Chapter-I

Introduction
There are two phases of analytical researches viz.

(1) To develop the techniques for chemical analysis.
(2) To study the mechanism and theory of these techniques.

Ion exchange is a wide spread phenomenon in analytical chemistry. New materials which exhibit ion exchange behaviour are being synthesized at a rapid rate. Ion exchange processes are useful in separation, removal and recovery of ionic species. These processes may also find utility in ion transport devices fuel cell preparations and catalysts development. A better understanding of these processes can be developed by thermodynamic and Kinetic studies in order to relate theories with experiments.

Theory of ion exchange and the underlying mechanism involved in the exchange process can be understood by the knowledge of thermodynamics and kinetics respectively. The thermodynamic study is of course the study of chemical equilibria. Rigorous thermodynamics however gives an inherently abstract treatment devoid of the mechanical or microscopic images which would lead one to a feeling of greater intimacy and understanding of the phenomena. The most successful treatments have been based on the model which incorporates observed physical characteristics. Yet properties of any particular model are reflected not only in the form of equations obtained but usually also in the physical
interpretation to which these equations lead. In the case of organic exchangers the most successful models take into account the swelling observed when the resin change the environment or the ionic form. Hence various theories and models were developed in this respect having their own merits.

In one approach attempts have been made to correlate the activities with some measurable quantities with the thermodynamic equations. The earliest approach was based on semi-empirical or empirical equations to fit in experimental results. Gans\(^1\) gave the first quantitative formulation of ion exchange equilibria using the law of mass action in its simplest form which was extended by Kielland.\(^2\) The formula did not involve the concept of activity coefficient. A suitable choice of the general treatment was given by Gaines and Thomas.\(^3\) However Gregor was able to relate selectivity to hydrated ionic volumes in his semi-quantitative model. Rigid structure, negligible swelling pressure and a differential selectivity has made the study simple on inorganic exchangers. When an exchanger in counter ion A form is placed in a solution of counter ion B there will be an equilibrium set up for the distribution of A and B between the exchanger and the solution phase according to their
selectivity for the exchanger phase. At equilibrium this exchange process may be represented as

\[ \overline{A} + B \text{(aq)} \rightleftharpoons \overline{B} + A \text{(aq)} \]  \hspace{1cm} (1)

Where bar represents the ion in the exchanger phase. For the sake of convenience the effect of co-ion on the equilibrium may be neglected. The thermodynamic equilibrium constant for the above reaction may be written as

\[ K_a = \frac{\gamma_B a_B}{\gamma_A a_A} = \frac{[B][A]}{[A][B]} \times \frac{f_A}{f_B} \]  \hspace{1cm} (2)

Where \( \gamma \) represents the activity coefficient in the exchanger phase and \( f \) is the activity coefficient in the solution phase. Thermodynamic equilibrium constant is particularly used to find out the free energy changes of the ion exchange processes by the expression

\[ \Delta G = -RT \ln K_a \]  \hspace{1cm} (3)

The ionic selectivity is governed by the lowering of free energy of the system which gives the information about the preferential uptake of the counter ions by the exchanger. \( K_a \) values at different temperatures give the value of enthalpy change. Changes in the number and the strength of the bonds involved in the ion exchange reaction is directly related to
enthalpy changes. The ion exchange reaction (equation-1) provides that structural changes within the exchanger are small, the most important factor influencing the entropy of equally charged ions will be expected to result from changes in liberation entropy may also play an important role and the overall entropy will reflect changes in randomness in the ion exchange reaction, the driving force being the tendency for the system to go to the most probable i.e., the most random state.

The ion exchange equilibria of alkali metal ions was studied by Larsen and Vissers\textsuperscript{4} and Gal and Ruvarec\textsuperscript{5} on amorphous zirconium phosphate of various compositions and properties. Ion exchange thermodynamic studies have been extended on more defined semi-crystalline and crystalline zirconium phosphate for alkali cations.\textsuperscript{6-16} The thermodynamics was interpreted in terms of the bonding between alkali metal and the exchanger matrix. Recently the ion exchange equilibria on Co(II) hexacyanoferrate (II) have been made by Ceranic and Adamovic.\textsuperscript{17} Similar studies have also been reported on hydrous zirconia acting as anion exchanger by Nancollas.\textsuperscript{18} Studies on zeolites have also been made to a greater extent.
Thermodynamic studies for alkali metals on ferricantimonate\textsuperscript{19,20} niobium arsenate,\textsuperscript{21} Zirconium triethylamine,\textsuperscript{22} thorium tetracyclohexylamine\textsuperscript{23} were made in our laboratories. Some of the equilibrium studies on different ion exchange materials with various systems and their parameters are given in table 1.1.

Thermodynamic studies have also been performed on various anion exchangers. The reversibility of Br\textsuperscript{−}-NO\textsubscript{3} exchange on hydrous zirconia was demonstrated by Kraus.\textsuperscript{45} The thermodynamics of Cl\textsuperscript{−}-NO\textsubscript{3}, Cl\textsuperscript{−}-SCN\textsuperscript{−}, and SCN\textsuperscript{−}-NO\textsubscript{3} exchange on hydrous zirconium oxide was studied by Nancollas and Paterson.\textsuperscript{46} Ruvarec and Tartanj\textsuperscript{47} studied the thermodynamics of Cl\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} in NO\textsubscript{3} form of hydrous zirconia at 25-80\textdegree C. Thermodynamic equilibrium constant was evaluated and then the other parameters. The use of mixed solvent systems like methanol-water system changes the value of $\Delta G$, $\Delta H$, $\Delta S$ on hydrous Zirconia\textsuperscript{48} and hence the selectivity coefficient is affected. Misakard Mikhail\textsuperscript{49} studied the thermodynamics of NO\textsubscript{3}\textsuperscript{−}, Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, Br\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SCN\textsuperscript{−} exchange on hydrous Ceria. Various models like Eisenman model, may throw some light on the anion exchange phenomenon.
<table>
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<tr>
<th>Sl. No.</th>
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<th>Various Parameters</th>
<th>Reference</th>
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<td>-do-</td>
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<td>Sl. No.</td>
<td>Ion exchange material</td>
<td>Systems studied</td>
<td>Various Parameters</td>
<td>Reference</td>
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<td>Semi-crystalline zirconium phosphate</td>
<td>Li⁺, K⁺ and Cs⁺-H⁺</td>
<td>ΔG°, ΔH° and ΔS°</td>
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<td>10.</td>
<td>-do-</td>
<td>Cs⁺-Rb⁺, Cs⁺-K⁺</td>
<td>K, ΔG° and ΔH°</td>
<td>35</td>
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<td>11.</td>
<td>Semi-crystalline zirconium phosphate</td>
<td>Cs⁺-H⁺ and H⁺-Cs⁺</td>
<td>K</td>
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<td>12.</td>
<td>-Zirconium phosphate</td>
<td>K⁺-H⁺</td>
<td>Completed layer structure</td>
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<td>13.</td>
<td>-do-</td>
<td>Li⁺-Cs⁺, Na⁺-Cs⁺, K⁺-Cs⁺</td>
<td>K, ΔG° and ΔH°</td>
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<td>14.</td>
<td>-do-</td>
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<td>ΔG° (298°C)</td>
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<td>15.</td>
<td>Crystalline antimonio acid</td>
<td>H⁺-Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Ca²⁺</td>
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<td>16.</td>
<td>-do-</td>
<td>Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺-H⁺</td>
<td>Selectivity sequence</td>
<td>38</td>
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<td></td>
<td></td>
<td>reversibility X-ray studies</td>
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<td>17.</td>
<td>-do-</td>
<td>Mg²⁺, Sr²⁺, Ca²⁺, Ba²⁺ and</td>
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<td>(ln K_H)</td>
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<td>X_M → 0</td>
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Table 1.1 contd.

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<th>Various Parameters</th>
<th>Reference</th>
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<tr>
<td>18.</td>
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<td>NH\textsubscript{4}\textsuperscript{+}-H\textsuperscript{+}, CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}-H\textsuperscript{+}, C\textsubscript{2}H\textsubscript{5}NH\textsubscript{3}\textsuperscript{+}-H\textsuperscript{+}, (CH\textsubscript{3})\textsubscript{2}NH\textsuperscript{+}-H\textsuperscript{+}, iso-C\textsubscript{3}H\textsubscript{7}NH\textsubscript{3}\textsuperscript{+}-H\textsuperscript{+} and (C\textsubscript{2}H\textsubscript{5})\textsubscript{4}N\textsuperscript{+}-H\textsuperscript{+}</td>
<td>ln K, ΔG°, ΔH° and ΔS°</td>
<td>40</td>
</tr>
<tr>
<td>19.</td>
<td>-do-</td>
<td>H\textsuperscript{+}-Li\textsuperscript{+}, H\textsuperscript{+}-Na\textsuperscript{+}, H\textsuperscript{+}-K\textsuperscript{+}, H\textsuperscript{+}-Rb\textsuperscript{+} and H\textsuperscript{+}-Cs\textsuperscript{+}</td>
<td>ln K, ΔG, and X-ray studies</td>
<td>41</td>
</tr>
<tr>
<td>20.</td>
<td>Ferric antimonate</td>
<td>H\textsuperscript{+}-Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+} and Rb\textsuperscript{+}</td>
<td>K, ΔG°, ΔH°, ΔS°</td>
<td>20</td>
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<tr>
<td>21.</td>
<td>-do-</td>
<td>Na\textsuperscript{+}-Ba\textsubscript{2+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+} and Sr\textsuperscript{2+}</td>
<td>K, ΔG°, ΔH°, ΔS°</td>
<td>19</td>
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<td>22.</td>
<td>Niobium arsenate</td>
<td>H\textsuperscript{+}-Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Ba\textsuperscript{2+} and Sr\textsuperscript{2+}</td>
<td>K\textsubscript{m}, ΔG°, ΔH°, ΔS° and ΔS\textsubscript{EX}</td>
<td>21</td>
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<tr>
<td>23.</td>
<td>Ce(IV) phosphate</td>
<td>Li\textsuperscript{+}-H\textsuperscript{+}, Na\textsuperscript{+}-H\textsuperscript{+}, K\textsuperscript{+}-H\textsuperscript{+}</td>
<td>ΔH°</td>
<td>42</td>
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<td>24.</td>
<td>Ferriate (natural zeolite)</td>
<td>Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+}, Cs\textsuperscript{+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}ΔH°</td>
<td>K\textsuperscript{m}, NH\textsubscript{4}\textsuperscript{+} and Ag\textsuperscript{+}</td>
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<td>25.</td>
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but certain factors like non coulombic electrostatic attraction and oxide entropy changes have been ignored in this model.

Although thermodynamic studies of ion exchange helps in investigating the conditions at equilibrium, but it does not provide with any information about the mechanism of change from one state to the other and the time required there on. The kinetics of exchange takes these factors into consideration.

The kinetics depends on the surface area of the ion exchange particles. Thus where diffusion rate or Kinetics are of importance, Particle size and macro porosity of the exchanger become important parameters. The Kinetics of a simple homogeneous chemical reaction is governed by their differential rate of reaction depending on the disappearance of product or formation of reactant with time.

\[ A X + B Y \rightleftharpoons \text{product} \]
\[ \text{Rate} = K \cdot X^A \cdot Y^B \]

where \( K \) is the rate constant and \((X)\) and \((Y)\) are the concentrations of reacting species. The powers \( A \) and \( B \) are the orders of the reaction with respect to \( X \) and \( Y \) respectively.
The Ion exchange process is however quite different in many respect from such simple chemical reactions. In the first case it concerns a reaction which involves the transport of ions from solution to exchanger and vice versa i.e. ion exchange process constitutes a solid phase in aqueous solution and hence is heterogeneous. Secondly in dilute solutions there is effectively no electrolyte penetration into the exchanger and hence the co-ion has no part to play in the overall reaction mechanism, and thirdly the electroneutrality is maintained every time, hence, the exchange process is stoichiometric. This coupling of the flows of the entering and leaving ions simplifies the treatment of ion exchange kinetics.

For an exchanger in 'A' form placed in an solute with 'B' as counter ion, following steps may be considered.

1. Migration of counter ion 'A' from exchanger to the adhering film of the particle
2. Migration of 'A' from film to solution
3. Chemical reaction between 'A' and 'B'
4. Migration of 'B' from solution to film
5. Migration of 'B' from film to the particle.

Since the slowest step is the rate determining step hence all the above steps are considered. Thus three
distinct type of kinetic processes may be considered in an ion exchange process.

a. The film diffusion control (FDC) i.e. inter diffusion of counter ions in the adhered film.

b. Particle diffusion control (PDC) i.e. inter diffusion of counter ions in the ion exchanger itself.

c. Chemical reaction control between two types of counter ions.

It is important to note that till now all the kinetic studies were found to depend either on film diffusion or on particle diffusion and not on the chemical exchange reaction. Furthermore, the rate determining step also depends upon the experimental conditions.

Nachod and Wood\textsuperscript{50} have made the first serious attempt on the kinetic studies of ion exchange. They have studied the reaction rate with which ions from solutions are removed by the solid ion exchanger or conversely the rate with which the exchangeable ions are released from the exchanger. Later on Boyd et. al\textsuperscript{51} have studied kinetics of metal ions on the resin beads and have given a clear understanding about the particle and film diffusion phenomena which govern the ion exchange.
Reichenberg\(^5\) confirmed that at high concentration the rate is independent of ingoing ion (particle diffusion control). Nancollas\(^5\) studied the kinetics of Na\(^+\)-H\(^+\) exchange on crystalline zirconium phosphate. The exchange rate is initially fast and then becomes slow suggesting a change in crystal structure. Fuga and Kikindai\(^5\) studied the kinetics of ion exchange between alkali metals and Zirconium antimonate in H\(^+\) form at 25°C. They found that the rate of reaction increases with the atomic number of the cation.

Costantino\(^5\) et al have studied the self diffusion of Na\(^+\) and K\(^+\) ions on micro crystals of Zr(NaPO\(_4\)) \(_3\)H\(_2\)O and Zr(KPO\(_4\)) \(_3\)H\(_2\)O and modified Ficks equation to take into account the non-uniformity of the particle size. The equation obtained have been employed in a study of self diffusion rate of Na\(^+\) and K\(^+\) ions in the above exchange.

Some work on kinetics has also been done in our laboratories. A kinetic study of exchange of cations Ag\(^+\), alkaline earth metals, Y\(^3+\), and Th\(^4+\) was made on tantalum arsenate.\(^5\) It was a P.D.C. mechanism. The kinetic study of Ag\(^+\), Zn\(^2+\), Cd\(^2+\), Hg\(^2+\), La\(^3+\) and Th\(^4+\) ions on Fe(III) antimonate has been made at different temperatures. Here again the mechanism is P.D.C. Similar studies were made on Stannic arsenate.\(^5\) Various kinetic parameters have been evaluated.
Much of the kinetic studies have been done on the synthetic organic ion exchange resins by Junge et al\textsuperscript{59} and others.\textsuperscript{60-74}

The preparation of an anion exchange resin with good chemical and thermal stability remains an outstanding problem. The anion exchange resins are usually prepared by introducing an amine or ammonium group as a source of positive ionogenic groups into polystyrene divinyl benzene copolymer, through a Friedal-crafts condensation. The common ion exchangers are based on triethylamine. An inorganic ion exchanger can be prepared by introducing triethylamine group into the hydrous oxide of a trivalent or tetravalent metal ion. The amine group may also act as a chelating group to certain cations and hence such a material may be useful in two ways.

(1) As an anion exchanger

(2) As chelating ion exchanger

Conventional ion exchangers are practically insoluble cross linked polymers that contain either basic or acidic functional groups in a high concentration. These functional groups are tightly attached to the polymer matrix and are commonly introduced into the basic solid copolymer by a
substitution reaction. Practice however has proved this method to be seldom applicable in the synthesis of a chelating resin.

Above all the resin should have in addition to the demanded selectivity, sufficient mechanical and chemical stability especially towards acids and bases which are used for the regeneration of the resin. In the practical performance of a separation, dimensions of the column and the amount of resin required should be as small as possible, consequently a resin should have an effective exchange capacity of at least 1 meq/gm (referred to the air dried material).

Furthermore, it is necessary that the rate of the complexation be relatively high. According to considerations given by Gregor et al, the following properties are required for a chelating agent that is to be incorporated as a functional group into an ion exchange resin.

1. The chelating agent should yield (alone or with cross linking substances) a resin gel of sufficient stability or, it should be capable of being incorporated by substitution into a polymer matrix.
2. The chelating molecule must possess sufficient chemical stability so that during the synthesis of the resin the functional structure is not changed by polymerization or any other reaction.

3. The steric structure of the chelating molecule should be compact so that the formation of the chelate rings will not be hindered by the matrix.

4. Because the agents forming relatively stable complexes are at least tridentate. It is necessary that the ligand groups of the chelating molecule be situated appropriately so that the specific arrangement of the ligand will be preserved in the resin.

These theoretical considerations make it unlikely that many known chelating agents can be incorporated into a resin without the loss of their selective properties. The group of unsuitable agents would include all that do not form 1:1 complexes (for example anthranilic acid, 8-quinolinol, and 1-nitroso 2-napthol). Long chain molecules such as E.D.T.A. similarly prove to be unsuitable because of the improbability that the chelate configuration occurring in aqueous solution can be maintained on a cross linked polymer. It can be concluded that the building of highly
selective ion exchanger designed for a given separation problem is possible if a few essential requirements are met. 1. A careful choice of the structure of a ligand polymer not only of the chelating group involved but also of the molecular structure surrounding this group.

2. A precise determination of the relative formation constants of a corresponding chelate which must be different by more than one order of magnitude.

3. A maximum compatibility between the polymer and the medium obtained either by adjusting the polymer structure or by using mixed solvent media.

Recently a number of chelating ion exchangers have been synthesized to encourage the applications of ion exchange to a broader range of separation and for the recovery of certain metal ions selectively Table 1.2.

Thus the chelating ion exchanger may provide a convenient technique for the analytical concentrations of many of the more interesting trace elements from natural waters and collection of toxic elements from industrial waste waters. The selectivity of the most complexing agents predominantly depends on their ability to form chelates with
Table 1.2

SOME OF THE IMPORTANT LIGAND ION EXCHANGE RESINS

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Type of Exchanger</th>
<th>Sorption capacity m. moles/g</th>
<th>Selectivity</th>
<th>Reference</th>
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<tr>
<td>1.</td>
<td>Oxime and diethyl amino-resin</td>
<td>2.0</td>
<td>Cu²⁺</td>
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<tr>
<td>2.</td>
<td>8-hydroxyquinoline and 8-hydroxyquinoline resin</td>
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<td>Cu²⁺, Zn²⁺</td>
<td>77</td>
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<tr>
<td>3.</td>
<td>O-hydroxy oxime resin</td>
<td>-</td>
<td>Cu²⁺, Mo⁶⁺</td>
<td>78</td>
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<tr>
<td>4.</td>
<td>Thioglycolate resin</td>
<td>-</td>
<td>Ag⁺⁺, Bi³⁺, Sn⁴⁺, Sb³⁺, Hg²⁺⁺, U⁶⁺</td>
<td>79</td>
</tr>
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<td>5.</td>
<td>Amino acid type resin</td>
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<td>U⁶⁺, Cu²⁺, Ni²⁺, Fe³⁺</td>
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<td>6.</td>
<td>Phosphate type resin</td>
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<td>7.</td>
<td>N-Acylphenyl hydroxyl</td>
<td>0.45</td>
<td>-</td>
<td>81</td>
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<td>8.</td>
<td>Aluminium oxide</td>
<td>-</td>
<td>NH₄⁺</td>
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<td>9.</td>
<td>Alumina and silica gel</td>
<td>-</td>
<td>Ag⁺</td>
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<td>10.</td>
<td>Micoreticular resin</td>
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<td>Ag⁺</td>
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<td>Cellulosic exchanger</td>
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<td>Sb³⁺, Co²⁺</td>
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<td>Cation exchange resin</td>
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<td>Zn²⁺</td>
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<td>Sulphonated type resin</td>
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<td>Carboxylic ion exchanger</td>
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<td>Co(en)³⁺</td>
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<td>15.</td>
<td>Chilosan</td>
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<td>Cu²⁺</td>
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<td>Chelating resin (Dithio carbamate)</td>
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<td>Cu²⁺</td>
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<td>Sl. No.</td>
<td>Type of Exchanger</td>
<td>Sorption Capacity m. moles/g</td>
<td>Selectivity</td>
<td>Reference</td>
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<td>Acrylic resin</td>
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<td>Cu$^{2+}$</td>
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<td>Chelating resin</td>
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<td>Pd$^{2+}$, Pt$^{4+}$, Rh$^{3+}$, Ir$^{3+}$</td>
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<tr>
<td>(Semithio carbazide)</td>
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<td>819 mg/g</td>
<td>An$^{3+}$</td>
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<td>19.</td>
<td>Chelating resin</td>
<td>-</td>
<td>Cu$^{2+}$, Cd$^{2+}$</td>
<td>93</td>
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<tr>
<td>Poly (Vinyl benzylthio urea)</td>
<td></td>
<td>1.9</td>
<td>Cu$^{2+}$</td>
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<tr>
<td>20.</td>
<td>Chelating resin</td>
<td>-</td>
<td>M$^{2+}$, W$^{6+}$</td>
<td>94</td>
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<tr>
<td>Poly (hydroxamic acid)</td>
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<td>819 mg/g</td>
<td>An$^{3+}$</td>
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<tr>
<td>21.</td>
<td>Chelating resin</td>
<td>-</td>
<td>Cu$^{2+}$, Cd$^{2+}$</td>
<td>93</td>
</tr>
<tr>
<td>22.</td>
<td>Chelating resin</td>
<td>-</td>
<td>M$^{2+}$, W$^{6+}$</td>
<td>94</td>
</tr>
</tbody>
</table>
certain metal ions. For this purpose the development of complexing ion exchangers have taken place where the complexation equilibrium will play an important role such studies can be directed to the following three categories.

(1) An ion exchanger is used in appropriate metal ion form and the complexing agent is present as a solvent in the liquid phase.

(2) An exchanger containing a complexing agent functional group attached to the matrix is used and the metal ion is present in the liquid phase.

(3) The solid phase is a chelating exchanger and the liquid phase also contains a complexing agent as solute.

Implementation of the first and the second possibilities will involve directly the metal complex equilibria in heterogeneous phase, where as the third possibility is mainly advantageous of chelate exchange system. In this field the successful efforts have been made by Bayer and Coworkers, Blasius and Coworkers, Gregor et al., Kennedy et al. and many others. The complex formation in such reaction is based mainly on the use of N, S, and O as donor atoms.
for the formation of coordinate bonds. A donor atom must be of high electronegativity. Chelating ion exchanger with nitrogen as the sole donor atom are relatively less in number. Gold and Gregor\textsuperscript{125} prepared a chelating resin with aromatic nitrogen as the only functional group.

The number of chelating ion exchangers with nitrogen and oxygen as donor atoms is comparatively much large. Klyatschko\textsuperscript{126} prepared a material by fixing E.D.T.A. as a solid solution within a phenol-formaldehyde condensate. Many workers prepared such materials by fixing ligands to the \textit{C}_6\textit{H}_6 nucleus of the cross linked polystyrene.\textsuperscript{111,127} Blasius\textsuperscript{102} prepared such materials by the reaction of chloromethylated polystyrene with various aliphatic amines and subsequent reaction with chloroacetic acid. Stamberg\textsuperscript{125,128} prepared several resins with vicinal dioxime groups using polystyrene as a starting material. Incorporation of thiol groups has also be applied to prepare such materials\textsuperscript{113,129} with sulfur as the sole donor atom.

The number of such materials utilized for analytical applications is small. Nevertheless many different chelating resins have been prepared. The main difficulty in their use is restriction of effective simpler means and chemical stability of these materials.
Although a number of chelate ion exchanger resins have come in wide use but no comparative studies exists on inorganic ion exchangers containing such groups.

Solid liquid interaction have always been of interest for many workers because of the diversity of the phenomena involved and immense application in chemistry and related science.

When a solution containing some solute is brought into contact with a solid, some of the solute is taken up by the solid. This phenomena of the uptake of a solute by a solid is referred to as "Sorption". In sorption the solute molecules are sorbed either by the inner framework of the solid in contact with the solution or by its surface only. So when the solute is adsorbed by the surface only the process is called as "Adsorption" and when the solute is absorbed by the solid to inner layer the process is called as "Absorption".

Adsorption is a fundamental natural process. It is one of the most fascinating areas of chemistry. Since the molecules on the surface have an environment different from those in the bulk of the material, the surface energy is different from the energy of the bulk. Concentration of
the molecules of a gas or a liquid on the surface of the solid is termed as "adsorption". This process is different from absorption which results from the penetration of one component throughout the body of another.

The adsorbing material is called as adsorbate and the underlying material is called "adsorbent" or substrate. Adsorption is of utmost importance in the field of agriculture, industries, and analytical chemistry. Adsorption of pollutants by soil, of dyes by wool and cotton, and of impurities by insoluble precipitates are well known examples. Similarly adsorption indicators and adsorption chromatography are also well known in the chemical analyses. Another important application of adsorption is in catalysis. A surface can catalyse numerous reactions depending upon the configuration of the adsorbed molecule and the nature of the adsorbent. A study of adsorption phenomena helps us in understanding the process by means of a molecular model.

The photoelectron spectroscopy method such as E.S.C.A. can be applied to reveal some of the bonding properties of the adsorbed species. In surface studies this is normally referred as photoemission spectroscopy. Infrared absorption spectra can be obtained by using I.R. transparent material and a technique that involves the internal reflection.
Adsorption is of two types physical and chemical. The physical adsorption is called as "physisorption" and chemical adsorption as "chemisorption". In the former the molecules are adsorbed to a solid surface by essentially the physical forces. In chemisorption, however the molecule forms the chemical bonds with the solid surface. In case of physical adsorption there is a vander waal's interaction (for instance dispersion or polar interaction) between the surface and the adsorbed molecule. These are weak types of interaction and the amount of energy released when a molecule is physisorbed is of the order of 25 kJ mol\(^{-1}\) ie. the enthalpy of condensation. This energy can be absorbed by the vibration of the lattice and is dissipated as heat. A molecule bouncing across the surface will lose its kinetic energy and stick to the surface resulting in the rise in temperature of the system, ie. heat is evolved. In chemisorption which is shortening of chemical adsorption the molecules stick to the surface as a result of the formation of chemical bonds, usually covalent bonds and tend to find the site that increases their coordination number with the temperature. Thus the energy of attachment is greater than in that of physical sorption and is in the range of 200 kJ mol\(^{-1}\).
For a spontaneous process chemisorption must be exothermic (barring the exceptional case.). This can be explained as follows:

For a spontaneous process $\Delta G$ should be negative. As the species is adsorbed there is a reduction in its translational freedom so $\Delta S$ is also negative. Hence $\Delta H$ must be negative if $\Delta G = \Delta H + T \Delta S$ is to be negative and a negative $\Delta H$ value corresponds to the exothermic process. But sometimes the adsorbate dissociates at high temperature leading to breaking of bonds and thus has high translational mobility on the surface. As in case of the adsorption of hydrogen on the glass surface, enthalpy is small and positive.

A formal distinction between the chemisorption and physisorption was formerly the magnitude of the enthalpy of adsorbed ion. $\Delta H$ for physisorption is rarely more negative than about -25 kJ mol$^{-1}$ while that for chemisorption is usually more negative and sometimes much more negative than -40 kJ mol$^{-1}$.

Plotting of adsorption isotherms is the most convenient way of studying and understanding the nature of adsorption taking place in a particular system. The isotherms are obtained by plotting the amount adsorbed against the
equilibrium concentration at any instant at a particular temperature. Thus different types of curves with different slopes and initial portion of the curve are obtained. Based on these factors adsorption isotherms can be divided into four main classes and thereafter into subgroups. The main classes are as follows.

a. Langmuir isotherm or L curves.
b. S. type of isotherms
c. High affinity isotherm or H curves.
d. Constant partition or C curves.

Langmuir isotherms indicate that molecules are adsorbed flat on the surface or sometimes vertically oriented with strong intermolecular attraction. This is the best known isotherm. These curves occur in majority of cases of adsorption from dilute solution and for cases of the other types appear to have been previously recorded. The initial slope depends on the rate of change of site availability with increase in solute adsorbed. As more solute is taken up, there is usually progressively less chance that a bombarding solute molecules will find a suitable site on which it can be adsorbed. The initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to
find out a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from the solvent. The type of systems which give this curve have one of the following characteristics.

1. The adsorbed molecules are most likely to be adsorbed flat eg. resorcinol on alumina (2) if adsorbed end on they encounter little solvent competition eg. high polar solute on substrate or systems with monofunctional ionic substances with strong intermolecular attraction.

- S types curves indicates the vertical orientation of the adsorbed molecule at that surface. The initial part of the S curve shows that more solute is already adsorbed and it is easier for the additional amount to become fixed.

- High affinity curves are given by solutes adsorbed as ionic micelles and by high affinity ions exchanging with low affinity ions. This is a special case of L curve in which the solute has such high affinity that in dilute solution it is completely adsorbed or at least there is measurable amount remaining in the solution. Thus the initial part is vertical. The adsorbed species are often large units ie. ionic micelles or polymeric molecules, but sometimes they
are apparently single ions which exchange with other ions of much lower affinity for the surface e.g. sulfonated dye ions exchange with Cl⁻ alumina, cyanide dye on silver halide. In the most extreme cases the curve is a horizontal line running into the vertical axis.

And lastly the constant partition curves or the linear curves are obtained when the solute penetrates into the solid more readily than does the solvent. There is a constant distribution of solute between solution and substrate up to the maximum possible adsorption where an abrupt change to a horizontal plateau occurs. Such type of curves are obtained for the partition of a solute between two immiscible solvents. Favourable conditions for "C" curve to appear are

(a) A porous substrate with flexible molecule and regions of differing degree of crystallinity and a solute with (b) higher affinity for the substrate than the solvent has and with (c) better penetrating power by virtue of conditions (d) and of molecular geometry, into the crystalline regions of the substrate.

The subgroups of these classes are arranged according to the shape of the parts of the curves farther from the
origin, and the significance of plateau and changes of slope are described. Fundamentally the linearity shows that the number of sites for adsorption remains constant i.e. as more solute is adsorbed more sites must be created. Such a situation arises when the solute has a higher attraction for the absorbent than the solvent itself has. Thus the solute can break the inter substrate bond more readily than the solvent could, and if its molecular dimension were suitable could penetrate to the structure of the substrate in regions not already penetrated by the solvent. This action has been compared to the opening of a zip fastener, the fastening represents the intermolecular bonds of the substrate, and the slider represents the first molecule or group of molecule of solute to penetrate. This opens up the structure and allows more solute molecule to enter. This action stops abruptly when more highly crystalline regions of the substrate are reached. In fact the isotherms usually do suddenly change direction to give the horizontal plateau. Thus a linear isotherm indicate that the solute is penetrating the regions inaccessible to the solvent.

Nearly all sufficiently complete curves have either a plateau or an inflection (knee). Those that do not have plateau or knee are clearly incomplete i.e. surface
saturation is not reached probably because of experimental difficulties. The plateau or the beginning of the linear portion above the "knee" must represent the "first degree saturation" of the surface i.e. the condition in which all possible sites in the original surface are filled and further the adsorption can take place only in new surface. For convenience this degree of coverage may be called the formation of a complete monolayer but this does not necessarily imply that it is a close packed layer of single molecule or ions, as in a compressed monolayer on water. It may be so in some cases and when it is specific surface area determination can readily be made. Generally however the layer may (a) contain solvent as well as solute molecule or (b) consist only of isolated cluster of solute molecule adsorbed on the most active sites or (c) consists of ionic micelle either packed closely or well separated.

The significance of a long plateau must be that a high energy has to be overcome before additional adsorption can occur on new sites, after the surface has been saturated to the First degree. The solute has high affinity for the solvent but low affinity for the layer of solute molecule already adsorbed. Adsorption of ionic micelles give curves with long plateau. In this case the solid surface when
covered will tend to repel other micelles holding the same charge. A short plateau means that the adsorbed solute molecule expose a surface which has nearly the same affinity for more solute as the original surface had.

Second rise or plateau are attributed to the development of a fresh surface on which adsorption can occur. The second plateau represents the complete saturation of the new surface.

The different models for adsorption applicable to both gases and liquids, are available in literature. They are however being discussed in brief as follows.

1. **Langmuir Model**

   Langmuir proposed

   \[
   \frac{C_e}{A_m} = \frac{1}{K} \cdot \frac{1}{b} + \left(\frac{1}{b}\right) \cdot C_e
   \]

   Where \( C_e \) is the equilibrium concentration and \( A_m \) is the amount adsorbed per specified amount of adsorbent. \( K \) is the equilibrium constant and \( b \) is the amount of adsorbate required to form a monolayer. Hence a plot of \( \frac{C_e}{m} \) Vs \( C_e \) should be a straight line, with a slope equal to \( \frac{1}{b} \) and \\
   \[ 1 \] as intercept

   \[ K \quad b \]
(II) **Freundlich Model**

According to this model

\[ A_m = K \cdot C_e^{1/n} \]

\[ \ln A_m = \ln K + \frac{1}{n} \ln C_e \]

Where all the terms have the usual significance and \( n \) is an empirical constant. thus a plot of \( \ln A_m \) Vs \( \ln C_e \) should give a straight line with a slope equal to \( 1/n \) and intercept gives the value of \( \ln K \).

This model deals with the multilayer adsorption of the substance on the adsorbent.

(III) **BET Model**

This model was given by Brunaur Emmet and Teller for a multilayer adsorption. The derivation is a development of the langmuir argument and it assumes that each layer with an exposed surface is in equilibrium with the adsorbent.

Thus

\[
\frac{C_e}{A_m(C_0-C_e)} = \frac{1}{K} + \frac{1}{K(Ce/C_n)}
\]

This equation may also be written as

\[
\frac{Z}{(1-Z)A_m} = \frac{1}{K} + \frac{1}{K} \times Z
\]

where \( Z = C_e/C_i \)
\[ K = Am(\text{mon}) \times C \]

where \( Am(\text{mon}) \) is the amount of adsorbent adsorbed by the adsorbate for monolayer formation, \( C_0 \) is the initial concentration of the adsorbate, \( C \) is constant at any given temperature for a complete monolayer formation, it can be written as -

\[
\frac{(E_I - E_L)}{C} = \exp RT
\]

Where \( E_I \) = heat of adsorption of the first layer.
\( E_L \) = Heat of total adsorption
\( R \) = Universal gas constant
\( T \) = absolute temperature

When \( C \) is large (\( \sim 100 \)) the equation may be changed to

\[
\frac{AM}{Am(\text{mon})} \sim \frac{I}{I-Z}
\]

Thus a plot of \( \frac{I}{I-Z} \) Vs Z should be a straight line with slope equal to \( C-1/K \) and \( 1/K \) as intercept. Thus \( Am(\text{mon}) \) can be obtained and hence the total surface area of the adsorbent by using these equations.
(IV) Temkin Model

This model deals with the adsorption of solute on the adsorbents with the assumption that there are a number of energetically unequal adsorption sites present in the adsorbent. Thus equation for Temkin isotherm can be written as

\[ A_m = C_1 \ln (C_2 K C_e) \]

where \( C_1 \) and \( C_2 \) are constants, corresponding to the supposition that the enthalpy changes linearly with concentration.

The adsorbents which have been commonly studied are alumina, silica, carbon and cellulose. These were mainly used for the adsorption of hydrocarbon, alcohols, phenols, organic acids, dyes, pesticides and pollutants etc. Literature survey shows that even inorganic ion exchangers and organic synthetic resins have also been used for many adsorption studies Table 1.3.
### Table 1.3

**CERTAIN OXIDES, INORGANIC ION EXCHANGERS AND ION EXCHANGE RESINS USED AS ADSORBENTS**

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Ion exchanger</th>
<th>Adsorption of</th>
<th>Other studies</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>AV-17 MS</td>
<td>SDS from industrial waste water</td>
<td>ΔS sorption, kinetics of sorption.</td>
<td>131</td>
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<tr>
<td>2.</td>
<td>Hydrous TiO₂</td>
<td>alkaline earth</td>
<td>distribution coefficient, Ion exchange rate</td>
<td>132</td>
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<tr>
<td>3.</td>
<td>Hydroxylated silica</td>
<td>dioxane, acetone and H₂O from binary and ternary solution</td>
<td>-</td>
<td>133</td>
</tr>
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<td>4.</td>
<td>Zinc monoxide</td>
<td>alkali metals</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>5.</td>
<td>AB-16 GS (Ion exchange resin)</td>
<td>Colour removal from sugar juice</td>
<td>-</td>
<td>135</td>
</tr>
<tr>
<td>6.</td>
<td>Dowex-50 W-X8</td>
<td>Protonium, D₂O</td>
<td>BET isotherm were observed and ΔG was calculated</td>
<td>136</td>
</tr>
<tr>
<td>7.</td>
<td>- MnO₂</td>
<td>alkaline earth</td>
<td>Langmuir isotherm and apparent heat of adsorption Q was calculated</td>
<td>137</td>
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<tr>
<td>8.</td>
<td>-do-</td>
<td>Cd²⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺</td>
<td>Langmuir isotherm were studied and apparent heat of adsorption Q were calculated</td>
<td>138</td>
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<tr>
<td>9.</td>
<td>Zinc oxide</td>
<td>H₂S from natural gas</td>
<td>-</td>
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<tr>
<td>Sl.No.</td>
<td>Ion exchanger</td>
<td>Adsorption of</td>
<td>Other studies</td>
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<tr>
<td>10.</td>
<td>TiO₂</td>
<td>Amino acids like glutamic acid lysin cysteine (27-33 mg/gm) Proline, leucine phenylalanine</td>
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<td>11.</td>
<td>Semi-chelate CR-Z</td>
<td>Cr⁺⁶ from waste water</td>
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<td>12.</td>
<td>Amberlite XAD-7</td>
<td>Human serum</td>
<td>langmuir isotherm</td>
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<td>A-zeolite X-zeolite mordentite</td>
<td>fatty acids like heptonic acid oleic acid</td>
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<td>14.</td>
<td>Anion exchange resin like AN-31, AV-16G and Amphoteric ion exchanger ANKB-1 and ANKB-2</td>
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<td>Crosslinked polyacrylamidoxime resin</td>
<td>uranium from acidic eluent</td>
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<td>16.</td>
<td>Lead dioxide</td>
<td>Cl⁻, ClO₄⁻, SO₄²⁻, HSO₄⁻, H₂PO₄⁻, NO₃⁻</td>
<td>Freundlich isotherm was best fit</td>
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<td>Ion exchanger</td>
<td>Adsorption of</td>
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<td>17.</td>
<td>Anion exchanger SAN-1</td>
<td>Boric acid</td>
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<td>Strongly basic anion exchanger</td>
<td>Phenol</td>
<td>Freundlich isotherm</td>
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<td>Hydrated zirconium oxide</td>
<td>Pt(IV) Cl complex</td>
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<td>20.</td>
<td>Fly ash China clay</td>
<td>Cr(VI) from aq solution</td>
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<td>21.</td>
<td>Mordenite</td>
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<td>23.</td>
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<td>Dowex 50 W-X8 and Amberlite IRC-50</td>
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<td>Chelating resin containing dithiocarbamate groups</td>
<td>U from water sea water</td>
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<td>Sorption kinetics of $Li^+$</td>
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</tr>
<tr>
<td>43.</td>
<td>AP [2-aminopyridine resin]</td>
<td>Sorption of noble metal</td>
<td>-</td>
<td>173</td>
</tr>
<tr>
<td>44.</td>
<td>Duolite ES 467</td>
<td>Sorption kinetic of Ga from liquid from Zn ore leaching</td>
<td>-</td>
<td>174</td>
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</tbody>
</table>
The present work includes equilibrium and kinetic studies on synthetic ion exchangers and ligand ion exchangers.

A new chelating ion exchanger lanthanum-diethanolamine was prepared and equilibrium of sorption of Cu\(^{2+}\) on this material was studied in detail. Structural studies were carried out and the tentative structure was established by variety of modern techniques.

Detailed thermodynamic studies have been carried out on synthetic organic ion exchange resins Amberlite IRC-718 and Duolite ES-467. Kinetic studies have also been done on Amberlite IRC-718 and the mechanism of exchange was elucidated.
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