CHAPTER I

INTRODUCTION

PART I

General Discussion on Solvent Extraction

Solvent or liquid-liquid extraction is a technique in which a solution (usually aqueous) is brought into contact with a second solvent (usually organic), essentially immiscible with the first, in order to bring about a transfer of one or more solutes into the second solvent. It is necessary to make the fundamental principles of extractions clear particularly the various terms used for expressing the effectiveness of a separation.

Partition co-efficient :

For an analytical chemist the aqueous-organic solvent pair is of special interest since he is concerned with the analysis of the element present in the aqueous phase. If a solute is allowed to dissolve within two immisible or slightly 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 phase at equilibrium at particular temperature remains constant, provided that the molecular weight of the species will have the same in the both phases. This ratio is known as 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 is not thermodynamically rigid but it is a useful approximation (e.g. it takes no account of the activities of the various species, and for this reason would be expected to apply in very dilute solution, where the ratio of the activities approaches unity).

For an ideal case, the species distributes 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 Co-efficient (D) :

In the solvent extraction technique analysts are interested primarily 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 necessary to introduce a reliable quantity to describe the extraction, called 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 partioned between an organic phase and an aqueous phase, the extraction can be expressed as

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

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

Percentage extraction :

The percentage extraction (% E) is more useful. The relation between the distribution ratio and percentage extraction can be expressed as

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

V_{aq} and V_{org} represents the volumes of the aqueous and organic phases respectively. The equation on simplification,

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

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

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

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

Multiple extraction :

This is applicable when the extraction efficiency is less than 100%.

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

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

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., $[Ao]/[A_{aq}] = D$ 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 :

It becomes necessary to introduce a term separation factor (β), when the solution contains two species A and B. The separation factor (β) is related to their individual distribution ratios. Thus

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

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.

It is possible to achieve complete separation when one of the distribution ratios is very small and the other relatively large. When the separation factor will be unity, it is very difficult to separate as the two distribution ratios are equal. In these cases to carry out separation, counter current extractions are generally used.

Classification of Extration systems :

The most convenient way to classify the extraction systems is, on the basis of the nature of the extractable species because a particular system under certain conditions may be grouped under more than one class. Such a classification might be :

uncharged covalent species
simple molecules e.g., I_2, $Hgcl_2$, RuO_4, C_6H_5COOH
chelate complexes e.g., aluminium oxinate.

Uncharged electrovalent species (ion-association complexes)
Halometallic acids e.g., $HFeCl_4$
Amine-anionic complex compounds e.g., $R_3NH^+ \cdot FeCl_4^-$
Metal-acid ester complexes e.g., $La(DEHP)_3$.
Solvated acids and salts e.g, $NHO_3 \cdot TBP$; $VO_2(NO_3)_2(TBP)_2$
Non-solvated salts e.g., $(C_6H_5)_4As^+ \cdot FeCl_4^-$
(DEHP = di-2-ethyl hexylphosphate; TBP = tributyl phosphate)

These classifications are convenient from the point of view of theoretical discussion. For practical purpose, however, it is much 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 :

The three 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 .

Uncharged complex formation depends upon several factors.

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

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

where M^{+n} is an n valent metal ion and R^- is an anion of a suitable chelating or co-ordinating agent.

Examples : Germanium tetrachloride (simple co-ordination)
lead diethyldithiocarbamate (chelate)

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

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

$$MB_b^{n+} + nX^- \rightleftharpoons (MB_b^{n+},\ nX^-) \qquad \ldots (10)$$

Example : $\left[(n\text{-}C_4H_9)_4N^+,\ ReO_4^- \right]$

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

$$MX_{n+a}^{a-} + aY^+ \rightleftharpoons (aY^+,\ MX_{n+a}^{a-}) \quad \text{(Ion association)} \qquad \ldots (11)$$

Example : $\left[H^+,\ FeCl_4^- \right]$

The stability of a metal co-ordination complex depends on (a) the acidity of the metal ion (b) basicity of the co-ordination ligand and (c) special factors related to the configuration of the resultant complex. In the simple co-ordination complex the monofunctional ligands take part and in the chelate complex polyfunctional ligands are acting which occupy more than one position in the co-ordination sphere. The chelate complexes are mostly soluble in organis solvents and are 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 -(phenanthroline)-iron(II).

(ii) Chelates having one anionic and one uncharged basic group of the ligand i.e. neutral chelates e.g. Gallium 8-quinolinate.

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

Ion association complexes e.g. $[(C_6H_5)_4As^+, ReO_4]_2$ are soluble in organic solvents like chloroform, benzene etc. The extent of the 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) Interaction of the complex in the organic phase :

The chelate type complexes generally do not interact with the solvent. But in case of ion association complexes, polymerization (when concentration increases) and dissociation (in case of dilute solution) should be considered.

Methods of extraction :

In the analytical laboratory, three basic types of liquid-liquid extractions are generally utilized. They are :

a) Batch extraction
b) Continuous extraction
c) Discontinuous extraction

(a) Batch extraction is the simplest extraction procedure and is the most used for analytical separation. The method 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 untill equilibrium is attained, and the two layers are then separated. After separation the metal in each phase is estimated.

(b) The continuous extraction makes use of a continuous flow of immiscible solvent through the solution or a continuous counter current flow of both phases. In continuous extraction the spent solvent is stripped and recycled by distillation or fresh solvent is added continuously from a reservoir. This method is applicable when the distribution ratio is small.

(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 is the direct evaporation of organic solvent if the solvent is volatile and then the solute is estimated. If the solvent is not so volutile, it may be removed by heating with concentrated nitric and perchloric acid followed by estimation. Most recently the organic phase may be estimated by radiometric method[2].

(iii) Selectivity :

Use of oxidising or reducing agents increases the selectivity of an extraction system. For example chromium (III) is not extracted with diphenyl carbazide but chromium (IV) can be extracted from its solution. Sometimes suitable masking agents like cyanide, citrate, tartarate, EDTA etc. are also used to prevent extractions of undesired element.

(iv) Salting-out agent :

The extent of extraction may be enhanced with the help of salting-out agents, especially in case of ion-association complexes. The most popularly 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 difference 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.

Striping : Striping 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 determinated 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 necessary, 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.

<u>Back-washing</u> : Impurities present in the organic phase may be 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 concentrations 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 element 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 is the salicylaldoxime complex in chloroform; the organic extract is sprayed directly into an oxy-acetylene 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 et al[3] in 1958 in their report that when a dialkyl hydrogen phosphate $(RO)_2PO.OH$, is used in conjunction with certain neutral organophosphorous reagent e.g. TBP, the extracting powers of the mixture exceeds the sum of the /‾extracting powers of its components. This phenomenon of greatly enhanced_7 extraction or 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 (/3-isopropyltropolone) and a solvating solvent such as TBP, IBMK (isobutylmethyl ketone), DBSO (dibutyl sulphoxide) and (2) a dialkylphosphoric 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 neutralize the charge on the metal ion, preferably by forming a chelate.

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

(c) the solvent(s) should not itself be hydrophilic and co-ordinated less strongly than Hx.

(d) the maximum co-ordination 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_2TBP and $UO_2X_2(TBPO)_3$ respectively[7-9], from isopiestic and inframed measurements. The studies were extended to plutonium(VI), americum(III), europium(III) and thorium, and the species indentified were

$PuX_3(TBP)_2$, $AmX_3(TBP)_2$, AmX_3TBPO, $ThX_3(No_3)TBP$ and $ThX(No_3)_3$ TBPO.

Healy[10] reported on 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 (S = organophosphorus ester) :

$$UO_2^{2+} + 2HTTA + xS = UO_2(TTA)_2S_n + 2H^+ \qquad \ldots \ (12)$$

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 carbontetrachloride.

Dialkylphosphoric acid (Hx) - neutral phosphorous ester(s) system :

Important cases in this category are : di(2-ethylhexyl) 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), Cen(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.

Substoicheiometric extraction :

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

Liquid Ion-exchangers :

The use of liquid ion-exchange dates back to 1948 when 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 solvent such as chloroform, benzene or kerosene :

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

where A^- = anion of simple acid or complex metal acid e.g., $FeCl_4^-$, and

$$R_3NH^+A^-_{org} + B^-_{aq} \rightleftharpoons R_3NH^+B^-_{org} + A^-_{aq} \text{ (anion exchange)}$$

The amine salt[13] can undergo anion-exchange with an anion (β^-) 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 chromatography :

In reversed phase chromatography the organic extractant is immobilized on some stationary inert support such as kieselguhr, styrene-divinylbenzene 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.

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 complex :

Betteridge and West[33] described the selective extraction of microgram amounts of dibutylamine silver(I) with an ion-association complex (or ternary complex) with salicyclic 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 produce from reactor fuel by extraction with magnesium chloride[36,37] according to the reaction (for a tetravalent metal such as a lanthanide).

$$2M_{(m)} + 3MgCl_{3\,(s)} + 3Mg_{(m)} \qquad \ldots (14)$$

where the subscripts (m) and (s) denotes the metal and salt phase.

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 the 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, molybdenum, platinum, gold, copper, vanadium and palladium :

Numerous methods on spectrophotometric determination of iron, cobalt, molybdenum, gold, copper, vanadium and palladium 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.

(v) Choice of convenients and easier method of 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 variation of the colour of a system with change in concentration of some component forms the basis of what the chemist commonly terms colorometric analysis. The colour is usually due to the formation of a coloured compound by the addition of an appropriate 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.

Colorometry 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 generally used as a light source, and the determinations are usually made with a simple instrument termed a colorimeter or colour comparator. When the eye is replaced by a photoelectric cell (to eliminate the errors due to the personal characteristics of each observer) the instrument is termed a photoelectric colorimeter. In spectrophotometric analysis a source of radiation is used that extends into the ultraviolet region of the spectrum. For this, definite wavelength of radiations are chosen possessing a bandwidth of less than 1 nm. The process necessiates the use of a more complicated and consequently more expensive instrument. The instrument employed for this purpose is a spectrophotometer, which is actually 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 the light absorbed. Incident radiation is emitted from a suitable source and is passed via an optical system, which isolates a narrow band of wavelengths, through a homogeneous layer of the absorbing medium.

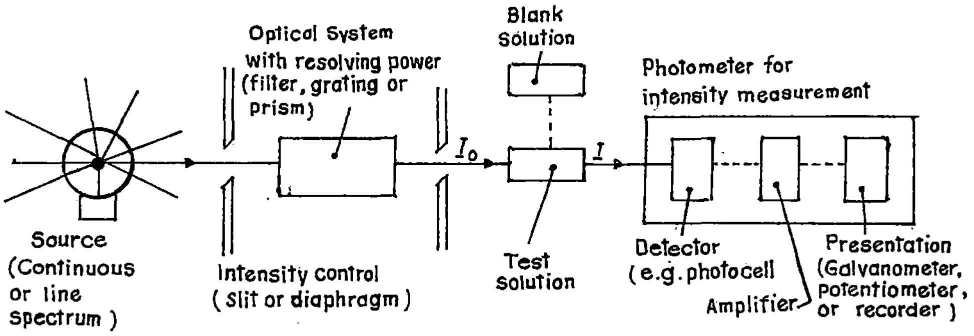

FIG. BASIC ELEMENTS OF ABSORPTIOMETRIC INSTRUMENTS (SINGLE-BEAM OPERATION)

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 wavelength 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/Io, termed the transmittance, T. The detection signal may be amplified and presented in various forms, such as percentage transmittance (100 T) or 100 I/Io or absorbance, A(-log T).

Two important properties are concerned in absorption measurements, wavelength 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 Bouguer's) law deals with optical path length. It states that the intensity of a beam of parallel monochromatic radiation decreases exponentially i.e., in geometric progression, as it traverses a thickness (or path length) of homogeneous absorbing medium.

$$I = Io\ e^{-Kl}$$

where l is the thickness, e the natural logarithm base and K is a constant for the medium at the particular wavelength. Rearranging the above equation

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

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

$$\log Io/I = Kl$$

where K = K/2.303 and is termed the extinction coefficient 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 parallel monochromatic beam decreases exponentially with the number of absorbing molecules encountered i.e., the concentration of the absorbing substance in a homogeneous solution. The solvent is assumed to be non-absorbing, in the simplest case. For general use the two laws are combined and, using the above mathematical treatment, the Beer-Lambert law may be expressed in the form

$$\log I_o/I = K'cl$$

$$\text{or} \quad A = K'cl$$

where c is the concentration of the absorbing solute l is the thickness and K', the extinction coefficient, 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 wavelengths. Both laws are held to be generally valid, though Kortum considered Beer's law to be a limiting law, valid only at low concentrations.

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

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

$$\text{or} \quad C \propto \log \frac{1}{T}$$

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

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 l in the above equation. The intensity units are immaterial and l is always in cm units. If the concentration is expressed in moles per litre, the constant is known as molar or molecular extinction coefficient

(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 dissolve 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 colourimetric 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.

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