simplest and most commonly used method, consists of extracting the solute from one immiscible layer into the other by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle before sampling. This is commonly used on the small scale in chemical laboratories. The most commonly employed apparatus for performing a batch extraction is a separatory funnel. Batch extractions may also be used with advantage when the distribution ratio is large.

B) Continuous extraction

The second type, continuous extraction, makes use of a continuous flow of immiscible solvent through the solution or a continuous countercurrent flow of both phases. Continuous extractions are particularly applicable when the distribution ratio is relatively small. Continuous extraction devices operate on the same general principle, which consists of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution being extracted. The extracting liquid separates out and flows back into the receiving flask, where it is again evaporated and recycled while the extracted solute remains in the receiving flask. When the solvent cannot easily be distilled, a continuous supply of fresh solvent may be added from a reservoir.

C) Countercurrent extractions

Extraction by continuous countercurrent distribution is the third general type and is used primarily for fractionation purposes. The separation through continuous countercurrent method is achieved by virtue of the density difference between the fluids in contact. In vertical columns, the denser phase enters at the top and flows downwards while the less dense phase enters from the bottom and flows upwards. The choice of method to be employed will depend primarily upon the value of the distribution ratio of the solute of interest, as well as on the separation factors of the interfering materials.

1.1.4 Factors Influencing the Extraction Efficiency

Primary requirement of solvent extraction for separation /removal purposes is a high distribution ratio of the solute of interest between the two liquid phases. It is useful to employ a number of different techniques for enhancing the distribution ratio. It depends on the nature of the species being extracted and extraction system. The attainment of selectivity in an extraction procedure is also very important. Some of the factors, which affect the distribution of solute of interest, are given below.

A) Choice of solvent

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 existed. 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 must be considered.

Use of a suitable solvent for effective separation is very important. Metal chelates and many organic molecules, being essentially covalent compounds do not impose many restrictions on the solvent and the general rules of solubility are the great use. In ion association systems and particularly in oxonium type ions, the role of solvents is very important. This is due to involvement of solvent in the formation of extractable species.

B) Acidity of an aqueous phase

The extractability of metal complexes is greatly influenced by the acidity of an aqueous phase, so it is necessary to assure optimum concentration of H^+ ions for maximum extraction. In the case of chelate extraction, the chelating reagent concentration is maintained constant; the distribution of the metal in a system is a function of pH. For this reason, curves of extractability versus pH at constant reagent concentration are of great analytical significance. Sometimes it is possible to achieve the desired characteristics of a solvent by employing a mixed solvent system.

C) Stripping

Stripping is the removal of the extracted solute from the organic phase for further processing or analysis. In many colorimetric procedures and even radioactive techniques, the concentration of solute is determined directly in the organic phase. However, where further separation steps are required, it is necessary to remove the solute from the organic layer to more stable medium. When organic layer is on the steam bath, care should be taken, 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, hydrochloric acid, nitric acid, perchloric acid or aqua regia is used.

The usual procedure is to shake the organic layer with a volume of water alone or water containing an appropriate concentration of acid, an oxidizing or reducing agent or masking agent. The metal ion is then back extracted in the stripping aqueous phase.

The conditions employed depends upon metal ion and the particular extraction system and are such that they promote the reversal of extraction. Pure water or water adjusted to an appropriate pH/ molarity of acid are the more popular and convenient stripping agents. Washing the organic layer with an oxidizing and reducing agent changes the metal ion to be stripped in an oxidation state in which it is not extracted under the specific conditions.

D) Use of masking agents

In the extraction procedures for metal pairs that are difficult to separate; masking or sequestering agents are introduced to improve the separation factor. Masking agents are themselves metal-complexing agents, which serve to prevent a particular metal from taking part in their usual reaction, and thus to 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 the application of masking agents, which include cyanide, tartarate, citrate, fluoride, and EDTA. 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 and the extraction agent.

EDTA, which has been proved as most useful masking agent, forms anionic complexes with a number of metal ions.

E) 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 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 favors the formation of the ion association complexes. Salting-out agents have been used with great success in separation involving the halide and thiocyanate systems.

In addition to enhancement of the extraction of the metal of interest using salting-out agents, it is also possible to decrease the extraction of impurities in the system. Thus, it is necessary to choose an agent that produces a favorable separation factor between the element of interest and the impurities. However, it must be remembered that anomalies sometimes result from specific interaction effects. Aluminium or calcium salts are strong salting-out agents, whereas ammonium salts are much weaker but analytically more convenient.

F) Backwashing

Backwashing is an auxiliary technique used with batch extractions to influence quantitative separations of elements. The combined organic phases from several extractions of the original aqueous phase contain practically all the desired elements and possibly some of the impurities that have been extracted to a much smaller extent. This combined organic phase when shaken with one or more small portions of a fresh aqueous phase containing the optimum reagent/salting agent concentration, acidity, etc., will result in a redistribution of the impurities in favor of the aqueous phase since their distribution ratios are low. Under optimum conditions, most of the elements of interest will remain in the organic layer, since their distribution ratios are high.

This technique is analogous in many respects to the re-precipitation step in a gravimetric precipitation procedure. With the proper conditions, most of the impurities can be removed by this backwashing operation, with negligible loss of the main component, thereby attaining a selective operation.

F) Variation of oxidation state

The selectivity of an extraction is increased by the modification of oxidation states of the interfering ions present in solution, in order to prevent the formation of their extractable metal complexes e.g. reduction of Cerium(IV) to Cerium(III) prevents extraction of this element from nitrate media, the extraction of Iron(III) from chloride solutions can be prevented by reduction to Iron(II), which is not extractable. Similarly, Antimony(V) may be reduced to the tetravalent state to suppress its extraction. Conversely, it is important in the preparation of a solution for extraction to adjust the proper valence state of metal ion required for the formation of the complex in order to ensure complete extraction of that element. Selectivity can also be achieved by variation of the oxidation state of the co-extracted interfering ions during the stripping operation.

G) Synergic Extraction

Synergism is defined as the combined action of two complexing reagents, which is greater than the sum of the actions of the individual reagents used alone. An example of the synergic extraction of Ce(III) with picrolonic acid and benzo-15-crown-5.

H) Use of organic acid media

Organic acid media are having ability of controlling the concentration of the complexing ligand, is one of the unique application, the ease of adjustment of pH and the wide difference in pH at which various metal ions form anionic complexes. The comparative ease of stripping of the complexes from the organic phase can be achieved by fully exploiting the differences in reactivity of various metals to backwash in the aqueous phase by mineral acid. It is known that organic acid media offers better separation of metals possibly due to high stability of metal organic acids complexes.

1.2 Introduction to spectrophotometry

Analysts have developed large number of instrumental techniques and which are extremely sensitive and can yield results rapidly to a high degree of accuracy. Among these instrumental analytical techniques, spectrophotometric technique occupies a unique position, because of its simplicity, sensitivity, accuracy and rapidity.

Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength [14].

Spectrophotometric method is the most important for determining metals in alloys, minerals and complexes, owing to its selectivity. In comparison with atomic emission spectroscopy, atomic absorption spectroscopy and similar techniques, offers the advantage of having calibration graphs that are linear over a wider range. A very extensive range of concentration of substances (10^{-2} - 10^{-8} M) may be covered.

The basis of spectrophotometric methods is the simple relationship between the absorption of radiation by a solution and the concentration of colored species in the solution (Lambert's-Beer's law). A molecule or an ion exhibits absorption in the visible or ultra-violet region when the radiation causes an electronic transitions in molecules containing one or more chromophoric groups. The color of a molecule may be intensified by substituents called auxochromic groups, which displace the absorption maxima towards longer wavelength (red shift) or towards shorter wavelength (blue shift). The color determining factors in many molecules is the introduction of conjugated double bonds by means of electron donor or electron acceptor groups [15].

1.2.1 Calibration Curve

The spectrophotometric technique requires the construction of a calibration curve for the constituents being determined. For the purpose, suitable quantities of the constituents are taken and treated in exactly the same way as the sample solution for development of the color, followed by the measurement of the absorption at the optimum wavelength. The absorbance is then plotted against concentration of the constituent. A straight line is obtained if Beer's law is followed. This calibration curve may then be used in future determinations of the constituents under the same conditions. The calibration curve needs frequent checking at intervals.

1.2.2 Sensitivity of spectrophotometric Methods

The sensitivity is often described in terms of the molar absorptivity (ϵ , $\text{Lmol}^{-1}\text{cm}^{-1}$) of the metal ligand complex. The awareness of the sensitivity is very important in spectrophotometric determination of trace metals. The numerical expression [16-18] is the molar absorptivity (max) of the colored species.

Molar absorptivity (ϵ) = A/cl

Sensitivity depends on the monochromaticity of the radiation. With monochromatic light of very narrow bandwidth corresponding to the wavelength of λ_{\max} , the maximum value of molar absorptivity is obtained.

Savvin [19] suggested a relation between sensitivity and molar absorptivity. He suggested a following criteria for describing the sensitivity.

Low sensitivity $\epsilon < 2 \times 10^4$ Lit. mol⁻¹ cm⁻¹

Moderate sensitivity $\epsilon = 2 - 6 \times 10^4$, Lit. mol⁻¹ cm⁻¹

High sensitivity $\epsilon > 6 \times 10^4$, Lit. mol⁻¹ cm⁻¹

It is generally stated [20] that the molar absorptivity will not exceed approximately beyond 10^5 . Other ways of specifying sensitivity are as specific absorptivity [21] or the Sandell's sensitivity [22]; both methods give the sensitivity in terms of mass of analyte per unit volume of solution. Such an approach is perhaps more convenient than using molar absorptivities as a basis of comparison. The Sandell's sensitivity is the concentration of the analyte (in μgmL^{-1}) which will give an absorbance of 0.001 in a cell of path length 1 cm and is expressed as $\mu\text{g cm}^{-2}$. Organic reagents with high molecular weights furnish maximum sensitivity if used as chromogenic agents.

1.3 Aims and objectives of the proposed work

The Platinum Group Metals (PGMs: Pt, Pd, Rh, Ir, Ru, and Os) are extremely scarce in comparison to the other precious metals due to only their low natural abundance but also to the complexity of the processes required for their extraction and refinement. In comparison with other precious metals (Au and Ag), these PGMs are of great technological importance as they have a number of important catalytic, mechanical, and oxidation-resistance properties, which are particularly seen at high temperatures. Their catalytic properties are presently being exploited in the development of catalytic converters for vehicles and this market now reached 60 % of the annual world production of Pt, Pd, and Rh [23]. The demand for these PGMs has led to increased interest in their recovery [24-27].

Platinum Group Metals are divided into primary platinum metals (Platinum and palladium) and secondary (ruthenium, rhodium, iridium and osmium). The primary platinum metals are appreciably more abundant than the other platinum group metals.

The world production of all six PGMs, silver and gold was only 281, 13818 and 2134 tonnes in 1992, respectively [28]. The largest sources were found in South Africa, Soviet Union, Canada, USA, China and Australia.

Recently, the emphasis on the removal of Platinum group metal ions has led to a considerable growth in the development of new methods in analytical chemistry for extraction, separation, and determination of various metal ions.

The direct determination of the trace metals in solid or a powder sample solution in complicated matrix by spectroscopic methods is often difficult due to their extremely low concentrations and matrix interferences. Therefore, a separation/pre-concentration step is required. Typically, the reason for performing a separation and/or preconcentration step is to bring the concentration of the trace element to a detectable level and/or separate it from interfering substances in the sample matrix. Several preconcentration procedures are available for this purpose, however, most of these are time consuming and costly, but, liquid-liquid extraction method still remains a standard method of separation and preconcentration, because of its simplicity, speed and applicability to both trace and macro-amounts of metal ions. The liquid-liquid extraction (LLE) technique has become increasingly popular in comparison with the other extraction methods because of its several major advantages, such as (i) simple to operate; (ii) high pre-concentration factor; (iii) rapid phase separation.

In order to develop or design highly selective reagents for Platinum group metals, we should take in to account the HSAB principle. The term "HSAB principle" which was suggested by R. G. Pearson refers to the rule that "hard acids" prefers to associate with "hard bases", and "soft acids" prefers to associate with "soft bases" [29-31]. Since the nitrogen atom has a high affinity for so-called "soft metals" such as gold, palladium, and ruthenium, a nitrogen containing reagent is expected to have a highly selective than cations and anion exchangers. Therefore, the extraction of these metals has become easily possible with enhanced efficiency in comparison to the non nitrogen extractants.

A large number of extractants have been commercially used in the field of hydrometallurgy. The most important factor in the solvent extraction of metals is high selectivity of the extractant for the recovery of a specified metal. Platinum group metals are always in association with base metals such as copper, nickel, iron and so on.

Furthermore, the separation of individual Platinum group metal is difficult because of the similarity of their chemical properties and chemical species in the chloride media; therefore, it is necessary to develop a more effective recovery process for their separation and purification.

Several factors need to be considered in the design of an extractant. For example, apart from both high lipophilicity and chemical stability, extractants should give rise to rapid complexation and decomplexation rates and ideally show selectivity for the metals of interest. Suitable solubility characteristics for use in the chosen two phase system are also necessary. However, the most important factor in the solvent extraction of metals is the selectivity of the extractants towards the specified metal ion to be recovered.

There are several general features which are essential for an extractant, if it has achieved the selective extraction of several metals. These are as follows:

- 1) To be selective for the required metal.
- 2) The ability to extract the metal at the desired acidity or pH.
- 3) Ease of formation of complex with metal of interest and high solubility of metal organic species in the organic phase.
- 4) Ease of recovery of the metal from the organic phase.
- 5) It must be stable throughout the principle stages of solvent extraction.
- 6) It is to be prepared in laboratory in large scale.
- 7) To have acceptable rates of extraction and stripping.
- 8) Regeneration of extractant for recycling in economical large scale processes.
- 9) There is no emulsion formation.

Due to high selectivity of nitrogen containing extractants towards the noble metals and as no substantial work has been done on the extraction of these metals, it is planned to synthesis water repellent nitrogen containing extractants for the effective separation and quantification of Platinum group metals from various alloy, synthetic mixtures,

real samples and pharmaceutical samples (Ayurvedic samples).

The present study is focused on the recovery of Platinum group metals with nitrogen containing extractant through solvent extraction technique. This subject is of great importance due to the high value and scarcity of platinum metals, consequently the need of developing and consolidating the new and effective extractant is necessary.

The summary of different extractants, containing donor atoms such as N/S/O/P which were used for liquid-liquid extractions of many metals from different aqueous solutions is presented in Table 1.4.

Table 1.4 Summary of the extractant systems used for solvent extraction

Extractants	Metal ion	Diluent	Medium
N-n- octylaniline	Au(III)	Xylene	Sodium malonate pH-10 [32]
Tri-n-octyl amine	Os,Ru(III)	Benzene	HCL [33]
Tri-n-octyl amine	Te	Xylene	NaI,HClO ₄ [34]
Tridodecyl amine	Th,Pa,Np,U	Benzene	Mixed mineral acids [35]
Tri-n-octyl amine	Np,Ta,Zr	Toluene chloroform	HCl,HF [36]
N-octylaniline	Noble metals	Xylene	Mineral acids [37]
Tridodecyl amine	Pu, U	Benzene	HCl or HBr H ₂ SO ₄ [38]
Tridodecyl amine	Cr(IV)	Chloroform	Orthophosphoric acid [39]
N-octylaniline	Mo,W,Cu(II), Ni(II),Co,Mn	Toluene	HCl [40]
Alamine336	Zn(II)	Xylene	HCl, HBr [41]
Aliquat336	Pb	Xylene	Chloride [42]
Alamine336, Aliquat336,Amberlite LA-1, Primene JMT	Zn,Cd,Hg,In and Tl	Benzene Chloroform	NH ₄ SCN [43]
Aliquat336	Am,Eu	Cyclohexane	NaOH [44]
Tricarpyl methyl amine	U,Np	Xylene	HCl,HBr [45]
Tridodecyl amine	Th,Pu	Xylene	HNO ₃ [46]
Tri-n-octyl amine	Ga(III),In(III)	Chloroform	Tartaric acid[47]
Tri-n-octyl amine	Al(III)	Chloroform	Tartaric acid Oxalic acid [48]
Aliquat336	Mn,Ni(II),Co ,Cu(II)	Benzene	SCN [49]
Aliquat336	Cd(II)	Benzene	SCN [50]
Aliquat336	Np,Pu,U	Chloroform	HCl [51]
TOA	Zr	Benzene	HCl [52]
Tridodecyl amine trioctyl amine	Np,U	Chloroform	Acetic acid [53]
Tri-n-octyl amine	Ac	Cyclohexane	HCl, HNO ₃ [54]
N-octylaniline	Noble metals	-	Mineral acids [55]
Aliquat336	Ac,Eu	-	Alkaline[56]
TOA	Zn(II)	Chloroform CCl ₄	HCl, HBr[57]
TOA	V	Benzene	HCl[58]
Tri-n-octyl amine	Fe(III)	Chloroform Toluene CCl ₄	HCl[59]

Aliquot336	In(III)	-	Malonate[60]
Aliquot336	Zn(II), Cd(II)	Chloroform	Mineral acid, citric acid [61]
Aliquot336	Th(IV)	Benzene	Succinate [62]
Aliquot336	Y, Nd	Benzene	Succinate [63]
Amberlite LA-1	Zr	Xylene	Citrate [64]
Amberlite LA-1	Ti	Xylene	Malonate [65]
Octyl aniline hydrochloride	Ir,Ru(III), Rh(III)	Toluene	H ₂ SO ₄ [66]
Tri-n-octyl amine	Al(III)	Chloroform	Tartaric acid, citric acid [67]
Tri-n-octyl amine	Nb, Ta	Kerosene	HF [68]
Aliquot336, Trioctyl amine, tri-iso-octyl amine	Bi(III)	Benzene	Succinate [69]
Tribenzyl amine	Co(II), Mn(II)	Chloroform	SCN [70]
Tri-n-octyl amine	Zn(II)	Benzene	HCl [71]
Decylamine	Lanthanides Actinides	Chloroform	NH ₄ HCO ₃ [72]
Octadecyl amine	Rare earth	Chloroform	Pyrophosphate [73]
Tri-n-octyl amine	Y, Nd, Sm	Benzene	Succinate [74]
Amberlite Al-2	Zn(II), Cd(II), Sm	1,2-dichloro-ethane	HCl, NaCl [75]
N-n-octylaniline	Zn(II), In(II)	Benzene	HCl [76]
N-n-octylaniline	Ga(III),In(III),Ti	Benzene	HCl [77]
n-octylaniline	Ga(III),In(III),Ti	Chloroform	HCl, HBr, HI [78]
N-n-octylaniline	Pb(II), Cd(II)	Benzene	HCl, HBr, HI [79]
n-octylaniline	Ru(III)	Di-isobutyl ketone	HCl+H ₄ BO ₄ +BeCl ₂ [80]
4-octylaniline	Noble metals	Toluene	HCl [81]
4-octylaminopyridine	Platinum group metals	Chloroform	HCl [82]
Aliquot336	Au(III)	Di-isobutyl ketone	NaCN [83]
Octylaniline	Au(III), Ag(I)	Toluene	HCl [84]
Long chain primary amine N octanol	Ir(IV)	Dichloroethane	HCl [85]
Alamine336, Aliquot336	Pd(II), Pt(IV)	Isodecanol benzene	pH 1-5 [86]
Aliquot336 or Tri-n-octylamine hydrochloride	Pd(II)	Chloroform	pH 3-6 [87]

Alamine308, TBP/DDSO	U	Benzene	HCl [88]
Trioctylamine	Pt(IV)	Kerosene	HCl [89]
Tetrabutyl1,3 Xylenediphosphate	Au(III)	1,2 DCE	HCl [90]
Alamine304	Au(III), Pt(IV)	Xylene	HCl [91]
N-n-hexyl aniline	Bi(III)	Xylene	H ₂ SO ₄ [92]
n-octylaniline	Bi(III)	Chloroform	HCl & HBr [93]
2-octylamino pyridine	Ga(III)	Chloroform	HCl [94]
Alamine336	Ni(II)	Xylene	HCl [95]
Benzothiazoyl sulfoxide	Pd(II)	Benzene	HCl [96]
Triphenyl phosphene oxide	Fe(III)	Acetone	Thiocynate [97]
Triphenyl phosphene oxide	Cu(II)	Chloroform	Aqueous solution [98]
Glyoxime	Pd(II)	Chloroform	HNO ₃ [99]
Triphenyl phosphene	PGMs	Chloroform	HCl [100]
1,12-Di-2-Thienyl-2,5,8,11- tetrathiododecane	Pd(II)	Chloroform	Aqua regia [101]
N,N-Dialkyl-N-benzoyl- thioureas	Pd(II),Au(III)	Chloroform	HCl [102]
Benzo-15-crown-5	Au(III)	Chloroform	HCl [103]
2,4-dihydroxyacetophenone	Mo(IV)	Benzene	HCl [104]
2,4,6-trihydrazinopyrimidine	In(III)	Benzene	Acetate Buffer [105]
p-tert-butylcalix[4]arene	Hg(II)	Chloroform	HCl [106]
N,N-dimethyl-2,7-dihexyl- 3,6-diazooctanic acid diethyl ester	Ag(I)	Chloroform	Aqueous solution [107]
Calyx[4]arene	Ag(I), Au(III)	Chloroform	Aqueous solution [108]
Tri-n-octylphosphene oxide	U	Chloroform	HNO ₃ [109]
Tris(2,6- dimethoxyphenyl)phosphene	Fe(III), Au(III)	Toluene	HCl [110]
3-(4-methoxyphenyl)-6-oxo- 4H-1-benzopyran	W	Dichloromethane	Perchloric acid [111]
Triphenyl phosphene	Hg(II)	Toluene	pH 5-6 [112]
Crown ether 12-crown-4	Ir(IV)	Chloroform	HCl [113]
Cyanex 923	Zn(II)	Toluene	Sulphate [114]
1,3 bis(2-acetoxymethyl thiobutyl-3-thiobutylpropyl)- 6-methyl uracyl	Au(III)	Chloroform	HCl [115]

p-[4-(3,5-dimethylisoxazolyl)azophenyl azo calyx(4)arene	Pd(II)	Chloroform	HNO ₃ [116]
D(2-ethylhexyl)dithiophosphoric acid	Ca(II)	Chloroform	HCl [117]
2-hydroxy-5-methylacetophenone isonicotinoyl hydrazone	Cu(II)	Chloroform	Citrate buffer [118]
1-benzoyl-3-[6-(3-benzoylthioureido)-hexyl]thiourea	Pd(II)	1,2DCE	HNO ₃ [119]
Calix[4,6]arenes	Pd(II)	Chloroform	HCl [120]
N,N-dimethyl N,N-diphenyltetradecylmalonamide	Rh(III)	Chloroform	HCl [121]
5-chloro-2-hydroxythio-benzahydrazide	Ru(III)	MIBK	HCl [122]
5-amino-1,2,4 thia diazole derivatives	Pd(II)	1,2 DCE	HCl [123]
N,N-dipentylethylenediamine-N-thio carbaldehyde	Pt(II)	Chloroform	HCl [124]
1-(2,4-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol	Au(III)	1,2 DCE	HCl [125]
Cynex 301	Co(II), Ni(II)	Chloroform	Sulphate [126]
Tris(2-ethylhexyl)amine(TEHA)	Co(II), Zn(II)	Xylene	HCl [127]
1, 10 Phenanthroline	Cu(II)	1,2 DCE	HCl [128]
Bis-(2,4,4-trimethylpentyl)phosphinate	Pd(II)	Toluene	HCl [129]

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