

LECTURE # 9

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”.

$$D = [X]_1 / [X]_2 \quad (1)$$

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;

$$D = [X]_{\text{org}} / [X]_{\text{aq}} \quad (2)$$

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,

$$\alpha = D_A / D_B \quad (3)$$

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

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

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 .

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 into 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).

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. The 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 consist 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.

General Features of Extractant

There are several general features which are essential for an extractant,

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.