1. INTRODUCTION

1.1 Scope and object :

When an ion exchange resin is placed in contact with a solution, one or more of the following phenomena may occur :

1. ion exchange,
2. sorption of strong electrolytes,
3. sorption of weak or nonelectrolytes

and 4. sorption of solvent or swelling of the resin.

In this study, the interest has been in the first three directions.

The object has been to contribute towards the understanding in the above directions and the application to the separation of mixtures.

1.2 Ion exchange materials : (1 to 10)

Introduction :

Ion exchange materials are of a wide variety. These may be inorganic or organic and of different shape and size. The common general structural principle is a framework with electric surplus charge and mobile counter ions. However, the various types of materials behave markedly differently.

Inorganic ion exchange materials :

Most natural ion exchange materials are crystalline aluminosilicates with cation exchange properties. The zeolites have a rigid three-dimensional framework structure with cavities and channels permeable to counter ions. Clays have a layer structure and the counter ions move in between the layers. Glauconites have a dense, three-dimensional framework structure and the exchange can occur essentially only at the crystal surface. A few minerals such as apatite can act as natural inorganic anion exchangers.

Synthetic aluminosilicate cation exchangers have been prepared by fusion and precipitation methods. Recently, zeolites with regular crystal structure have been prepared. These are useful as molecular sieves as these can sorb small molecules, but exclude molecules which may be larger than the channel width. Interesting cation and anion exchangers, have also been prepared from zirconium and tin hydroxides.

Organic ion exchangers :

Organic ion exchange resins are the most significant of the ion exchange materials. These are gels and the matrix consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains. The ionic groups attached to the matrix may be of various types such as,

$$-SO_3^{-} \qquad -COO^{-} \qquad -PO_3^{--} \qquad -AsO_3^{--}$$

for cation exchangers and

$$-NH_3^{+} \qquad >NH_2^{+} \qquad >\overset{+}{N}< \qquad -\overset{+}{S}<$$

for anion exchangers. Hence, ion exchange resins are crosslinked polyelectrolytes. They are insoluble, but have a limited swelling in water, depending on the crosslinking. The ion exchange behaviour of the resins is mainly dependent on the nature of the fixed ionic groups.

Certain coals are natural weak acid cation exchangers. Others may be converted into ion exchangers by chemical treatment, such as sulfonation. Many other natural or synthetic materials can act as ion exchangers or can be converted into ion exchangers, by introducing fixed ionic groups or by crosslinking. Ion exchange papers and phosphorylated cotton are of interest.

Commercial ion exchangers are insoluble solids. Recently liquid ion exchangers, such as long chain aliphatic amines and fatty acids or alkyl phosphates have become of great interest.

Organic synthetic resins in general, have superior chemical and mechanical stability, exchange capacity, exchange rates and versatility. Inorganic materials possess better thermal stability and resistance to radiation.

Preparation :

A wide variety of organic ion exchange resins have been prepared and some are available commercially under various trade names. Tables (1.2.1 and 1.2.2) give the trade names and the manufacturers of commercially available ion exchange resins.

The synthesis of ion exchange resin should yield a three-dimensional, crosslinked matrix of hydrocarbon

Table 1.2.1

Some common commercial cation exchange resins

Matrix	Ionic group	Trade name	Manufacturer	Physical form	Remarks
Crosslinked polystyrene.	$-SO_3^-$	Amberlite IR-120	Rohm and Haas Co.	Spherical beads	Standard resin, 8 % DVB.
Strongly acidic.		Amberlite 200	Rohm and Haas Co.	Sph.Beads.	Higher mech.and chem.stability.
		Amberlyst 15	Rohm and Haas Co.	Sph.Beads.	Macroreticular resin.
		Dowex 50	Dow Chemical Co.	Sph.Beads.	Dowex 50 X 2 has 2 % DVB etc.
		Imac C-12	Activit Hollands.	Sph.Beads.	Standard resin, 8% DVB.
		Permutit Q	Permutit Co.,U.S.A.	Sph.Beads.	Standard resin.
		Zeo-Karb 225	Permutit Co.,England	Sph.Beads.	Standard resin, 8 % DVB.
Vinyl addition polymers.	-COOH	Amberlite IRC-50	Rohm and Haas Co.	Sph.Beads.	

Table 1.2.1 (Continued)

Matrix	Ionic group	Trade name	Manufacturer	Physical form.	Remarks
Weakly acidic		Duolite CS-101	Chemical Process Co.	Sph.Beads.	
		Zeo-Karb 226	Permutit Co.,England.	Sph.Beads.	
Vinyl addition polymers.		Permutit C	Permutit A.G., W.Germany.	Sph.Beads.	
Weakly acidic		Permutit H-70	Permutit Co., New York.	Sph.Beads.	
Phenolic resins.	$-SO_3^-$	Duolite C-10	Chemical Process Co.	Granules.	More porous
		Zeo-Karb 215	Permutit Co.,England.	Granules.	
	-COOH	Duolite CS-100	Chemical Process Co.	Granules.	
		Permutit H	Permutit Co., New York.	Granules.	
		Zeo-Karb 216	Permutit Co.,England.	Granules.	

Table 1.2.2

Some common commercial anion exchange resins

Matrix	Ionic group	Trade name	Manufacturer	Physical form	Remarks
Crosslinked Polystyrene	$-\mathrm{N}(\mathrm{alkyl})_3^+$	Amberlite IRA-400	Rohm and Haas Co.	Spherical Beads.	Standard resin,8% DVB.
		De-Acidite FF	Permutit Co., England.	Sph.Beads.	Standard resin,7-9% DVB.
		Dowex 1	Dow Chemical Co.	Sph.Beads.	Standard resin, Dowex 1-X8
		Dowex 21 K	Dow Chemical Co.	Sph.Beads.	Improved mech.Stability.
		Duolite A-101	Chemical Process Co.	Sph.Beads.	Improved resins.
		Permutit S-1	Permutit Co., New York.	Sph.Beads.	
	$-\mathrm{N}(\mathrm{alkylol})-$ $+$ $(\mathrm{alkyl})_2$	Amberlite IRA-410	Rohm and Hass Co.	Sph.Beads.	Standard resin,(∽ 8% DVB)
		Dowex 2	Dow Chemical Co.	Sph.Beads.	Standard resins, Dowex 2-X8.
		Duolite A-102	Chemical Process Co.	Sph.Beads.	Improved resins.
		Permutit S-2	Permutit Co., New York.	Sph.Beads.	

Table 1.2.2 (Continued)

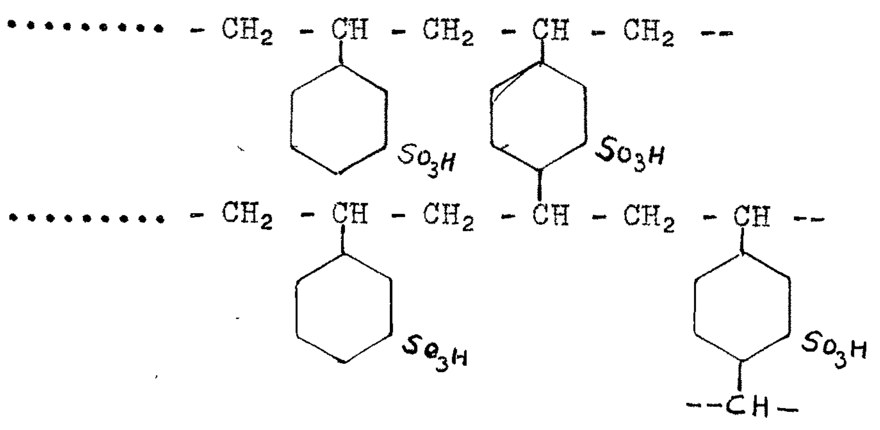
Matrix	Ionic group	Trade name	Manufacturer	Physical form	Remarks
”	Weak base Amino groups	Amberlite IR-45	Rohm and Hass Co.	Sph.Beads.	
		De-Acidite M	Permutit Co., England.	Sph.Beads.	Polyamine groups.
		De-Acidite G	Permutit Co., England.	Sph.Beads.	$-N(C_2H_5)_2$ groups only.
		Dowex 3	Dow Chemical Co.	Sph.Beads.	
Condensation polymers.	$-N(alkyl)_3^+$	Imac S-3	Activit Holland	Granules.	Highly porous resin.
	Weak base Amino groups	Amberlite IR-4B	Rohm and Haas Co.	Granules.	
		Duolite A-2	Chemical Process Co.	Granules.	
	Strong and weak base groups	Permutit A	Permutit Co., New York.	Granules.	

chains carrying ionic groups. The resins can be prepared by condensation polymerisation or addition polymerisation and the ionogenic groups can be introduced, before, during or after the polymerisation. These groups may be of one or more types giving monofunctional or multifunctional cation exchange or anion exchange or amphoteric resins.

Most of the earlier cation exchange resins were condensation products of phenol derivatives and aldehydes.

Most of the present commercial resins are addition polymers prepared from vinyl monomers. These resins have a better chemical and thermal stability than the condensation polymers and their degree of crosslinking and particle size can be more easily controlled.

The monofunctional sulfonic acid cation exchange resins available are crosslinked polystyrenes with sulfonic acid groups, introduced by sulfonation of the polymer. The crosslinking agent used is divinylbenzene. Amberlite IR-120, Dowex 50, Nalcite HCR, Permutit Q, Duolite C-20 and C-25 and Lewatit S-100 are resins of this type. The structure may be imagined as :



Pure divinylbenzene is not readily available ; hence the resins are prepared with a commercial product consisting of a mixture of the different divinylbenzene isomers (about 40 to 55 %) and ethylstyrene (about 45 to 60 %). Ethylstyrene is also incorporated into the matrix.

By varying the divinylbenzene content, the degree of crosslinking can be adjusted in a simple and reproducible manner. The nominal DVB content is used to indicate the degree of crosslinking ; it refers to mole percent of pure divinylbenzene (not of the commercial product) in the polymerisation mixture. Resins with low degree of crosslinking, swell strongly and are soft and gelatinous. Resins with high DVB content swell much less and are tough and mechanically more stable.

The copolymer beads are prepared by the pearl polymerisation technique. The monomers, from which stabilisers have been removed, are mixed and a polymerisation catalyst, such as benzoylperoxide is added. The mixture is then added to a thoroughly agitated aqueous solution at a required temperature (usually 85° to 100°C). The mixture forms small droplets, which remain suspended. A suspension stabiliser (gelatin, polyvinylalcohol etc.) in the aqueous phase prevents agglomeration of the droplets. The size of the droplets depends mainly on the nature of the stabilizer, the viscosity of the solution and the agitation and can be varied within wide limits. The polymer is obtained in the form of fairly uniform beads.

The sulfonation of the beads is simple, if proper precautions are taken. The cracking of beads may be avoided by first swelling the beads in an organic solvent such as toluene, nitrobenzene etc. It is advisable to transfer the sulfonated beads first to a highly concentrated electrolyte solution, which causes less swelling and then to dilute the solution stepwise. Sulfonation with concentrated sulfuric acid or chlorosulfonic acid results in practically complete monosulfonation of all the benzene rings.

Highly porous, macromolecular ion exchange resins are prepared by a variation in the conventional pearl polymerisation technique. An organic solvent, which is a good solvent for the monomers, but a poor solvent for the polymer is added to the polymerisation mixture. As polymerisation progresses, the solvent is squeezed out by the growling copolymer regions. In this way, spherical beads are obtained with wide pores which permit access to the interior of the beads even when nonpolar solvents are used. The recent Amberlyst ion exchange resins are of this type .

Cation exchangers with specific preference for certain cations can be made by introducing groups which form strong complexes, preferably chelates with these cations. Resins with chelating iminodiacetic acid are now commercially available.

Most of the earlier anion exchange resins were condensation products of aromatic or aliphatic amines and aldehydes, dihaloparaffins or haloepoxides. Most of these contain weakly basic groups.

The more important anion exchangers are cross-linked polystyrenes, into which strong or weakly basic groups are introduced by chloromethylation and subsequent amination. Reaction with tertiary alklyamines gives strong base quaternary ammonium groups and reaction with primary or secondary alkylamines or ammonia gives weak base amino groups. Anion exchangers with strong base quaternary phosphonium and tertiary sulfonium groups have also been prepared.

Amphoteric ion exchangers contain both acidic and basic groups. Snakecage polyelectrolytes are a novel variety of amphoteric resins. These are prepared from conventional ion exchangers by polymerisation of monomeric counter ions within the resin.

For specific purposes ion exchangers in the form of pellets, rods, belts etc. have been prepared by cementing ion exchange particles together with an inert binder or by impregnating suitable supporting carriers.

Ion exchange membranes have been prepared by various methods. The membranes may be homogeneous or heterogenous and have become of significant interest recently, particularly for desalting of water.

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