Transport properties of organic derivatives of zirconium molybdate

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An amorphous inorganic ion exchanger zirconium molybdate (ZM) and its organic derivatives have been prepared by anchoring ortho and para chlorophenol onto it, termed as ZMoCP and ZMpCP respectively. The materials have been assessed for chemical stability in several acidic, basic and organic media. Further they have been characterised for elemental analysis, thermal analysis and FTIR spectroscopy. Protonic conductivity in these materials were determined at various temperatures using SOLARTON SI 1260 Impedance analyser. The protonic conductance values obtained have been discussed and compared for ZMoCP and ZMpCP.

Frequency dependent measurements of the ac conductivity have been recognized as an important tool for the study of ionic properties of the solids. In recent years there has been intense research aimed at discovering new proton conductors and the mechanism of conductance in solids. This renewed activity has been driven by the potential use of such compounds in fuel cells, sensors, water electrolysis units and other electrochemical properties.

The underlying science of fast conduction of electrical charge through solids by proton (H+), migration is approaching maturity and application of proton conducting materials in devices such as fuel cells and electronic displays is being seriously investigated. Protonic conduction is often present in systems in which it may not be anticipated such as—smectite clays conduct protons due to the acidity of hydrated interlayer cations, the operation of the glass membrane (pH) electrode depends on protonic conduction in soda glass and protonic conduction is even found in some oxide ceramics. Proton conduction and devices employing it can be considered in three temperature ranges—(a) near ambient temperature, (b) medium temperature (150-300°C) and (c) high temperature (>600°C).

Protonic conductors at near ambient temperatures are hydrated (with H+ migration by protons hopping between H2O and H3O+ or OH-) and include materials as diverse as H-form inorganic ion exchangers, heteropoly acids and NAFIONS. In inorganic systems, conduction via the surfaces of particles often dominates conduction through a sample.

Studies in the medium temperature ranges have established protonic conduction in H3O+ exchanged and phosphoric acid bonded forms of known alkali ion conductors such as NASICON (Na_{1-x}Zr_{x}Si_{3-x}P_{3-x}O_{12}, 0 < x < 3) and in anhydrous salts such as M_{2}O_{3} doped (M=Y, rare earth) BaCeO_{3} ceramics with a perovskite structure. Protonic conductivity in such materials is a result of reactions with moisture and/or H_{2}. It is reported that the glasses in the lithium oxyfluorophosphate system [LiF - Li_{2}O - Al(PO_{3})_{3}] show unusually high conductivity at elevated temperatures.

Inorganic ion exchangers of the type of acid salts of tetravalent metals have the general formula M(IV) (HXO_{4})_{2} nH_{2}O, where M = Zr, Ti, Ce, Th, etc; and X = P, Mo, W, As, Sb, etc. They possess structural hydroxyl groups which are responsible for their ion exchange behaviour. These materials have been extensively studied in the field of separation science and catalysis. However, attempts have also been made to study the transport properties of these materials. They can behave as protonic conductors because of the presence of structural hydroxyl groups. When these -OH groups are hydrated, the protons can easily move on the surface, accounting for their conductivities which depend strongly on relative humidity, surface area, and degree of
crystallinity\(^{13}\). The conductivity in layered \(\alpha\)-zirconium phosphates has been studied\(^{12}\) in detail. Alberti et al.\(^{17}\) have shown that the surface conducts protons thousand times faster than the interior.

A new class of ion exchange materials has emerged\(^{14}\) having the general formula \(\text{Zr}(\text{O}_\text{P}-\text{R})_\text{nS}\) (\(\text{R}\) is organic radical and \(\text{S}\) is solvent molecule) formed due to intercalation of the organic moiety within the layers of the inorganic matrix such as \(\alpha\)-zirconium phosphate (\(\alpha\)-ZrP). These compounds have been in general termed as inorgano-organic ion exchangers. Because of the large variety of organic groups that can be attached to the inorganic backbone, there are more possibilities of Owing to their protonic conductivity, amorphous or microcrystalline powders of \(\alpha\)-ZrP were initially mixed to organic binders to prepare heterogeneous inorgano-organic membranes\(^{15,16}\). A literature survey shows that very few investigations of the protonic conductivity of these compounds have been investigated\(^{17-22}\). Protonic conduction of amorphous inorganic ion exchangers has been investigated in our laboratory\(^{23}\). However there are no reports on the protonic conduction of amorphous inorgano-organic materials.

In the light of the recent advances in the field of protonic conduction, the present endeavour deals with the synthesis, characterization and study of the transport properties of an amorphous inorganic ion exchanger zirconium molybdate (ZM) and of organic molecules, i.e., ortho chlorophenol and para chlorophenol anchored onto ZM, termed as ZMoCP and ZMpCP respectively. ZM, ZMoCP and ZMpCP have been assessed for their chemical stability in various acidic, basic and organic media. They have been characterised for elemental analysis, TGA and FTIR spectroscopy. Further protonic conductivity in these materials have been determined at various temperatures and compared.

**Experimental Procedure**

**Preparation of the materials**—Zirconium molybdate was prepared by the method reported earlier\(^{24}\). ZMoCP and ZMpCP were prepared by heating under reflux ZM (1g) with o-chlorophenol/p-chlorophenol each for 2h. The excess of the phenols were decanted and the exchanger was washed several times with ethanol and dried at 40°C, at a relative humidity of 80%. The decanted phenols were retained in order to estimate the amount of phenols anchored onto the matrix. This has been determined on the basis of the difference between the residual and initial concentration of the reagent by the bromination method\(^{25}\).

**Chemical stability**—The chemical stability of the materials was assessed by soaking the exchangers in several mineral acids, bases and organic solvents.

**Elemental analysis**—The samples were analysed for zirconium and molybdenum gravimetrically as zirconium oxide by cupferron method and molybdenum oxide by the \(\alpha\)-benzoin oxime method respectively. Carbon and hydrogen content were determined by Coleman analyser model 33.

**Thermal analysis**—The thermogravimetric analysis of the samples were performed on a Shimadzu DT-30 thermal analyser at a heating rate of 10°C/min.

**Fourier Transform Infrared Spectroscopy**—FTIR spectra of the samples were performed using a KBr wafer on a Perkin Elmer model 1720X with Epson Hi 80 printer/plotter.

**Conductivity measurements**—The electrical conductivity of the solids were measured on pellets of 10 mm diameter and 1.5-2 mm thickness, with a relative humidity of 80%. The opposite sides of the pellets were coated with conducting silver paste to ensure good electrical contact. Impedance measurements were taken using Solarton SI 1260 Impedance analyser, over a frequency range 10 Hz - 32 MHz at a signal level below 1V, interfaced to a mini computer for data collection. In all cases, since the impedance plots of the materials consist of single depressed impedance semi-circle, the pellet conductivity was calculated by arc extrapolation to the real axis, taking into account the geometrical size of the pellets. The measurement was made in the temperature range 25-120°C at a relative humidity of 80%.

**Results and Discussion**

It is observed that the colour of ZM changed from pure white to brownish yellow when treated with o-chlorophenol/p-chlorophenol, which resembles the colour of organic resins. This gives an indication that the organic moiety is anchored on to the inorganic matrix.

ZM was found to be stable in mineral acids such as HCl (2N), \(\text{H}_2\text{SO}_4\) (4N), HNO\(_3\) (2N), bases such as NaOH (2N) and KOH (0.5N). ZMoCP and ZMpCP were found to be stable in HCl (2N),
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$\text{H}_2\text{SO}_4$ (4N), $\text{HNO}_3$ (2N), bases, $\text{NaOH}$ (0.5N) and $\text{KOH}$ (0.5N). ZM, ZMoCP and ZMpCP were further found to be stable in ethanol, acetone and diethyl ether.

Chemical analysis indicate the composition of Zr:Mo to be 1:1. Based on this and the TGA data, the molecular formula of ZM is proposed to be $\text{ZrO}_2 \cdot \text{MoO}_4 \cdot 15\text{H}_2\text{O}$. The number of water molecules was determined using Alberti's formula. The carbon and hydrogen content in ZMoCP and ZMpCP were found to be $\% \text{C} = 4.908; \% \text{H} = 2.480$ and $\% \text{C} = 5.316; \% \text{H} = 2.371$ respectively.

The thermogram of ZM (Fig. 1 a) indicates an 8% weight loss within the temperature range of 80-180°C corresponding to the loss of external water molecules after which a slow change in weight loss is observed till about 600°C. This may be due to the condensation of structural hydroxyl groups.

The TGA of ZMoCP and ZMpCP (Fig.1 b&c) indicate a ~10% weight loss at a temperature of ~60°C which could be attributed to the loss of adsorbed moisture and traces of solvents used for washing the exchanger after the reflux period. A gradual decrease in weight occurs upto 500°C indicative of the dissociation and decomposition of the organic part from the inorganic support and to the condensation of the structural hydroxyl groups.

The FTIR spectrum of ZM (Fig.2 a) shows broad bands in ~3400 cm$^{-1}$ region characteristic of the asymmetric and symmetric hydroxo $-\text{OH}$ and aquo $-\text{OH}$ stretches. A medium band at ~1620 cm$^{-1}$ is characteristic of the $\text{H}-\text{O}-\text{H}$ bending frequency. A shoulder at ~935 cm$^{-1}$ is observed characteristic of the Zr-O stretching frequency.
The FTIR spectra of ZMoCP and ZMpCP (Fig. 2 b&c) show additional bands in the 1580-1460 cm\(^{-1}\) region characteristic of the C = C skeletal inplane vibrations. Bands in the 1390-1330 cm\(^{-1}\) region are due to the interactions of the OH bending and C - H stretching vibrations. Weak bands in the 1410-1310 cm\(^{-1}\) region and at 1200 cm\(^{-1}\) are due to the C-O stretching frequency.

Table 1—Variation of specific conductance (\(\sigma\)) with temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ZM ((\Omega \cdot \text{cm})^{-1})</th>
<th>ZMoCP ((\Omega \cdot \text{cm})^{-1})</th>
<th>ZMpCP ((\Omega \cdot \text{cm})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.12x10^5</td>
<td>6.77x10^7</td>
<td>3.98x10^6</td>
</tr>
<tr>
<td>30</td>
<td>1.08x10^5</td>
<td>5.86x10^7</td>
<td>3.17x10^6</td>
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<tr>
<td>60</td>
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<td>3.03x10^7</td>
<td>2.12x10^7</td>
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<tr>
<td>90</td>
<td>5.20x10^7</td>
<td>2.64x10^7</td>
<td>1.57x10^8</td>
</tr>
<tr>
<td>120</td>
<td>3.39x10^8</td>
<td>1.81x10^7</td>
<td>9.25x10^9</td>
</tr>
</tbody>
</table>

It is seen that the value of specific conductivity (\(\sigma\)) of ZM at 25°C is 1.12x10^5 \((\Omega \cdot \text{cm})^{-1}\) whereas for ZMoCP and ZMpCP the value of \(\sigma\) is 6.77x10^7 \((\Omega \cdot \text{cm})^{-1}\) and 3.98x10^6 \((\Omega \cdot \text{cm})^{-1}\) respectively.

The nature of the graphs in ZMoCP and ZMpCP are the same. Temperature and frequency dependent complex impedance plots for a particular case ZMpCP are exhibited in Fig. 3. For all the three materials, specific conductivity decreases with increasing temperature (Table 1). This is attributed to the loss of water of hydration as well as the condensation of structural -OH groups. This suggests the mechanism of transportation as a Grotthus type\(^{27}\) where the conductivity depends on ability of the water located on the surface to rotate and participate in a Grotthus type transport. It is also required that the hydronium ion must reorient to the proper position for the proton transfer to occur. This fact is also in keeping with the suggestion that protons are not able to diffuse along an anhydrous surface where the spacing of the -OR groups is high\(^{28}\). Moreover it is reported that in case of amorphous zirconium phosphate, swelling occurs in water and hydronium ions may form\(^{29}\), allowing for a Grotthus transport mechanism. Besides the fact that the loss of proton resulting from the hydroxyl condensation causes a considerable decrease in conductivity, indicates that the conduction is protonic also.

The ac conductivity experiments of different compounds reported earlier revealed that the ac conductivity of phases obtained from intercalation and thermal de-intercalation of 1,4 amino butanol in \(\alpha\)-ZrP at 150°C was 3x10^-6 S cm\(^{-1}\) which is about two orders of magnitude higher than that of anhydrous \(\alpha\)-ZrP\(^{30}\). Suitable guest molecules when intercalated in the interlayer region of \(\alpha\)-Zr(\(\text{HPO}_4\))\(_2\). \(\text{H}_2\text{O}\) affect the proton transport, acting as bridges between the phosphate ionogenic groups. High activation energy and low
conductivity were observed for intercalation compounds containing as guests, relatively strong Bronsted bases probably due to the proton localization, whereas a significant improvement in conductivity was obtained after intercalation of hydrazine. Ac conductivity in the intercalation compounds with imidazole and pyrazole show a remarkable increase. Similar values were obtained for compounds containing pyrazine, pyrimidine and pyridazine. Lowest conductivity was observed in case of the compounds containing 3,4 diamino groups in layered materials, the bulk contribution to the conductivity is negligible because the main part of the measured conductivity is related to the surface P-OH groups. The very low bulk conductivity at room temperature could be due to lack of orientation and polarization of the P-OH groups present in the interlayer region of α-zirconium phosphate. On the other hand, the P-OH groups present on the surface have much more freedom to rotate than the internal ones and transport is assisted by water molecules forming a bridge between the acid groups.

In the present case, however the transport of the surface protons of ZM is sterically blocked due to the presence of organic moieties on the surface. As a result, the orientation and polarization of the M-OH groups on the ZM surface is disturbed leading to a decrease in the specific conductance for ZMoCP and ZMpCP as compared to that of ZM. Further, it is also observed that conduction in case of the ortho derivative ZMoCP is less as compared to that of the para compound, ZMpCP. This may be due to the location of the phenolic –OH at the ortho position in ZMoCP which causes more steric's hindrance as compared to that in the para derivative ZMpCP.

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References