ION EXCHANGE CHROMATOGRAPHY

What is it ? It is a special category of column chromatography in which the stationary phase is an ion exchange resin.

PRINCIPLE

Ion exchange is a process in which an interchange of ions of like signs takes place between a solution and an insoluble solid (ion exchanger) in contact with the solution. This process is utilised to separate a mixture of ions. Here, a reversible exchange of ions takes place between ions in a liquid phase (mobile phase) and an ion exchange resin (an insoluble substance containing ionic sites) which is the stationary phase.

TYPES OF RESINS

Ion exchange resins are granular insoluble orgnic compounds with giant moleucles with exchangeable ions. The ion exchange resins are of two types. They are i) cation exchange resin and ii) anion exchange resion. A *cation exchange resin* can be represented as (Res A⁻) B⁺ where Res is the acidic polymer of the resin to which is attached

the anion A and mobile cation B. The cation exchanger exchanges its mobile cation with the cation of the solution.

Example

$$2(Res\ SO_3)\ Na^+ + Ca^{2+} \rightleftharpoons (Res\ SO_3^-)_2\ Ca^{2+} + 2\ Na^+$$

An *anion exchange resin* can be represented as (Res B⁺) A . Anion exchanger exchanges its mobile anion with the anion of the solution.

Example

$$[Res\ N(CH_3)_3\ ]OH + H^+Cl^- \rightleftharpoons [Res\ N(H_3)_3\ ^+]Cl^- + H_2O$$

Each of these are subdivided as follows:

i) *Strongly acidic cation exchange resins* : E.g. Su!phonated polystyrene resins. They are useful in the pH range of 1 - 14. These are used to separate cations, inorganic compounds, lanthanides, vitamins, peptides and amino acids.

ii) *Weakly acidic cation exchange resins:* E.g. Carboxylic polymethacrylate resins. They are useful in the pH range of 5 - 14. These are used to separate cations, biochemical compounds, transition elements, aminoacids, antibiotics and organic bases.

iii) *Strongly basic anion exchange resins:* E.g. Quarternary ammonium polystyrene resins. These are useful in the pH range 0 - 12. These are used to separate anions, halogens, alkaloids, vitamin B complex, fatty acids etc.

iv) *Weakly basic anion exchange resins:* E.g. Phenol formaldehyde and polyamine polystyrene resins. These are useful in the pH range of 0 - 9. These are used to separate anionic complexes of metals, anions of different valencies, vitamins and aminoacids.

REQUIREMENTS OF A GOOD RESIN

1. It must be sufficiently cross linked to have only a negligible solubility.

2. It must be suffiently hydrophilic so as to permit diffusion of ions through the structure at a constant and finite rate.

3. The swollen resin must be denser than water.

4. It should be chemically stable.

5. It must contain a sufficient number of accessible ionic exchange groups.

ACTION OF ION EXCHANGE RESINS

Ion exchange resins behave as a porous network, carrying a surplus electric charge, which is distributed over the surface and throughout the pores. The surplus charge is compensated by ions of opposite charge. Thus ion exchange resins comprise of static ions attached to the resin-part and mobile ions. These mobile ions are exchanged with similar ions during ion exchange process. In this ion exchange process, no chemical bonds are formed as the available heat of exchange is low. The actual ion exchange process is taking place by diffusion occurring in two different ways.

1. Film diffusion : In this method diffusion of ions takes place across the liquid film which is adjacent to the resin particle. This method dominates in dilute solutions and with small ions.

2. Particle diffusion: In this method diffusion of ions takes place within the pores of the resin particles. This method dominates in concentrated solutions and with large ions.

EXPERIMENTAL TECHNIQUES

The ion-exchange chromatography is carried out in a chromatographic column. The column consists of a burette provided with a sintered glass disc or glass wool plug at the lower end. The column is packed with wet ion-exchange resin uniformly. The top of the resin bed is covered with a glass wool pad. The column should never be allowed to drain out.

Let us suppose that we wish to replace the Cl^- ions by OH^- ions. The resin column is washed with a concentrated solution of NaOH to ensure the column contains only OH^- ions and no other anion. The solution contianing Cl^- ions is run through the column. Cl^- is exchanged by OH^-. The effluent will contain a quantitative yield of the hydroxide compound. The same process occurs when a cation exchanger is used.

If a mixture of small quantities of two or more different cations X, Y, etc., is passed through an ion-exchange column, they get separated. If cation X is held more firmly by the exchange resin than cation Y, Y will flow out of the bottom of the column before X. This separation technique is called ion-exchange chromatography. The liquid entering the column is called *influent.* The liquid leaving the

column is called the *effluent*. The process by which the absorbed ion are removed from the column is known as *elution*. The solution us for elution is *eluent* and the solution obtained as a result of elution called the *eluate*.

If a solution of suitable eluent is passed through a colum containing an ion X, the effluent is continuously analysed, and concentration of X is plotted against the volume of eluate, an elutic curve is obtained. (Figure 16 b)
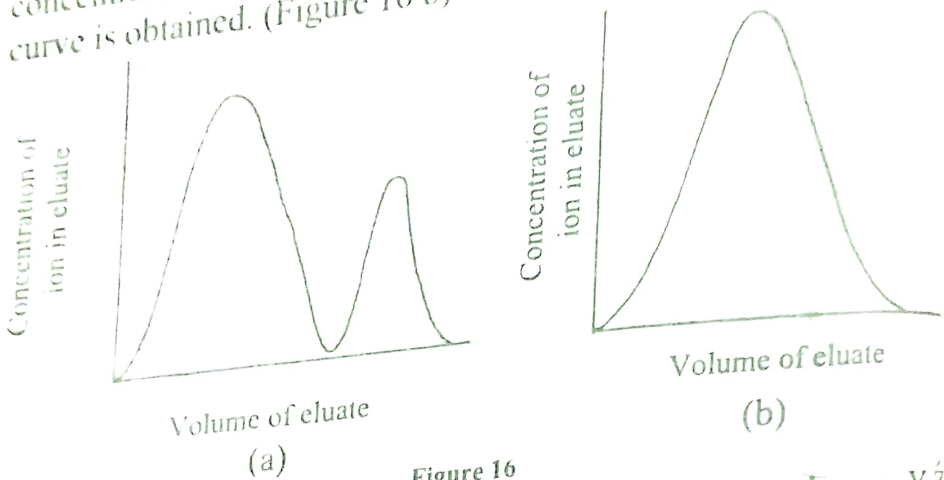

(a)

Volume of eluate

Volume of eluate

(b)

Figure 16

If the column contains several ions of similar charge, Y,Z etc., elution curves are obtained for each ion by the use of suitable eluents. It the elution curves are sufficiently far apart, (fig 16 a) quantitative separation is possible. If the elution curves overlap, only incomplete separation is possible.

APPLICATION

Ion-exchange chromatography is used in the separation of rare-earths, actinides, transition metals, phosphates, complex ions and even isotopes. It serves as a standard method in the discovery and isolation of trace amount of actinides. Industrially, it is used in the metal finishing industry, extraction of metals from ores and separation of rare earths.

Some specific examples are given below:

Separation of rare earths : A column is packed with an acid resin and treated with hydrochloric acid first to ascertain that all exchange centres were occupied by hydrogen ions. A mixture of rare earths (lanthanides) as their chlorides is sent down the column. The rare earth ions get exchanged with hydrogen ions. Later, the rare earth

ions are eluted with a solution of citric acid. The cations form complexes with citric acid. Depending upon the stability of these complexes, these ions are eluted at different rates.

SEPARATION OF Zn AND Mg

Principle : Zinc is absorbed from 2M HCl acid by a column of anion exchange resin while megnesium is not. Zinc in 2M HCl forms negatively charged chloro complex.

Procedure : A column of the anion exchange resin using 15g of zerolit FF in the chloride form is prepared. The column is made up in 2M HCl. The mixture is allowed to flow through the column at a rate of about 5cc / minute. The column is washed with 50 cc of 2M HCl. Care is taken not to permit the level of the liquid to fall below the top of the column of the resin. The effluent is collected in a receiver (conical flask). This will contain all the magnesium. The receiver is changed. Now Zinc is eluted with 30cc water followed by 80cc of approximately 0.25 M HNO_3. Thus zinc and magnesium are separated.

SEPARATION OF CHLORIDE AND BROMIDE IONS

Principle : An anion exchange resin originally in the choloride form is converted into the nitrate form by washing it with sodium nitrate solution. A concentrated solution of the chloride and bromide mixture is intorduced at the top of the column. The halide ions exchange rapidly with nitrate ions in the resin forming a band at the top of the column. Now this band is eluted with sodium nitrate solution. Chloride ions are more rapidly eluted than bromide ions. Thus they are separated.

Procedure : A column of the anion exchange resin using 40 g of Zerolit FF in the chloride form is prepared. The column is washed with 0.6 M sodium nitrate until the effluent contains no chloride ions. Now the column is washed with 50cc of 0.3M sodium nitrate solution. The mixture of chloride and bromide is mixed with 0.3 M sodium nitrate and the mixture is placed at the top of the column. 0.3 M sodium nitrate is passed through the column at the rate of 1 cc / minute. Chloride ions are eluted first. Bromide ions are eluted next. Thus they are separated.

SEPARATION OF Co AND Ni
Principle : Cobalt forms a monovalent complex anion

(probably $[CoCl_4]$) in 9M HCl while nickel does not. This anion is rapidly extracted from its solution by a strongly basic anion exchanger such as zerolit FF. The anionic chloro complex of nickel is not retained by the resin, as it is not stable. It can be washed out of the column with 9M HCl. Later, the column is eluted with water. The cobalt complex is decomposed and passes out in the effluent as cobalt (III) chloride.

Procedure : A column of the anion exchange resin using 30g of zerolit FF in the chloride form is prepared. 50cc of 9M HCl is passeed through the column . 10cc of the mixture of Co and Ni is placed at the top of the column with the aid of a pipette. A small amount of 9M HCl is added. The mixture reaches the upper part of the column. 100cc of 9M HCl is passed through the column. Nickel is eluted out. It is collected. Then 50 cc water is passed through the column at the rate of 5cc/ minute. The anionic cobalt chloro complex is decomposed and comes out of the column as cobalt (III) chloride. It is collected . Thus cobalt and nickel are separated.

SEPARATION OF Cd AND Zn

Principle : Cadmium and Zinc form negatively charged chloro complexes which are adsorbed by a strongly basic anion exchange resin such as zerolit FF. Zinc is eluted with 2M NaOH containing 20 g of NaCl/ dm³. Cadmium is retained on the resin. It is later eluted with 1M HNO_3.

Procedure : A column of the anion exchange resin using 30g of Zerolit FF in the chloride form is prepared. The column is washed with 0.12 M HCl containing 100g/dm³ AR NaCl (reagent I) The mixture of Cd and Zn is placed on the top of the column. It is brought into the column with the help of reagent I. 150 cc of 2 M NaOH containing 20 g of AR NaCl/dm³ (reagent II), is passed through the column at the rate of 4cc/ minute. Zn is eluted out. It is collected. The resin is washed to remove NaOH. Now 150cc of 1 M HNO_3 is passed through the column at the rate of 4cc/minute. Cd is eluted out. It is collected. Thus Zn and Cd are separated.

Advantages of ion-exchange chromatography : i) The exchange capacity of the resins is very high. So separation can be effected fairly quickly.

ii) The recovery of ions from the column is nearly 100% complete. So expensive materials can be separated by this technique so that there would be no loss. Also , quantitative works could be carried out since separation is nearly 100% complete.

Factors determining the distribution of ions between an ion exchange resin and a solution : i) *Nature of exchanging ion :* At low aqueous concentrations and at ordinary temperatures, the extent of exchange increases with increasing valency of the exchanging ion,

i.e., $Na^+ < Ca^{2+} < Al^{3+} < Th^{4+}$

iii) Under similar conditions and constant valency, for univalent ions, the extent of exchange increases with decrease in size of the hydrated cation, i.e., $Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$, while for divalent ions, the ionic size is an important factor but the incomplete dissociation of salts of bivalent metals also plays a part. The order is : $Cd^{2+} < Be^{2+} < Mn^{2+} < Mg^{2+} = Zn^{2+} < Cu^{2+} = Ni^{2+} < Co^{2+} < Ca^{2+} < Sr^{2+} < Pb^{2+} < Ba^{2+}$