SUMMARY
“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 [1-4].

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).

TMA salts are cation exchangers, possessing the general formula M(IV) (H\text{XO}_4)_2.n\text{H}_2\text{O}, where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X = P, Mo, As, Sb, W etc. They possess structural hydroxyl groups, the H\text{+} of the –OH being the exchangeable sites, due to which they exhibit cation exchange properties. TMA salts can be prepared in both amorphous and crystalline forms that exhibit selectivity for certain metal ions, are granular in nature, obtainable in a range of mesh sizes, very suitable for column operations. They 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.

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 a 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. 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 that when the organic functionalities possess ionogenic groups (–OH, –COOH, –SO₃H etc.), the surface area and hence surface acidity can be modified.

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, –SO₃H etc.), phosphonic acids are obtained, which when treated with tetravalent metal ions such as Zr⁴⁺, Ti⁴⁺, Sn⁴⁺, Th⁴⁺, Ce⁴⁺ etc. gives rise to metal phosphonates [5, 6].

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.
TBMA salts possess structural hydroxyl groups (the H⁺ of the –OH being the exchangeable sites), due to which they behave as cation exchangers. The potential applications of these materials can be explored as ion exchangers in separation science. Further, due to presence of structural hydroxyl protons, surface acidity is expected giving rise to solid acid characteristics. TBMA salts can therefore be explored as environment friendly solid acid catalysts. 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 indicate good potential for TBMA salts to exhibit solid state proton conduction.

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 I of the thesis is a brief introduction to TMA salts. Mixed materials and inorgano organic hybrids of the class of TBMA salts have also been discussed and their possible applications as ion exchangers in separation science, as solid acid catalysts and solid state proton conductors has been proposed.

Chapter II of the thesis deals with the synthesis and characterization of amorphous (A) and crystalline (C) phases of advanced inorganic materials - zirconium titanium phosphate (ZTPA), zirconium phosphate (ZPA), titanium phosphate (TPA), zirconium titanium phosphate (ZTPC), zirconium phosphate (ZPC) and titanium phosphate (TPC); novel hybrid materials (amorphous phase) - zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP), zirconium hydroxy ethylidene diphosphonate (ZrHEDP) and titanium hydroxy ethylidene diphosphonate (TiHEDP) and lithium exchanged phases of advanced inorganic materials – LiZTPA, LiZPA, LiTPA, LiZTPC, LiZPC and LiTPC. All
the materials have been synthesized by sol-gel route. 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. Further, Ion exchange capacity (IEC) of the synthesized materials have also been determined and the effect of calcination on IEC studied.

From the various characterizations, it is concluded that the materials possess structural hydroxyl groups (H⁺ of the -OH being the exchangeable site). NH₃ TPD also reveals that the materials exhibit surface acidity.

Chapter III of the thesis deals with the applicability of ZTPA and ZTHEDP as cation exchangers. The equilibrium exchange of Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ ions with H⁺ ions contained in ZTPA and ZTHEDP have been studied varying temperature, at constant ionic strength. Various thermodynamic parameters such as equilibrium constant (K), standard Gibbs energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) have been evaluated. Further, forward and reverse ion exchange kinetics of Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ ions with H⁺ ion contained in ZTPA/ZTHEDP has been studied varying temperature, applying the Nerst-Planck equation. Kinetic parameters such as self-diffusion coefficient (D₀), energy of activation (E_a) and entropy of activation (ΔS*) have been evaluated under the conditions favouring a particle diffusion-controlled mechanism.

The study shows that the exchange of H⁺ for M²⁺ (alkaline earth metal ions) is spontaneous, the mechanism being an ion exchange process. Further, the forward and reverse ion exchange kinetics reveal the mechanism of exchange to be a particle diffusion.
Distribution coefficient ($K_d$), for various metal ions, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$ (d-block), $\text{Cd}^{2+}$, $\text{Hg}^{2+}$, $\text{Pb}^{2+}$, $\text{Br}^{3+}$ (heavy metal ions) and $\text{La}^{3+}$, $\text{Ce}^{3+}$, $\text{Th}^{4+}$, $\text{UO}_2^{2+}$ (f-block) towards ZTPA and ZTHEDP has been determined in aqueous as well as various electrolyte media/concentrations. Selectivity/affinity of a particular metal ion is explained based on (1) the ion exchanger, (2) the exchange media and (3) the exchanging metal ion. The observed selectivity order towards ZTPA, amongst d-block metal ions is, $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$; amongst heavy metal ions, $\text{Pb}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+} > \text{Br}^{3+}$ and amongst f-block metal ions, $\text{Th}^{4+} > \text{Ce}^{3+} > \text{UO}_2^{2+} > \text{La}^{3+}$. In case of ZTHEDP the selectivity order, amongst d-block metal ions is, $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$; amongst heavy metal ions, $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+} > \text{Br}^{3+}$ and amongst f-block metal ions, $\text{Ce}^{3+} > \text{La}^{3+} > \text{Th}^{4+} > \text{UO}_2^{2+}$. Both, ZTPA and ZTHEDP exhibit efficient selectivity for $\text{Pb}^{2+}$. In addition, ZTPA also exhibits good selectivity for $\text{Cu}^{2+}$. ZTHEDP exhibits good selectivity for all the transition metal ions.

Elution behaviour of various metal ions towards ZTPA and ZTHEDP exhibit, ~77 to 99% metal ion recovery. Acids in general, are better eluants. The study shows that, metal ion exchange and elution are easy and possible on ZTPA/ZTHEDP exchanger using various electrolytes.

Based on the differential selectivity of various metal ions towards ZTPA/ZTHEDP, binary separations for all possible metal ions pairs (Table 1) and a few ternary metal ion separations ($\text{Cu}^{2+}$-$\text{Zn}^{2+}$-$\text{Ni}^{2+}$ d-block, $\text{Hg}^{2+}$-$\text{Cd}^{2+}$-$\text{Pb}^{2+}$ heavy metal ions and $\text{La}^{3+}$-$\text{Th}^{3+}$-$\text{Ce}^{4+}$ f-block metal ions) have been carried out.
In binary separations using ZTPA, separation efficiency is in the range 68-92 %, 62-78 % and 72-90 % for d-block, heavy and f-block metal ions respectively. While using ZTHEDP, separation efficiency is in the range 68-92 %, 60-78 % and 67-82 % for d-block, heavy and f-block metal ions respectively.

In ternary separations using ZTPA, separation efficiency is in the range 55-66 %, 56-64 % and 55-58 % for d-block, heavy and f-block metal ions respectively. While using ZTHEDP, separation efficiency is in the range 62-68 %, 58-67 % and 51-55 % for d-block, heavy and f-block metal ions respectively.

Separation efficiency and percentage recovery of metal ions are explained based on $K_d$ values, breakthrough curves and nature of elution curves (Langmuirian and non Langmuirian).

**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 in terms of surface acidity and turn over number (TON).
Amongst monoesters, catalytic activity/TON increases with increasing chain length of alcohol and the trend in TON is BzA>BA>PA>EA. Higher yields of BzA obtained could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. Amongst diesters, high yields in case of DEM, compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step. When homogeneous liquid acids are used as catalysts for synthesis of DOP and DBP, the result is a product that is coloured and of a poor quality. In the present work, the advantage is that the diester is the unique product and colourless. The study shows, amorphous materials exhibit enhanced catalytic activity compared to crystalline materials and mixed materials exhibit enhanced catalytic activity compared to their single salt counterparts. Further, ZTHEDP exhibits less catalytic activity compared to ZTPA. Probably lack of orientation and polarization of the P-OH groups and hence less availability of protons, as well as restriction of diffusible protons due to steric hindrance in the HEDP moiety are the responsible factors. The activity of the regenerated catalyst was reduced by ~10%. The work outlined herein reveals the promising use of ZTPA and ZTHEDP as solid acid catalysts in the synthesis of monoesters and diesters, the advantages being operational simplicity, mild reaction conditions and eco-friendly nature.

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 LiZTPA and LiZTPC have been investigated and compared with single salt counter parts, (LiZPA, LiTPA) and (LiZPC, 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 have been investigated and compared with single salts counterparts, ZrHEDP and TiHEDP as well as ZTPA.

The proton transport properties of above mentioned materials have been explored by measuring specific conductance at different temperatures in the range of 30 - 150 °C at °C intervals, using Solartron Impedance Analyzer (SI 1260) over a frequency range 1 Hz - 32 MHz at a signal level below 1 V.

For all the materials, it is observed that specific conductivity decreases with increasing temperature and the mechanism of conduction is suggested to be of Grotthuss type.

Mixed metal phosphate of the class of TBMA salts, ZTPA and ZTPC, exhibit enhanced proton conductance compared to their single salt counterparts, ZPA, ZPC and TPA, TPC. Further, amorphous materials exhibit higher conductance compared to crystalline phases.

In lithium-exchanged phases of TBMA salts, conductance is probably due to a contribution from both H⁺ as well as Li⁺. This conductance is also retained up to fairly high temperatures. The study reveals the possible application of lithium-exchanged phases as solid electrolytes for medium and high temperature applications.

Mixed metal phosphonate of the class of TBMA salts, ZTHEDP exhibits enhanced proton conduction compared to its single salt counterparts, ZrHEDP and TiHEDP as well as ZTPA. The study clearly reveals that modifying the number of surface protons, results in enhanced proton conduction.
REFERENCES


