SOLVENT EXTRACTION

PRESENTED
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FOR SEM 6(H) STUDENTS, PAPER – DSEA4, DATE-23.02.2023

30.10 Extraction Methods

1. Introduction

Although solvent extraction method is known for a long time to the chemists, it has received the recognition of chemists as a method of separation recently. This method has much in common with fractional distillation.

(Solvent extraction involves the partition or distribution of a solute between two immiscible liquids in contact with each other.) The process has become increasingly important in the analysis of metals because it furnishes clean separations in a short span of time and has the further advantages of simplicity of technique and equipment.

The distribution of a solute between two immiscible phases is an equilibrium process that can be treated by the law of mass action. Equilibrium constants for this process vary enormously among solutes, thus making possible many useful separations based on extraction. The extraction technique has been widely used to separate the components of organic systems. For example, carboxylic acids are readily separated from phenolic compounds by extracting a nonaqueous solution of the sample with dilute aqueous sodium bicarbonate. The carboxylic acids are almost completely transferred to the aqueous phase, while the phenolic constituents remain in the organic phase.

The process of solvent extraction with solvents is generally employed either for the isolation of dissolved substances from solutions or from solid mixtures or for the removal of undesired soluble impurities from mixtures. The latter process is known as washing.

2. Theory

The partition of a solute between two immiscible solvents is governed by the *distribution law*. If we assume that the solute species A distributes itself between an aqueous and an organic phase, the resulting equilibrium may be written as

$$A_{aq} \rightleftharpoons A_{org}$$

where the subscripts aq and org refer the aqueous and organic phases, respectively. Ideally the rations of the activities of A in the two phases will be constant and independent of the total quantity of A. That is, at any given temperature

$$K = \frac{[A_{org}]}{[A_{aq}]} \tag{30.1}$$

where the equilibrium constant K is the *partition coefficient* or *distribution coefficient*. The terms in brackets are strictly the activities of A in the two solvents, but molar concentrations can frequently be substituted without serious error. Often, K is approximately equal to the ratio of the solubility of A in each solvent.

The solute may exist in different states of aggregation in the two solvents. Then, the equilibrium becomes

$$x(A_y)_{aq} \rightleftharpoons y(A_x)_{org}$$

and the partition coefficient takes the form

$$K = \frac{\left[(A_x)_{org}\right]^y}{\left[(A_y)_{aq}\right]^x}$$

Partition coefficients make it possible to establish the experimental conditions required to transfer a solute from one solvent to another. For example consider a simple system that is adequately described by Equation 30.1. Suppose, further, that we have V_{aq} mL of an aqueous solution containing a_0 mmol of A and that we propose to extract this with V_{org} mL of an immiscible organic solvent. At equilibrium, a_1 mmol of A will remain in the aqueous layer, and we may write

$$[A_{aq}]_1 = \frac{a_1}{V_{aq}}$$

It follows, then, that

$$[A_{org}] = \frac{(a_0 - a_1)}{V_{org}}$$

Substitution of these quantities into Equation 30.1 gives upon rearrangement

$$a_1 = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)a_0 \tag{30.2}$$

The number of millimoles, a_2, remaining into Equation 30.1 gives upon rearrangement

$$a_2 = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)a_1$$

When this expression is substituted into Equation 30.2, we obtain

$$a_2 = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^2 a_0$$

After n extractions, the number of millimoles remaining is given by the expression

$$a_n = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^n a_0 \tag{30.3}$$

Equation 30.3 can be rewritten in terms of the initial and final aqueous concentration of A by substituting the relationships

$$a_n = [A_{aq}]_n V_{aq} \qquad \text{and} \qquad a_0 = [A_{aq}]_0 V_{aq}$$

where $[A_{aq}]_n$ is the concentration in the aqueous phase after n extractions. Substitution of these relationships into Equation 30.3 gives

$$[A_{aq}]_n = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^n [A_{aq}]_0 \tag{30.4}$$

As shown in the example that follows, the exponential nature of Equation 30.4 indicates that a more efficient extraction is achieved with several small volumes of solvent than a single large one.

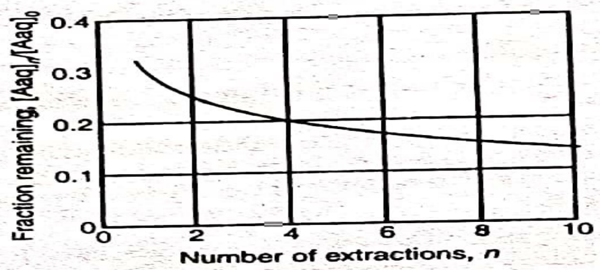


Fig. 30.1 : Plot of Equation 27.4 assuming $K = 2$ and $V_{aq} = 100$. The total volume of the organic solvent was also assumed to be 100, so that $V_{org} = 100/n$.

Figure 30.1 demonstrates that the improved efficiency brought about by multiple extractions falls off rapidly as the number of subdivisions increases. Clearly, little is gained by dividing the extracting solvent into more than five or six portions.

SOLVED EXAMPLES

Example 1. Calculate the mg of iron (III) left unextracted from 100 ml of a solution having 200 mg of Fe^{3+} and is 6 M in HCl after three extractions with 25 ml of ethyl ether. The value of D for this extraction is 150.

Sol. On substituting the given data in Eq. 30.4 we get

$$[A_{aq}]_n = 200\left(\frac{100}{150 \times 25 + 100}\right)^3 = 200\left(\frac{100}{3850}\right)^3$$

$$= 200 \times (0.026)^3 = 3.5 \times 10^{-3} \text{ mg.}$$ **Ans.**

Example 2. Calculate the amount of iron left in the iron–ether system of example 1 if only one extraction with a 75 ml portion of ether had been used.

Sol. In this case $[A_{aq}]_n = 200\left(\frac{100}{150 \times 75 + 100}\right) = 200\left(\frac{100}{11350}\right)$

$$= 200 \times 8.8 \times 10^{-3} = 1.8 \text{ mg}$$ **Ans.**

Thus, it is evident that three extraction with 25 ml portions are approximately 500 times more effective than one extraction with 75 ml of ether.

Example 3. The distribution coefficient of I_2 between CCl_4 and H_2O is 85. Calculate the concentration of I_2 remaining after extracting 50.0 mL of an aqueous 1.00×10^{-3} M solutions of I_2 with (a) 50.0 ml, CCl_4, (b) two 25.0 mL portions of CCl_4 and (c) five 10.0 mL portions.

Sol. Substituting into equation (30.4)

a. $$[I_{2aq}]_1 = \left(\frac{50.0}{50 \times 85 + 50}\right)^1 \times 1.00 \times 10^{-3} = 1.16 \times 10^{-5}$$

b. $$[I_{2aq}]_2 = \left(\frac{50.0}{25 \times 85 + 50}\right)^2 \times 1.00 \times 10^{-3} = 5.28 \times 10^{-7}$$

c. $$[I_{2aq}]_5 = \left(\frac{50.0}{10 \times 85 + 50}\right)^5 \times 1.00 \times 10^{-3} = 5.29 \times 10^{-10}$$

30.11 Sequence of the Extraction Process

Although the actual reactions may vary from system to system, all extraction processes may involve the following three basic steps :

1. Formation of a distributable species : In the first step, there occurs the reaction of the metal ion in the water phase with the complexing agent to form either a neutral molecular species or an extractable ion pair. If a neutral molecular species is assumed to be formed, the reaction may be represented as follows:

$$M + nL \rightarrow MLn \qquad (30.5)$$

where M is a metal ion and L is ligand. In reaction (*i*), charges have been omitted for simplicity. If more than one ligand is involved, complexes will be formed in steps and there may be appreciable quantities of intermediate species present. Further, the metal may undergo reactions with other complexing agents to form other complexes like MAn and may also undergo hydrolysis to form M(OH)*n*. Each of these interfering reactions may also occur in steps.

Suppose an ion pair is formed by incorporating the metal into a larger positive organic ion. These reactions may be represented as follows :

$$M^{n+} + xL \rightarrow ML_x^{n+} \qquad (30.6)$$

$$ML_x^{n+}\ nA^{+} \rightarrow [ML_x^{n+}.\ nA^{-})$$

It is also possible to write similar equations for the formation of a negative metal complex ion and ion pair. Also, intermediates may be formed and the metal ion may undergo reaction with other complexing agents to undergo hydrolysis.

2. Distillation of the distributable species : After the formation, the distribution species moves across the boundary until an equilibrium is established and the equilibrium concentrations satisfy the distribution law. This may be represented as follows :

$$(MLn)_o \rightleftharpoons (MLn)_w$$

In the above reaction, the parentheses represent active concentrations while the superscripts *o* and *w* refer to the organic and water phases respectively. The usual practice is to substitute molar concentrations by activities in most extraction calculations.

3. Interactions in the organic phase : After moving across the phase boundary, the extractable complex may undergo polymerisation or dissociation or may undergo interaction with other components in the organic phase. All these possible interferences will affect the distribution and may result significant differences between D and K_d.

30.12 Extraction Technique

1. Batch extraction : This is the most common type of extraction technique in which the organic liquid is added to the solution to be extracted in a separating funnel (Fig. 30.2). After agitation for sufficient length of time, the layers are allowed to separate. Now the top is opened and the lower heavier layer is allowed to drain through the stop–cock. If more extractions are required and the lower layer is the organic layer, a second portion of the organic liquid is added and the process is made to repeat. If the organic layer is present in the upper layer, the aqueous layer is transferred to a second separating funnel and a second portion of the organic liquid is added. The process is made to repeat as many times as required to ensure satisfactory separation. The method for calculating the efficiency of batch separations has been illustrated in examples 1 and 2.

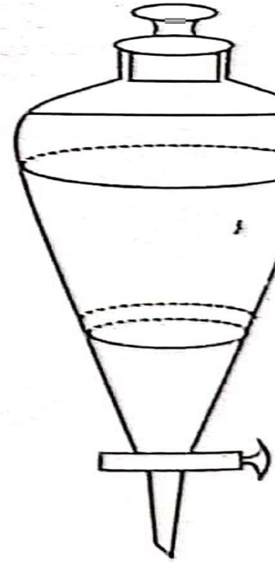


Fig. 30.2

2. Stripping or back extraction : After the material is extracted into organic layer, the usual practice is to return the extracted material to water for the analytical procedure to be used in the determination. This block extraction is known as *stripping*. For the systems sensitive to pH, the usual practice is to agitate the organic solution with an aqueous solution which has been adjusted to a pH value which is below the pH range in which the metal is extracted into the organic phase. In some cases, the organic liquid having the solute is agitated with an aqueous solution having a complexing agent which reacts with metals to form metal complexes that are more soluble in water than in the organic liquid used in the extraction.

3. Continuous extraction : For satisfactory separation, the usual practice is to have a large number of multiple batch extractions which are made possible by the use of continuous extraction procedure. Extraction equipments have been devised for continuous extraction using organic solvents which are lighter than water or heavier than water. Such equipments have been shown in Fig. 30.3 (*a*) and (*b*).

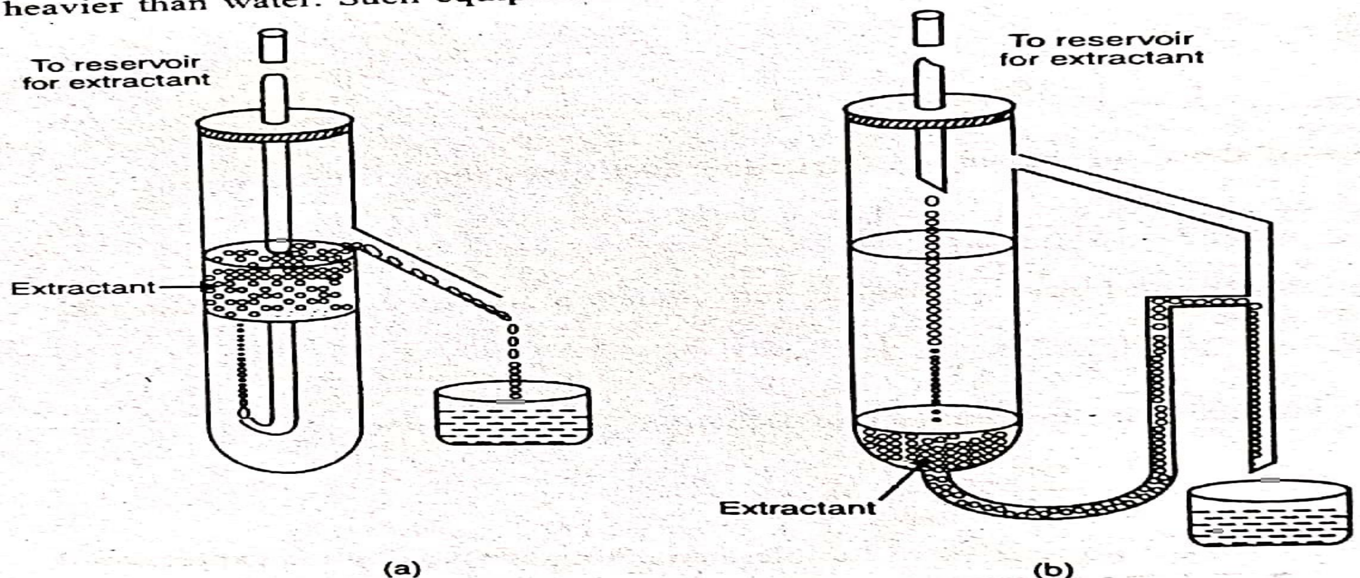


Fig. 30.3 : Continuous–flow solvent extractors (*a*) for extractants lighter than water and (*b*) for extractants heavier than water.

The apparatus shown in Fig. 30.3 (*a*) is used when the organic solvent is lighter than the solution to be extracted while the apparatus shown in Fig. 30.3 (*b*) is used for organic liquids heavier than the solution to be extracted.

The usual practice is to agitate the solutions during extraction. Alternatively, the entry tube for the solvent may be rotated to have more uniform distribution and more efficient extraction. For systems having tendency to produce emulsions, the agitation should be minimal.

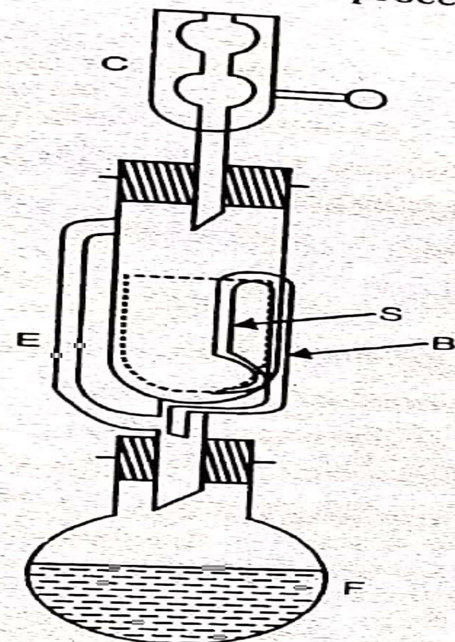
4. Counter–current extraction : In a true counter–current extraction, the two immiscible solvents contact each other as they flow through one another in opposite directions. Such extractions procedures have been found to be very difficult because fresh extractant is brought into contact with the solute depleted phase and the solute–enriched extractant is brought into contact with fresh aqueous solution. The amount of solute in either phase after any number of contact steps can be calculated from a Binominal expansion.

For carrying out counter–current extractions, various devices have been proposed.

5. Extraction of Solids. Even though the extraction or leaching of solids is not a true liquid–liquid portioning process, it is considered to be an important example of an extraction phenomenon. In the

...plest procedure, the solid is covered with the liquid, and, after agitation for a suitable period the liquid ... solid are separated by decantation, centrifugation or filtration. Most continuous extraction procedures ... solids utilise the Soxhlet extractor shown in Fig. 30.4. Soxhlet extractions may be allowed to run ...bserved for long time and save analyst time.

Soxhlet extractors are mainly used for analysing biological and other samples for fats and oils. ...vever, they are seldom used for inorganic extraction procedures.



...4 : Soxhelt extractor C = condenser, E = extractor, S = Siphon, B = boiling vapours and F = flask

...pplications of Extraction Procedures

...n extraction is often more attractive than a classic precipitation for separating inorganic species ...ocesses of equilibration and separation of phases in a separatory funnel are inherently less tedious ...e–consuming than precipitation, filtration, and washing. In addition, problems of coprecipitation and ...cipitation are avoided. Finally, and in contrast to the precipitation process, extraction procedures ...lly suited for the isolation of trace quantities of a species.

...ganic Separations

...her extractions of metal chlorides. The data in Table 30.3 indicate that a substantial number of ...lorides can be extracted into ether from 6 M hydrochloric acid solution; equally important, a large ... of metal ions are either unaffected or extracted only slightly under these conditions. Thus, many ...eparations are possible. One of the most important of these is the separation of iron (III) (99% ...d) from a host of other cations. The greater part of iron from steel or iron ore samples can be ... by extraction prior to analysis for such trace elements as chromium, aluminium, titanium or nickel ...cies extracted has been shown to be the ion pair H_3O^+ $FeCl_4^-$. It has also been found that the ...ge of iron transferred to the organic phase is dependent upon the hydrochloric acid content of ...ous phase (little is removed from solutions that are below 3 M and above 9 M HCl) and, to some extent, upon the iron content. Unless special precautions are taken, extraction of the last traces of iron is incomplete.

Extraction of nitrates. Certain nitrate salts are selectively extracted by ether as well as other organic solvents. For example, uranium is conveniently separated from such elements as lead and throium by ether extraction of an aqueous solution that is saturated with ammonium nitrate and has a nitric acid concentration of about 1.5 M; the uranium must be in the +6 oxidation state. Bismuth and iron(III) nitrates are also extracted to some extent under these conditions.

Table 30.3 : Ethyl Ether Extractions of Various Chlorides from 6 M Hydrochloric Acid

Percent Extracted	*Elements and Oxidation State*
90–100	Fe(III), 99%; Sb(V), 99%; Ga(III), 97%; Ti(III), 95%; Au [III] 95%
50–90	Mo(VI), 80–90%; As(III), 80%; Ge(IV), 40–60%
1–50	Te(IV), 34%; Sn(II), 15–30; Sn(IV), 17%, Ir(IV), 5%; Sb(III), 25%
< 1 > 0	As(V), Cu(II), In(III), Hg(II), Pt(IV), Se(IV), V(V), V(IV), Zn(II)
0	Al(III), Bi(III), Cd(II), Co(II), Be(II), Fe(II), Pb(II), Mn(II), Ni(II), Os(VIII), Pd(II), Rh(III), Ag(I), Th(IV), Ti(IV), W(VI), Zr(IV)

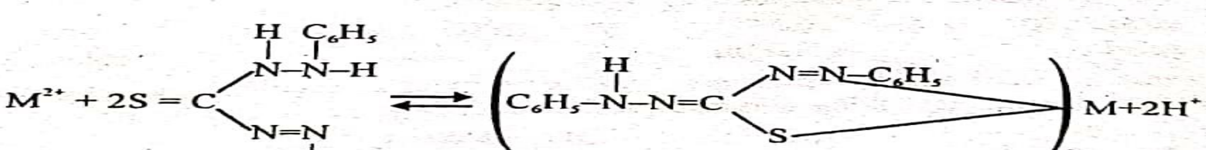
Extraction of chelate compounds. Many of organic reagents form chelates with various metals ions; these chelates are frequently soluble in such solvents as chloroform, carbon tetrachloride benzene, and ether. Thus, quantitative transfer of the metals ions to the original phase is possible.

A reagent that has widespread application for extractive separation is 8, hydroxyquionoline. Most of its metal chelates are soluble in several organic solvents. The reaction which occurs when an aqueous solution of a divalent metals ion M^{2+} is extracted with an organic solvent containing 8–hydroxyquinoline (symbolized as HQ) can be formulated as

$$2(HQ)_{org} + (M^{2+})_{aq} \rightleftharpoons (MQ_2)_{org} + 2(H^+)_{aq}$$

where the subscript indicates the phase. The equilibrium is clearly pH dependent thus, separations among metals having different formation constant with the ligand are possible through control of the pH of the aqueous phase. The latter has proved particularly useful for separation of traces of metals.

Another useful reagent for separating minute quantities of metal ions is dithiozone (diphenylthiocarbazone). Its reaction with a divalent metallic ion can be written as



dithizone

Both dithizone and its metal chelates are soluble in a variety of organic solvents. As with 8–hydroxyquinoline, the equilibrium between the metal ion and the reagent is pH dependent; thus, by controlling the pH of the aqueous phase, various separations of metallic ions are possible.

The dithizone complexes of many metal ions are intensely colored. Spectrophotometric measurement of the organic extract often serves to complete the analysis after the separation has been performed.

Information concerning the use of other organic chelating agents for separations by extraction can be found in several reference works.

Determination of iron as 8–hydroxy quinolate : It is possible to extract ferric ion from aqueous solutions with a 1% solution of 8–hydroxy–quinoline in chloroform by double extraction. The optical density of chloroform layer is determined the using a spectrometer. This process may be repeated with further oxine solutions and the optical density is again measured.

It is important to remember that the pH of the aqueous solution should lie between 2 and 10.

Determination of uranium as 8–hydroxy quinolate : It is possible to determine uranium as 8–hydroxquinolate in the presence of some EDTA at pH 8.8. The EDTA masks the interfering ions like Fe, Al, etc. Now the optical density is determined as usual.

Similarly it is possible to estimate other cations by using suitable organic reagents. For example

(*i*) Determination of nickel as dimethyl–glyoximate complex.

(*ii*) Determination of molybdenum by thiocyante methods.

(*iii*) Determination of lead by dithizone method.

(*iv*) Determination of copper as diethyldithiocarbamate, etc.

Solvent Extraction

Amongst the various methods of seperation, solvent extraction, or liquid - liquid extraction, is considered to be the most versatile and popular method of seperation. The main reason for its usefulness is that seperations can be carried out on a macrolevel as well as on a microlevel. One does not need any sofisticated apparatus or instrument except a seperatory funel. It is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents such as benzene, carbon tetrachloride, or chloroform. In limiting cases, the solute can be more or less transferred into the organic phase. The technique can be useful for the purpose of preparation, purification, enrichment, seperation and analysis on all scales. It has come to the forefront in analytical chemistry four decades ago, as it is elegant, simple, rapid and is applicable at tracer and macrogram concentrations of metal ions.

2005

① Define the distribution co-efficient of a solute between two solvents.
On which factors does it depend?

⇒ The concentration of a solute distributed between two phases at equilibrium at a constant temperature always bears a fixed ratio and the molecular state of the solute must be the same in both the phase.

$$K_D = \text{Distribution Co-efficient or partition co-efficient} = \frac{\text{Conc. of solute in solvent a}}{\text{Conc. of solute in solvent b}}$$

Factors:

① The temperature must be kept constant.

② Molecular state of the solute in the both solvents must be same.

③ The two solvents must be immiscible to each other.

④ No chemical reaction should occur between the solvents and the solute.

[2004]

The partition co-efficient 'K' of a substance A in a particular chromatography column is greater than that for a substance 'B'. Which compd be more strongly retained in chromatography column?

⇒ Partition co-efficient or distribution co-efficient 'K' often indicates the ratio of solubilities of a substance in two solvents. Since, here K value of A is greater than that of B, so, the tendency to go into the solvent of A is greater than B, i.e., B is more strongly retained in the chromatography column.

[2003]

Define and contrast: Distribution co-efficient and distribution ratio

⇒

Distribution Co-efficient	Distribution ratio
1. $K_D = \frac{(C_A)_a}{(C_A)_b}$ Where K_D = Partition/distribution co-efficient. $(C_A)_a$ = Conc. of A in solvent a $(C_A)_b$ = " " A " " b	1. $D = \frac{(C_A)_a}{(C_A)_b}$ D = Distribution ratio.
2. In the expression of K_D, molecular state of the substance in both the solvents must be same.	2. In the expression of D, molecular states of the substance are regardless. Here all the forms of the substance are considered.
3. It has less practical value.	3. It is of great importance for practical purpose.

Discuss the equilibrium involved in the extraction of metal chelates.

⇒ The consideration of an extraction equilibrium of the metal chelate gives ~~imf~~ information about experimental parameters which play an important role in selectivity of extraction.

Let us consider extraction by chelation. The reac^n occurring, when an aqueous phase containing metal ions is contacted with an organic phase containing a chelating ligand. The chelating ligand distributed between two phases.

Now, if the metal ion has the valency 'n' and HR is the chelating ligand.

$$HR_{aq} \rightleftharpoons HR_{org}$$

$$K_{DR} = \frac{[HR]_{org}}{[HR]_{aq}} \quad \text{--- (i)}$$

The chelating ligand dissociates as

$$HR \rightleftharpoons H^{+} + R^{-}$$

$$K_a = \frac{[H^+][R^-]}{[HR]} \quad \text{--- (ii)}$$

The chelating anion combines with metal ion M to form extractable chelate

$$M^{n+} + nR^{-} \rightleftharpoons MR_n$$

$$K_f = \frac{[MR_n]}{[M^{n+}][R^-]^n} \quad \text{--- (iii)}$$

The chelates distributes in two phases, hence

$$MR_{n(aq)} \rightleftharpoons MR_{n(org)}$$

$$K_{D_x} = \frac{[MR_n]_o}{[MR_n]_{aq}} \quad \text{--- (iv)}$$

However, distribution ratio (D) can be evaluated if metal chelate MR_n in the org phase and M^{n+} in the aq. phase is known,

$$\therefore D = \frac{[M]_{org}}{[M]_{aq}} = \frac{[MR_n]_{org}}{[M^{n+}]_{aq}} \quad \text{--- (v)}$$

From (iv), $[MR_n]_{org} = K_{Dx} \cdot [MR_n]_{aq}$

From (iii), $[MR_n]_{aq} = K_f \cdot [M^{n+}][R^-]^n$

$[MR_n]_{org} = K_{Dx} \cdot K_f \cdot [M^{n+}][R^-]^n$

Again from (ii), $[R^-] = K_a \cdot \dfrac{[HR]}{[H^+]}$

$$\therefore [MR_n]_{org} = K_{Dx} \cdot K_f \cdot [M^{n+}] \, K_a^n \dfrac{[HR]^n}{[H^+]^n}$$

$$= \dfrac{K_{Dx} \cdot K_f \cdot K_a^n}{(K_{DR})^n} \cdot \dfrac{[M^{n+}]}{[H^+]^n} \cdot [HR]^n_{org}$$

From (v),

$$D = \dfrac{K^*}{[M^{n+}]} \cdot [M^{n+}] \dfrac{[HR]^n_{org}}{[H^+]^n} = K^* \dfrac{[HR]^n_{org}}{[H^+]^n}$$

Where $K^* = \dfrac{K_f \cdot K_a^n \cdot K_{Dx}}{(K_{DR})^n}$

Now if we keep [HR], reagent concentration constant, then,

$$D = K^* [H^+]^{-n} \quad \text{------ (vi)}$$

$$\therefore \log D = \log K^* + n\,pH \quad \text{------ (vii)}$$

When, $V_w = V_o$, then we have

[V_w = volume of water
V_o = " " organic solvent]

$$D = \dfrac{E}{100 - E} \quad \text{---- (viii)}$$ [Where E = % of the extracted solid]

From (vi) & (vii), $\dfrac{E}{100-E} = K^* [H^+]^{-n} = D$

$$\therefore \log D = \log E - \log(100 - E) = \log K^* + n\,pH$$

When E = 50, the pH for 50% extraction is

$$pH_{1/2} = -\dfrac{1}{n} \log K^* \quad [\because \log D = 0] \quad \text{---- (ix)}$$

$(pH_{1/2} = -\dfrac{1}{n} \log K^* + \log [HR]$ if [HR] varies)

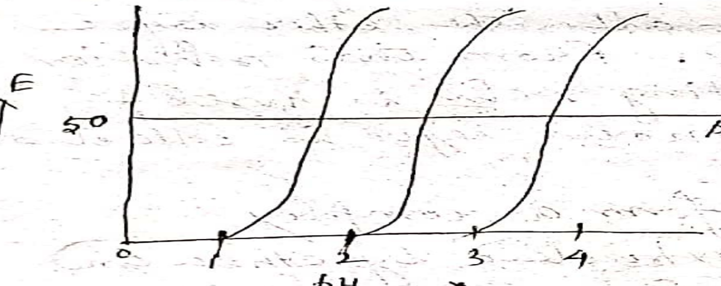
The eqn (ix) shows that pH at half extraction is constant for the same concentration of a given chelating lig (HR). The magnitude of pH is dependant only on the valency of the ion and stability const (K^*)

Write down the effect of pH on the solvent extraction

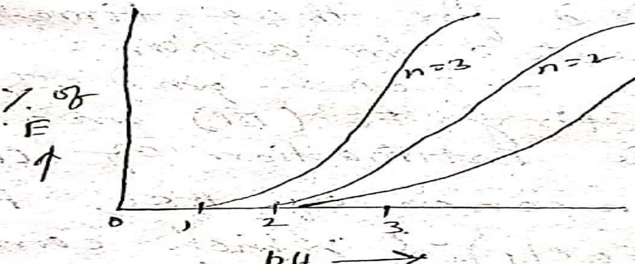
⇒ From the extraction equilibria we have,

$$\log D = \log E - \log(100 - E) = \log K^* + n\,pH$$

The distribution of the metal in chelation extraction is a function of the pH alone. The eqn represents a family of sigmoid curve when E is plotted against pH.



This figure shows how the position of the curves depend upon the magnitude of K^*



This figure shows how slope depends upon 'n'.

If the $pH_{1/2}$ values are sufficiently far apart, then ~~solvent~~ excellent seperation can be achieved by controlling the pH of the extraction.

[2001]

How are Fe (III) and Cu (II) are seperated by solvent extraction process ?

⇒ The mixture of Cu (II) and Fe (III) solⁿ is taken in a seperatory funel. The 12 (N) HCl of the same volume of the sample solⁿ is taken within the funel. The funel is allowed ~~to~~ sometimes to cool. After this measured amount of ether solⁿ is added in the seperatory funel.

The funel is shaken for sometimes and then it is allowed to settle the two layer. Here ether layer is the upper layer and the aqnous layer is lower layer. Ether layer is collected and after this the aqnous phase is again taken in funnel and the process is repeated for three times and all the ether layer is collected in a same beaker. From this solution ether is removed and the resulting solⁿ is used for estimating Fe (III) and the aqnous layer is collected for the estimation of Cu (II).

In presence of HCl, Fe (III) form a complex $\{H^+(FeCl_4)^-\}$ which can be extracted by ether and copper remains in aqnous solⁿ. In presence of ether, the formed complex of Fe (III) is

$$\{H^+(\text{ether})[FeCl_4]^-(\text{ether})\}$$

[2000]

Calculate the distribution ratio 'D' when Fe (III) is extracted from HCl solⁿ with tributyl phosphate if $V_o = 10$ ml ; $V_w = 25$ ml , $E = 99.8$

⇒ We have the formula,

$$D = \frac{E}{100-E}\left(\frac{V_w}{V_o}\right)$$

where D = Distribution ratio of the solute in organic phase and aqnous phase.

E = % of extracted solute

V_w = volume of water

V_o = volume of organic phase.

$$D = \frac{99.8}{100-99.8}\left(\frac{25.0}{10.0}\right)$$

$$= 1247.5$$

1998

Discuss the theory of liq-liq extraction

⇒ Liquid - liquid extraction is a technique in which a soln (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 ~~salts~~ solutes into the second solvent. The seperation that can be performed are simple, clean, rapid and convenient. In many cases separation may be effected by shaking in a separatory funnel for a few minutes. The technique is equally applicable to trace level and large amount of material.

1996

What are the advantages of solvent extraction technique?

⇒ ① Such seperations are simple, clean, rapid and convenient.

② The technique is equally applicable to trace level and large amount of materials.

③ Although solvent extraction has been predominantly used for the isolation and seperation of a single chemical species, it may also be applied to the extraction of group of metals prior to their determination

④ The solvent extraction can be also used to concentrate a species which in aq. soln is too dilute to be analysed.

2006

2. (a) **What are the criteria for a good solvent in liquid - liquid extraction?**

⇒ ① The solvent must be immiscible with another solvent.

② It would be better case if the colour (or refractive index) of the solvent is different from other.

③ The solvent must undergoing complexation with the substrate which is to be extracted.

2010 [2007]

Calculate the distribution ratio when a metal was extracted from 25 ml aqueous soln to an organic liquid of volume 10 ml and percentage of extraction was 99.8

$\Rightarrow$ $V_w = 25$ ml ; $V_o = 10$ ml

$E = 99.8\%$

$$D = \frac{E}{100-E}\left(\frac{V_w}{V_o}\right) = \frac{99.8 \times \left(\frac{25}{10}\right)}{100-99.8}$$

$=$

Proof : $D = \frac{E}{100-E}\left(\frac{V_w}{V_o}\right)$

$\Rightarrow$ Let x_o gm of a substance remains in V_w ml of aqueous soln and this is extracted with V_o ml of organic solvent. Now, if x_1 g is the amount of solute be unextracted

$$\therefore D = \frac{\text{conc. of solute in org}}{\text{conc. of solute in aq.}}$$

$$= \frac{\frac{x_o - x_1}{V_o}}{\frac{x_1}{V_w}} = \frac{(x_o - x_1) V_w}{x_1 V_o}$$

$$\Rightarrow D x_1 V_o = x_o V_w - x_1 V_w$$

$$\Rightarrow x_o V_w = x_1 (D V_o + V_w)$$

$$\Rightarrow \frac{x_1}{x_o} = \frac{V_w}{D V_o + V_w}$$

$$\Rightarrow 1 - \frac{x_1}{x_o} = 1 - \frac{V_w}{D V_o + V_w}$$

$$\Rightarrow \frac{x_o - x_1}{x_o} = \frac{D V_o}{D V_o + V_w}$$

$$\Rightarrow \frac{x_o - x_1}{x_o} \times 100 = \frac{D V_o}{D V_o + V_w} \times 100$$

$$\frac{x_1}{x_o} \times 100 = \frac{D V_w}{D V_w + V_o} \times 100$$

$$\Rightarrow E = \frac{D V_o}{D V_o + V_w} \times 100$$

$$\Rightarrow E D V_o + E V_w = 100 D V_o$$

$$\Rightarrow D (E V_o - 100 V_o) = - E V_w$$

$$\Rightarrow D = \frac{E}{100 - E} \left(\frac{V_w}{V_o} \right)$$

Proof : → Successive extraction is more efficient than single extraction

⇒ See P. C. Rakshit

A generalised formula can be easily suggested for the amount remaining unextracted after a given number of operations. Let V c.c. of a solution containing x_0 gms of substance be extracted with L c.c. of a solvent. Let x_1 gms of substance remain unextracted in water layer. Then

conc. of the substance in solvent $= \frac{x_0 - x_1}{L}$; and in water $= \frac{x_1}{V}$

Distribution coefficient, $K = \frac{\frac{x_1}{V}}{\frac{x_0 - x_1}{L}}$

$$\text{or} \quad x_1 = \frac{KV(x_0 - x_1)}{L} = x_0 \frac{KV}{KV + L}$$

If second extraction again with L c.c. solvent is made, the quantity unextracted would be

$$x_2 = x_1 . \frac{KV}{KV + L} = x_0 . \frac{KV}{KV + L} . \frac{KV}{KV + L} = x_0 \left(\frac{KV}{KV + L} \right)^2$$

Similarly after *n*-th extraction, the quantity left behind would be

$$x_n = x_0 \left(\frac{KV}{KV + L} \right)^n \qquad \text{....(A)}$$

If the entire quantity of the extracting solvent be used in one lot, then unextracted,

$$x = x_0 \left[\frac{KV}{KV + nL} \right] \qquad \text{.....(B)}$$

Since the quantity within the parantheses is less than unity, (A) is smaller than (B) and x_n will be smaller the greater the value of n; Hence it is more economical to use the solvent in portions.

Problem : The partition coefficient of an alkaloid between chloroform and water is 20, the alkaloid being more soluble in chloroform. Compare the weights of the alkaloid remaining in aqueous solution after 100 c.c. containing 1 gram has been shaken (a) with 100 c.c. chloroform and (b) with two successive quantities of 50 c.c. chloroform.

Distribution coefficient $K = \dfrac{Conc. in \;\; water}{Cone. in \;\; chloroform} = \dfrac{1}{20}$

(a) When 100 c.c. chloroform is used in one lot, the amount unextracted,

$$x_n = 1 \times \left(\frac{KV}{KV + L} \right) = \left(\frac{\frac{1}{20} \times 100}{\frac{1}{20} \times 100 + 100} \right) = \frac{5}{105} = 0.0476 \text{ gm.}$$

(b) When 50 c.c. chloroform is used in each of two stages, the amount unextracted,

$$x_n = 1 \times \left(\frac{KV}{KV + L} \right)^2 = \left(\frac{\frac{1}{20}.100}{\frac{1}{20} \times 100 + 50} \right)^2 = \left(\frac{5}{55} \right)^2 = 0.0083 \text{ gm}$$

Problem : An organic compound is extracted from aqueous solution with successive quantities of 25 c.c. chloroform. The original volume of solution is 500 c.c. and the distribution coefficient of the compound is 20 between chloroform/water. Calculate the number of extractions needed for at least 95% recovery of the compound.

$$K = \frac{conc. in \; water}{conc. in \; chloroform} = \frac{1}{20}$$

The amount left behind (*i.e.*, 5%) after *n*-th extraction required for separating the required 95% is given by

$$\frac{5}{100} = \left(\frac{KV}{Kv + 25} \right)^n = \left(\frac{\frac{1}{20} \times 500}{\frac{1}{20} \times 500 + 25} \right)^n = \left(\frac{1}{2} \right)^n$$

or $$n = \frac{\log 5/100}{\log \frac{1}{2}} = 4.3$$

Hence to obtain a minimum of 95% separation we need at least 5 successive extractions.

Reference Books

1. Mendham, J., *A. I. Vogel's Quantitative Chemical Analysis 6thEd.*, Pearson, 2009.
2. Willard, H.H. *et al.*: *Instrumental Methods of Analysis*, 7th Ed. Wardsworth Publishing Company, Belmont, California, USA, 1988. 3. Christian, G.D. *Analytical Chemistry*, 6th Ed. John Wiley & Sons, New York, 2004.
4. Harris, D.C.: *Exploring Chemical Analysis*, 9th Ed. New York, W.H. Freeman, 2016.
5. Khopkar, S.M. *Basic Concepts of Analytical Chemistry*. New Age International Publisher, 2009.
6. Skoog, D.A. Holler F.J. & Nieman, T.A. *Principles of Instrumental Analysis*, Cengage Learning India Ed.
7. Mikes, O. *Laboratory Hand Book of Chromatographic & Allied Methods*, Elles Harwood Series on Analytical Chemistry, John Wiley & Sons, 1979.
8. Ditts, R.V. Analytical Chemistry; Methods of separation, van Nostrand, 1974.