SUMMARY

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 [**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).

1.2 SALIENT FEATURES OF TETRAVALENT METAL ACID (TMA) SALTS

- TMA salts are cation exchangers, possessing the general formula M(IV) $(HXO_4)_2.nH_2O$, 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.
- TMA salts have shown a great promise in preparative reproducibility and ion exchange behaviour
- TMA salts exhibit both thermal and chemical stability

When a tetravalent metal is treated with phosphoric acid/Na salts of phosphoric acid, M – O – P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H^+ of the P – OH contributing to cation exchange [**5**]. TMA salts are prepared by sol gel routes of different compositions and crystallinities [**6-9**] 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 cation exchange capacity (CEC) thus depends on preparation procedure/parameters varied and hence performance in various applications like ion exchange, catalysis and proton conduction.

From our laboratory, TMA salts have been widely explored as cation exchangers [**10-26**], as solid acid catalysts [**27-40**] and solid state proton conductors [**41-46**]. A literature survey as well as works conducted in our laboratory (outlined above) reveals that phosphates of Zr, Sn and Ti have been widely explored as ion exchangers, solid acid catalysts and solid state proton conductors. However, very few reports are available on synthesis, characterization and application of cerium (IV) phosphate (CP) and thorium (IV) phosphate (TP) as ion exchangers, solid acid catalysts and solid state proton conductors. Much of the works available in literature is related to solving the structures of crystalline CP and TP.

The foregoing discussions have been described in **Chapter I** of the thesis. TMA 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 TMA salts CP and TP can be explored as **cation exchangers** in separation science. Due to presence of structural hydroxyl protons in TMA salts, surface acidity is expected giving rise to solid acid characteristics. TMA salts CP and TP can therefore be explored as **environment friendly solid acid catalysts** and **solid state proton conductors**.

Chapter II of the thesis is entitled is "***Synthesis and Characterization of Cerium (IV) and Thorium (IV) Phosphates***". Amorphous CP and TP have been synthesized by sol-gel route. Further, the gels were subjected to microwave (MW) irradiation for optimum time and temperature to yield CP_M and TP_M. These materials were subjected to

physical methods of characterization {appearance, percentage moisture content, particle size, apparent density, true density, nature of exchanger and chemical stability}, **ion exchange methods of characterization** {CEC, effect of calcination on CEC, void volume fraction, concentration of fixed ionogenic groups and volume capacity of the resin}, **instrumental methods of characterization** {elemental analysis (ICP-AES), thermal analysis (TGA and DSC), spectral analysis (FTIR), X-ray diffraction studies, SEM and EDX}, and **Catalyst characterization** {surface area measurements (BET method) and surface acidity (NH_3-TPD method)}.

Based on physico-chemical, ion exchange and instrumental methods of characterization, it can be concluded that both CP and TP exhibit promising ion exchange characteristics - good CEC value (retained upto 150 ºC), granular nature (30-60 mesh size) suitable for column operation, good chemical (insoluble in aqueous, acid and organic solvent media) and thermal stability. Evaluation of surface acidity (retained upto150 ºC) indicates good potential for CP and TP to be used as environment friendly solid acid catalysts and as solid state proton conductors.

Chapter III of the thesis is entitled as ***"Applicability of Cerium (IV) and Thorium (IV) Phosphates as Cation Exchangers"***. The equilibrium exchange of transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and heavy metal ions (Cd^{2+}, Hg^{2+}, Pb^{2+}) ions with H^+ ions contained in CP and TP have been studied varying temperature (303 K, 313 K, 323 K and 333 K), at constant ionic strength. Thermodynamic parameters equilibrium constant (K), standard Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been evaluated and correlated.

In the present study, equilibrium constant (K) values increase with increase in temperature for all metal ions under study, indicating that the metal ions have higher affinity for the exchanger and that the mechanism is ion exchange [**23, 24**]. $\Delta G°$ values for all the exchange reactions are negative and become more negative with increasing temperature indicating increase in feasibility and spontaneity of the exchange process. $\Delta H°$ is positive in all cases indicating complete dehydration of ions for exchange to take place. $\Delta S°$ values are also found to be positive in all cases and follows same trend as $\Delta H°$.

Adsorption of metal ions (under study) has been performed by varying metal ion concentration, pH, contact time and temperature and Langmuir constants (b and V_m), Freundlich constants (K and $1/n$) (using Langmuir and Freundlich isotherms respectively), and R^2 values (goodness of fit criterion) have been computed by linear regression for both types of isotherms. For both CP and TP, R^2 values are found to be close to unity (for both Langmuir and Freundlich isotherms) providing a good fit to the experimental data for sorption of all the metal ions studied.

Distribution coefficient (K_d) has been determined (batch process) at optimized conditions (optimum pH, optimum metal ion concentration and optimum equilibrium time) in aqueous as well as various electrolyte media/concentration (HNO_3, NH_4NO_3, $HClO_4$ and CH_3COOH of 0.2 M and 0.02 M).

Breakthrough curves have been plotted, breakthrough capacity (BTC) determined (column method) and compared with K_d values to confirm the selectivity order of metal ions.

CP follows the order: $Zn^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+}$ (transition metal ions)
$Pb^{2+} > Cd^{2+} > Hg^{2+}$ (heavy metal ions)
} aqueous medium

TP follows the order: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ (transition metal ions)
$Pb^{2+} > Cd^{2+} > Hg^{2}$ (heavy metal ions)
} aqueous medium

In the present study, K_d and BTC are observed to follow the same selectivity order, for both CP and TP.

Elution behaviour of metal ions has been studied using acids and electrolytes (HNO_3, NH_4NO_3, $HClO_4$ and CH_3COOH of 0.2 M and 0.02 M). Elution of various metal ions performed towards CP and TP exhibits, 81-97 % and 77-96 % elution efficiency (% E) respectively. In conclusion, acids in general, are better eluents, and metal ion exchange and elution are easy and possible with both CP/TP using various electrolytes.

Based on the separation factor α a few binary and ternary metal ion separations have been performed. Binary and ternary metal ion separations performed have been presented as given in **Table 1**.

For CP and TP, efficient binary separations in terms of (elution efficiency % E) is observed in all cases, attributed to high α values and symmetrical bell shaped curves. In ternary metal ion separations, for both CP and TP, in all cases, three distinct peaks are observed, however, with tailing effects for every metal ion eluted. % metal eluted is also lower as compared to single and binary metal ion separations.

Table 1 *Metal ion separations performed using CP and TP*

	Binary Separations performed	Separation Factor (α)	Separation/Elution Efficiency range (% E)	Ternary Separations performed	Separation/Elution Efficiency range (% E)
CP	Co^{2+}-Zn^{2+}	1.5	79-87 %	Ni^{2+}-Cu^{2+}-Zn^{2+}	47-55 %
	Cu^{2+}-Zn^{2+}	1.5			
	Ni^{2+}-Zn^{2+}	1.3			
	Hg^{2+}-Pb^{2+}	121.3	73-92 %	Hg^{2+}-Cd^{2+}-Pb^{2+}	41-62 %
	Hg^{2+}-Cd^{2+}	15.8			
	Cd^{2+}-Pb^{2+}	7.6			
TP	Co^{2+}-Cu^{2+}	3.1	84-92 %	Ni^{2+}-Co^{2+}-Cu^{2+}	48-52 %
	Ni^{2+}-Cu^{2+}	1.6			
	Ni^{2+}-Zn^{2+}	1.1			
	Hg^{2+}-Pb^{2+}	29.8	80-92 %	Hg^{2+}-Cd^{2+}-Pb^{2+}	44-50 %
	Cd^{2+}-Pb^{2+}	9.7			
	Cd^{2+}-Hg^{2+}	3.0			

The most promising property of the materials CP and TP is their high selectivity for lead (Pb^{2+}). Lead is a toxic metal requiring stringent regulations to be applied to its content in wastes and water streams. An extremely high affinity of CP and TP towards Pb^{2+} suggests the possibility of their application for lead separation from other pollutants.

To explore the performance ability, CP and TP have been regenerated and reused. It is observed that % retention in K_d values is almost ~100 % upto 4 cycles, indicating that materials could be regenerated and reused without much decline in performance.

Chapter IV of the thesis is entitled as ***"Applicability of Cerium (IV) and Thorium (IV) Phosphates as Solid Acid Catalysts"***. The potential use of CP, TP, CP_M and TP_M as solid acid catalysts has been explored by studying esterification and acetal formation as model reactions.

Monoesters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzAc) and diesters diethyl malonate (DEM), diethyl succinate (DES), dibutyl phthalate (DBP), dioctyl phthalate (DOP) have been synthesized. Esterification reaction conditions were optimized by varying several parameters such as reaction time, catalyst amount and mole ratio of reactants.

Amongst monoesters, order of % yield is BzAc > BA > PA > EA could be explained due to increase in carbon chain length in the respective alcohols used for ester formation. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapor phase and not be available in the liquid phase. This is the reason why the heavier alcohols react more than the lighter ones. Turn over number (TON) reflects the effectiveness of a catalyst and this also follows the order of ester formation. Amongst diesters, high yields in case of DEM and DES, compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate/succinate formed in the first step.

A simple, efficient and highly eco-friendly protocol is described for the acetalization of benzaldehyde, cyclohexanone, acetophenone and benzophenone with pentaerythritol (PET) by varying several parameters such as reaction time, catalyst amount and mole ratio of reactants. In all the reactions, acetal derivative of benzaldehyde (dibenzal acetal) was obtained with high % yield. This is probably due to the fact that aldehyde undergoes nucleophilic addition more readily than ketones. Compared to benzophenone and acetophenone, benzophenone being more bulky than acetophenone, shows the lowest reactivity and thus low yields.

The order of esters (mono and diesters) and diacetal derivatives formed with reference to performance of catalyst is $CP_M > CP > TP_M > TP$ could be attributed to higher surface acidity as well as protonating ability.

A study on regeneration and reuse of catalysts has been performed. The catalysts could be regenerated and reused upto two catalytic run without significant loss in % yield of esters and acetals.

A reaction mechanism has been proposed and discussed for solid acid catalyzed esterification and acetalization reactions.

Chapter V of the thesis is entitled as ***"Applicability of Cerium (IV) and Thorium (IV) Phosphates as Solid State Proton Conductors"***. Proton transport properties of CP, TP, CP_M and TP_M have been investigated. The proton transport properties of CP, TP, CP_M and TP_M have been explored by measuring specific conductance at different temperatures in the range of 30 - 120 °C at 10 °C intervals, using Solartron Impedance Analyzer (SI 1260) over a frequency range 1 Hz - 32 MHz at a signal level below 1 V.

The order of specific conductance at 30°C is found to be CP_M (3.17×10^{-6} Scm^{-1}) > CP (4.57×10^{-7} $S \cdot cm^{-1}$) > TP_M (2.76×10^{-7} $S \cdot cm^{-1}$) > TP (3.33×10^{-8} $S \cdot cm^{-1}$). This trend is also in keeping with the CEC values (in parenthesis), CP_M (2.90) > CP (2.45) > TP_M (2.41) > TP (1.48). Higher CEC as well as surface acidity values indicate more exchangeable protons and hence more conducting protons.

Activation energy (E_a) (in kcal/mol) values (in parenthesis), follow the order TP (7.30) > TP_M (4.86) > CP (2.10) > CP_M (1.15) in the temperature range 90-120 °C. A lower value of E_a indicates ease of conduction. In the present study trend in E_a and specific conductivity (σ) are supportive to each other.

Trends in specific conductivity and E_a in all the materials are as observed earlier [**41-46**]. Decrease in specific conductivity with increasing temperature, loss of water of hydration as well as condensation of structural hydroxyl groups with increasing temperature, supported by study of the effect of heating on CEC, where CEC values decrease as calcination temperature increases suggests the mechanism of transportation to be of Grotthuss type [**47**], where the conductivity depends on the ability of the water located on the surface to rotate and participate.

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