CHAPTER IV
DISCUSSION
INTRODUCTION

The results of exchange studies of $\text{ClO}_4^-$-Cl$^-$, $\text{CNS}^-$-Cl$^-$, I$^-$_Cl$^-$ and $\text{NO}_3^-$-Cl$^-$ on strong base exchangers such as Dowex 1-X8, Dowex 1-X4 and Tulsion A-27 (macroreticular), and also the exchange studies of $\text{ClO}_4^-$-Cl$^-$ and $\text{NO}_3^-$-Cl$^-$ on weak base exchangers such as Amberlyst A-21 (macroreticular) and Tulsion A-2X (gel) in aqueous and 2-isopropoxyethanol-water mixed media of various compositions are discussed in this Chapter. The results are discussed in terms of models proposed by Diamond$^1$ and Reichenberg$^2$ under the following headings:

1. Selectivity behaviour in
   a. aqueous medium; and
   b. 2-isopropoxyethanol-water mixed medium;

2. Effect of dielectric constant of the solvent on selectivity;

3. Effect of variation of cross-linkage (%DVB) of the exchanger on selectivity;

4. Effect of changing the resin fixed ion on selectivity;

The factors that contribute to the ion exchange selectivity are discussed in Chapter II of the thesis. Among all these, solvent medium of the external solution phase plays a dominant role. In this context solvent properties of importance are the dielectric constant of the medium, protic or aprotic and
polar or nonpolar nature of the solvent. The general assumption of the solvent medium as a dielectric continuum no longer accepted particularly with electrolyte solution. The solvent structure (microscopic), especially of water, plays a dominant role in exchange processes\textsuperscript{3}. The above fact is based on the experimental evidence of ion exchange. The addition of foreign species such as ions, inert molecules or another solvent is known to alter the hydrogen bonding nature of water, and hence its structure. Diamond \textit{et al}\textsuperscript{1} have reported that \textit{water-structure-enforced ion pairing} plays a significant role in exchange process and the degree of water-structure-enforced ion pairing depends upon the extent of water structure which is generally affected by the addition of organic solvent. A number of anion exchange studies have been carried out in mixed solvent media using protic and aprotic solvents of varying dielectric constants.

Bhat\textsuperscript{4} studied the effect of addition of methanol (a protic solvent) on simple monovalent anion exchange, and Narke\textsuperscript{5} investigated the influence of addition of dioxane (an aprotic solvent) on the monovalent anion exchange. Narke and coworkers have extended the study to other water soluble solvents such as formamide\textsuperscript{6}, ethylene glycol\textsuperscript{7}, DMP\textsuperscript{8}, 2-ethoxyethanol\textsuperscript{9}, propan-2-ol\textsuperscript{10}, acetone\textsuperscript{11} and 2-methoxyethanol\textsuperscript{12}.

Krishnan \textit{et al}\textsuperscript{13} have reported the results of anion exchange studies in mixed ethanol-water media. The capacity to form hydrogen bonding in case of alcohols is quite similar to that of water but to a lesser degree. It is a known fact that the
length of hydrocarbon chain attached to carbon containing the alcoholic group determines the hydrophobic ion pairing in water. Hoskeri\textsuperscript{9} and Patil\textsuperscript{12} studied the monovalent anion exchange process in 2-ethoxyethanol and 2-methoxyethanol mixed medium respectively. They reported that 2-methoxyethanol and 2-ethoxyethanol behaved more like aprotic solvents, and aprotic nature is more in the case 2-ethoxyethanol than in 2-methoxyethanol. Extending their studies it was thought worthwhile to study the exchange behaviour in mixed medium involving 2-isopropoxyethanol which has substitution of isopropoxy group comparatively larger in size.

4.1 SELECTIVITY BEHAVIOUR IN AQUEOUS MEDIUM

The details of average and corrected selectivity coefficients of all the anions studied on strong base exchangers such as Dowex 1-X8, Dowex 1-X4 and Tulsion A-27 (MP) are presented in Table IV.1.

It is obvious from Table IV.1 that the ionic selectivity sequence in aqueous medium is ClO$_4^-$ > CNS$^-$ > I$^-$ > NO$_3^-$ > Cl$^-$. This is the order expected from their crystallographic radii and the data in the literature\textsuperscript{11}. From the available free energy data (Table IV.2) and change in standard free energy values the selectivity sequence observed is also the same. This selectivity sequence is in good agreement with data reported by previous investigators\textsuperscript{4-12}, and can be explained by the models proposed by Diamond and Reichenberg.
TABLE IV.1
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS FOR ANIONS ON DOWEX 1-X8, DOWEX 1-X4 AND TULSION A-27 (MP)
IN 2-ISOPROPOXYETHANOL-WATER MIXED MEDIUM AT 303±1K

<table>
<thead>
<tr>
<th>Anion (B⁻)</th>
<th>log $K_{B}^{a} a_{Cl}^{-}$ in % of 2-isoproxy ethanol (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>00</td>
</tr>
<tr>
<td>-----------</td>
<td>-----</td>
</tr>
<tr>
<td>DOWEX 1-X8</td>
<td></td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>1.21</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>1.18</td>
</tr>
<tr>
<td>I⁻</td>
<td>1.17</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.57</td>
</tr>
<tr>
<td>DOWEX 1-X4</td>
<td></td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>1.20</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>1.13</td>
</tr>
<tr>
<td>I⁻</td>
<td>1.11</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.52</td>
</tr>
<tr>
<td>TULSION A-27 (MP)</td>
<td></td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>1.37</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>1.33</td>
</tr>
<tr>
<td>I⁻</td>
<td>1.24</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.69</td>
</tr>
</tbody>
</table>

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Diamond considers ion-water and water-water interaction differences (apart from other interactions) between the resin phase and the external aqueous phase to play an important role in ion exchange selectivity. A small ion with high charge density such as Cl$^-$ has more negative free energy of hydration compared to a larger one like ClO$_4^-$ with low charge density. Cl$^-$ will therefore prefer the external aqueous phase to satisfy hydration better. The quaternary ammonium group in the resin phase is a big hydrophobic ion with a low charge density. This ion will create a cavity resulting in tightening of water structure which in turn decreases the entropy of the system. A bigger ion such as ClO$_4^-$ with low charge density also tries to create a cavity and tighten up the water structure, which might further reduce the entropy of the system. But in order to avoid this further decrease in entropy, the two ions (R$^+$ and bigger ClO$_4^-$ anion) are forced to share a single cavity, thus favouring the formation of an ion pair. This is known as water-structure-enforced ion pairing. The crystallographic radii are in the following order:

$$\text{ClO}_4^- > \text{CNS}^- > \text{I}^- > \text{NO}_3^- > \text{Cl}^-$$

Hence the selectivity order in aqueous medium observed in the present investigation is the same as above.

Though the Diamond model explains ion exchange selectivity qualitatively it is unable to give quantitative basis. The formal thermodynamic treatment attempts to provide a quantitative basis.
An ion exchange reaction in aqueous medium can be conveniently represented as follows:

RA + B\(^{−}\) \(\rightleftharpoons\) RB + A\(^{−}\)  \(\ldots\) 4.1

where RA and RB are A and B forms of an ion exchange resin respectively;

A\(^{−}\) and B\(^{−}\) are counter-ions.

The thermodynamic equilibrium constant \(K_{B/A}^{−}\) for such reactions is given by:

\[
\ln K_{B/A}^{−} (h) = - \frac{1}{RT} (\Delta G_{A}^{0 B^{−}} (h)) \ldots 4.2
\]

\[
\ln K_{B/A}^{−} (h) = - \frac{1}{RT} [(\Delta G_{RB}^{0} - \Delta G_{RA}^{0}) + (\Delta G_{A}^{0 −} (h) - \Delta G_{B}^{0 −} (h))] \ldots 4.3
\]

where \(\Delta G_{A}^{0 B^{−}} (h)\) is the corresponding change in the standard free energy of the process;

\(\Delta G_{RB}^{0}\) and \(\Delta G_{RA}^{0}\) are the standard free energy change of B and A forms of the resin;

\(\Delta G_{A}^{0 −} (h)\) & \(\Delta G_{B}^{0 −} (h)\) are the standard free energy change of hydrated ions A\(^{−}\) and B\(^{−}\) respectively in the external phase with respect to the ideal ionic gas state.

From equation 4.3 it is evident that the thermodynamic equilibrium constant \(K_{B/A}^{−} (h)\) for an ion exchange reaction in aqueous medium is given by the electrostatic interaction difference 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.

According to the free energy of hydration consideration, the system attains stability by pushing the counter-ion with more negative free energy of hydration into the external solution phase, where hydration is better satisfied, and in turn, bringing the counter-ion with less negative free energy of hydration from the external solution into the resin phase. This means that the ions of higher negative free energy of hydration will be preferred less by the resin. The free energy of hydration for a few common anions and cations are given in Table IV.2 and IV.3 respectively. It can be seen that NO$_3^-$, I$^-$, CNS$^-$ and ClO$_4^-$ have relatively less negative free energy of hydration compared to Cl$^-$. The expected selectivity order in aqueous medium should be ClO$_4^-$ > CNS$^-$ > I$^-$ > NO$_3^-$ > Cl$^-$. The selectivity order in aqueous medium observed in the present investigation (Table IV.1) is in good agreement with the expectation.

Dominance of free energy of hydration in governing selectivity has also been observed in cation exchange processes$^{15}$. Free energies of hydration for alkali ions are shown in Table IV.3. Selectivity order of ions is

Li$^+$ < Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$

because the ion with more negative free energy of hydration is less preferred by the resin phase.
### TABLE IV.2

$\Delta G^\circ_1$ (h)

OF MONOVALENT ANIONS AND $\Delta G^\circ_1$ B$^-$ VALUES

FOR EXCHANGES ON STRONG BASE EXCHANGERS AT 303±1K

<table>
<thead>
<tr>
<th>Anion</th>
<th>Radius (Crystal-</th>
<th>Free energy of hydration</th>
<th>Diff. between free energies of hydration</th>
<th>Calculated standard free energy changes of an ion exchange reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(lographic)</td>
<td></td>
<td></td>
<td>$\text{RCI} + \text{B}^- \rightleftharpoons \text{RB} + \text{Cl}^-$</td>
</tr>
<tr>
<td>B$^-$</td>
<td>1.20</td>
<td>267.77</td>
<td>-67.66</td>
<td>$\Delta G^\circ_1$ B$^-$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>1.33</td>
<td>447.68</td>
<td>117.15</td>
<td>$\Delta G^\circ_1$ F$^-$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.81</td>
<td>330.53</td>
<td>0.00</td>
<td>$\Delta G^\circ_1$ Cl$^-$</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>1.96</td>
<td>301.24</td>
<td>-29.28</td>
<td>$\Delta G^\circ_1$ Br$^-$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>2.20</td>
<td>288.69</td>
<td>-61.84</td>
<td>$\Delta G^\circ_1$ I$^-$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>2.0-2.5</td>
<td>288.69</td>
<td>-61.84</td>
<td>$\Delta G^\circ_1$ NO$_3^-$</td>
</tr>
<tr>
<td>CNS$^-$</td>
<td>--</td>
<td>230.12</td>
<td>-100.41</td>
<td>$\Delta G^\circ_1$ CNS$^-$</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>2.90</td>
<td>209.20</td>
<td>-121.33</td>
<td>$\Delta G^\circ_1$ ClO$_4^-$</td>
</tr>
<tr>
<td>I$_2^-$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>$\Delta G^\circ_1$ I$_2^-$</td>
</tr>
</tbody>
</table>

- Estimated

l - Present Work.

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TABLE IV.3

$\Delta G^0$ OF MONOVALENT CATIONS AND $\Delta G^0_{Na^+}$ VALUES FOR EXCHANGE ON STRONG ACID EXCHANGERS AT 303K

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (Crystallographic)</th>
<th>Free energy of hydration</th>
<th>Difference between the Free energies of hydration</th>
<th>Standard free energy change of cation exchange equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^*$</td>
<td>- $\Delta G^0_T(h)$</td>
<td>$\Delta G^0_{Na^+}(h) - \Delta G^0_{B^+}(h)$</td>
<td>$-\Delta G^0_{Na^+}(h)$</td>
</tr>
<tr>
<td></td>
<td>(in $\AA$)</td>
<td>(in KJ mole$^{-1}$)</td>
<td>(in KJ mole$^{-1}$)</td>
<td>(in KJ mole$^{-1}$)</td>
</tr>
<tr>
<td>H$^+$</td>
<td>--</td>
<td>1087.84</td>
<td>676.13</td>
<td>0.96</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.70</td>
<td>510.86</td>
<td>99.16</td>
<td>1.51</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.97</td>
<td>411.70</td>
<td>0.00</td>
<td>--</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.33</td>
<td>337.23</td>
<td>-74.47</td>
<td>-1.08</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>1.49</td>
<td>315.89</td>
<td>-95.81</td>
<td>--</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>1.67</td>
<td>283.67</td>
<td>-128.03</td>
<td>-1.38</td>
</tr>
</tbody>
</table>


From Table IV.2 and Table IV.3 it is clear that the expected selectivity order agrees well with the experimental observations, but quantitative agreement between fourth and fifth column in Table IV.2 and Table IV.3 is poor, e.g., $\Delta G^{\circ}_{Na}$ difference in free energy of hydration calculated is -74.47 KJ mole$^{-1}$ (Col 4 of Table IV.3), whereas the corresponding change in free energy obtained from exchange equilibria is only -1.08 KJ mole$^{-1}$ (Col 5 of Table IV.3), which is about 70 times less.

The situation in anion exchange process is no way better, e.g., in $NO_3^-$-$Cl^-$ exchange, the calculated free energy of hydration is -41.84 KJ mole$^{-1}$ (Col 4 of Table IV.2), whereas the corresponding value obtained from ion exchange equilibria is -3.31 KJ mole$^{-1}$, which is about 12 times less.

The poor agreement in quantitative comparison may be due to the various approximations made in evaluating $\Delta G^o$ of exchange reaction in experimental treatment and/or the large uncertainties in the available data for the hydration energies, electrostatic energies, entropy of formation of anions, etc., which appear in the equation 4.3.

4.2 SELECTIVITY BEHAVIOUR IN MIXED MEDIUM

With addition of 2-isopropanol, the water structure in the external solution phase is destroyed to a greater extent, because solvent occupies some space and molecules form much less
three-dimensional hydrogen bonding. At the same time, structure of water in the resin phase is affected to a lesser extent. Consequently the difference in the water in the two phases decreases with increased 2-isopropropoxyethanol content. Further, there is a change of predominance from water-structure-enforced ion pairing in aqueous medium to Bjerrum type ion pairing in mixed solvent medium. Hence the selectivity of the preferred anion in aqueous medium should decrease with increase in 2-isopropropoxyethanol content.

It can be seen from Table IV.1 and figures 4.1, 4.2 and 4.3 that there is decrease in selectivity of all anions on all the resins studied with increase in 2-isopropropoxyethanol content. The decrease in selectivity with an increase in 2-isopropropoxyethanol content is rather steep in the case of ClO$_4^-$ and CNS$^-$ compared to that of I$^-$ and NO$_3^-$.

There is a crossover of selectivity between CNS$^-$ and I$^-$ on Dowex 1-X8 and Dowex 1-X4 at about 5% and on Tulsion A-27 (macroreticular) at about 15% solvent compositions (Figs. 4.1 to 4.3). Further crossover between ClO$_4^-$ and I$^-$ is also observed on Dowex 1-X8, Dowex 1-X4 and Tulsion A-27 at about 65%, 30% and 50% solvent compositions respectively.

The selectivity reversal of NO$_3^-$ is observed on Dowex 1-X8 and Dowex 1-X4 at about 65%, 55% solvent compositions. Selectivity reversal is not significant on Tulsion A-27 because of macroporous nature of the resin maintaining higher selectivity of preferred ion.
Fig 4: $\log K'_{ac}$ vs % 2-isopropanol (w/w) on Dowex 1-X8
Fig 4.2: $\log K_{act}^p$ vs. % 2-isopropoxyethanol (w/w) on Dowex 1-X4.
Thus the selectivity sequence in aqueous medium ClO_4^- > CNS^- > I^- > NO_3^- > Cl^- changes to ClO_4^- > I^- > CNS^- > NO_3^- > Cl^- on all the resins in mixed medium beyond 15% solvent composition. At higher compositions beyond 65% because of crossovers and selectivity reversal the selectivity sequence observed is I^- > ClO_4^- > CNS^- > Cl^- > NO_3^- . However on Dowex 1-X4 the sequence becomes ClO_4^- > I^- > CNS^- > Cl^- > NO_3^- due to second crossover taking place between I^- and ClO_4^- at about 70% solvent composition (Figs. 4.1 to 4.3).

Patil has reported similar crossover between CNS^- -Cl^- and I^- -Cl^- in mixed medium (2-methoxyethanol-water) on strong base resins (Dowex 1-X8 and Dowex 1-X2). However, on Dowex 1-X4 the cross over is reported at higher solvent composition. Bhat has also reported similar crossover between CNS^- and I^- in water methanol mixed medium.

V.T. Athawale et al, in their cation exchange studies on strong and weak base cation exchangers have reported change in the order of affinities Li^+ < Na^+ < NH_4^- < K^+ in aqueous medium to Li^+ < NH_4^- < Na^+ < K^+ in mixed solvent media. They attribute the anomalous behaviour of NH_4^- to its nonspherical shape. The anomalous behaviour of CNS^- in mixed medium in the present investigation may, therefore, be attributed to its nonspherical shape. Further, greater CNS^- -2-isopropoxyethanol (ion-solvent) interaction in mixed solvent medium may also contribute significantly to the crossover behaviour of CNS^-.
Selectivity reversal in the case of \( \text{NO}_3^–-\text{Cl}^- \) exchange at higher 2-isopropoxyethanol composition on all the three strong base exchangers could be explained on the basis that at higher concentration of organic solvent in the external phase, the relative concentration of water in resin phase will be higher than in the external solution phase resulting in predominance of water structure enforced ion pairing. Such an observation in the case of water-dioxane was reported by Diamond et al\(^\text{17}\).

An ion exchange reaction in solvent \( S \) can be conveniently represented as follows:

\[
\text{RA} + \text{B}^-_{(s)} \rightleftharpoons \text{RB} + \text{A}^-_{(s)} \quad \ldots \quad 4.4
\]

where \( \text{RA} \) and \( \text{RB} \) are \( \text{A} \) and \( \text{B} \) forms of resin respectively, and \( \text{A}^- \) and \( \text{B}^- \) are counter-ions.

The equilibrium constant for such a reaction is given by

\[
\ln K^{\text{B}^-_{(s)}}_{\text{A}^-(s)} = \left[ (\Delta G^\circ_{\text{RB}} - \Delta G^\circ_{\text{RA}}) + (\Delta G^\circ_{\text{A}^-_{(s)}} - \Delta G^\circ_{\text{B}^-_{(s)}}) + (\Delta G^\circ_{\text{RB}_{(t)}} - \Delta G^\circ_{\text{RA}_{(t)}}) + (\Delta G^\circ_{\text{A}^-_{(t)}} - \Delta G^\circ_{\text{B}^-_{(t)}}) \right]
\quad \ldots \quad 4.5
\]

where, the first term in the RHS of the equation represents the electrostatic interaction energy difference in aqueous medium of \( \text{RB} \) and \( \text{RA} \) ion pairing in the resin phase at equilibrium.

Second term corresponds to the difference between free energies of hydration of counter-ions \( \text{A}^- \) and \( \text{B}^- \) at infinite dilution in water.
The third and the fourth terms respectively, denote the differences in the corresponding free energies of transfer of the two resinates RB and RA, and the two counter-ions A' and B' form infinitely dilute aqueous solutions to that of infinitely dilute mixed solvent solutions.

Selectivity is governed either by the electrostatic interaction energies or by ion-solvent interactions or by both. The magnitude of electrostatic interaction energy is determined largely by the field strength of the resin fixed ion (ionogenic groups and the counter-ions). For strong base anion exchangers, the resin fixed ion, being a quaternary ammonium group, has a very low field strength. Exchangeable counter-ions in the case of anion exchangers (except F') are also of low field strength compared to cations. Hence the electrostatic interaction free energy difference term will not contribute significantly to \( K_{A'}^{B'} \). Thus the selectivity in the case of low field strength co-ionic exchangers (i.e., strong acid and strong base ion exchangers) is governed by the difference in the free energies of transfer from aqueous medium to mixed solvent medium.

Two important changes in water medium could be considered as contributing upon the addition of 2-isopropoxyethanol. Firstly, it would affect the water structure through the hydrogen bond breaking consequently affecting the water-structure-enforced ion pairing. It also changes the magnitudes of solvation free energy of ions by replacing some of the water molecules in the coordination sphere by the 2-isopropoxyethanol species. The other
important change in aqueous medium upon the addition of 2-isoproxyethanol would be the significant reduction in the dielectric constant of the medium from that of pure water to 80% w/w 2-isoproxyethanol composition.

4.3 EFFECT OF DIELECTRIC CONSTANT OF SOLVENT ON SELECTIVITY

As mentioned in Chapter I, various investigators have studied selectivity behaviour of simple monovalent anions in various water-soluble organic solvents, both protic and aprotic, having comparable dielectric constants. Results of their investigations are presented in Table IV.4, which gives $\log K_{Cl}^{+}$ values on Dowex 1-X8 resin for $\text{ClO}_4^-$-$\text{Cl}^-$ exchange in aqueous and various compositions of mixed solvent media with different solvents having different dielectric constants.

Dielectric constant is a macroscopic property of liquids. It is a well known fact that the strength of ion pair formation between two oppositely charged ions is determined largely by the effective dielectric constant of the medium. The dielectric constant of pure water is 78.54 ($\varepsilon=78.54$) at 298K, and that of 2-isoproxyethanol is 10.5 ($\varepsilon=10.5$). Hence dielectric constants of various compositions of water-2-isoproxyethanol mixed medium would lie between these two extreme values. Thus there will be continuous decrease in dielectric constant from 78.54 to 10.5 upon the addition of 2-isoproxyethanol to water. If the dielectric constant of the solvent medium is the dominant factor
in the determination of selectivity, the addition of 2-isopropoxyethanol to water should decrease the selectivity coefficients on the resin system quite radically with the increase in 2-isopropoxyethanol content.

The magnitude of selectivity coefficient was observed to decrease with increase of 2-isopropoxyethanol content. So apparently at first sight this seems to support the above contention. However on closer examination this correlations seems to fail. For example, propan-2-ol (ε=18.3) and acetone (ε=20.7) have nearly the same value of dielectric constants. But the exchange behaviours of these two solvents for the same ion pair ClO₄⁻-Cl⁻ is different (Table IV.4 and Fig. 4.4). The decrease in selectivity in propan-2-ol-water system is from 1.28 (aqueous medium) to 0.95 (70% w/w propan-2-ol). The corresponding values for water-acetone medium are 1.31 (aqueous medium) and -0.75 (80% w/w acetone). Selectivity in acetone-water decreases rather drastically (Table IV.4 and Fig. 4.4) than in propan-2-ol-water. This is because acetone which is aprotic in nature destroys water structure to a greater extent than propan-2-ol does. The gradual decrease in selectivity in case of protic propan-2-ol is because it forms hydrogen bonding with free water molecules present, which enhances water structure of the medium. At the same time, the hydrocarbon moiety of the alcohol tries to destroy the water structure. As the proportion of organic solvent increases, the destruction of water structure becomes more and more pronounced compared to the strucure formation due to hydrogen bonding.
<table>
<thead>
<tr>
<th>% of Organic solvent (w/w)</th>
<th>Dioxane (E=2.2)</th>
<th>Acetone (E=20.7)</th>
<th>Formamide (E=109.0)</th>
<th>Propan-2-ol (E=18.3)</th>
<th>2-Methoxy Ethanol (E=17.2)</th>
<th>2-Isooproxy Ethanol (E=10.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.64</td>
<td>1.31</td>
<td>1.35</td>
<td>1.28</td>
<td>1.56</td>
<td>1.21</td>
</tr>
<tr>
<td>20.00</td>
<td>1.29</td>
<td>1.23</td>
<td>1.36</td>
<td>1.52</td>
<td>1.32</td>
<td>1.07</td>
</tr>
<tr>
<td>20.20</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>40.00</td>
<td>1.15</td>
<td>0.78</td>
<td>1.41</td>
<td>1.18</td>
<td>1.25</td>
<td>0.88</td>
</tr>
<tr>
<td>44.00</td>
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</tr>
<tr>
<td>60.00</td>
<td>--</td>
<td>0.24</td>
<td>--</td>
<td>1.03</td>
<td>0.98</td>
<td>0.61</td>
</tr>
<tr>
<td>70.00</td>
<td>0.51</td>
<td>--</td>
<td>1.39</td>
<td>0.95</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>70.20</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>80.00</td>
<td>0.06</td>
<td>-0.75</td>
<td>0.82</td>
<td>--</td>
<td>0.56</td>
<td>0.35</td>
</tr>
</tbody>
</table>


(log_{Cl^-}^{ClO_4^-} \text{values on Dowex 1-X4})


f - Present Work (estimated).
Fig. 4.4 Effect of dielectric constant of the solvent on selectivity
Fig. 4.5 Effect of chemical nature of solvent on selectivity

\[ \log K^{\text{CTD}} \]

% composition of organic solvent

2-Methoxyethanol
2-isoproxyethanol

Log aqueous medium (for 2-isoproxyethanol study) is at \( N_{wv} = 0.5 \)
Therefore, selectivity of preferred ion decreases rather slowly in protic solvents compared to that in aprotic solvent. Selectivity in 2-isopropoxyethanol ($\varepsilon=10.5$) should have been less than that in acetone, but the selectivity coefficient values in 2-isopropoxyethanol-water are always higher than those in acetone at higher solvent composition.

In Table IV.4 dioxane is the solvent with lowest dielectric constant ($\varepsilon=2.2$). Hence it would have shown maximum decrease in selectivity on increasing solvent content. But the experimental results show that the selectivity coefficient values in dioxane-water system are higher than the corresponding values in acetone-water (Table IV.4).

In Table IV.4 formamide has highest dielectric constant ($\varepsilon=109$). The effective dielectric constant of different solvent compositions will be higher than that of water. Hence preferred ions should have shown higher selectivity with increased formamide content. But experimental data do not support this contention.

A cursory examination of data indicates that dielectric constant of the medium is not the sole factor governing selectivity, and in fact, chemical property of added organic solvent, such as protic or aprotic nature, polarisation, etc., rather than dielectric constant, has a greater influence on the selectivity (Table IV.4 and Fig. 4.5).
Further in 2-methoxyethanol and 2-isopropoxyethanol, the protic nature of alcohols decreases due to +I effect of -OCH$_3$, and -OC$_3$H$_7$ respectively. Among these two substituted alcohols, due to +I effect 2-isopropoxyethanol seems to behave more like aprotic than 2-methoxyethanol. Accordingly, the decrease in selectivity in 2-isopropoxyethanol may be expected to be more than 2-methoxyethanol. Results in Table IV.4 and Fig. 4.5 agree well with expectations.

4.4 EFFECT OF VARIATION OF CROSS-LINKING (%DVB) OF THE EXCHANGER ON SELECTIVITY

To understand the effect of cross-linking (% DVB) on selectivity behaviour, studies were carried out on differently cross-linked resins like Dowex 1- X8 and Dowex 1-X4 and results were compared with those on Tulsion A-27 (macroreticular). Table IV.1 gives logK$^{B -}_{a_{Cl}}$ values for ClO$_4^-$, CNS$, I^-$ and NO$_3^-$ in aqueous and mixed media of various compositions on these resins. Variations of logK$^{B -}_{a_{Cl}}$ as a function of 2-isopropoxyethanol content of the medium for each cross-linkage is shown in Figures 4.6, 4.7, 4.8 and 4.9.

The number of water molecules available per exchange site in an exchanger generally decreases with an increase of cross-linkage, because there is decrease in swelling of resin bed with increase in the DVB content. In other words, the electrolyte concentration in the resin phase increases with cross-linkage, Fig. 4.6.
Fig. 4.6 $\log K_{\text{act}}$ vs $\%$ 2-isopropanol (w/w) on Tulsion A-27 (MP), Dowex 1-X8 and Dowex 1-X4
Fig. 4.7 $\log K_{\alpha T}^{\infty}$ vs % 2-isopropoxyethanol (w/w) on Tulsion A-27 (MP), Dowex 1-X8 and Dowex 1-X4
Fig. 4.8 $\log K_{CT}^{*}$ vs % 2-isoproxyethanol (w/w) on Tulsion A-27 (MP), Dowex 1-X8 and Dowex 1-X4.
Fig 4.9: $\log K_{\text{act}}^{\text{NO}}$ vs % 2-isopropoxyethanol (w/w) on Tulsion A-27 (MP), Dowex 1-X8 and Dowex 1-X4
and therefore, the selectivity of preferred ion should increase with increase in cross-linkage irrespective of the solvent composition in the external phase.

When cross-linking is the only parameter varied, keeping all other constant (like resin fixed ion, counter-ions and the medium), change in the electrolyte concentration in the resin phase is the most important factor expected. The effect of the four terms in equation 4.5, remains in the same ratio, the net free energy change being more negative with increase of cross-linking. Similar observation of the effect of cross-linking with cations and anions on corresponding strong exchangers were reported by Myers et al.^{19}

The selectivity sequence of ClO$_4^-$ on these resins in aqueous medium is Tulsion A-27 (MP) > Dowex 1-X8 > Dowex 1-X4. The higher selectivity of ClO$_4^-$ on Tulsion A-27 (macroreticular) on aqueous medium is because of its macroporous nature. This facilitates free movement of bigger ClO$_4^-$ ion in the resin phase, resulting in predominance of water-structure-enforced ion pairing. As the organic solvent content increases, the external solution phase becomes rich in 2-isopropanol. The bigger ClO$_4^-$ ion is better solvated in external phase resulting in drastic decrease in selectivity of ClO$_4^-$ ion. This type of behaviour is not found in highly cross-linked resin Dowex 1-X8, and therefore, selectivity sequence of ClO$_4^-$ in mixed medium at higher solvent composition is Tulsion A-27 (MP) = Dowex 1-X8 > Dowex 1-X4 (Fig. 4.6).
As for the CNS\(^-\) ion, the expected sequence Tulsion A-27 (MP) > Dowex 1-X8 > Dowex 1-X4 is observed in aqueous medium and very low solvent compositions. At higher solvent compositions the cross-linking effect is not significant for this ion (Fig. 4.7).

For I\(^-\) and NO\(_3\)^-, the expected cross-linking effect is observed both in aqueous and mixed solvent medium (Figs. 4.8 and 4.9).

4.5 EFFECT OF CHANGING RESIN FIXED ION ON SELECTIVITY

To understand the selectivity behaviour on changing the nature of the resin fixed ion from strongly basic (quaternary ammonium) to weakly basic (tertiary ammonium) on the exchange studies of ClO\(_4\)^-Cl\(^-\) and NO\(_3\)^-Cl\(^-\) were carried out on weak base resins Tulsion A-2X (gel) and Amberlyst A-21 (macroreticular). Since these resins undergo hydrolysis at higher pH exchange studies were made in acidic medium with H\(^+\) as co-ion. The results obtained are summarised in Table IV.5 and Figs. 4.10 to 4.13.

Substitution of tertiary amine (NR\(_2\)H\(^+\)) group for the quaternary group (NR\(_3\)) yields a weak base resin. The tertiary ammonium ion is also a large ion, but differs in the respect that it has a proton which probably carries much of the charge of the ion, and this can form hydrogen bond with water and other molecules of the base and the anion. Thus resin fixed ion in weak base resin provides a hydrophilic site which is missing in strong
base resins containing quaternary ammonium group as a resin fixed ion. Due to this reason the tertiary ammonium group \((\text{NR}^+)_2\text{H}^+\) cannot participate in water-structure-enforced ion pairing as much as quaternary ammonium ion \((\text{NR}^+)_3\) can.

The selectivity order in weak base exchangers Tuslion A-2X (gel) and Amberlyst A-21 (macroreticular) in aqueous medium is \(\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^-\), which is the same as on strong base exchangers. In the case of Tuslion A-2X (gel) the selectivity values of \(\text{ClO}_4^-\) and \(\text{NO}_3^-\) gradually decrease with increase in 2-isopropanol content. The selectivity reversal is observed around 55% solvent composition for \(\text{NO}_3^-\)-\(\text{Cl}^-\) exchange, where \(\text{Cl}^-\) being preferred to \(\text{NO}_3^-\). The initial large difference in the selectivity magnitudes of \(\text{ClO}_4^-\) and \(\text{NO}_3^-\) goes on decreasing as solvent composition increases because of greater ion solvent interaction for \(\text{ClO}_4^-\) ion in mixed solvent medium. The selectivity values of \(\text{ClO}_4^-\) and \(\text{NO}_3^-\) are lower than those on strong base exchangers in aqueous medium and at all compositions in mixed medium. However, at higher solvent compositions the change is not significant for \(\text{NO}_3^-\) ion.

In the case of Amberlyst A-21 too selectivity of \(\text{ClO}_4^-\) and \(\text{NO}_3^-\) decreases with increase in 2-isopropanol content. The selectivity reversal is observed around 75% solvent composition for \(\text{ClO}_4^-\) and around 65% for \(\text{NO}_3^-\). The initial large difference in selectivity magnitudes of \(\text{ClO}_4^-\) and \(\text{NO}_3^-\) goes on decreasing as solvent composition increases as in the case of Tuslion A-2X (gel).
### TABLE IV.5
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS FOR ANIONS ON AMBERLYST A-21 AND TULSION A-2X (GEL) IN 2-ISOPROPOXYETHANOL-WATER MIXED MEDIUM AT 303±1K

<table>
<thead>
<tr>
<th>Anion (B⁻)</th>
<th>log K_B⁻/a_Cl⁻</th>
<th>0%</th>
<th>20%</th>
<th>40%</th>
<th>60%</th>
<th>80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td></td>
<td>1.18</td>
<td>1.08</td>
<td>0.72</td>
<td>0.28</td>
<td>-0.06</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td></td>
<td>0.57</td>
<td>0.45</td>
<td>0.23</td>
<td>0.04</td>
<td>-0.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AMBERLYST A-21 (MP)</th>
<th>TULSION A-2X (GEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td>1.04</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1.00</td>
</tr>
</tbody>
</table>

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Fig. 4.10 $\log K_{oe}^H$ vs % 2-isopropoxyethanol (w/w) on Tulsion A-2X
Fig. 4.11 $\log K_{\text{wct}}^R$ vs % 2-isopropoxyethanol (w/w) on Amberlyst A-21 (MP)
Fig. 4.12 $\log K^{\text{CE}}_{\text{CT}}$ vs % 2-isopropoxyethanol (w/w) on Amberlyst A-21 (MP) and Tulsion A-2X

Amberlyst A-21 (MP)
Tulsion A-2X

Fig. 4.12 $\log K^{\text{CE}}_{\text{CT}}$ vs % 2-isopropoxyethanol (w/w) on Amberlyst A-21 (MP) and Tulsion A-2X
Fig. 4.13 $\log K_{x/y}$ vs % 2-isopropoxyethanol (w/w) on Amberlyst A-21 (MP) and Tulsion A-2X
The selectivity values of these ions on Amberlyst A-21 (macroreticular) are higher than those on Tulsion A-2X (gel). The higher selectivity of $\text{NO}_3^-$ on Amberlyst A-21 than on strong base exchangers is rather difficult to understand. Macroreticular resins contain pores or channels several hundred nanometers in diameter even in dry state. Increase in the usable capacity of macroporous resins is due to the penetration of electrolyte in the grains by Donnan equilibrium. The diffusion theory is less predominant in the case of macroreticular resins due to its high porosity. As these are hard, rigid, furrowed sponges of channels, it follows therefrom that a great proportion of functional sites is found to be in direct contact with the solution, and that distribution is partly replaced by the easier migration in the solution contained in the pores of grains.

CONCLUSION

The observed results of the exchange behaviour of simple anions in water-2-isopropanol mixed solvent media are explained qualitatively on the basis of models proposed by Diamond and Reichenberg. The factors such as electrostatic interaction, ion-water interaction and medium effect on the resin phase and in the external solution phase which contribute significantly in the anion exchange process are rather difficult to explain quantitatively due to the lack of necessary thermodynamic data. However, some general remarks can be drawn from the observed experimental results.
Firstly, the macroscopic dielectric constant value of the solvent medium no doubt, affects the degree of ion-pair formation, and hence influences the transport and thermodynamic properties of the electrolyte solutions. But it appears that protic and aprotic nature of the solvent is more dominating factor than its dielectric constant in governing ion exchange selectivity.

Further, among 2-methoxyethanol and 2-isopropoxyethanol, the latter is more aprotic due to +I effect of -OCH₃ than -OCH₃. Accordingly, selectivity magnitudes are generally lower in 2-isopropoxyethanol compared to those in 2-methoxyethanol. Thus, we may expect lower selectivity magnitudes in the case of -OC₄H₉ substituted 2-butoxyethanol than 2-isopropoxyethanol due to more +I effect of -OC₄H₉. Further study in water-2-butoxyethanol mixed medium would throw light on this contention.

The cross-overs between CNS⁻ and I⁻ in mixed medium is attributed to the non-spherical nature of CNS⁻ and greater CNS⁻-2-isopropoxyethanol interaction (ion-solvent interaction).

Evaluation of selectivity coefficients on the basis of the measured capacities and concentration of only one ion in the external solution phase is likely to introduce unavoidable errors in the calculation of \( K^B \). Such discrepancies could be avoided by estimating both the counter-ions simultaneously taking into consideration of volume changes in the external solution during the exchange process. Determination of activity of water in
water-2-isopropoxyethanol media by isopiestic method would greatly facilitate the interpretation of the exchange behaviour in water-2-isopropoxyethanol mixed media. A theory which can provide a quantitative description of ion exchange selectivity in terms of physicochemical properties of both resin and external solution phase is of great need.
REFERENCES


2. D. Reichenberg. (ibid Chapter 7).


