UNIT 17 SEPARATION TECHNIQUES

Structure

17.1 INTRODUCTION

For an analysis some form of pretreatment of a sample is usually required so as to remove interference of the other substances. The most important pretreatment procedure in chemical analysis is the separation of components into the form used for the easy determinations.

The analytical chemists make use of a number of separation methods based on transfer of matter from one phase into another.

When a single stage of material transfer gives a quantitative separation, the procedure such as: precipitation, volatilization, and solvent extraction may be used successfully.

But when a single stage of material transfer is not sufficiently quantitative than the modern methods based on multistage separation procedures are used. In these procedures one phase that is stationary is brought repeatedly into contact with fresh portion of the second that is mobile which is either replaceable fraction wise or more continuously. Methods included in this category are: solvent extraction, chromatography and ion exchange. In this unit our discussion will be confined to these three methods only.

Objectives

After studying this unit, you will be able to

- understand the technique and principle of chromatography,
- learn the classification of chromatography,
- explain the general terminology of chromatography,
- learn the details of paper, thin layer and column chromatographies,
- understand the general theory of ion exchange, and
- explain the application of these chromatographies to environmental analysis.

17.2 SOLVENT EXTRACTION

You are aware that most of the organic reactions normally do not go to completion. The reaction mixture contains unreacted reactants and unwanted side products besides the desired product. In such a situation one of the products (wanted or unwanted) may need to be separated. One of the methods, which can be used to perform such a separation, is called as solvent extraction. This method is based on the principle of phase distribution. It exploits the differential solubility of a given solute in two immiscible solvents to separate it from a given mixture. Let us briefly understand the technique.

Suppose a substance 'X' has different solubilities in two immiscible solvents. If we take a solution of the substance in any of the solvents and shake with the second solvent then it distributes itself in two solvents depending on its solubility in these. For example acetanilide is soluble in ether as well as in water. If we take its solution in water and shake with ether then part of acetanilide goes to the ether layer. The two layers can be separated and the ether layer can be evaporated to get acetanilide. We can repeat the process a number of times whereby more and more of acetanilide would come to ether and eventually all the acetanilide from aqueous layer would get 'extracted'.

This definition of distribution coefficient holds only if the solute remains in same molecular state in both the solvents. If, however, the solute associates or dissociates in one or both the solvents the defining equation has to be modified. You can refer to any standard text on physical chemistry for these equations.

The extracting efficiency of the solvent depends on the distribution coefficient of the solute in the two solvents. Distribution coefficient is defined as the ratio of the concentration of the solute in two solvents.

$$K = \frac{\text{conentration of the solute in solvent 'A'}}{\text{concentration of the solute in solvent 'B'}}$$

$$= \frac{\text{solubility of the solute in solvent 'A'}}{\text{solubility of the solute insolvent 'B'}}$$

It is obvious that higher the value of 'K' higher is the extracting efficiency, i.e., in event of extraction more amount of the solute would be transferred. Thereby smaller volume of extracting solvent would be required. A good extracting solvent should have the following properties.

- It should be a good solvent for the substance being extracted i.e., solute should have high solubility in this solvent,

- It should have low boiling point so that the extracted substance can be recovered easily,
- It should not be expensive,
- It should not react with the solute or the other solvent, and
- Of course, it should be immiscible with the other solvent.

Suppose you want to separate acidic and basic compounds respectively from their mixtures with neutral substances. To accomplish such an extraction the mixture is normally taken in an organic solvent and is shaken with an aqueous solution of a base or an acid. This process is called as acid base extraction. Let us take an example of separation of an acidic component from the rest in a mixture to understand the process of acid base extraction. When we shake such a mixture with an aqueous solution of a base the acidic compound gets extracted into aqueous phase as its salt. The extraction process can be visualized as follows.

When we mix the organic solvent (containing acid) with aqueous solution of the base, the acid distributes itself into organic and aqueous layer depending on its distribution coefficient. The base present in aqueous layer immediately converts the acid into its salt, Eq.17.1.

$$RCOOH + MOH \longrightarrow RCOOM + H_2O \quad \ldots \quad (17.1)$$

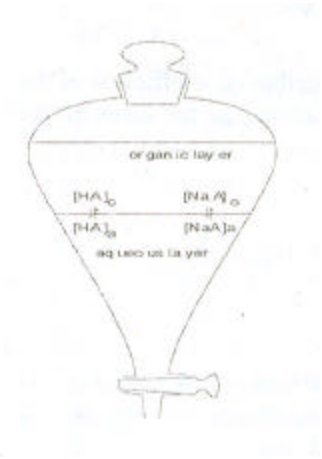
Organic solvents like chloroform and carbon tetrachloride form lower layer with water while, solvents like either, and petrol form upper layer with water in seporatory funnel.

Separation of a mixture of Benzoic Acid, 2 – **Pephthol** and 1,4 – Dimethoxy-Henzene by solvent extraction and identification of their Functional groups.

The extent of conversion depends on the strength of the base. In any case the concentration of free acid in aqueous layer becomes very small. As a consequence, to maintain the distribution coefficient more acid comes into the aqueous phase and gets converted into the salt. This process continues till the base is able to perform this conversion completely. The salt formed in this process also distributes itself into the two solvents. Due to very large solubility of the salt in aqueous phase as compared to organic phase, most of the salt stays in the aqueous layer. That is, a very little amount of acid goes back into organic layer as salt.

The net result of these processes brings most of the acid into aqueous phase. The amount of acid, which comes to the aqueous layer, depends on the amount and nature of the base (weak or strong). If sufficient quantity of appropriate base is present then practically all the acid from the organic layer comes into aqueous layer and we get a good (!) extraction. The equilibria involved in these processes are represented schematically in Fig. 17.1

p*K*a, as you know is an index of the strength of an acid. It is defined as $-\log K_a$ where K_a is dissociation constant of the acid. Higher the pK_a value weaker the acid.



$[HA]_a$: Concentration of acid HA, in aqueous layer

$[HA]_0$: Concentration of acid HA, in organic layer

$[NaA]_a$: Concentration of the salt NaA in aqueous layer

$[NaA]_0$: Concentration of the salt NaA in organic layer

Fig. 17.1: Schematic representation of the equilibria involved in the extraction of an acidic compound from organic to aqueous layer.

The appropriate base refers to the one, which can effectively convert the acidic compound into its salt. As a rule of the thumb a basic solution whose pH is atleast 4 pH units more then the pK_a of the acid to be extracted can afford an almost complete extraction. For example, benzoic acid (pK_a 4) can be extracted quite effectively by a 5% aqueous solution of sodium bicarbonate (pH – 11). The approximate pK_as of common organic acids or bases and the pH of the common extracting solutions are given in Table 17.1 and 17.2 respectively. These would be of help to you in devising the extraction strategy to separate any other mixture.

Table 17.1: Approximate p*K*a values of some common acidic/basic compounds

Class of compound	Approximate pK_a	Examples
Mineral acid	<1	HCI, HNO_3
Aromatic carboxylic acid	4	benzoic acid
Aliphatic carboxylic acid	5	acetic acid, Propionic acid
Anilines	5	aniline, toluidine
Pyridines	6	pyridine
Phenols	10	1 – naphthol, phenol 2 – naphthol
Aliphatic amines	11	methylamine, Ethylamine

Table 17.2 Approximate pH values of the solutions (5-10 % by weight) commonly used for acid-base extraction

Compounds	Approximate PH
HCI; H_2SO_4	0
Acetic acid	3
$NaHCO_3$	8
Na_2CO_3, K_2CO_3	11
NaOH, KOH	14

Needless to say that the other species (which are not acidic) would stay in organic layer. Only a small portion would come into the aqueous layer depending on its solubility and distribution coefficient. These are removed in the event of acidification or crystallization. Further, you may be wondering that we wanted to separate acid and have landed up with a solution containing salt of the acid. Don't worry the acid can be recovered quite easily by acidifying the solution with mineral acid (pH = 1).

Similarly, we can understand the extraction of a basic compound say an amine from an organic solvent by using an aqueous solution of an acid. Again as a rule of the thumb the pH of the extracting acid solution should be at least 4 pH units away from (pK_a of conjugated acid, RNH = 11 can be effectively extracted by a 5-10% solution of acetic acid (pK_a = 3). The acetate salt so obtained can be converted back to the amine by using aqueous solution of sodium hydroxide.

17.3 CHROMATOGRAPHY - A HISTORY

Chromatography is the most versatile technique of all the different types of separation methods. It is proved to be extremely valuable technique, since compounds which are similar enough in properties and defy separation by other methods often resolved by chromatography.

In the broad sense chromatography is a technique which affects a separation through the distribution of sample between two immiscible phases. One phase is stationary while the second is mobile and percolates through the first phase.

With the help of chromatography the components can be separated in both extremes, that is, very small quantities as well as very large quantities.

In 1906, Mikhail Tswett, a Russian botanist and physical chemist, reported a separation process for leaf pigments. In his experiment, different coloured constituents of leaves were extracted in petroleum ether and the extract was passed through a column of calcium carbonate. Addition of pure petroleum ether was continued through the column. After some time different coloured zones (of chorophyl A, chorophyl B, xanthophylls and caroteins) appeared on the column. Tswett gave the name CHROMATOGRAPHY to this process from the Greek words "chromatus" and "graphein" meaning "colour" and "to write". The method was not recognized for decades and further development did not occur until early 1930(s). In 1931, Kuhn and Lederer applied the method for the successful separation of **caroteines**. In 1941, Martain and Synge developed partition chromatography and in 1944 Consten, Martin and Gordon developed paper chromatography. In 1952, Martin and James developed gas chromatography. Various other types such as thin layer chromatography, gel chromatography, affinity chromatography and, ion exchange chromatography were developed in the following years.

17.4 THEORY OF CHROMATOGRAPHY

17.4.1 Definition

Chromatography is referred to any of a diverse group of techniques that effect a separation through a distribution of sample between two immiscible phases. One phase is stationary whereas the second is mobile which percolates through the first phase. The stationary phase may be a solid or a liquid while the mobile phase may be a liquid or a gas.

17.4.2 Classification

There are various ways to classify chromatography.

1. On the basis of **physical states of mobile phase** the chromatography is classified into two broad groups.
   - Liquid chromatography in which mobile phase used is in the form of a liquid.
   - Gas chromatography in which mobile phase used is a gas.

2. On the basis of physical states of stationary phase and its working principle, chromatography is classified as:
   - Adsorption chromatography in which stationary phase is solid and works as an adsorbent.
   - Partition chromatography in which stationary phase is a liquid or a liquid supported on an inert solid, and the movement of solute is based on the partition coefficient of the solute into two phases.
   - Ion exchange chromatography in which stationary phase is an ion exchanger and the distribution of solute is based on the ion exchange principle.
   - Gets chromatography in which stationary phase is gel and separation is based on its sieving action.

3. On the basis of the types of column it may be classified as:
   - Column chromatography in which a closed column containing the stationary phase in cylindrical tube is employed.
   - Sheet chromatography using an open column system in which separations are achieved on sheets of filter paper or thin layers of certain fine solid particles supported on glass or plastic plates.

17.4.3 Principle

Chromatography is essentially a separation process, which affects a separation by distributing the sample into two phases. One phase is stationary and second is mobile and flows through the stationary phase. During the process of movement of mobile phase, small differences in adsorption-desorption or partitioning or ion-exchange behaviour of each component of a mixture are multiplied many fold and these parameters distinguish between the different solutes. The ability of chromatography to separate two solutes, depends on the selectivity of the process and the degree to which the system can distinguish between the two solutes. The magnitude of the distribution is determined by the physico chemical nature of the solute and that of the mobile and stationary phases, beside various physical interaction (such as: hydrogen bonding, dipole moment etc.) of the solute with stationary and mobile phases.

SAQ 1

Define Chromatography.

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17.5 Terminology of Chromatography

Various terms are frequently used and they form the language of chromatography techniques. These are explained below:

17.5.1 Mobile phase

The moving component in the chromatography technique is called mobile phase, which is normally a liquid or mixture of liquid except in gas chromatography where gas is employed.

17.5.2 Stationary Phase

The fixed medium is called stationary phase. The fixed or solid part of the system is generally called **ad**sorbent. Because **it Adsorbs the solute not Absorb the solute**. Here it is very important to understand the difference between the **ad**sorbent and **ab**sorbent. In **ab**sorption the solute (substance to be separated) is taken up and held within the other substance which is called **ab**sorbent. For example a sponge **ab**sorbs water. While **ad**sorption is the ability of solid to attract solute to its surface and to hold them at the surface. The solid which hold the solute is called **ad**sorbent. The **ad**sorbent release the **ad**sorbed substance easily.

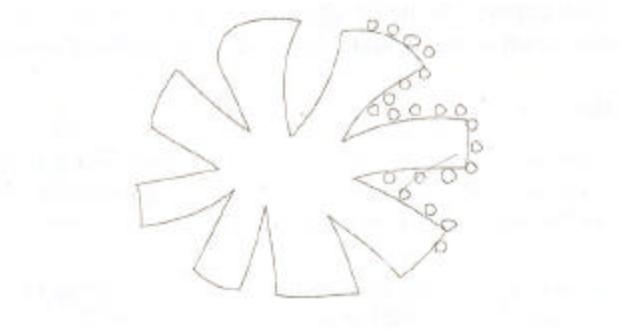

Fig. 17.2 spherical adsorbent particle with pores and adsorbed molecules

The good **ad**sorbent should have following properties:

(i) the adsorbent should not react with the solute being separated

(ii) the adsorbent must not dissolve in mobile phase

(iii) the adsorbent must not react with mobile phase

(iv) the adsorbent must release the solute with mobile phase

The commonly used adsorbents are: silica, gel, alumina, cellulose and animal charcoal.

17.5.3 Sample

The mixture of compounds to be separated is called sample

17.5.4 Components or Solute

The individual constituents of the sample is called components or solute.

17.6 SOME FUNDAMENTAL CONCEPTS

17.6.1 Retardation Factor (Rf)

R_f, in general, applicable to all chromatographic systems is defined to consider the motion of the point of maximum concentration relative to that of the eluting agent and is given by the equation

$$R_f = \frac{ds}{dm} = \frac{\text{distance moved by the center of the solute zone}}{\text{distance moved by the solvent front}}$$

Small R_f values indicate little tendency to move with solvent and thus reflect strong solute-adsorbent interaction. Large R_f value conversely indicate a lower polarity of solute and weaker solute-adsorbent attraction (provided the solvent is less polar then the adsorbent). The R_f values, for the given conditions of experiment, may be roughly regarded as constant and may be used for the identification of components. However, for precise measurements they can not be accepted without the use of reference standards under the identical conditions.

17.6.2 Chromatogram

A chromatogram, in general, can be described as a plot of concentration of the sample components against the elution volume (or elution time). If a detector that responds to the solutes is placed at the end of the column, the detector response is directly used as a measure of concentration. In liquid chromatography elution volume is preferred. For a good chromatogram zones should be compact, well defined and well separated.

17.6.3 Resolution

Resolution is the ability to separate certain pair of solutes. For a high resolution the zones should be well separated i.e. there should be an appreciable distance between the zone centres and no overlap between the zones.

In general, resolution is affected by column length and distribution coefficient. Hence resolution can alter the experimental conditions. For example, increase in column length increases the resolution.

SAQ 2

Look at the separation of the mixture of aceptophenanace and hexadeconol (See the fig.). Calculate the R_f value of a) accetaphenane b) hexadecanol

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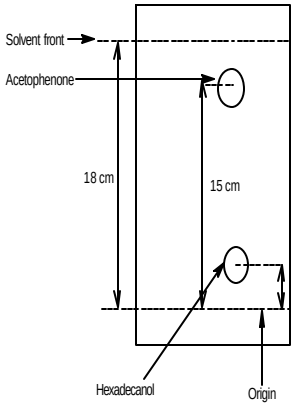

17.7 ADSORPTION SYSTEM

An adsorption system consists of a stationary phase, a mobile phase and the components to be separated.

The *stationary phase* is almost invariably highly polar, typically silica gel or alumina, which will adsorb molecules strongly. In silica gel, the adsorption sites are the oxygen atoms and silanol groups (Si – OH) which readily form hydrogen bonds with polar molecules. If the sample components are adsorbed too strongly, they may be difficult to remove (**elute**) with a suitable solvent (mobile phase). Conversely, if solutes lack polarity, e.g. hydrocarbons, and the solvent is sufficiently polar, then elution will occur too rapidly with little or no separation.

Turning to the *mobile phase*, it is again important to appreciate the polarity of the individual molecules. This leads to the construction of an **elutropic series** as given in Table 17.1 where solvents are arranged in order of increasing eluting power. The most polar among the solvents is listed at the bottom.

Table 17.1 Part of an Elutropic Series

Increasing eluting power ⇩

Hexane
Petroleum spirit
Cyclohexane
Tetrachloromethane
Methylbenzene
Benzene
Ethoxyethane (diethyl ether)
Trichloromethane
Dichloromethane
Tetrahydrofuran
Propane
Ethyl ethanoate
Cyanomethane
Pyridine
Propan-2-o1
Ethanol
Methanol
Water
Organic acids

To use an appropriate solvent to give good separation of a specific mixture components, you should consider the following two points:

1. A solvent, which is strongly polar, will compete for adsorption sites on the surface of the stationary phase with the solutes to be separated. These solutes will therefore be easily displaced and produce shorter retention times, i.e. the time taken for a solute to emerge from a TLC plate or column. If the retention time of various components is reduced, then the poorer separations result.

2. Solvents, which are poorly adsorbed due to low polarity, do not compete effectively with solute molecules. Hence they do not displace solute molecules from the surface as rapidly, and so retention times become too long. Again this will lead to poor separations.

In practice, the best separations are achieved by eluting with the least polar solvent possible.

SAQ 3

Arrange the following in order of increasing eluting power.

i)	cyclohexane	ii)	ethylehtanoate
iii)	benzene	iv)	propan-2-ol
v)	dichloromethane	vi)	propane

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17.8 THIN LAYER CHROMATOGRAPHY

Thin layer chromatography was introduced by Izmailov and Schreiber in 1938 by the name of 'Drop chromatography'. Nearly after a decade Meinhardt and Hall used adsorbent coated glass plates and named 'Surface chromatography'. However, it has been used more extensively since 1958 with the systematic approach of Stahi who devised a method involving standard size glass plates, an apparatus for the preparation of layers and a standard adsorbent, silica gel mixed with plaster of Paris. Stahi called the method 'THIN LAYER CHROMATOGRAPHY' and this name is now widely accepted with its abridged form TLC.

Literally, TLC is any chromatographic system in which the stationary phase, is in the form of a thin film (generally silica gel or alumina of an adsorbent bond to a plate of glass, plastic or metal foil) and mobile phase a liquid. It is an excellent technique for small laboratories which do not have access to more sophisticated chromatographic equipment. TLC possesses the advantages of high speed and easy variation of stationary phase.

17.8.1 Preparation of TLC Plate

To obtain reproducible R_f values and for accuracy in quantitative work, it is necessary to have a uniform coating of adsorbent. Coating can be made manually as well as automatic which is relatively expensive. The layer thickness may vary from 2 to 10 mm. However, the most popular are 2.5 mm and 5 mm for qualitative and quantitative analyses respectively.

The common adsorbents used for coating are silica gel and alumina. Other adsorbents are cellulose, polyamide, charcoal, magnesium oxide, gels and ion exchangers.

17.8.2 Development of Chromatogram

Development of chromatogram refers to the separation of the mixture on the plate by allowing the liquid phase to move up the adsorbent on the plate. Liquid sample can be applied directly to plate, 1 cm above the base with the help of capillary tube. A micropipette is used for the quantitative work where 1-25 microlitre of the sample can be applied at the plate to a minimum spot area. Solid sample cannot be applied directly to the plate so they must be dissolved in a suitable solvent before applying.

After the spot had sufficiently dried the plate is placed in a glass chamber containing the developer liquid (mobile phase), Fig. 17.3. The glass chamber may be a closed jar of an especially designed cylindrical or rectangular tank. Chambers may be designed to develop one plate or several plates that means more than one plate can be developed in the same tank by the use of same developing solvent.

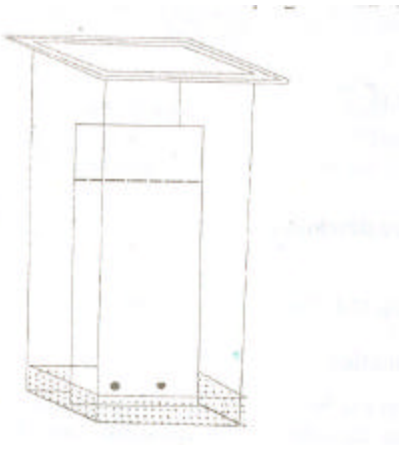

Fig. 17.3

As the solvent moves upwards the individual components in a sample mixture will begin to travel upwards as well, with least strongly adsorbed component moving the greatest distance. Eventually if the choice of solvent was correctly decided, then the series of spots traveling up the plate will be observed, provided the solutes are coloured. When the solvent moves to a required distance (or time) the plate is removed from the chamber, dried and spots are visualized directly, or in U.V. light or after spraying with a detector. R_f values are calculated by measuring the distance of the centre for the spot from the spotting line and the distance moved by the solvent.

17.8.3 Detection of Spots

Coloured zones are easily located by sight. However, that rarely happens, and it is usually necessary to use some spraying reagents to find the positions of spots. These visualizing reagents can be sprayed on developed and dried plates to locate the spots. The visualizing agents should form a coloured reaction product with the sample components.

Those compounds which absorb UV radiation can be located by holding the developed plate under a UV lamp where the component zones are located as dark spots. However, the compounds which fluoresce, are appeared under UV lamp as shining zones.

Ripening process may be used where the plates after development are placed in a tank containing certain gases e.g. NH_3, SO_3, Br_2 and I_2. Sometimes radioactive detectors are used for both detection and determination of radioactive components.

17.8.4 Identification of Components

We can identify the compound by comparing its R_f value with the pure compound (standard compound). Suppose you have a mixture containing compounds A, B & C. You also have pure standard compounds A, B and C. If the mixture is spotted alongside of the pure standard sample, then the comparison of R_f values will reveal the nature of the compound in the mixture. You can understand this situation by studying Fig. 17.4. The mixture contains three components, one (A) of which can be identified as it has the same R_f value as one of the standard samples. Similarly remaining can also be identified.

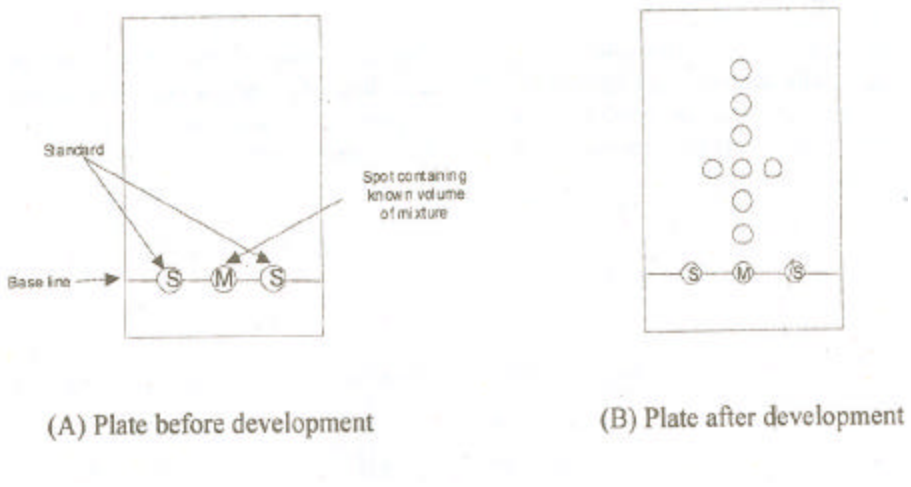

Fig. 17.4: Comparison of Rf value of unknown and standard.

17.8.5 Quantification

A rough estimation can be achieved by a simple visual technique as which consists of comparison of the intensity of the coloured zone of sample component with the standards by placing the plate of sample component between two standards with intensities very close to the sample component. One of the standards must have lower intensity and the other higher than the sample component. The method is not very reliable as errors upto 10% or even more are quite frequent.

Spectrophotometeric methods give better choice for obtaining results with less error. These methods are the most favoured methods for the quantification of thin media chromatograms because for the sensitivity, accuracy and reproducibility of these methods.

A recently devised, fully automatic TLC-scanner method is vary accurate and sensitive method. This involves the detection of radioactively labeled substances after separation by TLC.

SAQ 4

What are visualizing agents? Name any three visualizing agents.

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17.9 COLUMN CHROMATOGRAPHY

In general way column chromatography designates a liquid-solid adsorption technique. The basic principle of column chromatography is same as that of TLC. Column chromatography is a technique, which can be applied to separate many complex mixtures. It is a chromatographic system in which the stationary phase is contained in column. The sample is applied to the top of the column and the mobile phase flows down through the column.

The success of separation by column chromatography depends on the choice of the stationary phase and mobile phase. A choice of the mobile phase depends on the nature of the substance and how strongly it is adsorbed. In a number of cases (such as alumina and silica gel as the adsorbent) the mobile phase is generally non-polar solvent such as petrol and benzene. It is because polar solvent having polar group such

as hydroxyl group in water and in ethanol would cause **desorption**. Eluents containing two or more groups may be used for better results. In such cases the polarity is increased by adding a polar solvent with a non-polar one as discussed in section 17.7.

Consider a column as shown in Fig. 17.5 prepared by placing the stationary phase material as a slurry in a cylindrical glass tube that is plugged at the bottom by glass wool or cotton wool.

Let us suppose that we wish to separate a mixture of two coloured components A and B having the distribution coefficient K_A and K_B respectively. Where K is the ratio of concentration of the solute in the stationary phase to that in the mobile phase (K = Cs/Cm). Further let $K_A < K_B$

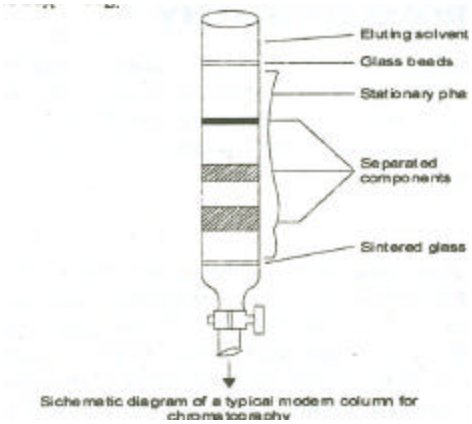


Fig. 17.5: Chromatographic column.

A small amount of the sample solution is applied at the top of the column. First a narrow band is formed at the top of the column. The eluting agent (developer or mobile phase) is now poured into the column and is allowed to proceed through the column. As the eluting reagent percolates over the stationary phase, some of the solute molecules are moved from the stationary phase and are transferred to the developer. As $K_A < K_B$ naturally the developer will be richer in A. Thus when the developer leaves the narrow band it is richer in A than B. The developer now comes in contact with fresh stationary phase and when it leaves the stationary phase, each time it becomes richer and richer in A. Soon after the well separated bands are obtained and that can be visualized by their respective colours. If the development further proceeds, the components are eluted out of the column. Solute A which has smaller K emerges first followed by B which as a large K. The various stages of chromatographics process are shown in Fig. 17.6.

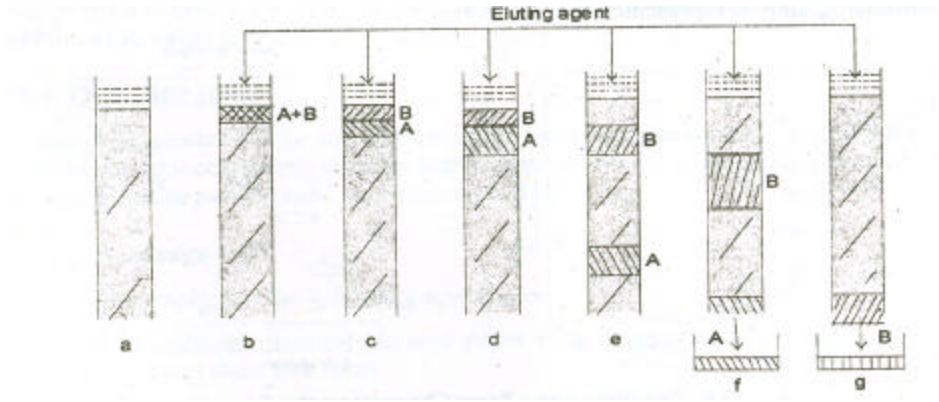


Fig. 17.6: Stages in the separation of a two component mixture.

The effluent can be analysed and concentration may be plotted as a function of effluent volume, a liquid chromatogram is obtained as given in Fig. 17.7.

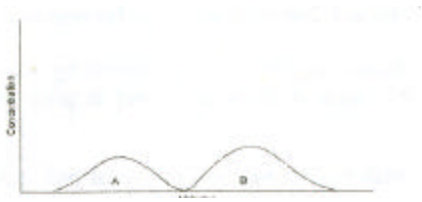


Fig. 17.7: Liquid Chromatogram.

17.10 PAPER CHROMATOGRAPHY

Paper chromatography was introduced by Consden, Gordon and Martin in 1944. It has proved to be a sensitive and inexpensive means for the separation and identification of different classes of compounds and can also be applied in environmental analysis. Although quantitative analysis is possible by this method but, the main application is in qualitative identification.

17.10.1 Principle

The separations by paper chromatography are based, mostly on the distribution ratios between the water saturated cellulose (stationary phase) and the developing liquid (mobile phase). Cellulose, as present in the form of filter paper commonly works as an inert support. Although the dominant factor is the partition, adsorption also plays some role in many of the separations affected by paper chromatography. Thus, the stationary phase in paper chromatography is either paper itself (adsorption) or the system consisting of cellulose and a liquid (partition).

It is evident that on a paper chromatogram, the rate of flow of developer (mobile phase) is slow and the process of distribution of solutes between two phases is repeated many times. Ascending of the developer on the paper is by capillary action and the solutes move up the paper at different rates, which is based on the distribution of solute between stationary and mobile phases. The relative rate of movement of solute in comparison to solvent is measured in terms of R_f values.

Separating power is increased by using TWO DIMENSIONAL CHROMATOGRAPHY in which a square piece of paper is spotted at a corner of the paper. It is first developed with one developer. After drying this is turned 90° and again developed with a second developer. This method is useful for separating complex mixtures which are not developed by one developer. Paper chromatogram of a hypothetical mixture of 10 components resolved by two dimensional chromatography is represented in fig. 17.8.

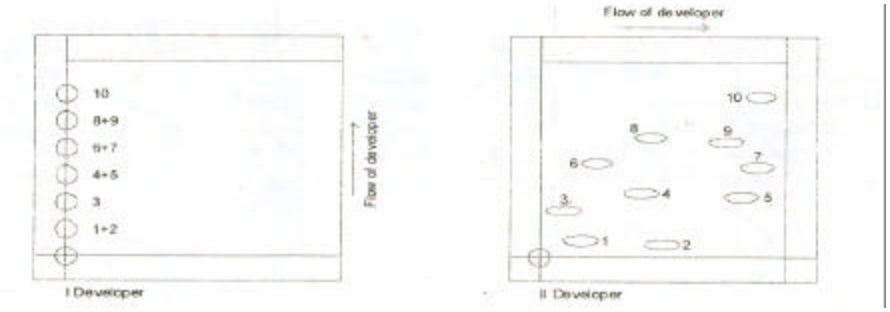


Fig. 17.8: Two Dimensional Paper Chromatographic Separation of a mixture of 10 components (Hypothetical).

17.10.2 Developing the Chromatogram

The direction of flow of the developer on paper gives three different kinds of procedures: ascending, descending and circular with the movement of the developer up, down and in horizontal manner respectively. The ascending technique is more popular because of being simpler than the other two procedures.

The paper chromatography set up for ascending procedure is shown in Fig. 17.9. A filter paper (for example Whatman No.1) is cut in the required size. A pencil line is drawn across the paper nearly one cm from one of the ends of the paper. The center of the line is marked with a pencil point and the sample is spotted at this point with the help of a capillary tube. The sample spot must be as small as possible to obtain good result. The spot is allowed to dry and the paper is placed in the chromatographic jar which contains a suitable developer. The developer is allowed to ascend along the paper till it reaches to a particular height and zones of solutes are distributed across the paper. The paper is taken out of the jar, the solvent over it is allowed to be evaporated. In general, the paper is treated with a suitable detector to visualize the zones corresponding to the solutes of the samples. A pencil mark is made around each zone and its R_f value is calculated.

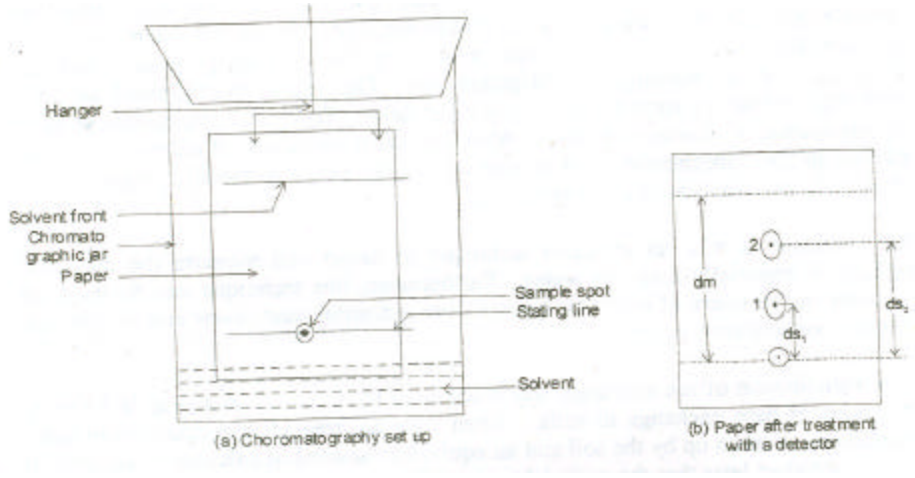


Fig. 17.9: Representation of Ascending Paper Chromatography.

17.10.3 Detection of Spots

If the solutes are coloured they can be visualized easily. UV light may be used to detect the solutes that show fluorescence. More often, the use is made of detecting reagents, which form coloured compounds with solutes. For examples, ninhydrin solution is used to detect amino acids. A pencil line is drawn around the spots for the calculation of R_f value and permanent identification.

17.10.4 Quantification

The quantity of a solute can be roughly estimated by (i) the size of the spot or (ii) the intensity of the spot comparing visually with a scale calibrated by means of standards chromatographed in parallel runs, as discussed in TLC.

17.10.5 Advantage

Paper chromatography has the following advantages:

(i) Reliable results are possible because paper is homogeneous, relatively stable, translucent and sheet like form.
(ii) Minute quantities in nanogram range can be handled.

(iii) Greater separation power can be achieved by using two dimensional paper chromatograph, for complex mixtures.
(iv) Greater selectivity can be achieved by the use of ion exchange impregnated papers for the separation of ionic substances.

17.10.6 Limitations

The limitations of paper chromatography are:

(i) Longer development time as compared to TLC
(ii) Zones are not always sharply defined
(iii) Reproducibility is low
(iv) Accuracy in quantitative analysis is not high.

17.11 ION EXCHANGE CHROMATOGRAPHY

The technique of ion exchange with a reorganization in recent past has proved to be one of the most versatile techniques especially for the removal and recovery of ionic species from aqueous solutions. Its need was first felt in the chemical industries where a chemically pure water was invariable required. Water of suitable purity is undoubtedly required by a civilized community for various purposes, such as, drinking, bathing, washing and irrigation etc. The years that followed saw ion exchange technology stepping into many other fields. Today, ion exchangers serve in the production of pharmaceuticals, combat the disastrous effects of ulcers and cardiac edema, in the concentration and recovery of some precious metals, preparation of chemicals, deionization of sugar syrups etc.

Ion exchange is now an impotent technique to detect and measure the dissolved pollutants, especially ionic, in water. Furthermore, this technique can be used for removal and recovery of polluting species from industrial wastewater and for analysis of trace contaminants in water.

The phenomenon of ion exchange was discovered by Thomson and Way in 1850 by the name of base exchange in soils. When soils are treated with ammonium salts, ammonium is taken up by the soil and an equivalent amount of calcium is released. It was established later that the materials responsible for this phenomenon were mainly clays, zeolites, gluconites and humic acids present in solid.

Gans (1905) recognized the practical utility of the ion exchange phenomenon for water softening using zeolites and clays. An interesting discovery began in 1935 when Adams and Holmes synthesized organic ion exchange resins which had much better properties than any of the previous products. These resins are stable towards acids and easy to handle.

The structure can be varied as desired, therefore, the difficulties observed with zeolites and clays were removed by the introduction of resins. Since then these organic ion exchangers have been used both in laboratory and on industrial scale for separations, recoveries of metals, purification of water, concentration of electrolytes and in so many other ways.

The use of ion exchange process for pollution control, for the first time probably was suggested in Germany in 1939 with the use of a pilot plant for recovery of copper from cuprammonium waste liquors. With the development of improved ion exchange resins the importance of ion exchange for valuable metal ion recovery was recognized by 1946. The ion exchangers prepared by polymerization of styrene and divinyl-benzene with suitable ionogenic group proved superior to all the previous ion exchangers.

SAQ 5

Fill in the following blanks

a) Ion exchange occurs between ions of ……..…….sign.
(opposite/same)

b) Ion exchange is a …….process.
(stoichiometric/non-stoichiometric)

c) Almost always ion exchange is a ……process.
(reversible/irreversible)

17.11.1 ION EXCHANGE MATERIALS

An ion exchanger is made of two parts: one known as MATARIX constitutes the framework and contains surplus charge fixed as ionogenic group and the other known as COUNTER IONS are mobile and exchangeable stoichiometrically with the ions of like charge. Counter ions have the charge opposite to that of the matrix and reside in the pores in sufficient numbers so that to make the exchanger as a whole electrically neutral. Carriers of exchangeable cations are called as **cation exchangers** whereas carriers of exchangeable anions as **anion exchangers**. For example, a **cation exchanger,** in general, can be represented as shown in Fig. 17.10.

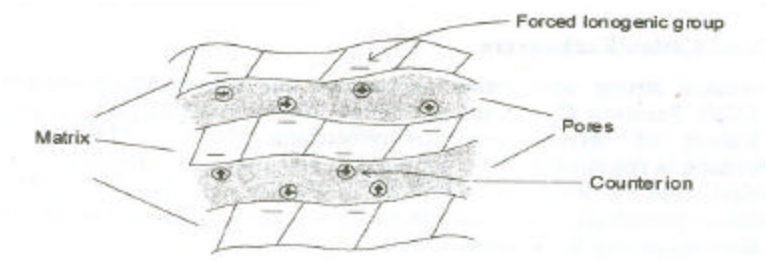


Fig. 17.10: Representation of a cation exchanger.

The ion exchange materials can be grouped as:

1. Synthetic organic ion exchange resins
2. Natural and synthetic zeolites
3. Synthetic inorganic ion exchangers
4. Chelate ion exchangers

In 1935 Adam and Holmes prepared first synthetic resin by condensation of phenol sulphonic acid with formaldehyde.

In this course we will discuss only synthetic organic ion exchange resin.

1. Synthetic Organic Ion Exchange Resins

The most important commercial exchangers are polymer of polystyrene divinyl-benzene with fixed ionogenic groups attached with the matrix and counter ions residing in the pores. They are chemically robust and have well defined characteristics such as swelling, exchange capacity and selectivity. A schematic representation is shown in Fig. 17.11.

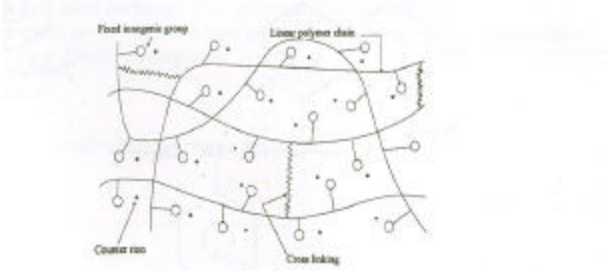


Fig 17..11

The common ionogenic groups used for cation exchangers are: sulphonate ($-SO_3^-$), phosphonic ($-PO_3^{2-}$) and carboxalate ($-COOH$); and for anion exchangers are: amines ($-NH_2^+, -NHR^+, -NR_2^+$) and quaternary amines ($-NR_3^+$).

Depending on the nature of the fixed ionogenic group, the ion exchange materials are of four types:

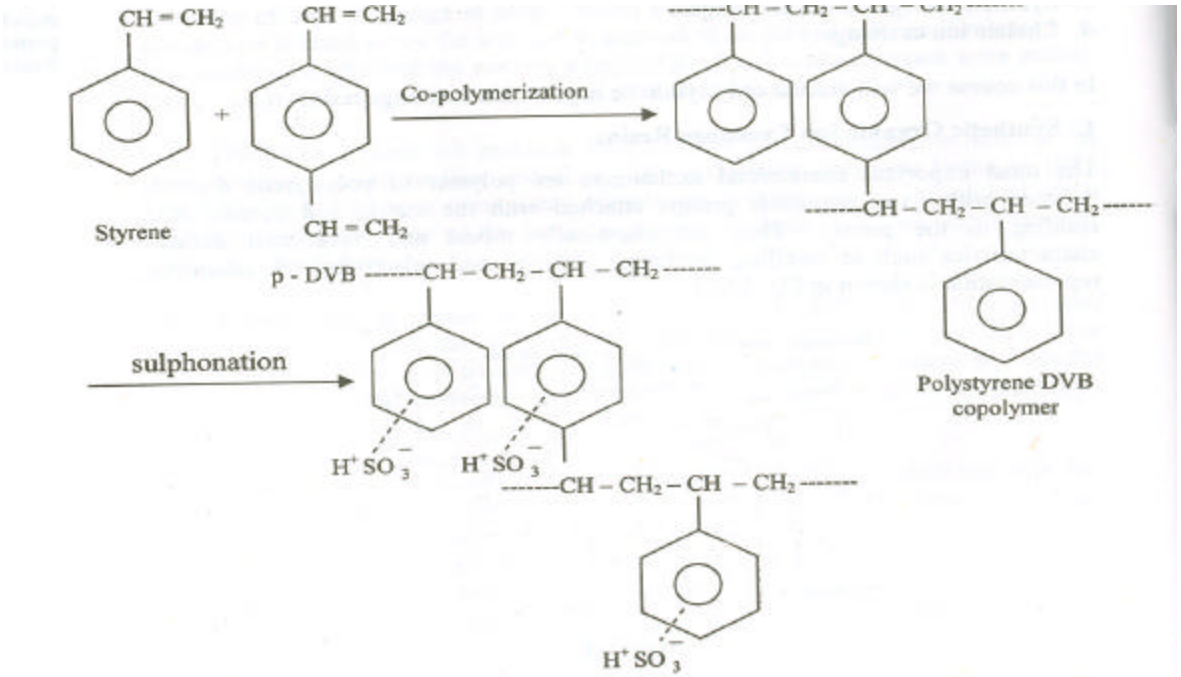
(i) strongly acidic cation exchanger
(ii) weakly acidic cation exchanger
(iii) strongly basic anion exchanger
(iv) weakly basic anion exchanger

For example an exchanger having $-SO_3^-$ group which is obtained from a strong acid, is referred to as a weak acid cation exchanger and that having –COOH group is referred to as a weak acid cation exchanger. Strong base anion exchangers are based on the introduction of quaternary ammonium ionogenic groups and the weak base anion exchangers contain primary or secondary amine ion ionogenic groups. Some of the important properties of these materials depend upon the nature of the ionogenic group.

Strong Acid Cation Exchangers

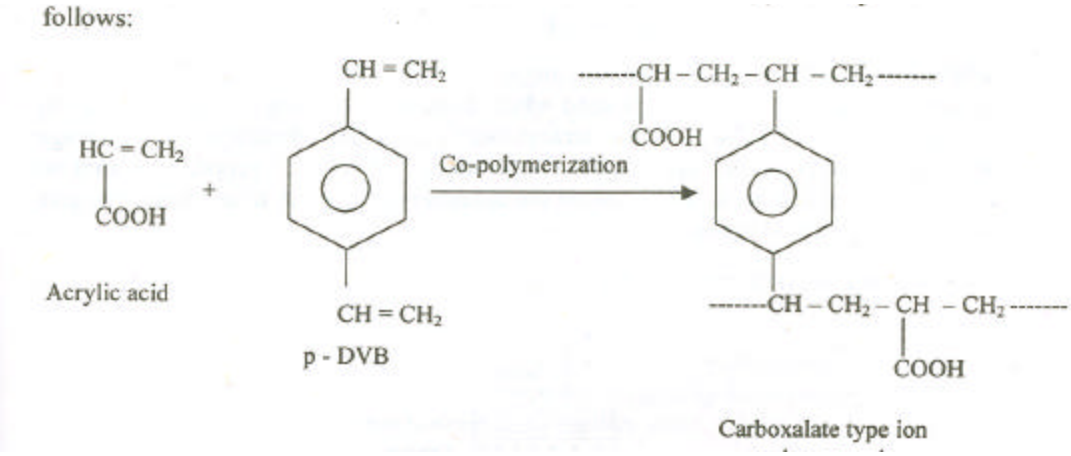
Some common strong acid cation exchangers are Dowex-50, Amberlite IR-120, Duolite C-20, Permutit Q and many others. These materials are prepared by co polymerization of styrene and divinylbenzene (DVB). The percentage of divinylbenzene is responsible for cross linking and may range from 2 to 20 per cent, with a selection of 8% for common type of ion exchangers. The pearl polymerization results almost completely spherical beads which can be prepared in varied range of particle sizes according to the requirement.

The beads are now sulphonated by refluxing with sulphuric acid or chlorosulphuric acid. The each benzene ring of the polymer is sulphonated by substitution reaction. $-SO_3^-$ group is attached with the matrix and produces the negative charge on it. H^+ ions remain as mobile ions and behave as the counter ions. The reactions may be represented as follows:



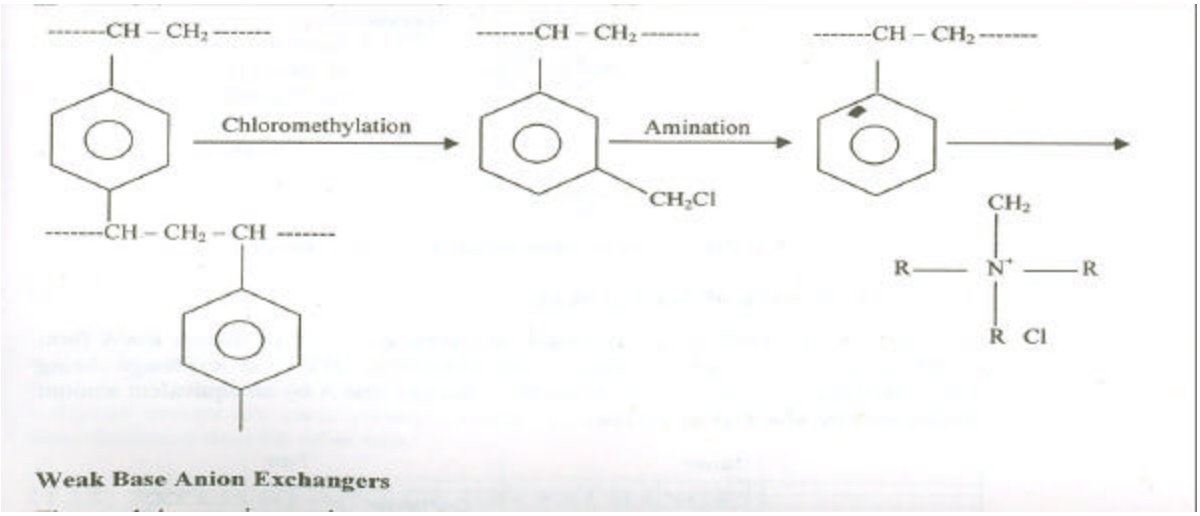
Weak Cation Exchangers

Wofalte C and Amberlite 45C are examples of weak cation exchanger. These materials are prepared by introducing a weak acid carboxylate functional group in the polymer network. They are prepared by co polymerization of mixture of acrylic acid or methacrylic acid with divinylbenzene. The reactions may be represented as follows:



Strong Base Anion Exchangers

The strong base anion exchange materials are prepared by the addition of quaternary ammonium group by chloromethylation of the cross linked polymer through a Friedel-Crafts condensation reaction followed by amination. The reaction may be written as:



Weak Base Anion Exchangers

The weak base anion exchange resins are prepared by the addition of a primary or secondary amine group. The weak base ion exchangers do not work well with weak acids, but are preferred for strong acids.

SAQ 6

What are the main advantages of organic ion exchange resins?

……..

……..

……..

17.11.2 Ion Exchange Process

Ion exchange is a process in which an insoluble material (ion exchanger) when comes in contact with an electrolyte solution ions of positive or negative charge and releases other ions of like charge from the exchanger phase into the solution phase.

$$2RH + CaCl_2 \longrightarrow R_2Ca + 2HCl$$

where R represents the unit of ion exchanger.

In general, a column operation is used which consists of passing the sample solution through an ion exchanger. This arrangement offers the advantage of multistage separation process with ease of phase separation. Because of proper regeneration (eqn. above), which is carried out when the column is exhausted, these ion exchangers can be used over and again.

$$R_2Ca + 2HCl \longrightarrow 2RH + CaCl_2$$

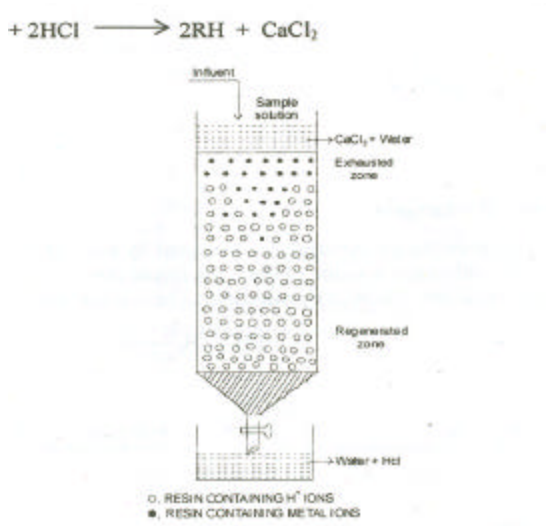


Fig. 17.12: A simple cation exchanger column in service.

17.11.3 MECHANISM OF ION EXCHANGE

Let us consider the uniform and spherical ion exchanger beads in counter ion A form placed in a well stirred solution of an electrolyte Bγ. Ion exchange being stoichiometric process gives a replacement of counter ions A by an equivalent amount of other counter ions B (Fig. 17.13a).

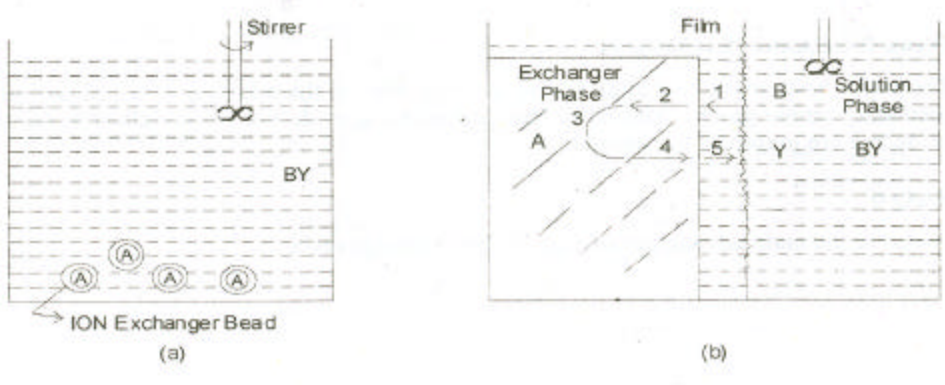


Fig. 17.13: Ion Exchange in Beads in A form and well stirred solution of B γ

The Donnan potential checks the entry of co-ions, but this does not hinder the entry of counter ions. Electroneutrality is maintained and the charge transfer by counter ions A is balanced by an equivalent charge transfer by counter ions B.

The ion exchange may be explained with the help of Fig. 17.13b as a stepwise mechanism.

1. Migration of counter ion B from the solution into the film.
2. Migration of counter ion B from the film into the exchanger particle.
3. Chemical exchange between A and B.
4. Migration of counter ion A from the particle into the film.
5. Migration of counter ion A from the film into the solution.

17.11.4 ION EXCHANGE CAPACITY

For characterizing an ion exchange material and to find the quantitative application of the ion exchanger in an experimental operation the capacity is of prime importance. The ion exchange capacity may be defined in various ways. However, the following three ways are in general use.

i) Weight Capacity

It is defined as the number of ionogenic groups per specified amount of dry ion exchanger. It is expressed in meq per gram of dry ion exchanger. A cation exchanger is taken in H^+ form and an anion exchanger in CI^- form to measure this capacity. The value of the weight capacity is a constant and does not depend on the experimental conditions. It may be used for characterizing ion exchangers. It is also known as scientific weight capacity and the maximum capacity. For common ion exchangers the weight capacities are between 1 and 5 meg/g.

ii) Volume Capacity

It is defined as the number of or inorganic groups per unit volume of packed bed (completely swollen exchanger). It is expressed in meq. per ml. Volume capacity depends on the water content of the ion exchanger.

iii) Apparent or Effective Capacity

It is defined as the number of exchangeable counter ions per specified amount of dry ion exchanger. It is expressed as meg/g of H^+ or CI^- form of ion exchanger. It depends on experimental conditions and is lower than the weight capacity when ionogenic groups are incompletely ionized. For practical applications this type is more important than the other two.

17.12 APPLICATIONS OF ION EXCHANGE

Ion exchange has number of applications as softening and deionization of water, concentration of ionic trace constituents, dissolution of sparingly soluble salts, ion selective electrodes, preparation of reagents, removal of interfering cations or anions, catalysis, redox reactions, selective uptake of certain ions, water pollution control, metal ion removal and recovery etc.

For the purpose of environmental analysis the discussion will be made only on the softening and deionization, pollution control of water and metal ion removal and recovery; though the treatment by other methods is also possible, ion exchange offers six advantages: (1) easy practical applicability (2) minimization of wastes (3) recovery and removal of metals (4) making water for reuse (5) possible regeneration of ion exchanger and (6) less recurring cost.

17.12.1 Softening and Deionization of Water

The complete removal of all ions from solution or hard water is known as deionization. For this process a twin bed system is used. The first column contains a cation exchange resin in hydrogen form and the second an anion exchange resin in hydroxyl form.

Hard water or aqueous solution containing ionic species is admitted first to a column of cation exchange resin in H^+ form. As the solution percolates through the exchanger bed, the cations in solution are taken by the resin and equivalent amount of hydrogen ions is released from it. The effluent of this column contains hydrogen ions and the anion which were originally present with the hard water or aqueous solution. The exchange reaction can be represented as follows.

$$2R_CH + SO_4^{2-} + 2H^+ \qquad Ra_2\,SO_4 + 2H_2O$$

where M is a metal and R_c is the matrix unit of a cation exchange resin.

The effluent of the first column is now admitted to the second column containing an anion exchange resin; in hydroxyl form. As this solution percolates through the column, the anions present in the solution are taken by the exchanger replacing an equivalent amount of hydroxyl ions which react with hydrogen ions released from the first column stoichiometrically. The effluent of the second column is deionized or pure water. The reaction is as follows:

$$2R_aOH + SO_4^{2-} + 2H^+ \qquad R_{a2}\,SO_4 + 2H_2O$$

where R_a is the matrix unit of anion exchange resin. Deionized water so obtained is comparable with a double or triple distilled water and can be checked by conductivity measurement.

When the resin beds are exhausted they are regenerated by a suitable acid and a bases respectively e.g. regeneration of cation exchanger column can be achieved by 4M hydrochloric acid solution and regeneration of anion exchanger by 1M sodium hydroxide solution.

17.12.2 Ion Exchange is Pollution Control

The study of pollution of water has a great importance because of multiple use of water for human consumption, agriculture, power generation and fisheries. In India the main source of water is the river water. But the rivers are continuously being polluted by the waste disposal in various ways, for example, by oil refining, oil drilling, paper industries, fertilizer industries, sugar industries and distilleries, municipal wastes, coal fields & mining, nuclear reactors, pesticide and other chemical industries.

Increasing knowledge with time, a realization of the effect of the presence of toxic materials in water has increased. This led to the careful investigation of water to fight and eliminate such contamination and developed the interest for the suitable water to be used with safety to the public health.

A novel approach is the use of ion exchange materials that can be used to remove the ionic species. The contaminated water should be treated before it is allowed to pour into. main stream

i) Treatment of Brackish Water: Use of Weak Ion exchangers

The growing energy shortage demands that water treatment process be more efficient than in past. Increased environmental restrictions on waste streams must be met. The treatment method selected should be one that will convert the waste water to the required quality of water at the minimum cost.

Conventional deionization has been widely used for many years in water treatment practices. However, this has been normally limited to water with less than 500 ppm ($CaCO_3$) hardness level. When the salinity is higher than this level, the operation cost increases due to larger amount of regenerate needed.

Weak ion exchangers can often be used advantageously ahead of conventional deionization when the salinity is high e.g. sea water, industry waste water, the use of weak ion exchange resins with their excellent chemical efficiencies can significantly reduce regenerate usage and minimize wastes without loss of product quality. These exchangers offer opportunities for increased selectivity and efficiency of operation in many water conditioning applications.

An economical deionization technique known as "Desal Process" has been developed recently for the treatment of brackish water. The method is based on the use of two weak ion exchange resins. First a weak anion exchange resin in bicarbonate form and then a weak cation exchange resin in hydrogen form.

The anions of brackish water replace bicarbonate from the first column containing weak acid anion exchanger and known as the ALKALIZATION COLUMN, since it releases bicarbonate making the solution alkaline. The reaction is illustrated by taking an example of calcium chloride as the hardness creating salt.

$$2(\text{R-NH})HCO_3 + CaCl_2 \longrightarrow 2(\text{R-NH})Cl + Ca(HCO_3)_2$$

where $(\text{R-NH})HCO_3$ represents the unit of a weak anion exchange resin in bicarbonate form.

The effluent of the first column contains the bicarbonate salts of metal ions. That is now passed over a second column containing a weak cation exchange resin in hydrogen form. The metal ions replace hydrogen ions which react stoichiometrically with bicarbonate to form carbonic acid. The alkalinity of water, the influent to the second column, is removed by this column denoted by the following equation:

$$2\text{R-COOH} + Ca(HCO_3)_2 \longrightarrow (\text{R-COO})_2Ca + 2H_2CO_3$$

where R-COOH represents the unit of a weak cation exchanger in hydrogen form.
The effluent of the second column passes through a degasifier system where CO_2 is released and processed water is used for domestic, industrial and agricultural purposes. The released CO_2 is used for regenerating the first column.

The process is illustrated with the help of a block diagram in Fig.17.14.

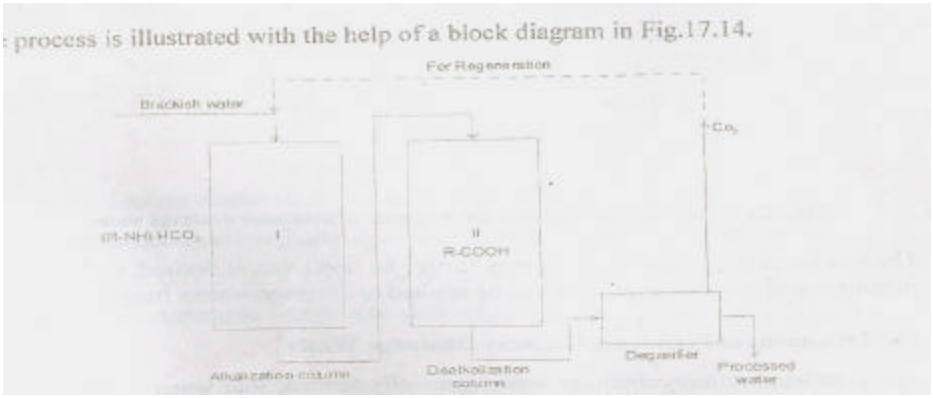


Fig. 17.12: Desal Process for Treatment of Brackish Water.

Regeneration: When the resin columns are exhausted, the regeneration is accomplished in the following manner.

The alkalization column is regenerated in two steps. In the first step it is converted to free base form by NaOH or $Ca(OH)_2$ solution.

$$(R\text{-}NH)Cl + NaOH \longrightarrow R\text{-}N + NaCl + H_2O$$

In the second step the free base form of the resin is converted to bicarbonate form with CO_2 released from the degasifier system.

$$(R\text{-}N) + H_2O + CO_2 \longrightarrow (R\text{-}NH)HCO_3$$

The dealkalization column is regenerated with a suitable and cheaply available acid.

$$(R\text{-}COO)_2 + 2HCl \longrightarrow 2(R\text{-}COOH) + CaCl_2$$

Modifications of this process can be incorporated to treat acid mine drainage waters and industrial waste waters.

ii) Treatment of Acid Mine Drainage Water

Drainage water from mines containing acids can be passed through a weak anion exchange resin column in bicarbonate form in reverse manner. The resin takes all the anions replacing bicarbonate ions which react with hydrogen ions present in the acid mine drainage water, to form carbonic acid.

$$(R\text{-}NH)HCO_3 + HNO_3 \longrightarrow R\text{-}NH)NO_3 + H_2CO_3$$

The effluent is passed through degasifier system which releases CO_2 and produces water free from acids. CO_2 obtained as by-product may be used to regenerate the resin column.

The process is illustrated in Fig.17.15 with the help or block diagram.

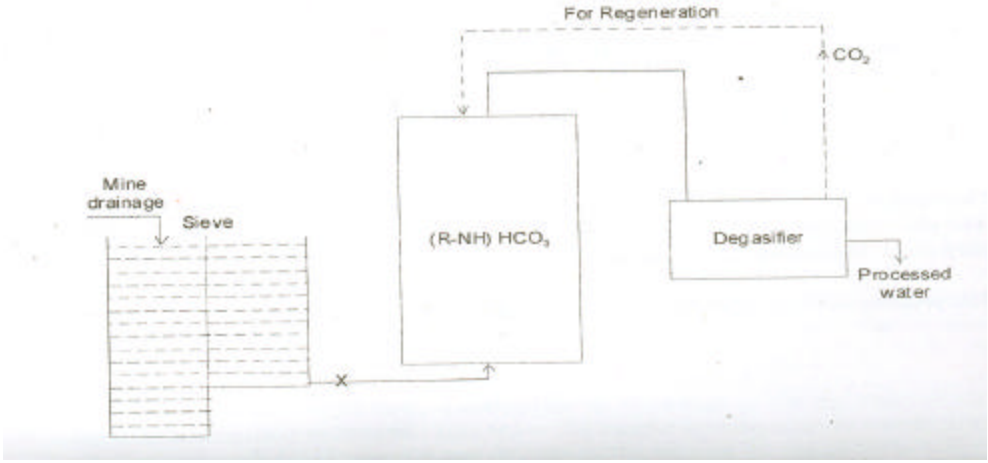


Fig. 17.15: Desal resin process for the treatment of acid mine drainage water.

The quality of the processed water may further be improved, if desired, through a lime treatment softening. The process can be applied to drainage waters from coal mines.

iii) Treatment of Petroleum Refinery Drainage Water

The petroleum refinery drainage water, generally termed, sour water, contains varied amounts of ammonia, hydrogen sulphide, phenols and some inorganic cations. In the refining operations, catalytic cracking and thermal cracking of heavy oils introduces the foul smelling pollutants and pollution characteristics of sour water are of great concern.

A process based on the use of weak electrolyte ion exchange resins is a highly effective process for renovating the sour water. The whole arrangement consists of two columns one of weak cation exchanger in hydrogen form and the other of a anion exchanger in free base form with a degasifier system placed between the two columns (Fig. 17.16)

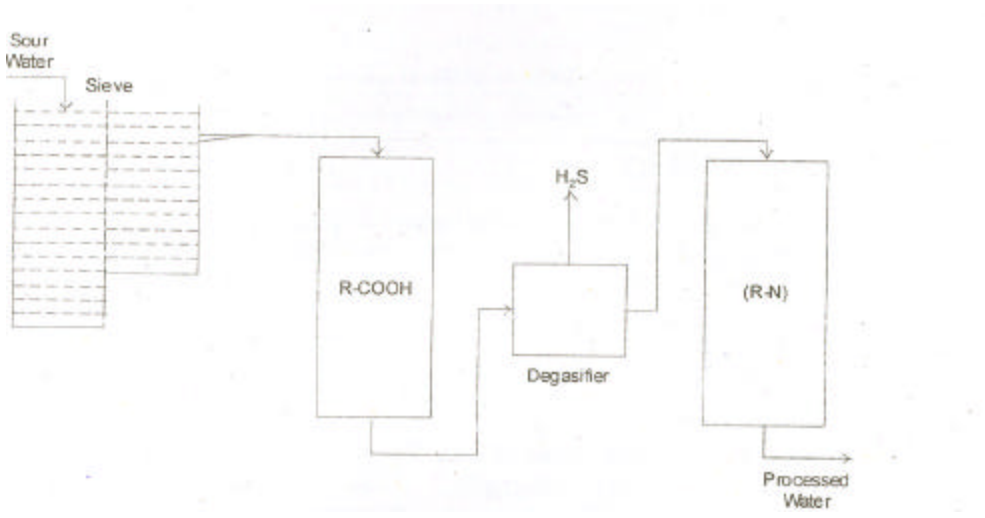


Fig. 17.16:

Hydrogen sulphide and ammonia, present in sour water, combine to form ammonium hydrogen sulphide which ionizes in water as NH_4^+ and HS^-. The NH_4^+ ions on a weak cation exchanger and liberating H_2S which can be stripped by conventional methods using a degasifier system.

$$R\text{-}COOH + NH_4HS \longrightarrow R\text{-}COONH_4 + H_2S$$

H_2S is collected as a by-product and can be used to prepare sodium sulphide or ammonium sulphide. Inorganic cations, if present are also exchanged on the column of weak cation exchanger. The effluent after the degasifier system is passed through the second column containing weak anion exchange resin in the free base form which adsorbs phenols. The processed water can now be discharged to a river.

Regeneration of the cation exchanger is accomplished with sulphurous acid which is obtained from the refinery by the dissolution of SO_2 (from flue gas) in water.

$$2R\text{-}COONH_4 + H_2SO_3 \longrightarrow 2R\text{-}COOH + (NH_4)_2SO_3$$

The regeneration of anion exchanger is accomplished by alcohol to remove adsorbed phenols. Later on, the mixture of alcohol and phenols may be separated to recover these compounds by fractional distillation.

SAQ 7

Fill in the following blanks w ith appropriate word.

a) The petroleum refinery drainage water contains mainly the impurities of

……...……

b) A cation exchanger membrane will allow to pass through ……..…… and not ……...

c) Conventional deionization is not a suitable method if the hardness level is

…….ppm ($CaCO_3$)

SAQ 8

What are the advantages in using ion exchange for treatment of wastewaters than the other methods?

……..

……..

……..

17.13 SUMMARY

- Solvent extraction is based on principle of phase distribution. It exploits the differential solubility of a given solute in two immiscible solvents to separate it from a given mixture.
- Chromatography is a separation technique based on the distribution of sample between the two immiscible phase. One is stationary phase and other is mobile which percolates over the stationary phase.
- In this course we have discussed only three common chromatography technique i.e. thin layer chromatography, column chromatography and paper chromatography. Some basics regarding these techniques are discussed.
- Rf is the ratio of the distance moved by the solute spot to the distance moved by the solvent front.
- Development of chromatogram refers to the separation of mixture on the plate or column by allowing the liquid phase to move on the adsorbent.
- Coloured compounds are easily located by sight but for colourless compounds some spraying reagents are used to find the positions of spots on TLC plate.
- Quantification can be roughly estimated by simple visual comparison technique or spectrophotometeric method.
- There are many types of ion exchange material, but in this unit we have discussed only synthetic ion exchange resin and chelate ion exchange resin.
- Ion exchange finds its utility in various processes but we have discussed only for the purpose of environmental analysis e.g. softening and deionization of water, pollution control of water and metal ion removal and recovery.
- Although quantitative analysis is possible by TLC and paper chromatography but the main application is in qualitative identification.
- The separation by paper chromatography are based, mostly on the distribution ratio between the water saturated cellulose (stationary phase) and the developing liquid.

17.14 TERMINAL QUESTIONS

1. What is distribution coefficient?
2. What are the properties of good adsorbent?
3. What are the properties of good chromatogram?
4. What are the limitations of paper chromatography?
5. An aqueous solution of sodium chloride was passed through a column prepared by 2 g of Dowex-50 resin in hydrogen form till all H^+ ions were replaced by

Na+ ions. The total effluent collected consumed 84 ml of O.IN NaOH for complete neutralization, Calculate the ion exchange capacity of Dowex-50 resin.

17.15 ANSWERS

Self -Assessment Questions (SAQs)

1. Please see sub-Section 17.4.1

2. We know Rf = $\frac{\text{Distance moved by spot}}{\text{Distance moved by solvent}}$

$$\text{Rf value of acetophenone} = \frac{15}{18} = 0.83 \text{ cm}$$

$$\text{and Rf value of hexadecanol} = \frac{5}{18} = 0.28 \text{ cm}$$

3. Increasing order of eluting power is i), iii), v), vi), ii), iv)

4. For colourless component we use some spraying reagent to find the position of the spot which is known as visualizing agent. The common visualizing agents are: ur light, I2, NH3 etc.

5. a) same b) stoichiometric c) reversible

6. Organic ion exchange resins are mechanically more stable, the preparation can be varied at will, the bead form is suitable for column operation and they can be regenerated without loss of ion exchange capacity.

7. a) NH_3, H_2S & phenols
   b) cations, anions
   c) > 500

8. Easy practical applicability, minimization of waste, recovery and removal of metals, making water for reuse, possible regeneration of ion exchange column and economic.

Terminal Questions (TQs)

1 Distribution coefficient is the radio of the concentration of the solute in two solvent

2 The good adsorbent should have following properties:

(i) the adsorbent should not react with the solute being separated
(ii) the adsorbent must not dissolve in mobile phase
(iii) the adsorbent must not react with mobile phase
(iv) the adsorbent must release the solute with mobile phase

3 For a good chromatogram zone should be compact, well defined and well separated

4 The main disadvantages are:

- The separation time in much more than TLC
- Recovery of the separated components is difficult
- Accuracy and reproducibility is low.

5 Ion exchange capacity = no. of meq of counter ion/g
= no. of meq of H^+ liberated/g
= no. of meq of OH^- consumed/g
= (8.4 × 0.D/2 = 4.2 meq/g of resin