CHAPTER - I

GENERAL INTRODUCTION

INTRODUCTION

Chromatography is a technique for the resolution of a mixture of compounds and for the isolation and partial description of the separated substances. The importance of chromatography lies in its use as an analytical tool.

In a chromatographic unit, the components to be separated are distributed between two phases, the mobile and the stationary phase. The mobile phase is a gas or liquid which is inert with respect to the sample. It flows at a more or less constant rate in one direction through the stationary phase, which may be a solid with a large surface to volume ratio or a high-boiling liquid on a solid support. The sample may be a gas, solid or liquid which however, must be soluble in the mobile phase. The term detector includes any unit capable of determining whether or not a substance is present in the mobile phase. Detectors range from high resolution mass spectrometers coupled to computers to very simple thermal conductivity cells. The material may be collected at the detector end and subjected to further separations or chemical tests.

The transfer of mass between the mobile phase and stationary phase occurs either because the molecules of the mixture are adsorbed on particle surfaces or adsorbed into particle pores, or they participate into pools of liquid held on surfaces or within pores. The general process is known as sorption.

Separation of a component in a sample is based on the partition of the molecule between the mobile phase and the stationary phase. Thus the partition coefficient of each component determines how much of it is present in the mobile phase at any time and thus the overall time spent in the stationary phase.

VARIOUS TYPES OF CHROMATOGRAPHIC METHODS

Depending on the mobile phase and the stationary phase one could have various combinations such as liquid-liquid, liquid-solid, gas-liquid and gas-solid chromatography. The various chromatographic methods could be classified as partition chromatography, adsorption chromatography, gas-solid and gas-liquid chromatography, exclusion chromatography and ion exchange chromatography.

Adsorption chromatography, the oldest of the various chromatographic methods based on the retention of solute by surface adsorption, is one of the simplest and most effective ways of separating methods of rather non polar substances such as liphophilic substances and constituents of low volatility.

In liquid-liquid partition chromatography, separation of a solute into its individual components is by distribution of the sample ingredients between a stationary liquid phase, usually held in place by an inert scaffold of solid particles, and a mobile liquid phase.

Gas chromatography differs from other methods of chromatography in that the mobile phase is a gas and the solutes are separated as vapours. The sequence of operations in a gas chromatograph can be visualised as a sample is injected into a heating block maintained at a high enough temperature so as to immediately vaporise the sample and is swept as a plug of vapour by the carrier gas stream into the column inlet.

Molecular sieves are synthetic zeolites which offer a novel method of separation of permanent gases. This chemical selectivity is due to the precise pore dimensions of the molecular sieves, while inorganic zeolites find applications in the separation of small molecules, organic xerogels are useful in the case of high molecular weight substances particularly biological molecules and polymeric materials. Apart from synthetic zeolites there are also naturally occurring zeolites.

Ion exchange chromatography is a powerful tool for chemical separations. Columns of ion exchange materials are used to separate all manner of inorganic ions from one another, as well as organic ions and organic compounds, that are not ionised at all. The wide scope of ion exchange chromatography is the product of the labours of many people.

Synthetic ion exchangers are used in analytical chemistry, hydrometallurgy and water treatment[1]. Many ion exchangers owe their origin to petroleum products and there is a continual increase in their cost. It is, therefore, necessary to prepare cheaper exchangers to identify substitutes which can partly replace the polymeric content of the exchangers to a considerable extent without causing deterioration of the properties of the parent polymers. Attempts have been made to synthesise newer cationic exchangers from renewable source of materials like rice husk[2], bagasse[3], coconut fibre[4], groundnut shells[5] and wheat husk charcoal[6].

The exchange capacity determined by EDTA titrations for Ca^{+2}, Zn^{+2} were found to be higher than that of Na^{+}. There was a continuous decrease in exchange capacity of composites and the fall was not much upto 20% of charcoal in the resin. The substitution of charcoal converted from rice husk, bagasse, coconut fibre, wheat rusk and groundnut shell was found to be economical upto 20%. Since the exchange capacity composite is acceptable.

ION EXCHANGE MATERIALS

Ion exchange separations are limited to samples containing ionised or partially ionised solutes. Ion exchange is a chemical reaction in which free mobile ions of a solid, the ion exchanger, are exchanged for different ions of similar charge in solution. The exchangers are insoluble in the solvents containing ions to be exchanged, and they are resistant to chemicals at temperatures below 100^0C. Along their basic physical properties, hardness and resistance to abrasion are the most desirable.

All ion exchangers have the same basic structure. This fundamental frame work is a three dimensional network that is fixed and chemically insensitive to the surrounding electrolytes. It acts like a semipermeable membrane through which charged species can diffuse. The site of exchange is attached to this inert matrix. The site of exchange is hydrophillic and contains functional groups that are ionisable and mobile counter ions. These counter ions can be replaced when brought in contact with an external solution containing ions of suitable charge and size. The fixed functional groups determine the nature of the exchange process. Thus the ion exchange materials are categorised as cation exchangers and anion exchangers. The cation exchangers are capable of exchanging cations and the anion exchangers can exchange anions with the surrounding electrolytes.

To obtain cation exchange resin, styrene monomers are first polymerised to give linear chains of the polystyrene, which are then covalently bonded to each other through divinyl benzene bridges, forming a three dimensional matrix. When this co-polymer is reacted with sulphuric acid, sulphonic groups are introduced into the structure and the resulting cation exchanger has the following structure, (fig.1-a) and it can be converted to the ammonium form (fig. 1-b).

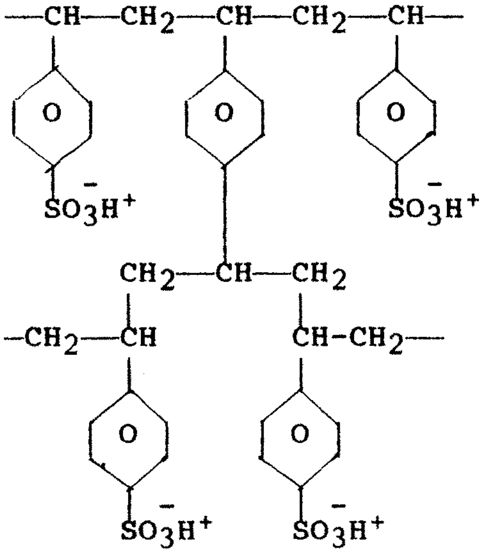

Fig. 1.a

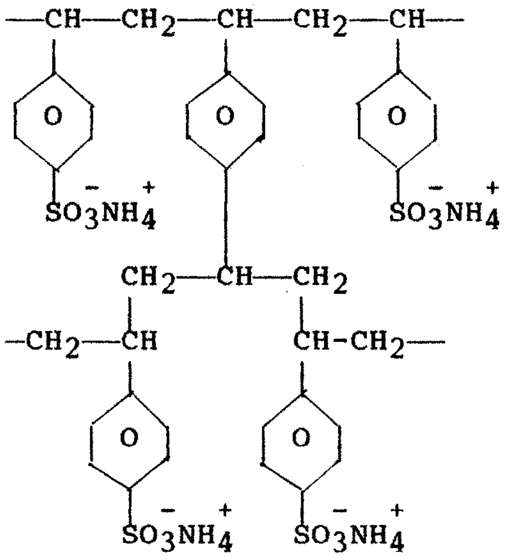

Fig. 1.b

Ion exchange resin has polymeric skeleton, held together by linkages crossing from one polymer chain to the other. The polymeric skeleton has ion exchange groups. The degree of cross-linking determines the physical properties. Highly cross-linked resins are brittle, harder and more impervious than the highly cross-linked materials. The preference of a resin for the ion is influenced by the degree of cross linking. Anion-exchanger is likewise cross-linked, high molecular weight polymer containing amine or quaternary ammonium groups and an equivalent amounts of anions such as chloride, hydroxyl or sulphate ions.

Depending upon the nature of the exchangeable ions, the cation exchanger may represent either an acid or a salt and the anion exchanger a base or salt. Cation exchanger is in the hydrogen form, it behaves as an acid whose strength is determined by the binding energy between the exchangeable hydrogen and the anion structure of the exchanger, when anion exchangers are in hydroxyl form, the anion exchange substances form a series of bases of varying strength. Anion exchange resins show an inferior chemical stability compared with cation exchange resins.

ION EXCHANGE PROCESS

Ion exchange reactions involve ionic equilibria and are therefore subject to rules governing these reactions. The reaction proceed stoichiometrically as,

$$R\overset{-}{A}\,\overset{+}{B} + \underset{(Sol^{n})}{\overset{+}{C}} \longrightarrow R\,\overset{-}{A}\,\overset{+}{C} + \overset{+}{B}\ \text{(solution)}$$

For every C^{+} ion removed from the external solution, a stiochiometrically equivalent numbers of B ions diffuse out of the resin. Because of the requirement that electrical neutrality be maintained at all times, the exchange capacity of an ion-exchange resin is indirectly dependent on the electrical charge of the functional groups attached to the organic backbone rather than on the nature of the mobile ions.

The displacement of NH_4^+ ions by Mg^{2+} ions in a sulphonate resin is given by

$$2\ R\ SO_3^-\ NH_4^+ + Mg^{++}(sol^n) \rightleftharpoons (R\ SO_3)_2^-\ Mg^{++} + 2\ NH_4^+\ (sol^n)$$

The reaction is reversible, by passing a solution containing ammonium ion through the product, the magnesium ions may be removed from the resin and the original ammonium form is restorted. The exchange capacity is virtually independent on the pH of the solution in this type of resin. In case of a weak acid cation exchanger, ionisation occurs to any appreciable extent only in alkaline solution.

EXPERIMENTAL

REAGENTS, SOLUTIONS AND APPARATUS

ION EXCHANGE RESIN

A cation exchange resin, Amberlite IR-120 was used in the ammonium form. Ammonium form resin obtained by treating Amberlite IR-120 in H^+ form, in column successively with 2N HCl before use. The resin was then converted into NH_4^+ form by treating with 10% NH_4Cl solution in 10% liquor ammonia (Sp.gr. 0.91) and then washing with distilled water till the effluent was air dried by suction on a sintered bed and stored. The capacity and moisture contents were 5.1 meq/g and 51.4% respectively.

THE GLASS COLUMNS

For all separation work Corning glass columns were used. The resin was filled in the columns by preparing a slurry of it in the water. The column was open on one end and at the other end, there was a nozzle with a stop cock, with the help of which one can control the drop-rate of the effluent. The glass column had a length of ≃ 560 mm and uniform inner diameter of ≃ 14 mm. A column of resin bed can rest easily on a sintered glass porous support at he botom. The height of the resin bed can be varied easily. A care was always taken that the resin bed will always remain beneath the water level at the top.

SOLUTIONS

Standard solutions were prepared from A.R.Grade reagents of B.D.H,S.R.L (India):Koch - Light Labarotary England, Fluka A.G.,Switzerland and Sarabhai M. Chemicals, India.

E.D.T.A.

0.1 M, 0.01 M and 0.001 M standard solutions of E.D.T.A were prepared by dissolving 37.225 g, 3.723 g and 0.372 g of A.R grade E.D.T.A.

METAL SALTS

0.1 M stock solutions of Cobalt, Cadmium, Copper, Mercury, Nickel, Zinc, Manganese, Magnesium, Calcium, Barium, Strontium, Aluminium, Lead, Thorium were prepared from A.R grade salts as follows.

1. $Co(No_3)_2\ 6H_2O$ —— 29.104 g dissolved in 1000 ml
2. $CdCl_2\ .H_2O$ —— 20.132 g dissolved in 1000 ml
3. $Cu(No_3)_2.3H_2O$ —— 24.16 g dissolved in 1000 ml
4. $HgCl_2$ —— 27.150 g dissolved in 1000 ml
5. $NiCl_2.6H_2O$ —— 23.771 g dissolved in 1000 ml
6. $Zn(No_3)_2.6H_2O$ —— 29.747 g dissolved in 1000 ml
7. $MnCl_2.4H_2O$ —— 19.792 g dissolved in 1000 ml
8. $MgCl_2.6H_2O$ —— 20.331 g dissolved in 1000 ml
9. $Ca(No_3)_2.4H_2O$ —— 23.616 g dissolved in 1000 ml
10. $BaCl_2.2H_2O$ —— 24.431 g dissolved in 1000 ml
11. $SrCl_2.6H_2O$ —— 26.662 g dissolved in 1000 ml
12. $Al(No_3)_3.H_2O$ —— 23.1 g dissolved in 1000 ml
13. $Pb(No_3)_2$ —— 33.123 g dissolved in 1000 ml
14. $Th(No_3)_2.6H_2O$ —— 58.815 g dissolved in 1000 ml

The solutions were standardised by using literature methods.

BUFFER SOLUTION (pH = 10)

70 g of A.R. grade Ammonium Chloride was dissolved

in 568ml of Concentrated ammonia and diluted to 1000 ml with distilled water.

INDICATORS

1) **Eriochrome Black T:-** The indicator solution was prepared by dissolving 0.29 of dyestuff in 15 ml of triethanolamine with the addition of 5 ml of absolute alcohol to reduce the viscocity.

2) **Xylenol Orange:-** The indicator solution was prepared by dissolving 0.5 g of Xylenol orange in 100 ml of distilled water.

3) **PAN 1-(2-pyridylazo)-2-naphthol:-** The indicator solution was prepared by dissolving 0.1 g of PAN in 100 ml of methyl alcohol.

4) **Phthalein Complexone:-** The indicator solution was prepared by dissolving 0.1 g of phthalein complexone in 100 ml of distilled water containing a little ammonium hydroxide

5) **Murexide Indicator:-** The indicator solution was prepared by dissolving 1 g of murexide in 50 ml of distilled water.

6) **Ammonium citrate solution:-** 1M stock solution of ammonium citrate was prepared by dissolving 226.20 g of ammonium citrate in 1000 ml of distilled water.

ESTIMATION OF METAL IONS

1) Estimation of Copper[7]

10 ml of nearely neutral solution of copper chloride was pipetted in a 250 ml conical flask. 1 ml of glacial acetic acid and 3-4 drops of 0.1 % PAN indicator solution were added.

The solution was titrated with 0.01M E.D.T.A solution. The end point indicated by a colour change from red to yellowish green. A violet or blue colour appears before the end point if more than few milligrams of copper are present.

1 ml 0.1M E.D.T.A = 6.354 mg cu

2) Estimation of Nickel[7]

Nickel was determined by a direct titration with EDTA, using murexide as indicator. Ammonium hydroxide was added to the nickel solution untill the nickel is converted to the tetramine complex. Diluted mixture and 3-6 drops of a saturated aqueous solution of murexide are added for each 100 ml of solution , and titrated with a standardized 0.1M solution of EDTA. The end point is indicated by a colour change from orange-yellow to purple.

1 ml 0.1M EDTA = 5.869 mg of Ni

3) Estimation of Cobalt[8]

10 ml of the coblat nitrate solution was diluted to 25 ml with distilled water and 3 drops of Xylenol orange indicator was added followed by very dilute sulphuric acid until the colour just changes from red to yellow . To this solution powdered hexamine was added with shaking until the deep red colour was restorted (pH =6). The solution was warmed to about 40^0c and titrated with standard EDTA solution until the colour changes from red to yellow orange. The addition of titrant should be made dropwise near the end point; Since the colour change is normally not altogether sharp. The amount of cobalt was calculated by using the relation.

1ml 0.1M EDTA = 5.9993 mg Co.

4) Estimation of Manganese[8]

10 ml of manganese chloride was pipetted out in a conical flask, 0.5 gm of hydroxyl ammonium chloride was added to prevent oxidation of managaese ion. The solution was then diluted to 50 ml with distilled water. 3 ml of triethanolamine, 2 ml of buffer solution (pH = 10) and several drops of Eriochrome Black-T indicator was added and the mixture was titrated with 0.1 M EDTA solution unitl the colour changes from wine red to sky blue. The amount of manganese was calculated using the relation.

1 ml of 0.1 M EDTA = 5.494 mg of Mn.

5) Estimation of Lead[8]

The lead ions were estimated titrimetrically using standard EDTA solution. 10 ml of lead chloride solution was pipetted out in a conical flask and it was diluted to 50 ml with distilled water, three drops of xylenol orange indicator were added. If the colour of solution is red, dil. H_2SO_4 is added until the solution acquires yellow colour, powdered hexamine is added in order to change yellow colour of solution to intensely red.

This step ensures that the solution has the correct pH (about 6). The mixture was titrated with 0.1 M EDTA solution until the colour changes from red to yellow. The amount of lead was calculated by using the relation.

1 ml of 0.1 M EDTA = 20.721 mg of Pb

6) Estimation of Magnesium[8]

The magnesium ions were estimated titrimetrically using standard EDTA solution 10 ml of magnesium salt solution was pipetted out in a concial flask and it was diluted to 50 ml with distilled water. 4 ml of buffer solution (pH = 10) and a few drops of Eriochrome Black-T indicator was then added and the mixture was titrated with 0.1 M EDTA solution, until the colour changes from wine red to blue. The amount of magnesium was calculated by using the relation.

1 ml of 0.1 M EDTA = 2.432 mg of Mg

7) Estimation of Calcium[8]

The calcium ions were estimated titrimetrically using standard EDTA solution. The procedure for estimation of calcium ions is the same as that of magnesium ions. The amount of calcium was calculated by using the relation.

1 ml of 0.1 M EDTA = 4.008 mg of Ca

8) Estimation of Strontium[7]

The solution containing the strontium was mixed with an equal volume of ethyl alcohol and for each 100 ml of the mixture 2-3 drops of 0.1% aqueous solution of phthalein complexone containing a little ammonium hydroxide and 5 ml of concentrated ammonium hydroxide was added. The solution was titrated immediately with 0.1 M EDTA solution. At the end point, the red colour of the mixture disappears abruptly

1 ml of 0.1 M EDTA = 8.763 mg of Sr

9) Estimation of Barium[7]

The titration of barium with phthaleincomplexone was carried out at pH 11. At pH 10, the colour of the indicator is substantially weaker. At higher concentrations the colour change is not sharp, due to small difference in the stabilities of metal-indicator and metal EDTA complexes. The determination is improved by adding 30 to 50 % alcohol.

In the presence of alcohol, the carbonates of the metals may precipitate. For this reason a back titration is recommended. An excess of EDTA is added and the excess titrated with standard barium chloride solution. The indicator is coloured in basic solution, with the result that, at the end point of the titration, the solution remains rose coloured

1 ml of 0.1 M EDTA = 13.738 mg of Ba

10) Estimation of Zinc[8]

10 ml of the zinc chloride solution was diluted to about 75 ml with distilled water and 3 drops of xylenol orange indicator solution were added. To this solution powdered hexamine was added with shaking until it acquires an intense red colour. Titrated with the standard EDTA solution until the colour changes from red to yellow.

1 ml of 0.1 M EDTA = 6.539 mg of Zn

11) Estimation of Cadmium[8]

The cadmium ions were estimated titrimetrically using standard EDTA solution. 10 ml of cadmium chloride solution was pipetted out in a conical flask and it was diluted to 50 ml with distilled water, three drops of xylenol orange indicator were added. If the colour of the solution is red, dil H_2SO_4 is added until the solution acquires yellow colour, powdered hexamine is added in order to change yellow colour of solution to intensely red. This step ensures that the solution has the correct pH (about 6). The mixture was titrated with 0.1 M EDTA solution until the colour changes from red to yellow. The amount of cadmium was calculated by using the relation.

1 ml of 0.1 M EDTA = 11.242 mg of Cd

12) Estimation of Mercury[7]

To 10 ml of the mercury chloride solution ran, from a burette a small excess of standard EDTA solution. Buffer (pH-10) and Eriochrome black-T indicator were added. The excess EDTA titrated with standard zinc or magnesium sulphate solution. Mercury also determined by adding an excess of magnesium - EDTA complex in an amount atleast equivalent to mercury present and then after adding the buffer and indicator, the magnesium formed in the replacement reaction was titrated with standard EDTA solution.

1 ml of 0.1 M EDTA = 20.061 mg of Hg

13) Estimation of Aluminium[8]

To 10 ml of the aluminium chloride solution ran from a burette a slight excess of 0.01 M EDTA solution and adjusted the pH between 7 to 8 by the addition of ammonia solution. The solution was boiled for a few minutes to ensure complete complexation of the aluminium, the solution was cooled to room temperature and adjusted the pH to 7-8.

Then a few drops of Eriochrome black-T indicator were added and the solution was titrated rapidly with standard 0.01 M zinc sulphate solution until the colour changes from blue to wine red.

Every ml difference between the volume of 0.01 M EDTA added and the 0.01 M zinc sulphate solution used in the back titration corresponds to 0.2698 mg Al.

14) Estimatiion of Thorium[8]

10 ml of thorium nitrate solution was pipetted in a 250 ml conical flask and diluted with about 25 ml distilled water. The pH was adjusted to a value of 2-3 by the addition of dilute nitric acid. To the solution introduced 3 drops of xylenol orange indicator solution and the solution was titrated with standard EDTA solution until the colour changes from red to yellow.

1 ml 0.1 M EDTA = 23.265 mg of Th

PRESENT WORK

Some elements are known to be harmful and their presence may cause toxic, carcinogenic or other undesirable effects. Cu, Co, Ni, Mn, Pb, Ba, Cd, Hg and Zn are indicated as toxic elements by Morrison (G.H. Morrison, CRC, Crit.

Rev.Anal. Chem., 1979, 8, 287). The distribution of these trace elements in our environment, food chain, water resources, industrial effluents may cause some serious harm to human life. Attempts are being made to separate the toxic metal ions by using ion exchange chromatography technique. The interesting results were obtained by using Amberlite IR-120 (NH_4^+) form in aqueous acetone-ammonium citrate media. The results are mentioned in the dissertation and are discussed in the light of different theories.

The work done on different aspects of ion exchange chromatography is divided into three chapters.

The theory of ion exchange chromatography and the general experimental procedure is mentioned in the first chapter.

In order to find out the optimum conditions for analytical separations, the kinetic studies and ion exchange of Mg, Ca, Sr and Ba metal ion on Amberlite IR-120 (NH_4^+) resin in aqueous acetone - ammonium citrate media were carried out. The kinetic parameters such as half exchange time $(t\frac{1}{2})$, interdifusion coefficient (D) were calculated at 0.002, 0.004, 0.006 and 0.008 molarities of metal ions and at 0, 30, 50 and 70 percentages of acetone. The kinetic studies were continued at 303, 308, 313 and 318^{0k} for Sr, Ba at 0.002 and 0.004M. The kinetic parameters are calculated. The rate of ion exchange reactions was found to obey the first order law, The rate constant (K) for these reactions was computed. The results, presented in chapter 2 are useful in discussing the mechanism involved in the kinetics of ion exchange.

The multicomponent mixture separations were carried out by ion - exchange chromatography technique, The distribution coefficients were found out at various percentages of acetone and at various concentrations of ammonium cirtare solutions . The effect of concentration of acetone on the distribution coefficients is discussed with the help of the various theories. The data of the distribution coefficients was used to find the possibility of the separations and the separations were tried on these guide lines. The results of the separations are presented in the chapter 3.

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