4. INTRODUCTION:

The results of exchange studies of \( \text{ClO}_4^- \), \( \text{CNS}^- \) and \( \text{NO}_3^- \) against systems, on strong base exchangers such as Dowex 1-X8, Dowex 1-X2 and Tulsion A-27 (Strong base anion exchangers) and also \( \text{ClO}_4^- \) and \( \text{NO}_3^- \) against \( \text{Cl}^- \) on Amberlyst A-21 and Tulsion A-2X (macroreticular weak base anion exchangers) in aqueous and sulfolane-water mixed medium of various compositions are discussed in this chapter. All the exchange studies are carried out at 303±1K at an ionic strength of 0.05M. The results were discussed in terms of models proposed by Diamond\(^1\) and Reichenberg\(^2\) under the following headings.

1. Selectivity behaviour in
   i) Aqueous medium and ii) Sulfolane-water mixed medium.

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

3. Influence of the cross linkage of the exchangers (i.e the variation of the DVB content) on selectivity.

4. Effect of changing the resin fixed co-ion on selectivity

Among different factors that contribute to the anion exchange selectivity (of 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 solvent. The general assumption of solvent medium as a dielectric constant is no longer accepted particularly with electrolyte solution. Experimental evidence of ion exchange results have accumulated to prove convincingly that the solvent structure (microscopic) especially of water plays a dominant role in anionic and cationic exchange processes\(^3\). 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 it’s 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 magnitude and disturbance of water structure by the addition of an organic solvent. Bhat studied the effect of addition of methanol (a protic solvent) on simple monovalent anion exchange, 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 formamide, ethylene glycol, DMF, 2-ethoxy ethanol, propan-2-ol, acetone, 2-methoxy ethanol, and 2-butoxy ethanol.

Alcohols in general are very similar in their capacity to form hydrogen bonding but to a lesser degree than in water. Addition of simple alcohols such as methanol or ethanol, therefore will effectively reduce the degree of hydrogen bonding in the mixed solvent medium. Krishnan et al., have reported their results of anion exchange studies in ethanol-water medium. It is known that the length of the hydrocarbon chain attached to the carbon containing the alcoholic group determines the hydrophobic ion pairing in water. Math studied the simple monovalent anion exchange process in water-propan-2-ol mixed medium. Hoskeri and Patil studied the monovalent anion exchange process in 2-ethoxy ethanol and 2-methoxy ethanol-water mixed medium respectively. They reported that the two solvents 2-ethoxy and 2-methoxy ethanol behaved more like aprotic solvents, and aprotic nature is more in the case of 2-ethoxy ethanol than in 2-methoxy ethanol. Kumi studied the anion exchange process in 2-butoxy ethanol and the results showed that 2-butoxy ethanol also behaved more like aprotic solvent and the aprotic nature being more in the case of 2-butoxy ethanol than 2-ethoxy ethanol and 2-methoxy ethanol.
4.1 SELECTIVITY BEHAVIOUR IN:

· i) Aqueous medium

ii) Sulfolane-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-X2 and Tulsion A-27 (Macroreticular) are summarised in table IV.1.

The order of selectivity observed in the present work, on the three strong base exchangers in aqueous medium is ClO$_4^-$ > CNS$^-$ > NO$_3^-$ > Cl$^-$. This is the order expected from their crystallographic radii and the data in the literature$^{15}$. From the available free energy data (Table IV.2) and change in standard free energy values, the selectivity observed is also the same i.e. ClO$_4^-$ > CNS$^-$ > NO$_3^-$ > Cl$^-$. This selectivity order can be explained by the models proposed by Diamond$^1$ and Reichenberg$^2$, and is also in good agreement with the data presented by previous investigators$^{4,13}$.

Diamond considers ion-water and water-water interaction different (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 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 up 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 will reduce the entropy of the system further. But in order to avoid further decrease in entropy, the two ions (R$^+$ and bigger ClO$_4^-$ 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$_4^-$ > CNS$^-$ > NO$_3^-$ > Cl$^-$. Hence the observed
### TABLE IV-1
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS FOR ANIONS ON DOWEX 1-X8, DOWEX 1-X2 AND TULSION A-27 (MP) IN SULFOLANE – WATER MIXED MEDIUM AT 303±1K

<table>
<thead>
<tr>
<th>ANION (B⁻)</th>
<th>logK_{ac}</th>
<th>IN % OF SULFOLANE (W/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>00.0</td>
<td>20.0</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>1.13</td>
<td>1.25</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>1.07</td>
<td>0.68</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.54</td>
<td>0.65</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>0.74</td>
<td>0.90</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>0.73</td>
<td>0.61</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.45</td>
<td>0.59</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>1.31</td>
<td>1.49</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>1.21</td>
<td>0.93</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.81</td>
<td>0.84</td>
</tr>
</tbody>
</table>
selectivity order ClO\(^-\) > CNS\(^-\) > NO\(_3^-\) > Cl\(^-\) 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.

\[ RA + B^{\prime}(b) \rightleftharpoons RB + A^{\prime}(b) \]  \hspace{1cm} 4.1

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 \( K_{a^{\prime}}^{B^-} \) for such reactions is given by:

\[ \ln K_{a^{\prime}}^{B^-} = -\frac{1}{RT} \left( \Delta G_{a^{\prime}}^{B^-}(b) \right) \]  \hspace{1cm} 4.2

\[ \ln K_{a^{\prime}}^{B^-} = -\frac{1}{RT} \left[ (\Delta G_{a^{\prime}}^{B^-} - \Delta G_{a^{\prime}}^{A^-}) + (\Delta G_{a^{\prime}}^{B^-} - \Delta G_{a^{\prime}}^{A^-}) \right] \]  \hspace{1cm} 4.3

Where, \( \Delta G_{a^{\prime}}^{B^-} \) \( \Delta G_{a^{\prime}}^{B^-} \) is corresponding change in the standard free energy of the process.

\( \Delta G_{a^{\prime}}^{B^-} \) and \( \Delta G_{a^{\prime}}^{B^-} \) are the standard free energy change of B and A forms of the resin.

\( \Delta G_{a^{\prime}}^{B^-} \) and \( \Delta G_{a^{\prime}}^{B^-} \) 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 equation (4.3), it is evident that the thermodynamic equilibrium constant $K_{A^{+}(h)}$ 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.

From the consideration of the free energy of hydration, it can be seen that 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 brings the one 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 the table IV.2 and IV.3 respectively. It can be seen that $\text{NO}_3^-$, $\text{CN}^-$ and $\text{ClO}_4^-$ have relatively less negative free energy of hydration compared to $\text{Cl}^-$. The expected selectivity order should be $\text{ClO}_4^->\text{CN}^->\text{NO}_3^->\text{Cl}^-$. 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 selectivity has also been observed in cation exchange process\textsuperscript{16}. The free energies of hydration for alkali ions are shown in Table IV.3. The selectivity order of ions $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ is because the ion with more negative free energy of hydration is less preferred by the resin phase.
### Table IV.2

| Anion | \( \Delta G^{\circ} \) (J/mol) | \( \Delta G^{\circ} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) | \( \Delta G^{\circ}_{\text{c}} \) (KJ/mol) |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Cl"   | 644.42         | 133.88         | 447.68         | 330.93         | 201.22         | 100.41         | 50.12           | 0.00           | -29.28         | -97.66          | 3.138           | -100.41         | -121.33         | -84.2           |
| Br"   | 2.0275         | 1.96           | 267.77         | 238.69         | -41.64         | 2.90           | 209.20          | 9.83           | -121.33        | -100.41         | -121.33         | -84.2           | 10.20           |
| NO₃   | 2.90           | 2.20           | 209.20         | 9.83           | -121.33        | -100.41        | -121.33         | -84.2          | 10.20           |                   |                 |                 |                 |
| CN⁻   | 6.31           | 8.01           | 11.25          | 9.51           | 8.40           | 7.80           | 8.82            | 10.20          |                   |                 |                 |                 |                 |
| CO₃²⁻ | 6.27           | 6.21           | 6.96           | 2.73           | 7.60           | 6.69           | 8.70            | 7.30           | 9.05           | 9.36           | 9.05           | 9.36           | 9.05           |
| F⁻    | 1.33           | 1.17           | 1.11           | 0.00           | 0.00           | 0.00           | 0.00            | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           | 0.00           |

### Notes
- * - Estimated
- l - Present Work.
**TABLE IV.3**

\[ \Delta G^{\circ} (h) \text{ OF MONOVALENT CATIONS AND } \Delta G^{\circ}_{Na^+} \text{ VALUES FOR EXCHANGE ON STRONG ACID EXCHANGES AT } 303K \]

<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>( \text{B}^+ )</td>
<td>( * ) ( r ) (in Å)</td>
<td>( \Delta G^{\circ} (h) ) (in KJ mole(^{-1}))</td>
<td>( \Delta G^{\circ}<em>{Na^+} - \Delta G^{\circ}</em>{B^+} ) (in KJ mole(^{-1}))</td>
<td>( \Delta G^{\circ}_{Na^+} ) *** (in KJ mole(^{-1}))</td>
</tr>
<tr>
<td>( \text{H}^+ )</td>
<td>--</td>
<td>1087.84</td>
<td>676.13</td>
<td>0.96</td>
</tr>
<tr>
<td>( \text{Li}^+ )</td>
<td>0.70</td>
<td>510.86</td>
<td>99.16</td>
<td>1.51</td>
</tr>
<tr>
<td>( \text{Na}^+ )</td>
<td>0.97</td>
<td>411.70</td>
<td>0.00</td>
<td>--</td>
</tr>
<tr>
<td>( \text{K}^+ )</td>
<td>1.33</td>
<td>337.23</td>
<td>-74.47</td>
<td>-1.08</td>
</tr>
<tr>
<td>( \text{Rb}^+ )</td>
<td>1.49</td>
<td>315.89</td>
<td>-95.81</td>
<td>--</td>
</tr>
<tr>
<td>( \text{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 experimental observations, but quantitative agreement between 4th and 5th column in Table IV.2 and Table IV.3 is poor. For example $\Delta G^{oK^+}$ 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 $\text{NO}_3^-$- $\text{Cl}^-$ 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 anion exchange equilibria is $-3.13$ KJ mol$^{-1}$, which is about thirteen 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, the entropy of formation of anions etc., which appear in the equation 4.3.

4.1.2 WATER - SULFOLANE (MIXED MEDIUM):

According to the Diamond’s model the anion selectivity in the case of strong base anion exchangers is determined by ion-solvent, solvent-solvent interactions. Any changes in either or both interactions will greatly affect the selectivity. Addition of an organic solvent to water would change the magnitude of these two interactions and depending upon the degree of this change, the selectivity should also change. Therefore to study the effect of organic solvent on ion-exchange selectivity, Sulfolane-water mixture was chosen.

The exchange studies of simple monovalent anions in mixed solvent media enable a better understanding of the origin of ion selectivity. Such studies done by earlier workers have produced interesting results. An aprotic media can provide a marked effect on selectivity when it goes from pure aqueous to mixed aprotic solvent.
media. A protic organic solvent-water media do show such effect on selectivity but the magnitude of such effect is small compared to the former.

In general, selectivity decreases with the increase in organic solvent content in the external solution phase.

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

It is seen from the table IV.1 and Fig. 4.1 to 4.3 that there is a decrease in the selectivity of all anions on all the resins studied with increase in sulfolane content. In case of ClO$_4^-$ and NO$_3^-$ ions, selectivity increases initially around 20% of sulfolane content on all strong base resins Dowex 1-X8, Dowex1-X2 and Tulsion A-27.

The decrease in selectivity with an increase in Sulfolane content is rather steep in case of ClO$_4^-$ and CNS$^-$ compared to that of NO$_3^-$. Charge density of perchlorate ion is less than NO$_3^-$ and CNS$. In case of ClO$_4^-$ and NO$_3^-$ ions, the selectivity increases around 20% Sulfolane content and is due to the free water molecule present in water aggregate.

Sulfolane is a polar solvent. The addition of 20% solvent makes water more structured and water-structure enforced ion pairing is more predominant than what one finds in pure water.

Subsequent addition of the solvent decreases the selectivity because of the bigger hydrocarbon moiety of the solvent. It breaks the water structure and hence the selectivity decreases (hydrogen bond accepting capacity).

CNS$^-$ ion is cylindrical in nature. So, it is not allowing the aggregation of water molecules. It contributes to the destruction of water structure.

There is also a selectivity reversal (negative log K values) for NO$_3^-$ on all the resins. But selectivity reversal is not seen on Dowex-1X8 for ClO$_4^-$ and on
Tulsion A-27 (MP) for CNS\(^-\) and ClO\(_4^-\). The selectivity reversal could be explained on the basis that at higher solvent composition the proportion of water molecules is more in the resin phase\(^{14}\) due to swelling effect. Therefore chloride becomes the preferred ion as it satisfies hydration better on the resin phase giving higher selectivity resulting in selectivity reversal. There is also selectivity reversal (negative log K values) for CNS\(^-\) on Dowex 1-X8 and Dowex 1-X2 at around 80% composition.

The selectivity reversal is also observed in case of NO\(_3^-\) on Dowex 1-X8 and Tulsion A-27 at around 80%. In case of Dowex 1-X2 the selectivity reversal is also observed at around 60% composition. But there is no crossover selectivity between ClO\(_4^-\) - Cl\(^-\), NO\(_3^-\) - Cl\(^-\) and CNS\(^-\) - Cl\(^-\) on Dowex 1-X8, Dowex1-X2 and Tulsion A-27 resins.

An ion exchange reaction in solvent S can be conveniently represented as follows;

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

Where, RA and RB are A and B forms of resin respectively, and \(A^-\) and \(B^-\) are counter-ions.

The standard free energy change \(\Delta G^\circ_{A^-}^{B^-}\) for the above reaction is

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

\[
= -RT \ln K_{A^-}B^- 4.5
\]

Where, \(\Delta G^\circ_{i(s)}\) is the standard free energy of formation of \(i\)th species with respect to the ideal ionic gas state.

In the case of ion exchange reaction in aqueous medium, equations 4.5 and 4.6 can be rewritten as:

\[
-RT \ln K_{A^-}B^- = \Delta G^\circ_{A^-}^{B^-} 4.7
\]

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From the equation (4.8) it is evident that the thermodynamic equilibrium constant $K_{A}^{+}$ for an ion 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 system 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 the 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 (4.4) in mixed solvent media can be rewritten as follows:

$$-RT \ln K_{A}^{+} = \Delta G_{A}^{o}$$

$$= \left( \Delta G_{RB}^{o} - \Delta G_{RA}^{o} \right) + \left( \Delta G_{A}^{+} - \Delta G_{B}^{+} \right)$$

$$+ \left( \Delta G_{RB}^{o} - \Delta G_{RA}^{o} \right) + \left( \Delta G_{A}^{+} - \Delta G_{B}^{+} \right)$$

Here $\Delta G_{i}^{o}$ refers to the standard free energy change of transfer of the $i^{th}$ species from the infinitely dilute aqueous solution to the infinitely dilute solution in mixed solvent.

The first term on the right hand side of equation (4.10) gives the difference in the electrostatic interaction energies between the two counter ions with the resin ion in aqueous medium. The second term refers to difference between the free energies of hydration of counter ions. The third and the fourth term deals with the difference between the free energies of transfer of the two resinates and two counter ions respectively from a reference state in aqueous phase to that in the corresponding solvent medium.

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Fig 4.1 $\log K_{a_{CG}}^{-B}$ Vs % Sulfolane (w/w) on Dowex 1-X8
Fig 4.2 log $K_a$ vs % Sulfolane (w/w) on Dowex 1-X2

% Sulfolane (w/w)

$\log K_a$
Fig 4.3 log $K_{\text{aqCl}}$ $V_s$ % Sulfolane (w/w) on Tulsion A – 27(MP)
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 in nature with some solvents having comparable dielectric constants. The results of their investigations are presented in Table IV.4. It gives log $K_{\text{ClO}_4}^-$ values on Dowex 1-X8 resin for ClO$_4^-$-Cl$^-$ exchangers 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 the dielectric constant of the medium on selectivity in ion exchange reaction is clearly seen in Table IV. 4.

The dielectric constant of pure water is 78.54 at 298 K and that of Sulfolane is 43.3. Hence, Dielectric constant of various compositions of water-Sulfolane 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 organic solvent content. If the dielectric constant is the sole factor governing selectivity$^{20}$, then the selectivity coefficient values should be comparable for solvents having comparable dielectric constant values. On a closer observation of Table IV.4, it is clear that this explanation does not hold good.

For example, methanol ($\varepsilon = 32.6$) 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 ClO$_4^-$-Cl$^-$ is different (Table IV.4). The selectivity decrease in DMF-water is more steep than that in methanol-water media. Similarly, sulfolane ($\varepsilon = 43.3$) and DMF ($\varepsilon = 37.6$) have nearly the same dielectric constant values but the exchange behaviour of these two solvents for the same ion pair ClO$_4^-$-Cl$^-$ is
different (Table IV.4) The selectivity decrease in DMF-water media is more steep than that in sulfolane-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 selectivity coefficient values in dioxane-water system are higher than the corresponding values on DMF-water mixed media (Table IV.4).

In Table IV.4, Formamide has the 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 Sulfolane is 43.3 and that of formamide and methanol is 109 and 32.6 respectively (both these solvents being protic in nature). If the dielectric constant is an important parameter governing selectivity, the selectivity values of Sulfolane should lie between those of formamide and methanol. But the experimental results obtained in the present investigation do not support this contention. (Table IV. 4)

Again when the selectivity behaviour is considered among aprotic solvents such as dioxane ($\varepsilon=2.2$), DMF ($\varepsilon=37.6$) and Sulfolane ($\varepsilon=43.3$), the expected selectivity of the preferred ion in the mixed media involving these solvents should be in the order Sulfolane > DMF > dioxane as per Ghodstein21 contention. But the observed selectivity behaviour is dioxane > Sulfolane >DMF (fig. 4.4). Further among Sulfolane, propan 2-ol and methanol, the selectivity is low in Sulfolane. This is attributed to more aprotic nature of the solvent and absence of hydrogen bond forming groups (Fig. 4.5).

A cursory examination of the data indicate that the dielectric constant of the medium is not the sole factor governing selectivity and in fact chemical properties of the added organic solvent such as protic or aprotic nature, polarisation etc. have a greater influence on selectivity rather than dielectric constant.
### TABLE IV. 4

AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS IN ORGANIC SOLVENT – WATER MEDIUM ON DOWEX 1–X8 (Cl) FORM AT 303 ±1 K (TOTAL IONIC STRENGTH = 0.05M)

<table>
<thead>
<tr>
<th>% of organic solvent (w/w)</th>
<th>logK&quot;a_{Cl}^{COG}</th>
<th>Dioxane</th>
<th>DMF</th>
<th>Acetone</th>
<th>Formamide</th>
<th>Methanol</th>
<th>Propan-2-ol</th>
<th>Sulfolane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ε =2.2)</td>
<td>(ε =37.6)</td>
<td>(ε =20.7)</td>
<td>(ε =109)</td>
<td>(ε =32.6)</td>
<td>(ε =18.3)</td>
<td>(ε =43.3)</td>
<td></td>
</tr>
<tr>
<td>00.00</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
<td>e</td>
<td>f</td>
<td>g</td>
<td></td>
</tr>
<tr>
<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>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.00</td>
<td>1.29</td>
<td>0.81</td>
<td>1.23</td>
<td>1.36</td>
<td>-</td>
<td>1.52</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>20.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.49</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40.00</td>
<td>1.15</td>
<td>0.33</td>
<td>0.78</td>
<td>1.41</td>
<td>-</td>
<td>1.18</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>44.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.39</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>60.00</td>
<td>-</td>
<td>-0.44</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>1.03</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>70.00</td>
<td>0.51</td>
<td>-</td>
<td>-</td>
<td>1.39</td>
<td>-</td>
<td>0.95</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>70.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.09</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>80.00</td>
<td>0.06</td>
<td>-0.91</td>
<td>-0.75</td>
<td>0.82</td>
<td>-</td>
<td>-</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

d. Y. P. Vyasamudri and C.S. Narke, Karnataka University Journal (Sc) Vol. XXXII(1988)
g. Present Work

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Fig 4.4 Effect of solvent dielectric constant on selectivity

% Organic solvent

log $K_{\text{Cl}^-}^{*}$ vs % Organic solvent

- ♦ Sulfolane
- ■ DMF
- ▲ Dioxane
Fig. 4.5 Effect of solvent dielectric constant on selectivity.
4.3 EFFECT OF VARIATION OF CROSS-LINKING (%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-X2 and Dowex 1-X8. Table IV.1 gives the log $K_{aCr}^{B'}$ values for ClO$_4^-$, CNS$^-$ and NO$_3^-$ in aqueous and mixed media of various compositions on strong base anion exchange resins viz. Dowex 1-X2, Dowex 1- X8 and Tulsion A-27 at 303±1K. Variations of log $K_{aCr}^{B'}$ as a function of Sulfolane content of the medium for each cross linkage is shown in figures 4.6 to 4.8. The general observations on all these figures are that, the selectivity coefficient of preferred ion generally increases with an increase in percentage of DVB.

The number of water molecules available per exchange site in an exchanger generally decrease with the increase of cross linkage, 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 cross linkage. Therefore the selectivity of preferred ion should increase with increase in cross linkage irrespective of solvent compositions in the external phase. The observations made in the present investigations are in good agreement with the above contention. (Table IV.1, figures 4.6 to 4.8)

When cross linkage is the only parameter varied keeping all other parameters such as fixed co-ion, counter ions and the medium constant, the change in the electrolyte concentration in the resin phase is the most important effect expected. The effect of the four terms in the equation (4.10) remains in the same ratio, the net free energy change being more negative with increase of cross linkage. A similar observation of the effect of cross linkage with cations and anions on corresponding strong exchangers were reported by Myers et al.21.

As expected, the selectiviy sequence of ClO$_4^-$, CNS$^-$ and NO$_3^-$ on the resins studied is Dowex 1-X8 > Dowex 1-X2 in both aqueous and mixed medium case of Tulsion A-27 (macroreticular) resin, the selectivity of the preferred ions is more than...
Fig 4.6 log $K_{\text{ClO}_4}^{\text{aq}}$ Vs % Sulfolane (w/w) on Tulsion A-27(MP), Dowex 1-X8 and Dowex 1-X2
Fig 4.7 $\log K_{aCl}^{\text{CNS}^-}$ Vs % Sulfolane (w/w) on Tulsion A-27(MP), Dowex 1-X8 and Dowex 1-X2
Fig 4.8 $\log K^\text{NO}_3$ $\text{vs}$ % Sulfolane (w/w) on Tulsion A-27(MP), Dowex 1-X8 and Dowex 1-X2

% Sulfolane (w/w)

$\log K^\text{NO}_3$ $\text{vs}$ % Sulfolane (w/w) on Tulsion A-27(MP), Dowex 1-X8 and Dowex 1-X2
Dowex 1-X8 and Dowex 1-X2 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 upto 100m$^2$/g. Hence larger molecules can easily penetrate the interior and selectivity of preferred anions is more. The selectivity sequence of ClO$_4^-$, CNS$^-$ and NO$_3^-$ on the resins studied is Tulsion A-27 (macroreticular) > Dowex 1-X8 > Dowex1-X2 in both aqueous and mixed medium (Figures 4.6 to 4.8).

4.4 SELECTIVITY BEHAVIOUR OF WEAK BASE RESINS

In order to understand the selectivity behaviour on changing the nature of the resin fixed ion from strongly basic (quaternary ammonium) to weakly basic (tertiary ammonium) ion 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 are summarised in Table IV.1 and Figures 4.9 to 4.12.

The selectivity order in the weak base exchangers in aqueous medium is ClO$_4^-$ > NO$_3^-$ > Cl$^-$ which is the same as on strong base exchangers. In case of Tulsion A-2X (gel) the selectivity values of ClO$_4^-$ - Cl$^-$ and NO$_3^-$ - Cl$^-$ are lower than those on strong base exchangers, in aqueous and at all compositions in mixed media. The selectivity of ClO$_4^-$ - Cl$^-$ and NO$_3^-$ - Cl$^-$ gradually decreases with increase in the Sulfolane content. In case of Tulsion A-2X (gel) the selectivity values of ClO$_4^-$ - Cl$^-$ and NO$_3^-$ - Cl$^-$ gradually increases upto 20% w/w Sulfolane content, then decreases with increase in Sulfolane content. The selectivity reversal is observed in ClO$_4^-$ - Cl$^-$ and NO$_3^-$ - Cl$^-$ exchange at around 60% and 40% of solvent composition respectively. There is no crossover of selectivity between ClO$_4^-$ - Cl$^-$ and NO$_3^-$ - Cl$^-$ exchange at around 60% and 40% of solvent composition respectively. In case of Tulsion A-2X (gel) the selectivity values of NO$_3^-$ - Cl$^-$ is lower than ClO$_4^-$ - Cl$^-$. 

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TABLE IV-5
AVERAGED AND CORRECTED SELECTIVITY COEFFICIENTS FOR ANIONS ON AMBERLYST A-21 AND TULSION A-2X (GEL) IN SULFOLANE – WATER MIXED MEDIUM AT 303±1K

<table>
<thead>
<tr>
<th>ANION</th>
<th>AMBERLYST A-21 (MP)</th>
<th>TULSION A-2X (GEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log(\text{log}K_b^{\text{Cl}^-})</td>
<td>log(\text{log}K_b^{\text{Cl}^-})</td>
</tr>
<tr>
<td></td>
<td>(B^-)</td>
<td>0.0</td>
</tr>
<tr>
<td>ClO_4^-</td>
<td>0.59</td>
<td>0.67</td>
</tr>
<tr>
<td>NO_3^-</td>
<td>0.40</td>
<td>0.53</td>
</tr>
<tr>
<td>ClO_4^-</td>
<td>0.29</td>
<td>0.46</td>
</tr>
<tr>
<td>NO_3^-</td>
<td>0.22</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Fig 4.9 $\log K_{\text{acr}}$ Vs % Sulfolane (w/w) on Tulsion A - 2X(gel)

% Sulfolane (w/w)

$\log K_{\text{acr}}$

- Perchlorate
- Nitrate

Fig 4.9 $\log K_{\text{acr}}$ Vs % Sulfolane (w/w) on Tulsion A – 2X(gel)
Fig 4.10 $\log K_{aCl^{-}}$ Vs % Sulfolane (w/w) on Amberlyst A - 21(MP)

% Sulfolane (w/w)

Fig 4.10 $K_{aCl^{-}}$ $\log B^{-}$ Vs % Sulfolane (w/w) on Amberlyst A - 21(MP)
Fig 4.11 \( \log K_{aCl^-} \) Vs % Sulfolane (w/w) on Amberlyst A-21(MP), Tulsion A-2X(gel)
Fig 4.12 $\log K_{\text{NO}_3}^{\text{ac}}$ Vs % Sulfolane (w/w) on Amberlyst A-21 (MP) and Tulsion A-2X(gel)
Substitution of tertiary amine (-NR$_2$H$^+$) group for the quaternary group (-NR$_4^+$) 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 the resin fixed co-ion, in weak base resin provides a hydrophilic site which is missing in the strong base resins containing quaternary ammonium group as resin fixed co-ion. Due to this reason, the tertiary ammonium group (-NR$_2$H$^+$) cannot participate in water-structure enforced ion pairing as much as quaternary ammonium group (-NR$_4^+$) can. Hence it is expected that the weak base resin should show somewhat enhanced selectivity for smaller basic anions (NO$_3^-$) and somewhat reduced affinity for a large hydrophobic ion like ClO$_4^-$.

In case of Amberlyst A-21 the selectivity in general decreases with increase in Sulfolane content. In case of Amberlyst A-21, the selectivity values of ClO$_4^-$-Cl$^-$ and NO$_3^-$-Cl$^-$ gradually increases upto 20% w/w Sulfolane content then, decreases with increase in Sulfolane content. The selectivity reversal is observed in case of ClO$_4^-$-Cl$^-$ and NO$_3^-$-Cl$^-$ exchange at around 80% and 60% of the solvent composition respectively. There is no cross over of selectivity. In case of Amberlyst A-21, the selectivity values of NO$_3^-$-Cl$^-$ is lower than ClO$_4^-$-Cl$^-$ . However, the selectivity magnitudes are always higher than those on Tulsion A-2X (gel). Amberlyst A-21 is a macroreticular weak base resin, which contains pores or channels of several hundred nanometers 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 equilibrium. The diffusion theory is less predominant in the case of macroreticular resins due to its higher porosity. As it is a hard, rigid, furrowed sponges of channels, it follows thefrom that a great proportion of functional sites is found to be in direct contact with the solution and that this 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 macroreticular nature of resin.
The higher selectivity of ClO$_4^-$-Cl$^-$ over NO$_3^-$-Cl$^-$ 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 recent investigation in sulfolane-water medium has qualitatively fulfilled the expectations based on the models proposed by Diamond$^1$ and Reichenberg$^2$. Quantitative explanation of the results was not possible because of lack of thermodynamic data.

From classical thermodynamics, an equation is presented (similar to that of Reichenberg’s) showing that the frequency of an ion exchange reaction in mixed solvent media is the result of the free energy changes contributed by

(i) electrostatic interactions
(ii) ion-water interactions
(iii) medium effect in the resin phase.
(iv) medium effect in the external solution phase.

An evaluation of individual terms would contribute significantly towards the better understanding of origin of ion exchange selectivity.

Factors such as enthalpy changes determined from calorimetric studies, uncertainty of the absolute capacity in going from one anion pair to another and from one solvent composition to other; preferential solvent uptake (may be determined by refractive index values of the aqueous and mixed solvent compositions before and after equilibrium), etc., also help greatly in explaining selectivity behaviour in mixed solvent medium.

However, some general remarks are drawn from observed experimental results. The macroscopic dielectric constant values of the solvent medium no doubt affects the degree of ion pair formation and hence influence the transport and the
thermodynamic properties of the electrolyte solution. But the influence of dielectric constant of the medium is not the dominating factor in the anion exchange behaviour. It appears that the protic and aprotic nature of the added organic solvent has greater influence than the dielectric constant in governing the ion exchange selectivity.

For Ex: The dielectric constant of sulfolane is 43.3 and that of dioxane and DMF is 2.2 and 37.6 respectively.

If the dielectric constant is the sole factor governing selectivity, then the selectivity order in mixed solvent would have been sulfolane>DMF>dioxane. But the observed selectivity behaviour in these media is dioxane > sulfolane > DMF.

The selectivity reversal observed in mixed medium is attributed to the aprotic nature of the solvent, non-spherical nature of CNS- and greater ion-solvent interactions.

The present investigation evaluated the selectivity coefficients based on the measured capacity of the resin and the concentration of one of the counter ions in the external solution phase at equilibrium. This introduces unavoidable errors in the calculated $K_{cA}^{B-}$. Such errors can be rectified if the composition of the counter ions in the external solution phase at equilibrium is determined simultaneously. Determination of water activity in water–sulfolane solution by isopiestic method would greatly facilitate the interpretation of water-sulfolane 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.
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Present study is an investigation to understand the exchange behaviour of ClO_4^-, CNS^- and NO_3^- against Cl^- on strong base anion exchangers, Dowex 1-X8, Dowex 1-X2 and Tulsion A-27 (macroreticular) and on weak base anion exchanger Tulsion A-2 (gel) and Amberlyst A-27 (macroreticular) in sulfonate water mixture at different solvent composition (0, 20, 40, 60, 80% sulfolane w/w)

The study covers a wide range of loading on these resins. The data are expressed in terms of models proposed by Diamond and Reichenberg.