

**SYNTHESIS, CHARACTERIZATION AND ION EXCHANGE
BEHAVIOUR OF A COMPOSITE ION EXCHANGER:
POLYANILINE ZIRCONIUM(IV) TUNGSTOPHOSPHATE**

**A MAJOR PROJECT SUBMITTED IN PARTIAL FULFILLMENT
FOR THE DEGREE OF**

**MASTER OF ENGINEERING
IN
POLYMER TECHNOLOGY**

BY

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111. H.J.C. Tendeloo Hydrophobic Colloids 83, Nordemann Publishing Co.(1937).
112. H.P.Gregor, J. Am. Chem. Soc., 73, 3537, (1951).
113. Gregor, H.P., J.Belle, and R.A. Marcus, J. Am. Chem. Soc., 76, 1984, (1955).
114. H.P.Gregor, J.Belle, and R.A. Marcus, J. Am. Chem. Soc., 77, 2713, (1955).
115. H.P.Gregor, J.I.Bregman, F.Guttoff, R.Broadley, D.Baldwin, and G.Overberger, J. Colloid Sci., 6, 20, (1991).
116. L.Wiklander L. Acta Agr. Scand 1, 190 (1951).
117. L.E.Davis; Soil Sci. 54, 199 (1942).
118. W.C.Bauman, and J. Eichhorn, J. Am. Chem. Soc., 69, 2830, (1947).
119. H.P.Gregor, Photo. Engg. 2, 102, (1951).
120. G.Kuehne and F.Martinala; VGB Kraftwerkstechnik 57, 173 (1977).
121. L.P.Evsinova, N.S.Kurolap, V.A.Uglyanskaya and O.N.krysina; Teor. Prakt. Sorbtion. Protsessov 7, 110 (1972).
122. V.P.Meleshko, L.P.Evsinova and O.N.Krysina; See ref. 80, 114 (1974).
123. K.M.Olshanova et al. ; IZV. Vyssh. Ucheb. Zaved. Khim. I. Khim. Tekhnol. 15, 1463 (1972).
124. J.Mathev, S.N.Tandon and J.S.Gill ; Radiochem. Radioanal. Lett. 30, 381 (1977).
125. L.zsunka, L.szirtes and Stenger ; Radiochem. Radioanal. Lett. 4, 257 (1970).

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CERTIFICATE

This is to certify that **Mr. Vinod kumar**, a student of **M.E. (Polymer Technology)**, **Delhi College of Engineering, Kashmere Gate, Delhi**, has completed his major project entitled, "**Synthesis, Characterization and Ion Exchange Behaviour of a Composite Ion Exchanger: Polyaniline Zirconium (IV) tungstophosphate**" for the partial fulfillment of **M.E. (Polymer Technology)**. To the best of our knowledge, the thesis is an original work of **Mr. Vinod Kumar**, which has not been submitted to any Institute or University or Organization to award any degree.

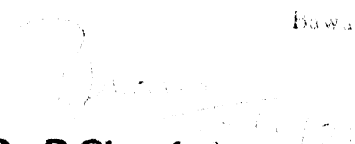
We wish him all the best and every success in life.


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*Dedicated to My Parents
&
Sister
who has given me
the strength to achieve the goal*

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Chapter-1

INTRODUCTION

1.1 General Introduction:

The early ion exchanger were largely inorganic in origin. It is interesting to note that the first systematic studies on ion exchange were carried out on the naturally occurring inorganic materials, viz, the clay fractions of the soil, which were investigated as long as 1850. Furthermore, the first industrial applications of the synthetic ion exchangers for water softening also employed inorganic materials. Later on the ion exchange scene was dominated by the synthetic organic resins because of the ease with which reproducible preparation of appropriate mechanical and chemical stability could be made. In recent years, interest in the inorganic exchanger has been revived with the need for the high temperature separation of ionic components in radioactive wastes. In order to make such separations, highly selective exchangers are required, which are not only stable at high temperatures but which also have exchange properties unaffected by acidity and high levels of radiation. Organic resins are unsuitable for such applications as change in selectivity and exchange capacity occur on exposure to radiation, and degradation takes place at the high temperature of interest.

The synthetic inorganic ion exchangers have revived considerable attention during the last few decades owing to their resistance to heat and

radiation and because they show some novel selectivities which are different from those of ion exchange resins. These materials have been used for

- The separation of metal ion.
- The purification of water
- The separation of organic compounds
- The preparation of ion selective membranes
- The preparation of artificial Kidney machine
- The preparation of fuel cell.

Some of the more important applications during last few years have been out lined.

- (I) Hydrometallurgy
- (II) Effluent treatment to control pollution

These ion exchange materials have been classified by Pekarek and Vesely as follows.

1. Hydrous oxides
2. Acidic salts of multivalent metals
3. Salts of heteropolyacids
4. Insoluble ferrocyanides
5. Synthetic alumino silicates
6. Certain other substance e.g. synthetic oppalites, sulfides and alkaline earth sulphates

Out of the various class outlined above the acidic salt of multivalent metals have attracted the greatest attention. They may be prepared by combining group IV oxides with more acidic oxides of groups V and IV.

Table-1

4th	5th	6th	14th	15th	16th
Ti	V	Cr	As	P	S
Zr	Nb	Mo	Ge	As	Se
Hf	Ta	W	Sn	Sb	Te
			Pb	Bi	Po

It was first shown by Boyd et. al that zirconium phosphate precipitated on silica exhibits ion exchange properties and could be used for the separation of uranium and plutonium from fission products, Later on Philips and Kraus found that Zirconium phosphate may be precipitated from acid solution of Zirconium salts or by treatment of Zirconium oxide with phosphoric acid. In the latter case the uptake of phosphate is irreversible and is considerable in excess of ion exchange capacity of the oxide. This was explained by proposing the Zirconium phosphate acts as an ion exchanger. Since then most of the work has been done on Zirconium phosphate.

The latest development in the discipline of inorganic ion exchanger has been taking place their conversion into composite ion exchanger materials. The preparation of composite ion exchangers is carried out with the binding of organic polymers i.e polyacrylonitrile, polyacrylic acid,

polystyrene, and polypyrrole etc. These polymer based composite ion exchanger materials show the improvement in a number of its properties. One of them is the improvement in its granulometric properties which makes more suitable for the application in column operations. In some of the cases it is observed the increase in number of cycles without affecting its ion exchange capacity as well as ion exchange equilibria. The binding of organic polymer also introduce the better mechanical properties in the end product i.e. composite ion exchangers.

1.2 Polymerization:

The process of polymerization were ~~devised~~ by Flory (1953) and Co-others (Mark 1940) into two groups known as condensation and addition polymerization or in more precise terminology, step reaction and chain-reaction polymerization.

1.2.1 Condensation (step-reaction) polymerization:

It is entirely analogous to condensation in low-molecular weight compounds. In this process two polyfunctional molecules condense to produce, one larger polyfunctional molecule with elimination of small molecule like water. The reaction continues until almost all of one of the reagent is used up, an equilibrium is established that can be shifted as will as high temperatures by controlling the amounts of the reactions and products.

1.2.2 Addition (chain) Polymerization:

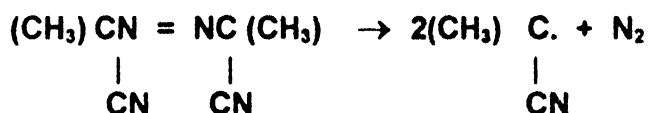
Addition or chain reaction polymerization involves chain reactions in which the chain carrier may be an ion or a relative substance with one unpaired electron called a free radical. A free radical is usually formed by the decomposition of a relatively unstable of reacting to open the double bond of a vinyl monomer and add to it, with an electron remaining unpaired. In very short time more monomers add successively to the growing chain. Finally, two free radicals react to annihilate each other's growth activity and form one or more polymer molecules.

1.2.3 Generation of Free Radicals:

Many organic reaction take place through intermediates having an odd number of electron and consequently, an unpaired electron. Such intermediates are known as free radicals. They can be generated in a number of ways, including thermal decomposition of organic peroxides or hydroperoxides or *azo* or *dialo* compounds.



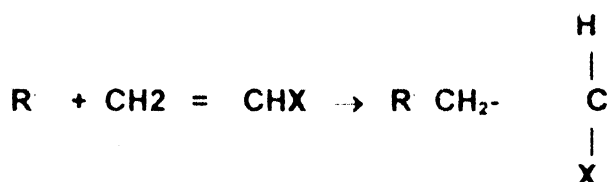
and of *azo* bis isobutyronitrile.



There are several radicals initiation process like photoinitiated polymerization, photochemical initiator, high-energy radiation, redox initiation, electro-chemical initiation etc.

- **Initiation:**

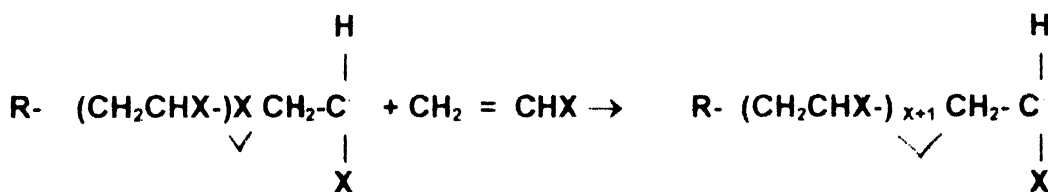
When free radicals are generated in the presence of a vinyl monomer, the radicals add to the double bond with the regeneration of another radical. If the radicals formed by decomposition of the initiator I is designated by R,



The regeneration of the radical is characteristic of chain reaction.

- **Propagation:**

The chain radicals formed in the initiation step is capable of adding successive monomers to propagate the chain.

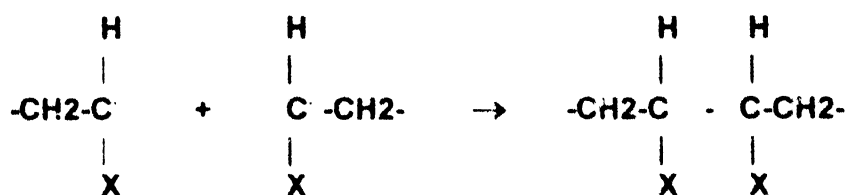


- **Termination:**

Propagation would continue until the supply of monomer was exhausted. In order to terminate a reaction, small concentration of radical species should be taken compared to monomer. Termination step is of two types.

- (1) Combination or coupling
- (2) Disproportionation

(1) Combination or coupling



1.2.4 Suspension polymerization (pearl polymerization):

This method is generally used to produce adhesive and coatings. ~~X~~

The water insoluble monomers are polymerized by this technique. The monomer is suspended in water in the form of droplets which are stabilized by suitable surfactant (soap, detergent) or by water soluble protective colloid. *wrong*

It can also be stirred or agitated. The size of the monomer droplet depends on aforesaid points such as monomer water ratio, concentration of monomer, *Answer* nature of stabilizing agent and quantum of agitation. Here water acts as a heat transfer medium. The entire bulk of the monomer gets distributed into innumerable tiny droplets. The polymer obtained in this method is in the form of beads or pearls. It has fairly narrow distribution of molecular weight. The separation of the product is easy because filtration only can provide it, surfactants or protective colloids are washed by water. After washing and drying of the product, it can be used for molding work. A number of polymers in the form of beads are prepared by this method using free radical initiators for example styrene, divinyl benzene copolymer beads (used for ION EXCHANGE COMPOSITE), polyvinyl acetate beads and expendable polystyrene beads (used to form Polystyrene foams) etc.

1.3 Synthesis of polyaniline:

Polyaniline (PAn), which has been used as a heat resistant paint ('aniline black'), has recently been applied to batteries, displays and anticharging materials [1]. Both the chemical and the electro chemical oxidation for PAn have been investigated from fundamental and practical points of view [2,3,4,5]. 2-5

Table 2 shows various chemical oxidative polymerization procedures for aniline, where [5-21] aniline salts such as anilinium chloride were oxidized by various oxidizing agents. The PAn powder prepared chemically in HCl (2M) using $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KIO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidizing agents showed that the maximum

Table-2

Chemical oxidative polymerization of aniline and its derivatives

Monomer	Oxidizing agent	Solvent	Reference
Aniline	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	HCl(aq)	5-9
Aniline	FeCl_3 , CuCl_2	H_2O	10-11
Aniline	$\text{Cu}(\text{BF}_4)_2$	$\text{CH}_3\text{CN}/\text{HBF}_4$	12
Aniline	$\text{Cu}(\text{ClO}_4)_2$	CH_3CN	13
Aniline	FeOCl		14
Aniline	$\text{K}_2\text{Cr}_2\text{O}_7$	HCl, H_2SO_4 (aq)	15,16
Aniline	$\text{P}_2\text{W}_{18}\text{O}_{62}^{-6}$	CH_3CN	22

conductivity was around 20 S cm^{-1} and that electroactivity was very similar to that for PAn prepared electrochemically, indicating that the type of

oxidizing agent influenced neither the conductivity nor the electroactivity of these materials [23].

Abe et al reported soluble, high molecular weight PAn species prepared by chemical oxidative polymerization at low temperature (-4°C) using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in acidic aqueous solutions [8]. After undoping aqueous ammonia, the Mw and Mn of the PAn were found to be 1.6×10^5 and 2.3×10^4 , respectively. The solubility of PAn prepared using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was also determined in various solvents [24].

PAn with a Mn of 3.7×10^3 was obtained (yield 17.7%) using FeCl_3 in aqueous HCl at 35°C [10]. In contrast to the preparation of PAn using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at -4°C , [8] a reaction did not occur with FeCl_3 even at 0°C . The molecular weight distribution of PAn prepared at various temperatures using FeCl_3 was bimodal.

The number average molecular weights for the higher and the molecular weight fraction of PAn prepared at an optimum temperature of 35°C was around 10^4 and 10^3 respectively. The lower molecular weight fraction could be obtained by the dimerization of cation radical of aniline, [10,25-27] where as the higher molecular weight species were prepared by the incorporation-oxidation mechanism, where monomeric aniline is incorporated into an oxidized aniline oligomer chain growth takes place by the insertion of the neutral monomer at the end of the oligomer. [16,28,29]. Note the lower HCl concentration, the higher the molecular weight and yield. At 0 mol dm^{-3} ,

the M_n and the yield were 2.04×10^4 and 51% respectively [10]. When PAn was synthesized using FeCl_3 in aqueous HCl at 35°C for 1 day under air and N_2 , the M_n obtained under air (3700) was higher than that N_2 (750), suggesting that the oxidation of aniline is promoted by oxygen present in air [10]. Gospodinova et. al. synthesized PAn using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in an aqueous dispersion stabilized by poly(vinyl alcohol-co-vinylacetate) without adding acids [30]. PAn was obtained only when the initial stage of the polymerization resulted in a drop in pH lower than 2.

Table-3

Polymerization of aniline with oxygen using copper salts as catalysts

Cu salt	Yield (%)		
	Isolated	Calc from O_2 consumed	TOF ⁺ (% day ⁻¹)
CuI	5	11	100
CuBr ₂	34	33	680
CuBr ₂	22	30	440
CuCl	26	29	520
CuCl	20	23	400
CuSO ₄	0	0	0

- Reaction of 50 mmol of aniline with 0.2 and 5 mmol of Cu salt in 20 Cm^3 of Acetonitrile / water (1/1 v/v at 30°C for 24h.
- Turnover frequency of the Cu salt catalyst for the isolated yield of the polymer per day
- Reaction for 73 h.
- White precipitates were obtained instead of PAn

White precipitates?

Table-4

Solvent dependence on the polymerization of aniline with oxygen using copper salts as catalyst.

Solvent	Ratio of CH ₃ CN/H ₂ O	Yield (g)
Acetonitrile/water	1:0	0.4
Acetonitrile/water	3:1	0.6
Acetonitrile/water	1:1	1.3
Acetonitrile/water	1:3	0.7
Acetonitrile/water	0:1	0.9
Ethanol	-	0.4
Methanol	-	0.2

Compared with these methods, the catalytic chemical polymerization of aniline has been investigated only very recently. Although the CuCl-AlCl₃-O₂ system did not work for the polymerization of aniline, CuCl₂ or CuBr₂ has been found to be an effective mediator under O₂ without acids. In this case, only neutral aniline gives good results when compared with anilinium chloride. Table 2 shows the chemical oxidation polymerization of aniline using various copper salts -O₂ system [31,32].

The catalytic activity of CuCl₂ depends on the solvents used for the reaction as shown in **Table 3**. The Acetonitrile-H₂O (1:1) solvent gave the highest yield, which was more than three times higher than that given Acetonitrile. However, the isolated polymer presumably contains a partially at 284°C (exothermic reaction) yielding a more stable material. The relatively low electrical conductivity observed was probably due to the disordered structure. Based on UV-VIS spectra for the reaction solution at molar ratios

of aniline to Cu(II) ion, a possible mechanism is provided in **Fig.1.2**. Here, aniline forms a complex with Cu(II) in the initial stages of the polymerization. Cu(II) accepts one electron from aniline in the complex, yielding the radical cation of aniline.

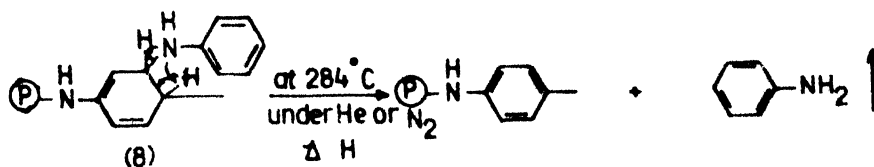


Figure-1.1 A possible scheme for the thermal degradation of PAN prepared using CuCl_2 as a catalyst.

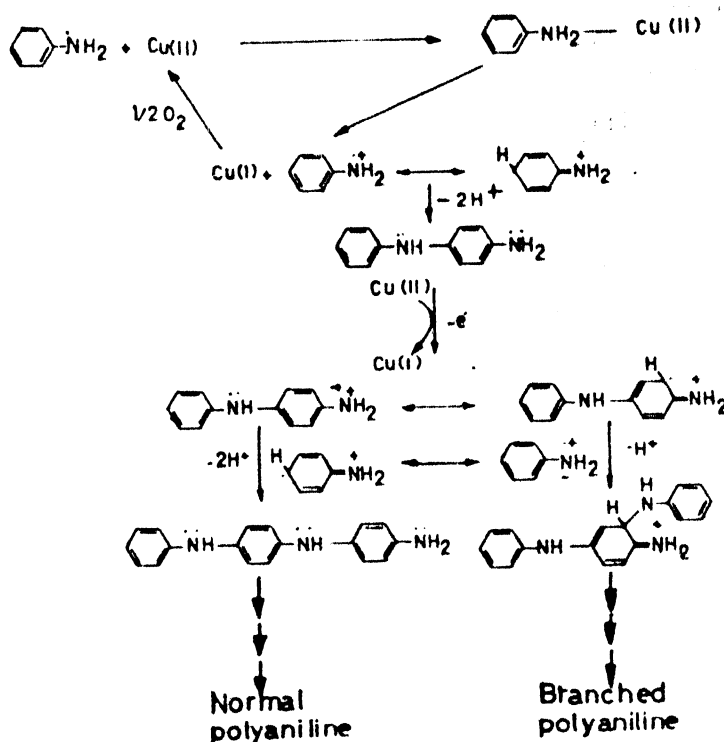


Figure-1.2 A possible mechanism of polymerization of aniline catalyzed by Cu(II).

The radical cation of aniline. The radical cation forms a dimer followed by a subsequent oxidation-step by Cu(II). The resulting Cu(I) is then deoxidized to Cu (II) by O₂. The succeeding coupling reaction includes some formation of branch structure. This process might also be used for the polymerization of aniline derivatives such as 2,6-xylydine. Poly(2,6-xylydine)

synthesized by this method was practical with that obtained by electro-polymerization.

3,5-xylydine cannot be polymerized by this method (CuCl₂-O₂) because of copper complex formation. When a stronger oxidizing agent -Ce(SO₄)₂- was applied to the reaction instead of CuCl₂-O₂, a polymer (yield : 46%) was obtained at 80°C, 8h. This strong oxidizing agent was also applicable for the 2,6-, 2,5-, and 2,3- xylydine monomers.

The chemical polymerization of aniline using FeSO₄ in acidic aqueous H₂O₂ can be achieved under mild conditions [33]. The isolated powdery emeraldine base, a form of PAn, was blue-black and exhibited high solubility in organic solvents. The Mn of the polymer was 1.3-1.7x10⁴ and the molecular weight distribution was relatively sharp (M_w/M_n =1.6-2.2). The similar method using Fe(III) also provided the polymer blend colloids containing PAn or PPy by oxidative polymerization [34] as well as the emeraldine base polymer by oxidation of leucoemeraldine, the reductive form of polyaniline [35,36].

The electrochemical polymerization of aniline provides films exhibiting a well-defined fibril morphology in some cases. This has not been reported for PPy and PTh. This morphology strongly depends on preparation conditions such as the type of electrolyte, the electrode and the electrochemical procedure used. PAn prepared electrolyte, the electrolyte and the electro-chemically and chemically, like other conducting polymers, exhibits electrochromic behavior. The approximate composition corresponding to a given color was studied in detail [37].

The thickness of PAn films prepared electro-chemically, measured by spectroscopic ellipsometry, increased linearly with anodic charge density of the films [38]. The concentration of electroactive moieties, as determined by cyclic voltammetry, was found to be constant over the range of film thickness studied. Rutherford back-scattering spectroscopy analysis showed a uniform distribution of chloride species, electroactive sites, within the PAn film. The thicker films possessed more chloride than thinner films, suggesting some HCl entrapment within the thicker films.

Aniline derivatives such as 4-aminobiphenyl, diphenylamine and N-phenyl-1-naphthylamine can also be electropolymerized in acidic and organic media [39,40]. The first two monomers afford poly(4-aminobiphenyle) and poly(diphenylamine) (poly DPA), respectively, with similar cyclic voltammeter and IR spectra. The third monomer gave poly(N-phenyl-1-naphthylamine) (PNA) exhibiting a lower conductivity ($10^{-3} \text{ S cm}^{-1}$) and

a lower doping level (30%) than those for poly DPA (2Scm^{-1} and 53%, respectively). Both poly DPA and poly PNA showed very interesting electrochemistry.

A number of conducting polymers together with new synthetic procedures have been prepared and others can be expected in the future. Chemical polymerization processes are desirable from the viewpoint of mass production but we also need to restrict by-products and waste materials in order to keep our global environment clean and safe.

Catalytical polymerization described in this review is suitable for an environment- friendly chemical process. Catalytic activities and the properties of the obtained polymers, however, are not sufficient at the present time. It is necessary to devise newer synthetic methods for conducting polymers based on highly catalytic systems. Looking back at the development of polyethylene (PE) and polypropylene (PP), research and development on catalysts has improved both the reaction efficiencies and the properties of these polymers. For the case of conducting polymers, especially PPP, PPy, PTh and PAn cited in this review, it will be necessary to undertake additional studies on catalytic systems.

1.4 Literature Review:

The literature survey reveals that a good number of references have been piled up in the field of inorganic ion exchanger as well as of ion

cation?

exchange resins pertaining to their ~~action~~ exchange and anion exchange behavior. In case of inorganic ion exchangers these have been reviewed by a number of workers from time to time. Here in this project work our interest is to review mainly work on Zirconium (IV) phosphate, Zirconium (IV) tungstate, Zirconium (IV) tungstophosphate materials related to this work as well as of some composite ion exchangers obtained by the employment of organic polymers in one way or the other. Beside this some cases where organics have been taken to prepare these ion exchange materials are being considered.

As per our understanding with these materials Zirconium (IV) phosphate is one of the most exhausted materials. The studies [41-56] on Zirconium phosphate have been reported in last few years pertaining to the preparation of different phases ion exchange behavior, kinetics and mechanism of ion exchange, the application in the separation of metal ions effluent treatment and recovery of some metals Pu, Po etc. from radioactive waste. Few of the publications appeared in the literature regarding the crystal lattice studies and the change in the crystal lattice pattern on drying at high temperatures.

The synthesis, characterization and ion exchange behavior of Zirconium (IV) tungstophosphate [57] have been reported in the literature. It has been employed to separate Cs^+ and Rb^+ from others metals ions.

Recently Gupta et al [58-61] have been published their findings on Zirconium (IV) tungstophosphate a cation exchanger. Its synthesis characterization, ion exchanger behavior, kinetics and mechanism of ion exchange, chelation with tetracycline hydrochloride and drying effect have been carried out in our laboratories.

Rawat et al [62,63] Zirconium Bis (triethyl amine) reported their studies regarding the synthesis of the material ion exchange behavior, thermodynamic behavior and the ion exchange equilibria of $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$ and MnO_4^- system at 30, 40, 45, and 60°C. The system shows S shaped curves. The overall thermodynamic data have been reported. The kinetics studies of $\text{K}_2\text{Cr}_2\text{O}_7$ and K_2CrO_4 have also been performed on this inorganic anion exchanger bis (tri ethylamine) Zirconium in Cl⁻ form.

The mechanism is found to be particle diffusion control various parameters viz. effective diffusion coefficient (D_i), diffusion coefficient (D_o), energy of activation (E_a) and entropy of activation (ΔS^*) have been evaluated.

Few years ago a very much interesting work has been published by Clearfield et al [64] on the polyether derivatives of Zirconium phosphate. γ -Zirconium phosphate, $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, with a 12.2 Å⁰ interlayer spacing is known to react with ethylene glycol solution to form glycol ester of Zirconium phosphate. It has been shown that the α - polymorph with a smaller interlayer distance (7-6Å⁰) also behaves similarly with highly crystalline

sample of α - Zirconium phosphate reaction takes place only at the surface. However if the interlayer distance is first increased so that ethylene oxide can diffuse into the interior, complete reaction ensues. Less crystalline samples were found to react directly with ethylene oxide, either as a gas or as a solution. Attempts to form long polyether chains by direct reaction were unsuccessful.

However by the preparation of the first polyether phosphate and then the reaction of these compound with Zr (IV) species, polyether analogous of α -Zirconium phosphate were prepared. These derivative incorporate electrolytes and form novel colloidal dispersions.

Ion exchange behavior of some amine intercalates of α -tin (IV) hydrogen phosphate monohydrate has been carried out by Hudson et. al. [65] in the presence of transitional metal ion. The behavior of these intercalates depends upon whether the guest mole is a mono or a polyamine. For each of the intercalation samples, the rate of uptake of metal ion rapid ($T_{1/2} < 5$ min) when the guest mole is a water-sol. Primary monoamine the uptake of the metal ion is accompanied by the loss of the amine in the form of a sol alkyl ammonium ion. The resultant solid product of this reactions essentially amorphous due to the delamination of the lamellar α -SnP. The surface, areas however are approximate. the same (α -SnP 51.6 and the delimitation product 55.9 m^2/g). The retention capacities of the α -SnP / alkylamine intercalate for Ni^{2+} , Co^{2+} , and Cu^{2+} were 6.3, 5.9, and 3.5 meq/g

respectively. This intercalate appeared to be selective for Cu^{2+} esp. at low Cu concentration in mixed solutions. Intercalation compounds with polyamines (e.g. 1,2 diaminoethane) also react rapidly with aq. transition metal ions but this reaction accompanied by a loss of the intercalated amine or by dealmination and the characteristic do O_2 ions absorbed was $\leq 20\%$ of the theoretical cation exchange capacity.

Composite ion exchanger of the investigations on an organic binding polymer based on polyacrylonitrile (PAN) with amm. molybdophosphate have been carried out by Sebesta et. al. [66]. PAN was used in the preparation of the composite exchanger contg. NH_4 molybdophosphate as the active component. Due to the improvement of granulometric properties of powder AMP with a binding polymer, an exchanger suitable for the application in column operations was prepared. Study of the properties of the exchanger AMP-PAN proved that kinetics of Cs sorption, capacity of the exchanger for Cs and desorption of sodium are not influenced by the binding polymer. The composite exchanger AMP-PAN described is therefore suitable for the selective separation and concentration of Cs and purification of radioactive wastes from ^{137}Cs .

• Objectives and Scope of the present work:

A composite material is made by combining two or more dissimilar materials. They are combined in such a way that the resulting composite

material or composite ³⁰⁰ possesses superior properties which are not obtainable with a single constituent material. In this way the composite is a multiphase material which differs in composition or form which remain bonded together. The components do not dissolve or completely merge they maintain an interface between each other and in concert to provide improved. Specific or synergistic characteristics not obtainable by any of the original components acting singly.

In view of the above mentioned facts it was kept in mind to prepare a composite ion exchange materials with the inorganic ion exchanged based on Zirconium and an organic polymer i.e. polyaniline, polystyrene polypyrrole and polyacrylonitrile etc. Here in present case Zirconium (IV) tungstophosphate was chosen an inorganic ion exchanger and polyaniline as organic polymer, these two were taken in the composite ion exchange material Polyaniline Zirconium (IV) tungstophosphate a cation exchanger.

The new composite ion exchange possesses a number of improved properties i.e. ion exchange capacity, ion exchange behavior and granulometric properties. This improvement helps in its functional column parameters. Towards its applications in the disciplines stated in under the heading of the applications.

Chapter-2

THEORY AND MECHANISM OF ION EXCHANGE

2.1 Introduction:

Before discussing any of the specific mechanisms it is some academic interest to consider whether ion exchange phenomenon should be classified as adsorption or as absorption processes. If we consider adsorption process strictly as confined to changes occurring at an interface or surface and absorption as those processes involving solids engulfing substances throughout their entire structure, then ion exchange phenomenon may fall into both categories and might therefore be more safely considered as a sorption process, a term that avoid the controversy between the devotees of the ad or ab prefix. Most students of ion exchange however used the term adsorption since the early work in the field of ion exchange was limited to non porous minerals where the exchange of ion exchange crystal surfaces confusion in terminology arises when consideration is given to materials, ion exchange resins for example, in which exchange of ions occurs throughout the entire ion exchange particle. Since the physical chemistry of the ion exchange processes of the two cases are identical since the energy considerations of ion exchange are more closely related to true adsorptive processes.

2.2 Crystal lattice theory:

The classic work of Pauling [67,68] and Bragg [69] on the crystal on the crystal structure of silicates exhibiting the phenomena of ion exchange in conjunction with the modern concept of the nature of ionic solids has considerably increased our understanding of ion exchange. The most recent concept of the nature of an ionic solids considers the constituent of the crystal lattice to be present as ions instead of molecules. In other words, an ionic solid may be considered to be completely dissociated. A crystal of sodium chloride contains no molecules of sodium chloride, only sodium ion and chloride ions. Each ion of the crystal is surrounded by a fixed number of ions of the opposite charge, as determined by the coordination number of ion, and is subject to certain coulomb attractive forces that are dependent on the relative charges of the ions and the distance between of the reaction. It follows that an ion at the surface of the crystal is subject to less attractive forces than a similar ion beneath the crystal surface. If placed in a highly polar medium such as water, the net attractive forces binding the ion to the crystal diminished to such a degree that an exchange to this ion for another ion or reaction with another ion in solution is quite possible. The ease with which the surface ions may be replaced by another ion depends therefore on (1) the nature of the forces binding the ion to the crystal, (2) the concentration of the exchanging ion, (3) the charge of the exchanging ion (4) sizes of the two ions, (5) the accessibility of the lattice ions, and (6) solubility effects.

The exchange of these crystal lattice ions is analogous to the mixing of two soluble electrolytes, such as sodium chloride and potassium nitrate. According to the modern concepts of electrolytes solutions each chloride ion of a sodium chloride solution is surrounded by sodium ions in a manner similar to a sodium chloride crystal. Similarly, each sodium ion is surrounded by chloride ions. As potassium nitrate is added to a solution of sodium chloride, the sodium ions must exchange with the added potassium ions and the chloride ions with the nitrate ions. This exchange of the ions is quite similar to the exchange of crystal lattice ions and ions of an electrolytic solution.

2.3 Base Exchange Capacity of Natural Silicates as a Function of Degree of Grinding:

There are many examples that may be cited as evidence for the exchange of crystal lattice ions. Kelley and Jenny [70] and Brown [71] Trough and Jackson [72], and many others [73-78] have found that, although it is difficult to exchange the lattice ions of silicates as the micas and feldspars, the cations of these silicates can be readily exchanged after a prolonged grinding of these minerals to a fine state of subdivision.

However, the structures of several minerals are such that a large fraction of the cation in the structure may be replaced by cations of an electrolyte solution without grinding. The zeolite minerals and several clays are examples of such structures. In other words, a substance need not be in

a fine state of subdivision to exhibit the phenomenon of ion exchange to an appreciable extent. The structure, however, must be porous enough to permit an exchanging ion to diffuse into the lattice. Dense structures such as feldspars and micas will not permit the exchange of ions unless they are in a fine state of subdivision,

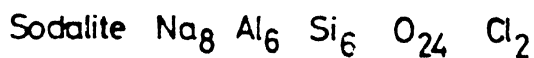
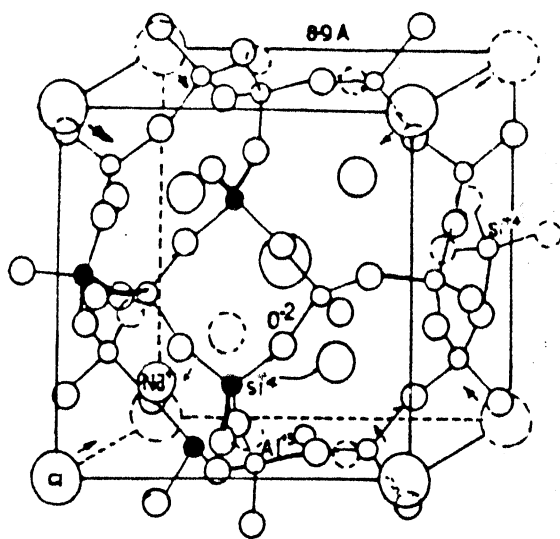


Figure-2.1 Portion of aluminium silicate framework in the structural unit of sodalite that is present in a distorted form in chabazite.

Whereas less dense structures such as the zeolites and ultramarine will permit ion exchange without a prior reduction to a fine state of subdivision. The zeolites such as chabazite ($\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$), heulandite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$), analcime ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), and sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_2 \cdot 4\text{Cl}_2$) are highly porous chain-like silicate structures in which the sodium and calcium ions are readily accessible by means of these fine pores. [79-85] Ions small enough to diffuse through these pores may then exchange with the sodium and calcium of the Crystal. In several instances it has been quite possible to exchange reversibly all the sodium and calcium of these minerals. These exchangeable ions occupy essential lattice sites, and there can be no question about the exchangeability of lattice ions in these cases [80,83,84]. These natural zeolites are most interesting in nature and have aroused considerable attention over the years. In many ways they are similar to the tightly cross-linked ion exchange resins. Barrer and his Co-workers [79-84] in England have found that the fixed pores of these zeolites are sufficiently uniform for the uses as "molecular sieves" for the fractionation of gaseous mixtures. These investigators also found that the pores could be modified by varying the exchangeable ion and that the zeolites could be synthesized. Efforts applied along these lines by the Linde Air Company in the United States have led to the commercial availability of such material in various grades of porosity.

The clay mineral montmorillonite *figure-2.1* also exhibits the exchange of lattice ions. This mineral is quite unusual in that when hydrated it is capable of swelling along its crystallographic c-axis. The structure of this mineral is such that the swelling results in the further separation of the two plates, each consisting of a silica layer and an alumina layer held together by the monovalent and divalent cations, sodium, potassium, calcium, and magnesium. When hydrated other cations may diffuse between the layers and exchange with these cations. In many of the silicates minerals, the exchange capacity and the seat of exchange have been related to the constitution of the silicate lattice-in particular, structural changes in the Si-O and Al-O chains. If a silicon atom, having the charge deficiency must be balanced by the presence of some cation. It is this cation that becomes exchangeable. This mode of substitution explain the ion exchanger phenomenon in many silicate minerals. The substitution of Mg^{+2} for Al^{+3} gives rise to the same effect as the substitution of Al^{+3} for Si^{+4} . Hendricks and Ross have analyzed many silicate clay minerals and have found that can account quantitatively for the exchange capacity of these clays in this manner.

The exchange of crystal lattice anions as well as cation is also quite possible, and in certain cases the exchange of both anions and cations may occur in the same crystal. Substances exhibiting the lattice phenomenon have been called amphoteric exchangers. The exchanger of anions in crystalline solids has been demonstrated in the silicate clay mineral, Kaolinite, by Stout [86] and in soils and montmorillonite by Mattson and his

co-workers [87-100] The hydroxyl ion of these ionic solids can exchange with chloride, sulfate and phosphate ions. The exchange of anions and cations in the clay mineral montmorillonite at various pH values is illustrated in **figure-2.2**. As is true for all amphoteric electrodes, the adsorption or exchange of cations increases with increasing pH, the reversed true for the anions. The oxides by other anions such as fluoride and sulfate has been demonstrated [87-89].

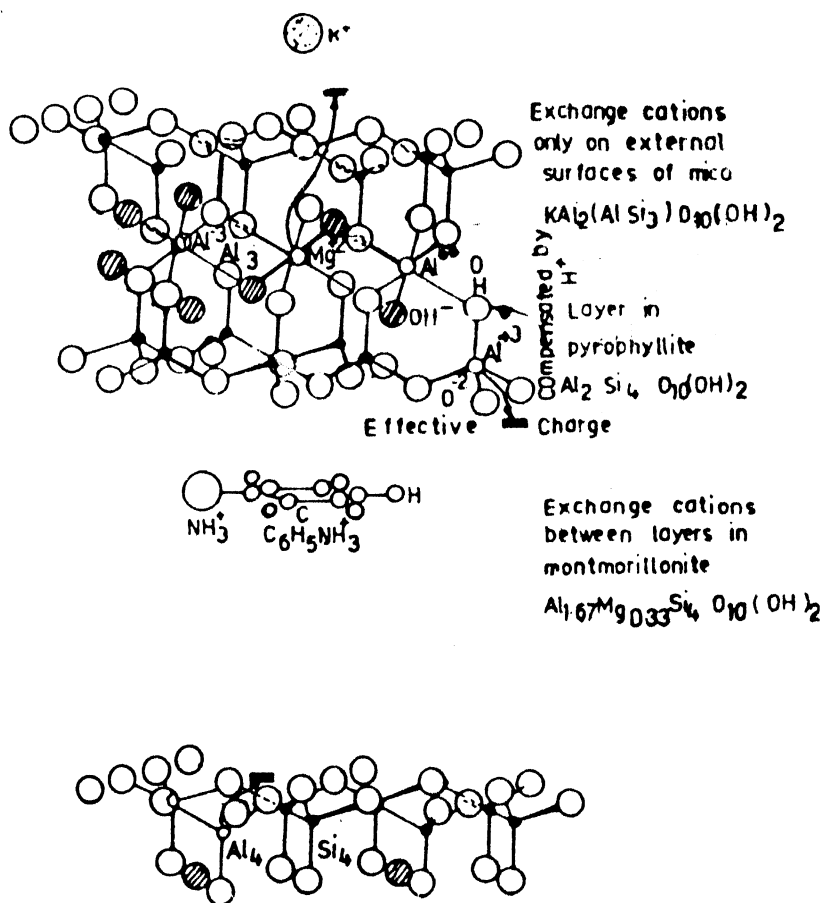


Figure-2.2 Structural layer of pyrophyllite and its modification in the micas and montmorillonite.

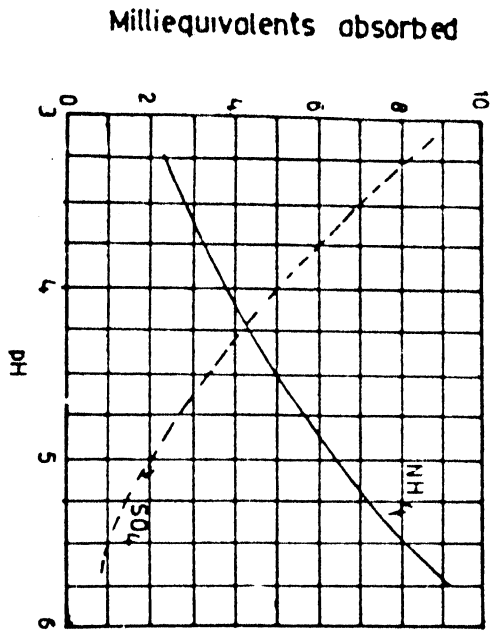


Figure-2.3 Amphoteric nature of ion exchange in bentonite.

It is important to note that, although an ion may be accessible for exchange with another ion, it is difficult to ascertain, a priori, that an exchange of ions will take place readily unless we are able to calculate the

relative binding energies of the exchanging ions in the particular lattice. To date, very little consideration has been given to this subject in the phenomenon of ion exchange.

Though lacking in crystalline, the mechanism of ion exchange in ion exchange resins is quite analogous to the exchange crystal lattice ions. The various cation and anion exchange resins may be considered as insoluble high molecular weight polymeric electrolytes. The cation exchange resins owe their capacity for exchanging ions to such functional groups as the sulfonic, carboxylic, and phenolic groups. It is most interesting to note that the capacity of the various sulfonic acid cations exchange resins may be quite accurately accounted for by the sulfur content of the resins **table-5**. This indicates quite decisively that the exchange of the ion with these resins takes place throughout the whole gel structure of the resin and is not limited merely to surface effects. Similarly, we may account for the exchange capacity of the carboxylic and phenolic cation exchanger resins.

Table-5

Total Cation Exchange Capacities and Sulfur Contents of Sulphonic Acid Cation Exchange Resins

Resin	%S	Total Exchange Capacity	
		Theoretical , meq/g	Experimental, meq/g
Amberlite IR-100	5.4	1.68	1.70
Amberlite IR-105	8.1	2.53	2.55
Amberlite IR-120	14.4	4.49	4.58

Although the exchange of anion exchange resins has been demonstrated by Kunin and Myers [101], Griessbach [102,103] and Wiklander [104], many still consider this phenomenon as the mere covalent adsorption of acid. However, it has been amply demonstrated that these anion exchange resins are polyamines in which the amine groups have reacted with a hydronium ion in a manner analogous to the system $\text{NH}_3\text{-H}_2\text{O}$, and that a hydroxyl ion exists somewhat dissociated from the substituted ammonium ion in a which may be exchanged for the other anions. It is quite interesting to note that, as in the case of the cation exchange resins, practically all the amine content of the anion exchange resin may be accounted for by the exchange capacity **table-6**. Since most available anion exchange resins have been of the weak-base type, however, the existence of exchangeable hydroxyl groups has been quite difficult to demonstrate.

Table-6

Total Anion Exchange Capacities and Nitrogen Contents of Sulphonic Acid Anion Exchange Resins

Resin	%N	Total Exchange Capacity	
		Theoretical meq/g	Experimental meq/g
Amberlite IR-4B	14.2	10.1	10.0
Amberlite IR-A400	5.8	4.1	3.9

However the fact that the rate and equilibrium are dependent on the anion concentration and not the acid concentration is indicative of the occurrence of anion exchange in the weakly basic resins. The preparation of quaternary type resinous exchangers has furnished the necessary evidence that atleast some amine type resins functions as true anion exchangers.

The exchange of ions in heterogeneous systems is quite common and should occur to some extent whenever any ionic solid comes in contact with any electrolyte but the exchanger of cluster lattice ion may be observed in many instances by solubility effects and by the unavailability of ions to penetrate the crystal lattice.

2.4 Double layer theory of ion exchange:

The double layer theory originally proposed by Helmholtz [105] and later modified by Gouy and Stern [106] as an explanation of the electrokinetic properties of collides, has been considered by many as an explanation for the various phenomena associated with ion exchange. Although many have considered the extensive electro-kinetic measurements of various collides studied since the classic work of Quince [105] in 1856 as proof of the existence of the double electrical layer at the surface of most colidals the origin and structure of this layer are still fundamental problems in colliide chemistry . The classic Helmholtz double layer consists of two digit electrical layer analogous because of later work of Gouy and Stern . Like the Helmholtz

model, the models of Gouy and Stern of an inner fixed layer , with a diffuse and mobile outer layer of charges. These charges layer owe their existence to absorbed ions , this may be quite different from ions that are already present in the inner portion in the colloid and that determines much of the electro kinetic properties of the colloidal system . The ions present in the diffused outer layer of the colloid extend into the external liquid medium. There is no sharp boundary between the ions in the diffuse outer layer and those in the equilibrium external medium, and we may consider the concentration of the ions constituting the diffuse layer as varying continuously and depending on the concentration and pH of the external solution. If we change the concentration of the ions in the external solution by the addition of foreign ions, The equilibrium is upset and a new equilibrium is obtained. Some of the new ions will enter the diffuse outer layer replacing some of the ions previously held in this layer. However since the law of electro neutrality must be maintained , the exchange is stoichiometric.

Although there is some similarity at crystal lattice sites and double layer exchange fundamentally the mechanism are quite different. As long as no crystallization occurs, The relation between theoretical total exchange capacity and pH or concentration is quite different for the two systems. Crystal lattice exchange assumes a fixed number of exchange sites that must be satisfied regardless of change in pH or concentration, However, in double layer exchange , this is not true , since the capacity of the diffuse double layer is dependent on both concentration and pH. In many systems both

types of chains may occur simultaneously. The relation between the electrokinetic properties of colloidal systems and ion exchange has been quite extensively studied by Wiegner [107-109], Jenny [110], Mattson [88-90], Verwey, De Kuryt and others [111].

2.5 Donnan membrane theory:

The third theory of ionic exchange is essentially a special case as the Donnan membrane theory [112-116,119]. The Donnan theory pertains to the unequal distribution of ions on the two sides of the membrane; one side contains an electrolyte, one of whose ions is not able to diffuse through the membrane. Such a system is obtained on placing a solution of the sodium salt of Congo-red on one side of a colloid membrane and a solution of sodium chloride on the other. Since the colloidal anion of the dye can not diffuse through the membrane only the sodium and chloride ions may distribute themselves. However this distribution must be unequal because of the usability of the anion of the dye to diffuse through the membrane. Mathematically, the relationship can be derived easily, since at equilibrium the number of impacts Na and Cl must be the same for the side of the membrane.

$$[\text{Na}^+]_1 [\text{Cl}^-]_1 = [\text{Na}^+]_2 [\text{Cl}^-]_2$$

In order for the principle of electroneutrality to be obeyed,

$$[\text{Na}^+]_2 = [\text{Cl}^-]_2 \text{ and } [\text{Na}^+]_1 = [\text{Cl}^-]_1 + [\text{An}^-]_1$$

$[\text{Na}^+]_2 [\text{Cl}]_2 = [\text{Cl}]_2^2$ and $[\text{Na}^+]_1$ must be greater than $[\text{Cl}]_1$

Since $[\text{Cl}]_2^2 = [\text{Na}^+]_1 [\text{Cl}]_1$

then $[\text{Cl}]_2 > [\text{Cl}]_1$

Or, in other words, the concentration of NaCl is greater on the side that is free the non-diffusible ion. If we let $[\text{Na}^+]_2 = [\text{Cl}]_2 = X$ and $[\text{Cl}]_1 = Y$ and $[\text{An}]_1 = Z$, then

$$X^2 = Y(Y + Z)$$

If a second cation, K^+ is added to the system, the following two conditions must be obeyed:

$$[\text{Na}^+]_1 [\text{Cl}]_1 = [\text{Na}^+]_2 [\text{Cl}]_2$$

and

$$[\text{K}^+]_1 [\text{Cl}]_1 = [\text{K}^+]_2 [\text{Cl}]_2$$

Dividing the two equation, we obtained:

$$\frac{[\text{Na}^+]_1}{[\text{K}^+]_1} = \frac{[\text{Na}^+]_2}{[\text{K}^+]_2}$$

$$[\text{Cl}]_1 = [\text{Na}^+]_2 [\text{Cl}]_2$$

For pairs of ions of unequal valence such as Na^+ and Ca^{2+} , the expression becomes.

$$\frac{[\text{Na}^+]_1}{[\text{Ca}^{2+}]_1^{1/2}} = \frac{[\text{Na}^+]_2}{[\text{Ca}^{2+}]_2^{1/2}}$$

These relationships simply state that an exchange of ions must take place until the concentration ratios are equal in both places. The Donnan concept early explains. The inability of free electrolyte to enter the resin phase of resin having a high exchange capacity. The effect of valency. The effects of solution volume and electrolyte concentration and the effect of fixed ion concentration of the resin phase.

In this derivation, the actual concentration has been employed rather than the thermodynamic activities. For a more rigorous application of the Donnan theory, thermodynamic activities must be employed instead of actual concentrations.

On extending this theory of membrane equilibria to the phenomenon of ion exchange, the assumption is made that the colloidal micelle, to which is attached the extendible ion, is considered to be the non-diffusible ion.

Although no membrane is encountered in ion exchange equilibria, the interface between the solid and liquid phases may be considered as a membrane. Although the conditions for ion exchange are not readily apparent from the previous derivation, by the appropriate choice of conditions exchange of ions will occur. The exchange of ions in living cells and across cellophane or parchment membrane has been shown to follow the Donnan theory. Does not conflict with the crystal lattice theory but merely offer a quantitative relationship governing the exchange of ions. In many simple ionic solids of ions, maybe capable of diffusion, and hence the Donnan theory cannot be applied. However, in the complex silicates, phosphates,

resins, etc.... one ion is always a high polymeric non-diffusible ion. Mattson and his student [94,99] and Davis [117] have found the Donnan theory to be quite useful in explaining exchange phenomena in silicates, phosphates, humate, and resins.

The Donnan membrane theory has been most useful in explaining the availability of an ion exchange material to exclude free, diffusible electrolyte. If we take anion exchange material having a high exchange capacity, or fixed ion concentration, and immerse this material in a dilute electrolyte solution, very little free electrolyte can diffuse in to the electrolyte material. For example, the sodium salt of sulfonic acid cation exchange resin having a fixed ion concentration of 5M when equilibrated with a 0.1N solution of NaCl will have but a negligible chloride content. This must follow if we consider the fact that at equilibrium, the $(\text{Na})_i \times (\text{Cl})_i = (\text{Na})_o \times (\text{Cl})_o$. The high fixed ion concentration of the resin, a condition resulting from the high capacity of the resin, excludes the entrance of free electrolyte into the resin phase from a solution having concentrations considerably below that corresponding to the fixed ion concentration. It is this phenomenon that forms the basis of the ion exclusion principle associated with ion exchange resins and the permselective character of ion exchange membranes.

Bauman and Eichhorn [118], applying a Donnan membrane equilibrium approach similar to that employed by Mattson [94], visualize the resin as a concentrated electrolyte solution in which the ion exchange

equilibrium is determined by the differences in activity coefficients of the outside solution and the resin phase. They also apparently exclude the specific affinity of one ion over another ion as having any effect on equilibria.

Essentially all the ion exchange theories are quite similar in that the exchange of ions must satisfy the law of electroneutrality. The only differences in the various theories then are the position and the origin of the exchange site. In all cases this site is essentially a fixed nondiffusible ionic grouping capable of forming an electrostatic bond with small diffusible ion of opposite charge. The ease with which this latter ion may be replaced depends on the strength of the bond, which varies in a manner similar to the dissociation of weak and strong electrolytes. The laws governing the exchange of ions in these heterogeneous systems are therefore quite analogous to those governing the solutions electrolytes.

Chapter-3

PROPERTIES OF COMPOSITE ION EXCHANGER

3.1 Chemical Stability:

According to the nature of degradation processes which occur during the chemical corrosion of ion exchangers, the following types of reactions may occur

- a) Degradation of the macromolecule chain between the special bridges.
- b) Chemical changes in groups belonging indirectly to the macromolecule chain. The inorganic groups remain unaffected.
- c) Substitution or degradation of the functional groups.
- d) Formation of new (especially weakly acidic) functional groups.

From the point of view of the chemical stability of ion exchanger, the most important characteristic is their resistance towards oxidizing agents [120].

If the resin is degraded in its polymer matrix because of insufficient oxidation resistance, its cross-linking is decreased. The resin swelling increased and in a limiting case, the resin is desolved. The phenol-formaldehyde skeletons under go this degradation more easily then the styrene-DVB matrix. The degree of degradation of the styrene-DVB depends on the amount of the DVB present in the polymer as well as on the purity of the monomer used in their synthesis. The effect of the DVB isomer used has also been observed.

Resin of lower DVB content exhibit a higher oxidation degradation. The degradation process is accelerated by the presence of element which are able to act as catalysts (especially iron, copper).

Strongly basic anion exchangers are especially sensitive to hydrogen peroxide. Resin containing the pyridinium groups are more resistant other strongly basic sorbents.

If the resin are contacted with acidic solution of chromate's, permanganates and vanadates, the anion mentioned are mostly reduced with oxidation of some component of the resin [121-123].

macro reticular, strongly basic anion exchanger exhibit a higher stability to alkaline solution than do gel-like resins.

Ion exchanger are not appreciably damaged by the usual organic solvents (at room temperature). How ever, a loss of small amount of organic material occurs which may (in some cases) interfere with further analytical procedures.

3.2 Radiation Stability:

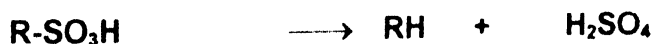
Due to low a swelling ability of these exchangers there is no substantial difference between the degradation of a dry or swollen sorbent. No considerable changes were observed when most of these exchangers had adsorbed a dose of 10^7 Gy. A dose of 2×10^6 Gy. led to a decrease in the silica gel exchange capacity by approximately 15%. It is thought that suitable

types of inorganic ion exchangers can work at doses up to 10^7 - 10^8 Gy. where the use of organic type ion exchangers is excluded [124-126]. The ion exchangers based on treated types of coal are generally stable towards ionizing radiation. Irradiation up to 10^7 Gy causes no substantial changes in their exchange properties. Due to a low swelling ability, there is no great difference between the stability of dry and wet exchanger.

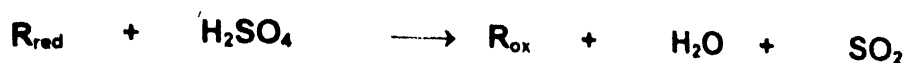
3.3 Thermal stability:

The thermal stability of ion exchangers depends on the type of resin skeleton, its degree of cross linking, the type of inorganic group and their counter ion. The stability of the ion exchangers is affected by their synthesis.

The ion exchanger stability becomes especially evident in change of the volume exchange capacity, the loss in inorganic groups, swelling changes, in the formation of new groups (especially weakly acidic) or in the destruction of the resin skeleton to various degrees. The exchange capacity of the resin decreases with increasing temperature due to increasing desulphonation:



With rise in temperature desulphonation process accelerates and at temperatures $> 150^\circ\text{C}$, a reaction between the sulfuric acid formed and oxidation resin components begins and sulfur dioxide is formed



Desulphonation, together with other reactions, as a consequence of the air heating of the resin was also observed for styrene-DVB cation exchangers. For this type of exchangers (H⁺ form), differential thermal analysis reveals three endothermic changes due to dehydration (100-200°C), desulphonation (270-310°C) and oxidative degradation of the matrix at temperatures above 430°C. In addition to these three endothermic effects, an exothermic effect at 370°C was observed due to depolymerization of the skeleton.

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3.4 Radiation stability of organic ion exchanger:

According to their resistance towards ionizing radiation, cation exchangers can be divided in the following groups.

6689 KOT

- (a) Sulphonated, monofunctional, strongly acidic cation exchanger of the polymer type;
- (b) Sulphonated, polyfunctional, strongly acidic cation exchanger of the polycondensation type;
- (c) Phosphorylated, mono-and polyfunctional medium acidic cation exchangers of the polymer and polycondensation types;
- (d) Weakly acidic, mono and polyfunctional, cation exchanger of the polymer and polycondensation types;

3.5 Determination of ion exchanger particle size and particle distribution by mesh analysis:

The size and distribution of ion exchanger particles are determined by the method of mesh analysis. The sample of the exchanger taken for the analysis should be in a standard state (the Na^+ form for cation exchangers) and should be either air dried or fully swollen in water. It is more convenient to use the fully swollen sample.

If exchanger in ionic forms other than standard ones are analyzed, certain small deviations in the size distribution should be expected

Approximately 100g of the air dried ion exchanger in a standard state (strongly acidic cation exchangers in the Na^+ form an exception ?) are sieved mechanically or manually through a series of standard sieves for 30 minutes. Portion retained by individual sieves are transferred quantitatively into a suitable vessel and weight with to three decimal places. Using the values of the weight of the individual fractions, the distribution curve (integral or derivative) can be plotted. Note; it is advantageous to add approx. 50 Mg of an antistatic substance to the analyzed sample.

3.6 Purification of ion exchanger:

Organic high molecular-weight of ion exchanger are delivered mostly in a wet state, in a sealed polyethylene bags or bottles. Inorganic ion exchanger and cellulose based ion exchanger are delivered mostly in a dry

state in appropriate packing. The packing prevent contamination of the ion exchanger during its transport and storage.

The process of purification leads also to a certain release of functional groups from the ion exchanger skeleton and, at the same time, the ion obtains the necessary "training".

The ion exchanger is poured into a beaker of an appropriate size, filled to approximately 1/3 of its volume with distilled water. An amount of water is added such that its level is at least 10 cm above the ion exchanger layer. The ion exchanger is rest to swell for several hours. After mixing the swollen ion exchanger, followed by its determination, water is removed by decanting. The process of decantation is repeated several times. The final washing water should be clear and colorless. A 3-4M solution of hydrochloric or sulfuric acids is added to the ion exchanger (the ion exchanger must not contain ions forming insoluble precipitates in these solutions). The total concentration of H^+ ions (cation exchangers) or of appropriate anions (anion exchanger) should exceed the expected total capacity of the whole ion exchanger amount by approximately 25%. A suspension of the ion exchanger in the acid solution is left to stand for 1-2 hours and mixed occasionally. The acid is then decanted and the ion exchanger washed with distilled water until a neutral reaction of the washing water occurs.

The purified ion exchanger is then converted to the Na^+ (OH) form with 1-2M sodium hydroxide solution. After standing for 1-2 hours, the ion exchanger is thoroughly washed with water and converted into the H^+ (Cl⁻ or

SO_4^{2-}) form by the method described above. The whole purification cycle is repeated 2-3 times.

If a considerable determination of the ion exchanger of the ion exchanger in the sodium hydroxide solution occurs, it is possible to use sodium. Its pH value is lower than the hydroxide solution and thus the dissolution of the ion exchanger in an alkaline medium can be prevented.

3.7 Ion Exchange Columns:

The dynamic ion exchange separation is carried out in an ion exchange column. The ion exchange column is a tube of appropriate design and filled with the ion exchanger. In the simplest case, the ion exchange column may be represented by a glass tube of suitable size containing a swollen resin.

Glass or quartz are the most suitable materials for the manufacture of laboratory ion exchange columns. In the case of corrosion danger (e.g. presence of hydrofluoric acid etc.) the column is made of other appropriate materials (teflon, prospect and other plastics, stainless steel, etc.). The material should be resistant towards solutions flowing through the column.

3.7.1 Shape of the column:

The column should be designed so that the solutions passing through flow steadily through its whole cross section. This is the reason why precision

glass columns (especially of smaller diameter) are often drilled into glass rods or are made of precision capillary tubes.

The ion exchanger layer sits in the column on a flat support plate. It is recommended to use a fritted glass disc of appropriate porosity which is fused into the bottom part of the column. In cases when the fritted glass disc can not be used, stainless steel or platinum net may be applied. In the case of small and thin columns, it is sufficient to seal their lower part with glass wool, porous teflon, polyurethane or another suitable material.

3.7.2 Size of the column:

The height of the ion exchanger column is determined by the separation factor of the ions under the given conditions. Extension of the height of exchanger column beyond the optimum conditions leads to an improvement in the separation. At the same time, the amount of effluent is increased leading to an improvement in the elution curve.

The approximate column height can be calculated using equilibrium data or results from a preliminary experiment.

The column cross section is chosen according to the amount of substance to be separated. For non-chromatographic, simple applications, exchangers columns having the diameter/height ratio of 1:10-1:20 as used. Ratio of 1:100-1:200 are chosen in the case of difficult separation of more complicated mixtures.

3.7.3 Filling of the ion exchange column:

The column is filled, as a rule, with a fully swollen resin. If the column contains a dry resin which swells in contact with water, the glass column may easily be ruptured due the great volume change of the exchanger.

3.7.4 Rate of flow:

The flow rate of the liquid during chromatographic separation should be chosen so that the working conditions are close to the equilibrium state. Higher flow rates can be used in the case of non-chromatographic separations where the requirement of equilibrium need not be so strictly kept. A generally valid rule is that increased temperature and decreased ion exchanger particle size leads to a possibility of increasing the liquid flow rate through the column. and the good separation ability of the ion exchanger column is retained.

3.8 Application of composite ion exchanger:

The composite ion exchanger shows some better granulometric properties which facilitates its suitability in column operations especially for separation, filtration and preconcentration of ionic species. The column operation suitability make it more convenient in regeneration of exhausted beds also. As in general their materials have their applications in following disciplines direct on indirect.

- Water softening.

- Separation of ionic species.
- Preconcentration of metal ion.
- Synthesis of organic Pharmaceuticals compound.
- Catalysis.
- Redox system.
- Hydrometallurgy.
- Effluent treatment.
- Ion selective electrodes.
- Chemical and Bio sensors.
- Ion exchange fibers.
- Ion exchange membranes.
- Membrane technology etc.

Chapter-4

EXPERIMENTAL

4.1 Preparation of Composite Ion Exchanger:

A new material Polyaniline Zirconium (IV) tungstophosphate (PZWP) was prepared by mixing the solutions of 0.1M sodium tungstate, 0.1M ammonium sodium hydrogen ortho phosphate, and 0.1M zirconium oxychloride at pH - 1 to 2. The mixture was heated up to boil and then left to acquire room temperature. The polymerization of aniline was done at a temperature of 0°C to 5°C in the presence of ammonium per sulphate (APS) as a catalyst. The so obtained green colored gel confirming the polymerization of aniline was left for over night.

This gel was filtered, washed with 1M HCl, Deionized water (DIW) and finally with diethyl ether. The washed gel was dried at 40°C (± 2) and converted into granules by the addition of DIW. These granules were finally converted into H⁺ form by placing in 3M HNO₃ for two days. The so obtained material after washing was again dried at 40°C (± 2).

4.2 Determination of the ion exchange capacity (IEC):

A series of terms used to express the exchange capacity of exchangers exists. The weight capacity (QA) is a characteristic constant of the individual ion exchanger. Theoretically, it should be independent of the

method of determination. However small discrepancies have been found when comparing capacities determined by various measuring techniques.

In addition to the weight capacity, the quantity 'volume capacity', expressed in mmol/cm^3 of swollen resin, has often been used.

Before determining the capacity, the exchanger should be purified and cycled. However it is also possible to use a shortened purification whereby a small amount of exchange resin ($5\text{-}10 \text{ cm}^3$) is first decanted with deionised water, the cation exchanger is converted to the Na^+ form with 3% sodium hydroxide solution and then to the H^+ form with 5% hydrochloric acid solution. Anion exchangers are converted to the OH^- form with 2% NaOH solution and then to the Cl^- form with 5% HCl solution. Inorganic ion exchangers are usually converted to the H^+ form with nitric acid, the concentration of which depends upon the character of the exchanger. 3-7% nitric acid is used as a rule. the conversion of these exchangers to the Na^+ form with sodium hydroxide solution does not find application as the majority of modern synthetic, inorganic ion exchanger are not stable at pH values greater than 6-8.

Exchanger treated in the way mentioned above can be considered as a starting form the determination of their exchange capacity.

Considering the uncertainty in the moisture-content determination, the exchange capacity is related to the dry exchanger dried under certain conditions. The exchange capacity is usually determined with an error of $\pm 1\%$.

The choice of the method of the determination depends on the functional group and ion exchanger reaction rate.

4.3 Determination of the total weight exchange capacity:

1.000 - 2.000 g of the air-dried exchanger in the H^+ form are allowed to swell in deionised water. It is also possible to use 1-3 g of a wet exchanger which has been formerly sucked on a Buchner funnel. At the same time, 0.300 - 1.000 g of the exchanger are weighed to determine the dry substance. The swollen resin is transferred to an ion exchange column (6-10 cm in height, approx. 1 cm in diameter). A known amount (20ⁿ to 300 cm³) of 0.1M sodium hydroxide solution is passed through the exchanger-resin column at a flow rate of 2-3 cm³/min. The effluent is collected in a 500 cm³ volumetric flask. After the total amount of sodium hydroxide solution has passed through the column, the residual liquid present in the column is ejected to the volumetric flask with pressure air. Washing of the exchanger with water can lead to the hydrolysis of the former.

In an determined by titration with 0.1M HCl and the total weight capacity, expressed in M mole H^+ g⁻¹ of dry exchanger, is calculated.

4.4 Electron Spectrometer For Chemical Analysis (XPS):

The use of ESCA as an analytical technique. The different level of sophistication, qualitative and quantitative element analysis; elemental state

and structural analysis are dealt with in turn in order to give an overview of the analytical information available in spectra its extraction and interpretation. Also we review the types of material for which ESCA provides new analytical information because of its surface sensitivity.

- **Quantitative Analysis:**

The simplified expression of Wendt [127,128] relating measured photoelectron intensity to fundamental parameters, for an infinitely thick sample, gives-

$$I_j(\alpha) = \frac{K_{\alpha} N_j}{S_j} \quad (a)$$

Where I_j is the intensity for photoelectron j , α_j is the emissivity of the atom j (approximated by the atomic photoelectric cross-section), N_j is the number of these atoms per cubic centimeter. K is an instrument response function dependent on the KE (E) of the photoelectron and S_j is the total photoelectron scattering coefficient in cm^{-1} . With in the region sampled no attenuation of the X-ray intensity is assumed. Expansion of the S_j terms gives:

$$S_j = \sum a S_j(M_1) + b S_j(m_2) + \dots \quad (b)$$

where $S_j(M)$ represents a particular scattering mechanism with in the solid matrix and the associated coefficient (a, b, \dots) represents its fractional contribution to the total scattering coefficient. For KEs typical of ESCA single

electron-electron scattering generally dominates, but other mechanism can be important, as discussed bellows.

Electron Scattering accounts for the surface sensitivity of ESCA and S_i is inversely related to the inelastic mean free path (IMFP) or escape depth, λ . Compilation plots of λ/E data show that in the region of interest for ESCA λ is a function of E (approximately $E^{1/2}$). The K term in the equation (a) is also a function of E varying approximately as E^{-1} for instrument employing fixed analyzer transmission (FAT) energies or as E^{-1} for those employing fixed retardation ratios (FRR) of emitted and analyzer pass energies.

The former to be more common ; in these cases both λ and S_i terms are related to E^{-1} resulting in some degree of cancellation in equation (a) and the possibility that I_j will correlate reasonably with α_j . Relative I_j values (usually related to F is = 1.00) have been compiled by several workers using FAT instrument [129-131]. The correlate reasonably with α_j values calculated directly [130-133] or from X-ray mass absorption coefficients.

4.5 Infra red spectroscopy:

The range in the electromagnetic spectrum extending from 0.8 to 200 μ is refereed to as the infrared. However, discussion in this chapter will be restricted to those region from 0.8 to 50 μ which can explored with commercial infrared instruments, and where in spectra originate primarily from the vibration stretching and bending modes with in molecules. Most

organic and inorganic material shows absorption and in all but a few cases, this absorption includes several characteristic wavelength. In fact, the infrared spectrum is one of the most characteristic properties of a compound. It provides a finger prints for identification and a powerful tool for the study of molecular structure. Empirical correlation of vibrating groups with specific observed absorption bands offer the possibility of chemical- identification and coupled with intensity measurement of quantitative determinations.

Infrared spectroscopists use both wavelength and wave numbers as units to describe a position in the absorption spectrum. The wavelength λ is usually measured in micron μ . The wave number $\bar{\nu}$ is the "true" frequency divided by the speed of light. It is the reciprocal of the wave-length. It indicates the number of wavelength for 1 cm of distance traversed (cm^{-1}). A simple reciprocal relationship exists between these units, namely both units will be employed in the text.

$$\bar{\nu} \text{ (in cm-1)} = \frac{10^4}{\lambda(\text{in } \mu)}$$

The position of absorption band can be predicted from the mechanical theory of harmonic oscillators that is a simple spring obeying Hook's law. The classical Modal of a vibrating diatomic molecule represent the simplest case. When two adjacent atoms, thought as approximating to point masses m_1 and m_2 and connected by a spring representing the strength of the band,

execute a simple harmonic motion about an equilibrium point, while linkages with the remaining atoms are ignored the frequency will be given by.

$$\nu \text{ (in cm}^{-1}\text{)} = \frac{1}{2\pi c} \sqrt{\frac{K(m_1+m_2)}{m_1 m_2}}$$

Where

K = The restoring force per unit displacement (dynes cm⁻¹) from the equilibrium point.

m₁m₂ = in grams

The frequency is the greater the smaller the mass of the vibrating nuclei and the greater the force restoring the nuclei to the equilibrium position.

4.6 Thermogravimetric analysis (TGA):

Data are obtained as continuously record curves which may be considered as thermal spectra. This thermogram characterize a system, single or multicomponent in term if the temperature dependencies of its thermodynamics properties & physico-chemical reaction kinetics.

Thermogravimetric analysis involves change in weight of a system under investigation as the temperature is increased at a predetermined rate. Differential thermal analysis consist of measuring changes in heat content, as a function of the difference in temp. between the sample under investigation

and a thermal inert reference compound, as the two material are heated to elevated (or cooled to subnormal temperature at predetermined rate.

In this manner enthalpic changes, Such as melting, vaporization, crystallographic phase transition, or chemical changes are detected from the endothermic and exothermic bands and peaks that appear on the thermograms.

Interest in thermogravimetry has increased in recent years because of the commercial availability, Continuous recording thermobalances which are rugged, reliable, and accurate. In dynamic thermogravimetry a sample is subjected to condition of continuous increase in temperature usually linear with time , where as in isothermal or constant temp. for a period of time during during which any change are noted.

Plateaus on the decomposition curve indicative of constant weight, represent stable phases over the particular temperature interval. An inflection may imply the formation of an intermediate compound, or the adsorption of a volatile production (or in) the new solid phase.

Correction must be applied for the apparent weight change of the empty sample pan to arrive at the actual weight change occurring in the specimen. This procedure considered to be more satisfactory than the ice of tare container in a separate furnace, in view of the possible nonuniformity of the hot zone of the two furnaces. This apparent change in weight is caused by the interplay of a complex combination of several factors, such as air buoyancy, convection effect with in the furnace, container geometry, radiation

effects, the atmosphere in the furnace, and the fact that the specimen support is subjected to a temperature gradient within the furnace.

The shape of the corrected Thermogravimetric curve is influenced for a particular compound by-

- (a) the heating rate
- (b) the sample
- (c) the crucible
- (d) the atmosphere

At any given temperature, the extent of decomposition is greater at a slow rate of heating than for a similar sample heated at a faster rate. The heat of reaction will affect the difference between the sample temperature and furnace temperature, causing the sample temperature to lead or lag the furnace temperature depending on whether the reaction is exothermic or endothermic. The use of a small finely divided sample is preferred. Equilibrium between sample and product gas and with the furnace temperature will be governed somewhat by the bulk of the material in the crucible. The environmental atmosphere immediately surrounding the reactive particles influence the curve. even small change in the composition of the atmosphere can affect the thermogram.

- **Application:**

The widest application of the thermogravimetry analysis has been in the investigation of analytical procedures.

- (a) In investigating suitable weighing forms for many elements.

- (b) In testing materials that are actual or potential analytical standard.
- (c) In the direct application of the technique to analytical determinations.

Thermogravimetry is regularly used for determining the drying range of precipitates. However the dynamic nature of the technique must be considered when interpreting the best drying temperature, the most reliable information will be gained by using several different heating rate or a slow rate of heating, possibly with preliminary air drying. Plateaus for hydrates sometimes depends on the initial water content.

The apparent pattern of thermal decomposition of pure compounds may suggests reaction scheme to account for the degradation. The breakdown of organic polymer has received much attention. The sample is heated in an inert atmosphere or under vacuum.

Thermogravimetric data can be used to evaluate kinetic parameters of weight change in reactions. Graphical methods for the determinations of the reaction X and the activation of energy (E_A) can be obtained from the equation

$$\frac{-E_A/(2.303) R \Delta T^{-1}}{\Delta \log W_r} = \frac{-x + \Delta \log (dW/dt)}{\Delta \log W_r}$$

where R is the gas constant, T is the absolute temperature, and $W_r = (W_c - W)$, where W is the weight loss at time 't' and W_c is the weight loss at completion of the reaction. Either by plotting a graph of

$$\frac{\Delta \log (dW/dt)}{\Delta \log Wr} \quad \text{vs} \quad \frac{\Delta T^{-1}}{\Delta \log Wr}$$

4.7 X-Ray method:

When a beam of electron impinges on a target material, the electrons in general will be should down by multiple interaction with the electron of the target. The energy will be converted in to a continumm of x- radiation, with a sharp minimum wavelength λ_{\min} (maximum frequency) corresponding to the maximum energy of the electron which can not be exceeded. This cut of wavelength is given (in angstrom) by

$$\lambda_{\min} = \frac{hc}{ev} = \frac{12,400}{v}$$

where

h = Plank's constant.

c = velocity of electromagnetic radiation in vacuum.

e = electronic charge.

v = Accelerating potential across x-ray tube in volts.

As the potential is increased, a point is reached where the energy is sufficient to knock a planetary electron completely of the target atom. Then as another electron falls back into the vacancy, a photon of x- radiation is emitted with a wavelength dependent on the energy level involved the electron closest to the nucleus are the principal once effected. Thus a K

electron may be ejected and its place taken by an electron from the L cell. Since these inner electron are not concerned with state of chemical combination of the atoms (acceptor the lighter). It follows that x-ray properties element are independent of chemical combination or physical state. The wavelength corresponding to such high energies are small, of the order of 10^{-2} to 10\AA . The range of 0.7 to 2.0\AA includes the wavelengths most useful for analytical purposes.

X-ray wavelength were formerly given in terms of $k\alpha$ units, where $1\text{ }k\alpha$ unit = 1.00202\AA .

If the excitation is brought about by fluorescence, i.e. irradiation with x-rays of shorter wavelength, the continuum does not appear. Only the characteristic lines are present. This is a favorable situation for x-ray emission analysis, greatly increasing the signal-to-noise ratio.

• **Application:**

For analytical purposes x-radiation may be utilized in several distinct way

- (1) The absorption of x-ray will give information about the absorbing material, just as will absorption in other spectral regions.
- (2) The diffraction of x-ray permits analysis of crystalline substance with a high degree of specificity and accuracy.
- (3) Wavelength measurement will identify elements in the sample which is undergoing excitation.

(4) Measurement of radiant power at a given wave-length can give a quantitative of the composition of the sample.

4.8 Distribution behavior:

The distribution behaviour of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions. The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase. The distribution coefficients (K_d values) increase with dilution of the solution may be expressed as follows

$$K_d (\text{ml /g}) = \frac{\text{Amount of metal ion in exchanger phase g}^{-1}}{\text{Amount of metal ion in solution phase ml}^{-1}}$$

In other word, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion exchange material and mathematically can be written as

$$K_d (\text{ml /g}) = \frac{I - F}{F} \times \frac{V}{W}$$

where 'I' is the total of metal ions initially in the solution,

- 'F' is the amount of the metal ions left in the solution after equilibrium,
- 'V' is the volume of the solution and
- 'W' is the weight of the exchanger

4.9 Separation factor:

Before carrying out the chromatographic separation it is necessary to adsorb the mixture of the ions to be separated on the top of the separating column. The most effective separation is achieved when the amount of ions to be separated is low. The volume of the exchanger column retaining the separated ions should be about 3-5% of the total volume of the exchanger column. However, when especially difficult separation operations are to be carried out, this volume should not exceed 1% of the column volume.

The column efficiency for adsorption can be increased by up to 50% of its capacity in the case of selective separations when only one of the separated ions is eluted.

A small amount of the sample is placed directly on the ion exchanger by a small pipette. Previous to this the liquid level is lowered to the level of the top of the exchanger column. A known volume of the solution is allowed to infiltrate into the exchanger either in gravity or under pressure. The column walls are then rinsed with water for several times. However, this sample technique can not be used in the case of operations under high

pressure. In that case the method involving a sample loop is generally applicable.

Due to a large local pH change in the adsorption zone of the column (especially in the case of H^+ or OH^- forms of the resins) during adsorption, the elution of adsorbed ions may occur. This be prevented by the addition of an appropriate buffering mixture of the solution.

The separation factor is the preference of the ion exchanger for one of the two counter ions is often. The quantity is particularly convenient for practical applications, e.g. for the calculation of column preference. The separation factor has been calculated by

$$\text{Separation Factor } (\alpha_B^A) = \frac{\text{K}_d \text{ value of metal ion A}}{\text{K}_d \text{ value of metal ion B}}$$

Chapter-5

RESULTS AND DISCUSSION:

A number of sample of Polyaniline - Zirconium (IV) tungstophosphate were prepared. Out of these one prepared by the mixing of 0.1M sodium tungstate, 0.1M ammonium sodium hydrogen phosphate and 0.1M Zirconium oxychloride at pH 1-2. The aniline was polymerized in the gel of Zirconium tungstophosphate in the presence of APS at temperature 5°C. In the last green colored gel obtained which was kept for aging overnight. This gel was filtered, washed with 1M HCl, DIW and finally with diethyl ether. The washed gel was dried at 40°C and broken into granules with the immersion in 3M HNO₃ which convert it into H⁺ form.

The material shows ion exchange capacity (meq g⁻¹) as. [Na⁺ = 1.46, K⁺ = 0.82, Mg²⁺ = 2.00, Ca²⁺ = 1.38, and Sr²⁺ = 0.86]. It shows that the capacity varies along the hydrated radii of the cation.

The ESCA analysis gives the % composition of this composite material as. Zr(7.10), O(11.25), C(1.40), N(0.25), W(44.0), P(19.2), H(16.8). It reveals the presence of polyaniline in the material investigated

Table-7

**Composition of Polyaniline Zirconium (IV) tungstophosphate
(PZWP){ESCA}**

Elements	Zr	O	C	N	W	P	H
%	7.1	11.25	1.4	.25	44.0	19.2	16.8

Table 8 shows the details of I.R. spectrum of Polyaniline-Zirconium (IV) tungstophosphate. Beside other quite interesting is the evidence of absorption peaks due to bending and rocking of N-H bonds and substituent sensitive vibration in benzene ring. The I.R. studies supports the presence the aniline in composite ion exchange.

The thermogravimetric analysis data are shown in the **table 9**. Which reflects that is only 2.5 % gel water adhered to the material. It is a very salient feature of this composite ion exchanger because there shall be no appreciable change in its ion exchange capacity upto 100°C. The loss upto 200°C is due to the condensation of hydroxyl groups and the loss at higher temperatures is due to the conversion of phosphate in their corresponding oxides and the oxidation of polyaniline.

The ion exchange capacity of PZWP for different cations is shown in table 10. Which clearly reflects the variation of ion exchange capacity with hydrated ionic radii. As the hydrated ionic radii of cation decreases its ion exchange capacity decreases. It shows that the exchange is taking place in the unhydrated form of the cation.

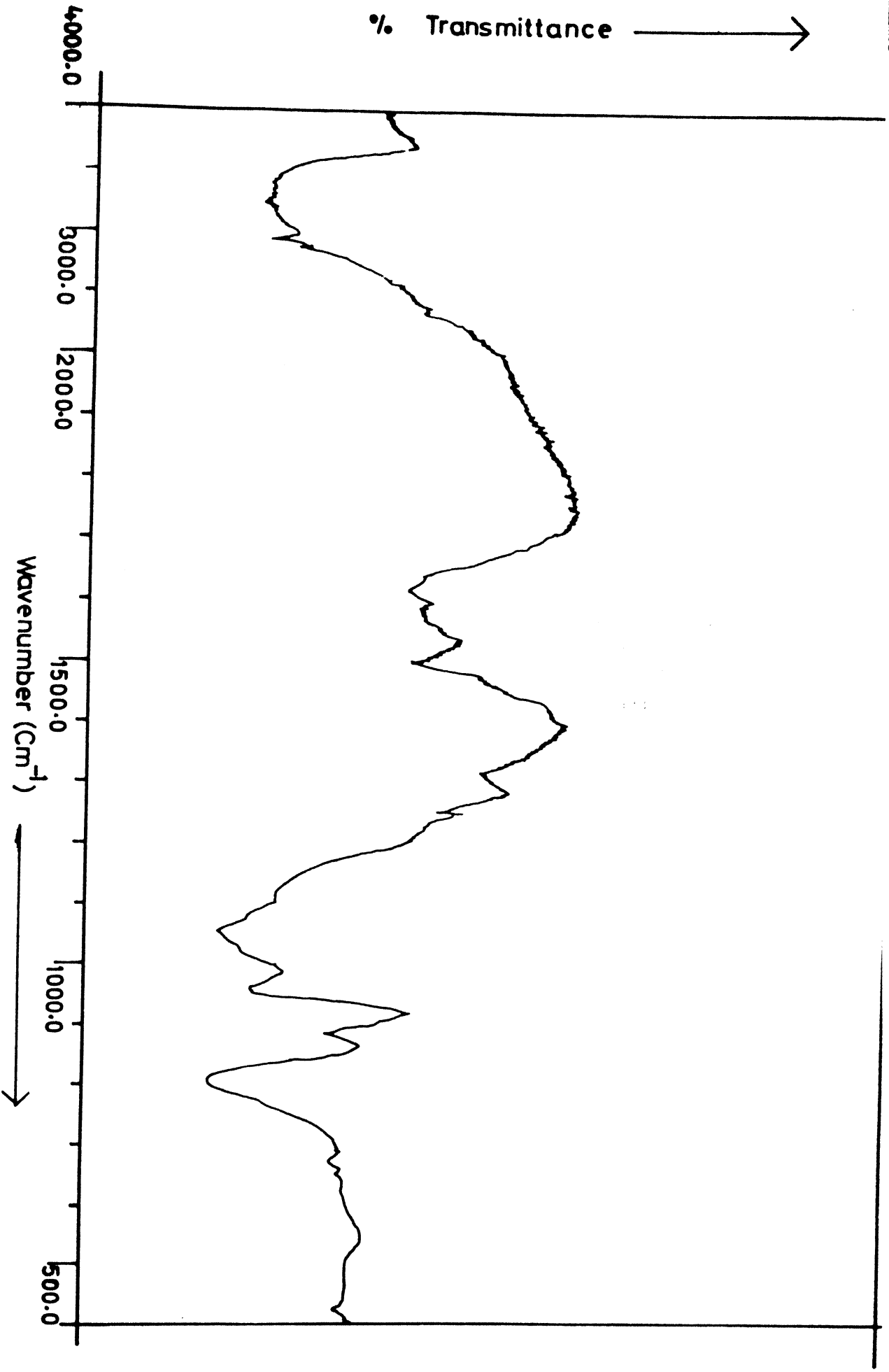


Fig. 5-1 I. R. Spectra of Polyaniline Zirconium (IV) Tungstophosphate

Table-8**Details of IR spectra of Polyaniline Zirconium (IV) tungstophosphate (PZWP)**

Wave No (Cm ⁻¹)	Appearance	Designation
3600-3100	Broad	Hydroxo stretching vibrations [ν_1 (OH)]
3000-2900	Medium	Deformation vibrations of coordinated water [δ_1 (H ₂ O) cord.]
1630-1600	Medium	Deformation vibration of interstitial water [δ_2 (H ₂ O) inter.]
1500	Sharp	Bending of N-H and Rocking of N-H bonds.
1250 1320-1300	Sharp Medium	Superposition of metal oxygen, stretching vibrations [ν_2 (W-O, and P-O)] and aqua wagging twisting and rocking modes.
1080-1020 880 960	Medium Sharp Medium	Superposition of metal substituent sensitive vibrations in benzene ring. [ν_2 (W-O, Zr-O and P-O)] and aqua wagging twisting and rocking modes.

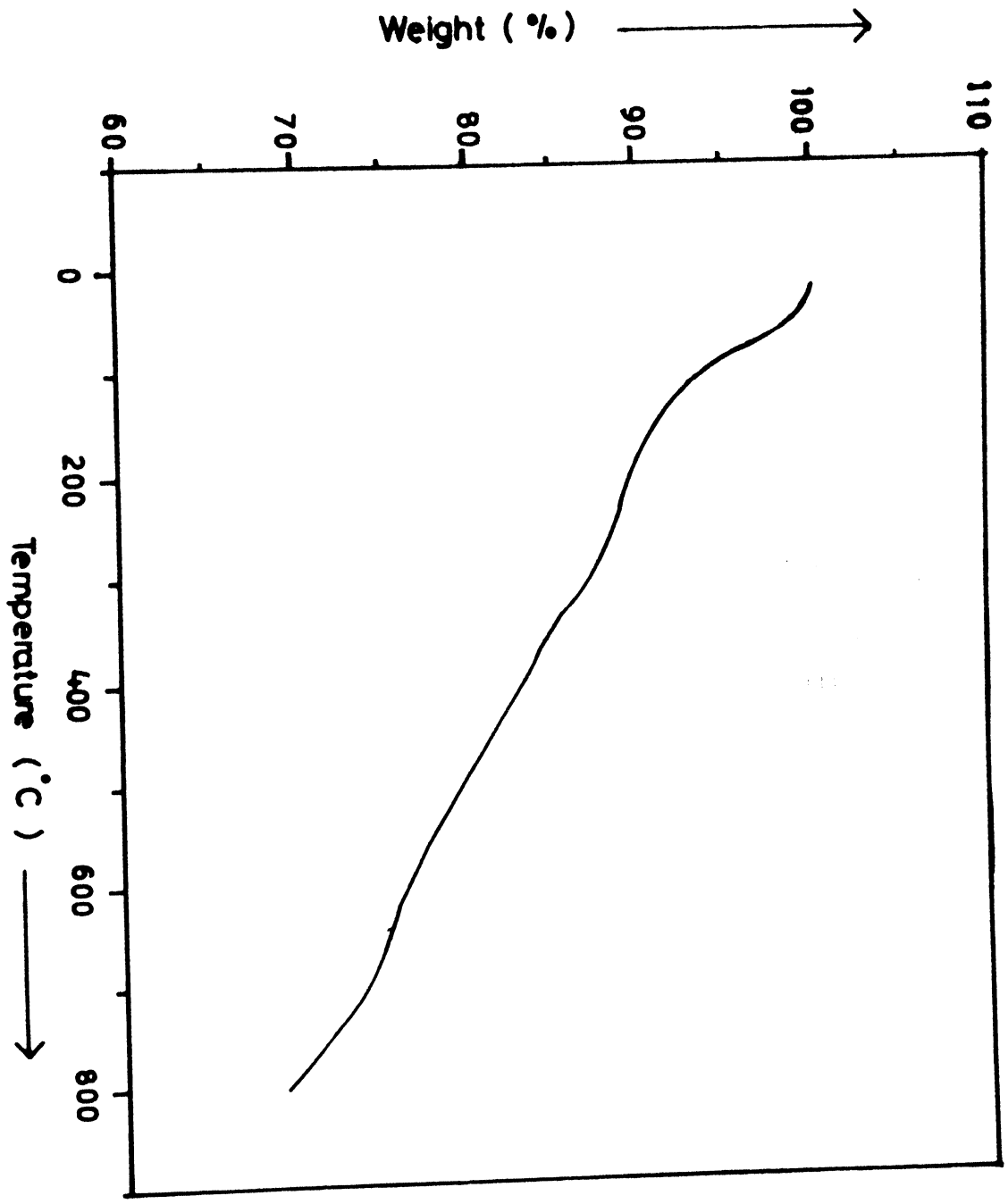


Fig. 2 TGA Curve of polyaniline Zirconium (IV) Tungstophosphate

Table-9

Details of TGA curve analysis of Polyaniline Zirconium (IV) tungstophosphate (PZWP)

Temperature	% Weight loss
40°C	0
100°C	2.5
200°C	9.0
300°C	12.5
400°C	16.0
500°C	20.0
600°C	23.0
700°C	26.0
800°C	31.0

X-ray diffraction pattern shows the poor crystalline nature of the material under study.

The material is quite chemically stable in DIW, 1M HCl, 3M HNO₃, 1M NH₄NO₃, Acetone, Chloroform, DMF and DMSO. Therefore its distribution

Handwritten note: *Handwritten*

Table-10

Ion exchange capacity of Polyaniline Zirconium (IV) tungstophosphate for different cations

Cations	pH	Hydrated ionic radius (Å ⁰)	Ion exchange capacity (meq /g) dry exchanger
Na ⁺	6.7	7.9	1.46
K ⁺	6.8	5.3	0.82
Mg ²⁺	6.5	10.8	2.00
Ca ²⁺	6.5	9.6	1.38
Sr ²⁺	6.5	9.4	0.86

Studies can be carried out safely without the interference of dissolved species from the composite.

Table-11

Distribution coefficients (K_d Values) of metal ions on Polyaniline Zirconium (IV) Tungstophosphate (PZWP) [at $25 \pm 2^\circ\text{C}$]

Metal ions	DMW	pH-3 ($1 \times 10^{-3}\text{M}$) HNO_3	DMF	n-butanol
Mg^{2+}	32.6	37.3	86.9	322
Ca^{2+}	3.0	29.3	135	605
Sr^{2+}	4.0	1.0	30.3	119.1
Ba^{2+}	3.8	10.1	67.7	616.7
Th^{4+}	1966.7	1140	313.3	113.8
La^{3+}	163.3	140	295	1.2
U^{4+}	0.6	264	122	1147

Table-12

Separation factors of metal ions on Polyaniline Zirconium(IV) tungstophosphate (PZWP)

Separation factors	DIW	pH-3 ($1 \times 10^{-3}M$) HNO_3	DMF	n-butanol
$\alpha_{Mg^{2+}}^{Th^{4+}}$	60.3	52.7	22.6	6.1
$\alpha_{Ca^{2+}}^{Th^{4+}}$	655.5	67.12	14.56	3.2
$\alpha_{Sr^{2+}}^{Th^{4+}}$	491.6	1966.7	64.9	16.5
$\alpha_{Ba^{2+}}^{Th^{4+}}$	617.5	194.7	29.05	3.1
$\alpha_{La^{3+}}^{Th^{4+}}$	12.04	14.04	6.6	1638.8
$\alpha_{U^{4+}}^{Th^{4+}}$	3277.8	7.4	16.1	17.1
$\alpha_{Mg^{2+}}^{La^{3+}}$	5.0	4.37	1.87	0.5
$\alpha_{Ca^{2+}}^{La^{3+}}$	54.4	5.57	1.7	0.2
$\alpha_{Sr^{2+}}^{La^{3+}}$	40.8	163.3	5.38	1.3
$\alpha_{Ba^{2+}}^{La^{3+}}$	42.9	16.1	2.4	0.2
$\alpha_{U^{4+}}^{La^{3+}}$	272.1	0.6	1.3	1.4

Table 11 shows the K_d values of 7 cations in DIW, 1×10^{-3} M HNO_3 , DMF, n-butanol system. The exchanger shows its higher uptake towards Th^{4+} , La^{3+} and U^{4+} ions comparatively alkaline earth metal ions. The preference towards higher charge cations indicate the exchanger takes place in unhydrated form.

On account of K_d values a number of separation factors pertaining to the separation of La^{3+} and Th^{4+} have been evaluated and shown in **table 12**.

At a glance of separation factors, the utility of this composite ion exchange material may be explored towards the separation of La^{3+} or Th^{4+} from others. It may be employed in the preparation of La^{3+} or Th^{4+} selective electrodes membrane or chemical sensors etc.

• Summary and Conclusion:

Polyaniline-Zirconium (IV) tungstophosphate a cation exchange material has been synthesized with the polymerization of aniline in the presence of APS. The dark colored product has been assessed for its ion exchange capacity.

It has been characterised using IR, TGA, DTA, DSC, ESCA(XPS) and SEM techniques. The composite shows the composition % (w/w). [Zr = 7.10, O=11.25, C=1.40, N=0.25, W=44.0, P=19.2, H=16.8].

It shows different ion exchanger behavior of the Zirconium (IV) tungstophosphate. It shows its affinity towards, La^{3+} , Th^{4+} , U^{4+} .

Which may prove its utility either in the separation of these metals from others i.e. Th^{4+} from Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , La^{3+} , U^{4+} , and La^{3+} from Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , U^{4+} or it may act as an electroactive constituent in the preparation of ion selective electrodes, ion exchange membranes, ion exchange fibers and in chemical sensors.

Chapter- 6

REFERENCES

1. J.S.Miller, *Adv.Matter*, 5, 587 (1993).
2. E.M. Genies, M.Lapkowski and C.Tsintavis, *N.J.Chem.* 12, 181 (1988).
3. E.M.Genies, A.Boyle, M Lapkowski and C.Tsintavis, *Synth. Met.* 36, 139 (1990).
4. R.De Surville, M.Jozefowicz, L.T.Yu, J.Perichon and R.Buvet, *Electrochim. Acta.* 13, 1451 (1993).
5. A.G.MacDiamid, J-C.Chiang, A.F.Richter, N.L.Sobasiri and A.J.Epstern, *Conducting Polymers* 105, Reidel (1987).
6. A.G.MacDiamid, J-C.Chiang, *Synth. Met.* 13, 193 (1986).
7. A.Andreatta, Y.Cao, J.-C.Chiang, A.J. Geager and P.Smith, *Synth. Met.* 26, 283 (1988).
8. M.Abe, A.Ohtani, Y.Umemoto, S.Akizuki, M.Ezoe, J.Higuchi, K.Nakamoto, A.Okuno and Y.Noda, *J. Chem. Commn.* 1736 (1989).
9. A.P.Monkman and P.Adams, *Synth. Met.* 40, 87 (1991).
10. A.Yasuda and Shimidzu, *Polym. J.* 25, 329 (1993).
11. M.Mehta, and I.Hashuda, *J. Appl. Polym. Sci.* 41, 1073 (1990)
12. O.Ando, H.Ono and O.Suzuki, *Mitsubshi Kasei R & D Rev.* 3, 81 (1988)

13. W.R.Salaneck, I.Lundstrom, T.Hjertberg, C.B.Duke, E.Conwell, A.Paton, A.G.MacDiamid, N.L.D.Somasiri, W.S.Huang, and A.F.Richter, *Synth. Met.* 18, 291 (1987).
14. M.G.Kanatzidis, C.-G.Wu, H.O.Marcy, D.C.DeGroot, C.R.Kannewurf, A.Kostikas, and V.papaefthymiou, *Adv. Mater.* 2, 364 (1990)
15. A.Pron, F.Genoud, C.Menardo and M.Nechtscheiu, *Synth. Met.* 24, 193 (1988).
16. J.P.Travers, J.Chroboczek, F.Devreux, F.Genoud, M.Nechtschein, A.Syed, E.M. and C.Tsintavis, *Mol. Cryst.* 121, 195 (1991).
17. L.Wang, X.Jing and F.Wang, *Synth. Met.* 41, 745 (1991).
18. M.Leclerc, J.Guay and L.H.Dao, *Macromolecules* 22, 649 (1991).
19. L.H.Dao, J.Y.Bergeron, J.W.Chevalien, M.T.Nguyen and R.Paynter, *Synth. Met.* 41, 655 (1991).
20. L.H.Dao, M.T.Nguyen and R.Paynter, *Synth. Met.* 41, 649 (1991).
21. N.B.Inoue, B.F.Velazquez and M.Inoue, *Synth. Met.* 24, 223 (1988).
22. M.Lapkowski, G.Bidan and Fournier, *Synth. Met.* 41, 411 (1991).
23. M.A.Rodrigues and M.A.DePaoli, *Synth. Met.* 41, 2957 (1991).
24. M. Angelpoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A.G.MacDiamid, M.Akhtar, Z.Kiss and A.J.Epstein, *Mol. Cryst. Liq. Cryst.* 160, 151 (1988).
25. E.M.Genies and C.Tsintavis, *J. Electroanal. Chem.* 195, 109 (1985).
26. E.M.Genies and M.Lapkowski, *J. Electroanal. Chem.* 236, 189 (1987).

27. E.M.Genies, J.F.Pennean, M.Lapkowski and A.Boyle. *J. Electroanal. Chem.* 269, 63 (1989).
28. K.Sasaki, M.Kaya, J.Yano, A.Kitani and A.Kunai, *J. Electroanal. Chem.* 215, 401 (1986).
29. K.Sasaki, J.Yano, A.Kitani and A.Kunai, *J. Electroanal. Chem.* 221, 69 (1987).
30. N.Gospodinova, P.Mokreva and L.Terlemezyan, *Polymer* 34, 2438 (1993).
31. H.Yan, M.Ishiwatari and N.Tohima, *Polym. Prepr. Jpn.* 42, 2848 (1993).
32. H.Yan, M.Ishiwatari and N.Tohima, *Bull. Chem. Soc. Jpn.* 67 1947 (1994).
33. D.-K.Moon, K.Osakada, T.Maruyama and T.Yamamoto, *Makromol. Chem.* 193, 1723 (1992).
34. C.-F.Liu, D.-K.Moon, T.Maruyama and T.Yamamoto, *Polym. J.* 25, 775 (1993).
35. D.-K.Moon, K.Osakada, T.Maruyama and T.Yamamoto, *Chem. Lett.* 1633 (1991).
36. D.-K.Moon, M.Ezuka, K.Osakada, T.Maruyama and T.Yamamoto, *Makromolekules* 26, 364 (1993).
37. W.S. Huang, B.D.Humphery and A.G.MacDiamid, *J.Chem.Soc. Faraday Trans.*, 82, 2385 (1986).
38. A. Guisepp i- Elie, S. ARE. Pradhan, A. M. Wilson, D. L.Allara, P. Zhang, R.W.Collins and Y.-T.Kim, *Chem. Mater.* 5, 1474 (1993).

39. J. Guay and L.H. Dao, *J. Electroanal. Chem.* 135, 173 (1982).
40. J. Guay, R. Payter and L.H. Dao, *Macromolecules* 23, 3598 (1990).
41. G.H. Nancollas and V. Pekarek, *J. Inorg. Nucl. Chem.*, 27, 1409 (1965).
42. L.G. Nagy, G. Torok, N. Vajeda and I. Gerlei, *J. Radioanal. Chem.*, 58, 215 (1980).
43. J. Albertsson, *J. Acta Chem. Scand.*, 20, 1689 (1966).
44. G. Alberti and E. Torracca, *J. Inorg. Nucl. Chem.*, 30, 317 (1968).
45. Javed Iqbal, Latif M. Mirza and N. Sareecha, *J. Chem. Soc. Pak.*, 16, 20 (1994).
46. Javed Iqbal, Latif M. Mirza and F. Fatima, *Sci. Int.*, 5, 29 (1993).
47. M. Zomain, T. Shaheen and A. Dyer, *J. Radioanal. Nucl. Chem.*, 182, 323 (1994).
48. M. Zomain, T. Shaheen and A. Dyer, *J. Radioanal. Nucl. Chem.*, 182, 335 (1994).
49. M. Zomain, T. Shaheen and A. Dyer, *J. Radioanal. Nucl. Chem.*, 182, 345 (1994).
50. A. Clearfield and J.A. Stynes, *J. Inorg. Nucl. Chem.*, 26, 117 (1964).
51. S. Oosumi, K. Sugivra and Kato, *Jpn. Kokai Tokkyo Koho.*, 48, 713 (1994) and 92, 220 (1992).
52. A. Clearfield, L. Kulberg and A. Oskarsson, *J. Phys. Chem.*, 12, 78 (1974).
53. R. Kataoka, Y. Watanabe and Y. Yamabe, *Jpn. Kokai Tokkyo Koho.*, 8003, 337 (1970).

54. I.S.C. Churms, S. African, Ind. Chemists, 19, 26, 48, 87, 148 (1965).
55. J. Prospert, Comn. Energie At. (France, Repptt.) CEA-R, 2835 (1966).
56. V.F. Tikavyi and L.I. Tsukovova, Kzv. Acad. Nauk. USSR, Neorgan, Matter., I, 108 (1965).
57. S. Ahrland, J. Albertsson, B. Nihlgard and L. Nilsson, Acta. Chem. Scand., 18, 707 (1964).
58. A.P.Gupta and Pradeep K. Varsney, Reactive Polymers., 31, 111 (1996).
59. A.P.Gupta and Pradeep K. Varsney, Reactive Polymers.,[in press] Netherland.
60. A.P.Gupta and Pradeep K. Varsney, Synth. React. Inorg. Metal-org. Chemistry (Commnicated) USA.
61. A.P.Gupta and Pradeep K. Varsney, J. of Transitional Metal Chemistry (Communicated) UK.
62. J.P.Rawat, Masood Alam, Hasam M. Abdul Aziz, and Balbir Singh; Bull. Chem. Soc.Jpn., 60, 2619-2626 (1987).
63. J.P.Rawat, and Chitra; Bull. Chem. Soc.Jpn., 61, 2668, (1988).
64. C.Y.Ortiz-Avila and A. Clearfield Inorganic Chemistry; 24, 1773, (1985).
65. M.J.Hudson, E. Castellon, P. Sylvester, Hydro metallurgy 24, 77, (1990).
66. F.Seppestra. V.Stefula; J. Radional Nuccl. Chem., 140,15, (1990).
67. L.Pauling J. Am. Chem. Soc 49, 765 (1927).
68. L.Pauling Proc. Nat. Acad. Sci. U.S. 16, 139 (1930).
69. W.L.Bragg, Atomic Structure of Minerals, Cornell University Press, (1939).

70. W.P.Kelley and H.Jenny, Soil Sci. 41, 367 (1936).
71. W.P.Kelley, H.Jenny and S.M.Brown, Soil Sci. 41, 259 (1936).
72. W.P.Kelley Cation Exchange in Soils, Reinhold Publishing Corp., (1948).
73. M.E.Harward, and N.T.Coleman, proc. Soil Sci. Am., 17, 339, (1953)
74. R.P.Mitra J. Indian Chem. Soc. 23, 386 (1947).
75. P.H.Plesch and R.H.S.Robertson Nature 161, 1020 (1948).
76. R.Rost Vestnik Stat. Geol. Ustavu Ceskoslov. Rep. 22, 334 (1947).
77. D.H.Sieling Soil Sci. Soc. Amer., Proc. 11, 161 (1948).
78. M.Vendt Roy. Hung. Palatine-Joseph Univ. Tech. Econ. Sci. Pub. Dept.
Ming and Met. 15, 344 (1943).
79. Barrer, R.M., diffusion in and through solids, Cambridge Univ. Press,
1941
80. R.M.Barrer, J. Chem. Soc., 1948, 127
81. R.M.Barrer, Discussions Farady Soc., 1949, 7, 1935.
82. R.M.Barrer, Quarterly revs. (London), 3, 135.
83. R.M.Barrer, and D.B. Ebitison, Trans. Farady Soc., 40, 206, 1944.
84. R.M.Barrer, and D.W. Riley, J. Chem. Soc., 133, 1948.
85. P.H.Emmett, and T.W. Dewitt, J. Am. Chem. Soc., 65, 1253, (1943).
86. P.P.Stout Soil Sci. Soc. Am. Proc. 4, 177 (1939).
87. S.Mattson J. Agr. Research, 33, 553 (1926).
88. S.Mattson Soil Sci., 28, 179 (1929).
89. S.Mattson Soil Sci., 30, 459 (1930).
90. S.Mattson Soil Sci., 31, 57 (1931).

91. S.Mattson Soil Sci., 33, 41 (1932).
92. S.Mattson Ann. Agr. Coll. Sweden., 4, 1 (1937).
93. S.Mattson Ann. Agr. Coll. Sweden., 5, 261 (1938).
94. S.Mattson Soil Sci., 49, 109 (1940).
95. S.Mattson Ann. Agr. Coll. Sweden., 10, 56 (1942).
96. S.Mattson Jgl. Lantbruks-Hogskol. Ann., 15, 308 (1948).
97. S.Mattson and Y.Gustafsson Ann. Agr. Coll. Sweden., 2, 1 (1935).
98. S.Mattson and E.Koutler-Anderson Ann. Agr. Coll. Sweden., 11, 104
(1943).
99. S.Mattson and K.G.Larsson Soil Sci., 61, 313 (1946).
100. S.Mattson and L.Wiklander Ann. Agr. Coll. Sweden., 4, 169 (1937).
101. R.Kunin and R.J.Myers, Discussions Faraday Soc. 7, 114 (1949).
102. R.Griessbach, Melliand Textil., 20, 577, (1939).
103. R.Gruessbach, Uber die Herstellung and Anwendung neuer
Austauschadsorbienten, insbesondere auf Harzbasis, Berlin, Verlag
Chemie, 1939; Angew. Chem., 52, 215, (1939).
104. L.Wiklander Ann. Royal Agr. Coll. Sweden 14, 1 (1946).
105. Helmholtz, H.Von; Ann. Phys. Chem. 7, 337 (1879).
106. O.Stern Z. Elektrochem 30, 508 (1924).
107. G.Wiegner J. Soc. Chem. Ind. 50, 65 (1931).
108. G.Wiegner J. Soc. Chem. Ind. 50, 103T (1931).
109. G.Wiegner J. Soc. Chem. Ind. 50, 105 (1931).
110. H.Jenny, J. Phys. Chem. 36, 2217 (1932).

126. E. Born and G. Paul ; *Atomkernenergie* 31, 57 (1978).
127. R.C. Wendland and W.M. Riggs, *Surface Analysis by XPS*, Presented at the Eastern Analytical Symposium, New York (1971).
128. R.S. Swingle II *Anal. Chem.* 47, 21 (1975).
129. C.D. Waginer *Anal. Chem.* 44, 1050 (1972).
130. V.I. Nefedov et al. *J. Electron Spectrosc.* 2, 383 (1973).
131. N. Berthou and C.K. Jorgensen *Anal. Chem.* 47, 482 (1975).
132. F.M. Chapmann and L.L. Lohr *J. Am. Chem. Soc.* 96, 4731 (1974).
133. J.H. Schofield, Lawrence Livermore Laboratory Rep. VCRL-51326 (1973).