Preparation and properties of styrene supported zirconium(IV) tungstophosphate: A mercury(II) selective inorganic-organic ion exchanger

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A new phase of mixed material, styrene supported zirconium(IV) tungstophosphate, prepared in the granular form suitable for column preparation has been characterized by elemental analyses, TGA, XRD and IR studies. Its ion exchange behaviour, pH titration and distribution behaviour have been studied. Distribution studies reveal the exchanger to be highly selective for Hg^{2+}.

Inorganic ion exchangers of single and double salts as well as organic resins are being increasingly used for separation of metal ions, the former being more stable to high temperature and radiations than the latter. Selectivity towards a particular metal ion by inorganic ion exchangers is one of the important factors for their development, while in the case of organic resins it is uniformity and chemical stability. In order to achieve stable materials with chromatographic properties interest has been generated in organic-inorganic ion exchange materials. In the present study a styrene supported zirconium(IV) tungstophosphate (SZWP) cation exchanger has been synthesized. Ion exchange properties have been studied on its surface.

Experimental

Zirconyl chloride (ZrOCl_{2}.8H_{2}O) and sodium tungstate (Na_{2}WO_{4}.2H_{2}O) were of AR grade. Orthophosphoric acid (H_{3}PO_{4}) was obtained from CDH Product (India) while styrene was a GSC product. All other reagents and chemicals were of Analar grade.

A pH meter model Li-10 Elico' (India); spectrophotometer model U- 2000 Hitachi, IR, Perkin Elemer model 783; TGA, Perkin Elemer USA; X-ray diffractometer, Philips (Holland) model PW-1700 and Elemental analyzer Perkin Elemer USA were used for analysing and characterising the materials. Heating effect on the ion exchange capacity and weight loss was studied manually in a muffle furnace.

Stock solutions of zirconium oxychloride (1M), sodium tungstate (1M) and orthophosphoric acid (1M) were prepared in demineralized water. Working solutions were obtained by dilution to the desired concentration with demineralised water. Styrene solution (10%) was prepared in ethyl alcohol.

Samples of the ion exchanger were prepared by mixing the solutions of zirconyl chloride, styrene, sodium tungstate and orthophosphoric acid in varying volume ratios with constant stirring. Gels so obtained were subjected to sulphonation, nitration or hydrochlorination and digested in their respective mother liquor for 24h at room temperature. After filtering, the excess acid was removed from gels by washing with demineralised water till the pH of the washing was ~6. The samples were dried at 50°C in an oven. The dried gel samples were then broken into small granules by putting in demineralised water. The H^{+} form was obtained by treating with 1M HNO_{3} for 24h and finally washed with demineralised water and dried in oven. Table 1 indicates the experimental details of the synthesis of various samples of the material. On the basis of Na^{+} ion exchange capacity, appearance and reproducibility, sample no. 2 was selected for further studies. IR spectra were recorded in KBr discs at room temperature. TGA analysis was carried out by heating the exchanger from 40 to 920°C at the rate of 15 deg/min.

About 0.5 g of the exchanger was dissolved in 10 ml of HF by heating on a water bath. Demineralised water (10.0 ml) and HNO_{3} (20.0 ml) were then added dropwise. After the reaction subsidised the solution was diluted to 100 ml with demineralised water. The amount of zirconium and tungsten were determined by AAS while phosphorous was determined titrimetrically by standard method. Carbon and hydrogen contents of the exchange material were determined.
by elemental analyses. The molar composition of the material was found to be Zr: styrene : W : PO₄⁻³ = 2:1:3:6.

To determine the extent of dissolution of the material in different solvents, 250mg portions of the sample were treated with several solvents for 24h at room temp. with intermittent shaking. The supernatant liquid was analysed quantitatively for the zirconium, tungsten and phosphate contents using standard spectrophotometric methods.

pH-titrations were performed by method of Topp and Pepper. About 500mg portions of the exchanger were placed in 250 ml conical flasks and equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios were added, the final volume being 50ml to maintain a constant ionic strength. The pH of the solution was recorded after every 24h until equilibrium was attained which needed approximately 11 days and pH at equilibrium was plotted against the milliequivalent of OH⁻ ions added. The results are shown in Fig. 1.

**Ion exchange capacity**

The exchanger (H⁺- form, 1g) of uniform mesh size (50 - 100) was placed in a glass tube (int.dia. ~1cm) fitted with glass wool at its bottom. NaNO₃ solution (1M, 250 ml) was passed through it at a very slow flowrate (~0.5 ml min⁻¹). The effluent was titrated against standard alkali solution to determine the total H⁺ released. The ion exchange capacity (in meq gm⁻¹ dry material) for Li⁺, K⁺, Na⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ are 1.55, 2.10, 2.32, 2.50, 2.74, 2.70 and 3.38 respectively.

To study the effect of eluant concentration on ion exchange capacity, NaNO₃ solutions of varying concentrations (0.2 - 1.4 M) were passed through the column. The H⁺- ions thus eluted were titrated against a standard 0.1M NaOH. The ion exchange capacity of dry material in meq g⁻¹ at different concentrations was found to increase with increase in concentration of the eluant as follows:

1.40 (0.2M); 1.74 (0.4M); 2.00 (0.6M); 2.20 (0.8M); 2.32 (1.0M); 2.32 (1.2M); 2.34 (1.4M).

**Distribution and separation studies**

Nearly 200 mg of the exchanger beads in the H⁺ form were equilibrated with 20ml of the selected solvents at room temperature for 24h. The initial metal ion concentration in the solution was adjusted by elemen al analyses. The molar composition of the material as found to be Zr: styrene : W : PO₄⁻³ = 2:1:3:6.

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**Table 1 - Synthesis of various samples of styrene supported zirconium(IV) tungstophosphate as cation exchanger.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mixing volume ratio</th>
<th>Acidification</th>
<th>Na⁺ ion exchange capacity (meq gm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr (0.1M) W (0.1M) P (0.1M) Styrene (10%)</td>
<td>(100°C, 1h)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1 1 3  Nil</td>
<td>Nil</td>
<td>1.88</td>
</tr>
<tr>
<td>2</td>
<td>1 1 3  1</td>
<td>Sulphonation in mother liquor</td>
<td>2.32</td>
</tr>
<tr>
<td>3</td>
<td>1 1 3  1</td>
<td>Nitrification in mother liquor (100°C, 1h)</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>1 1 3  1</td>
<td>Hydrochlorination (HCl) in mother liquor (100°C, 1h)</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>1 1 3  1</td>
<td>Nil</td>
<td>1.65</td>
</tr>
<tr>
<td>6</td>
<td>1 1 3  1</td>
<td>Sulphonation in mother liquor (without heat)</td>
<td>2.25</td>
</tr>
</tbody>
</table>
so that it does not exceed 3% of the total ion exchange capacity of the material. The determinations were carried out volumetrically using EDTA as the titrant. Distribution coefficients \( K_d \) were calculated by formula.

\[
K_d = \frac{(I - F)}{F \times V/m (ml/g)}
\]

where \( I \) is the initial amount of the metal ion in the solution phase, \( F \) is the final amount of the metal ion in the solution phase; \( V \) is the volume of the solution (ml) and \( m \) is the amount of the exchanger (g).

Several alkali, alkaline earth and transition metal ions were tested. The solvents chosen were the following: Demineralised water, \( \text{HNO}_3 \) (0.01, 0.1 and 1\( M \)), \( \text{HCl} \) (0.01, 0.1 and 1\( M \)), \( \text{HClO}_4 \) (0.01, 0.1 and 1\( M \)), \( \text{CH}_3\text{OH}, \text{C}_2\text{H}_5\text{OH}, 1\% \text{citric acid and } 1\% \text{oxalic acid}.

The exchanger in \( \text{H}^+ \)-form (mesh size 50-70, 2g) was used for column operation in a glass tube having an internal diameter of \( \sim 0.6 \text{cm} \). The column was washed thoroughly with demineralised water and the mixture was loaded. After recycling 2 or 3 times to ensure complete adsorption of the mixture on the column bead, the metal ions were eluted at a flow rate \( \sim 2-3 \text{ drops min}^{-1} \) using eluants selected on the basis of the \( K_d \) values obtained. The metal ions in the effluent were determined quantitatively by EDTA titrations and results are summarized in Table 2.

### Results and discussion

A new organic-inorganic ion exchanger, SZWP, has been developed which possesses a higher ion exchange capacity (2.32 meq/dry gm) as compared to simple zirconium(IV) tungstophosphate (1.88 meq/dry gm) and other similar materials, i.e., double salts of some tetravalent metals\(^5\). The material has also been regenerated three times and its ion exchange capacity was found to be 1.95 meq/gm for each time. On heating the exchanger (1g) at different temperatures for one hour ion exchange capacity was found to be 2.32, 1.98, 1.02, and 0.06 meq/g at 50, 100, 200, 400 and 600\( ^\circ C \) respectively indicating its thermal stability. It was found to be highly resistant to \( \text{HNO}_3 \) and \( \text{HCl} \) with slight solubility in \( \text{H}_2\text{SO}_4 \) and alkaline media.

The material possesses maximum ion exchange capacity at an eluant concentration of 1\( M \) and requires about 150ml of 1\( M \) \( \text{NaNO}_3 \) for the complete elution of \( \text{H}^+ \) ion from a column of 1g.

IR studies show the presence of the external water molecules in addition to the metal-oxygen and metal-OH stretching bands in the material. Absorption bands at 530 cm\(^{-1}\) and 1100 cm\(^{-1}\) are due to the presence of \( \text{PO}_4^{-3} \) and \( \text{HPO}_4^{-2} \) groups\(^10\). The absorption band at 3600 cm\(^{-1}\) is due to the presence of external water molecules while the band at 1600 cm\(^{-1}\) identifies the water of crystallization\(^10\). The sulphonation was confirmed by the presence of high intensity band at 1100 cm\(^{-1}\) due to the presence of \( \text{SO}_3^- \) group in the styrene moiety\(^10\). A band at 630 cm\(^{-1}\) represents the C-S stretching frequency\(^10\). X-ray studies show the exchanger to be amorphous.

Thermogravimetric analysis shows an inflection point at \( \sim 145^\circ C \) which signifies the removal of water molecules corresponding to 12% weight loss\(^11\). The

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal ions</th>
<th>Amt. loaded (( \mu )g)</th>
<th>Amt. found (( \mu )g)</th>
<th>Error (%)</th>
<th>Solvent</th>
<th>Vol (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hg(II)-Ni(II)</td>
<td>Hg(II), 1404.2</td>
<td>1354.0</td>
<td>-3.5</td>
<td>1( M ) \text{NH}_4\text{Cl}</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni(II), 587.0</td>
<td>587.0</td>
<td>0.0</td>
<td>0.1( M ) \text{HClO}_4</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Hg(II)-Fe(III)</td>
<td>Hg(II), 1354.0</td>
<td>1304.0</td>
<td>-3.7</td>
<td>1( M ) \text{NH}_4\text{Cl}</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe(III), 293.0</td>
<td>293.0</td>
<td>0.0</td>
<td>1( M ) \text{HCl}</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>Ni(II)-Fe(III)</td>
<td>Ni(II), 469.6</td>
<td>484.3</td>
<td>+2.1</td>
<td>0.1( M ) \text{HClO}_4</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe(III), 195.3</td>
<td>195.3</td>
<td>0.0</td>
<td>1( M ) \text{HCl}</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Hg(II)-Pb(II)</td>
<td>Hg(II), 1604.8</td>
<td>1554.6</td>
<td>-3.1</td>
<td>1( M ) \text{NH}_4\text{Cl}</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb(II), 1450.4</td>
<td>1502.2</td>
<td>+3.5</td>
<td>0.1( M ) \text{HClO}_4</td>
<td>50</td>
</tr>
</tbody>
</table>
weight loss of 22% between 145°C and 520°C may be due to the decomposition of the organic part of the material. An abrupt loss of weight of 52% between 520°C and 630°C may be due to the rapid expulsion of oxygen, produced due to the condensation of phosphate to $P_2O_7$. A plateau is reached after 630°C, indicating the complete formation of the pyrophosphate phase. Based on the thermogravimetric and IR studies, the tentative formula of the compound is proposed as $[(ZrO_2)_2(WO_3)_3(C_8H_7SO_3H)(H_3PO_4)_6]nH_2O$.

The pH titration curves obtained under equilibrium conditions shown in Fig. 1 for LiOH / LiCl, NaOH/ NaCl and KOH / KCl systems indicate bifunctional behaviour of the material. It appears to be a strong cation exchanger as indicated by a low pH(~2.5) of the solution when no OH$^-$ ions were added. The bifunctional behaviour becomes prominent in the case of $H^+$.Na$^+$ and $H^+$.K$^+$ exchange. The theoretical ion exchange capacity in the case of these ions are found to be ~3.8 meq/g. However bifunctional behaviour is less prominent in the case of the $H^+$.Li$^+$ exchange. The ion exchange capacity in this case is found to be ~2.5 meq/g.

Distribution studies for fourteen metal ions, viz., Al$^{3+}$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Hg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Fe$^{3+}$ and Cd$^{2+}$ have been performed on SZWP in different media. On the basis of these studies, the material was found to be highly selective for Hg$^{2+}$ which is a polluting metal ion. The potential of this material has also been demonstrated by achieving some important separations such as Hg(II) - Ni(II), Ni(II) - Fe(III), Hg(II) - Fe(III) and Hg(II) - Pb(II). Table 2 illustrates the salient features of these separations.

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References