CHAPTER II

ION EXCHANGERS,
THEORIES AND MODELS OF ION EXCHANGE
AND
REVIEW OF LITERATURE
2. INTRODUCTION

The earliest research work on ion exchange was reported in the mid nineteenth century in the field of agricultural chemistry. Since then ion exchange has found increasing demand in Science and technology. During past few decades ion exchange process has attained a unique position for unit operations in process and separation techniques mostly because of ease of operation, adoptability, flexibility and simplicity of equipment required for different types of operational convinces.

Ion exchange has proved its utility in recent years in the laboratory as well as industry. As a result chemists and engineers are being faced with the task of investing its applicability in their own particular field of work. Separations of rare elements from a host of other impurities are carried out by using ion exchangers. Among other tasks the catalysis of organic reactions and decontamination of nuclear reactor coolant systems are some of the major area of applications. Recent developments in the field of ion exchanger membrane stretch its application into physico-chemical fields. The importance of ion exchange in analytical chemistry is a well established fact. Another potential area of application is the utility of exchangers in the field of preparative chemistry. However the main use of ion exchangers is in the purification and demineralization of water.
2.1 ION EXCHANGERS

There are different types of ion exchangers which may be either organic or inorganic. They may be natural or synthetic. The solid organic polymeric ion exchangers are usually called ion exchange resins, and are more predominant in technical applications. One cannot, at the same time, ignore the importance of inorganic ion exchangers, especially in the light of their better mechanical, thermal and electrical properties, and also because of their important role in soil sciences.

Thus, today, one can have a wide choice of ion exchange materials and it is more appropriate and necessary today than ever before to have a comprehensive knowledge of different kinds of ion exchangers available. The knowledge of different types of ion exchangers will help in selecting appropriate ion exchanger for the purpose of any given process.

2.1.1 INORGANIC ION EXCHANGERS

Historically, it was inorganic ion exchangers that were first studied for the practical applicability of ion exchange. Majority of the natural ion exchangers are crystalline aluminosilicates with cation exchange properties. The main representatives of this group are the zeolites, in fact the earliest known ion exchanger was the inorganic mineral zeolite. These minerals have relatively open three dimensional structures with channels and interconnecting cavities. Their lattices are made up of SiO₄ and AlO₄ tetrahedra with corner oxygen sharing. The lattices carry a net negative charge which is balanced by alkali or alkaline earth cations which do not occupy fixed positions and are free to move in the channel of lattice framework. These act as counter-ions necessary for the replacement with other cations from solutions.

Certain aluminosilicates can also act as anion exchangers. The mineral anion exchangers which have been used for practical purposes are apatite \([\text{Ca}_5(\text{PO}_4)_3\text{OH}]^4\). The natural inorganic ion exchangers exhibit ion exchange properties typical of weak acid or weak base exchangers. They have been used extensively as molecular sieves for a number of industrial applications.

The first synthetic inorganic exchangers of theoretical importance were fusion permutits prepared by the fusion of soda, potash, feldspar and kaolin or similar components. Later on cation exchangers with improved properties were prepared which are known as gel permutits.
Recent developments in this area provide ion exchangers with much more satisfactory properties. A combination of oxides of elements group (IV) with more acidic oxides of group (V) and group (VI) elements provide ion exchangers with improved properties. Such as thermal stability, resistance to radiation, etc. These exchangers are gaining increasing importance as a result of the developments of radiochemical engineering that necessitate the use of ion exchange materials that are resistant to heat and radiation.

2.1.2 ORGANIC ION EXCHANGERS

Organic ion exchange resins are insoluble polymerised or polycondensed products of high molecular weight containing functional groups which are capable of acting as exchangeable ions. The high molecular weight three dimensional supporting matrix for the functional groups is a divinylbenzene-styrene co-polimers, a phenol formaldehyde polymer or the like. Cation exchange functional groups include sulfonic acid (-SO₃H), carboxylic acid (-COOH), phenolic (-OH), sulphydrl (-SH), arsonic (-ASO₃H₂), phosphoric (-PO₃H₂) and phosphorous (-PO₂H₂). The anion exchange resins contain functional groups like primary, secondary or tertiary amino groups (-NH₂, = NH, = N), quaternary ammonium compound (≡N⁺), a pyridine group ( ), quaternary pyridine bases ( ), quaternary phosphonium (≡P⁺) and sulphonium groups (≡S⁺). For example, for a copolymeric styrene divinylbenzene sulphonlic acid cation exchangers the quasi-constitutional formula would be

\[
\begin{align*}
\text{SO}_3\text{H} & \quad \text{SO}_3\text{H} \\
\end{align*}
\]
and for a styrene divinylbenzene quaternary ammonium anion exchanger the quasi-constitutional formula would be

\[
\begin{align*}
\text{CH} \quad & \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} \\
\text{CH}_2\text{N(CH}_3\text{)}_3\text{OH} \quad & \text{CH} \quad \text{CH}_2 \\
\end{align*}
\]

A common depiction of the basic structure of synthetic ion exchange resins based on styrene and divinylbenzene with their anionic fixed groups in the case of cation exchangers, or cationic fixed groups in the case of anion exchangers, is by figures showing schematically the charged matrix including the exchangeable ions in a circular outline to suggest the bead form of such ion exchangers.

The chemical, thermal and mechanical stability of the resin depends upon the structure and degree of cross linking of the resin and the nature and number of ionogenic groups. For example, the resin beads take up the solvent when in contact with the solvent medium and swell. The degree of swelling decreases with the increasing DVB content.

### 2.1.3 TYPES OF ION EXCHANGERS

Depending upon their porosity, ion exchangers are either gel type, macroporous (macroreticular) or isoporous. Resin having homogeneous network which is elastic in nature
and contains solvent from manufacturing process is called *gel type* of resin. In other words, gel type resin refers to polymer matrices that do not contain pores. During production of the resin from monomers, use of solvent gives porous matrix structure to the resin formed and the resin so formed is called *macroponous* or *macroporous* resin. The cross-linking and pore structure in the macroporous resin can be modified to obtain polymers with substantially uniform pore size. Such a resin is called *isoporous* ion exchange resin.

Ion exchange resins are manufactured as beads or granules. It is also possible to form resins in other shapes such as films, fibres, fabrics, tubes, foams, plates, etc. The whole material in all these cases, however, consists of same polymer or co-polymer which has been converted into an ion exchanger. Such resins are called *pellicular ion exchangers*.

In what are known as *snake cage resins* a polymeric linear snake is formed by polymerisation of suitable monomers with a given charge, such that it is located in a polymeric cross linked cage of opposite charge. Such ion exchanger was developed to facilitate the removal of salts from a single polyelectrolyte and regenerate the exhausted resin with water.

*Specific ion exchangers* are the ion exchangers containing the active group having the properties of specific reagent. The chemical structure of the ion exchanger itself determines this specificity. Specificity of an ion exchanger should not be confused with the selectivity of the ion exchanger. Selectivity is the process in which the ion exchangers sorbs one ionic species preferentially over the others, while specificity is the phenomenon in which the ion exchanger sorbs one species of ions to the exclusion of the others.

While the physical properties of the matrix substantially determines the characteristic of an ion exchanger, its chemical mode of action is decided by its ionogenic groups. Depending on the acidity or basisity of the ionogenic group, ion exchangers are distinguished as *strong acid ion exchanger* and *weak acid ion exchangers* and as *strong base ion exchangers* and as *weak base ion exchangers*.

*Partial ionogenic ion exchange resins* such as partially sulfonated cation exchange resins, though have low capacity, are quite helpful in avoiding difficulties in performing chromatographic separations.
Monofunctional ion exchanger is an ion exchanger containing one type of ionogenic group, while bifunctional ion exchanger contains two types of ionogenic groups. In general, an ion exchanger containing more than one type of ionogenic group is called polyfunctional ion exchanger, or preferentially, multi-ionic ion exchanger.

2.1.4. CELLULOSE ION EXCHANGERS

In addition to these synthetic resins many different types of ion exchange celluloses are now available. The degree of structure order may vary from amorphous to highly crystalline type fibers. Aggregates of glucosidic chains are held together by inter chain bonding which provides dimensional stability to matrix. Various functional groups are introduced by chemical treatments of the matrix.

Cellulose exchangers find wide spread use in purification of biological macromolecules such as enzymes, oligonucleotides and mononucleotides and hormones. Dextran exchangers when used as ion exchangers have application similar to those of cellulose ion exchangers.

In general, the synthetic resins are superior to natural ones in their physical and chemical stabilities, exchange capacity, the rate of exchange etc. They owe their characteristic properties to their structure.

2.1.5 GEL TYPE ION EXCHANGE RESINS

Gel type or microreticular resins are the resins having no pores in their polymer matrices. They are transparent spherical beads. The amount of cross-linking agents used during polymerisation has marked effect on the property of swelling of the ion exchanger. It has been observed that an ion exchanger containing low proportion of cross-linking agent in its matrix swells much strongly in aqueous solution than an ion exchanger containing higher proportion of cross-linking agent in its matrix. Therefore, gel type resins having high proportion of cross-linking agents are frequently unsuccessful in anhydrous solutions of low polarity. This is because the resin does not swell or swells only partially, as a result of which ion exchange rate process or the penetration of the non-electrolyte into the resin is curtailed. Other basic properties of gel type ion exchangers, also depend on the amount of cross-linking. Mechanical strength of the
resin, for example, decreases with the decrease in the amount of cross-linking agent used. Therefore, it is obvious that the properties of gel type ion exchangers can be controlled by use of individual monomers in appropriate proportions, during its synthesis.

Styrene and divinylbenzene copolymerisation is frequently used for the manufacture of gel type ion exchange resins. Use of divinylbenzene in low proportions (<10%) results in a resin which swells strongly in aqueous solutions while its use in higher proportions (>10%) results in resin with substantially low degree of swelling properties. These types of resins swell in polar solvents and usually contain 5 to 50 Å channel widths depending on the degree of cross-linking. These channels in the gel type resins are analogous to the pores in macroporous resins, and they determine the size of species, ion or molecule that may enter the resin structure. Thus resin containing low proportion of DVB swells considerably in suitable medium and opens up its structure widely, permitting large ions to diffuse easily and rapidly into the exchanger.

2.1.6. MACRORETICULAR OR MACROPOROUS ION EXCHANGERS

Macroreticular or macroporous ion exchangers are those in which porous matrix structure is formed by use of solvent during its production from monomers. Even in dry state such resins contain pores of several thousands of angstrom in size. The macroreticular resin structure can be seen as agglomerate of very small microspheres of gel. They are extremely uniform in external shape and in contrast to the gel type resins, they are opaque.

Though large proportion of cross-linking agents is necessary to prevent collapse of the structure of these resins, the same has many advantages due to the large internal porosity of the resin. Because of the existence of larger pores, the internal surface area of the resin is much higher than the gel type resins. This facilitates easy and complete sulfonation of the structure. Further, they have smaller swelling differences in polar and non-polar solvents; they have smaller loss of volume during drying; and they have higher oxidation resistance. Their suitability for catalytic purposes is unique. Therefore they are preferred in industrial applications though they have lower capacities and higher regeneration cost.
2.1.7 LIQUID ION EXCHANGERS

Various basic and acidic organic liquids of high molecular weight can be used as ion exchangers. They are essentially uni-functional. The behaviour of these ion exchangers is identical to that of solid ion exchanger, except that their organic phase is highly hydrated in contrast to the anhydrous organic phase of the solid ion exchangers. Liquid ion exchangers have a significant role to play in uranium and aluminium hydrometallurgy, and in thorium and rare earth recovery. Weakly basic liquid ion exchangers have wider applications than their weakly acidic counterparts.

2.1.8 STRONG AND WEAK BASE RESINS

A cation exchanger is described as a solid acid with high molecular weight anion, and an anion exchanger as a solid base with high molecular weight cation. They can exchange their hydrogen or hydroxyl ions for equally charged ions in the solution and get converted into high molecular weight salts. Seen in this light, we have two types of ion exchangers. In the first type, the ionogenic group is essentially completely dissociated in all normal conditions. In the other, the extent of dissociation is highly dependant on pH, corresponding to whether the ionogenic groups represent strong or weak acid or base. In terms of activity, the ion exchangers which are either strong acids or strong bases are active over wider pH range than those which are either weak acids or weak bases.

In the present work both strongly basic and weakly basic gel and macroporous ion exchangers are used.

2.2 ION EXCHANGE SELECTIVITY

Selectivity is a property of an ion exchangers to exhibit a preferential activity for certain ions in a solution containing several ions. When the ion exchanger takes up the ions with different readiness, the ion can mutually displace each other. The exchange reactions may be represented as follows.

Cation exchange reaction: \[ RNa^+ + KCl_{aq} \rightleftharpoons RK^+ + NaCl_{aq} \]  \hspace{1cm} (2.1)

Anion exchange reaction: \[ RCl^- + KNO_3_{aq} \rightleftharpoons RNO_3^- + KCl_{aq} \]  \hspace{1cm} (2.2)

where R represents the co-ion of the resin i.e., nonexchangeable ion fixed on the resin matrix. The ions in the solution having the same charge as R are also called co-ions, whereas the exchangeable ions in solutions and on the resin are called counter ions. The concentration of
the exchangeable ions, milliequivalents per gram of the resin is called specific capacity of the resin.

Ion exchanger exhibits all the characteristics of equilibrium and follow the law of mass action. If one ignores the penetration of co-ions into the resin, it can be said that the ion exchange tends towards equilibrium, wherein, the quotient of concentration ratios of two exchangeable ions on the exchanger and the solution becomes independent of concentration. This state is characterised by constant called selectivity coefficient \( K_c \). \( K_c \) is the ratio of ionic fractions of the exchanging ions in the two phases. If \( A \) and \( B \) are the exchanging ions, and \( Y \) is concentration in the resin and \( X \) is the concentration in the solution, then:

\[
K_c = \frac{Y_B}{Y_A} \times \frac{X_A}{X_B} \quad \ldots \quad 2.3
\]

\( K_c \) is not a thermodynamically defined equilibrium constant, but it is only a coefficient defined according to the practical requirements, in as much as ion activity in the resin phase cannot be determined. Further, \( K_c \) is not a constant in true sense of the word, but is influenced by a number of factors such as:

1. **Nature of resin**:
   a. Properties of exchangeable ions, i.e., their size and charge;
   b. Properties of exchanger, i.e., particle size, degree of crosslinking, specific capacity, type of ionogenic groups, nature of resin matrix, magnitude of swelling, etc.

2. **Nature of external solution phase**:
   a. Nature of ions, both capable and incapable of exchange, e.g., total concentration and concentration ratios; and
   b. Nature, type and quantity of other substances in the solution;

2.3 **THERMODYNAMIC TREATMENT**

Like any other phenomenon, ion exchange equilibrium can be studied by different approaches. The various approaches of the study of ion exchange equilibria fall broadly into two distinct, though complementary, categories.

1. The rigorous thermodynamic treatment requiring no models and no assumptions with respect to the ion exchange mechanism.

2. Treatment consisting of the introduction of models having particular properties similar to those of the ion exchanger to permit derivation of equations revealing the action of various physical forces during the exchange process.
2.3.1 EVALUATION OF THERMODYNAMIC EQUILIBRIUM CONSTANT

For the sake of simplicity our discussion will be centered around the simplest type of system, i.e., uni-univalent exchange in dilute solution, which can be represented as:

RA+ B\textsuperscript{-}(aq) $\rightleftharpoons$ RB + A\textsuperscript{-}(aq)  \hspace{1cm} ... 2.4

Then, the equilibrium constant $K_8^A$ for the reaction is given by

$$K_8^A = \frac{[RB]}{[RA]} \frac{[A^-]_{aq}}{[B^-]_{aq}} \hspace{1cm} ... 2.5$$

Where $[ ]$ refers to the active mass of the respective species. If we replace the active masses in the equation 2.5 by the corresponding equivalent fractions of species, then the equilibrium constant $K_8^A$ becomes selectivity coefficient $K_{cA}^{B^-}$. The value of selectivity coefficient is a dimensionless number when both A and B are ions of same valency.

The process is usually represented in terms of RA, RB, XA and XB, because single ion activities are indeterminate. Thus we have,

RA+ XB\textsuperscript{(aq)} $\rightleftharpoons$ RB + XA\textsuperscript{(aq)}  \hspace{1cm} ... 2.6

At equilibrium, the resin phase may be considered as uniform solid solution of A and B forms of the resin, namely, RA and RB, while, XA and XB are electrolytes present in the external solution. The equilibrium constant $K_{A}^{B^-}$ can be given by

$$K_{A}^{B^-} = \frac{M_{XA} w_{A}^{\pm XA}}{M_{XB} w_{B}^{\pm XB}} \frac{w_{RA} f_{RB}}{w_{RB}^{\pm RB}} \frac{w_{RA}}{w_{RB}} \hspace{1cm} ... 2.7$$

Where,

- $N_{RA}$ and $N_{RB}$ represent the equivalent fractions of RA and RB forms of the resin respectively.
- $M_{XA}$ and $M_{XB}$ represent the molality of XA and XB in the external solution phase.
- $w_{RA}$ and $w_{RB}$ refer to the activity coefficients of RA and RB forms of the resin respectively in water medium.
- $w_{A}^{\pm XA}$ and $w_{B}^{\pm XB}$ are the mean molal activity coefficients of XA and XB respectively in water medium.
To evaluate the constant $K_{aB}$, the corresponding $K_{cB}$ values are determined experimentally at constant temperature and constant ionic strength of external solution for various ratios of $M_{XA}$ and $M_{XB}$ over wide range so that $\bar{N}_{RB}$ values shall vary as widely as possible between 0 and 1. The corrected selectivity coefficients $K_{aB}^*$ at each resin composition are then calculated using the formula

$$K_{aB}^* = K_{cB}^* \left( \frac{w_{XA}^F}{w_{XB}^F} \right)^2$$

The values of $K_{aB}^*$ are plotted against $\bar{N}_{RB}$ over the range 0 to 1. Assuming that the standard states for resin components as those when the pure resinates are equilibrated with such a dilute solution of an electrolyte that the state of water and not that of the resin phase is affected thereby. Then applying the Gibbs-Duhem equation, $\log K_{aB}^*$ of the exchange reaction is calculated using equation

$$\log K_{aB}^* = \int \log K_{aB}^* \, d\bar{N}_{RB}$$

Bonner and his co-workers have reported for $K_{aB}^*$ for large number of ions on sulphonic acid ion exchangers of different cross-linkages. Hogfeldt, Gaines and Thomas, and Davidson and Argersinger have modified the above treatment taking into consideration water in the resin phase as an additional component as discussed by Holm. These treatments differ mainly in the selection of standard states. Gaines and Thomas have given us the treatment which is thermodynamically more rigorous and further enables the determination of activity coefficients in the resin phase independently of the concentration of counter-ions in the external solution. According to Gaines and Thomas:

1. A solid exchanger has a fixed number of exchange sites per unit mass. It is capable of absorbing solvent, but no co-ions from the external solution. (The case in which it absorbs co-ions from the external solution is dealt with separately by the said authors).

2. The ion exchange process is heterogenous reaction involving electrolytes $XA$ and $XB$ dissolved in a solvent, and the resinates $RA$ and $RB$ in the solid solution.

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3. The solvent on the resin phase is also a variable in addition to the resinates and the electrolytes.

4. The system is closed one and the vapour phase is also a part of the system at equilibrium. Then the thermodynamic equilibrium constant $K_{A}^{b-}$ for the ion exchange reaction 2.6 is given by

$$\ln K_{A}^{b-} = \int_{0}^{1} \ln K_{A}^{b-} dB - \int \frac{\ln a_{w}}{a_{w}} \frac{dB}{DB} \left[ a_{w} (\bar{N}_{RA} = 1) - 1(a_{w} (\bar{N}_{RB} = 1)) \right]$$

$$a_{w} (\bar{N}_{RB} = 1) = \int n_{w} \ln a_{w} + \int n_{w} \ln a_{w} \quad \ldots \quad 2.10$$

Where, $n_{w}$ is the number of moles of water associated with the one equivalent of the exchanger, and

$$a_{w}$$ is the activity of water.

Gupta\textsuperscript{19} has extended this treatment to ion exchange in mixed solvent media by adding correction term for the medium effect, according to which $\ln K_{A}^{b-}$ is given by the equation

$$\ln K_{A}^{b-} = \int_{0}^{1} \ln K_{A}^{b-} dB - \int \frac{\ln a_{w}}{a_{w}} \frac{dB}{DB} \left[ a_{w} (\bar{N}_{RA} = 1) - 1(a_{w} (\bar{N}_{RB} = 1)) \right]$$

$$a_{w} (\bar{N}_{RB} = 1) = \int n_{w} \ln a_{w} + \int n_{w} \ln a_{w} \quad \ldots \quad 2.11$$

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This $K^{b\text{-}}_{A^-}$ is with respect to pure water as solvent. $K^{b\text{-}}_{A^-}$ is the selectivity coefficient after making the activity coefficient correction in the external solution for the particular solvent composition. $a_{w}(X_{B}, (\bar{N}_{RB} = 1)$ refers to water activity in m molal solution of XB containing $X_{B}$ mole fraction of water (m is the ionic strength). Terms $a_{w}^{0}(X_{B}, (\bar{N}_{RB} = 1)$ represent water activities in infinitely dilute solutions of XB in the mixed solvent containing $X_{B}$ (mole fraction) of water. For the purpose of our discussion, the following assumptions are made:

1. The standard state for the electrolyte is that of infinite dilution in water.
2. The standard state for the resin is that of monoionic form of the exchanger in equilibrium with water; and
3. The activities of water inside the resin and in the external solution are equal.

As it is not possible to evaluate individually all the terms except the first in equation 2.11, the same must be rewritten combining integrals 2.7 as follows:

$$\ln K^{b\text{-}}_{A^-} = \int_{0}^{1} \ln K^{b\text{-}}_{A^-} \ d\bar{N}_{RB} + \ln Q$$

where, $Q$ includes solvent activity terms and activity coefficient correction for the differences in the standard states for the resin and the external solution phase.

Further approximating that the ionic activity coefficients are a function of total ionic strength only, and that they are independent of ionic composition of the solution, the activity terms in $\ln K^{b\text{-}}_{A^-}$ in equation 2.12 are taken outside the integral when ionic strength is $\leq 0.1$.

Then,

$$\ln K^{b\text{-}}_{A^-} = \int_{0}^{1} \ln K^{b\text{-}}_{A^-} \ d\bar{N}_{RB} + 2\ln \frac{s_{X_{A}}}{s_{X_{B}}} + 2\ln \frac{m_{A}}{m_{B}} + \ln Q$$

where, $s_{X_{A}}$ is the mean molal activity coefficient of XA in mixed solvent referred to the standard state of infinite dilution in mixed solvent.

$m_{f}$ term corrects this standard state of infinite dilution in water.

$K^{b\text{-}}_{A^-}$ is the selectivity coefficient in terms of concentrations at a given solvent composition.
Gupta is of the opinion that second, third and fourth terms in equation 2.11 do not contribute significantly compared to the other three terms. Ghate et al. determined $K_{A}^{B^-}$ for $\text{Li}^+ - \text{H}^+$, $\text{Na}^+ - \text{H}^+$ and $\text{K}^+ - \text{H}^+$ equilibria in methanol-water medium using equation 2.13, and have shown the importance of solvent activity terms.

In equation 2.13 correction for activity coefficient terms of the resinates for the difference in the corresponding standard states when the external solution changes from water to mixed solvent has not been taken into consideration. This has been considered by Starobinets et al. Gupta has treated the ion exchange equilibria in nonaqueous and mixed solvents in thermodynamically rigorous manner. Using the concept of standard free energy of transfer of ions and resinates from water to mixed solvents (or nonaqueous solvents), the thermodynamic equilibrium constants $K_{A}^{B^-}$ for exchange equilibria in mixed solvents have been correlated with the equilibrium constants in aqueous systems.

### 2.3.2 STANDARD FREE ENERGY CHANGE OF AN ION EXCHANGE REACTION IN MIXED SOLVENT MEDIUM

Ion exchange process in solvent medium can be considered as a thermodynamic equilibrium of exchangeable ions between an external electrolyte solution and electrolyte solution inside resin phase. It can be conveniently represented as

$$
\text{RA} + \text{B}^{-}_{(s)} \rightleftharpoons \text{RB} + \text{A}^{-}_{(s)} \quad \ldots 2.14
$$

where, $\text{A}^{-}_{(s)}$ and $\text{B}^{-}_{(s)}$ are solvated counter-ions.

RA and RB are A and B forms of the resin, respectively.

The equilibrium constant for the above ion exchange reaction is given by

$$
\ln K_{A}^{B^-} = \frac{-\Delta G_{A}^{R^{B^-}}}{RT} = \frac{-1}{RT} \left[ (\Delta G_{\text{RB}_{(s)}}^{-} - \Delta G_{\text{RA}_{(s)}}^{-}) + (\Delta G_{A}^{R^{-}_{(s)}} - \Delta G_{B}^{R^{-}_{(s)}}) \right] \quad \ldots 2.15
$$
where, $K_{A(s)}^{B^-}$ is the thermodynamic equilibrium constant for the reaction 2.14 at a given temperature.

$\Delta G_{A(s)}^{B^-}$ is the corresponding change in the standard free energy for the process.

$\Delta G_{A_1(s)}^{RB} & \Delta G_{A_2(s)}^{RB}$ are the standard free energy change of A and B forms of resin.

$\Delta G_{A_1(s)}^{A-} & \Delta G_{A_2(s)}^{A-}$ are the standard free energy change of solvated ions, A$^-$ and B$^-$ respectively in the external phase with respect to the ideal ionic gas state.

The second term of equation 2.15 would be equal to the difference in the standard free energy of hydration of the two ionic species A$^-$ and B$^-$ in the given medium. Thus, equation 2.15 can be rewritten as:

$$\ln K_{A(s)}^{B^-} = -\frac{\Delta G_{A(s)}^{B^-}}{RT}$$

From the equation 2.16 it is evident that the thermodynamic equilibrium constant $K_{A(s)}^{B^-}$ for anion exchange reaction is given by the electrostatic interaction differences ($\Delta G_{A_1(s)}^{RB} - \Delta G_{A_2(s)}^{RA}$) between the counter ions with the resin ion and the difference in the standard free energy of hydration ($\Delta G_{A_1(h)}^{A^-} - \Delta G_{A_2(h)}^{B^-}$) of the two counter ions in the aqueous medium. In a mixed solvent the corresponding term in that solvent medium has to be used.

To compare the equilibrium constant in mixed solvent medium with that in aqueous, it is necessary to have a common reference state chosen. Here the standard state for the electrolyte is that of infinite dilution in water and standard state for the resin phase is that of homoionic form of the exchanger in equilibrium with water. Then the standard free energy change for the reaction 2.14 in the mixed solvent media can be rewritten as

$$RT \ln K_{A(s)}^{B^-} = -\frac{\Delta G_{A(s)}^{B^-}}{RT} = -\left(\Delta G_{A(s)}^{RB} - \Delta G_{A(s)}^{RA} + (\Delta G_{A_1(h)}^{A^-} - \Delta G_{A_2(h)}^{B^-}) + (\Delta G_{A_1(h)}^{A^-} - \Delta G_{A_2(h)}^{B^-})\right)$$

where, $\Delta G_{i(0)}$ refers to the standard free energy change of transfer of $i^{th}$ species from infinitely dilute aqueous solution to the infinitely dilute solution in the mixed solvent.
The first term on the right hand side of equation 2.17 gives the difference in the electrostatic interaction energies between the two counter ions with the resin ion in aqueous medium. The second term refers to the difference between the free energies of hydration of counter ions. The third and the fourth deal with the difference between the free energies of transfer of the two resinates and the two counter ions respectively from a reference state in the aqueous phase to that in the corresponding mixed solvent medium.

From thermodynamic equilibrium constant $K_{A}^{B^{-}}$, the standard free energy change ($\Delta G^\circ$) for the exchange at a given temperature is given by the relation

$$\Delta G^\circ = -RT \ln K_{A}^{B^{-}} \quad \ldots 2.18$$

The standard enthalpy change ($\Delta H^\circ$) for the exchange is evaluated from the temperature coefficient of $K_{A}^{B^{-}}$ or by calorimetric studies, which give more precise results. The standard entropy change for the exchange is then computed using the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \ldots 2.19$$

Redinha and Kitchner have determined changes in free energies, enthalpies and entropies of ion exchange reactions between $H^+$, $Na^+$ and $Ag^+$ with a series of polystyrene sulphonic acid resins of varying cross-linkages. Some of the results are given in the following table.

### TABLE II.1

<table>
<thead>
<tr>
<th>% DVB</th>
<th>EXCHANGE</th>
<th>$\Delta G^\circ$ (KJ per gm.eq. of resin)</th>
<th>$\Delta H^\circ$</th>
<th>$T\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.0</td>
<td>Ag$^+$ - H$^+$</td>
<td>6.527</td>
<td>6.276</td>
<td>-0.251</td>
</tr>
<tr>
<td>8.0</td>
<td>Ag$^+$ - H$^+$</td>
<td>4.477</td>
<td>4.602</td>
<td>0.125</td>
</tr>
<tr>
<td>4.5</td>
<td>Ag$^+$ - Na$^+$</td>
<td>2.259</td>
<td>0.000</td>
<td>-2.259</td>
</tr>
<tr>
<td>2.0</td>
<td>Ag$^+$ - H$^+$</td>
<td>1.631</td>
<td>0.000</td>
<td>-1.631</td>
</tr>
</tbody>
</table>
It is shown that the exchange selectivity is governed entirely by enthalpy change in 
Ag⁺ - H⁺ systems (16% and 8% DVB) and entropy change in Ag⁺ - Na⁺ system (4.5% DVB) 
and Ag⁺ - H⁺ system (2% DVB).

2.4 MODELS

The thermodynamic description of the ion exchange phenomenon requires no model. 
But the other theories of ion exchange start from some model. Few of such models are 
summerised here.

2.4.1 DONNAN MEMBRANE MODEL

Donnan's original treatment 27,28 applied to solutions separated by semipermeable 
membrane extended to resin-electrolyte systems by incorporating some of the assumptions29 
like

1. The swelling energy due to stretching of polymer network is a function only of its 
specific volume;
2. Chemical free energy term depends only on the nominal molality of the ions; 
and
3. The ions are incompressible.

An ion exchange reaction represented in equation 2.6 may be considered as Gibbs- 
Donnan membrane equilibrium and its thermodynamic equilibrium constant is given by

\[ 2.303 \, RT \log K_{A/B}^B = \pi (\nabla_A - \nabla_B) \]

where

- R is the gas constant.
- T is temperature in Kelvin.
- \( \pi \) is the osmotic type swelling pressure.

\( \nabla_A \) and \( \nabla_B \) are the partial molal volumes of A and B respectively in the resin phase.

On substituting experimentally determined selectivity coefficient \( \log K_{A/B}^B \) into the 
thermodynamic equilibrium constant \( \log K_{A}^{B^-} \) in equation 2.20, one gets after rearranging the 
terms.
\[
\log K_{c_{A}^{-}c_{B}^{+}} = \frac{\pi (\bar{V}_{A} - \bar{V}_{B})}{2.303 \, RT} + \log \frac{w_{RA}}{w_{RB}} - 2\log \frac{f_{\pm XA}}{f_{\pm XB}} \quad \ldots \, 2.21
\]

This simple picture is beset with many difficulties. It fails to explain some observed selectivities such as \( K_{\text{Ag}^{+}} \) and also it is difficult to evaluate experimentally the partial molal volumes of the ions in the resin phase. Boyd and Bunzl have determined volume changes which accompany ion exchange reactions employing Carlesberg dilatometer with a view to correlate the volume changes with the effect of ions on the short range order in water.*

The relative importance of the individual terms of Gibbs-Donnan equation 2.21 is investigated extensively by Glueckauf\(^{30}\) Boyd and other\(^{31-34}\), and Soldano and others\(^{35-37}\). In evaluating these terms several approximations are made, many of which are not based on firm thermodynamics.

From isopiestic swelling data on the pure resinates, Glueckauf\(^{30}\) estimated semiempirically applying Hamed's Rule\(^{38}\). Soldano and others\(^{35-37}\) have criticised some of the assumptions made by Glueckauf, and determined the same employing Gibbs-Duhem equation. This treatment agrees better with the experimental results than that of Glueckauf. However, some empirical fittings had to be employed. The work is confined to monoatomic and monovalent ions, and the empirical interaction coefficients are not related to fundamental structural properties.

Boyd and others\(^{31-34}\) have obtained experimentally \( K_{c_{A}^{-}c_{B}^{+}} \) values for alkali ions, tertramethyl ammonium ion and some anions as a function of cross linkage of strong ion exchangers. They have also evaluated the different terms of equation 2.21 individually. Here both the osmotic type pressure and resin activity coefficient ratio \( \left( \frac{w_{RA}}{w_{RB}} \right) \) were evaluated from the equivalent water contents of resins of different cross-linkages, measured as a function of water activity and resin composition. The partial molal volume differences between two exchanging ions \( A \) and \( B \) in the resin phase (\( \Delta \bar{V} \)) was determined by pyknometric equivalent volume measurements at varying resin compositions. The mean molal activity coefficient ratio term for the two ions \( \left( \frac{f_{\pm XA}}{f_{\pm XB}} \right) \) in mixed electrolytes in the external aqueous phase was obtained from the literature with proper corrections\(^{39}\).

* as reported in G.E. Boyd and K. Bunzl "Binding of Ions by Ion Exchangers - The Volume Change Criterion" (private communication).
The $K_{c}^{b-}$ values of alkali ions\textsuperscript{32} and halide ions\textsuperscript{33} thus evaluated agreed fairly well with the experimental ones in the case of low cross-linked exchangers. But the disagreement in case of the high cross-linked exchangers was attributed to chemical heterogenities in them.

The theoretical $K_{c}^{b-}$ of tetramethyl ammonium ion against Na\textsuperscript{+} agreed with the experimental one, where there is a reversal of selectivity with increase of cross linkage which is unusual for normal alkali ions. This is explained as due to the large increase in the configurational free energy ($\pi \Delta \overline{V} / 2.303 RT$) of the polymer molecular network when the large quaternary ammonium ion enters the exchanger.

Marinsky\textsuperscript{40} has re-examined the Gibbs-Donnan equation (2.21) as applied to ion exchange reactions. He adopted Fietelson’s\textsuperscript{41} procedure of calculating $w_{RA}^{f} / w_{RB}^{f}$, who applied Fuoss, Katchalsky and Lifson\textsuperscript{42-43} polyelectrolyte theory as modified by Kagawa and Gregor\textsuperscript{44}. Hydration parameters obtained via polyelectrolyte model appear to enhance quantitative estimate of $w_{RA}^{f} / w_{RB}^{f}$ and of swelling pressure effects as well.

Marinsky and co-workers\textsuperscript{45-48}, in a series of publications have extended this treatment to several tracer cation studies. Michael Goldsmith et al.\textsuperscript{49} determined the Donnan potentials of single ion exchanger beads with micro-electrodes.

Fessler and strobel’s\textsuperscript{50} modification of equation 2.21 to explain ion exchange selectivity in mixed solvent media will be referred to later.

Demirgian\textsuperscript{51} et al. have experimentally examined solvent and ion selectivity behaviour in mixed media, and have shown that the Gibbs-Donnan model is as useful for the prediction of ion exchange behaviour in mixed media as it is in aqueous systems.

The models ascribing the driving force for the ion selectivity to the osmotic type pressure of the polymer network of the resin matrix and the effective ionic sizes had partial success in predicting the relative selectivity order. But they failed to explain several experimental results, including the large influence of water-organic mixed solvents on the selectivity and the observed similar selectivity order in liquid ion exchangers and gel type resins.
2.4.2 MODELS UTILISING SOLVENT STRUCTURE

The inadequacies of the models based on osmotic pressure-volume as the origin of selectivity in the ion exchange process lead to statistical models utilising various types of solute-solute, solute-solvent and solvent-solvent interactions. Among the large number of contributors, Diamond and Whitney\textsuperscript{52-53}, Eisenman\textsuperscript{54}, Reichenberg\textsuperscript{55} and Steigman and Dobrow\textsuperscript{56} have laid emphasis on ion-solvent and ion-ion interactions. They describe these interactions in terms of thermodynamic quantities that are less ambiguous than the solvated ionic radii and solvation numbers\textsuperscript{29-30}. Though they differ in the details, certain aspects of the solvent structure and solute-solvent interactions are common.

### 2.4.2.1 INTERACTIONS AMONG IONS AND SOLVENTS

Ions are charged bodies, and an assembly of such charged bodies will undergo several types of interactions. The attractive forces of importance even in vacuum are (decreasing in magnitude) ion-ion, ion-dipole, ion-induced dipole, dipole-dipole, dipole-induced dipole, the dispersion forces and also the short range repulsive forces which are proportional to \( r^{-12} \). Magnitude of these interactions are changed by the dielectric constant (\( \varepsilon \)) of the medium. Thus the change of solvent may affect these interactions.

Classical description of ion interactions in dilute aqueous solution was culminated in the famous Debye-Hückel theory of strong electrolytes. According to this theory, the ion interactions are so far as they contribute to thermodynamic properties were determined by the “ionic atmosphere”, solvent merely acting as a dielectric continuum. Direct ion-water interactions and ion-ion pair formation was not recognised. The inadequacy of this theory except as a limiting case at infinite dilution is well known and requires no elaboration. All the present models recognise this deficiency of considering the solvent as dielectric continuum, but differ in their details in treating this aspect.

Ions in aqueous solutions are surrounded by water molecules. The charge on the ions will interact on the dipoles of water molecules. The magnitude of interaction depends on the charge, size and polarisability of the ions and dipole moment of the water molecules. In addition, water structure also contributes to overall energy of interactions. A more useful description of ions in water is given by Frank and Wen\textsuperscript{57}.

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Frank and Wen have described three distinct zones of water around an ion as a result of ion-water interactions. They are:

1. Water dipoles in the immediate region of an ion are highly oriented. They called these as immobilization (or stationary) region. The extent of this region is determined by the charge density of the central ion.

2. Structure of the water in the region next to the immobilized (or stationary) region is broken. This is because of the opposing effects of the ion-induced dipoles and the water dipoles surrounding the broken region. The broken region consists of comparatively free, and almost monomeric water molecules.

3. In the third region, water is undisturbed and has its normal structure.

This concept provides an insight into the nature of hydration, though qualitative in nature. The description is valid only for dilute solutions, because the interaction of one solute ion over another is not considered.

Ion-water interactions have been dealt with in great details in a number of monographs^{58-62}. The free energy of hydration, $\Delta G^o_{A(h)}$ of ion A is defined as follows.

$$
\Delta G^o_{A(h)} = \mu^o_{A(aq)} - \mu^o_{A(g)}
$$

... 2.22

where, $\mu^o_{A(aq)}$ and $\mu^o_{A(g)}$ are standard chemical potentials of A in aqueous solution and in gas phase, respectively.

As the single ion hydration free energy is not directly measurable, relative ion hydration free energies taking aqueous ion as the reference have been evaluated from the measured enthalpy and entropy of hydration of electrolytes^{63-65}. To illustrate the utility of such information $\Delta G^o_{A(h)}$ of alkali ions listed below are taken from Robinson and Stokes^{39}.

<table>
<thead>
<tr>
<th>ION</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta G^o_{A(h)}$</td>
<td>505.42</td>
<td>405.84</td>
<td>331.79</td>
<td>310.45</td>
<td>278.23</td>
</tr>
<tr>
<td>(KJ mol$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

26
\( \Delta G^{\circ}_{\text{A(h)}} \) can be considered as an indication of the ion-water interactions. More negative this quantity is, the more negative will be the hydration. As can be seen from the above list, \( \text{Li}^+ \) ion should exhibit the maximum hydration. This conclusion is in agreement with the intuitive reasoning that the smaller \( \text{Li}^+ \) ion with its small ionic radius should have the highest charge density, and hence, the maximum hydration interactions.

Solvents in general, and protonated solvents in particular, are far from being a medium of dielectric continuum. They have a definite structure, and this structure plays a significant role in determining the thermodynamic properties of the solutes in them. Water is, probably, the extreme example of such solvents\(^62\). Because of the omnipresence of aqueous solutions in general and its vital importance in many aspects of human endeavour, water and aqueous solutions have been extensively investigated. Our knowledge of these two have undergone several revisions during the past four decades. Yet we have only partial answers to several questions regarding them.

The anomalous behaviour of liquid water compared to other hydrides of VI group elements is well known. Many of these properties like high melting and boiling points, high dielectric constant, etc., are explained on the basis of hydrogen bonding between water molecules. Even after invoking a simple hydrogen bonding concept, its unusual heat capacity and especially its maximum density at 277 K cannot be explained. To explain such unique properties of liquid water several models have been proposed, starting from Bernal’s\(^66\) modified ice-like picture to the models proposed by Nemethy and Scheraga\(^67\). The degree of success that these statistical models have achieved has been amply discussed in several monographs\(^60-62\). A very brief description of one such model is presented here.

The most satisfactory of all the above models appears to be the one proposed by Nemethy and Scheraga\(^67\), based on Frank and Wen’s\(^57\) flickering cluster model. They have derived the thermodynamic parameters of liquid water by means of statistical thermodynamic treatment. The calculated free energy, enthalpy and entropy values of liquid water between 273K and 343K agreed well with experimental ones.

Liquid water consists of monomers and short lived clusters of hydrogen bonded molecules. Monomers participate in strong dipole-dipole and London interactions with their neighbours to form clusters. The clusters melt because of local energy fluctuations. Thus there is
an equilibrium between the highly hydrogen bonded clusters and non-hydrogen bonded monomers. At a given temperature, this equilibrium is determined by the requirement that the free energy of the system as a whole should be minimum. The dissolution of solute, whether it is an electrolyte or a nonelectrolyte, is going to interfere with this equilibrium concentration, thereby influence the thermodynamic properties of the solution significantly.

2.4.2.2 ELECTROSTATIC MODELS

According to Rice and coworkers\textsuperscript{68-70} as well as Katchalsky and others\textsuperscript{71-73}, some of the counter-ions are bound to the fixed sites and the binding is governed by the mass action type of relation. The mass action constant is different for the two counter-ions. The swelling equilibrium is assumed to be governed by balance between the mutual electrical repulsions of the fixed sites on the resin and configurational entropy of the network. The former is treated by using screen Coulomb potential and the latter by modification of Flory\textsuperscript{74} treatment of swelling of the uncharged cross-linked polymer.

Rice's treatment differs slightly from Katchalsky in computation of electrostatic interaction energy. Rice assumes the distribution of fixed ionic groups within the exchanger to be practically uniform. He considers the interactions between the nearest neighbours only, without differentiating whether they are on the same or on the adjacent chains. Katchalsky considers the interactions between all groups on one and the same chain disregarding interactions between those of neighbouring chains.

The model proposed by Rice correctly predicts that swelling increases with the decrease of cross-linkage and solution concentration as well as with increase of specific capacity of resin. The model is not applicable to low cross-linked gels, wherein, the distance between the adjacent chains becomes very great. In such a case the lattice model used for the computation of the electrostatic interactions becomes unrealistic. The behaviour of resins of this type is more adequately described by Katchalsky's model which cannot be applied to high cross-linked resins, because interactions between neighbouring chains are disregarded. But the success of either as a general model is rather limited.
2.4.2.3 DIAMOND’S MODEL

As discussed earlier Debye and Hückel’s limiting law was adequate in explaining thermodynamic properties of electrolyte solutions only at infinitely low concentrations. Various other assumptions like those of Bjerrum’s ion pair formation, Robinson and Harned’s localised hydrolysis etc. have been proposed from time to time to explain the behaviour of the solutions at finite concentrations. Diamond considers yet another type of interaction to explain the activity and osmotic pressure coefficients of large univalent ions like NR₄⁺, ClO₄⁻, ReO₄⁻, AuBr₄⁻, FeCl₄⁻, and SbCl₆⁻. If an ion small in size with high charge density is introduced into highly hydrogen bonded and structured water, it orients the water molecules around it. On the other hand, if the ion is large in size with low charge density, the bulky chargeless hydrocarbon part fails to orient the water dipoles around it. But at the same time, it forces its way by pushing the immediate neighbours a little closer. In the process the water around the big ion is more ordered, i.e., more hydrogen bonded, than in the bulk. This is known as tightening of water structure. Frank et al. and Nemethy and Scheraga have termed this interaction as hydrophobic bonding. But this ordering of neighbouring water molecules by a big ion is distinctly different from that by a small ion having a high charge density. The entry of a big hydrophobic ion into water thus results in decrease in entropy of water. Tightening of water structure should increase with the size of the tetra substituted ammonium ion. In agreement with this the experimentally observed order of activity and osmotic coefficients (viz., NMe₄⁺ < NEt₄⁺ < NPr₄⁺ < NBu₄⁺) increase with increasing size of the tetra substituted ammonium ions. Diamond further considers a situation where both cation and anion are big and hydrophobic, like NR₄⁺ and ClO₄⁻. In such cases, water structure forces the two big ions into a single cavity instead of providing two separate cavities. By doing so, water structure reduces the loss of entropy (as this process reduces the disturbance to the water structure). Diamond calls this as water-structure-enforced ion pair formation, which is different from Bjerrum type ion pair formation. This can occur only in highly structured solvents.

Diamond has proposed a model for ion exchange selectivity in general, taking resin phase as a concentrated electrolyte solution differing significantly from external dilute electrolyte solution in three aspects:
1. The functional group in the resin matrix is fixed;
2. The electrostatic forces are stronger in the resin phase; and
3. Water molecules in the resin phase have less co-operative structure, i.e., water molecules are on the average, hydrogen bonded to a smaller number of other water molecules in the resin than in the external dilute solution.

Diamond considers the ion-water and water-water interaction differences between the resin and the external aqueous phase (apart from other interactions) to play an important role in the ion exchange selectivity. A small and highly charged ion which has more negative free energy of hydration compared to big and lowly charged ion will prefer the external aqueous phase to satisfy its hydration better. The water structure in the resin phase is disturbed partly due to resin matrix. The benzyltrimethyl ammonium ion in a strong anion exchanger is large and hydrophobic. Hence a large and lowly charged anion like ClO$_4^-$ which requires less hydration prefers the resin phase. In the resin phase the residue water structure forces this ion and the resin cation into a single cavity, thus favouring the formation of an ion pair. Diamond’s model thus explains the higher selectivity of ClO$_4^-$ over I$^-$.

Myers and Boyd$^{32}$ found that the selectivity coefficients of alkali ions on a strong cation exchange resin approach unity as cross linkage decreases to 0.5% DVB. Those of halide ions$^{33}$ on strong anion exchange resins decrease with decreasing cross linkage, but to a lesser extent than in the case of alkali ions. Diamond explains the above by assuming that the Bjerrum type of ion pairing is mainly responsible in cation exchange selectivity for alkali ions and water-structure-enforced ion pairing in anion exchange selectivity for halide ions.

Selectivity of tetra substituted ammonium ions on strong cation exchange resins increases with their size$^{77-79}$. Diamond explains this on the basis of their capacities to form water-structure-enforced ion pairs. This capacity increases with the size of large hydrophobic ion in solution, which increases with its crystallographic size.

A weak base exchanger can act as an anion exchanger only in acidic solutions, when the resin ion will be NR$_3$H$^+$. The entire charge is concentrated on the proton and can form hydrogen bond with other highly basic ions. This resin is less hydrophobic than the one in strong base resin. Therefore, in weak base resin water-structure-enforced ion pairing cannot be as predominant as in the strong base one. Accordingly, a weak base exchanger should exhibit
somewhat enhanced selectivity for smaller anions and somewhat reduced affinity for big and hydrophobic ions. This was borne out by Jensen and Diamond by studying the distribution coefficients of traces of F\(^-\), Br\(^-\) and I\(^-\) as a function of lithium chloride molarity on strong and weak base anion exchangers. In dilute solution, the relative selectivity coefficients of F\(^-\), Br\(^-\) and I\(^-\) against Cl\(^-\) on strong base exchanger are 1 : 55 : 280 and on weak base exchanger, 1.0 : 3.7 : 10.0.

It is well known that selectivity of cation generally increases with their valency, on strong cation exchanger, because of the predominance of Bjerrum type ion pairing. But this need not to be the case with anion exchange system with strong anion exchangers wherein water-structure-enforced ion pairing is predominant. As polyvalent anions have more negative free energy of hydration compared to that of monovalent anions of similar size and structure, the system should try to attain minimum free energy by pushing the lowly charged ions into the resin phase and keeping polyvalent ions in the dilute external solution. To test this, Diamond et al. have studied the selectivity coefficients of \(\text{ReO}_4^{2-}\), \(\text{CrO}_4^{2-}\) and \(\text{WO}_4^{2-}\) (traces) against Cl\(^-\) as the macro anion and those of \(\text{Cr} (\text{CN})_6^{3-}\), \(\text{Co} (\text{CN})_6^{3-}\) and \(\text{Fe} (\text{CN})_6^{3-}\) (traces) against macro concentration of CN\(^-\) on strong anion exchangers. They were particular in selecting ions of similar size and structure but differing only in charge. They found that selectivity decreases with increase in charge of counter-ion. They, therefore, concluded that Bjerrum type ion pairing is not important in governing selectivities of these anions on strong base resins.

Diamond's concept of water-structure-enforced ion pairing, though qualitative in nature, explains many observed ion exchange selectivity orders.

### 2.4.2.4 STEIGMAN'S MODEL

Steigman and Dobrow have proposed a new hypothesis that the anion selectivities on ion exchange resins in water are strongly influenced by antagonistic or co-operative interactions of two water atmospheres, namely, one surrounding quaternary ammonium ion of the resin and the other surrounding the entering anion.

Three kinds of ion-water interactions are considered to characterise the two types of interactions of the water atomosphere:
1. Structure formers according to Gurney\(^83\): Ions with high charge density such as Li\(^+\) and F\(^-\) orient strongly the water dipole around them.

2. Structure breakers according to Gurney\(^83\): Ions with low charge density such as Cs\(^+\) and I\(^-\) destroy the hydrogen bonded water structure in their immediate vicinity.

3. Tightening of water structure according to Diamond\(^52\): Big organic ions like quaternary ammonium ions produce stable cages of hydrogen bonded water structures around their non-polarizing moieties\(^57\), as evidenced by high positive heat capacities and high positive viscosity coefficients (\(\beta\)-\(^84\)) of their aqueous solutions.

Ions belonging to both groups 1 and 3 are structure formers, though the way in which the water is organized is different. Those belonging to the second group are structure breakers. Electrolytes with ions which have different and mutually incompatible effects on the structure of water in which they are dissolved are known as antagonistic. If a structure breaking ion in an electrolyte provides more loose water for structure forming ion of opposite sign to organise, the interaction is of cooperative type, and such an electrolyte is cooperative one.

Taking the condition of water in concentrated quaternary ammonium salt solutions\(^85\)\(^-\)\(^89\) as guide for the condition of water in the resin phase, they stated that water in the immediate vicinity of fixed charge site in the resin is organised, eventhough the ratio of water molecules to sites is not large. They differ from Diamond's postulation that water in the resin phase is largely disorganised by the high concentration of resin ions, counter-ions and hydrocarbon matrix.

Their studies on salting in and salting out effects in mixtures of electrolytes in water gave experimental support for the antagonistic and cooperative effects of water atmospheres proposed by them.

They have extended this concept in deciding whether an ion in external solution is preferred or not by the resin cation in anion axchange resin. On a strong base anion exchange resin, F\(^-\) is less preferred while I\(^-\) and ClO\(_4\)^- are more preferred over Cl\(^-\) ion\(^53\). This is explained on the basis that F\(^-\) forms an antagonistic electrolyte while the other two form cooperative electrolyte with quaternary ammonium ions of the resin.
Reichenberg applied the concept of field strength defined by Eisenman in his model of ion exchange processes with glass membranes to ion exchange selectivity of organic exchangers. Among his several assumptions the following two require special attention:

1. Hydration of ions is recognised as of key importance and is considered in terms of energetics rather than in terms of hydrated ionic radii or volumes.

2. Electrostatic interactions are considered as primary cause of cross overs and affinity reversals.

Let us consider the transfer of counter-ion $B^-$ from the external solution into the vicinity of resin co-ion $R^+$. This will result in

1. The electrostatic interaction energies between $R^+$ and $B^-$, both being non-polarisable point charges, each at the centre of an incompressible sphere, is

$$\frac{e^2}{r_{R^+} + r_{B^-}}$$

where $e$ and $r$ are electronic charge and radius of ion respectively.

2. The free energy change required to remove from (or to rearrange around) the fixed grouping $R^+$ and the counter-ion $B^-$, as many water molecules as necessary to permit the contact (or close approach) of the fixed grouping $R^+$ and the counter-ion $B^-$, such free energies would be closely related (if not actually proportional) to the standard free energies of hydration of fixed group $R^+$ and counter-ion $B^-$. If these free energies are $\Delta G_{R^+}$ and $\Delta G_{B^-}$, the total free energy involved in this removal (or rearrangement) of water molecules is $\Delta G_{R^+} + \Delta G_{B^-}$

The total gain of free energy of the system when the ion is brought from the bulk of dilute aqueous solution into contact with the fixed grouping $R^+$ is therefore,

$$- \frac{e^2}{r_{R^+} + r_{B^-}} + \Delta G_{R^+} + \Delta G_{B^-}$$

Since this process is purely hypothetical, it cannot occur on its own. It should be accompanied by another process in which a counter-ion $A^-$ in contact with $R^+$ should be
removed from the resin into the bulk dilute solution. The gain in free energy by the system due
to this latter process is
defined as
\[
\frac{e^2}{r_{R^+} + r_{A^-}} - \Delta G_{R^+} - \Delta G_{A^-} \quad \ldots \ 2.24
\]

The overall gain in free energy of the system after the exchange (where the ion B' is
removed from the bulk of the solution, exchanged for ion A' at the fixed grouping and ion A'
transferred to the bulk of the solution) is, therefore,
\[
\Delta G_{B^- A'} = \left[ \frac{e^2}{r_{R^+} + r_{A^-}} - \frac{e^2}{r_{R^+} + r_{B^-}} \right] - (\Delta G_{A^-} - \Delta G_{B^-}) \quad \ldots \ 2.25
\]

But,
\[
\Delta G_{B^- A'} = -RT \ln K_{B^- A'} \quad \ldots \ 2.26
\]

Equations 2.25 and 2.26 enable predictions of more penetrating character to be made
than those we have discussed in connection with Gregor's theory. Consider the case where \(r_{R^+}\)
is large. Eisenman describes this as the case of fixed grouping of low field strength. Regardless
of the counter-ion involved \(\frac{e^2}{r_{R^+} + r_{A^-}} - \frac{e^2}{r_{R^+} + r_{B^-}}\) will be small and \(\Delta G_{B^- A'}\) will be
determined by the term \(- (\Delta G_{A^-} - \Delta G_{B^-})\) which as described above is related to the
difference of the standard free energies of hydration of the counter-ions. Consider the counter­
ions potassium (A\(^+\)) and sodium (B\(^+\)) \(\Delta G_{B^+ A^-}\) is numerically less than \(\Delta G_{A^+ B^-}\) and hence,
\(\Delta G_{B^- A'}\) will be negative. \(K_{B^- A'}\) will, therefore, be greater than unity, i.e., potassium will be
preferred to sodium. This is the normal selectivity order observed. Similarly in case of anion
exchange of Cl\(_{104}^-\) - Cl\(^-\), the difference in total electrostatic energy is only 43.51 KJ mol\(^{-1}\),
whereas, the difference of hydration free energies is 127.61 KJ mol\(^{-1}\). Hence, the latter plays a
predominant role in governing the selectivities. In agreement with this, Cl\(_{104}^-\) is preferred over
Cl\(^-\) on strong base anion exchangers. According to Eisenman, as field strength increases, the
differences in the electrostatic interaction terms become more and more significant. In the case
of weak cation exchangers (high field strength), the selectivity order of alkali ions is just reverse
of that observed on strong cation exchangers, showing the predominance of the electrostatic
interactions over that of the hydration energies. In case of anions Reichenberg\(^{55}\) has studied the
exchange of Cl\(^-\), Br\(^-\), I\(^-\) and Cl\(_{104}^-\) on tribasic sulphate of lead and found a reversal of selectivity

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order of Cl\(^-\), Br\(^-\) and I\(^-\) compared to that on strong base exchangers, indicating the significance of the electrostatic interaction. Higher selectivity of ClO\(_4\)^- is still attributed partly to the field strength not becoming significantly high, and partly to the other interactions governing selectivity\(^{55}\).

2.5 ION EXCHANGE SELECTIVITY IN MIXED SOLVENT MEDIA

The above discussion lays stress on the significance of solvent properties like dielectric constant, polarity, presence of hydrogen-bond, solvation energies of the ion, etc. in determining the selectivity of an ion on a given resin. Therefore, right from its inception, the scientists have given attention towards the improvement of resin characteristics in order to improve their selectivity and separability. Dorfner has presented the characteristics of the commercially available resins\(^{90}\). Thus, by controlling the solvent properties, the efficiency of separation can be increased\(^{91-92}\). Mixtures of water and various organic liquids in solvent media were exploited to achieve excellent analytical separation of closely related ions\(^{92-93}\). The majority of the publications are concerned more with achieving separation than with answering origin of separation. Even among those which have reported, the thermodynamic study in mixed solvent media, cation exchange investigations out number the anion exchange investigations.

Even in case of water, the most investigated solvent, our understanding of ion exchange phenomenon is yet incomplete. In mixed solvents, only a beginning has been made. A rigorous theoretical treatment of ion exchange equilibria in mixed solvents is difficult on account of two reasons:

1. The available data on ion exchange selectivity in well characterised system is limited.
2. The exact physico-chemical nature of the mixed solvents is still not well defined. In this connection a few qualitative observations are made here.

There is a linear relationship between selectivity coefficient and the reciprocal of solvent dielectric constant\(^{91}\). Another remark is concerned with solvent sorption. Ion exchange resins are osmotic system, wherein cross-linked matrix which restricts the fixed ions to the resin phase, functions analogous to the membrane in a refined Donnan system. This means that it is subjected to certain limitations, osmosis will occur resulting in resin swelling. Where mixed solvent media
are used, the possibility of preferential osmosis arises resulting in differential solvent composition across the resin membrane. This effect increases with decrease in dielectric constant. In other words, when the mixed solvent media are made of water and organic liquids like alcohol, dioxane, DMF, etc, resin phase solvent may become water rich in comparison. This preferential water sorption is more prevalent in cation exchanges than in anion exchanges. In explaining the difference in behaviour in cation and anion resins in the same mixed solvents, this factor should be considered.

Ghodstinat et al. studied cation exchange in DMF-water mixture. They showed that in general the logarithm of exchange coefficient vary with the reciprocal of dielectric constant, as would be predicted for Coulombic interactions. Their results agree with conclusions of other investigations that the dielectric constant of the medium is the most significant factor in solvent effects. Other factors including ionic solvation do play a significant role. Their results appear also to be reflected by changes in solvent composition in the resin and solution phases, and by the resin swelling effects.

Mody and Thomas and Vernon have reviewed the inorganic ion exchangers in organic and aqueous-organic solvents. Gupta correlated the thermodynamic equilibrium constants in nonaqueous and mixed solvent systems with the corresponding equilibrium constants in aqueous systems. The free energies of transfer of resinates from water to mixed solvent have been formulated in terms of free energies of swelling. Application of this theory to the data obtained for Li⁺ - H⁺, Na⁺ - H⁺ on Amberlite IR-120 and for Na⁺ - H⁺ on Dowex 50W in methanol-water mixture have been discussed. From selectivity data of Li⁺ - Na⁺ in methanol water on Dowex 50W Schwarz arrived at standard free energy, enthalpy and entropy changes, and concluded that the increased selectivity in methanol compared to that in water was due to sodium-sulfonate interaction stabilization by the release of methanol molecules from the solution sphere of Na⁺.

Starobinets et al. studied the effect of the nature of solvation on the selectivity of anion exchange in mixed aqua-organic solvent media, viz., Water-DMF and water-methanol. In methanolic solutions of low methanol concentrations, the selectivity of anion exchange increased in the order Cl⁻ < Br⁻ < NO₃⁻ < I⁻ < CNS⁻. In DMF-Water solutions at higher mole
fractions of the organic component ($>0.6$) the order was $F^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$. The reverse order of selectivity in DMF-Water system was attributed to weak solvation of anions in the aprotic amide.

In their further studies Starobinets et al. have shown that affinity of halide and thiocyanate ions to high alkali anionites in aqueous solution increases in the series $F^- < Cl^- < Br^- < I^- < CNS^-$. During the same exchange processes with strong exchanger Dowex-1, in DMF-water mixture the exchange constant of the halide with nitrate increases in the reverse series as $CNS^- < I^- < Br^- < Cl^- < F^-$ due to dipole-ion solvation of both CNS$^-$ and I$^-$. Barbier and Rossett studied the equilibrium and kinetics of exchanges in aqua-organic solvent system on Dowex 50W and macroporous exchanger Amberlyst-15 for water-dioxane and water-propanol. Selectivity coefficients for the exchange of several alkylammonium ions with $H^+$ or $Li^+$ on sulfonic acid resin were shown to be a function of solvent composition in water-methanol system$^{101}$. The exchange of alkyl anilium ions on a sulfonic acid exchanger have been studied in this solvent medium$^{102}$, and it is observed that ion exchange constants increased with increase in methanol content. Separation of several organic bases on a cation exchanger in mixed solvent systems has lead to a novel method of separations$^{103}$. Alkali metal ion exchange in ethanol-water and dioxane-water, and barium ion exchange in acetic acid-water solvents have been investigated$^{104}$. The authors explain the changes in selectivity coefficients with solvent on the basis of dielectric constant. However, changes in the selectivity order at low water concentrations are accounted for on electrostatic grounds only, if the ion solvation changes in an appropriate manner. Cation exchange in DMSO has been the subject of several papers, and the exchange distribution suggest that DMSO-Water mixtures will be promising media for cation separations$^{94,105,107}$. Ogawa and Tsuji$^{108}$ are first to study exchange of $Cl^-, Br^-, I^- vs NO_3^-$ on strong base exchangers in water-methanol, water-ethanol and water-acetone media. They observed an increase in selectivity for $Cl^-$ and $Br^-$, but decrease in selectivity for $I^-$ with increase in organic solvent content. Davydov$^{109}$ has derived relation for the ratio of activity coefficients of counterions in the resin phase from the observed change in the selectivity coefficients in mixed solvents.
Krishnan and Ramanathan\textsuperscript{110} studied the selectivities of CNS\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−} and OH\textsuperscript{−} against Cl\textsuperscript{−} on strong base exchangers of varying cross-linkages in aqueous and mixed solvent media. There was a decrease in selectivity in all the above three systems with the increase in organic solvent content of the solution phase. The results were explained on the basis that the predominance of water-structure-enforced ion pair formation in aqueous medium changes over to Bjerrum type in mixed solvent media.

Bhatnagar et al.\textsuperscript{111} have investigated the exchange of halides against OH\textsuperscript{−} and attributed the observed decrease in selectivity of halides to resin matrix contraction. It may be pointed out that there is a disagreement in the data for Cl\textsuperscript{−} - OH\textsuperscript{−} exchange reported by the two teams\textsuperscript{110-111}.

Phipps\textsuperscript{107} observed the same selectivity order of anions against NO\textsubscript{3}\textsuperscript{−} (viz., Br\textsuperscript{−} > Cl\textsuperscript{−} > I\textsuperscript{−} > NO\textsubscript{3}\textsuperscript{−} > CNS\textsuperscript{−} > ClO\textsubscript{4}\textsuperscript{−}) in DMSO as well as in liquid ammonia. According to him, Reichenberg treatment\textsuperscript{55} will be better suited to explain the observed anion exchange selectivity order. Sherrill\textsuperscript{112} et al. reported an exchange study of Cs\textsuperscript{+} and R\textsubscript{4}N\textsuperscript{+} on strong base exchangers in methanol-water, propan-2-ol-water and showed that the measured log \( K_c \) correlated with the reciprocal of the dielectric constant.

Selectivity in mixed solvents have been studied by number of investigators\textsuperscript{113-122} from a mechanistic point of view. Cations were absorbed more strongly with respect to the hydrogen ions, as the proportion of organic solvent (eg., methanol, ethanol, acetone) increased. Smites\textsuperscript{115} et al. in a careful study of Rb\textsuperscript{+}, Mg\textsuperscript{2+}, H\textsuperscript{+} in Water-DMSO, related the exchange equilibria to the Walden product, and thus, to hydration.

Though pellicular and macroporous resins have been used, yet the data available is quite insignificant. It seems that their attractive mechanical properties and relatively fast reactions have overshadowed the potential disadvantage of specific lower selectivity\textsuperscript{123}. In one of the reports\textsuperscript{124}, a comparison of distribution and exchange rates in macroporous resins with those of gel type deserve special reference.

Bhat\textsuperscript{125} has reported exchange studies of I\textsuperscript{−}, CNS\textsuperscript{−}, ClO\textsubscript{4}\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} against Cl\textsuperscript{−} in water-methanol media and described the results in terms of Diamond’s model. Diamond and Jensen\textsuperscript{126} have investigated the exchange equilibria of F\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−} and ReO\textsubscript{4}\textsuperscript{−} on Dowex 1-X4
and Dowex 3-X4 in water-dioxane. They have adopted the tracer method using LiCl as the macroelectrolyte (0.01-0.1M). The partial replacement of water by dioxane makes the solvent poorer and poorer solvating agent for anions. This mixed external solution becomes poorer solvating agent, and hence the preference of the smaller ions to the external solution medium should decrease. Thus the ion most in need of solvation decreasingly prefers the external solution. Therefore, the separation factor should get smaller and smaller. This was confirmed experimentally. However, this observation was complicated by the fact that the resin phase absorbs water preferentially. In other words, relative amounts of water in the resin phase is higher than the corresponding external solution phase. This results in the increase of non-exchange or resin invasion of electrolyte. The large decrease in the dielectric constant introduces a competition between Bjerrum type ion pairing and water-structure-enforced ion pairing. This fact should be taken note of. Within this constraint it has been shown that the Diamond-Reichenberg model adequately explains the observations.

Narke et al.\textsuperscript{27} carried out a systematic study of the exchange behaviour of simple monovalent ions such as ClO\textsubscript{4}\textsuperscript{-}, I\textsuperscript{-} and CNS\textsuperscript{-} against Cl\textsuperscript{-} in water-dioxane solvent mixtures on strong base anion exchangers. The results were discussed in terms of models proposed by Diamond and Reichenberg. They showed that the experimental results agree qualitatively with the above models, but fail to provide quantitative agreement.

Bhatnagar and Jain\textsuperscript{128} have studied the anion exchange equilibrium distribution of 15 metal ions in aqueous nitrite and aqueous-methanol- nitrite media on Dowex - 21K (nitrate form). Their study in aqueous nitrite media indicated the following selectivity sequence of common transition and post transition ions

\begin{align*}
\text{Hg (II)} & > \text{Cd (II)} > \text{Ag (I)} > \text{Pb (II)} > \text{Cu (II)} > \text{Zn (II)} > \text{Co (II)} > \text{Ni (II)}
\end{align*}

However, Hg(II), Cd (II) and Ag (I) have high K\textsubscript{d} values and have suggested the separation possibilities for many metal ions by ion exclusion technique.

Bhatnagar and Mishra\textsuperscript{129} have studied the exchange selectivity of halate ions on the nitrate form of strong base exchanger Amberlite IRA-400. They have reported the increase in selectivity coefficient with the increase in acetone content for ClO\textsubscript{4}\textsuperscript{-} and BrO\textsubscript{3}\textsuperscript{-}, but decrease in selectivity coefficient for IO\textsubscript{3}\textsuperscript{-}.
Taylor\textsuperscript{130} et al. have studied the exchange of simple monovalent cations Na\textsuperscript{+} - H\textsuperscript{+} and Na\textsuperscript{+} - Li\textsuperscript{+} with Dowex 50-X8 and one anion exchange I\textsuperscript{−} - Cl\textsuperscript{−} with Dowex 1-X8 in water-methanol mixtures. They have used Gupta's equation and showed that the selectivity trends in cation exchange systems were mainly due to the salt and medium effect activity coefficient ratios in external solution phase. But by contrast it was the resin phase activity coefficients which contributed significantly to the selectivity trend in I\textsuperscript{−} - Cl\textsuperscript{−} exchange.

Deoki Nandan\textsuperscript{131} et al. have recently investigated the exchange behaviours of some simple monovalent anions in water and methanol. The thermodynamic equilibrium constants in water ($K_w$) and in methanol ($K_g$) were found to follow the ionic selectivity sequence $I^− > NO_3^− > Br^− > Cl^−$, $K_g$ being generally lower than $K_w$.

Clifford Dennis\textsuperscript{132} et al. have examined and quantified influence of ion solvation parameters in the affinity of monovalent anions for strong base anion resins.

Katale\textsuperscript{135}, Vyashamudri\textsuperscript{133}, Math\textsuperscript{137}, Bhavikatti\textsuperscript{134}, Hoskeri\textsuperscript{136}, Sangolli\textsuperscript{138} and Patil\textsuperscript{139} have studied anion exchange behaviour in Water-DMF, water-formamide, water-propan-2-ol, water-ethylene glycol, water-2-ethoxyethanol, water-acetone and water-2-methoxyethanol, respectively. Comparison of dielectric constants and magnitudes of selectivity coefficients prompted them to believe that dielectric constant is not the sole factor governing selectivity. It was, in fact, the protic or aprotic nature of the solvent that determines the selectivity behaviour.

Recently, Bhatnagar et al. have carried out equilibrium studies with BrO\textsubscript{3}\textsuperscript{−}\textsuperscript{140} and ClO\textsubscript{3}\textsuperscript{−}\textsuperscript{141} ions in mixed solvent medium, viz., aq.- methanol, aq.- ethanol and aq.- isopropanol using strong base anion exchangers in nitrate form, and they have drawn conclusions regarding the variation of corrected selectivity coefficient with solvent compositions. Distribution studies of halides and thiocynate ions in aq.- acetone media\textsuperscript{142} were reported by the same authors. Changes in the affinity sequence with percentage of acetone in solution were derived from distribution data.

It is evident from this brief review of this literature that the data on ion exchange available till today is rather inadequate to understand ion exchange phenomenon on synthetic resins. Additional data of simple anion exchange behaviours in mixed solvents with wide range of solvent properties would greatly add to the understanding of this process.
There is hardly any data available concerning ion exchange selectivity in Water-Acetonitrile. Hence a systematic study of simple monovalent anions such as $\text{ClO}_4^-$, $\text{CNS}^-$, and $\text{NO}_3^-$ against $\text{Cl}^-$ on strong base exchangers like Dowex 1-X8, Dowex 1-X2, Tulsion A-27 (macroreticular) and also $\text{ClO}_4^-$ and $\text{NO}_3^-$ against $\text{Cl}^-$ on weak base exchangers like Tulsion A-2X (gel) and Amberlyst A-21 (macroreticular) with wide range of loadings ($N_{\text{lb}}$ 0-1) in Water-Acetonitrile media of varying compositions was carried out.
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