CHAPTER II

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

Although the possibility of desalting brackish water was suggested in the Holy Bible, by ancient Greeks and by Sir Francis Bacon, 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 convenience.

Ion exchange has proved its utility in recent years in the laboratory as well as in industry. As a result, chemists and engineers are being faced with the task of investigating its applicability in their own particular field of work. Separation of rare elements from a host of other impurities is 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 application. Recent development in the field of ion exchange membranes stretch its application into physico-chemical and biophysical 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 demineralisation of water.

2.1 Ionexchangers and ion exchange selectivity

Ion exchange has become a general operating technique today. Ion exchange was investigated first with inorganic materials, these materials found some industrial use, but were almost completely displaced by synthetic ion exchange resins. The demand for ion exchange materials that would satisfy the most diverse requirements led to the development of new products, which must be considered as separate ion exchanger types according to their special properties.

Among the available types, synthetic ion exchange resins have the greatest importance. But inorganic ion exchangers should not be neglected, since these have once again aroused interest because of their mechanical, thermal and chemical properties and because, in light of their mineralogical parallels, they offer information about numerous processes in soil science. The cellulose ion exchangers
represent a separate type with their own characteristics
related most closely to another group, i.e., the dextran ion
exchangers. Both types have been rapidly accepted in ion
exchange chromatography where they have become indispensable
for analytical as well as preparative work. In addition, ion
exchangers based on carbon have been produced and, together
with a number of other materials with ion exchanging
properties, have been investigated for their applicability.
Liquid ion exchangers as another type, probably are important
primarily because of the technological possibilities they
offer.

2.1.1 Inorganic Ionexchangers

Historically, it was inorganic ion exchangers that
were first studied for the practical applicability of ion
exchange\(^1\). 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\(^2,3\). These minerals have relatively open three
dimensional structures with channels and interconnecting
cavities. Their lattices are made up of SiO\(_4\) and AlO\(_4\)
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 alumino silicates can also act as anion exchangers. The mineral anion exchanger which have been used for practical purposes are apatite \([\text{Ca}_5(\text{PO}_4)_3]\text{F}\) and hydroxyl apatite \([\text{Ca}_5(\text{PO}_4)_3]\text{OH}\).

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-polymer, a phenol formaldehyde polymer or the like. Cation exchange functional groups include: sulfonic acid (\(-\text{SO}_3\text{H}\)), carboxylic acid (\(-\text{COOH}\)), phenolic (\(-\text{OH}\)), sulphhydryl (\(-\text{SH}\)), arsonic (\(-\text{ASO}_3\text{H}_2\)), phosphoric (\(-\text{PO}_3\text{H}_2\)) and phosphorous (\(-\text{PO}_2\text{H}_2\)). The anion exchange resins contain functional groups like primary, secondary or tertiary amino groups (\(-\text{NH}_2, =\text{NH}, =\text{N}\)) quaternary ammonium compounds (\(\equiv\text{N}^+\)) a pyridine group \(\left(\begin{array}{c} \text{N} \\ \end{array}\right)\), quaternary pyridine bases \(\left(\begin{array}{c} \text{N} \\ \end{array}\right)^{\equiv}\), quaternary phosphonium (\(\equiv\text{P}^+\)) and sulphonium groups (\(\equiv\text{S}^+\)). For example, for a copolymeric styrene divinylbenzene sulfonic acid cation exchangers the quasi-constitutional formula
would be

\[-\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \]
\[\text{SO}_3\text{H} \quad \text{CH} - \text{CH}_2 - \quad \text{SO}_3\text{H}\]

and for a styrene divinylbenzene quaternary ammonium anion exchanger the quasiconstitutional formula would be

\[-\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \]
\[\text{CH}_2\text{N}(\text{CH}_3)_3\text{OH} \quad \text{CH}_2\text{N}(\text{CH}_3)_3\text{OH}\]

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. Gel Type Ionexchange Resins

During polymerisation of styrene and DVB which yields products to be used as the skeleton of an ion exchanger, the network formed is obtained as a gel. The term gel here refers to the fact that, macroscopically, a homogeneous network has been synthesized that is elastic in nature and contains solvent from the manufacturing process. The properties of such copolymers or matrices can be varied by changing the ratios of the amounts of the individual monomers.
used during the synthesis. It is already obvious from this brief description that the form "gel type resins" refers to polymer matrices that do not contain pores. As a result it is important to pay close attention to the influence of the amount of crosslinking agent used during polymerisation, since this factor influences markedly the very important property of swelling. A gel ion exchanger whose matrix contains a low proportion of DVB swells strongly in aqueous solutions; this opens the structure widely, permitting large ions to diffuse easily into the exchanger, and at a rapid rate. Ion exchangers having matrices with higher proportion of crosslinking agent (> 10% DVB) swell to a substantially lower degree in aqueous solutions.

2.1.4. Macroreticular Ion exchange Resins

Macroreticular ion exchangers are types in which the solvent is used during production from the monomers, so that a porous matrix structure is formed in the course of polymerization. These macroporous structures, which have large internal surfaces, can be sulfonated very easily and completely and are much more resistant than gel type resins to osmotic shock. Furthermore, they are extremely uniform in external shape and, in contrast to the gel types, opaque.
Pore sizes of several hundred nanometers in diameter and surface areas of up to $100\,\text{m}^2/\text{g}$ and more can be obtained. To prevent collapse of the structure, a larger portion of crosslinking agent needs to be used. However, in connection with the large internal porosity, this leads to a number of advantages such as smaller swelling difference in polar and non-polar solvents, a smaller loss of volume during drying, and higher oxidation resistance. Because of their higher porosity, larger molecules can also penetrate the interior. The economy of macroporous ion exchangers is somewhat limited by their lower capacities and higher regeneration costs, but, their suitability for catalytic purposes is unique. Macroporous ion exchangers are fully developed products, which are in frequent use because of their advantages.

2.1.5. Liquid Ion Exchangers

In addition to ion exchange resins in solid form, various high molecular weight (in the range of 250 to 500) basic and acid organic liquids can be used as liquid ion exchangers. They are unifunctional. The liquid cation exchangers include alkyl phosphonic and sulphonic acids and the liquid anion exchangers are represented by various primary, secondary, tertiary and quaternary ammonium amines.
The behaviour of the liquid ion exchangers are similar to the solids except that in the case of the former the organic phase is anhydrous whereas in the latter case it is highly hydrated. The weakly basic liquid exchangers have been found to have a wider scope of application than the weakly acidic materials. Some of the major applications of liquid ion exchangers are in uranium and aluminium hydrometallurgy, thorium and rare earth recovery etc.

2.1.6 Cellulose Exchangers

In addition to these synthetic resins many different types of ion exchange celluloses\textsuperscript{11} are now available. The degree of structure order may vary from amorphous to highly crystalline type fibres. Aggregates of glucosidic chains are held together by inter chain bonding which provides dimensional stability to the 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\textsuperscript{12} 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 structures.

2.1.7. Ion exchange selectivity

As already stated earlier, the ion exchangers have three dimensional network of hydrocarbon matrix (hydrophobic) carrying ionogenic groups (relatively hydrophilic) such as -SO_3H^+, -COOH, -N(CH_3)_3Cl^- etc. One ion of the ionogenic group remains fixed to the resin matrix whereas the other (called the counter ion) being free to move within the exchanger, exchanges with ion of the same charge present in the solution phase in contact with the resin. The exchange reactions may be represented as follows.

Cation exchange reaction

\[ \text{RN}_a + \text{KCl}_{aq} \leftrightarrow \text{RK} + \text{NaCl}_{aq} \quad 2.1 \]

Anion exchange reaction

\[ \text{RCl} + \text{KNO}_3_{aq} \leftrightarrow \text{RNO}_3^- + \text{KCl}_{aq} \quad 2.2 \]

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 exchange reactions are generally reversible. At equilibrium the ratio of the concentrations of the two counter ions in the external solution phase will be different from that in the resin phase. In other words the resin prefers one counter ion over the other. This is called selectivity. It is influenced by size and charge of counter ion, presence of other ions in the external solution, nature of the solvent, degree of cross linkage, nature of the resin ion, total ionic strength of the solution etc.

There are several reviews\textsuperscript{13-20} and monographs\textsuperscript{21,22,23} dealing with the varied aspects of ion exchange phenomenon. The theoretical developments that have taken place during last three decades are briefly reviewed below.

2.2 Thermodynamic Treatment

A number of attempts made to explain and predict ion exchange equilibria can be broadly classified into two
categories. The first refers to the rigorous thermodynamic treatment that requires no models and no assumptions with respect to the mechanism of exchange process. The second consists of the introduction of models with particular properties resembling those of the ion exchanger to permit the derivation of equations which reflect the action of various physical forces in the exchange process. These two categories are complimentary to each other.

2.2.1. Evaluation of Thermodynamic Equilibrium Constant

For the sake of simplicity an ion exchange reaction involving only uni-univalent ions is considered here. It is represented as follows

\[ \text{RA} + \text{B}^-_{\text{aq}} \rightleftharpoons \text{RB} + \text{A}^-_{\text{aq}} \]  \hspace{1cm} 2.3

Then the equilibrium constant \( K^B_A \) for the reaction is given by

\[ K^B_A = \frac{[\text{RB}] [\text{A}^-]_{\text{aq}}}{[\text{RA}] [\text{B}^-]_{\text{aq}}} \]  \hspace{1cm} 2.4

Where [ ] refers the active mass of the respective species. In equation (2.4) if the active masses are replaced by the corresponding equivalent fractions of species then the
equilibrium constant $K_{A}^B$ becomes the selectivity coefficient $K_{A}^B$. The value of $K_{A}^B$ is a dimensionless number when $A$ and $B$ are of equal valency.

Since single ion activities are indeterminate, the ion exchange process is usually represented in terms of $R_A$, $R_B$, $X_A$, and $X_B$. Thus

$$R_A + X_B \underset{\text{aq}}{\rightleftharpoons} R_B + X_A \underset{\text{aq}}{\rightleftharpoons}$$

At equilibrium, the resin phase is considered as a uniform solid solution of $R_A$ and $R_B$ which are $A$ and $B$ forms of the resin. $X_A$ and $X_B$ are the electrolytes present in the external solution.

The equilibrium constant $K_{A}^B$ is given by,

$$K_{A}^B = \frac{\bar{N}_{RB}}{\bar{N}_{RA}} \frac{M_{XA}}{M_{XB}} \frac{w^f_{RB}}{w^f_{RA}} \frac{w^{f2}_{+XA}}{w^{f2}_{+XB}}$$  \hspace{1cm} (2.6)

Where $\bar{N}_{RB}$ and $\bar{N}_{RA}$ are the equivalent fractions of the $R_B$ and $R_A$ forms of the resin respectively; $M_{XA}$ and $M_{XB}$ represent the molality of $X_A$ and $X_B$ in the external solution phase, $w^f_{RA}$ and $w^f_{RB}$ refer to the activity coefficients of $R_A$ and $R_B$ forms of the resin and $w^{f2}_{+XA}$ and $w^{f2}_{+XB}$ are the mean molal activity coefficients of $X_A$ and $X_B$ respectively.
To evaluate $K_{a_A}^{B^-}$ the corresponding $K_{c_A}^{B^-}$ values are determined experimentally at constant temperature and constant ionic strength of external solution, varying the ratio $\frac{M_{XA}}{M_{XB}}$ over a wide range, so that $\bar{N}_{RB}$ values vary as widely as possible from 0 to 1. The corrected selectivity coefficients $K_{a_A}^{B^-}$ at each resin composition are then calculated using the equation (2.7)

$$
K_{a_A}^{B^-} = K_{c_A}^{B^-} \left( \frac{w_{f+}^{XA}}{w_{f+}^{XB}} \right)^2
$$

The values of $K_{a_A}^{B^-}$ are plotted against $\bar{N}_{RB} = 0$ to $\bar{N}_{RB} = 1$.

For all practical purposes, the standard states for the resin components are assumed as those when the pure resinates are equilibrated with such a dilute solution of an electrolyte, that it does not affect the state of the resin phase but affects only that of water. Then applying the Gibbs-Duhem equation, $\log K_{a_A}^{B^-}$ of the exchange reaction is calculated using equation 2.8

$$
\log K_{a_A}^{B^-} = \int_{\bar{N}_{RB}=0}^{\bar{N}_{RB}=1} \log K_{a_A}^{B^-} \ d\bar{N}_{RB}
$$
Using the above treatment, Bonner and his co-workers have reported $K_{A}^{B}$ for a large number of ions on sulphonic acid ion exchangers of different crosslinkages.

Hogfeldt, Gaines and Thomas as well as Davidson and Argersinger have modified the above treatment taking into consideration the water in the resin phase as an additional component as discussed by Holm. These treatments differ principally in the selection of standard states. The one given by Gaines and Thomas is thermodynamically more rigorous. In addition, it enables the determination of activity coefficients in the resin phase. These are independent of the concentration of the counter ions in the external solution.

According to Gaines and Thomas,

i) The solid exchanger has a fixed number of sites per unit mass. It is capable of absorbing solvent but not co-ions from the external solution. (The case in which it absorbs co-ions from the external solution is dealt with separately by them).

ii) The ion exchange process is heterogeneous reaction involving electrolytes $X_A$ and $X_B$ dissolved in a solvent.
and the resinates RA and RB in the solid solution.

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

iv) The system is a closed one and the vapour phase is also a part of the system at equilibrium. Then the thermodynamic equilibrium constant $K_{aA}^{B-}$ for the ion exchange reaction (2.5) is given by

$$
\ln K_{aA}^{B-} = \int_{0}^{1} \ln K_{aA}^{B-} d\bar{N}_{RB} - \int n_w d \ln a_w^{\bar{N}_{RA}=1} \\
- \int n_w d \ln a_w^{\bar{N}_{RB}=1} + \int a_w^{\bar{N}_{RA}=1} \ldots (2.9)
$$

Where $n_w$ is the number of moles of water associated with one equivalent of exchanger and $a_w$ is the activity of water.

Gupta has extended this treatment to ion exchange in mixed solvent media, by adding correction term for the medium effect, according to which $\ln K_{aA}^{B-}$ is given by equation (2.10).
In $K_B$ solvent.

This $K_{B}^A$ is with respect to pure water as the solvent. $K_{B}^A$ is the selectivity coefficient after making the activity coefficient corrections in the external solution for the particular solvent composition. $a_w(N_{H_2O})(\tilde{N}_{RB}=1)$ refers to water activity in m molal solution of XB containing $N_{H_2O}$ mole fraction of water ($m$ is the ionic strength). Terms like $a_w^*(N_{H_2O})(\tilde{N}_{RB}=1)$ represent water activities in an infinitely dilute solution of XB in the mixed solvent containing $N_{H_2O}$ (mole fraction) of water. It is assumed that,
i) The standard state for the electrolyte is that of infinite dilution in water.

ii) The standard state for the resin is that of the monoionic form of the exchanger in equilibrium with water and

iii) 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 (2.10), the same was rewritten combining integrals 2.6 as follows.

\[
\ln K_{B}^{B} = \int_{0}^{1} \ln K_{A}^{B} \, d\bar{N}_{RB} + \ln Q \quad \ldots \quad (2.11)
\]

Further approximating that ionic activity coefficients are a function of total ionic strength only and are independent of the ionic composition of the solution, the activity coefficient terms in \( \ln K_{A}^{B} \) in equation (2.11) are taken outside the integral when ionic strength is \( \leq 0.1 \).

Then,

\[
\ln K_{A}^{B} = \int_{0}^{1} \ln K_{A}^{B} \, d\bar{N}_{RB} + 2 \ln \frac{s_{B}^{+} XA}{s_{B}^{+} XB} + 2 \ln \frac{m_{B}^{f}}{m_{B}} + \ln Q
\]
Where $s^{f}$ is the mean molal activity coefficient of $X_A$ in mixed solvent, referred to the standard state of infinite dilution in mixed solvent. $m^i$ term corrects this standard state of infinite dilution in water. $K_{B}^{A}$ is the selectivity coefficient in terms of concentrations at a given solvent composition. Where $Q$ includes solvent activity terms and activity coefficient correction for the differences in the standard states for the resin and external solution phase. Gupta is of the opinion that 2nd, 3rd and 4th terms in equation (2.10) do not contribute significantly compared to the other three terms. Ghate et al., determined $K_{B}^{A}$ for $Li^{+}$-$H^{+}$, $Na^{+}$-$H^{+}$ and $K^{+}$-$H^{+}$ equilibria in methanol-water medium, using equation (2.12), and have shown the importance of solvent activity terms.

In equation (2.12), 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 non-aqueous and mixed solvent in a thermodynamically rigorous manner. Using the concept of standard free energy of transfer...
of ions and resinates from water to mixed solvent (or nonaqueous solvents), the thermodynamic equilibrium constants $K^B_A$ for exchange equilibria in mixed solvents have been correlated with the equilibrium constants in aqueous systems.

2.2.2 Standard free energy change of an ionexchange reaction in mixed solvent medium

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

$$\text{RA}(s) + B^-(s) \rightleftharpoons \text{RB}(s) + A^-(s) \quad \ldots \ldots \ldots \ldots \ldots (2.13)$$

Where $\text{RA}$ and $\text{RB}$ are $\text{A}$ and $\text{B}$ forms of the ion exchange resin respectively and $A^-(s)$ and $B^-(s)$ are counter ions. The equilibrium constant for the above ion exchange reaction is given by

$$\ln K^B_A = - \frac{\Delta G^B_A}{RT}$$

$$= \frac{1}{RT} \left[ (\Delta G^B_{\text{RB}(s)} - \Delta G^B_{\text{RA}(s)}) + (\Delta G^A_{\text{A}(s)} - \Delta G^A_{\text{B}(s)}) \right] \quad (2.14)$$
Where \( K_{BA}^- \) is the thermodynamic equilibrium constant for reaction (2.13) at a given temperature, \( \Delta G_{B^-}^o \) is the corresponding change in the standard free energy of the process, \( \Delta G_{RB(s)}^o \) and \( \Delta G_{RA(s)}^o \) are the standard free energy change of B and A forms of the resin and \( \Delta G_{A(s)}^o \) and \( \Delta G_{B(s)}^o \) 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.

In the case of anion exchange reaction in aqueous medium, equation (2.14) can be rewritten as

\[
\ln K_{BA}^- = - \frac{\Delta G_{B^-}^o}{RT} \]

\[
= \frac{1}{RT} \left[ (\Delta G_{RB}^o - \Delta G_{RA}^o) + (\Delta G_{A(h)}^o - \Delta G_{B(h)}^o) \right] \quad (2.14 \text{ A})
\]

From the equation (2.14 A) it is evident that the thermodynamic equilibrium constant \( K_{BA}^- \) for anion exchange reaction is given by the electrostatic interaction differences between the counter ions with the resin ion and the difference in the standard free energy of hydration of the two counter ions in aqueous medium.
To compare the equilibrium constant in a mixed solvent medium with that in aqueous, it is necessary to have a common reference state chosen. Here the standard state for 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 (2.13) in mixed solvent media can be rewritten as follows:

\[
-RT \ln K^B_{A(s)} = \Delta G^\circ_{A(s)}
\]

\[
= (\Delta G^\circ_{RB(s)} - \Delta G^\circ_{RA(s)}) + (\Delta G^\circ_{A(s)} - \Delta G^\circ_{B(s)})
\]

\[
+ (\Delta G^\circ_{RB(t)} - \Delta G^\circ_{RA(t)}) + (\Delta G^\circ_{A(t)} - \Delta G^\circ_{B(t)})
\]

(2.15)

(2.16)

Here, \( \Delta G^\circ_{i(t)} \) refers to the standard free energy change of transfer of \( i^{th} \) species from infinitely dilute aqueous solution to the infinitely dilute solution in mixed solvent.

The first term on the right hand side of equation (2.16) gives the difference in the electrostatic interaction energies between the two counterions 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 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 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.

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

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

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

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 crosslinkages. Some of the results are given in the Table 2.1. 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).

Table 2.1

<table>
<thead>
<tr>
<th>% DVB</th>
<th>Exchange</th>
<th>(-\Delta G^0)</th>
<th>(-\Delta H^0)</th>
<th>(-T\Delta S^0)</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>

2.3 Models

The thermodynamic description of the ion exchange phenomenon requires no model. But the other theories of ion exchange start from some model. A few of such models are summerised here.
2.3.1 Donnan Membrane Model

Donnan's original treatment\textsuperscript{40,41} applied to solutions separated by a semipermeable membrane is extended to resin electrolyte systems by incorporating some assumptions\textsuperscript{42} like:

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

An ion exchange reaction (equation 2.5) may be considered as a Gibbs-Donnan membrane equilibrium, when its thermodynamic equilibrium constant is given by,

\begin{equation}
2.303 \, RT \log K_a^B = \pi (\bar{V}_A - \bar{V}_B)
\end{equation}

Where

- \( R \) = The gas constant
- \( T \) = Temperature in K
- \( \pi \) = The Osmotic type swelling pressure
- \( \bar{V}_A \) and \( \bar{V}_B \) = The partial molal volume of A and B respectively in the resin phase.

On substituting experimentally determined selectivity coefficient \( K_{A^B} \) in equation (2.19) one gets after
rearranging,

\[
\log \frac{K_{B}^{C}}{K_{A}^{C}} = \frac{\pi(\bar{V}_{A} - \bar{V}_{B})}{2.303 \text{RT}} + \log \frac{w_{RA}^{f}}{w_{RB}^{f}} - 2 \log \frac{w_{XA}^{f+}}{w_{XB}^{f+}} \quad (2.20)
\]

This simple picture is beset with many difficulties as it fails to explain some observed selectivities such as \( K_{Ag^{+}}^{26} \) 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 Carlsberg dilatometer with a view to correlate the volume changes with the effect of ions on the short range order in water.

Further the most effective argument against the osmotic type pressure - volume effect as the origin of selectivity is that where measured, similar selectivity orders are obtained with the liquid ion exchangers*43,44, which have no resin matrix and hence can not have any pressure - volume effect.

*G.E. Boyd and K. Bunzl "The binding of ions by ionexchangers. The volume change criterion, Private communication."
The relative importance of the individual terms of Gibbs-Donnal equation (2.20) is investigated extensively by Glueckauf, Boyd et al., and Soldano et al. In evaluating these terms several approximations are made, many of which are not based on firm thermodynamics.

From the isopiestic swelling data on the pure resinates, Glueckauf estimated $w_f^{RA}/w_f^{RB}$ semiempirically applying Harned's rule. Soldano and others have criticised some of the assumptions made by Glueckauf and determined the same employing Gibbs-Duhem equation. This treatment agrees better with 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 et al. have obtained experimentally $K_{CA}$ values for alkali ions, tetramethyl ammonium ion and some anions as a function of crosslinkage of strong ion exchagers. They have also evaluated the different terms of equation (2.20) individually. Here both the osmotic type pressure and resin activity coefficient ratio ($w_f^{RA}/w_f^{RB}$) were evaluated.
from the equivalent water contents of resins of different crosslinkages, 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 \(\Delta V\) was determined by pyknometric equivalent volume measurements at varying resin compositions. The mean molal activity coefficient ratio term for the two ions \(\frac{W_{f+xA}}{W_{f+xB}}\) in mixed electrolytes in the external aqueous phase was obtained from the literature with proper corrections.54

The \(K_{CA}^B\) values of alkali ions and halide ions48 thus evaluated agreed fairly well with the experimental one in the case of low crosslinked exchangers. But the disagreement in the case of high crosslinked exchangers was attributed to chemical heterogeneities in them.

The theoretical \(K_{CA}^B\) of tetramethyl ammonium ion against \(Na^+\) 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 \((mAV/2.303 RT)\) of the polymer molecular net work when the large quaternary ammonium ion enters the exchanger.
Marinsky\textsuperscript{55} has reexamined the Gibbs-Donnan equation (2.20). He evaluated (\(W^f_{RA}/W^f_{RB}\)) by adopting Feitelson's\textsuperscript{56} application of the Fuoss, Katchalsky and Lifson\textsuperscript{57,58} polyelectrolyte theory, as modified by Kagawa and Gregor.\textsuperscript{59} Hydration parameters obtained via polyelectrolyte model appear to enhance the quantitative estimate of (\(W^f_{RA}/W^f_{RB}\)) and of swelling pressure effects as well.

Marinsky and Co-workers\textsuperscript{60-63} in a series of publications have extended this treatment to several tracer cation exchange studies. Michael Goldsmith et al.\textsuperscript{64} determined the Donnan potentials of single ion exchanger beads with microelectrodes.

Fessler and Strobel's\textsuperscript{65} modification of equation (2.20) to explain ion exchange selectivity in mixed solvent media will be referred to later.

Demirgian et al.\textsuperscript{66} have experimentally examined solvent and ion selectivity behaviour in mixed media and showed 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 selectivity order in the liquid ion exchangers and the gel type resins.

2.3.2 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 67,68, Eisenman 69, Reichenberg 70 and Steigman and Dobrow 71 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 42,45. Though they differ in the details, certain aspects of the solvent structure and solute solvent interactions are common and are presented here in brief.
2.3.2.1. 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 of the medium. Thus the change of solvent may effect these interactions.

Classical description of ion interactions in dilute aqueous solution was culminated in the famous theory of Debye-Huckel of strong electrolytes. According to this theory, the ion interactions so far, as they contribute to thermodynamic properties were determined by the "ionic-atmosphere" solvent merely acting as 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 required no elaboration. All the present day models recognise this deficiency of considering the solvent as a dielectric continuum but differ in their details in treating this aspect.
Ions in aqueous solutions are surrounded by water molecules. The charge on the ion will interact with the dipoles of water molecules. The magnitude of interaction depends on the charge, size and polarizability of the ions and the dipole moment of water molecules. In addition, water structure also contributes to the overall energy of interactions. A more useful description of the ions in water is given by Frank and Wen.

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 water in the region next to the immobilized (or stationary) region is broken. This is because of the opposing effects of ion-induced dipole 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 solution over another is not considered.

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

$$\Delta G_A^\circ(h) = \mu_A^{\text{aq}} - \mu_A^{\text{g}}$$

(2.21)

where, $\mu_A^{\text{aq}}$ and $\mu_A^{\text{g}}$ 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 the electrolytes. To illustrate the utility of such information, the $\Delta G_A^\circ(h)$ of alkali ions listed below are taken from Robinson and Stokes.

<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>$\Delta G_A^\circ(h)$</td>
<td>505.42</td>
<td>405.84</td>
<td>331.79</td>
<td>310.45</td>
<td>278.23</td>
</tr>
<tr>
<td>in kJ mol$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\( \Delta G^\circ_{A(h)} \) can be considered as an indication of the ion-water interactions, more negative this quantity, more will be the hydration. As can be seen from the above list, lithium ion should exhibit the maximum hydration. This conclusion is in agreement with the intuitive reasoning that the smaller 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, probably the extreme example of such a solvent. 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 last thirty years. Yet we have only partial answers to several questions regarding these two.

The anomalous behaviour of liquid water compared to other hydrides of VI\(^{th}\) 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 227K can not be explained. To explain such unique properties of liquid water several models have been proposed starting from Bernal's modified ice like picture to the Nemethy and Scheraga. The degree of success that these statistical models have achieved has been amply discussed in several monographs. A very brief description of one such model is presented here.

The most satisfactory model appears to be the one proposed by Nemethy and Scheraga based on the Frank and Wen's "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 273 to 343 K 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 a solute whether it is an electrolyte or a non electrolyte is going to interfere with this equilibrium concentrations, thereby influence the thermodynamic properties of the solutions significantly.

2.3.2.2 Electrostatic Models

According to Rice and Coworkers, as well as Katchalsky and others, some of the counterions 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 counterions. The swelling equilibrium is assumed to be governed by a 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 a modification of Flory's treatment of swelling of the uncharged crosslinked polymer.

Rice's treatment differs slightly from Katchalsky's in computation of electrostatic interaction energy.
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 decrease of crosslinkage and solution concentration as well as with increase of specific capacity of the resin. The model is not applicable to low crosslinked gels, wherein the distance between 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 can not be applied to high crosslinked resins because interaction between neighbouring chains are disregarded. But the success of either, as a general model was rather limited.
2.3.2.3 Diamond's Model

2.3.2.3.1 Water Structure Enforced Ion Pairing

As discussed earlier, Debye and Huckel's limiting law was adequate in explaining thermodynamic properties of electrolyte solutions, only at infinitely low concentrations.

Various other assumptions like Bjerrum's ion pair formation, Robinson and Harned's localised hydrolysis etc., have been proposed from time to time to explain the behaviour of these solutions at finite concentrations. Diamond considers yet another type of interaction to explain the activity and osmotic coefficients of large univalent ions like $\text{R}_4\text{N}^+$, $\text{ClO}_4^-$, $\text{ReO}_4^-$, $\text{AuBr}_4^-$, $\text{FeCl}_4^-$, and $\text{SbCl}_6^-$.

If an ion, small in size with a high charge density, is introduced into water, which is highly hydrogen bonded and structured, it orients the water molecules around it. On the other hand, if the ion is large in size with a low charge density as the tetra substituted ammonium ion the bulky hydrocarbon part (having no charge) 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 a big ion is more ordered (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 neighboring 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 a decrease in the entropy of water. As the concentration of tetra substituted ammonium salt increases, there is an increase in the tightening of water structure. This tightening up of water structure should increase with the size of the substituted ammonium ion. In agreement with this, the experimentally observed order of activity and osmotic coefficients (viz. NMe₄⁺ < NEt₄⁺ < NPr₄⁺ < NBut₄⁺) 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 it). Diamond calls this as "water structure enforced ion pair formation" which is different from Bjerrum type. This can occur only in highly structured solvents.
2.3.2.3.2 Origin of Ion Exchange Selectivity

Diamond\textsuperscript{92} has proposed a model for ion exchange selectivity, in general, taking resin phase as a concentrated electrolyte solution which differs significantly from the external dilute electrolyte solution in three aspects.

i) The functional group in the resin matrix is fixed

ii) The electrostatic forces are stronger in the resin phase

iii) The water molecules in the resin phase have less co-operative structures, i.e., the 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 phases (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 because of the resin matrix. The benzyltrimethyl ammonium ion in a strong anion exchanger is large and hydrophobic. So
a large and lowly charged anion like ClO\textsubscript{4}\textsuperscript{-}, which requires less hydration prefers the resin phase. In the resin phase, the residual water structure forces this ion and the resin cation into a single cavity, thus favouring the formation of an ion pair. In this way, Diamond's model explains well the higher selectivity of ClO\textsubscript{4}\textsuperscript{-} over I\textsuperscript{-}.

Myers and Boyd\textsuperscript{47} found that the selectivity coefficients of alkali ions on strong cation exchange resins approach unity as the crosslinkage decreases to 0.5\% DVB. Those of halide ions\textsuperscript{48} on strong anion exchange resins decrease with decreasing crosslinkage but to a lesser extent than in the case of alkali ions. Diamond explains the above by assuming that 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.\textsuperscript{93-95} Diamond explains this on the bases of their capacities to form water structure enforced ionpairs. This capacity increases with the size of the 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 \( \text{NR}_3^+ \), 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 the strong base resin. Therefore water structure enforced ion pairing can not be as predominant in the weak base resin as in the strong base one. According to this, a weak base exchanger should show a somewhat enhanced selectivity for smaller anions and somewhat reduced affinity for big and hydrophobic ions. This was borne out by Jensen and Diamond\(^96\) by studying the distribution coefficients of traces of \( F^- \), \( \text{Br}^- \) and \( I^- \) as a function of lithium chloride molarity on strong and weak anion exchangers. In dilute solution the relative selectivity coefficients of \( F^- \), \( \text{Br}^- \) and \( I^- \) against \( \text{Cl}^- \) on strong base exchanger are 1.0:55:280 and on weak base exchanger 1.0:3.7:10.

It is well known that the selectivity of cations generally increases with their valency on strong cation exchanger because of the predominance of Bjerrum type ion pairing. But this need not be the case with anion exchange systems with strong anion exchangers, wherein water structure enforced ion pair formation is predominating. 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 the 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 $\text{Cl}^-$ as the macro anion and those of $\text{Cr(CN)}_6^{3-}$, $\text{Co(CN)}_6^{3-}$ and $\text{Fe(CN)}_6^{3-}$ (traces) against macro concentration of $\text{CN}^-$ on strong anion exchangers. They were particular in selecting the ions having similar size and structure but only differing in charge. They found that the selectivity decreases with increase of charge of counter ion. They therefore calculated that Bjerrum type ion pairing is not important in governing selectivities of these large 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.

2.3.2.4 Steigman's Model

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

1. Ions with a high charge density, such as Li$^+$ and F$^-$, orient strongly the water dipoles around them (Structure formers according to Gurney$^{99}$).

2. Ions with a low charge density, such as Cs$^+$ and I$^-$ destroy the hydrogen bonded water structure in their immediate vicinity (Structure breakers according to Gurney$^{99}$).

3. Big organic ions, such as quaternary ammonium ions produce stable cages of hydrogen bonded water structures around their non-polarising moieties as evidenced by high positive heat capacities and high positive viscosity $\beta$-coefficients of their aqueous solutions (tightening of water structure according to Diamond$^{92}$). Ions belonging to both groups (1) and (3) are structure formers, though the way in which the water is organised is different. Those belonging to 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 the structure forming ion of opposite sign to organise, the interaction is a co-operative type and such an electrolyte is a co-operative one.

Taking the condition of water in concentrated quaternary ammonium salt solutions as a guide for the condition of water in the resin phase, they stated that water in the immediate vicinity of fixed charged site in the resin is organised, even though 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 co-operative effects of the 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 exchange resin. On a strong anion exchange resin, $F^-$ is less preferred while $I^-$ and $ClO_4^-$ are more
preferred over chloride ion. This is explained on the basis that F forms an antagonistic electrolyte while ClO₄⁻ and I⁻ form co-operative electrolyte with quaternary ammonium ions of resin.

2.3.2.5 Reichenberg's Treatment (Eisenman's Model)

Reichenberg applied the concept of field strength, defined by Eisenman in this 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 it is considered in terms of energetics rather than in terms of hydrated ionic radii or volumes.

2. Electrostatic interactions are considered as the 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 coion R⁺, this will result in:

i) The electrostatic interaction energies between R⁺ and B⁻, both being nonpolarisable point charges, each at the centre of an-incompressible sphere, is \( \frac{e^2}{r_{R^+} + r_{B^-}} \) where e and r are the
electronic charge and radius of the ion respectively.

ii) The free energies required to remove from (or, to rearrange around) the fixed grouping $R^+$ and the counter ion $B^-$, as many water molecules as are 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 $\Delta G_{B^-}$ and $\Delta G_{R^+}$, the total free energy involved in this removal (or rearrangement) of water molecules is $\Delta G_{B^-} + \Delta G_{R^+}$.

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

$$-\left[\frac{e^2}{r_{R^+} + r_{B^-}}\right] + \Delta G_{R^+} + \Delta G_{B^-}$$

Since this process is purely hypothetical it can not occur on its own. It should be accompanied by another process in which a counter ion $A^-$ incontact with $R^+$ should be removed from the resin into the bulk dilute solution. The gain of free energy by the system due to this latter process is

$$\left[\frac{e^2}{r_{R^+} + r_{A^-}}\right] - \Delta G_{R^+} + \Delta G_{A^-}$$
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

\[
\Delta G^0_{A^-} = \frac{e^2}{(r^+ + r^-)} A^- - \frac{e^2}{(r^+ + r^-)} A^+ - \left( \Delta G_A^- - \Delta G_B^- \right) \tag{2.22}
\]

and of course

\[
\Delta G^0_{A^-} = -RT \ln K_{A^-} \tag{2.23}
\]

Equations (2.22) and (2.23) enable predictions of more penetrating character to be made than those we have discussed in connection with Gregor's theory. Consider the case where \( r_+ \) is large, Eisenman describes this as the case of a fixed grouping of low field strength. Regardless of the counter ions involved \( \left[ \frac{e^2}{r^+ + r^-} - \frac{e^2}{r^+ + r^-} \right] \) will be small and \( \Delta G^0_{A^-} \) will be determined by the term \( -\left( \Delta G_A^- - \Delta G_B^- \right) \), 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 \( (B^+) \), \( \Delta G_{B^+} \), is numerically less than \( \Delta G_A^+ \) and hence \( \Delta G_{A^+}^+ \) will be
negative $K^B_{A^+}$ will be therefore greater than unity, i.e., potassium will be preferred to sodium.

This is the normal selectivity order observed. Similarly in the case of anion exchange of $\text{ClO}_4^- - \text{Cl}^-$, the difference in total electrostatic energy is only $43.51 \text{ kJ mol}^{-1}$ whereas the difference of hydration free energies is $127.61 \text{ kJ mol}^{-1}$ hence the latter plays a predominant role in governing the selectivities. In agreement with this $\text{ClO}_4^-$ is preferred over $\text{Cl}^-$ on strong anion exchangers. According to Eisenman, as the field strength increases, the difference in the electrostatic interaction terms becomes more and more significant. In the case of weak cation exchangers (high field strength) the selectivity order of alkali ions is just the reverse of that observed on strong cation exchangers showing the predominance of the electrostatic interactions over that of hydration energies. In the case of anions, Reichenberg has studied the exchange of $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$ and $\text{ClO}_4^-$ on tri basic sulphate of lead and found a reversal of selectivity order of $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ compared to that on strong base exchangers, indicating the significance of electrostatic interaction. Higher selectivity of $\text{ClO}_4^-$ is still attributed partly to the field strength not becoming
significantly high and partly to other interactions governing selectivity.70.

2.4 Ion Exchange Selectivity in Mixed Solvent Media

The discussion dealt above clearly shows the importance of solvent properties like dielectric constant, polarity, presence of hydrogen bond, solvation energies of the ions, etc., in determining the selectivity of anion on a given resin. Eversince the introduction of synthetic organic resins, emphasis is laid towards the improvement of the resin characteristics to enhance the selectivity and separability. Dorfner106 has presented the characteristics of the commercially available resins. Thus by controlling the solvent properties the efficiency of separation can be increased107,23. Mixture of water and various organic liquids as a solvent media were exploited to achieve excellent analytical separations of closely related ions23. The majority of the publications were concerned more in achieving separation than in answering the origin of separation. Even among those which have reported the thermodynamic study in mixed solvent media, cation exchange investigations, outnumber anion exchange investigations.
The thorough understanding of ion exchange phenomenon in water, the most investigated solvent is yet incomplete, and in mixed solvents, it has made a beginning. Rigorous theoretical treatment of ion exchange equilibria in mixed solvents is made difficult on two grounds:

i) The available data on ion exchange selectivity in well characterised system is limited.

ii) The exact physico-chemical nature of the mixed solvents is still not well describable. In this connection a few qualitative observations have been made here.

There is a linear relationship between selectivity coefficient and the reciprocal of the solvent dielectric constant. Another remark is concerned with the solvent sorption. Ion exchange resins are osmotic systems wherein crosslinked matrix which restricts the fixed ions to the resin phase, functions analogously to the membrane in a refined Donnan system. This means that, subject 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 of 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 composition. This preferential water sorption is more prevalent in cation exchangers compared to anion exchangers. In explaining the difference in behaviour of 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 in general, the logarithm of exchange coefficients vary with the reciprocal of the dielectric constant, as would be predicted for coulombic interactions. Their results agree with the conclusion of other investigations that the dielectric constant of the media is most significant factor in solvent effects. However, other effects 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 resin swelling results.

Moody 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 \( \text{Li}^+ - \text{H}^+ \), \( \text{Na}^+ - \text{H}^+ \) on Amberlite IR-120 and for \( \text{Na}^+ - \text{H}^+ \) on Dowex 50W in methanol-water mixture have been discussed. From selectivity data of \( \text{Li}^+ - \text{Na}^+ \) in methanol-water on Dowex 50W Schwarz arrived at standard free energy, ethalpy 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 \( \text{Na}^+ \).

Starobinets et al. studied the effect of the nature of solvation on the selectivity of anion exchange in mixed aq-organic solvent media viz., water-DMF and water-methanol. In methanolic solutions of low methanol concentrations, the selectivity of the anion exchange increased in the order \( \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{CNS}^- \). In DMF-water solutions at higher mole fractions of the organic component (\( \geq 0.6 \)), the order was as follows, \( \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{CNS}^- \). The reverse order of selectivity in DMF-water system was attributed to a weak solvation of anions in the aprotic amide.
In their further studies, Starobinets et al., showed that the affinity of halide and thiocyanate ions to high alkali anionites in aqueous solution increase 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 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 aq-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. The exchange of alkyl-anilium ions on a sulfonic acid exchanger have been studied in this solvent medium and observed that ion exchange constants increased with increasing methanol content. The separation of several weak organic bases on a cation exchanger in mixed solvent systems has led to a novel method for separations.
Alkali metal ion exchange in ethanol-water and in water-Dioxane and barium ion exchange in aceticacid-water solvents have been investigated. 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 subject to several recent papers and the exchange distribution suggests that DMSO-water mixtures will be promising media for cation separations.

Ogawa and Tsuji were the first to study the exchange of Cl\(^-\), Br\(^-\), I\(^-\), Vs NO\(_3^-\) on strong base exchangers in water-methanol 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. Davyдов has derived a relation for the ratio of activity coefficients of counter ions in the resin phase from the observed change in the selectivity coefficients in mixed solvents.

Krishnan and Ramnathan studied the selectivities of CNS\(^-\), NO\(_3^-\) and OH\(^-\) against Cl\(^-\) on strong base exchangers of
varying crosslinkage in aqueous and mixed solvent media. There was a decrease in selectivity in all the above three systems with increasing 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 solvant media.

Bhatnagar et al., \textsuperscript{124} 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 disagreement in the data for Cl\textsuperscript{−}-OH\textsuperscript{−} exchange reported by the two teams. \textsuperscript{123,124}

Phipps\textsuperscript{120} 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's treatment \textsuperscript{70} will be better suited to explain the observed anion exchange selectivity order. Sherrill et al.\textsuperscript{125} reported an exchange study of Cs\textsuperscript{+} and R\textsubscript{4}N\textsuperscript{+} on strong base exchangers in methanol-water, propan-2-01-water and showed that the measured log K\textsubscript{c} correlated with the reciprocal of the dielectric constant.

\[ \text{Reichenberg's treatment} \textsuperscript{70} \text{ will be better suited to explain the observed anion exchange selectivity order.} \]
Selectivity in mixed solvents have been studied by a number of investigators\textsuperscript{126-135} from a mechanistic point of view. Cations were absorbed more strongly with respect to the hydrogen ion as the proportion of organic solvent (e.g., methanol, ethanol, acetone) increased. Smites et al.\textsuperscript{128}, in a careful study of Rb\textsuperscript{+}, Mg\textsuperscript{++}, H\textsuperscript{+} in water-DMSO related the exchange equilibria with the Walden product and thus with hydration.

Pellicular and macroporous resins have been used but yet little data is made available. It seems that their attractive mechanical properties and relatively fast reactions have obscured the potential disadvantage of specific lower selectivity.\textsuperscript{136} In one of the reports\textsuperscript{137} a comparison of distribution and exchange rates in macroporous resins with those in gel type deserves special reference.

Bhat\textsuperscript{138} 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 result in terms of Diamond's model. Diamond and Jensen\textsuperscript{139} 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 macro-electrolyte (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 a poorer solvating agent and hence the preference of the smaller ions to external solution medium should decrease. Thus the ion most in need of solvation decreasingly prefers the external solution. Therefore the separation factors should get smaller. This was observed 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 Dimond-Reichenberg model adequately explains the observations.

Narke et al., carried out a systematic study of the exchange behaviour of the simple monovalent ions such as ClO$_4^-$, I$^-$, CNS$^-$ against Cl$^-$ 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{141} 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 i.e. Hg(II) > Cd(II) > Ag(I) > Pb(II) > Cu(II) > Zn(II) > Co(II) ≥ Ni(II). However, Hg(II), Cd(II) and Ag(I) have high $K_D$ values and have suggested the separation possibilities for many metal ions by ion exclusion technique.

Bhatnagar and Mishra\textsuperscript{142} have studied the exchange selectivity of halate ions on the nitrate form of strongly basic exchanger Amberlite IRA-400. They have reported the increase in selectivity coefficient with increase in acetone content for $\text{ClO}_3^-$ and $\text{BrO}_3^-$ but decrease in selectivity coefficient for $\text{IO}_3^-$. 

Taylor et al.\textsuperscript{143}, have studied the exchange of simple monovalent cations $\text{Na}^+\text{H}^+$ and $\text{Na}^+\text{Li}^+$ with Dowex 50x8 and one anion exchange, $\text{I}^-\text{Cl}^-$ with Dowex 1-X8 in water-methanol mixtures. They have used Gupta's equation and
showed that the selectivity trends in the 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 $I^- - Cl^-$ exchange.

Deoki Nandan et al.\textsuperscript{144}, have recently investigated the exchange behaviour of some simple monovalent anions in water and methanol. The thermodynamic equilibrium constants in water ($k_w$) and in methanol ($k_s$) were found to follow the ionic selectivity sequence $I^- > NO_3^- > Br^- > Cl^-$. $k_s$ being generally lower than $k_w$.

Recently Katale\textsuperscript{145}, Vyasamudri\textsuperscript{146}, Math\textsuperscript{147}, Bhavikatti\textsuperscript{148}, Hoskeri\textsuperscript{149}, Sangolli\textsuperscript{150} and Patil\textsuperscript{151} have studied the anion exchange behaviour in water-DMF, water-formamide, water-propan-2-01, water-ethyleneglycol, water-2-ethoxyethanol, water-acetone and water-2-methoxy ethanol respectively. Comparison of dielectric constants and magnitudes of selectivity coefficients prompted them to believe that the dielectric constant is not the sole factor governing the selectivity. It was in fact the protic or aprotic nature of the solvent that determines the selectivity behaviour.
It is evident from this brief review of literature that the data on ion exchange available till today is rather inadequate to understand the anion exchange phenomenon on synthetic resins. Additional data of simple anion exchange behaviour 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 anion exchange selectivity in water-2-butoxyethanol. Hence a systematic study of simple monovalent anions such as ClO$_4^-$, CNS$^-$ and NO$_3^-$ against Cl$^-$ on strong base exchangers like Dowex 1-X8, Dowex 1-X4, Tulsion A-27 (macrotectic) and also ClO$_4^-$ and NO$_3^-$ against Cl$^-$ on weak base exchangers, Tulsion A-2X (gel) and Amberlyst A-21 (macrotectic) with wide range of loading ($\tilde{N}_{RB}$ from 0 to 1) in water-2-butoxyethanol media of varying compositions was carried out.
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