CHAPTER I

INTRODUCTION
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A. History and Application of Ion Exchangers

The term ion exchange is generally understood to mean the exchange of ions of like charges between solution and a solid (highly insoluble substance) in contact with it. For a good ion exchange material the solid must have an open porous molecular structure so that the ions in the solid molecules (matrix) can move freely in and out of it. Many substances both natural and artificially prepared have ion exchange properties. All ion exchangers of significance have several properties in common; they are almost insoluble in water, are selective for ions that will exchange in a way that does not alter appreciably the surrounding solution without any appreciable physical change occurring in the solid exchanger material. The ion exchangers are of complex nature and are in fact polymeric. Two types of ion exchangers have been in use (i) organic ion exchangers (ion exchange resins) and (ii) inorganic ion exchanger ( sparingly soluble solids).

Both type of ion exchangers possess cation as well as anion exchange properties i.e. some of them possess tendency to exchange its cations with the cations present in the solution phase while the others possess tendency to exchange...
its anion; with the cation present in the solution. The former are known as cation exchangers and the latter as anion exchangers.

A brief description of the ion exchange resins is given below:

The ion exchange resins consist of small beads usually made of polystyrene cross-linked in a manner such that they produce an insoluble sponge-like network, the matrix of which contains chemical groups capable of exchanging cation or anions. Thus, one gets cation- and anion-exchange resins. Resins with highly ionised groups are known as strong exchangers, while resins with only partially ionised groups are called weak exchangers.

**Cation exchange resins:**

Cation exchange resins contain ions which are capable of exchanging with cations present in the surrounding medium without altering the major physical characteristics of the resin.

A widely used cation exchange resin is that obtained by co-polymerisation of styrene and a small proportion of divinyl benzene followed by sulphonation; it may be represented as:
Here the resin matrix contains sulphonic acid groupings
\(-\left(\text{SO}_3\right)\text{H}^+\) hydrogen ions \((\text{H})^+\) being those capable of exchange.

**Anion exchange resins:**

Anion exchange resins have similar structures, except that the resin matrix contains ions which are capable of exchanging with anions in the surrounding medium without altering the major physical characteristics of the resin.

A typical example is shown below:

Here the resin matrix contains a substituted ammonium hydroxide grouping \(-\text{N}\left(\text{CH}_3\right)_3\text{OH}^+\), hydroxyl ions \((\text{OH})^-\) being those capable of exchange with anions.

The basic requirements of a useful resin are:

(i) the resin must be sufficiently cross-linked to have a negligible solubility,
(ii) the resin must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate,

(iii) the resin must contain a sufficient number of accessible ionic exchange groups and must be chemically stable, and

(iv) the swollen resin must be denser than water

**Action of the ion exchange resins:**

The reaction between a cation exchange resin \( \text{Res} \) and \( \text{Na}^+ \) ions can be represented as:

\[
\text{Res} - \text{H}^+ + \text{Na}^+ \xrightarrow{\text{exchange}} \text{Res} - \text{Na}^+ + \text{H}^+
\]

while that of the anion exchange resin with chloride ions would be shown as:

\[
\text{Res} - \text{OH}^- + \text{Cl}^- \xrightarrow{\text{exchange}} \text{Res} - \text{Cl}^- + \text{OH}^-
\]

A similar mechanism holds true for class of the inorganic ion exchangers also. In general, the ion exchange reaction mechanism may be understood to involve the simultaneous exchange of ions present in the solid (Exchanger materials) with those of the ions present in solution.

Numerous inorganic ion exchangers both natural such as zeolites, aluminosilicates and clays and those artificially prepared are known; synthetic inorganic ion exchangers may be classified into the following class of compounds:

(i) Heteropoly acids and their salts,
Acidic forms of multivalent metals,

Hydrazides,

Insoluble ferricyanides,

Synthetic alumino silicates,

Sulphides, alkaline earth sulphates

The early ion exchangers were of inorganic origin, but the reproducibility in the preparation and the ion exchange properties of the organic resins dominated the ion exchange scene for quite a long time. Recently, the use of inorganic ion exchangers in separations involving high temperature and the radioactive waste disposals, diverted the attention of scientists towards investigating inorganic ion exchangers capable of withstanding conditions of high temperature without much loss in their exchange properties.

The ion exchange techniques were known from a very long time when these naturally occurring ion-exchangers were mainly used for the purpose of water softening. Cams 1 in 1905 first prepared sodium permangit based exchangers and used them for water softening. Synthetic zeolites were first used by Pollin and Bell 2 for the collection and separation of ammonia from biological wastes. Behrät 3 used the column techniques for the softening of natural...
water and also for the determination of its sulphate content.

However, the true industrial era of ion exchange began in 1955 with the synthesis of phenol- formaldehyde based cation exchange resins by Adams and Holmes. This technique has found applications not only in water purification but also in analytical chemistry involving separation and isolation of new elements, in hydrometallurgy and of course, in many specialised fields related to the utilization of atomic energy.

The excellent book on inorganic ion exchangers by C.B. Amphlett and J.A. Marinsky and Y. Marcus and review articles by Churms and Materova et al. and that by Vesely give a consolidated account of the work involving synthetic inorganic ion exchangers.

B. Ion exchange equilibria

The ion exchange reactions take place by way of exchange of similarly charged ions between a solution and a solid and therefore, these reactions may be considered as taking place in a heterogeneous system. The solid ion exchange materials are essentially electrolytic substances and possess an ability to exchange its cations or anions freely and rapidly.

$K_d$ and $K_A$ are the two practical quantities which represent the extent of exchange of ions under well defined experimental conditions. $K_d$ and $K_A$ are known as
distribution coefficient and the selectivity quotient respectively and can be determined experimentally.

\( K_d \), the distribution coefficient gives a measure of distribution of the ions in the solid and the solution phases and may be written as:

\[
K_d = \frac{\text{Amount of the ion}(A) \text{ exchanged per gram of the exchanger material in m. equivalents}}{\text{Amount of the ion}(A) \text{ remaining in the solution per ml. in m. equivalents}}
\]

In cases where the amount of the exchanger materials used is not one gram the following formula is used for calculating the \( K_d \) values:

\[
K_d = \frac{100 - X}{X} \times \frac{V}{m}
\]

where \( X \) stands for the \% amount remaining in solution, \( V \) stands for the volume of the solution in ml., \( m \) stands for the mass of the exchanger material in gms.

Another quantity, \( q_0 \), the saturation capacity of the exchanger material gives the total number of milli equivalents of exchangeable ions present per gram of the exchanger material. Conventionally, the uptake of the exchanging ions by the exchanger material has been represented by the notation \( q_A \) which corresponds to the amount of the ion \( A \) in m. equivalents taken up by one gram of the exchanger material under well specified experimental
conditions. However, in the body of the thesis $q_A$ refers to the uptake of the exchanging ion in m. equivalents per 100 mgs or 250 mgs of the exchanger material.

The preference of the exchanger material for an ion $B^+$ relative to an ion $A^+$ between a selected pair of the similar ions at equilibrium is quantitatively expressed by the selectivity quotient $K_A^B$ which is calculated by employing the following relations:

$$K_A^B = \frac{[B^+][A^+]}{[A^+][B^+]}$$

where Barred quantities are the equilibrium concentrations of the two ions in the exchanger phase and others to their concentrations in the solution phase.

The position of the equilibrium in the aforementioned equation has been found to depend on the nature of the exchanging ions $A^+$ and $B^+$ and upon the external conditions of solution such as concentration and pH.

Ion exchangers of all types possess a tendency to exchange with just any type of cation or anion present in the solution, due to which reason the ion exchange process is not a very selective one. However, such selectivity as may exist, sometimes forms the basis of ion
exchange separations of metallic and non-metallic elements even with very similar properties. Keeping in view the practical utility of the ion exchange materials and also for understanding the basic factors contributing to it, many attempts have been made to elucidate the selectivity patterns of various ion exchangers for very many ions. During the last two decades large number of the inorganic ion exchange materials have been prepared under varying experimental conditions and the studies are still in progress in search of ion exchangers possessing very high selectivity for an ion or for a group of ions.

The present day knowledge of the selectivity effects may be summarized as:

(i) At low aqueous concentrations and at ordinary temperatures the extent of exchange increases with increasing valency of the exchanging ions:

\[ \text{Na}^+ < \text{Ca}^{+2} < \text{Al}^{+3} < \text{Th}^{+4} \]

(ii) Under similar conditions the extent of exchange increases with decrease in size of the hydrated univalent cation:

\[ \text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Rb}^+ < \text{Ca}^+ \]

(iii) At higher concentrations the extent of the exchange of the ions of similar valency do not
increase with increasing atomic number but are very similar or even decrease.

(iv) Complex metallic ions and cations exhibit usually high exchange affinity.

(v) Selectivity is affected only slightly by temperatures except in certain cases where uptake of divalent ions relative to the univalent ions increases with temperature.

(vi) In general the selectivity pattern for most common cations are:

\[
\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}
\]

\[
\text{UO}_{2}^{2+} > \text{Tl}^{+} > \text{Ag}^{+} > \text{Cs}^{+} > \text{Rb}^{+} > \text{K}^{+} > \text{NH}_{4}^{+} > \text{Na}^{+} > \text{Li}^{+}
\]

and those for anions:

\[
\text{citrate} > \text{SO}_{4}^{2-} > \text{C}_{2}\text{O}_{4}^{2-} > \text{I}^{-} > \text{NO}_{3}^{-} > \text{CrO}_{4}^{2-} > \text{Br}^{-} > \text{SCN}^{-}
\]

\[
\text{Cl}^{-} > \text{Formate} > \text{acetate} > \text{F}^{-}
\]

C. Theory of ion exchange

Two important theories have been put forward to explain the ion exchange equilibria particularly in inorganic ion exchangers viz. (i) the double layer theory and (ii) concept of zeta potential. These theories are briefly described as:

(i) The double layer theory:

As has been stated earlier the ion exchangers
are like electrolytic substances possessing loosely held exchangeable ions (say A\(^+\)). These loosely held exchangeable ions are soluble in external liquid medium. When the ion exchanger is brought in contact with a polar solvent the exchangeable ion will form an outer charged layer around the oppositely charged exchanger matrix (M\(^-\)) and then it can be pictured as colloid:

\[
\begin{array}{c}
\text{A}^+ \\
\text{M} \\
\text{M}^{-} \\
\text{A}^+ \\
\end{array}
\]

The above concept was developed by Guoy\(^{37-38}\), Chapman\(^{39}\), Stern\(^{40}\) and later by Grahame\(^{41}\). According to this theory an inner fixed charged layer is surrounded by an outer diffuse and mobile charged layer which extends into the external liquid phase with no sharp boundary separating them. Thus the concentration of the ions in this layer varies continuously depending upon the external conditions of pH and concentrating of the ions in the external solution. Such a hypothesis can explain the change in the extent of exchange with change in the concentration and pH of the solution.

This theory successfully illustrates the change in \(q_A\) (exchange capacity) in various hydroxide type of
exchanger materials e.g. Zirconium hydroxide

$$\text{H}_2\text{O} + \text{Zr} - \text{OH} \rightleftharpoons \text{H}^+ \text{O}^- \text{Zr} - \text{OH}^-$$

In acidic medium the presence of $\text{H}^+$ ions in the external solution will suppress the dissociation of $\text{H}^+$ ions thereby causing an adverse effect on the exchange of $\text{H}^+$ ions with other cations in solution hence lowering the exchange capacity $q_A$.

$$\text{H}^+ \rightarrow \text{H}^+ \text{O}^- \text{Zr} - \text{OH}^- \leftarrow \text{H}^+$$

On the other hand, in basic medium the presence of $\text{OH}^-$ ions in the external solution will tend to draw the outer diffuse layer of $\text{H}^+$ ions in solution thereby facilitating the release of $\text{H}^+$ ions easily thus enhancing the exchange capacity, $q_A$.

It has been reported by R.K. Srivastava et al., that the exchange capacity $q_A$ increases with increase in all of the external solution.

$$\text{OH}^- \rightarrow \text{OH}$$

$$\text{H} \text{O}^- \leftarrow \text{H}^+ \text{O}^- \text{Zr} - \text{OH}^- \rightarrow \text{OH}^- \rightarrow \text{OH}^-$$
(i) **Concept of Zeta Potential:**

According to this theory developed by Murray and Puerstenau, when a solid is kept in contact with water a charge is, generally, generated on its surface. This charge and the counter ions, required for electroneutrality, constitute the electrical double layer and the ions are exchanged into and out of this double layer. In inorganic ion exchange materials the potential determining ions are $H^+$ and $OH$ ions. The thickness of the double layer varies with the pH and concentration of the exchanging ions in the external solution. T.W. Healy, K.A. Kraus, and C.B. Amphlett used this concept of zeta potential to explain the ion exchange behaviour of the inorganic ion exchangers.

**D. Ion Exchange Kinetics:**

During an ion exchange reaction mutual exchange of ions takes place between a solid (Exchanger) and solution. Due to the heterogeneity of the reaction process the exchange may not be instantaneously taking place (the ion exchange theory is also of a similar view). Thus the exchange reactions may be assumed to progress with a measurable speed and the speed of the reaction may be determined. However, the study of kinetics of ion exchange reactions is beset with the following problems which need
What is the mechanism of the process?
What is the rate determining step?
What laws govern the rate of exchange?
How can the rate be predicted theoretically?

A survey of the literature, shows that the rate of exchange is governed by diffusion either through the hydrostatic film around the exchanger when placed in water, referred to as 'film controlled' diffusion, or through the pores of the resin matrix called 'particle diffusion control'. The rate of exchange of ions in the former case depends upon the thickness of the film around the exchanger, while in the latter case it depends upon the charge and size of the ion and the electrical potential between the exchanging species and also on the environment through which the ion is diffusing.

The rate of exchange of ions in the exchanger particles is best represented by the following equation, known as Helfferich-Plaskett equation, earlier developed by Boyd and others. According to the equation - fractional attainment of the equilibrium, \( F \), at any time, \( t \), for a particle of radius \( r \), is related as below:

\[
F = 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{L}{n^2} \exp\left(\frac{-n^2Dt}{r^2}\right)
\]
where \( \frac{\pi^2 \gamma^2}{D} \) is \( B \), known as time coordinate and \( D \) is the diffusion coefficient of the ion in question and the hydrogen ions within the exchanger. \( F \) is a calculable mathematical function of \( B \). The above equation to a good approximation may be written as:

\[
P = 1 - \exp\left(\frac{\pi^2 \gamma^2 \Delta t}{D}\right)^\frac{1}{2}
\]

or

\[
D = -\frac{0.233 r_0^2}{t} \log \left(1 - P^2\right)
\]

It has since been established that in dilute solutions, the rate is controlled by the film diffusion and in concentrated solutions, by particle diffusion mechanism.

The conditions under which this equation can be applied are:

1. The mobility of the ingoing and the outgoing ions should be equal.
2. The concentration of the medium surrounding the particle should be constant.
3. The exchange should be carried in a well stirred solution.

However, the equation may be applied for the direct comparison of the diffusion coefficients of various ions when the ion initially present in the exchanger material is the same in all the cases.

D. E. Conway\textsuperscript{51} and G. H. Nancollas\textsuperscript{52} have determined the diffusion coefficient for Na\textsuperscript{+}/H\textsuperscript{+} exchange.
on titanium oxide and found them to be in the order
$4 \times 10^{-8}$ cm$^2$/sec, on sulphonic acid resins$^{51}$. 
$10^{-6}$ to $10^{-5}$ cm$^2$/sec and for amberlite IRA-50 to the
extent of $3.92 \times 10^{-9}$ cm$^2$/sec.

R.K. Srivastava et al., have studied exchange
kinetics on $\beta$-SnO$_2$ using certain ammiines of divalent
ions and found that the rate process is governed by the
film as well as particle controlled diffusion mechanisms.
The rate of film diffusion was found to increase with
decreasing particle radius of the exchanger materials.

E. Effect of irradiation on ion exchangers.

It has been reported by C.B. Amphlett$^{54}$ that Dowex-50
resin loses its ion exchange capacity by 15% to 35% when
exposed to a $^{60}$Co source. On the other hand, the inorganic
ion exchangers are generally, unaffected under these
conditions. However, the investigation of the effect of
exposure on a few inorganic exchanger materials (salts and
oxides) to a high flux of neutron and $\gamma$-ray irradiation
has shown certain alternations in the exchange properties.
For example, the exchange capacity of zirconium phosphate
on irradiation with $10^8$ roentgens of $\gamma$-rays from a $^{60}$Co
source (220 cell, Atomic energy, Canada) has been found
to increase from 1.19 to 1.98 m. equivalents per gram
and the exchange capacity of SiO$_2$, ZrO$_2$ and SnO$_2$ by about
It has been reported by Brij Bhushan\textsuperscript{55} that the exchange capacity of hydrous ferric oxide and ferric phosphate increases by 5.2\% and 6.6\% respectively on irradiation with $\gamma$-rays. W. Primak\textsuperscript{57-58} have shown that the neutron bombardment causes an increase in the lattice constant of quartz. Various inorganic solid materials have been exposed to high doses of radioactive rays and the sequence in their radiation stability was found to be:

$$\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO}$$

which corresponds to the order of increasing covalency in chemical bonding.

A number of authors\textsuperscript{59-60} have also reported an increase in the exchange rate on irradiated exchange materials. Thus there appears to be a good scope for an experimental investigation of irritation effects on the selected ion exchange materials.

P. Ion Exchange Chromatography

Ion exchange chromatography has been widely used for:

(i) Separation and concentration of the trace elements,
(ii) Separation of very similar elements such as rare earths, lanthanides and actinides,
(iii) Separation of co-ordination of common elements,
(iv) Separation of amino acids,
(v) Separation of alkaloids.
The pioneering work on chromatography was done in 1906 by Mikhail Tsvett61. Then the years 1910 to 1931 saw very little work in this field. The actual era of 'ion exchange chromatography' began with the development of synthetic or 'ionic exchange resins' by Adams and Holmes5 in 1935. Two prominent chromatographic techniques have since been developed.

(i) Adsorption Chromatography
(ii) Ion exchange chromatography

The former technique was used by Richard Kunin62 and coworkers for resolving plant carotenes. The resolution of naturally occurring mixtures of pigments, sugars and amino acids which has been tedious and normally impossible to achieve by classical methods of fractional crystallisation and distillation was attacked with great vigour by Kunin and coworkers - the separations being based on the different adsorption affinities for a particular adsorbent, those bound strongly adsorbed moving more rapidly than the more weakly adsorbed ones, a process known as adsorption chromatography.

In ion exchange chromatography true heteropolar bonds are formed reversibly between ionic components in the mobile and the stationary phases. The ion exchange chromatography
can be carried out in three different ways: column, paper and thin layer chromatography. Sheet method such as paper chromatography and the thin layer chromatography are very useful in analysis of known or unknown mixtures and when handling very small quantities of the materials.

The basic requirement, ensuring conditions favourable for a good separation by ion exchange column technique depends upon separation factor:

\[
\frac{C_A}{C_B} = \frac{D_A}{D_B}
\]

where \(C\) is the separation factor and \(D_A\) and \(D_B\) are the equilibrium distribution coefficients. For a good separation the value of \(C\) should be high enough to bring about a favourable retention of one of them by the exchanger materials and the other loosely bound ion could be eluted with a suitable eluting agent.

In order to obtain the high values of \(C\), two methods are known. In one of the methods ion selective groups such as phosphonous, phosphonic, dipicrylamine phenyl fluorone, diphenyl carbazide, dimethyl glyoxime and dipicol groups were attached to the polystyrene matrix. The other, was to search for inorganic ion exchangers with high affinity for
ion or group of ions. In this category, insoluble phosphates, molybdates, tungstates, arsenates, antimonates, silicates, many complex cyanides and heteropoly acids and their salts have been found to be selective for one or the other ion. 73-90

G. The Exchanger Materials

The heteropoly acids obtained by adding cerium(iv) ions to the mixture of (a) ammonium molybdate and sodium orthophosphate solution and (b) ammonium molybdate and sodium tungstate solution were used as ion exchanger materials. A brief survey of the literature on the heteropoly acids is given below.

Simple molybdates and tungstates: Simple molybdates and tungstates can be obtained by dissolving trioxides of molybdenum and tungsten in alkali metal hydroxides. In solutions they exist as $\text{M}_2\text{MoO}_4$ and $\text{M}_2\text{WO}_4$ and contain discrete tetrahedra of $\text{MoO}_4^{2-}$ and $\text{WO}_4^{2-}$ ions. 60 The normal molybdates and tungstates of many other metals can be prepared by such reactions.

When the solutions of molybdate and tungstate are made weakly acid, polymeric chains are formed while in strong acid solutions molyblic and tungstic acids are formed, but they do not contain $\text{H}_2\text{MoO}_4$ or $\text{H}_2\text{WO}_4$ molecules; broad line nmr spectrum shows that all the hydrogen present
is in the form of water molecules. A partial X-ray study of MoO₃·2H₂O shows the presence of sheet of MoO₆ octahedra sharing corners. An important characteristic feature of the chemistry of molybdenum and tungsten is the formation of large number of poly molybdates and poly tungstates which may be divided into two main groups:

(i) Iso poly acids - containing molybdenum, tungsten and hydrogen,

(ii) Heteropoly acids and anions - contain one or two atoms of other element in addition to molybdenum, tungsten oxygen and hydrogen.

All poly anions contain octahedral MoO₆ and WO₆ groups. Thus the conversion of tetrahedral MoO₄⁻² and WO₄⁻² anions into octahedral MoO₆ and WO₆ require an increase in coordination number of molybdenum and tungsten atoms.

Poly anions containing species such as Mo₇O₁₄⁻⁶, HW₆O₂₁⁻⁹ or Ta₆O₁₆⁻⁶ have been found to predominate over other anions. The polymerisation may be represented as:

\[
7 \left[ \text{MoO}_4 \right]^{-2} + 8 \text{H}^+ \xrightarrow{\text{propagation}} \left[ \text{Mo}_7\text{O}_{24} \right]^{-6} + 4\text{H}_2\text{O}
\]

and

\[
6 \left[ \text{WO}_6 \right]^{-2} + 7 \text{H}^+ \xrightarrow{\text{propagation}} \left[ \text{HW}_6\text{O}_{21} \right]^{-5} + 3\text{H}_2\text{O}
\]
In strong acid medium (pH< 1.5) the poly anions $\left[\text{Mo}_{8}^{0.26}\right]^{-4}$ and $\left[\text{W}_{12}^{0.41}\right]^{-10}$ have also been shown to be formed in solution. However, the polyanion in solution and solid phase may not have the same structure. Further, the poly anion such as $\left[\text{Mo}_{8}^{0.26}\cdot5\text{H}_{2}\text{O}\right]^{-4}$, $\left[\text{HWO}_{4}\right]^{-4}$, $\left[\text{W}_{2}^{0.7}(\text{OH})\right]^{-3}$, $\left[\text{MoO}_{12}(\text{OH})\right]^{-4}$, $\text{H}\left[\text{W}_{4}^{0.12}(\text{OH})\right]^{-6}$ and $\left[\text{W}_{6}^{0.20}(\text{OH})\right]^{-6}$ have also been identified to be formed in solution.

**Heteropoly Acids**:

These are formed when molybdate and tungstate solutions containing other oxoanions $(\text{PO}_{4})^{-3}, (\text{SiO}_{4})^{-4}$ or metal ions are acidified. At least 30 elements are known to be capable of functioning as hetero atoms. When crystallised from water, the heteropoly acids and salts are always obtained in highly hydrated conditions.

The synthetic chemistry of heteropoly acid and their salts have been extensively studied and methods for the preparation of wide variety of these compounds are known. H. Wu have prepared yellow crystals of 12-molybdo phosphoric acid with the molecular formula $\text{H}_{3}\left[\text{PO}_{4}(\text{Mo}_{3}^{0.7})_{4}\right]29\text{H}_{2}\text{O}$ and the isomorphous colourless crystals of 12-tungsto phosphoric acid with the molecular formula $\text{H}_{3}\left[\text{PO}_{4}(\text{W}_{3}^{0.9})_{4}\right]29\text{H}_{2}\text{O}$.

Recently, heteropoly acid and their salts containing heavy metal ion cerium have been prepared and
their molecular formula determined are:

Cerro molybdo phosphate \(^{85}\) = \(K_{15}[CeP_{11}Mo_{40}] \cdot 20H_2O\)

Cerro tungsto vanadate \(^{86}\) = \(K_{15}[Ce(\text{V}_3\text{W}_9\text{O}_{33})_2] \cdot 16H_2O\)

Cerium silico tungstate \(^{88}\) = \(K_{7}\text{H}_6[\text{H}(\text{CeO}_3)(\text{SiW}_9\text{O}_{34})_2]\)

Phosphorous Tungsto Molybdate \(^{89}\) = \(Na_9[\text{P}_8\text{W}_8\text{MoO}_{34}] \cdot 11H_2O\)

From the above studies it seems that a wide variety of heteropoly acids and their salts can be obtained with varying molecular formula. The purpose of the above discussion was just to explain that no fixed molecular formula can be assigned to poly molybdates and poly tungstates. One aspect is very clear that these materials are giant molecules containing a large amount of hydrated water. X-ray, TGA - DTA results \(^{89}\) showed that the compounds undergo dehydration and thermal decomposition on heating. More, \(^{88}\) has established that the compound \(K_{7}\text{H}_6[\text{H}(\text{CeO}_3)_3(\text{SiW}_9\text{O}_{34})_2]\) have a structure consisting of \(\text{SiW}_9\) units connected by a belt of three cerium atoms.

The selected exchanger materials:

Cerium molybdo phosphate and cerium molybdo tungstate were selected as the exchanger materials. As the properties and structure of these exchanger materials are very much
dependent on their method of preparation, necessary precautions were taken to maintain very similar experimental conditions during the preparation of the exchanger materials.

**Preparation of the exchanger materials:**

Stock solutions of ammonium ceric nitrate, ammonium molybdate, sodium phosphate and sodium tungstate each of 0.1 M concentration were obtained by dissolving the appropriate amount of the solids in deionised water. The work in the body of the thesis deals with the elucidation of the ion exchange properties of these materials (those possessing high exchange capacity will be more useful). For the purpose four varieties of the exchanger materials: cerium molybdo phosphate and cerium molybdo tungstate—were obtained by mixing the various components in the ratio of (i) 2 : 1 : 1, (ii) 4 : 3 : 1, (iii) 4 : 1 : 3 and (iv) 2 : 2 : 1. The exchanger materials thus obtained were washed thoroughly with deionised water till free from the ions. Finally, the exchanger materials were converted into H- form. The procedure followed is described below:

The precipitate obtained by mixing Ce(iv) ion solution to the mixture of (a) ammonium molybdate and sodium phosphate solution and (b) ammonium molybdate and sodium tungstate solution in varying but known proportions, were filtered and washed free of ions by washing with deionised water and then dried at 40°C in oven. The dried samples were brought to the required
size by grinding and sieving through standard sieves. The dried samples thus obtained were treated with dilute HNO₃ to bring the materials in H-form. The procedure adopted is described in detail. The dried samples of cerium molybdo phosphate and cerium molybdo tungstate were shaken with 50 ml. of 0.05 M nitric acid for half an hour, allowed the sample to settle down and removed the excess acid by decantation. This process was repeated five times, finally, the samples were washed free of the acid, dried at 40°C and stored in closed vessels.

The exchange capacity, qₐ, of all the samples thus obtained were determined by using copper ammine as exchanging ions. The results are presented in tables 1.1 to 1.4.
Table 1.1
Exchange of Cu-ammine on cerium molybdo phosphate as a function of time of shaking.

Amount of the exchanger materials = 100 mg.
Concentration of the exchanging ions = 0.05 M.
pH of the solution = 9.8; Total Volume = 10 ml.

<table>
<thead>
<tr>
<th>Time of hours</th>
<th>Exchange capacity $q_A$ in m. equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sample(i)</td>
</tr>
<tr>
<td>One</td>
<td>0.562</td>
</tr>
<tr>
<td>Two</td>
<td>0.733</td>
</tr>
<tr>
<td>Three</td>
<td>0.787</td>
</tr>
<tr>
<td>Four</td>
<td>0.787</td>
</tr>
<tr>
<td>Five</td>
<td>0.787</td>
</tr>
</tbody>
</table>
Table 1.2
Exchange of Cu- ammine on cerium molybdo tungstate Vs time of shaking.

Amount of the exchanger material = 100 mg.
Concentration of the exchanging ions = 0.05 M.

pH of the solution = 9.8 ; Total Volume = 10 ml.

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>Amount exchanged in m. equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample(i)</td>
</tr>
<tr>
<td>One</td>
<td>0.590</td>
</tr>
<tr>
<td>Two</td>
<td>0.650</td>
</tr>
<tr>
<td>Three</td>
<td>0.842</td>
</tr>
<tr>
<td>Four</td>
<td>0.842</td>
</tr>
<tr>
<td>Five</td>
<td>0.842</td>
</tr>
</tbody>
</table>
Fig. 1.1: pH-metric titration of the exchanger materials (Table 1.3)

1. NaOH vs. free acid
2. NaOH vs. cerium molybdo phosphate
3. NaOH vs. cerium molybdo tungstate.
The data presented in tables 1.1 and 1.2 show that the exchange capacity of the exchanger materials increases with increase in the time of shaking and attains a maximum value between two and three hours. The minimum time required for the maximum exchange was taken as the equilibration time throughout the experimental work.

Further, it is also indicated that the exchanger materials prepared by mixing the various components in the proportion:

\[
\begin{align*}
\text{Cerium}(0.10M) & : \text{Molybdate}(0.10M) : \text{Phosphate}(0.10M) \\
\text{Four} & : \text{One} : \text{Three}
\end{align*}
\]

\[
\begin{align*}
\text{Cerium}(0.10M) & : \text{Molybdate}(0.10M) : \text{Tungstate}(0.10M) \\
\text{Four} & : \text{One} : \text{Three}
\end{align*}
\]

i.e., the sample(iii) possessed high exchange capacity for the exchanging ions. Hence the sample(iii) was prepared in sufficient amounts and used throughout the experimental work presented in this thesis.
pH-metric studies:

One gram each of the samples of cerium molybdo phosphate and cerium molybdo tungstate were taken in two beakers (100 ml capacity) added 50 ml of deionised water and titrated pH-metrically with 0.05 M NaOH solution. NaOH solutions were added in fraction and after each addition the solutions were stirred till a constant pH was attained. The results are presented in Table 1.3 and figure 1.1.

Table 1.3
Volume of NaOH vs pH of the solution.
Concentration of NaOH solution = 0.05 M.
Amount of the exchanger materials = 1.0 gm.

<table>
<thead>
<tr>
<th>pH of solution</th>
<th>Volume of NaOH required in ml.</th>
<th>Blank</th>
<th>Cerium Molybdo phosphate</th>
<th>Cerium Molybdo Tungstate</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>7.00</td>
<td>0.20</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>7.50</td>
<td>0.30</td>
<td>1.60</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>8.00</td>
<td>0.40</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>8.50</td>
<td>1.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>9.00</td>
<td>2.00</td>
<td>5.50</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>9.50</td>
<td>4.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
</tr>
</tbody>
</table>

The data presented above shows that
more amounts of NaOH were required to raise the pH of the heterogeneous mixture containing cerium molybdo phosphate and cerium molybdo tungstate as compared with the blank. Consumption of more amount of NaOH clearly indicates the exchange of Na$^+$ ions (from solution) with H$^+$ ions of the exchanger materials and subsequent neutralisation of H$^+$ forming unionised water. From the curve 1.1 it is also clear that the amount of NaOH required to raise the pH of the heterogeneous mixtures from 6.00 to 8.00 is much less than the amount required to raise the pH of the heterogeneous mixtures from 8.00 to 9.50. This result supports the statement that the exchange of cations increases with increase in the pH of the solution.
Chemical analysis of the samples:

i. Elemental Analysis - The samples of the exchanger materials viz. cerium molybdo phosphate and cerium molybdo tungstate obtained by mixing various components in the ratio 4 : 1 : 3, were analysed for their elemental contents with the help of Inductive coupled plasma atomic emission spectrometer (ICP-AES) simultaneous and sequential (Jobin Yvon JY - 70 plus). The analysis showed that the sample cerium molybdo phosphate contained 29.73% of cerium, 12.1% of molybdenum, and 1.9% of phosphorous while the sample of cerium molybdo tungstate contained 28.3% cerium, 12.1% molybdenum and 11.57% of tungsten and the remaining amount corresponds to oxygen and hydrogen associated with the exchanger materials as oxido, hydroxide and water molecules. On the basis of which the empirical formula - $\text{Ce}_3\text{Mo}_2\text{P}_n\text{H}_{2n}$ and $\text{Ce}_3\text{Mo}_2\text{W}_n\text{H}_{2n}$ have been derived.

ii. I.R. Studies - The I.R. Analysis of the samples, cerium molybdo phosphate and cerium molybdo tungstate, were carried out on 'Bio - Rad Win' I.R. instrument. The absorption spectrum of the sample of cerium molybdo phosphate showed sharp absorption bands at 450 cm$^{-1}$, 600 cm$^{-1}$, 1100 cm$^{-1}$ and at 1650 cm$^{-1}$ corresponding to $\text{CeO}_2$, $\text{MoO}_4^{2-}$, $\text{PO}_4^{3-}$ and $\text{H}_2\text{O}$ molecules (hydration) respectively.

Similarly, the absorption of the spectrum of the sample of cerium molybdo tungstate showed sharp absorption
bands at 450 cm⁻¹, 900 cm⁻¹, 900 cm⁻¹ and at 1650 cm⁻¹ corresponding to CeO₂, MoO₄⁻², WO₄⁻² and H₂O molecules (hydration) respectively. A broad band at 3200 cm⁻¹ and at 3600 cm⁻¹ in both the spectra indicated the presence of free water and hydroxyl groups in the molecules.

iii. Structural Formula:

On the basis of the elemental and spectral analyses of the samples the following approximate structural formula may be assigned to cerium molybdo phosphate and cerium molybdo tungstate:

\[
H_6\left[(\text{CeO}_2)_3 (\text{MoO}_4)_2 \text{PO}_4\right] \cdot n\text{H}_2\text{O} \text{ and }
H_8\left[(\text{CeO}_2)_3 (\text{MoO}_4)_2 \text{WO}_4\right] \cdot n\text{H}_2\text{O}
\]

The probable structure may be shown as:

![Structural formula of cerium molybdo phosphate and cerium molybdo tungstate]
Here it seems that the tetrahedrons of all the three elements are joined through $-O-$ linkages as none of them have catenation power but possess a great tendency to polymerise through $-O-$ linkages.

Further, the presence of the large number of the water molecules attached with the exchanger materials may also cause an increase in the co-ordination number of molybdenum and tungsten atoms from 4 to 6. The available literature shows that all the heteropoly anions contain $\text{MoO}_6$ and $\text{WO}_6$ groups and therefore the structures cited above may be transformed to:

\[
\text{Cerium molybdo phosphate} - \text{H}_7\left[(\text{CeO}_2)_3(\text{MoO}_6)_2\text{PO}_4\right]\cdot\text{nH}_2\text{O}
\]

\[
\text{Cerium molybdo tungstate} - \text{H}_9(\text{CeO}_2)_3(\text{MoO}_6)_2\text{WO}_6\cdot\text{nH}_2\text{O}
\]

However, due to lack of data, the presence of $\text{MoO}_6$ and $\text{WO}_6$ groups, in the exchanger materials could not be confirmed.
iv. Thermal analysis: - the thermal analysis of the samples of cerium molybdo phosphate and cerium molybdo tungstate showed the loss in weight of about 24% at temperatures between 40° to 140° C, which may correspond to the loss due to water molecules adhered with the exchanger materials, as the materials have not been reported to decompose within the above temperature range.

Semi for further study:

As discussed in the previous section (G), a large amount of the work on the study involving the structural aspects of the heteropoly acids and their salts are available in the literature. The study shows that the method of preparation and the composition of the various components taken, play an important role in deciding the molecular formula and hence the structure of the heteropoly acids obtained. The presence of large number of the -O- linkages in the molecule indicated that the various components are joined through the oxygen linkages.

A very little work on the elucidation of the ion exchange properties of these materials has been reported in the literature and thus there is a scope for the systematic study of the ion exchange properties of cerium molybdo phosphate and cerium molybdo tungstate. The other
two aspects of the study such as ion exchange kinetics and the γ - ray irradiation. The latter are expected to throw some light on the mechanism of the ion exchange reaction and the possible use of these materials under intense radiation fields respectively.

I. The Exchanging Ions:

In order to understand the effect of shape and size of the exchanging ions on the ion exchange properties of the exchanger materials, the exchanging ions with definite size and shape are required. As most of the cations are largely hydrated in aqueous solutions and hence the ammine and the ethylene diamine complexes of the cations Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ which have well known geometry have been selected as the exchanging ions. A brief description of these ions is given below:

1. Ammine and ethylene diamine complexes of Copper:

In moderately concentrated solution of ammonia and ethylenediamine the copper complex has been found to exist as $[\text{Cu} (\text{NH}_3)_4 (\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu} (\text{en})_3]^{2+}$ ions with the octahedral symmetry. Further, due to the John Teller effect these complexes with d$^9$ electron system suffers distortions and are generally known to have staggered octahedral configurations with paramagnetic moments lying between 1.90 to 2.11 B.M.
2. Ammine and ethylene diamine complexes of Zinc and Cadmium:

Unlike copper, zinc and cadmium possess \(3d^{10}\) and \(4d^{10}\) configurations and have no ligand field stabilization energy and hence the stereochemistry of their complexes can be determined, among other considerations, by their size. Zn(II) and Cd(II) form tetrahedral complexes with excess ammonia e.g.,

\[ [\text{Zn} (\text{NH}_3)_4]^2^+ \] and \[ [\text{Cd} (\text{NH}_3)_4]^2^+ \] while in presence of ethylene they form diamagnetic octahedral complexes having the molecular formula \([\text{Zn} (\text{en})_3]^2^+\) and \([\text{Cd} (\text{en})_3]^2^+\).

3. Ammine and the ethylene diamine complexes of Nickel(II):

Ammonia and ethylenediamine replace all the \(H_2O\) groups from \([\text{Ni}(H_2O)_6]^2^+\) to form octahedral \([\text{Ni}(\text{NH}_3)_6]^2^+\) and \([\text{Ni}(\text{en})_3]^2^+\) ions. These complexes have characteristically blue colour in contrast to the bright green colour of \([\text{Ni}(H_2O)_6]^2^+\) ions. All of them have two unpaired electrons with para magnetic moment lying between 2.9 to 3.4 B.M. These complexes with \(t^6\) and \(e^2\) electronic configurations are expected to remain undistorted.
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