

1.1 INTRODUCTION

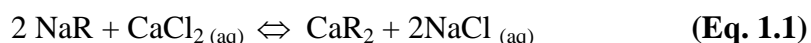
Separations are extremely important in synthesis, industrial chemistry, the biomedical sciences and chemical analysis. Separations isolate the analyte from potentially interfering constituents. The basic principles of a separation involves transport of material and spatial redistribution of the components. Separation always requires energy, because the reverse process, mixing at constant volume is spontaneous, being accompanied by an increase in entropy. The separation can be preparative or analytical. Different types of separation methods have been presented in **Table 1.1**. Amongst the various separation methods outlined ion exchange method of separation is making a huge impact.

Table 1.1 *Separation methods*

<i>Separation Methods</i>	<i>Basis of Method</i>
<i>Mechanical phase separation</i>	
<i>Precipitation and filtration</i>	<i>Difference in solubility of compounds formed</i>
<i>Distillation</i>	<i>Difference in Volatility of compounds formed</i>
<i>Extraction</i>	<i>Difference in solubility in two immiscible liquids</i>
<i>Ion Exchange</i>	<i>Difference in interaction of reactants with ion exchange resin</i>
<i>Chromatography</i>	<i>Difference in rate of movement of a solute through a stationary phase</i>
<i>Electrophoresis</i>	<i>Difference in migration rate of charged species in an electric field</i>
<i>Field-flow fractionation</i>	<i>Difference in interaction with a field or gradient applied perpendicular to transport direction</i>

1.2 ION EXCHANGE

Ion exchange is a process, whereby an insoluble substance removes an ion of positive or negative charge from an electrolyte solution and releases another ion of like charge into the solution in a chemically equivalent manner. The process occurs with no structural changes in the ion exchanger. At some point, during the exchange process, ion exchange equilibrium is established. A typical ion exchange reaction occurring in water softening is as presented below:



where, R represents the structural unit of the ion exchanger. Here the exchanger in the Na^+ form is converted to the Ca^{2+} form. Complete conversion to the Ca^{2+} form can be achieved by treating the exchanger with a sufficient excess solution of a Ca^{2+} salt.

Ion exchange is, with very few exceptions, a reversible process. In water softening, a cation exchanger which has lost all its Na^+ ions and thus has become exhausted, can be regenerated with a solution of sodium salt such as NaCl . In regeneration, the process is reversed, and the ion exchanger is reconverted to the Na^+ form.

Ion exchange resembles sorption in that, in both cases, a dissolved species is taken up by a solid. The characteristic difference between the two phenomena is that, ion exchange is a stoichiometric process while sorption is a non stoichiometric process. Every ion that has been removed from the solution is replaced by an equivalent amount of another ionic species of the same sign from the ion exchange material. In sorption, a solute/electrolyte is taken up without being replaced by an equivalent species. Though this difference is clear, it is difficult to distinguish between exchange and sorption, since every ion exchange process is accompanied by electrolytic sorption or desorption and most of the common sorbents such as alumina and activated carbon act in turn as ion exchangers.

Ion exchange materials have found extensive applications in analytical chemistry and industrial chemistry in view of their elegant characteristics such as insoluble matrix, stoichiometric exchange, good selectivity, specificity and applicability to column operations. Ion exchange is firmly established as a unit operation and is an extremely valuable supplement to other procedures such as filtration, distillation and adsorption.

Ion exchange process in general and ion exchange resin in particular are useful because of the insolubility of the resin phase. After contact with the ion-containing solution, the resin can be separated by filtration. They are also adaptable to continuous processes involving columns and chromatographic separations. Their insolubility renders them environmentally compatible since the cycle of loading/regeneration/reloading allows them to be used for many years.

Rapid industrial development has given way to environmental pollution caused by release of hazardous effluents from industries into natural water resources. Ion exchange materials play a vital role in the treatment of these environmental pollutants. Ion-exchange resins have also been used in water softening, wastewater treatment, hydrometallurgy, chromatography, and biomolecular separations.

1.3 A RETROSPECTIVE ON DEVELOPMENTS IN ION EXCHANGE

In the most ancient literature, references can be found to the description of ion exchange processes. Moses wrote that in the time of the wanderings, his people made drinkable water from undrinkable bitter water by using pieces of wood. Aristotle suggested filtration through certain types of soil for the improvement of water. Presumably in the improvement of the taste of water, the ion exchange property of wood cellulose played a role in the first case and that of silicates in the second one. Ion exchange processes were studied scientifically only in the middle of the last century, in connection with investigation of different soils. Thompson and Way observed that Ca^{2+} and Mg^{2+} ions of certain types of soil could be exchanged for K^{+} and NH_4^{+} ions. Later Eichorn showed that ion exchange properties of soil, arise from zeolites. The first synthetic aluminosilicate based ion exchanger was made by Harms and Rumpler in 1903. In the field of industrial production and technical application of ion exchangers, Gans pioneered the work. The first industrial product, applicable for technical purposes was Sodium Permutites, which was produced by fusing a mixture of clay minerals and alkalis. One of the most important events in the history of ion exchange is represented by the discovery of Adams and Holmes in 1935, that resins having good ion exchange characteristics, could be synthesized.

A review on ion exchange resins [1] by Spiro D. Alexandratos provides a historical perspective of the field through a chronological examination of the concepts central to ion exchange resins. As will be seen, the early papers develop applications with a limited number of resins while later papers expand the number of resins for new targeted applications.

An overview of 1909-1949 shows that the phenol-formaldehyde polymer was introduced and cation exchange was ascribed to the phenolic -OH group. The concept was extended to anion exchange by preparing a polymer from the reaction of formaldehyde with diaminobenzene. The polystyrene-based sulfonic acid cation-exchange resin and the trimethylammonium strong base anion-exchange resin were critical developments. The shift to polystyrene was due to the ability to form well defined beads via suspension polymerization and their applicability to column operations. Also developed was the methacrylate-based weak acid cation-exchange resin prepared as beads. The sugar industry became a major utilizer of ion-exchange resins for decolorization of sugar solutions [1].

An overview of 1950-1959 shows that it was proposed that ion-exchange resins could be selective for targeted ions by incorporating chelating groups into their structure. The sulfonic acid resin is most valuable when different ions all need to be removed from water. The carboxylic acid resin is good at separating the alkaline earth from the alkali ions. Both cannot be applied if a particular transition metal ion needs to be removed from a solution containing different transition metal ions. A *specific ion-exchange resin* was thus defined as “one that under proper experimental conditions is characteristic of one ionic species only [1, 2]. The preparation of a resin was described involving the condensation of *m*-phenylene diglycine dihydrochloride with formaldehyde.

An overview of 1960-1979 shows that macroporous and ultrafine ion exchange resins were introduced, greatly expanding their applicability. Resins were utilized for biomass conversion, the treatment of gaseous refinery streams, and the selective removal of boron from water [1].

An overview of 1980-1999 shows that chitosan, a ubiquitous form of biomass, was used as an alternative support for ion-selective resins. Bifunctional ion-exchange resins allowed for selectivity with rapid kinetics. Resins complexed with silver ions were used for olefin/paraffin separations. Metal ion separations were accomplished with different ligands [1].

Ion exchange is now a well established technique and is applied in many industrial processes and chemical laboratories. However, the criteria that govern the utility of an ion exchanger for a particular process or experiment are of great importance and should be taken into account before selecting the ion exchanger. Following are the criteria of an ideal ion exchanger:

- The exchanger should be insoluble in water and organic solvents, besides being stable in various acidic, basic and oxidizing media, where exchanger operates.
- The exchanger should be physically hard enough to withstand mechanical stress.
- The exchanger molecular structure should be open and permeable to ions and solvent molecules so that they can move freely in and out, during the exchange process.

- An ion exchanger, for analytical applications, should have good ion exchange capacity and differential affinity for several exchangeable ions.
- Thermal stability is one of the most important requirements of a good ion exchanger. There are several important ion exchange processes that occur at higher temperatures. For such cases, the exchanger in use should be able to withstand the temperature of the reaction system.
- An ion exchanger should be environmentally compatible with the cycle of loading/ regeneration/ reloading.
- It should be possible to regenerate and reuse the ion exchangers without much declined in performance.

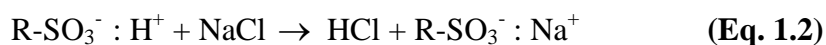
1.4 CLASSIFICATION OF ION EXCHANGERS

Ion exchange resins have been broadly classified as - **cation exchange resins**- those of the resins which are capable of exchanging cations and **anion exchange resins**- those which are capable of exchanging anions. Both cation and anion exchange resins are organic in nature. These resins have been further classified and categorized by the nature of functional groups attached to a matrix – (I) Strong acid and weak acid cation exchangers, (II) strong base, and weak base anion exchangers.

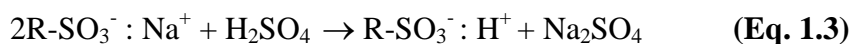
1.4.1 Cation Exchangers

Strong acid cation-exchangers (SAC)

Strong acid cation exchangers have generally sulfonic acid groups $-\text{SO}_3\text{H}^+$, attached to an insoluble matrix. These exchangers split neutral salts and convert them to the corresponding acid.



These exchangers can be regenerated with a strong acid such as H_2SO_4 or HCl .



The regeneration efficiency of these exchangers is 30-50 %. Examples of commercially available cation exchange resins – gel type- strongly acidic are - *DOWEX-50W-(X4/X8/X12/X16)* [strongly acidic cation exchangers with *S-DVB* matrix, where *S-DVB* = styrene divinylbenzene], *Amberlite IR-120* (8% styrene-DVB), *Amberlite IR-122* (10% styrene-DVB) etc.[3]

Weak acid cation exchangers (WAC)

Weak acid cation exchangers have generally carboxylic acid groups, $-\text{COOH}$, attached to the matrix. These exchangers cannot split neutral salts, but can remove cations associated with the water's alkalinity to form carbonic acid.



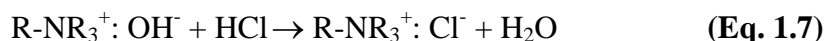
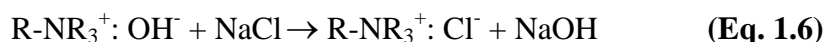
This exchanger can be regenerated with any acid, stronger than the functional group.



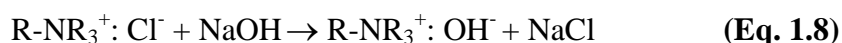
The regeneration efficiency of these exchangers is 100 %. Examples of commercially available weakly acidic cation exchangers-gel type- with carboxylic acid functionality are - *Duolite C-433 [acrylic-DVB type resins]*, *Bio-Rex 70 [weakly acidic cation exchanger with carboxylate groups on a macroreticular acrylic matrix]* etc. [3]

1.4.2 Anion Exchangers**Strong base anion exchangers (SBA)**

Strong base anion exchangers have quaternary ammonium group, R-NR_3^+ : OH^- , where R is alkyl/aryl.



These exchangers can be regenerated using NaOH.



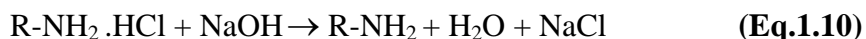
The regeneration efficiency of these resins is 30-50 %. Examples of commercially available strong base anion exchangers - macroreticular type – with quaternary ammonium functionality are - *Amberlite IRA-910 and 938 (Dimethylethanolamine styrene-DVB)*, *Amberlite IRA-958 (Acrylic-DVB matrix)* and *AG MP-1 (S-DVB matrix)* etc. [3]

Weak base anion exchangers (WBA)

These exchangers cannot split neutral salts but they can remove strong acids by adsorption. Weak base anion-exchangers may have primary, secondary, or tertiary amines as the functional group.



The resin is regenerated by treatment with excess of 1M NaOH solution or by NH_3 solution.



The regeneration efficiency of these resins is 100 %. Examples of commercially available weak base anion exchangers - gel type - weakly basic – with *polyamine functionality* are, DOWEX 4-X4 (*tertiary amines on an acrylic matrix*) or Amberlite IRA-68(*Acrylic-DVB matrix*) etc. [3]

1.4.3 Chelating Ion Exchangers

In chelating ion exchangers various chelating/functional groups are attached to the matrix. It is observed that only a few elements such as oxygen, nitrogen, sulphur, phosphorous or arsenic from these groups can function as electron donors. The affinity of a particular metal ion for a certain chelating resin, depends mainly on the nature of the chelating group and stability of the metal complexes formed on the exchanger under various pH conditions. The chelating resins complex with metals to mostly form tetra or hexacordinated complexes.

Chelating exchangers can also be called as specific ion exchangers. D-picrylamine was synthesised as a specific resin for potassium. Many compounds forming chelates (e.g. anthralinic acid and iminodiacetic acid groups) are incorporated into resin by polycondensation (phenol and aldehydes) and styrene type resin. Chelex 100 (chelating resin) shows unusually high preference for copper, iron and other heavy metals over such cations as sodium, potassium and calcium. Most of the chelating ion exchangers in use are synthetic chelating exchangers.

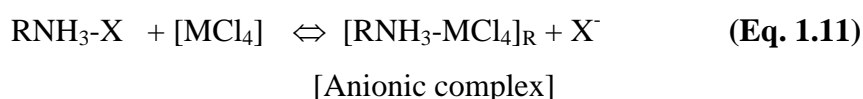
While synthesizing chelating exchangers the chelating group must have sufficient chemical stability. During the synthesis of the resin, its functional structure should not be changed by any reaction. The specific arrangements of the ligand groups should be preserved in the resin. This is particularly necessary since the complexing agent forming sufficient stable complexes must possess ability to form chealte rings uninfluenced by matrix during exchange reaction. The steric structure of the chelating group should be compact so that the formation of the chelate rings with cation is not hindered by the resin matrix. The affinity of particular metal ion to a functional group of certain chelating resin depends mainly on the nature of the chelating group, the size of the metal ion and its charge. Chelating resins behave similarly to weak acid cation exchange resins but exhibit a high degree of selectivity for heavy metal ions.

The exchange process in chelating exchanger is slower than that in ordinary type of exchanger. The high selectivity of these resins for some ions often leads to difficulties in quantitative elution of ions from them. In order to achieve quantitative recovery of absorbed ions, it is sometimes necessary to destroy the resins. The effectiveness of complete and selective separation by extraction method is achieved by increasing the number of extractions. Chelating resins can be regenerated for its use. Column extractions are accomplished with high number of theoretical plates so that the selectivity and efficiency of separation is maximum. Therefore, synthetic chelating resins play an important role in metal ion separation processes.

Examples of commercially available chelating ion exchangers are – *Chelex 100, Amberlite IRC 748, Lewatit TP 207, Lewatit TP 208, Purolite S 930 etc. (all exchangers contain iminodiacetate as functional group)* [3, 4].

1.4.4 Liquid Ion Exchangers

Like solid analogue, we have liquid anion exchangers and liquid cation exchangers. These are organic exchangers similar to solid resin but are present in liquid form. High molecular weight amines (HMWA) constitute a class of liquid anion exchangers. Depending upon the type of amine we have primary, secondary, tertiary and quaternary amines. They have 18 to 27 carbon atoms. Aliphatic amines are also used e.g Amberlite LA-1 and LA-2. The first is dodecyl (trialkyl methyl) amine while latter is lauryl (trialkyl methyl) amine. The liquid anion exchangers form salt as

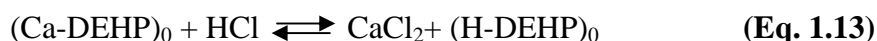


They all involve transfer of species of ions across liquid- liquid interface. The system is similar to solvent extraction by ion pair formation. They do have small solubility in water, large specific exchange capacity, large solubility in organic solvents, high selectivity, stability and small surface activity. They are more useful than solid analogues. They have faster exchange rate, possess no interstitial water, have no problem with suspended matter, provide facility for true counter current process and have greater permselectivity. Liquid cation exchangers are similar to solid cation exchanger resins as H_2R . They all have the replaceable group as H^+ . Since these resins are present in the liquid form, they are called liquid cation exchangers. The simplest examples are HDEHP (i.e ethyl hexyl) phosphoric acid and DNN (i.e.

dinonyl naphthalene sulphonic acid). They act like solid cation exchangers during separation of ions;



This represents exchange of calcium on cation exchange resin in the liquid form. One has to use inert diluents like xylene, toluene or benzene for the purpose of separation. Unlike solid cation exchange resins they can be converted back to H^+ from as



In above equation o- represents, organic phase. Many useful separations of rare earths have been accomplished by these liquid cation exchangers.

Commercially available liquid cation exchangers are - *DNS*, *HDEHP* (i.e. *dinonyl sulphonic acid* or *bis 2(ethyl hexyl) phosphoric acid* respectively) and anion exchangers are *Amberlite LA-1* (secondary amine containing two highly branched aliphatic chains), *Amberlite LA-2* (secondary amine of M.W. 353 to 395) [3, 4]

1.4.5 Organic Ion Exchangers

The framework of these materials, the so called matrix consists of an irregular, macromolecular, three dimensional network of hydrocarbon chains. They are of two types – cation exchangers and anion exchangers depending on the ionic groups present in the matrix. When the matrix carries ionic groups such as $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, $-AsO_3^{2-}$ they are known as cation exchange resins. A widely used cation exchange resin is that obtained by the copolymerization of styrene and a small proportion of divinyl benzene. Cation exchange resins include that prepared by the copolymerization of methacrylic acid with glycol bismethacrylate as the cross linking agent. This contains free $-COOH$ groups and has weak acidic properties.

When the matrix carries ionic groups such as $-NH_3^+$, $=NH_2^+$, $=N^+$, $=S^+$ they are known as anion exchange resins. A widely used anion exchange resin is prepared by copolymerization of styrene and a little divinyl benzene followed by chloromethylation and interaction with a base such as trimethylamine.

1.4.6 Inorganic Ion Exchangers

The last fifty years or so has seen a great upsurge in the researches on synthetic inorganic ion exchangers, the reason being probably due to some important characteristics of inorganic ion exchangers such as resistance to temperatures, oxidizing radiation and strongly oxidizing solutions, the main emphasis being development of new materials possessing thermal stability, chemical stability,

reproducibility in ion exchange behaviour and selectivity for certain metal ions important from analytical and environmental point of view. Important classes of inorganic ion exchangers are clay minerals, zeolites, heteropolyacid salts, oxides/hydrous oxides, hexacyanoferrates and tetravalent metal acid salts.

A partial listing of inorganic ion exchangers both natural and synthetic is given in **Table 1.2**.

Table 1.2 Principle classes of inorganic ion exchangers

Type	Example	Exchange capacity (meq.g ⁻¹)
Smectite clays	Montmorillonite	0.5 - 1.5
Zeolites	$Na_x(AlO_2)_x(SiO_2)_y \cdot ZH_2O$	3 - 7
Substituted aluminium phosphates	Silico aluminophosphates $(M_x^{n+}Al_{1-x}O_2)(PO_2)(OH)_{2x/n}$	depends upon value of x.
Hydrous oxides	$SiO_2 \cdot x H_2O$, $ZrO_2 \cdot x H_2O$	1 - 2
Group IV phosphates	$Zr (HPO_4)_2 \cdot H_2O$	4 - 8
Other phosphates	Uranium phosphate	8
Condensed phosphates	$NaPO_3$	
Heteropolyacids	$M_n X Y_{12} O_{40} \cdot nH_2O$ ($M=H^+, Na^+, NH_4^+$; $X=P, As.$) $Y = Mo, W$	0.2 - 1.5
Ferrocyanides	$M_{4/n}^{n+} Fe (CN)_6$ ($M=Ag^+, Zn^{2+} \dots$)	1.1 - 1.6
Titanates	$Na_2 Ti_n O_{2n+1} (n=2-10)$	2 - 9
Apatites	$Ca_{10-x} H_x (PO_4)_6 (OH)_{2-x}$	
Anion exchangers	Hydrotalcite	2 - 4
Miscellaneous types	Alkaline earth sulphates	1.5 - 3
Fast ion conductors	– alumina, NASICON	2 - 7

Clay minerals

The clay minerals comprise of a complex series of aluminosilicate structures. Basically, the aluminosilicate ‘backbone’ of the clays is composed of alternating, parallel, two dimensional layers formed from silicate tetrahedra and aluminate octahedra [5]. Depending on the arrangement of these units, three basic types of clay minerals, Kaolinite, Montmorillonite and Illite are recognized. The exchange in clay minerals is non stoichiometric and they have relatively low ion exchange capacity. Although their stability towards acid solution is limited, suggestions have been made that the clay minerals be used as ion exchangers in certain cases, particularly where specificity, cheapness, stability towards radiation or high temperature is concerned [6]. The clay minerals also peptise in some solutions. Industrial use is often difficult

due to the presence of impurities and inappropriate physical properties for packed bed operations. Many a time they also need chemical or thermal treatment.

Zeolites

The zeolites, both synthetic and natural, form another group of aluminosilicate minerals, the structures of which are built up from tetrahedral groupings AlO_4^{5-} and SiO_4^{4-} in such a way that corners of the tetrahedra are shared to give condensed three dimensional cage like structures. The isomorphous substitution of Aluminium (III) for Silicon (IV) makes the backbone negatively charged. To preserve electroneutrality, cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} etc. are inserted in the structure. These cations are usually hydrated and mobile and are responsible for the observed ion exchange properties.

Zeolites may exist as fibrous, layered or rigid three dimensional structures. It is the three dimensional network which is usually taken to represent the zeolites and it is this type which has been extensively studied for its ion exchange properties. The polyhedra in zeolites are packed in such a way that there are channels penetrating into the interior of the lattice. Their diameters are seen to vary from one type of structure to another and may even vary along the length of the channel. The porous structure of Zeolites makes it possible to use them as ion sieves. This type of ion sieve behavior makes it possible to carry out certain specific separations. Limitations to the use of zeolites are their instability in acid media and low abrasion resistance.

Heteropoly acid salts

These salts represent another class of inorganic ion exchangers. Ammonium phosphomolybdate was the first member of this class of exchangers to be studied in detail. Other members of this series include ammonium molybdoarsenate, molybdosilicate, tungstophosphate, tungstoarsenate etc. The parent acids of these compounds belong to the 12-heteropolyacids having the general formula $\text{H}_3\text{XY}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, where X may be one of the several elements including phosphorous, arsenic or silicon and Y a different element such as molybdenum, tungsten or vanadium.

Ammonium phosphomolybdate normally prepared is microcrystalline. The larger crystals normally breakdown in aqueous suspensions. Ammonium phosphomolybdate columns are used for the separation of heavier alkali metals from the lighter members and also from other multivalent cations in acid solutions.

Heteropoly acid salts usually show a high affinity for cesium and hence used for the recovery of cesium from irradiated nuclear wastes.

Oxides/ hydrous oxides

This class includes oxides and hydrous oxides of Zr, Ti, Fe, Al, Nb, Cr, Th, etc. Hydrous oxides are most active when freshly precipitated. They are however, least useful as regards to ion exchange column applications, mainly due to ion exchange capacities that are offset by their ease of dissolution in acids or bases and also the poor filtration characteristics of the precipitates [7, 8].

The use of oxides or hydrous oxides as a column material is obviously governed to a large extent by its resistance towards breakdown or dissolution when treated with various reagents. In general, the insoluble acid oxides and hydrous oxides are stable in acid solutions but dissolve readily at $\text{pH} > 7$. In contrast, the more basic hydrous oxides such as TiO_2 and ThO_2 dissolve readily in mineral acids above about 0.1 M concentration but are stable in less acidic solutions.

Insoluble hexacyanoferrates

Insoluble hexacyanoferrates of various metals have been studied for their ion exchange properties [9-11]. These materials act as cation exchangers with an especially high affinity for cesium [11]. Attempts to elute cesium, absorbed on hexacyanoferrates have been only partially successful, since it is accompanied by decomposition of the absorber. The exchange capacity depends strongly on the method of preparation.

The hexacyanoferrate ion exchangers are stable in mineral acids. However, when in contact with strong HNO_3 , a slight oxidation of Fe(II) to Fe(III) can occur. In alkaline solutions, a tendency to peptize has been observed [7, 8], but this can be greatly reduced by addition of neutral salts.

1.5 TMA (TETRAVALENT METAL ACID) SALTS AS CATION EXCHANGERS

“**Tetravalent metal acid (TMA) salts**” have been researched since the last 50 years, and have emerged as promising advanced materials owing to their good thermal stability, chemical resistivity, resistance towards ionizing radiations, and found important applications in the area of ion exchange, catalysis and solid state proton conduction. An

extensive literature on TMA salts, exists today, which have been reviewed and detailed in four books.

- ❖ Varshney K G and Khan A M, 1991, *Inorganic Ion Exchangers in Chemical Analysis*, (Eds.) Qureshi M and Varshney K G, CRC Press, Boca Raton, Florida.
- ❖ Clearfield A, 1982, *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, Florida.
- ❖ Clearfield A, Nancollas G H and Blessing R H, 1973, *Ion Exchange and Solvent Extraction*, (Eds.) Marinsky J H and Marcus Y, Marcel Dekker, Vol 5, New York.
- ❖ Amphlett C B, 1964, *Inorganic Ion Exchangers*, Elsevier, Amsterdam.

Systematic studies on their synthesis, structure elucidation and applications in the area of separation science, catalysis and solid electrolytes have been carried out by various groups – Dr. A. Clearfield (USA), Dr. G. Alberti, Dr. U. Costantino (Italy), Dr. D. Whittaker (UK), Dr. W. H. J. Hogarth (Australia), late Dr. M. Qureshi and Dr. K. G. Varshney (Aligarh Muslim University, India) and Dr. U. V. Chudasama (The M. S. University of Baroda, India).

Salient features of TMA salts

- TMA salts are cation exchangers, possessing the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$, where $M(IV) = Zr, Ti, Sn, Ce, Th$ etc. and $X = P, Mo, As, Sb, W$ etc.
- The materials possess structural hydroxyl groups, the H^+ of the $-OH$ being the exchangeable sites, due to which the material possesses cation exchange properties.
- TMA salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.
- The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.
- The materials are generally hard and range in physical appearance from totally opaque to transparent.
- TMA salts have shown a great promise in preparative reproducibility and ion exchange behavior.
- TMA salts exhibit both thermal and chemical stability.

Structural aspects of TMA salts

Almost all the possible combinations of tetravalent metals (such as Zr, Ti, Ce, Sn, Th etc) with polybasic acids (containing P, W, Mo, As, Sb etc) have been examined. Earlier work was carried out with amorphous materials. Much of the earlier work was focused on zirconium phosphate (ZP) [12]. Extensive information on the structure of ZP has been reviewed by C B Amphlett [6]. De Boers reported the structure of ZP as $\text{Zr}(\text{HPO}_4)_2$, but other workers suggested it to be $[\text{ZrO}(\text{H}_2\text{PO}_4)_2]$. Bluementhal (**Figure 1.1a**), Paterson (**Figure 1.1b**), Baestle and Pelsmaekers (**Figure 1.1c**), Nancollas and Pekarek (**Figure 1.1d**) and (**Figure 1.1e**) proposed various structural formula for ZP [6]. According to these structures, the H^+ of the structural –OH groups are the exchangeable protons. Much of the pioneering work in this area was done by the research group at the Oak Ridge National Laboratory led by K A Kraus [7] and in the United Kingdom by C B Amphlett [6].

The first crystalline α -ZP was prepared by Clearfield and Stynes [13]. Structure elucidation was first carried out in 1969 [14]. ZP has a layered structure. Three oxygen atoms of each phosphate, are bonded to three adjacent metal atoms, forming a distorted equilateral triangle [15]. Each zirconium atom is thus octahedrally coordinated by oxygens. An idealized picture of a portion of the layer is given in (**Figure 1.2**).

Zirconium phosphate, the most extensively studied TMA salt of the crystalline type can be prepared as fibrous, layered or as three-dimensional structures [13].

The layered acid salts, in turn, may be obtained in at least two different modifications, usually known as β -ZP and γ -ZP having the formula $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ respectively [17].

The structure of β -ZP (**Figure 1.3**) arises from the ABAB stacking of layers, each of which is formed by zirconium atoms lying in a nearly ideal plane and sandwiched between $-\text{O}_3\text{POH}$ groups, with the exchangeable proton pointing into the interlayer region as $\text{P}-\text{OH}$ [15]. These protons are responsible for ion exchange [18]. The layers of the β -ZP are made up of zirconium atoms laying in two parallel ideal planes and bridged by $-\text{PO}_4$ groups, while $-\text{O}_2\text{P}(\text{OH})_2$ groups are directed towards the interlayer region [19, 20]. The layers in the β -ZP are thus thicker (0.92 nm) than those in γ -ZP (0.64 nm), and the –OH groups bound to the same phosphorous atoms have different acidities.

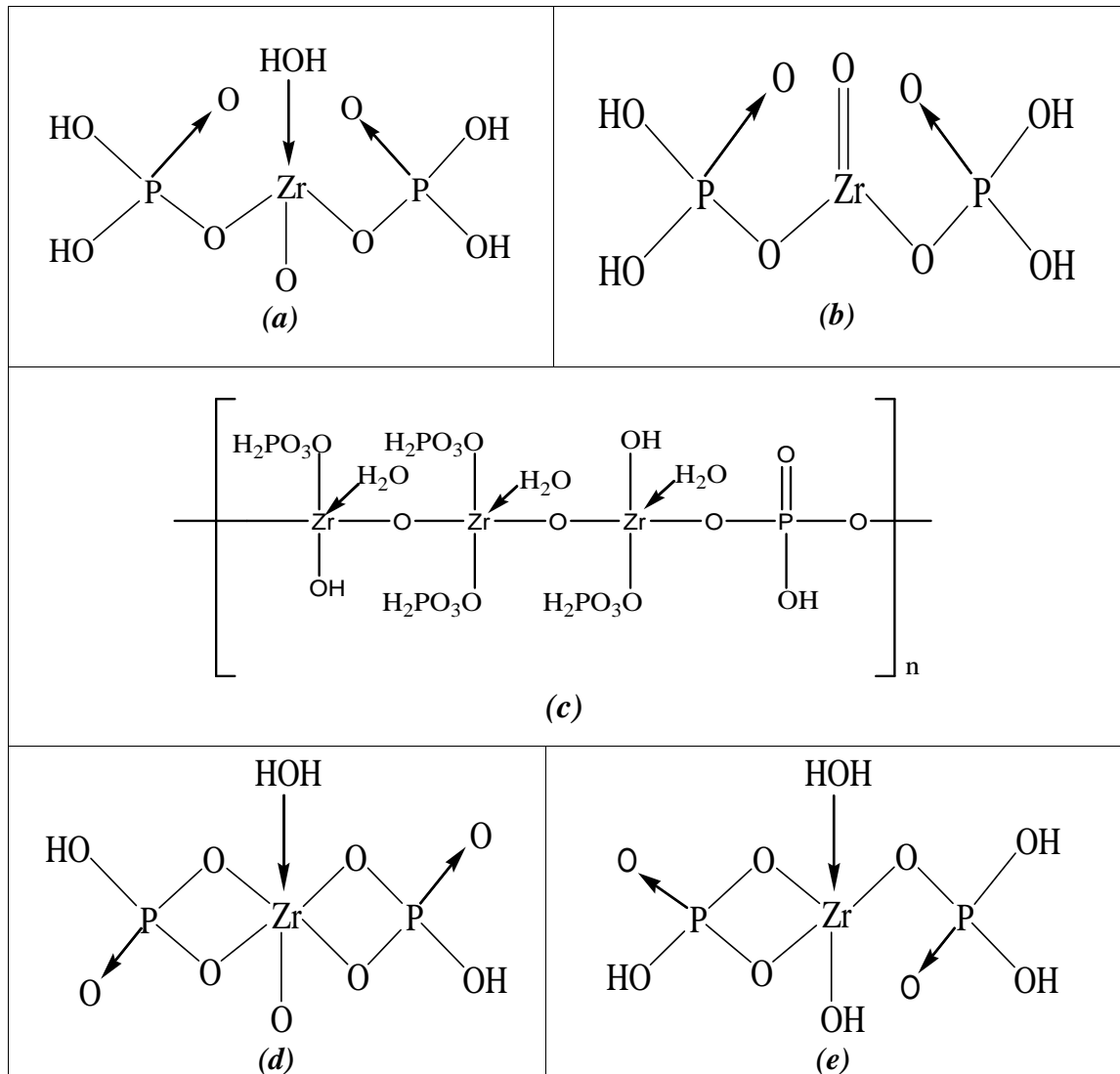


Figure 1.1 Structures of zirconium phosphate

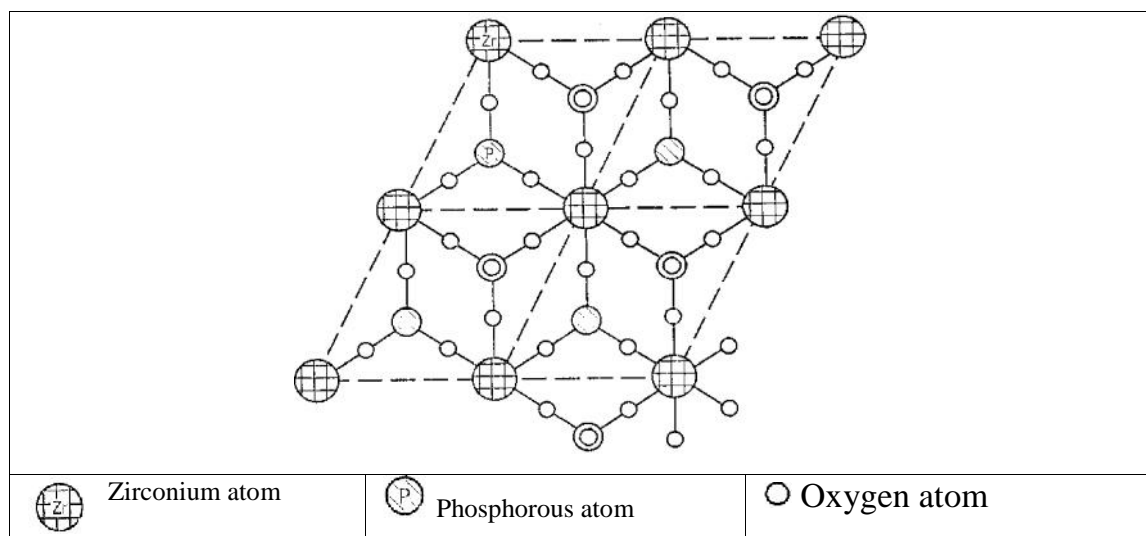


Figure 1.2 Idealized portion of ZP layer [25]

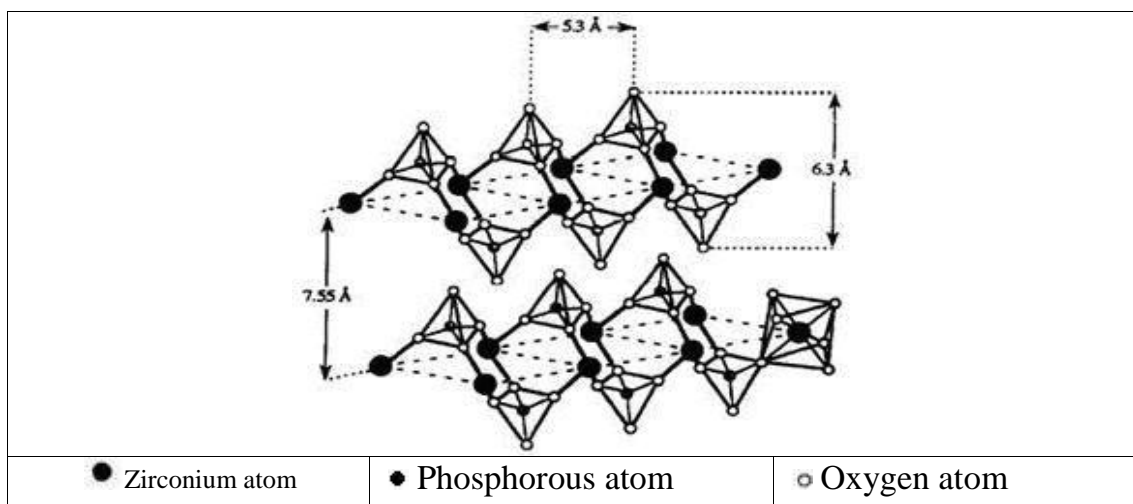


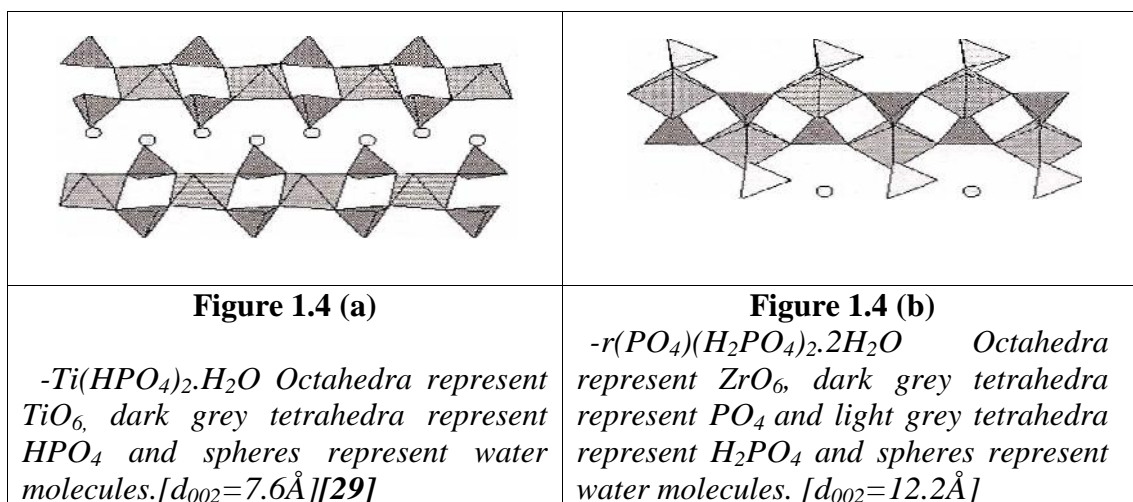
Figure 1.3 Schematic diagram of the arrangement of two adjacent macroanions in -ZP [16]

After -ZP, -titanium phosphate (-TP) is the most investigated material. It has been obtained independently in various laboratories and structural aspects investigated [21]. Since the length of the Ti–O bond is shorter than that of the Zr–O bond, the distance between fixed charges in the planar macroanion $[\text{Ti}(\text{PO}_4)_2]_n^{2n-}$ is shorter than in $[\text{Zr}(\text{PO}_4)_2]_n^{2n-}$. The unit cell dimensions are $a = 8.631 \pm 0.001 \text{ \AA}$, $b = 5.002 \pm 0.001 \text{ \AA}$, $c = 16.176 \pm 0.002 \text{ \AA}$, and $\beta = 110.20 \pm 0.01^\circ$.

Owing to its smaller unit cell, the dimensions of the windows connecting the cavities in -TP are correspondingly smaller and the density of the fixed charges higher, compared to -ZP. Thus, the steric hindrance to the diffusion of large cations is expected to be higher in -TP than in -ZP and the ion exchange rate is slower.

Owing to its high density of fixed charges, -TP tends to behave as a rigid layered exchanger and therefore it possesses more marked ion sieve properties than does -ZP. The ion sieve properties of -TP have been used [22] to effect separations of Cs^+ and K^+ ions from Na^+ . Ion exchange equilibrium between -TP and NaCl-KCl aqueous solution has been investigated by Kobayashi [23] who also considered the possibility of separating Na^+ and K^+ ions. The insoluble acid salts of tetravalent metals can be obtained with different layered structures, usually known as -structure. After $-\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, first obtained by Clearfield [24], another compound with formula $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ and showing marked analogies with -ZP, was prepared by Alluli et al [25].

Although the structure is as yet unknown, some indirect information has been obtained [26]. Both -ZP and -TP are able to take up stoichiometric amount of several polar organic molecules and the first d-values of these materials increase with increase in the length of these molecules. Furthermore, there is a discontinuous change of the first d-value during the dehydration of $-\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (from 12.2 to 9.4 Å) and of $-\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (from 11.6 to 9.2 Å). These properties provide strong evidence that the structure, like that of materials, is built up of polymeric macro anion $[\text{M}(\text{IV})(\text{XO}_4)_2]_n^{2n-}$, with negative charges neutralized by protons, while the hydration water, or other polar molecules can be accommodated between adjacent layers. It can probably be assumed that $-\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ is isostructural to $-\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$. Extensive information on the chemistry of group IV metal phosphates with and type structures has been compiled in reviews and books [27, 28]. Polyhedral layered phosphates in the *a-b* plane are presented in (Figure 1.4a & 1.4b).



When a tetravalent metal is treated with phosphoric acid/Na salts of phosphoric acid, M – O – P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H⁺ of the P – OH contributing to cation exchange. TMA salts are prepared by sol gel routes of different compositions and crystallinities [18, 30-32] varying parameters such as mole ratio of reactants M : X (M = tetravalent metal, X = polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), pH and rate of mixing. Variation in any of these parameters yields materials with different characteristics.

The cation exchange capacity (CEC) thus depends on preparation procedure/parameters varied and hence performance as an ion exchanger. From our laboratory, TMA salts have been widely explored as cation exchangers [33-39].

1.6 HYBRID ION EXCHANGERS

Different types of metal pollutants from chemical process industries necessitates finding new ion exchangers, that have good ion exchange capacity, stability towards temperature, ionizing radiation, and oxidizing solutions and that are capable of removing toxic substances from effluents. Heavy metals when present in water in concentrations exceeding the permitted limits are injurious to health. Hence, it is very important to treat such waters to remove the metal ions present before it is supplied for any useful purpose. Out of the several investigations on developing more effective processes to treat such waste streams, ion-exchange has been widely adopted for treating heavy metal containing wastewater. Most of the ion-exchangers currently being used are commercially mass-produced organic resins [40].

Although organic ion-exchangers have a wide applicability, a few limitations of the organic resins have been reported. One of the severest limitations of organic resin is its poor thermal stability; for instance, the mechanical strength and removal capacity of ordinary organic ion-exchange resins tend to decrease under high temperature conditions which are frequently encountered in processing liquid radioactive waste stream [41]. Since organic ion-exchangers were found to be unstable at high temperatures inorganic ion-exchangers were taken as alternatives for such cases. However, the inorganic adsorbents have their own limitations. For instance, these materials, in general are reported to be not very much reproducible in behaviour and fabrication of the inorganic adsorbents into rigid beads suitable for column operation is quite difficult. Further, they have generally worse mechanical and chemical strength than the organic counterparts because of their inorganic nature [42].

In order to overcome the above limitations of organic resins and inorganic adsorbents, many investigators have introduced inorgano-organic hybrid ion-exchangers consisting of inorganic ion-exchangers and organic binding matrices [43-49].

Anchoring of organic units on the backbone of TMA salts is of particular interest. From our laboratory inorgano-organic ion exchangers have been prepared by anchoring organic moieties onto various TMA salts [50-53].

Anchoring of organic molecules possessing ionogenic groups on an inorganic matrix such as TMA salts, could give rise to additional H^+ sites. In organic molecules possessing aryl $-OH$ or $-COOH$, the protons are more labile because of the presence of the electron- withdrawing phenyl group. These materials have the added advantage of both their counterparts in terms of thermal stability, ion exchange capacity and high selectivity for mono and multivalent cations.

Inorgano-organic ion exchangers have been synthesized by anchoring chromotropic acid (4,5-dihydroxynaphthalene-3,7-disulphonic acid, disodium salt) and tiron (1,2-dihydroxybenzene-3,5-disulfonic acid, disodium salt) onto TMA salts zirconium molybdate. The materials were subjected to ion exchange and instrumental methods of characterization. Distribution behaviour for several metal ions were studied and compared [50, 51].

Inorgano-organic ion exchangers were also synthesized by anchoring o-chlorophenol and p-chlorophenol onto zirconium tungstate abbreviated as ZWoCP and ZWpCP. The materials were subjected to ion exchange and instrumental methods of characterization. Distribution behaviour of several metal ions were studied and binary separations were performed. From the above studies it was concluded that the anchored ion exchangers reported presented characteristics of promising ion exchangers [52, 53].

1.7 NEW DEVELOPMENTS IN ION EXCHANGE MATERIALS

There is currently high interest in engineering mixed materials (organic / inorganic) where features of the organic and inorganic components complement/amalgamate/cooperate leading to the formation of new solid-state/lattice structures and materials with new composite properties, that have the potential to provide improved and tunable properties [54-58]. In all cases, there is promise of developing new materials that offer a wide range of interesting properties not seen in purely organic or purely inorganic solids. Such materials are termed as hybrid inorgano-organic compounds. This new field of materials science is expanding rapidly. Several international meetings are now devoted to this promising area of research and many review papers have been published [54-66].

The purpose of synthesizing such hybrid materials is to achieve properties that a single phase material cannot provide. In general, the organic component of such materials have good elasticity, toughness, formability and low density, while the

inorganic component are hard, stiff and thermally stable. Together, these components can produce hybrid materials that are chemically and thermally stable. To achieve the optimum balance of properties, phase separation between organic and inorganic components in the hybrid must not occur. Therefore, the nature of the chemical interaction between the organic and inorganic components during the processing of these materials plays an important role in avoiding such phase separation [67].

The synthesis of novel inorgano-organic hybrid materials, has received extensive attention in recent years [57, 68-71]. Hybrid materials in general can be obtained through intercalation/anchoring/pillaring/encapsulation or sol-gel method. The concept of “hybrid inorgano-organic” materials exploded with the birth of soft inorganic chemistry processes (“Chimie Douce”), where mild synthetic conditions allow versatile access to chemically designed hybrid inorgano-organic materials that enable the integration of useful organic and inorganic characteristics within a single molecular-scale composite [57]. Sol-gel technique, has been widely used for the preparation of inorgano-organic hybrid materials and has attracted a great deal of attention in material science. The synthesis of these hybrids with controlled functionality and hydrophobicity could open new avenues that offer a variety of exciting technological opportunities. Thus, inorgano-organic hybrid materials are expected to provide many possibilities as new composite materials [40].

A major advantage of inorgano-organic hybrid materials is the rigid inorganic backbone and flexibility of the organic groupings. This flexibility creates opportunity to design compounds with specific properties such as, when the organic functionalities possess ionogenic groups (-OH, -COOH, -SO₃H etc.), the surface area, ion exchange capacity (IEC), surface acidity etc. can be modified. Other important features are the simple reaction steps required to make them and the ability to affix the various organic groups on an inorganic solid support.

Organic derivatives of inorganic ion exchangers of the class of TMA salts are of particular interest. TMA salts as inorganic ion exchangers have been discussed in detail in section 1.5 of this chapter.

M(IV) phosphates have been widely used as cation exchangers and have shown a number of advantages as an ideal host lattice [72]. In the tetrahedral moiety of phosphoric acid, PO(OH)₃, if H or OH is replaced by R (where R = alkyl or aryl possessing ionogenic groups), phosphonic acids are obtained, which when treated

with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc. give rise to metal phosphonates [73, 74]. They are very insoluble compounds and their structure and reactivity, can be modified and tailored for specific purposes [57, 75]. Depending on the complexity of the phosphonic acid used, the resulting M(IV) phosphonate material gives rise to two or three dimensional hybrid polymeric structures. They can be described as molecularly engineered solids and represent a relatively new class of compounds [40, 42]. Their preparation is an example of soft chemistry route to new materials and are obtained at low temperatures, often from aqueous.

Though several metal(IV) phosphonates have been synthesized and characterized, the focus has been on structure elucidation [73, 31]. These materials are interesting because of their potential utility as sorbents and supports [76], in the area of catalysis [18], as ion exchangers [30], proton conduction [31], intercalation chemistry [29], photochemistry [32] and materials chemistry [77].

1.8 AIM AND SCOPE OF THE PRESENT WORK

Synthetic inorganic ion exchangers of class of (TMA) salts have been an area of considerable study owing to its high selectivity for certain metal ions and excellent ion exchange behaviour. Organic derivatives of inorganic ion exchanges of the class of TMA salts is of particular interest. A major advantage of inorgano- organic hybrid materials is the rigid inorganic backbone and flexibility of the organic groupings. This flexibility creates opportunity to design compounds with specific properties such as, when the organic functionalities possess ionogenic groups (-OH, -COOH, -SO₃H, etc.) the surface area, ion exchange capacity (IEC), surface acidity etc. can modified.

The importance of inorgano-organic hybrid materials in general and hybrid ion exchangers in particular prompted us to synthesize M(IV) phosphonates of the class of TMA salts.

Since M(IV) phosphates (where M(IV) = Zr, Ti, Sn, Ce, Th etc.) of the class of TMA salts have been widely explored as cation exchangers, it was thought of interest to explore the ion exchange properties of M(IV) phosphonates which have not been widely explored. Though the potential use of M(IV) phosphonates as ion exchangers has been suggested, a literature survey reveals that no systematic studies have been performed nor explored on the ion exchange characteristics of these materials.

Claw molecules of the type amino phosphonic acids have received considerable attention [78-80] due to diverse binding ability/chelating ability/effectiveness of donor group in the binding of tetravalent metal ions and contain multi-dentate building blocks. Further, the organic species incorporated in an inorganic phase, permits control of porosity, hydrophobicity/hydrophilicity, ion exchange characteristics (organic moiety containing ionogenic groups), using a sol-gel chimie douce approach.

Chapter II of the thesis is focused towards synthesis of amorphous novel hybrid metal amino phosphonates, ZrATMP and TiATMP (ATMP = amino tris methylene phosphonic acid) using a sol-gel method. ZrATMP and TiATMP have been subjected to physical, ion exchange and instrumental methods of characterization. To explore feasibility of ZrATMP and TiATMP as cation exchangers thermodynamics, kinetics and adsorption studies have been performed. The utility of ZrATMP and TiATMP as cation exchangers has been explored by performing distribution studies, elution studies as well as binary and ternary separations of metal ions [Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} (transition metal ions) and Hg^{2+} , Cd^{2+} , Pb^{2+} (heavy metal ions)].

The innumerable separation procedures published so far are almost exclusively based on the use of monofunctional ion exchangers, mostly strongly basic anion exchangers with quaternary ammonium groups and strongly acidic cation exchangers with sulfonic acid groups [81]. Amphoteric ion exchangers in contrast to conventional monofunctional exchangers contain anionic and cationic exchange sites, and under appropriate conditions, can retain/exchange simultaneously anions and cations from external solutions. Although it was surmised long ago [81], that simultaneous presence of anion and cation exchange groups may offer new interesting separation possibilities, very few attempts to exploit these possibilities in practice can be found in literature [81]. Some of these amphoteric ion exchangers are chelating resins with functional groups able to form complexes with several cations and are used for the preconcentration of trace elements. Since these complex forming groups contain basic nitrogen atoms that can be protonated, the resins may also act as weakly basic anion exchangers.

Chapter III of thesis deals with synthesis and characterization of new and novel, amorphous amphoteric chelating ion exchangers, by sol gel routes using

inexpensive and easily available chemicals, ZrOCl_2 and polyamines (D = diethylene triamine and T= triethylene tetraamine) to yield zirconium diethylene triamine (ZrD) and Zirconium triethylene tetraamine (ZrT). ZrD and ZrT have been subjected to physical, ion exchange and instrumental methods of characterization. Using ZrD and ZrT anion exchange capacity (AEC) for Cl^- , Br^- , $\text{Cr}_2\text{O}_7^{2-}$, F^- and AsO_4^{3-} has been determined, and distribution coefficient K_d for Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} (transition metal ions) and Hg^{2+} , Cd^{2+} , Pb^{2+} (heavy metal ions) has been evaluated by batch equilibration techniques in aqueous and various electrolyte media/concentrations. Based on the separation factor, a few binary separations have been achieved on a chromatographic column packed with ZrD/ZrT. The amphoteric behavior of ZrD and ZrT has been demonstrated by simultaneous exchange of cations (Cu^{2+} , Hg^{2+}) and anion (Cl^-) in CuCl_2 and HgCl_2 . The practical applicability of ZrD and ZrT as amphoteric exchangers has been highlighted by performing a case study.

Chapter IV of thesis deals with the applicability of zirconium tri-ethylene tetra-amine (ZrT) gel for fabrication of hybrid chelating membrane. In the present study hybrid chelating membranes, based on cross-linked ZrT gel and poly vinyl alcohol (PVA) has been reported. The chelating membranes have been designated as ZrTETA-45, ZrTETA-50 and ZrTETA-55, based on different weight percentage of ZrT gel used to prepare the membranes. The chelating membranes have been synthesized by an acid catalyzed sol-gel process followed by chemical crosslinking via formal reaction. The membranes have been subjected to (a) physicochemical methods of characterization which include water uptake, swelling, ion exchange capacity (IEC), fixed-ion concentration, oxidative stability and hydrolytic stability. (b) electrochemical methods of characterization which include, transport number, membrane conductivity, electro-osmotic permeability and metal ion transport studies and (c) instrumental methods of characterization which include spectral analysis (ATR-FTIR), thermal analysis (TGA/DSC), DMA, XRD, SEM and EDX. Metal ion transport studies have been performed for bivalent ions namely Mn^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} . The experiments have also been carried out using mixed metal electrolyte (equimolar) for achieving separations.

Amongst the chelating membranes prepared of varying gel composition, crosslinked ZrTETA-55 hybrid chelating membrane exhibits strong interaction towards all metal ions, specially Cu^{2+} . Thus, thermodynamic, kinetic and adsorption

studies were performed using ZrTETA-55 chelating membrane which involves effect of time, temperature, pH, adsorbent dose, and adsorbate concentration, towards adsorption of Cu^{2+} . Pseudo-first and pseudo second order kinetic models, thermodynamic parameters {(Standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°)} have been evaluated and adsorption isotherms (Langmuir and Freundlich) studied.

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