CHAPTER - 1

GENERAL INTRODUCTION

INTRODUCTION

Chromatography is a science of separation and is often referred to as an ' art of separation'. It deals with phenomena involved in separating and resolving different constituents of mixture by virtue of certain physical and chemical properties and forces of interaction. Chromatographic techniques are being used by all branches of Chemistry in some form or another. Chromatography is a physical process of separation in which components to be separated are distributed between, two phases-one is 'Stationary Phase' with large surfaces area and the other is 'Moving or Mobile Phase' which is always in contact with the former. Complex separation procedures are required for multicomponent samples. Most depend on the selective transfer of materials between two immiscible phases. Solvent extraction, gas chromatography, column chromatography, thin-layer chromatography, paper chromatography, ion-exchange chromatography, gel permeation chromatography and electrophoresis are the separation techniques in which different phase systems are associated. Ion-exchange chromatography deals with the separation of ionic materials in microgram to gram quantities by passage of a solution through a column or across a surface of a porous polymeric resin incorporating exchangeable ions.

Even though the first ion-exchangers were originally known and used more than a century age, the field of ion-exchange is still experiencing a phenomenol increase in its applications and importance. Today ion-exchange chromatography is used on an incomparably wider scale and is an integral part of many new technical and industrial processes. Indian research and industrial laboratories are fast following tracks of world wide trends and are employing chromatographic techniques for monitoring reactions and processes as well as to estimate individual components in sample mixtures.

Selection of the right chromatographic method starts with defining the problem correctly and laying out the purpose of analysis very clearly . Foreknowledge of nature and number of constituents of the sample matrix, chemical reactions and processes is absolutely essential. Degrees of structural and functional differences among the components to be separated play important roles in the choice of stationary phases, modes of chromatography and other conditions such as temperatures and solvents used in the analysis. Volatility of sample components, stability under analytical conditions, possibilities of interactions with chromatographic beds and components are other major considerations in deciding the right chromatography system for a particular application. The prominent use of ion-exchange is in softening of water which is used for domestic purposes whereas in industrial boilers it is used for demineralization of water. Many industrial waste solutions are treated with ion exchange resins to make them fit for discharge or reuse and sometimes for the recovery of valuable materials present in them. In nuclear energy products it finds use in the extraction of uranium from acid solutions, the separation of radioactive isotopes from atomic fission. Ion exchange chromatography holds a special position among the various methods used for the separation and identification of organic substances such as amino acids, carbohydrates, amines, nucleic acid components.

Ion exchange was discovered[1-2] in 1850 by H.S.Thomson and J.T.Way. They observed that soil can perform an ion-exchange reaction in which ammonia is displaced from a solution of its salts. Ion-exchange was hence recognised as a physico-chemical phenomenon. History of chromatography may be traced to ancient times, when the phenomena were employed for a variety of applications. The credit of discovery of chromatography[3] goes to Mikhail Tswett in 1906. He used a column of precipitated calcium carbonate to separate the pigments of green leaves. In 1905 R.Gans [4-5] used a fusion process to synthesize ion-exchange materials he called "Permutits". These sodium - aluminium silicates were capable of exchanging their constitutional sodium ions for some other ions like calcium and magnesium. These permutits were found to have undesirable properties and because of the scarcely available ion-exchange materials the scope of chromatography was limited. The event that marked the real birth of modern ion-exchange technology was happened in 1935, when Adams and Holmes[6] synthesised the first cation exchanging resin.

The use of ion-exchange in chemical analysis[7] was investigated systematically by O. Samulson in 1939. The separation of interferring cations and anions such as iron and phosphate was studied by absorbing the cation on a cation-exchange resin and replacing it in the solution by an non-interferring hydrogen ion. It was also shown that the total electrolyte concentration of a solution can be measured by passing the solution through a cation-exchange resin in the H^+form. The cations are exchanged with H^+ ions on the resin and corresponding amounts of H^+ ions are collected in the elute. The total molar concentration of H^+ ions in the elute corresponds to the total molar concentration of cations.

Ion exchange chromatography developed rapidly because of its unique applications in the materials required in atomic energy projects. The tremendous developments [8-11] in the technology of rare earths, preparation of very pure metals, separation of fission products and the chemistry of transuranic elements were possible.

The use of ion-exchange to analyse rocks and minerals[12] has been brought to high precision by Strelow and his associates. Reliable and accurate analysis of the chemical constituents of minerals were carried out by separation of the constituents and the estimations of the metal ions by EDTA titrations.

Ion-exchange technique is now a recognised technological tool. As a result of the continuous research activity new materials are being continuously added and diverse applications are being discovered. With the ever increasing scope for the technique and with the manufacturing of indigeneous equipments on the horizon. The future generations of scientists will have to continue their work in the ion-exchange phenomenon and we may expect better materials and specific applications in the problems of tomorrows scientific community.

THEORY OF ION - EXCHANGE PROCESS

(A) Chromatographic Mechanisms

During a chromatographic separation solute molecules are continually moving back and forth between the stationary and mobile phases. While they are in the mobile phase, they are carried forward with it but remain virtually stationary during the time they spend in the stationary phase. The rate of migration of each solute is therefore determined by the proportion of time it spends in the mobile phase or by its distribution ratio.

The process whereby a solute is transferred from a mobile to a stationary phase is called sorption. Chromatographic techniques are based on four different sorption mechanisms, namely surface adsorption, partition, ion-exchange and exclusion. The original method employed by Tswett involved surface adsorption where the relative polarities of solute and solid stationary phase determine the rate of movement of that solute through a column or surface. If a liquid is coated on to the surface of an inert solid support, the sorption process is one of partition and movement of the solute is determined solely by its relative solubility in the two phases. Both adsorption and partition may occur simultaneously, and the contribution of each is determined by the nature of the mobile and stationary phases, solid support and solute.

The third sorption phenomenon is that of ion-exchange. Here, the stationary phase is a permeable polymeric solid containing fixed charged groups and mobile counter ions which can exchange with the ions of a solute as the mobile phase carries it through its structure.

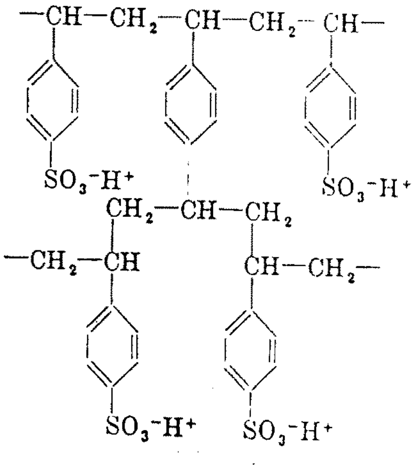
The fourth type of mechanism is exclusion in which separations occur because of variations in the extent to which the solute molecules can diffuse through an inert but porous stationary phase. This is normally a gel structure having a small pore size it allows small molecules to diffuse in and exclude the larger molecules from it.

(B) Ion-exchange Materials

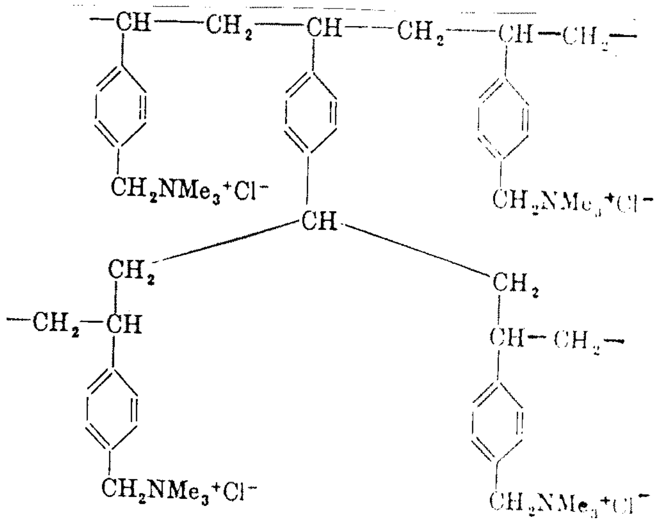
Ion-exchange separations are limited to samples containing ionized or partially ionized solutes. An ion-exchanger is a substance that is capable of reversible exchanges of its constitutional ions with some other external ionic species bearing the same charge. Ion-exchangers are insoluble in the solvents containing ions to be exchanged, and they are resistant to chemicals at temperatures below 100^{o}C. Among 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 hydrophilic and contains functional groups that are ionizable and mobile counterions. 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 ion-exchange materials are categorized 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 polymerized 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 copolymer is reacted with sulphuric acid, sulphonic groups are introduced into the structure, and the resulting cation exchanger has the following structure[13].



Since the linear polystyrene chains can be linked together at different points, different structures may result. The degree of cross-linking determines the physical properties. In polystyrene ion-exchangers, the degree of cross-linking is expressed as percentage of divinylbenzene contained in the polymer. Highly cross-linked resins are hard and brittle. Anion exchanger is likewise crossed-linked high molecular weight polymer containing amine or quaternary ammonium groups and an equivalent amounts of anions such as chloride, hydroxyl or sulphate ions.



Types of ion-exchange materials

Cation and anion exchangers are further subdivided into strong, moderately strong, and weak, depending on the nature of the functional groups.

Strongly acidic cation exchangers contain sulphonic acid groups and can be represented as $RSO_3^-H^+$ where R stands for the matrix, SO_3^- is the site of exchange, and H^+ is the mobile counter ion that is exchanged.

Substituted phosphoric acids $[-PO(OH)_2]$ are used as moderately strong acidic ion-exchangers. The carboxylic acid group is found in weakly acidic cation exchangers of the type RCOOH.

Strongly basic anion exchangers use tetra-alkyl ammonium groups and can be represented as $[R\ N(CH_3)_3]^+Cl^-$. Weakly basic anion exchangers usually contain tetra-alkyl ammonium groups $[R\ NH(CH_3)_2]^+Cl^-$ or secondary amine groups $[R\ NH_2\ CH_3]^+Cl^-$.

(C) Ion-Exchange Process

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

$$RA^-B^+ + C^+ \xrightarrow{(Solution)} RA^-\ C^+ + B^+\ (Solution)$$

For every C^+ ion removed from the external solution, a stoichiometrically equivalent number 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 directly 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 Na^+ ions by Mg^{2+} ions in a sulphonate resin is given by

$$RSO_3^-\ Na^+ + Mg^{++}(Soln.) \rightleftharpoons (RSO_3)_2^-\ Mg^{++} + 2Na^+\ (Soln.)$$

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

The carboxylic exchangers in the hydrogen form will adsorb strong bases from solution

$$RCOO^{-}H^{+} + Na^{+}\ OH^{-}\ \text{(Solution)} \rightleftharpoons RCOO^{-}Na^{+} + H_2O$$

Strongly basic anion exchange resins are largely ionised in both the hydroxide and salt forms. The following reactions occur with the resin.

$$2(RNM_e{}^{+}3)\ Cl^{-} + SO_4^{--}\text{(Soln.)} \rightleftharpoons (R\ N\ Me^{+}3)_2SO_4^{--} + 2\ Cl^{-}\text{(Soln.)}$$

$$(R\ N\ Me^{+}_3)\ OH^{-} + Cl^{-}\text{(Soln.)} \rightleftharpoons (R\ N\ Me^{+}_3)\ Cl^{-} + OH^{-}\ \text{(Soln.)}$$

These resins are similar to the sulphonate cation exchange resins in their activity, and their action is largely independent of pH.

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 a 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.

(D) Ion - exchange equilibria

The ion exchange process, involving the replacement of the exchangeable ions A_R in the resin by ions of like charge Bs from a solution, may be written as

$$A_R + B_S \rightleftharpoons B_R + A_S$$

The process is a reversible one. The extent to which one ion is absorbed in preference to another will determine the readiness with which two or more substances can be separated by ion-exchange and also the ease with which the ions can subsequently be removed from the resin. The distribution of ions between as ion exchange resin and a solution is determined by following factors[14].

(a) The extent of exchange increases with increasing valency of the exchanging ion at low aqueous concentrations and ordinary temperature - e.g.

$$Na^{+} < Ca^{2+} < Al^{3+} < Th^{4+}$$

(b) The extent of exchange increases with decrease in the size of the hydrated cation for univalent ion, e.g.

$$Li^{+} < H^{+} < Na^{+} < NH_4^{+}$$

The ionic size and the incomplete dissociation of salts decide the exchange in bivalent ions, e.g.

$$Cd^{2+} < Mg^{2+} = Zn^{2+} < Cu^{2+} = Ni^{2+} < Co^{2+} < Ca^{2+}$$

(c) Univalent anions appear to behave similarly to univalent cations with strongly basic anion exchange resins, e.g.

$F^- <$ acetate $<$ formate $< Cl^- < Br^- < I^- < SO_4^{2-} <$ citrate

(d) When a cation in solution is exchanged for an ion of different valency the relative affinity of the higher valent ion increases in direct proportion to the dilution.

(e) The absorption of ion will depend upon the nature of the functional groups in the resin. Selectivity also increases with increasing degree of cross-linking. At concentrations greater than 0.1 M, selectivity for monovalent over polyvalent ion increases. Ionic properties which determine resin affinity are complex involving hydration energy, polarizability and hydrated ionic radius.

Theoretical Plates

When much repetitive work is to be done the optimum Column dimensions may be calculated by the application of the plate theory of distillation as modified by various workers[15-17]. An ion-exchange column is considered as consisting of a number of theoretical plates[18] each being in equilibrium with the adjacent solution. Each plate can be considered to occupy a position of a column or longer lenght. The length is called the height equivalent to a theoretical plate (HETP). The HETP is a measure of the efficiency of a chromatographic column and is about 0.002 cm for a good partition column. According to the plate theory the elution curves are bell shaped and many points move down the column at a constant velocity which is inversely proportional to t/c.

This method, known as discontinuous counter current distribution[19], is devised by Craig and it enables the separation of substances with similar distribution ratios.

If we introduce 64 mg of solute in to the first equilibration on stage 1, after equilibration 32 mg will be in each phase. Now open the valve and allow the moving phases to flow to a second stage which contains only stationary phase. Simultaneously add a fresh portion of moving phase to stage 1. After equilibration, the amounts of solute will be distributed as shown in step 2. If the process is repeated through five steps, the solute can be seen to be distributed with a maximum concentration in the middle stage. If the system is extended to nine equilibrations and then to seventeen equilibrations, two additional curves will result.

From this we get three important conclusions, (a) A substance with a partition coefficient of 1, and thus equally distributed between the phases, will be found concentrated at the middle of the system. (b) If the number of equilibrations is increased, the solute will be concentrated in a smaller fraction of total system. (c) The distribution curve approximates a Gaussion distribution.

Contd. on next page......

	Stage-1	Stage-2	Stage-3	Stage-4	Stage-5
Step-1	32 mg				
	32 mg				
Step-2	16 mg	16 mg			
	16 mg	16 mg			
Step-3	8 mg	16 mg	8 mg		
	8 mg	16 mg	8 mg		
Step-4	4 mg	12 mg	12 mg	4 mg	
	4 mg	12 mg	12 mg	4 mg	
Step-5	2 mg	8 mg	12 mg	8 mg	2 mg
	2 mg	8 mg	12 mg	8 mg	2 mg

Fig.- Solute distributions which will result after various number of equilibrations.

COLUMN CHROMATOGRAPHY

Separation of mixtures in trace quantities is possible by passage of the sample through a column containing a stationary liquid or solid phase. Components migrate through the column at different rates due to differences in solubility, adsorption, size or charge.

Most separations are performed using vertical glass columns in which the sorption process are adsorption or partition, and the mobile phase is a liquid which passes through the column by gravity flow. A sample is introduced on the top of the column and the pure mobile phase is passed through it continuously until all the components have been eluted. The order of elution depends on the individual distribution ratios for each solute, and incomplete separation may occur where these are not sufficiently different.

Gradient elution, stepwise elution and complexing agents are the procedures[20] adopted in ion exchange column-chromatography. Gradient elution is a procedure whereby the conditions under which the sample is eluted are progressively varied throughout the separation so as to speed up the process. This can be achieved by altering the composition of the mobile phase or increasing the temperature or flow rate. The effect is to elute components more rapidly in the latter stages and sharpen their elution profiles. Stepwise elution is a similar procedure in which elution conditions are changed at predetermined times rather than continuously. In complexing elution a reagent which forms complexes of varying stability with sample components is included in the solution. Acids, bases, and buffers are the most widely used eluting agents.

Two other means of separating and removing components from a column are frontal analysis and displacement development. In frontal analysis sample is continuously applied to the top of the column, eventually as the stationary phase becomes saturated with the sample, the component with the smallest distribution ratio begins to emerge from the column followed by others in order of increasing distribution ratio but not separated as well as in the elution method. Displacement development involves the movement of a sample down the column by introducing a displacement agent which has a larger distribution ratio than any of the sample components. Again solutes leave the column in order of their distribution ratios, but with much less overlap than in frontal analysis. These methods are used in preparative work where large quantities are to be handled.

Capacity of the resin

The number of exchangeable ions is known as the capacity of the resin. It is determined by the degree of cross linking. The full capacity is never available due to non-ideal operating conditions. For column separation, the break through capacity is reached when an exchanging ion continuously introduced at the top of the column leaks through with the column effluent. The break through capacity depends on the dimensions of the column, the flow conditions, the nature of the ion exchangers, the size of the beads, the temparature of the system, and the composition of the external electrolytes[21].

DISTRIBUTION COEFFICIENT

The equilibrium between a metal ion in solution and that adsorbed on a cation exchanger is expressed by

$$Kd = \frac{M_R}{(M)} \qquad ..(1)$$

where

Kd = distribution coefficient

M_R = gram atoms of metal bound per unit weight of cation exchanger,

M = concentration of metal ion in solution.

The batch distribution coefficient Kd is difined as

$$Kd = \frac{\text{m equiv. metal on resin/g of dry resin}}{\text{m equiv. metal in solution/ml of solution}}$$

The formation of any soluble metal complex in the eluent makes it necessary to consider a second equilubrium involving the metal ion and the complexing ligand in addition to that involving the exchange reaction.

When the distribution coefficient Kd is considered as the ratio of concentration of a metal on resin to the total concentration of metal present in solution (free as well as bound) only a fraction of the total metal exists as free metal ions because of the following reaction.

$$M + nK_e \rightleftharpoons MK_en, \quad K = \frac{(MKen)}{(M)\ (K_e)^n} \quad ..(2)$$

Where K_e is the complexing enion.

In presence of the complexing agent, therefore,

$$K'd = \frac{M_R}{(M) + (MK_en)} \quad ..(3)$$

Substituting (1) and (2) in (3)

$$K'd = \frac{Kd}{1 + K\,(K_e)^n}$$

Where Kd represents distribution coefficient in the absence of any complexing agent.

If it is assumed that the most of the metal is bound as a complex

$$K'd = \frac{Kd}{K\,(K_e)^n} \qquad \text{.. (4)}$$

If the complexing acid (monobasic) is not completely dissociated

$$Hk_e \rightleftharpoons H^+ + K^-e, \; Ka = \frac{(H^+)\,(Ke^-)}{(HKe)} \qquad \text{.. (5)}$$

Thus, equation (4) becomes

$$K'd = \frac{Kd\,(H^+)^n}{K_a^n\,(HK_e)^n} \qquad \text{.. (6)}$$

Thus the distribution coefficient Kd, becomes proportional to the n^{th} power of H^+ concentration of the complexing acid and inversely proportional to the n^{th} power of the concentration of the complexing acid.

If we consider the separation factor for two metals forming similar complexes in the same solution the terms (K_e) (H^+), (HK_e) and Ka in (5) and (6) cancel out when raised to the same power for both metals.

EXPERIMENTAL

Reagents, Solution and Apparatus

Cation Exchange Resin Dowex 50 WX8 (20-50 mesh Na^+ form, BDH, England) analysed reagent resin is used in the measurement of distribution coefficient and column separations. The cation exchange resin is sulphonic acid type. The structure of the resin in H^+ form is as shown on page No.8. In Na^+ form of the resin H^+ ion is replaced by Na^+ ion.

The resin is purified by washing it by distilled water in a beaker. The solid granules of resin swell when placed in water, but the swelling is limited by the cross-linking. In the above example the divinyl benzene units 'weld' the polystyrene chains together and prevent it from swelling indefinite and dispersing. The resulting structure is a vast sopnge-link network with negatively charged sulphonate ions attached firmly to the frame work. These fixed negative charges are balanced by an equivalent number of hydrogen ions in the hydrogen form of the resin.

The resin is soaked in a breaker in about twice the volume of 2M hydrochloric acid for 45 minutes. The resin is occassionaly stirred in order to convert it into H^+ form. It is further washed several times with water. The fine particles of resin were removed by decantation.

Solutions :- All BDH chemicals were used.

EDTA :- 0.1 and 0.01M standard wolutions of EDTA were prepared by disolving 37.225 g and 3.7225 g of disodium salt of EDTA per litre of solution.

Metal Salts 0.05 M stock solutions of calcium, magnesium, cobalt, manganese, zinc, nickel, cadmium, copper, strontium, barium and aluminium chlorides and thorium, lead and mercuric nitrates were prepared as follows.

(1) $CaCl_2$. 5.5495 g. were dissolved in 1000 ml.
(2) $MgCl_2.6H_2O$ 10.1655 g. were dissolved in 1000 ml.
(3) $MnCl_2.4H_2O$ 9.896 g. were dissolved in 1000 ml.
(4) $CoCl_2.6H_2O$ 11.896 g. were dissolved in 1000 ml.
(5) $ZnCl_2$. 6.8185 g. were dissolved in 1000 ml.
(6) $CdCl_2.H_2O$ 11.8966 g. were dissolved in 1000 ml.
(7) $CuCl_2.2H_2O$ 8.524 g. were dissolved in 1000 ml.
(8) $NiCl_2.6H_2O$ 11.8855 g. were dissolved in 1000 ml.
(9) $SrCl_2.6H_2O$ 13.311 g. were dissolved in 1000 ml.
(10) $BaCl_2.2H_2O$ 12.215 g. were dissolved in 1000 ml.
(11) $AlCl_3.6H_2O$ 12.072 g. were dissolved in 1000 ml.
(12) $Th(NO_3)_4$, 39.500 g. were dissolved in 1000 ml.
(13) $Pb(NO_3)_2$ 16.5605 g. were dissolved in 1000 ml.
(14) $Hg(NO_3)_2$, 16.231 g. were dissolved in 1000 ml.

The solutions were standardized by using literature methods[22].

Buffer solution ($_p$H=10) Add 142 ml of concentrated ammonia solution to 17.5 g. of AR ammonium chloride and dilute to 250 ml with distilled water.

Sodiumthiosulphate ($Na_2S_2O_3$, $5H_2O$). 0.1 M sodium thiosulphate solution was prepared in distilled water. Sodium thiosulphate solution was standardised volumetrically.

Sodium hydroxide : (NaOH) 0.1 M Sodium hydroxide solution was

Prepared by dissolving 4 g. of it in 1000 ml. Sodium hydroxide solution was standardised with oxalic acid volumetrically.

Indicators

1) Eriochrome Black T. The indicator solution was prepared by dissolving 0.2 g of the dye stuff in 15 ml of triethanolamine with the addition of 5 ml of absolute enthanol to reduce the viscesity.

2) Xylenol Orange. The indicator solution was prepared by dissolving 0.59 g of xylenol orange in 100 ml of water.

3) Starch. The starch solution was prepared everyday by boiling starch soluble power in distilled water.

4) Phthalein complexone Indicator - 0.1 % aqueous solution.

Acid

1) Succinic acid. Succinic acid (BDH, AR grade) was used for preparing the solution of various strengths as per requirement.

Succinic acid in acetone-water mixtures.

The solutions of succinic acid of the desired molarities were prepared in various compositions of acetone-water mixtures (v/v) and the molar strengths of the stock solutions were determined volumetrically[24].

Estimation of Metal Ions.

1) Estimation of Calcium

The calcium ions were estimated titrimetrically [22] using standard EDTA solution. 10 ml of calcium nitrate solution was pipetted out in a conical flask and it was diluted to 50 ml with distilled water. 4 ml of buffer solution and a few drops of the 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 calcium was calculated by using the relation:

1 ml 0.1 M EDTA = 4.008 mg Ca

2) Estimation of Magnesium

The magnesium ions were estimated titrimetrically[22] using standard EDTA solution. The procedure for the estimation of magnesium ions is the same as that of calcium ions. The amount of magnesium was calculated by using the relation:

1 ml 0.1 M EDTA = 2.432 mg Mg

3) Estimation of manganese [22]

10 ml of manganese nitrate / chloride solution was pipetted out in a conical flask, 0.5 g of hydroxyl amine-hydrochloride was added to prevent oxidation of the solution. The solution was then diluted to 50 ml with distilled water. 3 ml of triethanolamine, 2 ml of buffer solution ($_{p}H=10$) and several drops of Erio-T indicator were added and the mixture was titrated with 0.1 M EDTA solution until the colour changes from red to blue. The amount of manganese was calculated by using the relation:

1 ml 0.1 M EDTA = 5.494 mg Mn

4) Estimation of Lead [22]

10 ml of lead nitrate solution was pipitted our in a conical flask and it was diluted to 50 ml with distilled water. 3 drops of xylenol orange indicator were added. If the colour of the solution is red, dil. H_2SO_4 is added until the solution aquires yellow colour. Powdered hexamine is added in order to change yellow colour of the solution to intensely red - this step ensures that the solution has the correct $_pH$ (about 6). The mixture was tirated with 0.1 M EDTA solution until the colour changes from red to lemon yellow. The amount of lead was calculated by using the relation:

1 ml 0.1 M EDTA = 20.721 mg pb.

5) Estimation of Cadmium.

The cadmium ions were estimated titrimetrically [22] using standard EDTA solution. The procedure for the estimation of cadmium ions is the same as that of lead ions. The amount of cadmium was calculated by using the relation:

1 ml 0.1 M EDTA = 11.242 mg Cd.

6) Estimation of Coppear.

The copper ions were estimated titrimetrically [22] using standard sodiumthiosulphate solution. 10 ml of copper nitrate solution was pipetted out in a conical flask. Ammonium hydroxide (1:1) solution was added dropwise till a slight permanent precipitate of cupric hydroxide was formed. Acetic acid (1:1) was then added till the precipitate just dissolves and clear light blue solution was obtained. 2 g solid KI was then added. The stoppered flask was kept aside for complete liberation of iodine. Iodine was titrated against standard sodium thiosulphate using starch as an indicator. The amount of copper was calculated by using the relation:

$$1 \text{ ml } 0.1 \text{ M } Na_2S_2O_3 = 0.06354 \text{ g Cu.}$$

7) Determination of cobalt [22] using Xylenol Orange as Indicator-

10 ml of the cobalt-ion solution was diluted to 25 ml with distilled water and added 3 drops of the indicator solution, followed by very dilute sulphuric acid until the colour just changes from red to yellow. To this solution added powdered hexamine with shaking until the deep red colour was restored ($_pH = 6$) The solution was warmed to about 40°C and titrated with standard EDTA until the colour changed 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.

$$1 \text{ ml } 0.1 \text{ M EDTA} = 5.8933 \text{ mg. Co.}$$

8) Determination of zinc [22] using Eriochrome Black T as indicator.

The zinc ions were estimated titrimetrically [22] using standard EDTA solution. The procedure for the estimation of zinc ions is the same as that of calcium ions. The amount of zinc was calculated by using the relation:

1 ml 0.1 M EDTA = 6.538 mg Zn.

9) Determination of nickel[22] using Eriochrome Black T as indicator (back - titration).

To 10 ml of the almost neutral nickel-ion solution, added from burette a slight excess of 0.1 M - EDTA solution (10 - 15 ml). The solution was diluted to about 50 ml, added 4 ml of the buffer solution ($_pH$=10) and a few drops of Erio T indicator. The solution was titrated, the excess of EDTA with standard 0.1M - zinc sulphate or magnesium sulphate solution until the colour changed from blue to wine red.

The reaction between the Ni-EDTA complex and Erio T takes place very slowly as long as there is an excess of EDTA present. As soon as the end point with $ZnSO_4$ or $MgSO_4$ is reached, the nickel forms a fairly stable complex with Erio T, so that over-titrated solution are lost.

Every ml difference between the volume of 0.1 M EDTA and the 0.1M metal-ion solution used in the back-titration corresponds to 5.871 mg of Ni.

10) Determination of thorium[22] using Xylenol orange as indicator.

10 ml. of thorium ion 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 (used indicator test paper or a $_pH$ meter). To the

solution introduced 3 drops of the indicator solution and titrated with standard EDTA until the colour changes from red to lemon yellow.

1 ml 0.1 M EDTA = 23.206 mg Th

11) Determination of aluminium[22] using Erichrome Black T as indicator (back-titration).

To 10 ml of the aluminium - ion solution ran from a burette a slight excess of 0.01 M EDTA and adjusted the $_pH$ to between 7 and 8 by the addition of ammonia solution (tested drops on phenol red paper or use a $_pH$ meter). The solution was boiled for a few minutes to ensure complete complexation of the aluminium; the solution was cooled to room temperature adjusted the $_pH$ to 7 - 8. Then added a few drops of Erio T indicator, and the solution was titrated rapidly with standard 0.01M zinc sulphate solution until the colour changes from blue to wine red.

After standing for a few minutes the fully titrated solution acquired a reddish-violet colour due to the transformation of the zinc dye complex into the aluminium - Erio T complex; this change was irreversible, so that over titrated solutions were lost.

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.

12) Determination of mercury [25].

Mercury was not titrated directly with EDTA, but was determined by back titration. After separation of mercury from other metals, a small excess of standard EDTA, buffer and indicator were added and the excess EDTA titrated with a standard zinc or magnesium(sulphate) solution. Mercury may also be determined by adding an excess of the magnesium EDTA complex in an amount at least equivalent to the mercury present and then, after adding the buffer and indicator, the magnesium formed in the replacement reaction was titrated with standard EDTA. One ml of 0.1M EDTA solution corresponds to 20.061 mg of mercury. This method may also be applied to the microdetermi--nation of mercury by using a 0.001 M solution of EDTA.

13) Determination of strontium [25].

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

The precipitation of strontium carbonate caused a turbidity, which redissolved only slowly after the end point was reached. This caused a reappearance of red colour. If this happened, the second titration was carried and most of the

EDTA was added before adding the alcohol and then the titration was completed.

1 ml of 0.1 M EDTA corresponds to 8.763 mg of strontium.

14) Determination of barium[25].

The titration of barium with phthalein-complexone indicator was carried out at $_pH$-11. At $_pH = 10$, the colour of the indicator was substantially weaker. The concentrations of the colour change was not very sharp, due to small difference in the stabilities of metal-indicator and metal-EDTA complexes. The determination was improved by adding 30-50% alcohol. In the presence of alcohol, the carbonates of the metal may be precipitated. For this reason a back titration was recommended. An excess of EDTA was added, and the excess titrated with standard barium chloride solution.

The indicator was coloured in basic solution, with the result that, at the end point of the titration, the solution remained rose coloured. This colour is compensated by adding other indicators.

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PRESENT WORK

The work in the thesis refers to the studies in ion-exchange separations. The thesis consists of four chapters. Theory of ion-exchange chromatography and the experimental procedures are covered in the first chapter. The studies of ion-exchange equilibria were carried out and the results of Hg^{2+}/H^{+}, Al^{3+}/H^{+} and Mn^{2+}/H^{+} exchanges in acetone and acetone-succinic acid media are reported in the second chapter. The equilibrium constants were calculated and the various factors, governing these constants, were found out. The results in the studies of kinetics of ion-exchange reacions are presented in the third chapter. The reactions of proton exchange with Cu, Zn, Co, Ni, Hg, Ca, Mg, Mn, Pb, Cd, Th (IV) and Al (III) ions in acetone and acetone-succinic acid media were carried out. The Kinetic Parameters such as half exchange time, diffusion coefficients, parabolic diffusion constant were found out. The studies of the Kinetics were carried out at various temperatures and the values of energy of activation, entropy were computed. The rate constants, are computed and the results are examined from the point of various exchange isotherms. The Kinetic studies lead to the conclusion of possible mechanisum of ion-exchange reactions under study.

The separations of binary mixtures of metal ions such as Cu, Zn, Ni, Co, Th(IV), Al(III), Hg, Sr, Ba, Ca, Mg, Mn, Pb and Cd in acetone-succinic acid were carried and the results are given in the fourth chapter. The optimum conditions such as concentration of metal ions, composition of the mixed solvents, the strength of the acid and the total time required were determined. The percentage recoveries of metal ions have been found out.

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