CHAPTER I

INTRODUCTION
INTRODUCTION

Ion exchange is a quasi heterogeneous phase reaction in which a solid colloidal electrolyte reacts with a solution. Ions can be exchanged and electrolytes and even precipitates can be removed by treating the solution with a solid ion exchanger. Nature makes extensive use of them and has done so before man attempted to elucidate and apply its principles and to copy and surpass the performance. A spectacular change began in 1935 with the discovery by two English Chemists, Adams ad Holms, that crushed phonograph records exhibited ion exchange property which eventually led the discoveries to synthesise organic ion exchange resins, and these were found to possess much better properties than any one of the previous products. Nearly all current industrial and laboratory applications of ion exchange are based on such resins. Today, ionexchange is firmly established as a unit operation and is an extremely valuable supplement to other procedures such as filtration, distillation and adsorption.

Thus the study of inorganic ion exchanger was in past over shadowed by the much greater interest in organic ion exchange resins, while the industrial applications of ion exchange have relied heavily on the latter material. The revived interest in inorganic exchangers stems largely from the fact that they are more stable than organic resins under certain conditions, such as high temperature, or the presence of ionising radiations. Apart from consideration of possible applications, study of many
Inorganic exchangers is of interest for the light which it throws upon problems such as the sorptions of ions by precipitate, the electrophoretic behaviour of the suspension, the diffusion of ions in the crystals, isotopic exchange in the heterogeneous systems and many other problems in the field of chemistry. This had led to considerable interest in the fundamental studies of this system some of which have been attempted in the present investigation.

Inorganic ion exchangers particularly those of Zirconium phosphate and Zirconium oxide types, are today undergoing a rapid development. Zirconium phosphate is extremely resistant to acids other than HF, H₂SO₄ and oxalic acid, all of which form complex Zirconium very effectively.

The interesting cation exchange property of the synthetic zirconium phosphate and the various fields of its application are the great stimulating incentives to the scientists for further research in this fascinating field of synthesis of inorganic ionexchange material. The present work with the experimental details as embodied in this thesis is the outcome of such incentive.

The properties and texture of synthetic Zirconium phosphate is very much dependent on the preparatory conditions. In the rapid precipitation method normally a gelatinous product is obtained which contains a definite amount of water in the structure resembling silica gel. The precise conditions which govern the physical nature of the product are not well understood although extensive work has been carried out on the effects of
variables in the preparatory work. Structural studies on Zirconium phosphate showed that the amorphous structure persists until at least $300^\circ C$ but that at $1000^\circ C$ the pattern is characteristic of Zirconium pyrophosphate. The changes are accompanied by irreversible loss of water from the material. Of course the phosphate does not give evidence of the existence of discrete hydrates.

Water is an essential part of the hydrogel structure and as such the dehydration behaviour depends on the nature of the bonds with the water molecules. This type of gel material usually shows continuous dehydration-rehydration behaviour although that is not a general rule. A greater part of the dehydration, however, involve removal of water molecules, held loosely in the main framework structure by secondary forces, and this permits partial dehydration and regain of its initial properties by heat treated materials as long as the lattice is not destroyed. The thermal characteristics of the base exchange materials usually depend on preheat temperature, the nature of the exchange cation and their hydration energies.

Systematic work on dehydration rehydration behaviour of Zirconium phosphate hydrogel as revealed from the literature is lacking. Water is lost at temperature in excess of $300^\circ C$ presumably due to the condensation of acid phosphate groups to pyrophosphate. Evidence in favour of the condensation of acid phosphate groups to pyrophosphate on heating is furnished by the infrared spectra of the samples. Part of the weight loss at
relatively low temperature is due to the constitutional water found on condensation of acid phosphate groups. The range of composition and structures may be quite wide and they are very sensitive to the method of preparation. From the studies on ion exchange it has been suggested that two replaceable hydrogen per molecule and would be more likely to loss water reversibly at low temperature without a drastic change in the X-ray pattern. X-ray data suggests that the crystalline material is composed of sheets of phosphate units in which some of the oxygen atoms are bound to Zirconium atom while others carry hydrogen atom. Half of the P-OH groups form hydrogen bonds with phosphate groups in the adjacent layers, while the others are hydrogen bonded to water molecules. The combined X-ray and titration data suggest that ion exchange occurs in two stages. In the first hydrogen ions are displaced from P-OH groups which are bonded to water molecules.

\[
P-OH \quad OH_2 + M^+ \rightarrow P - O\tilde{M}^+ + H_2O^+
\]

The interlayer spacing remains unchanged until the ratio of M : Zr equals 1 : 1, after which hydrogen ions are replaced in P-OH groups which are bonded to adjacent layers leading to an increase in spacing. The difference between the gel and the crystalline product is due to the fact that the former possesses a more disordered structure. The larger interplanar spacings and weaker interlayer hydrogen bonds in the gel will permit exchange of larger ions, and will also favour the hydrolysis of the phosphate groups.
Zirconium phosphate type materials are enjoying tremendous interest both from scientific and industrial world and the interest in these series is still increasing.

In the present investigation Zirconium phosphate hydrogel was synthesised by following the wet interaction technique in aqueous medium. The experimental variable was the molar ratio of ZrO_2 : P_2O_5. Other conditions were adjusted in such a manner as per with the expectation of obtaining a homogeneous gel structure. Through the study of differential thermal analysis the homogeneity of the sample with respect to hydrate formation was studied and also the temperature of expulsion of water from the system.

Dehydration rehydration behaviour of the hydrogel under equilibrium condition which is related to the thermal stability was studied as a function of temperature and humidity. Permanent change of reactivity of the samples was determined through the measurement of bulk density and CEC.

Kinetics of the particular endothermic process was studied through isothermal dehydration experiment. Kinetics belongs to the type of heterogeneous solid state reaction and the basis for the understanding the rate processes was the Arrhenius relationship which states that for many processes the logarithm of the reaction rate constant k is proportional to the reciprocal of absolute temperature. Thus the relative influence of the compositional ratio as well as the particle size and the
compaction were compared by the experiments under identical condition i.e. isothermal weight loss measurement. The kinetic parameters including the activation energies were determined for the expulsion of water from the gel structure.

Although various studies have been made on cation exchange phenomenon with the organic exchangers but the data on inorganic exchangers are extremely meagre which was mainly due to the low CEC value of the traditional inorganic exchangers. By the application of complexometric method of analysis of the exchanging cations and taking the synthesised Zirconium phosphate an attempt has been made to present a picture of the cation exchange phenomenon which embraces the different factors associated with the type of quasiheterogeneous phase reaction. Selectivity sequences of a number of cations for this phosphate structure have been drawn.

Ion exchange is a time dependent process and equilibrium is attained when an ion exchanger is placed in an electrolytic solution containing a counterion which is different from that in the ion exchanger. The mechanism of ion exchange is a redistribution of counterions by diffusion. The rate controlling steps in ion exchange is usually either diffusion of ions within the exchanger itself or within a thin film of solution surrounding the latter, depending on the physicochemical parameter of the system. Again the models of ion exchangers used by different
workers for explaining the kinetics of exchange in organic ion exchangers appear to be inadequate to explain such mechanism for rigid framework structure of the inorganic exchangers. Thus in the final part of the work kinetics of cation exchange process in zirconium phosphate hydrogel structure has been studied with respect to variation in the nature of the exchanging cations.