Ion Exchange Properties of Synthesized Cerium (IV) Phosphate

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ABSTRACT
Tetravalent metal acid salts are the most extensively studied group of synthetic inorganic ion exchangers. The cation exchange properties arise from the presence of readily exchangeable hydrogen ions associated with the anionic groups in these salts. An amorphous material cerium (IV) phosphate obtained in the present study, belongs to the class of tetravalent metal acid salt. Ceric sulphate and disodium hydrogen phosphate were mixed to obtain a material of optimum sodium exchange capacity. The selected material was characterized by FTIR, XRD, TGA/DTA, SEM, EDS and UV-Visible in addition to chemical stability and ion exchange studies. Ion exchange capacities for different alkali and alkaline earth metals were determined. Na⁺ exchange capacity was found to be 2.26 meq/g. The effect of heat on ion exchange capacity was also studied for the exchanger. The optical band gap obtained as per Tauc relation was 1.211 eV, which indicates that the material is a semiconductor.

Key words: Cation exchanger, cerium(IV) based material, ion exchange capacity.

Received 07/12/2013 Accepted 28/01/2014 © 2013 AELS, India

INTRODUCTION
Insoluble salts of tetravalent metals can be prepared both in crystalline and amorphous forms [1]. They can be obtained by the combination of tetravalent metal salts with anions like phosphate, molybdate, arsenate, antimonate, tungstate etc. They have the general formula M(IV) (HXO₄)₂.nH₂O where M(IV) = Zr, Ti, Sn, Ce, Th etc and X = P, Mo, W, As, Sb etc. These compounds have structural hydroxyl groups, the H of –OH being exchangeable sites. A number of cations can be exchanged with H⁺ due to which the materials possess cation exchange properties. Tetravalent metal acid (TMA) salts show great promise in preparative reproducibility and thermo chemical stability [1]. Such inorganic ion exchangers have multiphased applications owing to their properties such as selectivity for certain metal ions, high stability in strong acids, oxidizing solutions and ionizing radiations [3]. They are especially attractive for analytical applications were organic resins cannot be employed because of their degradability. Due to the presence of surface hydroxyl protons they can be successfully employed as Bronsted acid catalysts [4] and protonic conductors [5]. They can also be used as sorbents for the removal of dyes, pesticides, organic molecules etc [6]. They have been widely used for the removal of heavy metals from waste water which are generated as untreated or partially treated by-products of various industries [7]. In recent years lanthanides are in great demand as functional materials with diverse applications in electric, magnetic and catalytic fields originating from their unique 4f electrons and among the rare earths cerium is the cheapest [8]. The present study is devoted to the preparation, characterization and ion exchange properties of tetravalent cerium based material namely cerium (IV) phosphate.

MATERIALS AND METHODS
All chemicals, ceric sulphate, ammonium hepta molybdate, disodium hydrogen phosphate etc., were of Analar grade and used as received. Solutions of ceric sulphate were prepared in 0.5 M H₂SO₄. pH adjustments were achieved using dilute HNO₃ and NaOH solutions.

Preparation of the ion exchanger
Cerium Phosphate (CP) in the present study was prepared by adding aqueous solution of 0.1 M disodium hydrogen phosphate to half its volume of 0.5 M ceric sulphate slowly, with continuous stirring at pH~2. The gel obtained was stirred for another 1 hour and kept overnight at room temperature in contact with
the mother liquor for the growth of fine particles. The granular precipitate thus obtained was filtered, washed with conductivity water till free of chloride and sulphate ions and dried at 40°C. The material after drying were broken to desired particle size (ASTM, 30 – 60 mesh) by grinding and sieving. It was then converted to the hydrogen form completely by repeated treatment with 1 M HCl solution. Finally, washed thoroughly with conductivity water, till free of chloride ions, to remove any free acid remaining on the sample and dried at 40°C. To access chemical stability of the synthesized material, 500 mg of the exchanger was kept separately in 50ml of different solvents and the change in colour and weight were noted.

**Apparatus:** X-Ray diffractogram of the sample was taken from Bruker D8 Advance diffractometer using Cu Kα radiation. The elemental analysis and surface morphology was observed on a JEOL JSM 5600 LV SEM. Thermograms were taken with Perkin-Ermer Diamond Thermo Gravimetric Analyzer. FTIR spectrum was recorded on a Perkin Elmer Fourier Transform Spectrometer. UV-Visible spectrum of the compound was obtained from Shimadzu UV-2550 Spectrophotometer. Ion Exchange capacity (i.e.c) of the material was determined by column method [9]. The effect of heat on i.e.c of the sample was studied at different temperatures.

### RESULTS AND DISCUSSION

CP was obtained as a pale yellow solid. It was found to be stable in mineral acids like HCl, H₂SO₄ and HNO₃ up to ~7 M concentrations as evident by no change in colour, form or weight of sample used. CP was found to be stable in all concentrations of bases, in ethanol, diethyl ether, acetic acid and 1 M salt solutions. The amorphous nature of the material is evident from the absence of strong peaks in the X-ray diffractogram as seen in Fig. 1. The SEM image (Fig. 2) of CP shows the formation of aggregates of size 217 nm. Elemental analysis (Fig. 3) shows that CP contains 38.36% of cerium and 16.29% of phosphorous. The thermograms of CP (Fig. 4) shows a sharp change in weight around 100°C corresponding to the loss of external water molecules and a small weight loss around 200°C due to the removal of co-ordinated water molecules after which a gradual loss in weight is observed. This is attributed to the condensation of structural hydroxyl groups. DTA of the materials also shows endothermic peaks corresponding to these changes. Elemental analysis data gives the percentage composition of different elements in the material, from which the empirical formula can be calculated by usual methods [10]. Therefore, based on elemental analysis, the empirical formulae were proposed for CP is CeO₂ P₂O₅ . n H₂O.

The number of external water molecules ‘n’ in these compounds, were further calculated from TGA data using Alberti and Torracca formula [11].

\[ 18n = \frac{X(M + 18n)}{100} \]

M = molecular weight of the exchanger without water molecules, X = percentage weight loss upto 180°C. Based on the above formula it is found that n = 2 in CP.

FTIR showed bands around 3400cm⁻¹ due to –OH stretching, 1631cm⁻¹ due to bending vibration of water, 1068cm⁻¹ attributed to P=O stretching, and bands around 620-410cm⁻¹ due to metal-oxygen vibrations [12].

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**Fig. 1 XRD of CP**

**Fig. 2 - SEM of CP**
The UV-Visible spectrum of CP (Fig. 6) reveals that the material absorbs in the ultra-violet region of the spectrum which is usually observed in cerium-based materials [13]. The absorption edge around 250nm for the samples is an indication of the presence of band gap in the material. The value of optical band gap is obtained by best-fit method by plotting \((\alpha h\nu)^2\) versus \(h\nu\), as per the Tauc relation [14]. The band gap energy obtained for CP is 1.211 eV, which is found to be close to the value reported for the semiconductor commonly used namely Si (1.1 eV) [15].
The exchange capacities with other alkali and alkaline earth metals taken as their respective chloride salts are summarized in Table 1. The \( \text{iec(meqg}^{-1}) \) for alkali metals is in the order \( \text{Na}^{+} (2.26) > \text{K}^{+} (1.73) > \text{Li}^{+} (1.68) \) and for alkaline earth metals the preference is \( \text{Mg}^{2+} (4.60) > \text{Sr}^{2+} (3.73) > \text{Ca}^{2+} (2.59) > \text{Ba}^{2+} (1.07) \). The selectivity do not follow the order of ionic radii or hydrated ionic radii. The decrease in \( \text{iec} \) observed for CP on calcination (Table 2) is attributed to the condensation of structural hydroxyl groups at higher temperatures which is the usual behavior of inorganic ion exchangers [9]. The colour change of CP from cream to white is an indication of the reduction of Ce(IV) to Ce(III) [16].
Fig. 7 – Optical band gap by best-fit method

Table 1 - Exchange capacities for alkali and alkaline earth metal ions on CP

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Ionic radii (Å)</th>
<th>Hydrated ionic radii (Å)</th>
<th>i.e.c meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>68</td>
<td>600</td>
<td>1.68</td>
</tr>
<tr>
<td>Na⁺</td>
<td>97</td>
<td>450</td>
<td>2.26</td>
</tr>
<tr>
<td>K⁺</td>
<td>133</td>
<td>300</td>
<td>1.73</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>66</td>
<td>800</td>
<td>4.60</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>99</td>
<td>600</td>
<td>2.59</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>112</td>
<td>500</td>
<td>3.73</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>134</td>
<td>450</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 2 - Effect of heat on Na⁺ exchange capacity of CP

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>CP i.e.c (meq/g)</th>
<th>colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.13</td>
<td>cream</td>
</tr>
<tr>
<td>200</td>
<td>0.67</td>
<td>cream</td>
</tr>
<tr>
<td>300</td>
<td>0.45</td>
<td>cream</td>
</tr>
<tr>
<td>400</td>
<td>0.20</td>
<td>white</td>
</tr>
<tr>
<td>500</td>
<td>0.20</td>
<td>white</td>
</tr>
</tbody>
</table>

In the present work, CP shows high affinity for Na⁺ ions among the alkali metals studied. Such materials with high selectivity for Na⁺ find application in electro-deionization which is a desalination method based on a combination of ion exchange resin and ion exchange membrane [17]. It may also find application in the removal of sodium from natural and industrial brine in a reasonable period [18]. Analysis of nucleic acids frequently requires separation from various impurities commonly Na⁺ or K⁺ ions and inorganic ion exchangers with high sodium exchange capacity can be used for such purpose [19]. Among the alkaline earth metals studied, CP shows high affinity for Mg²⁺ and Ca²⁺ ions. Therefore, the material may also be
used in the removal of hardness of water. CP is stable with reasonable sodium exchange capacity even at high temperature.

CONCLUSION
Cerium (IV) Phosphate exhibits the characteristics of a promising cation exchanger with good chemical resistivity, thermal stability and ion exchange capacity. The material shows excellent chemical stability in high concentration of bases. The affinity for the semiconduction properties coupled with the UV absorption ability of the synthesized cerium based materials may enhance the potential use of the materials in electronic devices as well as in sunscreen applications.

ACKNOWLEDGEMENT
This work was supported by UGC (FIP Plan XI).

REFERENCES

Citation of This paper