Solvent Extraction

Part 2

For 5th sem students (DSE-2)

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Basic Principles of solvent extraction method:

- An extractant is a substance primarily responsible for the transfer of a solute from one phase to another
- 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----

$P+V=C+2$

Where, P= number of phases
V= the variance or degree of freedom and
C= number of components

In solvent extraction, $P=2$ (Aqueous and organic);$C=1$ (Solute); $V=1$ at constant temperature and pressure…

So, $2+1=1+2$ ie, $P+V=C+2$ ie, It follows Gibbs Phase rule

Distribution ratio:

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

$D= [X]_1/[X]_2$

Where, X represents the stoichiometric or formal concentration of a substance X and the subscripts 1 and 2 refer to the two phases.

As per analytical interest
$D= [X]_{org}/[X]_{aq}$

- Distribution ratio is dimensionless quantity
- Separation of two solutes by solvent extraction is expressed by the term separation factor (α) which is related to individual distribution ratio

$\alpha=D_A/D_B$

Where 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 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

$$K_D=D$$

Percent Extraction (%E):

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

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

Classification of extraction system:

On the basis of process of extraction

- Chelate extraction
- Extraction by solvation
- Extraction involving ion-pair formation
- Synergic extraction

1. **Chelate extraction**

- Proceeds by the formation of chelate or closed ring structure between the chelating agent and the metal ion to be extracted

Examples: 1. Extraction of Uranium with 8-hydroxyquinoline in chloroform
2. Extraction of Iron with cupferron in carbon tetrachloride

2. **Extraction by solvation:**

- Extraction proceeds by the process of solvation of the species which is extracted into organic phase
- Oxygenated organic solvents (alcohols, ketone, ether, ester) show some basicity therefore, directly solvate protons and metal ions and cause extraction

Examples: 1. Extraction of Uranium with tributyl phosphate from nitric acid
2. Extraction of Iron(III) with diethyl ether from hydrochloric acid

3. **Extraction involving ion-pair formation:**

- Extraction proceeds with the formation of neutral uncharged species which in turn gets extracted in to the organic phase
- In this case an ion pair is formed between complex of metal ion with high molecular weight amine and anionic species of mineral acids

Examples: 1. Extraction of Scandium and Uranium with trioctyl amine from mineral acid

4. Synergic Extraction:

The phenomenon in which two reagents, when used together, extract a metal ion with enhanced efficiency compared to their individual action is called “Synergism”

- In this process a metal ion is extracted by a mixture of an acidic chelating reagent and a uncharged basic reagent.

Examples: 1. Extraction of Uranium with tributylphosphate (TBP) as well as 2-thionyltrifluoroacetone

Factors affecting the extraction efficiency:

1. Choice of solvent
2. Acidity of an aqueous phase
3. Stripping
4. Use of masking agent
5. Salting out agents
6. Backwashing
7. Variation of oxidation state
8. Use of organic acid media

Problems:

1. Twenty milliliters of an aqeous solution of 0.10M butyric acid is shaken with 10 mL ether. After the layers are separated, it is determined by titration that 0.5mmol butyric acid remains in the aqueous layer. What is the distribution ratio? What is the percentage extracted?

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.

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 thiocynate systems.

In addition to enhancement of the extraction of the metal of interest using saltingout 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 neglisible 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.

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.