CHAPTER - I

I N T R O D U C T I O N

Part I

General Discussion on Solvent-Extraction:

Solvent or liquid-liquid extraction is a technique in which a solute is allowed to distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an organic solvent. It is necessary to clarify the fundamental principles of extractions particularly the various terms used for expressing the effectiveness of a separation.

Partition Coefficient:

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

$$K_D = \frac{\text{Metal ion Concentration in Organic Phase}}{\text{Metal ion Concentration in Aqueous Phase}} \quad \ldots (1)$$

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

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

Distribution ratio or Extraction Coefficient (D):

In the solvent extraction technique the primary interest of analysts lies in the fraction of the total solute in one or other phase, quite regardless of its mode of dissociation, association or interaction with other dissolved species. Hence it is required to introduce a reliable quantity to describe the extraction, known as the distribution ratio (D).

$$D = \frac{\text{Total metal concentration in the organic phase}}{\text{Total metal concentration in the aqueous phase}} \quad \ldots (2)$$

For a given metal M, present as various species M_1, M_2, M_3 ... M_n and partitioned between an organic phase and an aqueous phase, the extraction can be expressed as

$$D = \frac{[M_1]_{org} + [M_2]_{org} + [M_3]_{org} + \dots + [M_n]_{org}}{[M_1]_{aq} + [M_2]_{aq} + [M_3]_{aq} + \dots + [M_n]_{aq}} \quad \dots (3)$$

In case of polynuclear species, their concentrations are multiplied by the appropriate stoichiometric co-efficient. D and K_D are equal when there is no reaction between the species and other components in either phase.

Percentage extraction:

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

$$\%E = \frac{100\ D}{D + [V_{aq} / V_{org}]} \quad \dots (4)$$

V_{aq} and V_{org} stand for the volumes of the aqueous and organic phases respectively. On simplification this equation becomes,

$$D = \frac{V_{aq}}{V_{org}} \left[\frac{E}{100-E} \right] \quad \dots (5)$$

Where E is percentage extraction. When the volume of the organic phase is equal to the volume of aqueous phase

$$D = \frac{E}{100-E} \qquad \ldots (6)$$

When E approaches from 99 to 100%, the distribution ratio varies from 99 to infinity.

Multiple extraction :

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

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

$$L_A = \left[\frac{V_{aq}}{V_{aq} + V_o D} \right]^n \qquad \ldots (7)$$

For rapid and complete extraction, the distribution ratio (D) must be of very high values. In the above system, the partition isotherm is assumed to be linear i.e., $[A_o] / [A_{aq}] = D$

which remains constant for any value of $[A]$. To achieve good results V_o should be low and n should be of high value.

Separation Factor :

The term separation factor (β), is required to be introduced when the solution contains two species A and B. The separation factor (β) is related to their individual distribution ratios. It can be shown as,

$$\beta = \frac{[A]_o / [B]_o}{[A]_{aq} / [B]_{aq}} = \frac{[A]_o / [A]_{aq}}{[B]_o / [B]_{aq}} = \frac{D_A}{D_B} \quad \ldots (8)$$

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

Complete separation can be achieved when one of the distribution ratios is very small and the other relatively large. If the separation factor is unity, it will be very difficult to separate as the two distribution ratios are equal. In such cases, separation is generally carried out by using counter current extractions.

Classification of Extraction systems :

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

Uncharged covalent species
Simple molecules e.g., I_2, $HgCl_2$, C_6H_5COOH,
Chelate complexes e.g., aluminium oxinate.

Uncharged electrovalent (ion association complexes)
Halometallic acids, e.g., $HFeCl_4$
Amine-anionic complex compounds e.g., $R_3NH^+.FeCl_4^-$
Metal-acid ester complexes e.g., $La(DEHP)_3$
Solvated acids and salts e.g., HNO_3-TBP;
$VO_2(NO_3)_2(TBP)_2$.
Non-solvated salts e.g., $(C_6H_5)_4AS^+.FeCl_4^-$
(DEHP = di-2-ethyl hexyl phosphate;
TBP = tributyl phosphate).

From the view point of theoretical discussion such classifications are meant convenient. For practical purpose, however, it will be more useful to classify according to the type of reagent used, so that the possibilities for separation, etc. can be more easily seen.

Extraction Process :

Thus the main aspects of extraction process are:

(1) Uncharged complex formation.

(2) Distribution of such complex between the two liquid phases.

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

Unchargedcomplex formation depends upon several factors.

The complex may be of different types as (i) simple coordination complex, chelate complex or (ii) as ion association complex.

(i) $M^{+n} + nR^{-} \rightleftarrows MR_n$ (co-ordination) ... (9)

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

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

Gallium 8-quinolinate (chelate)

(ii) An ion association complex is formed by co-ordination in either the cation or the anion of the extractable ion pair.

$$M^{n+} + bB \rightleftarrows MB_b^{n+} \quad \text{(Ion-association)}$$

$$MB_b^{n+} + nX^{-} \rightleftarrows (MB_b^{n+} \cdot nX^{-}) \quad \ldots (10)$$

Example : $[(C_6H_5)_4P^+, Cl^-]$

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

$$MX_{n+a}^{a-} + ay^+ \rightleftarrows (ay^+, MX_{n+a}^{a-}) \text{ (Ion-association)} \quad \ldots (11)$$

Example : $[H^+, FeCl_4^-]$

The stability of a metal coordination complex depends on (a) the acidity of the metal ion (b) basicity of the coordination ligand and (c) special factors related to the configuration of the resultant complex. In the simple co-ordination complex the mono-functional ligands take part and in the chelate complex poly-functional ligands are acting that occupy more than one position in the coordination sphere. The chelate complexes are mostly soluble in organic solvents and hence used in the process of extraction. These chelates are either five or six-membered rings. They may be classified as follows:

(i) positively charged chelates having requisite number of uncharged basic groups of the ligand e.g., Tris (ethylenediamine)-Iron (II).

(ii) Chelates having are anionic and are uncharged basic group of the ligand i.e., neutral chelates e.g., Nickel dimethyl glyoximate.

(iii) Negatively charged chelates having negatively charged basic group of the ligand e.g. Alizarin derivative of Iron (III).

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

(2) In the second stage of extraction, the chelate complex or ion-association complex is distributed uniformly in the solvent depending upon their solubilities.

(3) The third stage is the interaction of the complex in the organic phase. The chelates are not generally interacting with the solvent. In case of ion-association complexes, polymerisation (when concentration increases) and dissociation (in case of dilute solution) should be considered.

Methods of extraction:

In the analytical laboratory the following three methods of liquid-liquid extractions are in use. They are:

a) Batch extraction

b) Continuous extraction

c) Discontinuous extraction

a) Batch extraction is the simplest method of extraction and is useful when the distribution ratio is large. In this method a given volume of metal salt solution is extracted with a given volume of the organic solvent in a separating funnel by mechanical shaking until equilibrium is attained, and the two layers are then separated. After separation the metal in each phase is estimated.

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

c) Craig[1] has used this technique for rapid separation and applied in fractionation of organic compounds having similar distribution ratios.

Techniques in extractions :

(i) Organic solvent :

The choice of solvent in the extraction procedure depends on many factors, mainly the solubility of the particular species to be extracted.

(ii) Analysis :

The amount of solute present in both the phases after extraction can be determined in various ways. One important method

is back extraction of solute from organic phase with water or acid followed by analysis. Another method consists of direct evaporation of organic solvent when the solvent is volatile and then estimation of the solute. If the solvent is not very volatile, it may be removed by heating with concentrated nitric and perchloric acids followed by estimation. Most recently the estimation of the organic phase may be carried out by radiometric method[2].

(iii) Selectivity :

The selectivity of an extraction system increases by using oxidising or reducing agents. For example, Chromium (III) is not extracted with diphenyl carbazide but chromium (IV) can be extracted from its solution. Sometimes suitable marsing agents such as cyanide, citrate, tartrate, EDTA etc. are also useful to prevent extractions of undesired element.

(iv) Salting-out agent :

Salting-out agents may also play an important role in enhancing the extent of extraction, especially in case of ion-association complexes. The most widely used salting out agents are chlorides and nitrates of ammonium, sodium, magnesium etc. This is probably due to high concentration of the complexing ion supplied by the salting-out agents.

Some Practical Considerations :

Solvent extraction is generally employed in analysis to separate a solute (solutes) of interest from substances which interfere in the ultimate quantitative analysis of the material; sometimes the interfering solutes are extracted selectively. The choice of solvent is governed by the following consideration:

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

(ii) Low solubility in the aqueous phase.

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

(iv) Low toxicity and inflammability.

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

Stripping :

Stripping is the removal of the extracted solute from the organic phase for further preparation for the detailed analysis.

In many colorimetric procedures involving an extraction process the concentration of the desired solute is determined directly in the organic phase by measuring the absorbance of a known volume of the solution of the coloured complex.

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

Back-Washing :

Impurities present in the organic phase may sometimes be removed by back-washing. The organic extract when shaken with one or more small portions of a fresh aqueous phase containing the optimum reagent concentration and of correct pH will result in the

redistribution of the impurities in favour of the aqueous phase, since their distribution ratios are low; most of the desired elements will remain in the organic layer.

Completion of the analysis :

Having separated a particular element or substance by solvent extraction, the final step involves the quantitative determination of the element or substance of interest. Simple colorimetric or better, spectrophotometric methods may be applied directly to the solvent extract utilising the absorption bands of the complex in the ultraviolet or visible region. A typical example is the determination of nickel as dimethylglyoximate in chloroform by measuring the absorbance of the complex at 366 nm.

With ion-association complexes, improved results can often be obtained by developing a chelate complex after extraction. An example is the extraction of uranyl nitrate from nitric acid into tributyl phosphate and the subsequent addition of dibenzoylmethane to the solvent to form a soluble coloured chelate.

Further techniques which may be applied directly to the solvent extract are flame spectrophotometry and atomic absorption spectrophotometry. An example of the former technique is the determination of copper as the salicylaldoxime complex in chloroform; the organic extract is sprayed directly into an oxyacetylene flame and the spectral emission of copper at 324.7 nm is measured.

Recent Developments :

1. Synergism : The term synergism was first coined by Blake etal[3] in 1958 in their report that when a dialkyl hydrogen phosphate $(RO)_2PO.OH$, is used in conjunction with certain neutral organophosphorous reagents, e.g., TBP, the extracting power of the mixture exceeds the sum of the extracting powers of its components. This phenomenon of greatly enhanced extraction of synergism due to a mixture of extractants has attracted considerable attention in recent years. The review articles by Marcus[4] and De[5] are of interest in this connection.

Synergic systems :

The most intensively studied systems are of the following types : (1) a chelating agent such as HTTA or IPT(-isopropyl-tropolone) and a solvating solvent such as TBP, IBMK (isobutylmethyl ketone), DBSO (dibutyl sulphoxide) and (2) a dialkyl phosphoric acid and a neutral organophosphorous ester(s).

Chelating agent-solvating solvent system :

Considerable work has been done in this area. Irving and Edgington[6] postulated that the conditions for synergic extraction are:

(a) one of the active reagents (HX) should be able to neutralise the charge on the metal ion, preferably by forming a chelate.

(b) the solvent(s) should display any residual coordinated water from the neutral metal complex, rendering it less hydrophilic.

(c) the solvent(s) should not itself be hydrophilic and coordinated less strongly than HX.

(d) the maximum coordination number of the metal and the geometry of the ligands should be favourable.

These postulates were valid for the U(VI)-HTTA-TBP and U(VI)-HTTA-TBPO (tributylphosphine oxide) mixtures, synergic enhancement factors of the order of 10^3 and 10^4 respectively were observed. The extracted species were assigned the composition UO_2X_2.TBP and UO_2X_2.$(TBPO)_3$ respectively[7-9], from isopiestic and infrared measurements. The studies were extended to plutonium (VI), americium (III), europium(III) and thorium and the species identified were PuX_3.$(TBP)_2$, AmX_3.$(TBP)_2$, AmX_3.TBPO, $ThX_3(NO_3)$.TBP and $ThX(NO_3)_3$.TBPO.

Healy[10] reported an synergic extraction of uranium (VI), thorium, lanthanides(III), actinides(III) and alkaline earth metals with HTTA-TBP, HTTA-TBPO and HTTA-TPP; TPP is triphenyl phosphate.

Healy[11] further suggested that the reaction for the system uranium (VI)-HTTA-S can be expressed as :

$$UO_2^{2+} + 2HTTA + xS = UO_2(TTA)_2S_x + 2H^+ \quad \ldots (12)$$

Sekine and Dyrssen[12-17] have reported extensive investigations on solvent extraction of metal ions with mixed ligand. They have described the adduct formation of Cu(II), Zn, Eu(III) and Th with HTTA and TBP or IBMK and with IPT and TBP or IBMK in chloroform and carbon tetrachloride.

Dialkylphosphoric acid (HX)-neutral phosphorous ester(s):

Important cases in this category are : di(2-ethyl-hexyl) phosphoric acid (HDEPH)-TBP, which was the first reported case of synergic extraction[3,18,19]; mono (2-ethylhexyl) phosphoric acid (H_2MEHP)-TBP[20]; dibutyl phosphoric acid (HDBP)-TBP[21] and HDBP-TOPO[22].

Peppard et al[20] investigated the system lanthanide(III), Y(III), Am(III), Cm(III), Th, U(VI)-H_2MEHP-S-diluent, where the synergic agent S was n-decanol, TBP or TOPO and the diluent was toluene, cyclohexane or n-decanol.

Substoichiometric extraction :

Ruzicka and Stary[23,24] first proposed this new technique of substoichiometric extraction and determination of metals, which is applicable to activation analysis and isotope dilution analysis.

In all conventional extraction separation procedures, an excess of the organic reagent is usually used to ensure quantitative separation of the desired metal. In substoichiometric method the organic reagent is added in less than the stoicheiometric amount required for the metal to be determined. By using the same amounts of organic reagent every time, it is possible to isolate always the same amount of the element in question irrespective of the amount of it actually present (subject to the condition that this must be an excess relative to the amount of extractant). This permits highly selective separations. The treatment is essentially that developed by Ruzicka and Stary[23,24].

Liquid Ion-Exchangers:

The use of ligand ion-exchange dates back to 1948 when Smith and Page[25] reported that high molecular weight amines (HMWA) can be used for extraction of acids because their acid salts are insoluble in water but readily soluble in organic solvents such as chloroform, benzene or kerosene :

$$R_3N_{org} + H^+_{aq} + A^-_{aq} \rightleftharpoons R_3NH^+A^-_{org} \text{ (extraction)} \quad \ldots (13)$$

where A^- = anion of simple acid or complex metal acid e.g., $FeCl_4^-$, and $R_3NH^+A^-_{org} + B^-_{aq} \rightleftharpoons R_3NH^+B^-_{org} + A^-_{aq}$ (anion exchange) The amine salt[13] can undergo anion-exchange with an anion (B^-) in the aqueous phase. The order of preference in the organic amine solution is similar to that in anion-exchange resins.

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

The earlier work for liquid anion-exchangers (HMWA) has been reviewed by Moore, Green and Prabhu[26-29].

Reversed-phase Partition Chromatography :

In reversed-phase partition chromatography the organic extractant is immobilized on some stationary inert support such as kieselguhr, styrenedivinylbenzene copolymer or simply filter paper. The technique was introduced by Fidelis and Siekierski[30] for the separation of the lighter rare earth on columns of kieselguhr impregnated with TBP, 15 M nitric acid being used as the mobile phase. They extended their work[31] to the heavier rare earths, which are usually difficult to separate. Fair separations were achieved with 11.5 M , 12.3M and 13 M nitric acid and concentrated hydrochloric acid as the mobile phases.

Combined Ion-Exchange-Solvent Extraction (CIESE) :

Korkisch[32] presented a novel separation technique, viz., combined ion-exchange solvent extraction (CIESE). This is based on simultaneous operation of ion-exchange and solvent extraction.

Ternary Complexes

Betteridge and West[33] described the selective extraction of microgram amounts of dibutylamine silver(I) with an ion-association complex (or ternary complex) with salicylic acid. Dagnall and West[34] described the extraction of a blue ternary complex Ag(I)-1,10-phenanthroline-Bromopyrogallol Red-as the basis of an extremely sensitive spectrophotometric procedure for trace of silver.

Ternary complexes have been reviewed by Babko[35].

Extraction from molten salts

The oldest examples of extractions of solutes from molten salts are the removal of impurities by slag formation in metallurgy, the fire-assay method for separation of gold. None of these is particularly useful in solvent extraction chemistry, although a process akin to slagging was used to remove fission products from rreactor fuel by extraction with magnesium chloride[36,37] according to the reaction (for a tetravalent metal such as a lanthanide).

$$2M_{(m)} + 3MgCl_{2(S)} \rightleftharpoons 2MCl_{3(s)} + 3Mg_{(m)} \quad \ldots (14)$$

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

The use of organic solvents in conjunction with molten salt was reported by Gruen and co-workers[38]. Marcus[39] has given an excellent review of this extraction from molten salts.

Extractive titrations and indicators

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

Programme of work with iron, cobalt, platinum, copper, palladium, nickel and Bismuth

Numerous methods on spectrophotometric determination of iron, cobalt, platinum, copper, palladium, nickel and Bismuth are available in the literature. Further attempt has been made to apply this technique for the spectrophotometric method of these elements, where the methods are simple.

The basic points of the scheme are:

(i) Review of the literature on spectrophotometric methods of these metals and on their separation from mixtures.

(ii) Choice of appropriate reagents for obtaining suitable complexes and also of solvents.

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

(iv) Actual experiments on extraction and separation.

Throughout the investigation effort has been put to minimise the wastage of chemicals, time and power and to prevent the loss of the precious metals.

Part II

Absorptiometry and Spectrophotometry : Analytical Basis

The colorimetric analysis is based on the variation of the colour of a system with change in concentration of some component. The colour displayed is due to the formation of a coloured compound by the addition of a suitable reagent or it may be inherent in the desired constituent itself. The intensity of the colour may then be compared with that obtained by treating a known amount of the substance in the same manner.

Colorimetry is concerned with the determination of the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of the substance. In visual colorimetry, natural or artificial white light is normally used as a light source, and determinations are carried out with a simple instrument called a colorimeter or colour comparator. When the eye is replaced by a photoelectric cell (thus largely eliminating the errors due to the personal characteristics of each observer) the instrument is termed a photoelectric colorimeter. This instrument is also known as filter photometer because it is employed with light contained within a comparatively narrow range of wavelengths furnished by passing white light through filters, i.e., materials in the form of plates of coloured glass, gelatin, etc., transmitting only a limited spectral region.

In spectrophotometric analysis a source of radiation is used that extends in to the ultraviolet region of the spectrum. From this, definite wavelengths of radiation are chosen possessing a bandwidth of less than 1 nm. This process necessitates the use of a more complicated and consequently more expensive instrument. The instrument employed for this purpose is a spectrophotometer, and this instrument is really two instruments in one cabinet- a spectrometer and a photometer.

Molecules or atoms which absorb radiation characteristically may be determined or studied by measurement of light absorbed. Light from a suitable source is allowed to pass via an optical system, that isolates a narrow band of wavelengths, through a homogeneous absorbing medium.

The layer is usually planer, liquids and vapours being enclosed in cylindrical or rectangular cells. The intensity of the radiation transmitted by the medium, I is compared with the incident intensity, Io, by allowing each in turn to pass to a suitable detector. Since cells and solvents may absorb radiation, and to compensate also for reflection and similar optical effects from the cell faces, a matched cell containing only the solvent medium is interposed in the beam during the measurement of Io. The detection is often a photoelectric cell (photo cell) sensitive in the required wave length region and forms part of the photometric device which measures the intensity. Since the detector

response is related to the radiant energy falling upon it, the instrument normally measures a ratio of the two intensities, I/I_o, termed the transmittance, T. The detection signal may be amplified and presented in various forms, such as percentage transmittance (100T) or 100 I/Io or absorbance, A(-log T).

Two important properties are concerned in absorption measurements, wave length and degree of absorption. The wave length at which absorption occurs are determined by the energy difference, ΔE, between the upper and lower energy states of each possible transition of the molecule (or atom) concerned.

The degree of absorption is expressed by means of an experimentally measured absorptivity per unit quantity of substance. This is termed the extinction co-efficient and is defined by means of Beer-Lambert law. This law is a combination of two absorption laws, which may be stated in a variety of ways.

Lambert's (or Beer's) law deals with optical path length. The law states that the intensity of the emitted monochromatic light decreases exponentially as the thickness of the absorbing medium increases arithmetically or that any layer of given thickness of the medium absorbs the same fraction of the light incident upon it. The law can be expressed as:

$$I = I_o e^{-kl}$$

Where Io = intensity of the incident light falling upon an absorbing medium.

l = thickness of the absorbing medium.

I = intensity of the transmitted light.

k = a constant for the wave length and the absorbing medium.

e = the natural logarithm base.

Rearranging the above equation,

$$\ln Io/I \text{ or } 2.303 \log Io/I = kl$$

or $$\log Io/I = kl/2.303$$

or $$\log Io/I = kl$$

Where K = k/2.303 and is termed the extinction co-efficient or absorbance index. Its value is characteristic at a given temperature for a pure homogeneous liquid or solid, provided it exhibits no directional absorption properties, but not for a gas or solution in which the number of molecules per unit thickness varies with pressure or concentration.

Beer's law deals with concentration. It states that the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. The solvent is assumed to be non absorbing, in the simplest case. This can be written in the form,

$$I = Ioe^{-kc}$$

For general use the two laws are combined and using the above mathematical treatment the Beer-Lambert law may be expressed in the form,

$$\text{Log} \quad Io/I = k'Cl$$

$$\text{or } A = k'Cl$$

Where c is the concentration of the absorbing substance as solute, l is the thickness and k', the extinction co-efficient, is a combination of constants. The property log Io/I is linearly related to concentration and path length and is termed the absorbance A; it is also known as the optical density (D).

The Beer-Lambert law is the basis of accurate analytical absorptiometry and spectrophotometry at all wave lengths. Both laws are held to be generally valid, though kortum considered Beer's law to be limiting law, valid only at low concentrations.

For matched cells (i.e., l constant) the Beer-Lambert law may be written as,

$$C \propto \log \frac{Io}{I}$$

$$\text{or } C \propto \log \frac{1}{T} \quad [\text{where T = transmittance}]$$

$$\text{or } C \propto A$$

Hence by plotting A (or log $\frac{1}{T}$) as originate, against concentration as abscissa, a straight line will be obtained and this will pass through the point C = 0, A = 0 (T = 100%). This calibration line may then be used to determine unknown concentrations of solution of the same material after measurement of absorbances.

Extinction co-efficient or absorptivities :

From Beer's law we have,

$$A = k'Cl$$

The numerical value of k' depends on the units chosen for expressing C and 1 in the above equation. The intensity units are immaterial and 1 is always in cm units. If the concentration is expressed in moles per litre, the constant is known as molar or molecular extinction co-efficient (European system) or molar absorptivity (U.S. system) and is written as ϵ , giving the form,

$$A = \epsilon Cl$$

Deviation from Beer's law:

Beer's law will generally hold over a wide range of concentration if the structure of the coloured ion or of the coloured non-electrolyte in the dissolved state does not change with concentration. Small amount of electrolytes, which do not react chemically with the coloured components, do not usually affect the light absorption; large amounts of electrolytes may result in a

shift of the maximum absorption and may also change the value of the extinction co-efficient. Discrepancies are usually found when the coloured solute ionises, dissociates or associates in solution, since the nature of the species in solution will vary with the concentration. The law does not hold when the coloured solute forms complexes, the composition of which depends upon the concentration. Also discrepancies may occur when monochromatic light is not used. The behaviour of a substance can always be tested by plotting log Io/I or log T against the concentration : a straight line passing through the origin indicates the conformity to the law.

Some aspects of Colorimetric Determination :

The choice of a colorimetric procedure for the determination of a substance will depend upon such considerations as the following:

1. A colorimetric method will often give more accurate result at low concentrations.

2. The method may frequently be applied under conditions when no satisfactory gravimetric or titrimetric procedure exists.

3. Speed and rapidity, provided the experimental conditions are rigidly controlled to avoid any serious sacrifice of accuracy.

The criteria for a satisfactory colorimetric analysis are:

(a) Specificity of the colour reaction

(b) Proportionality between colour and concentration

(c) Stability of the colour

(d) Reproducibility

(e) Clarity of the solution

(f) High sensitivity.

Proposed Investigation :

Most of the available extraction spectrophotometric methods for the determination of cobalt, palladium, nickel, bismuth, copper, platinum and iron are based on colour-forming reactions with various reagents - mostly organic. In majority of cases, after separation, determinations were carried out by measuring the absorption of the coloured metal complexes in the visible region. Methods based on such colour-forming reactions are always found to be dependent on various factors i.e., the pH of the medium, the reagent concentration, stability and extractability of the coloured complex as also the absorption of the reagent itself.

In the proposed investigation the above mentioned metal ions in micro quantities are made to react with a suitable ligand or ligands to give complexes in the form of coloured precipitates. The precipitates are readily soluble (except cases in Chapter VI and VII where determination procedures are accomplished using aqueous solutions) and extractable in certain immiscible organic solvents. The complexes in organic solvents or in aqueous

medium absorb considerably in the visible region and conform to Beer's law for a fairly wide range of metal ion concentration. Further, the solubility and the intensity of the colour systems are found satisfactorily high. Measurement of absorbance of the coloured extract at the wave length recording maximum absorption, has made possible development of new spectrophotometric methods for determination of the metal ions under investigation.

R E F E R E N C E S

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