CHAPTER I
INTRODUCTION
Ion exchange is the process in which depending on the nature of the ion exchanger, one of the ions, either the anion or the cation, is exchanged between the highly insoluble solid ion exchanger and the liquid solution with which it comes into contact. Thus, in an ion exchanger one of the two ions is a fixed ion, and the other ion is exchangeable and is called co-ion. If the cation is fixed ion, the resin exchanges anion and is called anion exchanger and vice versa. The exchange of ions is reversible, and there is no directly perceptible permanent change in the structure of the solid. Ion exchangers are widely used for water treatment. They are equally useful in analytical chemistry. Due to the convenience with which they can be used, ion exchangers are becoming more and more useful in most of the industrial processes such as hydrometallurgy, metal recovery, sugar manufacture, pharmaceuticals, biochemistry, biotechnology, food processing, etc.

Utility of ion exchange process depends on the ion exchanger used. Different ion exchangers have different thermal properties and stabilities and proper ion exchanger should be selected to answer the requirements of a particular process.

Ion exchange techniques are highly versatile because they are highly specific, and they are highly specific because ion exchangers are highly selective. Kitchner and Redinha\(^1\) define selectivity as follows:
"When an ionogenic surface is in equilibrium with a solution containing a mixture of counter ions, the proportion of different ions that are associated with the surface are not the same as their proportion in the bulk of the solution; the phenomenon is known as ion selectivity."

This fact that an ion exchanger has different affinity towards different ions in the solution with which it comes into contact, was known quite early in the history of ion exchange study. This property of an ion exchanger was exploited by inorganic chemists to separate chemically closely related ions such as alkali ions, lanthanides, etc., and fraction of closely related isotopes. Similarly selectivity is used for separating amino acids. In spite of the rapid progress in the synthesis of ion exchangers with improved specific selectivities the understanding of selectivity phenomenon is far from perfect. This dearth in knowledge is due to the highly complex nature of the phenomenon itself. Though there is a large number of publications appearing every year in this field of study, and there are several monographs and a journal exclusively devoted to the study of ion exchange, they are all concentrated mainly on the application of ion exchangers rather than on the fundamental principles and mechanisms of ion exchange. The knowledge of cation exchange behaviour is at present a little more advanced than the knowledge of anion exchange behaviour.
Initially, some empirical equations\textsuperscript{7-10} were proposed, which were thought of immense help in predicting the selectivity, were of little assistance in delineating its exact nature. Many mysteries of ion exchange phenomenon were unraveled by several studies conducted by researchers such as Gaines and Thomas\textsuperscript{11} (thermodynamic treatment); Gregor\textsuperscript{12}, Harris and Rice\textsuperscript{13} (mechanistic model); Stigman and Dobrow\textsuperscript{14}, Diamond\textsuperscript{15}, Jensen and Diamond\textsuperscript{16}, and Reichenberg\textsuperscript{17} (a combination of thermodynamic treatment and mechanistic model).

To improve the resolution and to increase the speed of separations a study of influence of water miscible organic solvents in the external phase on ion exchange reactions has been conducted\textsuperscript{2}. Extensive studies conducted by Fritz and Rettig\textsuperscript{18} and by Korkisch\textsuperscript{19} are worth mentioning. Thermodynamic treatment of ion exchange equilibria in aqueous medium have been extended to mixed solvent media by Fessler and Strobel\textsuperscript{20}, and Gupta\textsuperscript{21}. Mention may also be made of the studies conducted by Bonner\textsuperscript{22}, Fessler and Strobel\textsuperscript{20}, Athawale, et al\textsuperscript{23}, Pauley, et al\textsuperscript{24}, Jensen and Diamond\textsuperscript{16}, Reichenberg\textsuperscript{17} to explain the selectivity order in mixed solvents. Krishnan and Ramanathan\textsuperscript{25}, Phipps\textsuperscript{26}, Jensen and Diamond\textsuperscript{16}, Bhat\textsuperscript{27}, Narke and co-workers\textsuperscript{28-34} have given tentative explanations and suggestions regarding the effect of different types of water soluble organic solvents on anion exchange selectivity. The next Chapter presents a brief discussion of these developments.
In order to understand the selectivity behaviour of simple monovalent anions such as ClO$_4^-$, CNS$^-$, I$^-$ and NO$_3^-$ against Cl$^-$ in mixed solvent media, Narke and co-workers$^{28-34}$ have conducted several studies using different resins and water soluble solvents. Narke$^{29}$, Katale$^{30}$ and Sangolli$^{33}$ have used aprotic solvents like dioxane, DMF and acetone, respectively. Vyasamudri$^{29}$, Bhat$^{27}$, and Math$^{32}$ have used protic solvents like formamide, methanol, propan-2-ol respectively. Hoskeri$^{31}$ and Patil$^{34}$ have used substituted alcohols such as 2-ethoxyethanol and 2-methoxyethanol, respectively. All these studies have revealed that the chemical properties of organic solvents, viz., protic and aprotic, polar and non-polar nature have a marked influence over the anion exchange behaviour in mixed solvent media. It is also observed that protic and aprotic solvents have different behaviour with respect to selectivity. Dielectric constant of the above solvents exhibited comparatively less effect on selectivity in mixed media.

In order to understand the effect of substitution of isoproxy group in ethanol on selectivity, selectivity coefficients in water and water-2-isoproxyethanol at different loadings were gathered. The results so obtained were compared with those in 2-methoxyethanol$^{34}$ and other solvents. It was expected that 2-isoproxyethanol behaves as more aprotic solvent than 2-methoxyethanol$^{34}$.

All exchange studies were made with the Cl$^-$ form of the resin as the frame of reference with monovalent anions of
different shapes and sizes as counter ions. Spherically symmetric large polyatomic \( \text{ClO}_4^- \), cylindric polyatomic \( \text{CNS}^- \), \( I^- \) and, symmetric polyatomic \( \text{NO}_3^- \) were the counter-ions selected for the purpose of present study.

The exchange of these four anions against \( \text{Cl}^- \) \( (K_{\text{Cl}^-}) \) were investigated as function of organic solvent composition (0, 20, 40, 60 and 80 % w/w of 2-isopropoxyethanol) at 303±1K on strong base anion exchangers Dowex 1-X8, Dowex 1-X4 (crosslinking effect) and Tulsion A-27 (macroreticular). Studies on weak base anion exchangers Tulsion A-2X (gel) and Amberlyst A-21 (macroreticular) were conducted to know the possible effect of changing the resin fixed co-ions from quaternary ammonium in strong base to tertiary ammonium in weak base resins. Details of these experiments are presented in Chapter III and the results are analysed in terms of water-structure-enforced ion pair formation as well as field strength and solvation energy as applied to ion exchange equilibria and are presented in Chapter IV.

The results obtained in the present work substantiated the fact that dielectric constant is not a governing factor as far as selectivity is concerned. Selectivity is proved to be governed more by the protic or aprotic nature of the solvent.
REFERENCES


