CHAPTER 1
INTRODUCTION

Ion-exchange can be defined as a reversible exchange of ions between two immiscible phases; one of which having the ionogenic group, is termed as the ion exchanger. The ion exchanger may be a solid, liquid, membrane, fibre etc and can be organic or inorganic in nature.

The exchanger materials, either inorganic or organic, with fixed negative groups are capable of exchanging cations and are called cation exchangers. Materials with fixed positive groups and capable of exchanging anions are called anion exchangers. There are others which exchange either cations or anions depending on the pH of the medium and are termed amphoteric exchangers.

The conventional cation and anion exchangers are available either in solid or in liquid form. The theory of ion-exchange as well as synthesis and applications of various ion-exchange materials have been exhaustively described in literature. 1-10

Thompson 11 was the first to observe and publish a description of the phenomenon of ion-exchange. He reported that when a solution of ammonium sulphate was percolated through a column of soil, the effluent contained a large
amount of calcium sulphate. Way\textsuperscript{12} in his exhaustive studies of this phenomenon established it to be one of ion-exchange involving the complex silicates present in the soil. He made the important discovery that synthetic aluminosilicates prepared in the laboratory from a solution of alum and sodium silicate exhibited very similar behaviour and also reported the interesting observation that on aluminosilicates some ions were exchanged more rapidly than others.

These discoveries for water softening and other processes led to the use of natural and synthetic aluminosilicates by Harm and Rumpler\textsuperscript{13} and Gans,\textsuperscript{14} Adams and Holmes\textsuperscript{15} in 1934 discovered that in addition to the synthetic base exchange materials exhibiting ion-exchange properties, synthetic products could also be prepared from organic raw materials. This led to the synthesis of organic ion-exchange resins, which possessed superior properties over all other earlier products. The synthesis of organic resins made it possible to vary the properties of ion exchangers in a systematic manner.

Ion-exchange is established as a unit operation today. Numerous plants are in operation all over the world using these materials for applications ranging from recovery of
metals from industrial wastes to the separation of rare earths. In the laboratory, ion exchangers are also used in analytical and preparative chemistry. Ion-exchange membranes have further extended the application of these materials. Of the numerous applications of the membranes the most important is the desalination of brackish water. 16

1.2 Classification of ion-exchange materials

1.2.1 Inorganic ion exchangers

Mineral ion exchangers -

Most natural ion-exchange materials of this group are crystalline aluminosilicates with cation-exchange properties. All these materials have a three dimensional framework and aluminosilicate lattice. The lattice consists of AlO₄ and SiO₄ tetrahedra which have their oxygen atom in common. 17-24 Other aluminosilicates with cation-exchange properties were also reported. 25-34 Ferrous aluminosilicates which contain dense and rigid lattice exhibiting considerable cation-exchange capacity were also reported by Jonny and Bruce. 35-37

Certain aluminosilicates having anion-exchange capacity are montmorillonite, kaolinite and feldspars belonging to sodalite and cancrinite groups. 38-39 However for practical purposes like defluorination of water, the
mineral anion exchangers - apatite $\left[Ca_5\left(PO_4\right)_3\right]F$ and hydroxylapatite $\left[Ca_5\left(PO_4\right)\right]OH$ - have been used due to their high adsorption capacities. 40-42

Synthetic inorganic ion exchangers -

The successful large scale application of zeolites was developed by Harm and Rumpfer13 and Gans14 who synthesised inorganic material of the type $Na_2Al_2Si_3O_10$ in which sodium ion was available for exchange. Later, cation exchangers with improved properties viz gel permutes, were prepared and these were similar to the zeolites. 43-49

Various zeolites with completely regular crystal structure have been synthesised and studied. Because of their rigid and strictly uniform pore structure, they act as molecular sieves. 50-63 Literature survey on inorganic ion exchanger revealed the need for development of other inorganic ion exchangers.

Many hydrous oxide gels including $Fe_2O_3$, $Al_2O_3$, $Cr_2O_3$, $TiO_2$, $ZrO_2$, $ThO_2$, $SnO_2$, $MoO_2$ were synthesised and studied. They were amphoteric in nature and can be used as cation exchangers at pH values above their isoelectric point. 64-69

Amphlet, McDonald and Redman70 have reported synthetic inorganic ion-exchange materials based on hydrous metal oxides. Hydrous oxides of zirconium, thorium, aluminium and mixed hydrous oxide of aluminium and thorium were
synthesised and studied by Pai et al.\textsuperscript{71} and were used as anion exchangers. Cation exchangers with superior properties were prepared,\textsuperscript{72-75} for example, from zirconium phosphates with variable $ZrO_2 : P_2O_5$ ratios. Thus, phosphates of zirconium, thorium, titanium, zirconium antimonate, phosphoantimonic acid and other such cation exchangers were synthesised and studied by Pai et al.\textsuperscript{71}

1.2.2 Ion-exchange coals or carbonaceous exchangers

Idebknecht\textsuperscript{76} discovered that certain coals when treated with hot concentrated sulphuric acid yielded a product having ion-exchange properties, which, in addition, were physically and chemically stable towards acids and to some extent towards alkalies. Most lignite and bituminous coals and anthracites were converted into strong acid cation exchangers by sulphonation with fuming sulphuric acid to introduce sulphonic acid groups. Additional carboxylic groups were formed by oxidation. In certain respects, sulphonated coals resembled organic ion-exchange resins.\textsuperscript{77-81} For example the capacity of the sulphonated coals vary with the pH of the solution like organic ion-exchange resin.

1.2.3 Organic ion exchangers of natural and modified type

Natural substances like wool, horn, hair, leather and cellulose possess ion-exchange properties. The first
four being proteinaceous in nature, contain both basic and acidic residues and hence behave as amphoteric exchangers. Cellulose contains aliphatic alcoholic groups which are easily oxidised to carboxylic groups by sodium hypochlorite or nitrogen tetroxide. Consequently they exhibit weakly acidic cation-exchange properties. Natural products like, alginic acid contain carboxylic groups and act as weakly acidic cation exchangers.\textsuperscript{82-83}

1:2:4 Synthetic organic ion exchangers

The most important class of ion exchangers are the organic ion-exchange resins. Their framework or matrix consists of an irregular macromolecular three-dimensional network of hydrocarbon chain and carries ionic groups such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $\text{A}_3\text{O}_4^{2-}$, in cation exchangers, and $-\text{NH}_3^+$, $\text{NH}_2^+$, $\text{H}^+$, $-\text{S}^+$, in anion exchangers. Ion-exchange resins are thus crosslinked polyelectrolytes.

There are two general types of polymerisation reactions both of which can be used to synthesise organic ion-exchange resins. These are condensation polymerisation and addition polymerisation. Condensation polymers are formed by reacting polyfunctional molecules, in such a manner that new carbon-carbon, carbon-nitrogen or carbon-
oxygen bonds are formed with the elimination of water etc. In contrast, polymers prepared by addition polymerisation of olefinic compounds contain only carbon-carbon bonds as the links which join the monomers. These polymers have the same empirical compositions as the monomers used in their preparation and have a higher chemical and thermal stability than the condensation polymers. The degree of crosslinking and the particle size of the products are more readily controlled in this technique.

14.25 Liquid ion exchangers

Conventional ion exchangers are insoluble solids; however, as stated earlier, ion-exchange can also occur between two immiscible liquid phases. The liquid ion exchangers are prepared by dissolving compounds with ionogenic groups in an organic solvent such as chloroform, kerosene, trichloroethylene and xylene which are immiscible with water. Long chain aliphatic amines having hydrophobic groups are used as anion exchangers. Fatty acids and dialkyl phosphates are used as cation exchangers.

The advantages of liquid ion exchangers are (i) they can be easily prepared (ii) the concentration of the functional groups in the ion exchanger phase can be readily adjusted
(iii) high ion-exchange rates can be attained by efficient dispersion of the organic phase in the aqueous phase and (iv) continuous counter current operation is much simpler with liquid than with solid ion exchangers. However losses due to phase separation increase the handling losses as compared to solid exchangers.

1.2.6 Macroreticular ion-exchange resins

A modified resin structure different from conventional homogeneous gels and having a rigid macroporous structure similar to those of conventional absorbents has been synthesised by Kunin. These resins have been designated as macroreticular or isoporous ion exchangers and have very high specific surface area and are highly porous.

These resins are widely used in reactions involving nonaqueous media, where ordinary gel resins are unsuitable as they hardly swell in nonaqueous media. Because of their high porosity, macroreticular resins allow big molecules to penetrate inside the pores even when nonpolar solvents are used. This helps to increase the rate of catalytic reactions in nonaqueous media. These resins are prepared by the addition polymerisation technique.
Furthermore, the improved resistance characteristics of many of the macroreticular resins to physical and chemical attrition enables ion-exchange operations to be performed under controlled conditions. 95-102

**Specific ion exchangers**

These resins exhibit higher selectivities towards certain ions and are called specific ion exchangers. Many compounds which form chelates with metal ions have been incorporated into the resin matrix by polycondensation with phenols and aldehydes or other cross-linking agents. Examples are salicylic acid, 103 chromotropic acid, 104 anthranilic acid, 105-106 and o-amino phenol, 105-107 m-phenylenediaminetetra acetic acid, 108 and iminodiacetic acid. 109 & 110

Many other specific resins have been prepared with different groups, for example a resin with hydroxamic acid groups was prepared by Connaz and Hutschnaker. 111

Specific ion-exchange resins containing mercapto groups and groups of chlorophyll and haemin derivatives were prepared by Gregor, 112 Broser 113 and Leutich 114 respectively.

Comprehensive reviews of specific ion exchangers have been published by Hale, 115 Millar, 116 Hojo, 117 Rosset 118 and Schmuckler. 119
Electron exchangers are solid oxidation and reduction agents. They are insoluble but are able to swell in aqueous media to a limited extent. They are reversible agents, i.e. after having oxidised or reduced a substrate, the electron exchanger can be regenerated by suitable oxidising or reducing agent. The reactivity of electron exchangers is due to built-in functional components such as quinone/hydroquinone which can be reversibly oxidised or reduced.

Electron exchangers can be prepared by condensation or addition polymerisation technique. In either case, the reactive groups can be introduced into one of the monomers or after polymerisation in the crosslinked resin.

Redox ion exchangers are conventional ion exchangers into which reversible oxidation reduction couples such as Cu$^{2+}$/Cu$^+$, Fe$^{3+}$/Fe$^{2+}$, methylene blue/lucoumethylen blue are introduced. The oxidation reduction couples are held in the resin either as counter ions or by sorption or by complex formation. Ion-exchange or desorption may cause a gradual loss of redox capacity.
Redox ion exchangers are easily prepared from conventional cation or anion exchangers. Either the counter ion is replaced by an ion such as Cu$^{2+}$ or Fe$^{3+}$, SO$_3^{2-}$ etc which can act as an oxidation (or reduction) agent or an organic oxidation-reduction agent such as methylene blue is incorporated by sorption.

1:3 Application of ion-exchange resins

Applications of ion-exchange resins are extremely varied with regard to types of solutions treated and principles governing such treatments. However water softening and demineralisation are the major applications for these versatile tools. Recently ion-exchange technique has been used for the preparation of chemicals. Advantages of this technique over conventional methods are that it can be easily handled and pure product can be obtained. Potassium carbonate, potassium nitrate, and potassium silicate have been prepared by this technique. In various applications of ion-exchange the resins performed one or more of the following functions:

1) elimination of ionic impurities as for example in deionisation,

2) substitution of desirable for undesirable ions as for example in water softening (sodium for calcium and magnesium).
iii) isolation of desirable ionic constituents from contaminated solutions, for example, recovery of copper from cuprammonium waste,

iv) fractionation as in ion-exchange chromatography,

v) neutralisation as in deacidification of citrous juices, and

vi) catalysis as in esterification reaction.

1131 Preparation of acids by ion-exchange technique

The hydrogen forms of cation exchangers are useful in the preparation of different acids from their corresponding salts. Hirano and Kurobe prepared standard solutions of acids by dissolving known quantities of salts in a definite volume of water and passing the resulting solution through the cation exchanger in hydrogen form. Keattch prepared standard solutions of hydrochloric, sulphuric and acetic acids in a similar way, achieving a maximum concentration of 0.25 normality.

Simek and Novotony prepared standard solutions of hydrochloric acid and sodium hydroxide from sodium chloride by passing the solution over hydrogen form of a cation exchanger and hydroxide form of an anion exchanger respectively.

Almasy and coworkers prepared boric acid from a mixture of borax and boric acid by passing the
solution of the mixture over the hydrogen form of a
cation exchanger of the nuclear sulphonlic acid type at
80°C by circulating hot water around the resin column.
Brown and Jeffers\textsuperscript{147} obtained boric acid in a similar
way by using a cation-exchange resin having a carboxylic
group. Sodium sulphate was obtained as a by-product
while regenerating the resin with sulphuric acid.
Georgeta\textsuperscript{150} prepared boric acid from borax contain­
ing ore by employing ion-exchange technique in a
batch reactor. Three fold excess of the stoichiomet­
ric amount of cation-exchange resin was used. Solid
liquid ratio in the reactor was 1 : 10 and temperature
was adjusted to 60°C. Crude boric acid containing
sulphuric acid was purified by passing the solution
through an anion exchanger.\textsuperscript{150}

Thilo and Wetche\textsuperscript{151} prepared phosphoric acid from
ground apatite by shaking it with cation-exchange
resin in the hydrogen form in the presence of water
and found that the velocity of reaction was dependent
on the resin particle size. Eros\textsuperscript{152} prepared phosphoric
acid from Algerian and Jordanian phosphates by using
a cation-exchange resin in the hydrogen form. Cochran\textsuperscript{153}
lixiviated apatite with phosphoric acid, producing
calcium-dihydrogen phosphate and treated this solution
with a sulphonlic acid type of cation-exchange resin
to obtain phosphoric acid, Klement\textsuperscript{154} Vilukh and Bogatyrev\textsuperscript{155-157} prepared a number of acids by passing potassium or calcium salts of the corresponding acids through nuclear sulphonie acid type of cation exchangers in the hydrogen form. They also reported the preparation of periodic acid from potassium periodate.

The preparation of molybdc acid,\textsuperscript{158} tungstic acid,\textsuperscript{161} vanadic acid,\textsuperscript{159} thiotungstic acid and thiomolybdic acid\textsuperscript{160} from their sodium and ammonium salts, has been reported by Richardson,\textsuperscript{158} Mitra,\textsuperscript{159} Boch,\textsuperscript{160} and Vilukh et al.\textsuperscript{161} Production of hydrochloric acid from sodium chloride,\textsuperscript{162} potassium chloride,\textsuperscript{163} calcium chloride\textsuperscript{164} and preparation of nitrous acid\textsuperscript{165} have been described. Vilukh and Bogatyrev have described the preparation of hydrobromic acid from potassium bromide by using a cation-exchange resin of sulphonie acid type and employing both static and dynamic conditions. Mandalia has prepared hydrobromic acid from iron bromide using hydrogen form of zekarb-225.\textsuperscript{167}

1:3:2 Use of ion-exchange resin as an acid absorbent

Strongly basic anion-exchange resins are useful for the removal of weak and strong acids from their solutions. However, weak base anion-exchange resins
preferentially take up strong acids from solutions containing a mixture of strong and weak acids. Sorption of hydrochloric acid and sulphuric acid by anion-exchange resins was studied by Myers,168 Jenny169 measured nitric acid sorption on an anion-exchange resin. Kunin and Meyers170 presented graphically the sorption of a wide variety of acids as a function of solution pH. Sorption of halogen acids and nitric acid was reported by Yanovich171 and coworkers. Rizaev and Korolkov172 compared sorption isotherms for tartaric, citric and lactic acids on anion-exchange resins. They found that sorption capacity of an anion-exchange resin increased with decreasing flow rate. Bauman and Donald173 reported that the removal of hydrochloric acid from ethylene glycol was effected by passing the solution through an anion-exchange resin in the sulphate form. Removal of acid from milk sample by different anion-exchange resins was studied by Mirozova and coworkers.174 Deacidification of grape juice was investigated by Vibhakar and coworkers.175 Separation of polyacid from its salt was achieved by passing the solution through an anion-exchange resin by Hatch.176 Vilukh et al177 used an anion-exchange resin in gas masks to absorb halogens and hydrochloric acid vapours. Physical adsorption as well as exchange of hydrochloric, acetic and chloroacetic acid by base
exchange was reported by Bishop. Shapovalova and Skorokhod studied the sorption and exchange of benzoic acid and salicylic acid from their mixture by the chloride form of AV 17 anion-exchange resin.

Krasnov and Iv ovchinnikova studied the molecular sorption of formic acid on AV 17 anion-exchange resin. They found that the sorption of formic acid was higher on the hydroxide form than on the sulphate form and explained that basicity of the resin in the hydroxide form was higher than in sulphate form. They have also reported that sulphuric acid was not formed by the interaction of formic acid with the anion-exchange resin matrix and therefore its capacity was lower in the sulphate form than in the hydroxide form.

Samuelson, Soldatov, Valdimir and David studied the sorption of acetic, monofluoroacetic and trifluoroacetic acids on an anion-exchange resin and observed that these acids are strongly held by the anion-exchange resin, the stability increased in the order

\[ \text{trifluoroacetic} > \text{monofluoroacetic} > \text{acetic} \]

Donskaya and Libinson studied the sorption of aliphatic amines on the sulphuric acid cation exchanger KU₃.
They found that sorption increased with increase in chain length of the aliphatic part of the amine molecule in mono, di and tri substituted compounds.

Koganovaski and Nikitina\textsuperscript{183} studied the absorption of aromatic amines from aqueous solution by the sulphonic acid type cation exchanger KU 2 and found that the nondissociated amine molecules were absorbed by the hydrogen form of KU 2 resin. They also reported that protonization of amine in the resin phase was the reason for the absorption. The protonization of the amine molecule is due to the interaction of the amine molecule with the proton of the \( \text{SO}_3\text{H}^+ \) group of cation-exchange resin.

Krasnov and coworkers\textsuperscript{184} have studied the mechanism of amine sorption on cation-exchange KU 2 in \( \text{H}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \) and \( \text{Ca}^{++} \) forms under dynamic conditions using diethylamine solution. They found that reaction between amine and cation-exchange resin (in \( \text{H}^+ \) form) was only possible when pKa of the amine was \( \geq \) pKa of the cation-exchange resin. However in salt form (viz. \( \text{Na}^+ \), \( \text{K}^+ \) and \( \text{Ca}^{++} \)) only molecular sorption of amine was observed.

Recently Prokop\textsuperscript{185} and coworkers have studied the sorption of aliphatic amines on styrene divinyl benzene ion exchangers. They reported that sorption is a
function of the number and distribution of sulphonic acid groups of the exchanger.

1314 Softening of seawater

Softening of seawater by ion-exchange technique has been known from a very long time. Zeokarb - 225 cation-exchange resin is used to remove calcium and magnesium. Extensive research has been carried out by scientists in this field. Kunin has reported that methacrylic acid-divinyl benzene copolymers in alkali metal or ammonium form can be used to remove calcium and magnesium ions. Ohbayashi Osao reported that deterioration of the exchange capacity resulting from deposition of ferrous hydroxide could be prevented by subjecting the water to magnetic field and efficiency of softening could be enhanced. In this process, the feed water is subjected to a three-stage magnetic field in an iron pipe. Iron and other chemical species responsible to the hardness of water are magnetised to give diamagnetic species. The preparation of ion-exchange membranes has extended the application of the ion-exchange technique. A membrane could be defined as a solid film, liquid film or layer with thickness generally smaller compared to its surface. In fact in the most general terms, a membrane could be defined as a phase acting like a
barrier to the flow of molecular or ionic species present in the liquid and/or vapour contacting the two surfaces.

Membranes can be classified into three groups -

1) Homogeneous (2) Heterogeneous (3) Interpolymer

1) Homogeneous membranes are coherent ion exchanger gels in the form of ribbons, discs etc. (2) In heterogeneous membranes fine particles of ion-exchange resins are dispersed in an inert polymeric film forming binder. (3) Interpolymer membranes obtained by the molecular combination of two polymeric materials, one of which is a polyelectrolyte, have attracted wide attention from workers in this field.

The inherent quality of permselectivity and conductivity in membranes have enabled their usage in the electrodialysis application. Electrodialysis is defined as a process, in which ions migrate through a membrane or diaphragm separating two solutions, this migration being caused by an electrical potential difference applied between the two solutions. Desalination of seawater and brackish water is a major application of this process. However desalting of milk was carried out recently by Nakamura and coworkers. Harkare reported that this process can
be used for desalting of cheese whey and extended further for the preparation of chemicals like potassium nitrate and potassium carbonate. The same can also be used for the separation of sodium formate from pentaerythritol.

Khaseva had adopted this technique for the purification of rare earth element like neodymium hydroxide. Lysenko and coworkers have reported that this technique can be employed for the concentration of sodium hydroxide solution.

1.3.5 Basis for the work undertaken

1) Uptake of organic acids by weak base anion-exchange resins -

Literature survey showed that such work has been done on the uptake of organic acids by strong base anion-exchange resins. However, such work has not been reported regarding the uptake of organic acids by weak base anion-exchange resins. Hence, in the present investigation, uptake of tartaric, succinic, citric, formic, oxalic, acetic, propionic and butyric acids by weak base anion-exchange resins in different forms like chloride, sulphate and hydroxide was studied.

2) The uptake of organic acids by hydroxide form of Amberlyst A 21 in acetone, dioxane and ethanol
(nonaqueous media) was also studied because no such data is available in the literature so far.

3) Uptake of amines by cation-exchange resin -
Literature survey presented earlier in the introduction showed that no data is available regarding the uptake of ethylamine and triethylamine by cation-exchange resins. Therefore this work was undertaken with a commercial carboxylic resin and an indigenously prepared one for evaluating comparative performance.

4) Preparation of electrolytic grade boric acid -
It will be seen from literature that boric acid produced by conventional methods is contaminated with chloride impurity. The literature survey carried out showed that pure boric acid can be obtained by ion-exchange technique. Since, however, no detailed information regarding the preparation of electrolytic grade boric acid by ion-exchange technique was available, work was undertaken for standardising a suitable ion-exchange procedure for its preparation and various parameters such as effect of flow rate, effect of concentration of the influent and effect of resin bed height on breakthrough capacity were studied.

5) Softening of seawater -
Scale formation on the surface of the evaporator reduces the thermal efficiency of the process of sea
water distillation and increases the cost of the product water. Studies on softening of seawater by ion-exchange technique were undertaken using indigenously available cation-exchange resins.