CHAPTER IV

DISCUSSION
The results of exchange studies of $\text{ClO}_4^-$ - $\text{Cl}^-$, $\text{CNS}^-$ - $\text{Cl}^-$ and $\text{NO}_3^-$ - $\text{Cl}^-$ systems, on strong base exchangers such as Dowex 1-X8, Dowex 1-X4 and Tulsion A-27 (macroreticular) and also the exchange studies of $\text{ClO}_4^-$ - $\text{Cl}^-$ and $\text{NO}_3^-$ - $\text{Cl}^-$ on weak base exchangers Amberlyst A-21 and Tulsion A-2X in aqueous and 2-butoxyethanol-water mixed media of various compositions are discussed here. All the exchange studies are carried out at 303±1K and at an ionic strength of 0.05M. The results are discussed in terms of models proposed by Diamond and Reichenberg under the following headings.

I) Selectivity behaviour in
   i) Aqueous medium and
   ii) 2-butoxyethanol-water mixed medium.

II) Effect of Dielectric constant of the solvent on selectivity.

III) Effect of variation of cross linkage (%DVB) of the exchangers on selectivity.

IV) Effect of changing the resin fixed coion on selectivity.

Among different factors that contribute to the anion exchange selectivity (cf Chapter II of this thesis). The solvent medium of the external solution plays a dominant role. The solvent properties of importance in this context are the
dielectric constant of the medium, protic or aprotic, polar or non-polar nature of the solvents. The general assumption of solvent medium as a dielectric continuum is no longer accepted particularly with electrolyte solution. Experimental evidence of ion exchange have accumulated to prove convincingly that the solvent structure (microscopic) especially of water plays a dominant role in anionic and cationic exchange processes. The addition of foreign species such as ions, inert molecules or another solvent is known to alter the hydrogen bonding nature of the water and hence its structure. According to Diamond et al., "water structure enforced ion pairing" plays a significant role in ion 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 an organic solvent. Bhat studied the effect of addition of methanol (a protic solvent) on simple monovalent anion exchange and Narke investigated the influence of addition of dioxane (an aprotic solvent) on the monovalent anion exchange. Narke and co-workers have extended the study to other water-soluble solvents such as DMF, formamide, propan-2-01, ethylene glycol, 2-ethoxyethanol, acetone and 2-Methoxy ethanol.
Alcohols in general are similar to water in their capacity to form hydrogen bonding but to a lesser degree than in water. Addition of simple alcohols such as methanol and ethanol, therefore will effectively reduced the degree of hydrogen bonding in mixed solvent medium. Krishnan et al.\textsuperscript{13} have reported their results of anion exchange studies in ethanol-water medium. It is known that the length of hydrocarbon chain attached to the carbon containing the alcoholic group determines the hydrophobic ion pairing in water. Math\textsuperscript{8} studied the simple monovalent anion exchange process in water-propan-2-\textsubscript{0}1 mixed medium. Hoskeri\textsuperscript{10} and Patil\textsuperscript{12} studied the monovalent anion exchange process in 2-ethoxyethanol and 2-methoxyethanol mixed medium respectively. They showed that 2-ethoxy and 2-methoxyethanols behaved more like aprotic solvents, and aprotic nature is more in the case of 2-ethoxyethanol than 2-methoxyethanol. Extending their studies, it was thought worthwhile to study the exchange behaviour in mixed medium involving 2-butoxy ethanol which has substitution of butoxy group comparatively larger in size.

4.1 Selectivity Behaviour in

i) Aqueous medium.

ii) 2-butoxyethanol-water mixed medium.
4.1.1. Aqueous medium.

The averaged 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 (macrocyclic) are presented in Table IV.1.

The order of selectivity observed in the present work, on the three strong base exchangers in aqueous medium is $\text{ClO}_4^- > \text{CNS}^- > \text{NO}_3^- > \text{Cl}^-$. This is the order expected from their crystallographic radii and data in the literature. From available free energy data (Table IV.2) and change in standard free energy values, the selectivity observed is also the same i.e. $\text{ClO}_4^- > \text{CNS}^- > \text{NO}_3^- > \text{Cl}^-$. This selectivity order can be explained by the models proposed by Diamond and Reichenberg, and is also in good agreement with the data presented by previous investigators.

Diamond considers ion-water and water-water interactions 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 big ion such as $\text{ClO}_4^-$ with
TABLE IV.1
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS FOR THE ANIONS ON DOWEX 1-X8, DOWEX 1-X4 AND TULSION A-27(MP) IN 2-BUTOXYETHANOL-WATER MIXED MEDIUM AT 303±1K

<table>
<thead>
<tr>
<th>Anion (B⁻)</th>
<th>logKₐB⁻Cl⁻ in % of 2-Butoxyethanol (W/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00</td>
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<tr>
<td>ClO₄⁻</td>
<td>1.30</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>0.82</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.57</td>
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</table>

DOWEX 1-X8

<table>
<thead>
<tr>
<th>Anion (B⁻)</th>
<th>logKₐB⁻Cl⁻ in % of 2-Butoxyethanol (W/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td>1.10</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>0.72</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.40</td>
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</table>

DOWEX 1-X4

<table>
<thead>
<tr>
<th>Anion (B⁻)</th>
<th>logKₐB⁻Cl⁻ in % of 2-Butoxyethanol (W/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td>1.37</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>0.98</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.62</td>
</tr>
</tbody>
</table>

TULSION A-27(MP)
low charge density. Cl\textsuperscript{-} 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 up of water structure which in turn decreases the entropy of the system. A bigger ion such as ClO\textsubscript{4}\textsuperscript{-} with low charge density also tries to create a cavity and tighten up the water structure which might reduce the entropy of the system further. But in order to avoid further decrease in entropy, the two ions (R\textsuperscript{+} and bigger ClO\textsubscript{4}\textsuperscript{-} anion) are forced into 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 order ClO\textsubscript{4}\textsuperscript{-} > CNS\textsuperscript{-} > NO\textsubscript{3}\textsuperscript{-} > Cl\textsuperscript{-}. Hence the observed selectivity order ClO\textsubscript{4}\textsuperscript{-} > CNS\textsuperscript{-} > NO\textsubscript{3}\textsuperscript{-} > Cl\textsuperscript{-} in aqueous medium in the present investigation is thus explained quite satisfactorily by Diamond's model.

Though the Diamond's model explains the anion 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.
Where RA and RB are A and B forms of an ion exchange resin respectively and A^- and B^- are counter ions. The thermodynamic equilibrium constant $K_{A^-}^{B^-}$ for such a reaction is given by

$$\ln K_{A^-}^{B^-} = -\frac{1}{RT}(\Delta G_{A^-}^{B^-})_{h}$$

(4.2)

$$\ln K_{A^-}^{B^-} = -\frac{1}{RT}[(\Delta G_{RB}^{B^-} - \Delta G_{RA}^{B^-}) + (\Delta G_{A^-}^{B^-} - \Delta G_{B^-}^{B^-})]$$

(4.3)

Where $\Delta G_{A^-}^{B^-}$ is corresponding change in the standard free energy of the process, $\Delta G_{RB}^{B^-}$ and $\Delta G_{RA}^{B^-}$ are the standard free energy change of B and A forms of the resin and $\Delta G_{A^-}^{B^-}$ and $\Delta G_{B^-}^{B^-}$ 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 eq (4.3), it is evident that the thermodynamic equilibrium constant $K_{A^-}^{B^-}$ 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 \( \text{NO}_3^- \), \( \text{CNS}^- \), and \( \text{ClO}_4^- \) have relatively less negative free energy of hydration compared to \( \text{Cl}^- \). The expected selectivity order in aqueous medium should be \( \text{ClO}_4^- > \text{CNS}^- > \text{NO}_3^- > \text{Cl}^- \). The observed selectivity order in aqueous medium in the present investigation (Table IV.1) is in good agreement with the expectation.

The dominance of free energy of hydration in governing the selectivity has also been observed in cation exchange processes. The free energies of hydration for alkali ions are shown in Table IV.3. The selectivity order of ions is \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ \), because the ion with more
### TABLE IV.2

<table>
<thead>
<tr>
<th>Anion</th>
<th>Radius r (Crystallographic in Å)</th>
<th>Free energy of hydration (-\Delta G^\circ_{i}) in KJ mole(^{-1})</th>
<th>Diff. between free energies of hydration (-\Delta G^\circ_{i} \text{-} \Delta G^\circ_{\text{Cl}}) in KJ mole(^{-1})</th>
<th>Calculated standard free energy changes of an ion exchange reaction RC1 (\leftrightarrow) RB + Cl(^{-})</th>
<th>(\Delta G^\circ_{\text{Cl}}) in KJ mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^{-})</td>
<td>--</td>
<td>464.42</td>
<td>133.88</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>F(^{-})</td>
<td>1.33</td>
<td>447.68</td>
<td>117.15</td>
<td>--</td>
<td>-4.14</td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>1.81</td>
<td>330.53</td>
<td>0.00</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td>Br(^{-})</td>
<td>1.96</td>
<td>301.24</td>
<td>-29.28</td>
<td>--</td>
<td>2.38</td>
</tr>
<tr>
<td>I(^{-})</td>
<td>2.20</td>
<td>267.77</td>
<td>-67.66</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>NO(_3)^{-}</td>
<td>2.0 - 2.5</td>
<td>288.69</td>
<td>-41.84</td>
<td>3.138</td>
<td>3.01</td>
</tr>
<tr>
<td>CNS(^{-})</td>
<td>--</td>
<td>230.12</td>
<td>-100.41</td>
<td>6.82</td>
<td>7.86</td>
</tr>
<tr>
<td>ClO(_4)^{-}</td>
<td>2.9</td>
<td>209.20</td>
<td>-121.33</td>
<td>9.83</td>
<td>11.25</td>
</tr>
<tr>
<td>IO(_4)^{-}</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

* estimated

l. Present work.
### TABLE IV.3

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius r (Crystallo-Graphic) in Å</th>
<th>Free energy of hydraton ΔG( ^{\circ} _{T(h)} ) in KJ/mole</th>
<th>ΔG( ^{\circ} _{T(h)} ) - ΔG( ^{\circ} _{B(h)} ) in KJ/mole</th>
<th>Standard free energy change of cation exchange ΔG( ^{\circ} _{B(h)} ) Na</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>--</td>
<td>1087.84</td>
<td>676.13</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(^+)</td>
<td>0.70</td>
<td>510.86</td>
<td>99.16</td>
<td>1.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.97</td>
<td>411.70</td>
<td>0.00</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.33</td>
<td>337.23</td>
<td>-74.47</td>
<td>-1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>1.49</td>
<td>315.89</td>
<td>-95.81</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>1.67</td>
<td>283.67</td>
<td>-128.03</td>
<td>-1.38</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) K.H.Stern and E.S.Emis, Chem. Revs., 59 75 (1959)


negative free energy of hydration is less preferred by the resin phase.

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

The situation in anion exchange process is in no way better for example, in $NO_3^-$ - $Cl^-$ exchange, the calculated free energy of hydration is $-41.84$ kJ mol$^{-1}$ (column 4 of Table IV.2) whereas the corresponding value obtained from ion exchange equilibria is $-3.30$ kJ mol$^{-1}$ which is about twelve times less.

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

4.1.2 Mixed medium.

With the addition of 2-butoxyethanol, the water structure in the external solution phase is destroyed to a greater extent; because the 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 lesser extent. Consequently the difference in the structure of water in the two phases decreases with increased 2-butoxyethanol content.

Hence the selectivity of preferred anion in aqueous medium should decrease with increase in 2-butoxyethanol content because of the change from predominance of water structure enforced ion pairing in aqueous medium to Bjerrum type ion pairing in mixed solvent medium.

It can be seen from the Table IV 1 and Figs. 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-butoxyethanol content. The decrease in selectivity with an increase in 2-butoxyethanol content is rather steep in the
Fig. 4.1 $\log K_{aCl}^B$ vs % 2-butoxyethanol (w/w) on Dowex 1-X8.
Fig. 4.2 $\log K_{a_{Cl}}^{B}$ vs $2$-butoxyethanol (w/w) on Dowex 1-X4.
Fig. 4.3 log $K_{Cl}$ vs $\%$ 2-butoxyethanol (w/w) on Tulsion A-27 (MP)
case of $\text{ClO}_4^-$ and $\text{CNS}^-$ compared to that in the case of $\text{NO}_3^-$. There is also selectivity reversal (negative log $K$ values) for $\text{NO}_3^-$ on Dowex 1-X8 around 80% and on Dowex 1-X4 around 60%. For $\text{CNS}^-$, the selectivity reversal is around 80% solvent composition on Dowex 1-X8, and Dowex 1-X4.

As has been already seen, the selectivity order on all the strong base resins studied in aqueous medium is $\text{ClO}_4^- > \text{CNS}^- > \text{NO}_3^- > \text{Cl}^-$. However, there is crossover of selectivity between $\text{CNS}^- - \text{Cl}^-$ and $\text{NO}_3^- - \text{Cl}^-$ on Dowex 1-X8 and Dowex 1-X4 at higher 2-butoxyethanol content where the selectivity order is $\text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^- > \text{CNS}^-$. This observation is analogous with the observations made by Starobinets et al.,$^{16}$ in their anion exchange studies in water-DMF mixed medium. The reverse order of selectivity in water-DMF system was attributed to a weak solvation of anions in the aprotic amide. The change in the order of selectivity in present investigation can be attributed to 2-butoxyethanol behaving more like an aprotic solvent.

V.T.Athavale et al.,$^{17}$ in their cation exchange studies on strong and weak acid cation exchangers have reported similar change in the order of affinities $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+$ in aqueous medium to $\text{Li}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{K}^+$ in mixed
solvent medium. Bhat has reported similar crossover between CNS⁻ and I⁻ in water-methanol mixed medium. Athavale et al. attributes the anomalous behaviour of NH₄⁺ to its non-spherical nature. The anomalous behaviour of CNS⁻ in mixed medium in the present investigation may therefore be attributed to non-spherical nature of CNS⁻. Further, greater CNS⁻ - 2-butoxyethanol (ion-solvent) interaction in mixed solvent medium may also contribute significantly to the crossover behaviour of CNS⁻. The selectivity reversal in the case of NO₃⁻ - Cl⁻ exchange at 2-butoxyethanol rich compositions (60% and 80%) could be explained on the basis that at higher concentration of organic solvent in external phase, the relative concentration of water in resin phase will be higher than in the external solution phase. Such an observation in the case of water-dioxane was reported by Diamond et al.

4.2 Effect of dielectric constant of the solvent on the 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 with some having comparable dielectric constants. The
results of their investigations are presented in Table IV.4. Table IV.4 gives, $\log K^\text{\textsubscript{ClO}_4^- Cl}^-_{\text{AcI}}$ values on Dowex 1-X8 resin for ClO$_4^-$ - Cl$^-$ exchanges in aqueous and various compositions of 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 role played by dielectric constant of the medium on selectivity in ion exchange reaction is well seen in Table IV.4.

The dielectric constant of pure water is 78.54 at 298K and that of 2-butoxyethanol is 9.3. Hence, dielectric constants of various compositions of water-2-butoxyethanol mixed medium would be between these two extreme values. From Table IV.4 it is seen that the selectivity of preferred ion decreases with increase in the organic solvent content. If dielectric constant is the sole factor governing selectivity, then the selectivity coefficients values should be comparable for solvents having comparable dielectric
TABLE IV.4
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS IN ORGANIC SOLVENT-WATER MEDIUM ON DOWEX 1-X8 (Cl FORM) AT 303+1K (TOTAL IONIC STRENGTH = 0.05M)

<table>
<thead>
<tr>
<th>log $K_a$</th>
<th>% of organic solvent (w/w)</th>
<th>2-Butoxy ethanol</th>
<th>2-Ethoxy ethanol</th>
<th>2-Methoxy ethanol</th>
<th>Propan-2-ol</th>
<th>Methanol</th>
<th>Formamide</th>
<th>Acetone</th>
<th>DMF</th>
<th>Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(E=2.2)</td>
<td>(E=12.5)</td>
<td>(E=17.2)</td>
<td>(E=18.3)</td>
<td>(E=32.6)</td>
<td>(E=19)</td>
<td>(E=109)</td>
<td>(E=20.7)</td>
<td>(E=37.6)</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>1.64</td>
<td>1.45</td>
<td>1.31</td>
<td>1.35</td>
<td>1.98</td>
<td>1.28</td>
<td>1.56</td>
<td>1.33</td>
<td>0.57</td>
</tr>
<tr>
<td>20.00</td>
<td></td>
<td>1.29</td>
<td>0.81</td>
<td>1.23</td>
<td>1.36</td>
<td>--</td>
<td>1.52</td>
<td>1.32</td>
<td>1.33</td>
<td>0.75</td>
</tr>
<tr>
<td>20.20</td>
<td></td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>1.49</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>40.00</td>
<td></td>
<td>1.15</td>
<td>0.33</td>
<td>0.78</td>
<td>1.41</td>
<td>--</td>
<td>1.18</td>
<td>1.25</td>
<td>0.98</td>
<td>0.81</td>
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<td>44.00</td>
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<td>1.59</td>
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<td>60.00</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>1.03</td>
<td>0.98</td>
<td>0.81</td>
<td>0.57</td>
</tr>
<tr>
<td>70.00</td>
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<td>-0.44</td>
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</tr>
<tr>
<td>80.00</td>
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<td>0.06</td>
<td>-0.91</td>
<td>-0.75</td>
<td>0.82</td>
<td>--</td>
<td>0.56</td>
<td>0.57</td>
<td>0.57</td>
<td>0.42</td>
</tr>
</tbody>
</table>

* estimated

d. Y.P.Vyasmudri and C.S.Narke, Karnatak University Journal (Sc.) 1988 Vol. XXXII

i. Present work.
constant values. On closer examination of Table IV.4, it is clear that this expectation does not hold good.

For example, methanol ($\varepsilon = 32-63$) and DMF ($\varepsilon = 37.6$) have nearly the same values of dielectric constant. But the exchange behaviour of these two solvents for the same ion pair $\text{ClO}_4^-\text{Cl}^-$ is different. (Table IV.4). The selectivity decrease in DMF-water is more steep than that in methanol-water mixed media.

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 on DMF-water (Table IV.4).

In Table IV.4 formamide has highest dielectric constant ($\varepsilon = 109$). The effective dielectric constant of different solvent composition will be higher than that of water. Hence preferred ion should have shown higher selectivity with increase in formamide content. But experimental data do not support this contention.
The dielectric constant of 2-butoxyethanol is 9.3 and that of dioxane and DMF are 2.2 and 37.6 respectively. If the dielectric constant is an important parameter, governing selectivity, the selectivity values in 2-butoxyethanol should lie between those for DMF and Dioxane. But Table IV.4 and Figure 4.5 show that it does not hold good.

A cursory examination of the data indicates that the 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 selectivity.

Further, in 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol, the protic nature of alcohols decreases due to +I effect of $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ and $-\text{C}_4\text{H}_9$ respectively. Among these three substituted alcohols due to +I effect 2-butoxyethanol seems to behave more like an aprotic than 2-methoxy and 2-ethoxyethanols. Accordingly, the decrease in selectivity in 2-butoxy ethanol may be expected to be more than 2-methoxy and 2-ethoxyethanols. The results in Table IV.4 and Figure 4.4 agree well with the expectation.
Fig. 4.4 Effect of solvent dielectric constant on selectivity
Fig. 4.5 Effect of solvent dielectric constant on selectivity
4.3 Effect of variation of crosslinkage (% DVB) of the exchangers on selectivity

To understand the effect of cross linkage on selectivity behaviour, studies were carried out on different cross linked resins like Dowex 1-X4 and Dowex 1-X8. Table IV.1 gives the log $K^{B^-}_{aCl^-}$ values for $ClO_4^-$, $CNS^-$ and $NO_3^-$ in aqueous and mixed medium of various compositions on strong base anion exchange resins Dowex 1-X4 and Dowex 1-X8 at 303 ± 1K. Variations of log$K^{B^-}_{aCl^-}$ as a function of 2-butoxyethanol content of the medium for each crosslinkage is shown in Figures 4.6 to 4.8. The general observations on all these figures is that the selectivity coefficient of preferred ion generally increases with an increase in % DVB.

The number of water molecules available per exchange site in an exchanger generally decreases with the increase of crosslinkage, because there is decrease in swelling of the resin bead with increase in the DVB content. In other words the electrolyte concentration in the resin phase increases with crosslinkage. Therefore the selectivity of preferred ion should increase with increase in crosslinkage irrespective of the solvent compositions in the external phase. The
observations made in the present investigation are good agreement with this (Table IV.1 figures 4.6 to 4.8)

When crosslinkage is the only parameter varied keeping all other constant (like resin fixed coion, counter ions and the medium), change in the electrolyte concentration in the resin phase is the most important effect expected. The effect of the four terms in the equation (4.5), remains in the same ratio, the net free energy change being more negative with increase of crosslinkage. A similar observations of the effect of crosslinkage with cations and anions on corresponding strong exchangers were reported by Myers et al.20.

As expected the selectivity sequence of $\text{ClO}_4^-$, $\text{CNS}^-$ and $\text{NO}_3^-$ on the resins studied is $X_8 > X_4$ in both aqueous and mixed medium.

In the case of Tulsion A-27 (Macroreticular) resin the selectivity of preferred anions is more than Dowex 1-X4 and Dowex 1-X8 in aqueous as well as in mixed solvent media. This is because of its higher porosity. The pore sizes of macroreticular resins are of several hundred nanometers in diameter and surface area of upto 100 m$^2$/g. Because of this,
Fig. 4.6 log $K_{Cl}$ vs %2-butoxyethanol (w/w) on Tulsion A-27 (MP), Dowex 1-X8, and Dowex 1-X4.
Fig. 4.7 $\log K^*$ vs $\%$ 2-butoxyethanol (w/w) on Tulsion A-27

- Tulsion A-27 (MP)
- Dowex 1-X8
- Dowex 1-X4
Fig. 4.8 log $\frac{K^+NO_3^-}{a_{Cl^-}}$ vs %2-butoxyethanol (w/w) on Tulsion A-27 (MP), Dowex 1-X8, and Dowex 1-X4.
larger molecules can also penetrate the interior and selectivity of preferred anions is more. The selectivity sequence of $\text{ClO}_4^-$, $\text{CNS}^-$ and $\text{NO}_3^-$ on the resins studied is $\text{Tulsion A-27 (macoreticular)} > \text{Dowex 1-X8} > \text{Dowex 1-X4}$ in both aqueous and mixed medium (Figs. 4.6 to 4.8)

4.4. Effect of Changing the Resin Fixed Co-ion on Selectivity

To understand the selectivity behaviour on changing the nature of the resin fixed co-ion from strongly basic (quaternary ammonium) to weakly basic (tertiary ammonium) ion the exchange studies of $\text{ClO}_4^- - \text{Cl}^-$ and $\text{NO}_3^- - \text{Cl}^-$ were carried out on weak base resins Tulsion A-2X (gel) and Amberlyst A-21 (macoreticular). Since these resins undergo hydrolysis at higher pH, exchange studies were made in acidic medium with $\text{H}^+$ as co-ion. The results obtained are summarised in Table IV.5 and Figures 4.9 to 4.12.

The selectivity order in the weak base exchangers in aqueous medium is $\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^-$ which is the same as on strong base exchanges. In the case of Tulsion A-2X (gel) the selectivity values of $\text{ClO}_4^-$ and $\text{NO}_3^-$ are lower than those on strong base exchangers, in aqueous and at all composition in mixed media. The selectivity of $\text{ClO}_4^-$ and $\text{NO}_3^-$ gradually
TABLE IV.5
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS FOR THE ANIONS ON TULSION A-2X(gel) AND AMBERLYST A-21 IN 2-BUTOXYETHANOL-WATER AT 303±0 1K

<table>
<thead>
<tr>
<th>Anion (B⁻)</th>
<th>logK_B⁻_aCl⁻</th>
<th>0.00</th>
<th>20.0</th>
<th>40.0</th>
<th>60.0</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td></td>
<td>0.65</td>
<td>0.52</td>
<td>0.32</td>
<td>0.09</td>
<td>-0.26</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td></td>
<td>0.34</td>
<td>0.15</td>
<td>-0.03</td>
<td>-0.21</td>
<td>-0.35</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td></td>
<td>0.95</td>
<td>0.76</td>
<td>0.51</td>
<td>0.29</td>
<td>-0.13</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td></td>
<td>0.41</td>
<td>0.23</td>
<td>-0.05</td>
<td>-0.12</td>
<td>-0.33</td>
</tr>
</tbody>
</table>
Fig. 4.9 $\log K_{a\text{Cl}}^B$ vs %2-butoxyethanol (w/w) on Tulsion A-2X
Fig. 4.10 log $K_{aCl}^{-}$ vs % 2-butoxyethanol (w/w) on Amberlyst A-21
Fig. 4.12 \( \log K^\text{NO}_3^\text{aCl} \) vs \% 2-butoxyethanol (w/w) on Tulsion A-2X and Amberlyst A-21.
decreases with increase in the 2-butoxyethanol content. The selectivity reversal is observed around 80% composition for ClO$_4^-\text{-Cl}^-$ exchange and around 60% for NO$_3^-\text{-Cl}^-$ exchange. The initial large difference in selectivity magnitudes of ClO$_4^-$ and NO$_3^-$ goes on decreasing as solvent composition increases.

Substitution of tertiary amine (-NR$_2^+$) group for the quaternary group (-NR$_3^+$) yields a weak base resin. The tertiary ammonium ion is also a large ion but differ in the respect that it has the proton which probably carries much of the charge of the ion and this can form hydrogen bond to water and other molecules of the base and the anion. Thus the resin fixed coion, in weak base resin provides a hydrophilic site which is missing in strong base resins containing quaternary ammonium group as resin fixed coion. Due to this reason, the tertiary ammonium group (-NR$_2^+$) can not participate in water structure enforced ion pairing as much as quaternary ammonium in (-NR$_3^+$) can. Further more there is a possibility of hydrogen bonding although weakly to small basic ions such as F$^-$ and the resin phase can be more attractive to such ions than is the case with strong base resins. Hence it is expected that the weak base resin should show a somewhat enhanced selectivity for smaller basic anions (NO$_3^-$) and a somewhat reduced
affinity for large hydrophobic ions like $\text{ClO}_4^-$. In the case of Amberlyst A-21 the selectivity decreases with increase in 2-hydroxyethanol content. However, the selectivity magnitudes are always higher than those on Tulsion A-2X (weak base gel) but lower than those on strong base resins. Amberlyst A-21 is a macroreticular weak base resin which contains pores or channels several hundred nanometres in diameter even in the dry state. The increase in the usable capacity of macroporous resins is due to the penetration of electrolyte in the grains by Donnan's equilibrium. The diffusion theory is less predominant in the case of macroreticular resins due to its high porosity. As it is hard rigid, furrowed sponges of channels it follows there from that a great proportion of functional sites is found to be indirect contact with the solution and that distribution is partly replaced by the easier migration in the solution contained in the pores of grains. Thus the results obtained in this case are due to combined effect of weak base and macro reticular nature of resin. The higher selectivity of $\text{ClO}_4^-$ over $\text{NO}_3^-$ on Amberlyst A-21 (macroreticular) is attributed to larger pore size in bringing more water and resulting in predominance of water structure enforced ion pairing.
CONCLUSION

The results of the present investigation in aqueous and water-2-butoxyethanol mixed medium are explained qualitatively on the basis of models proposed by Diamond and Reichenberg. However, due to lack of necessary thermodynamic data, it is not possible to explain quantitatively the factor such as electrostatic interaction, ion-water interaction and medium effect in the resin phase and in the external solution phase that are contributing significantly to the anion exchange processes. An evaluation of these individual terms would contribute significantly towards the understanding the origin of selectivity.

However, some general remarks are drawn from observed experimental results. The macroscopic dielectric constant value of the solvent medium no doubt affects the degree of ion pair formation and hence influence the transport and thermodynamic properties of the electrolyte solutions. But the influence of the dielectric constant of the medium is not the dominating factor in the anion exchange behaviour. It appears that protic and aprotic nature of the added organic solvent has greater importance than the dielectric constant in
governing the ionexchange selectivity. For example, the dielectric constant of 2-butoxyethanol is 9.3 and that of dioxane and DMF are 2.2 and 37.6 respectively. If the dielectric constant is the sole factor governing the selectivity, then the selectivity order in mixed solvents would have been DMF ($\varepsilon = 37.6$) > 2-butoxyethanol ($\varepsilon = 9.3$) > Dioxane ($\varepsilon = 2.2$). But the observed selectivity behaviour in these mixed media is Dioxane > 2-butoxyethanol > DMF. Though there is a crossover between 2-butoxyethanol and dioxane at about 70% composition, the values in dioxane are much higher than those in DMF - an aprotic solvent with very high dielectric constant.

Further, among 2-methoxy, 2-ethoxy and 2-butoxyethanols, the 2-butoxyethanol behaves more like an aprotic due to more $+I$ effect of $-\text{C}_4\text{H}_9$ than $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$. Accordingly the selectivity magnitudes are generally lower in 2-butoxyethanol compared to those in 2-methoxy and 2-ethoxyethanols.

The selectivity reversal and crossovers between CNS$^-$ and NO$_3^-$ in mixed medium are attributed to 2-butoxyethanol behaving more like an aprotic solvent and the non-spherical
nature of CNS$^-$ and greater CNS$^-$-2-butoxyethanol (ion-solvent) interaction.

The present investigation, as is common with other investigations, involves the evaluation of selectivity coefficients on the basis of the measured capacities and the concentration of only one of the ions in the external solution phase at equilibrium. This introduces unavoidable errors in the calculated $K_{C_A}^{B^-}$. Such discrepancies can be overcome by determining both counterions in the external solution at equilibrium, simultaneously taking into consideration of volume changes of external solution during exchange process. Measuring the water activity in water-2-butoxyethanol solution by isopiestic method would greatly facilitate the interpretation of water-2-butoxyethanol solvent on the exchange selectivity. Therefore a theory which can provide a quantitative description of ion exchange selectivity in terms of the physico-chemical properties of both the resin and the external solution phase, is in great need.
REFERENCES


