CHAPTER 1

INTRODUCTION
1.1 TETRAVALENT METAL ACID SALTS

"Tetravalent Metal Acid (TMA) Salts" have been researched since the last 50 years, and have emerged as promising advanced materials owing to their good thermal stability, chemical resistivity and resistance towards ionizing radiations, and found important applications in the area of ion exchange, catalysis and solid state proton conduction. An extensive literature on TMA salts, exists today, which have been reviewed and detailed in four books.


Systematic studies on their synthesis, structure elucidation and applications in the area of separation science, catalysis and solid electrolytes have been carried out by various groups – Dr. A. Clearfield (USA), Dr. G. Alberti, Dr. U. Costantino (Italy), Dr. D. Whittaker (UK), Dr. W. H. J. Hogarth (Australia), late Dr. M. Qureshi and Dr. K. G. Varshney (Aligarh Muslim University, India) and Dr. U. V. Chudasama (The M. S. University of Baroda, India).

1.2 SALIENT FEATURES OF TETRAVALENT METAL ACID (TMA) SALTS

- TMA salts are cation exchangers, possessing the general formula M(IV) (Hxo4)2.nH2O, where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X = P, Mo, As, Sb, W etc.
• The materials possess structural hydroxyl groups, the H⁺ of the -OH being the exchangeable sites, due to which the material possesses cation exchange properties.

• TMA salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.

• The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.

• The materials are generally hard and range in physical appearance from totally opaque to transparent.

• These materials have shown a great promise in preparative reproducibility, ion exchange behaviour and stability towards thermal, chemical and ionizing radiations.

TMA salts with varying water content, composition and crystallinity [1-4] can be obtained, depending on varying parameters such as mole ratio of reactants M : X (M = tetravalent metal, X = polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), pH and rate of mixing. Variation in any of these parameters yields materials with different characteristics. The preparation procedure affects the structural hydroxyl groups, which is reflected in their performance in various applications like ion exchange, catalysis and proton conduction.

TMA salts possess structural hydroxyl groups, the H⁺ of the -OH being the exchangeable sites, due to which the material possesses cation exchange properties. The acid sites (surface protons/acidity) present in TMA salts indicate good potential for application as solid acid catalysts. Further, the supports used in heterogenised homogeneous catalysis are either organic or inorganic supports. Both kind of supports (organic/inorganic) have their own advantages and disadvantages, the main one being that though the method of anchoring (ion exchange) is both easy and leads to a stable interaction in organic (polymers) supports as compared to the inorganic (oxides) supports, their major disadvantage is poor heat transfer ability leading to degradation at
comparatively low temperatures. It would be ideal to search for a new material which combines the advantages of both types of supports. The answer to this is inorganic ion exchangers of the class of TMA salts, that can be used to advantage. TMA salts have thus, also been used as supports in heterogenised homogeneous catalysts. The protons present in the structural hydroxyl groups indicates good potential for TMA salts to exhibit solid state proton conduction. From our laboratory, TMA salts have been widely explored as cation exchangers [5-16], as solid acid catalysts [17-29], as supports in heterogenised homogenous catalysis [30-32], and solid state proton conductors [33-38].

1.3 STRUCTURAL ASPECTS OF TMA SALTS

Almost all the possible combinations of tetravalent metals (such as Zr, Ti, Ce, Sn, Th etc) with polybasic acids (containing P, W, Mo, As, Sb etc) have been examined. Earlier work was carried out with amorphous materials. Much of the earlier work was focused on zirconium phosphate (ZP) [39]. Extensive information on the structure of ZP has been reviewed by C B Amphlett [40]. De Boers reported the structure of ZP as \( \text{Zr(HP}_4\text{O}_4)_2 \), but other workers suggested it to be \( \text{[ZrO(H}_2\text{PO}_4)_2] \). Bluementhal (Figure 1.1), Paterson (Figure 1.2), Baestle and Pelsmaekers (Figure 1.3), Nancollas and Pekarek (Figure 1.4) and (Figure 1.5) proposed the following structural formula for ZP [40].

![Figure 1.1](image1)

![Figure 1.2](image2)
According to these structures, the $H^+$ of the structural $-\text{OH}$ groups are the exchangeable protons. Much of the pioneering work in this area was done by the research group at the Oak Ridge National Laboratory led by K A Kraus [41] and in the United Kingdom by C B Amphlett [40].

The first crystalline $a$-ZP was prepared by Clearfield and Stynes [42]. Structure elucidation was first carried out in 1969 [43]. ZP has a layered structure. Zirconium atoms lie slightly above and below the $ab$ plane as shown in (Figure 1.6) and are bridged by the phosphate groups. These are situated alternatively above and below the metal atom plane. Three oxygen atoms of each phosphate, are bonded to three adjacent metal atoms, forming a distorted equilateral triangle [44]. Each zirconium atom is thus octaheddally coordinated by oxygens. An idealized picture of a portion of the layer is given in Figure 1.7.
Figure 1.6 ab layer of α-ZP [45]

Figure 1.7 Idealized portion of ZP layer [43]

Figure 1.8 Schematic diagram of the arrangement of two adjacent macroanions in α-ZP [45].
Zirconium phosphate, the most extensively studied TMA salt of the crystalline type can be prepared as fibrous, layered or as three-dimensional structures [42]. The layered acid salts, in turn, may be obtained in at least two different modifications, usually known as α-ZP and γ-ZP having the formula Zr(HPO$_4$)$_2$. H$_2$O and Zr(PO$_4$)(H$_2$PO$_4$).2H$_2$O respectively [46]. The structure of the α-ZP (Figure 1.8) arises from the ABAB stacking of layers, each of which is formed by zirconium atoms lying in a nearly ideal plane and sandwiched between –O$_3$POH groups, with the exchangeable proton pointing into the interlayer region as P–OH [44]. These protons are responsible for ion exchange [1]. The layers of the γ-ZP are made up of zirconium atoms laying in two parallel ideal planes and bridged by –PO$_4$ groups, while –O$_2$P(OH)$_2$ groups are directed towards the interlayer region [47, 48]. The layers in the γ-ZP are thus thicker (0.92 nm) than those in α-ZP (0.64 nm), and the –OH groups bound to the same phosphorous atoms have different acidities.

After α-ZP, α-titanium phosphate (α-TP) is the most investigated material. It has been obtained independently in various laboratories and structural aspects investigated [49]. Since the length of the Ti–O bond is shorter than that of the Zr–O bond, the distance between fixed charges in the planar macroanion [Ti(PO$_4$)$_2$]$_n^{2n-}$ is shorter than in [Zr(PO$_4$)$_2$]$_n^{2n-}$. The unit cell dimensions are $a = 8.631 \pm 0.001$ Å, $b = 5.002 \pm 0.001$ Å, $c = 16.176 \pm 0.002$ Å, and $β = 110.20 \pm 0.01^\circ$.

Owing to its smaller unit cell, the dimensions of the windows connecting the cavities in α-TP are correspondingly smaller and the density of the fixed charges higher, compared to α-ZP. Thus, the steric hindrance to the diffusion of large cations is expected to be higher in α-TP than in α-ZP and the ion exchange rate is slower.

Owing to its high density of fixed charges, α-TP tends to behave as a rigid layered exchanger and therefore it possesses more marked ion sieve properties than does α-ZP. The ion sieve properties of α-TP have been used [50] to effect separations of Cs$^+$ and K$^+$ ions from Na$^+$. Ion exchange
equilibrium between α-TP and NaCl-KCl aqueous solution has been investigated by Kobayashi [51] who also considered the possibility of separating of Na⁺ and K⁺ ions.

The insoluble acid salts of tetravalent metals can be obtained with different layered structures, usually known as γ-structure. After γ-Zr(HP⁰₄)₂.2H₂O, first obtained by Clearfield [52], another compound with formula Ti(HP⁰₄)₂.2H₂O and showing marked analogies with γ-ZP, was prepared by Alluli et al [53].

Although the γ structure is as yet unknown, some indirect information has been obtained [54]. Both γ-ZP and γ-TP are able to take up stoichiometric amount of several polar organic molecules and the first d-values of these γ materials increase with increase in the length of these molecules. Furthermore, there is a discontinuous change of the first d-value during the dehydration of γ-Zr(HP⁰₄)₂.2H₂O (from 12.2 to 9.4 Å) and of γ-Ti(HP⁰₄)₂.2H₂O (from 11.6 to 9.2 Å). These properties provide strong evidence that the γ structure, like that of α materials, is built up of polymeric macro anion [M(IV)(XO₄)₂]_{2n}⁻, with negative charges neutralized by protons, while the hydration water, or other polar molecules can be accommodated between adjacent layers. It can probably be assumed that γ-Ti(PO₄)(H₂PO₄).2H₂O is isostructual to γ-Zr(PO₄)(H₂PO₄).2H₂O. Extensive information on the chemistry of group IV metal phosphates with α and γ type structures has been compiled in reviews and books [55, 56].

Polyhedral layered phosphates in the α-b plane are presented in Figure 1.9.
1.4 RECENT ADVANCES AND CURRENT TRENDS

There is currently high interest in engineering mixed materials leading to the formation of new solid-state/lattice structures resulting from cooperative interactions between the two interacting components, where there is a promise of developing new materials with properties not seen in the pure compound giving rise to composite as well as wide range of interesting properties. In this context, materials of the class of TMA salts i.e. compounds containing two different cations and an anion, are interesting since they could exhibit improved properties in comparison to their single salt counterparts. They are referred to as tetravalent bimetallic acid (TBMA) salts.

Zirconium phosphate and titanium phosphate of the class of TMA salts are now well-known inorganic ion-exchange materials. It was thought of interest, to synthesize a TBMA salt zirconium titanium phosphate and assess enhancement in properties by exploring their application in the area of ion exchange, catalysis and proton conduction.

In the area of mixed materials, inorgano-organic materials or hybrid materials, have been attracting attention as a significant class of materials. Hybrid inorgano-organic compounds are novel multifunctional materials that...
offer a wide range of interesting properties. This new field of materials science is expanding rapidly. Several international meetings are now devoted to this promising area of research and many review papers have been published [57-62].

Organic derivatives of inorganic ion exchangers of the class of TMA salts are of particular interest. A major advantage of these inorgano-organic hybrid materials is the rigid inorganic backbone and the flexibility of the organic groupings. This flexibility creates opportunity to design compounds with specific properties such as, when the organic functionalities possess ionogenic groups (−OH, −COOH, −SO$_3$H etc.), the surface area and hence surface acidity can be modified.

As already indicated earlier, zirconium phosphate and titanium phosphate of the class of TMA salts have been widely used as cation exchangers and have shown a number of advantages as ideal host lattices [63, 64]. In the tetrahedral moiety of phosphoric acid, PO(OH)$_3$, if H or OH is replaced by R (where R = alkyl or aryl possessing ionogenic groups −OH, −COOH, −SO$_3$H etc.), phosphonic acids are obtained, which when treated with tetravalent metals such as Zr$^{4+}$, Ti$^{4+}$, Sn$^{4+}$, Th$^{4+}$, Ce$^{4+}$ etc. gives rise to metal phosphonates [65, 66]. Metal phosphonates are obtained at low temperatures, often from aqueous. Their preparation is an example of soft chemistry route to new materials. They are very insoluble compounds and their structure and reactivity, can be modified and tailored for specific purposes [67, 68]. Depending on the complexity of the phosphonic acid used, the resulting M(IV) phosphonate, gives rise to two or three dimensional hybrid polymeric structures.

New phases of TMA salts are thus being continuously synthesized with an intention to prepare materials with good ion exchange capacity, having preparative reproducibility and stability both thermal and chemical. Though the potential use of metal phosphonates as ion exchangers has been proposed there
are no reports of their applications as ion exchangers in separation technology, in catalysis and solid state proton conductors.

Sol-gel processing is one of the promising routes to synthesis of inorgano organic hybrids using a “Chimie Douce”, low temperature approach, often from aqueous medium, involving hydrolysis and polycondensation. Using sol-gel route, it is possible to introduce a large variety of organic moieties into an inorganic matrix. The sol-gel route also includes hydrothermal/solvothermal reactions, in which various parameters such as temperature, pH, metal salt to reactant ratio, mode of addition and ageing etc. can lead to different structure, by changing any one of the parameters or all of them. A combination of property of the metal or phosphonate anions (or combination of the two) can be exploited as a coherent strategy towards synthesis of new materials.

It was thought of interest to study mixed metal hybrids of the class of TBMA salts, zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP) where HEDP is hydroxy ethylidene diphosphonic acid. HEDP, possessing five structural hydroxyl protons (H⁺ of the –OH being the exchangeable sites) as against three structural hydroxyl protons in the phosphate moiety, enhanced properties in terms of ion exchange characteristics as well as surface acidity are expected.

1.5 APPLICATIONS OF TBMA SALTS

TMA salts have been widely explored as an ion exchangers, solid acid catalysts and solid state proton conductors. In the present endeavour, it was thought of interest to explore the utility of mixed metal phosphates and phosphonates of the class of TBMA salts as ion exchangers, solid acid catalysts and solid state proton conductors.

TBMA salts as Ion exchangers

Ion exchange is an excellent technique for removal of toxic metals from effluents. Ion exchange materials have played a vital role in waste water treatment and found extensive application in analytical/industrial chemistry.
Various ion exchange materials are being studied, to improve efficiency and economy in its application to metal separations and removal/recovery. TBMA salts possess structural hydroxyl groups (the H⁺ of the –OH being the exchangeable sites), due to which they behave as cation exchangers. Further, TBMA salts may exhibit improved ion exchange properties and selectivity for particular metal ions compared to their single salt counterparts. The potential applications of TBMA salts can be explored as ion exchangers in separation science.

**TBMA salts as Solid Acid Catalysts**

Catalysts and catalyst based technologies have undergone tremendous changes and the present trends in catalysis research and industrial catalysis is the materials approach and catalysts that are environment friendly. In the ongoing search for catalysts that are environment friendly, solid acid catalysts are making a huge impact. Due to presence of structural hydroxyl protons in TBMA salts, surface acidity is expected giving rise to solid acid characteristics. TBMA salts can therefore be explored as environment friendly solid acid catalysts.

**TBMA salts as Solid State Proton Conductors**

Discovering new proton conductors and studying the mechanism of their conduction is an area of current interest, the potential use of such compounds being in fuel cells. The protons present in the structural hydroxyl groups indicates good potential for TBMA salts to exhibit solid state proton conduction.

### 1.6 AIM AND SCOPE OF THE PRESENT WORK

The present study is focused towards synthesis and characterization of advanced inorganic material, zirconium titanium phosphate (ZTPA) and a novel hybrid material, zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP) of the class of tetravalent bimetallic acid (TBMA) salts, and
exploring the utility of these materials as ion exchangers, solid acid catalysts and solid state proton conductors.

**Chapter II** of the thesis deals with the synthesis and characterization of following materials,

**Advanced inorganic materials (amorphous phase)**
- Zirconium titanium phosphate (ZTPA)
- Zirconium phosphate (ZPA)
- Titanium phosphate (TPA)

**Advanced inorganic materials (crystalline phase)**
- Zirconium titanium phosphate (ZTPC)
- Zirconium phosphate (ZPC)
- Titanium phosphate (TPC)

**Novel hybrid materials (amorphous phase)**
- Zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP)
- Zirconium hydroxy ethylidene diphosphonate (ZrHEDP)
- Titanium hydroxy ethylidene diphosphonate (TiHEDP)

**Lithium exchanged phases of advanced inorganic materials (amorphous and crystalline phases)**
- Lithium exchanged ZTPA (LiZTPA)
- Lithium exchanged ZPA (LiZPA)
- Lithium exchanged TPA (LiTPA)
- Lithium exchanged ZTPC (LiZTPC)
- Lithium exchanged ZPC (LiZPC)
- Lithium exchanged TPC (LiTPC)

The advanced inorganic materials (both amorphous and crystalline) and novel hybrid materials have been synthesized by sol-gel route while lithium exchanged phases have been prepared by ion exchange technique. All the synthesized materials were characterized for elemental analysis (ICP-AES), thermal analysis (TGA), spectral analysis (FTIR), X-ray diffraction studies, SEM, pore size/pore volume distribution (mercury porosimeter), surface area
measurements (BET method) and surface acidity (NH3 TPD method). Chemical stability/resistivity of the materials in various media (acids, bases and organic solvents) have been assessed. Ion exchange capacity (IEC) of the synthesized materials have also been determined and the effect of calcination on IEC studied.

Chapter III of the thesis deals with the applicability of ZTPA and ZTHEDP as cation exchangers. The equilibrium exchange of Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ ions with H$^+$ ions contained in ZTPA and ZTHEDP have been studied varying temperature, at constant ionic strength. On the basis of the exchange isotherms, various thermodynamic parameters such as equilibrium constant ($K$), standard Gibbs energy change ($\Delta G^\circ$), entropy change ($\Delta S^\circ$) and enthalpy change ($\Delta H^\circ$) have been evaluated. Further, forward and reverse ion exchange kinetics of Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ ions with H$^+$ ions contained in ZTPA/ZTHEDP has been studied varying temperature, applying the Nernst-Planck equation. Kinetic parameters such as self-diffusion coefficient ($D_0$), energy of activation ($E_a$) and entropy of activation ($\Delta S^*$) have been evaluated under the conditions favouring a particle diffusion-controlled mechanism. Distribution coefficient ($K_d$), for various metal ions, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ (d-block), Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Bi$^{3+}$ (heavy) and La$^{3+}$, Ce$^{3+}$, Th$^{4+}$, UO$_2^{2+}$ (f-block) towards ZTPA and ZTHEDP has been determined in aqueous as well as various electrolyte media/concentrations. Breakthrough capacity (BTC) and elution behaviour of metal ions have also been studied. Based on the differential selectivity, breakthrough capacity (BTC) and elution behaviour of various metal ions towards ZTPA/ZTHEDP, a few binary and ternary metal ion separations have been carried out.

Chapter IV deals with the applicability of ZTPA and ZTHEDP as solid acid catalysts, in the synthesis of monoesters {ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzA)}, and diesters {diethyl malonate (DEM), dioctyl phthalate (DOP) and dibutyl phthalate (DBP)}. HEDP (in ZTHEDP) possessing greater number of structural hydroxyl
protons compared to phosphate, enhancement in surface acidity and hence catalytic activity is expected. Monoesters and diesters have also been synthesized using ZTPC, in order to see the effect of crystallinity on the catalytic performance. In all cases, the catalytic activity of TBMA salts have been compared with single salt counterparts.

Chapter V deals with application of ZTPA and ZTHEDP as solid state proton conductors considering the following aspects:

- Proton transport properties of ZTPA and ZTPC have been investigated and compared with amorphous and crystalline phases of single salt counter parts, (ZPA and TPA) and (ZPC and TPC).

- Small ionic radii, low weight and high reduction potential of lithium ion, supports its potential use in high energy density batteries. Thus, lithium ion conductors are especially attractive. Ion transport properties of lithium exchanged phases of amorphous and crystalline zirconium titanium phosphate (LiZTPA, LiZTPC) have been investigated and compared with lithium exchanged phases of single salt counter parts, both amorphous and crystalline, zirconium phosphate (LiZPA, LiZPC) and titanium phosphate (LiTPA, LiTPC).

- Hybrid material, ZTHEDP has been synthesized with an aim to modify the number of surface protons and hence proton conductivity. Proton transport properties of ZTHEDP has been investigated and compared with single salts counter parts, ZrHEDP and TiHEDP as well as ZTP.
REFERENCES


Chapter 1 - Introduction


