CHAPTER \- 5

Synthesis, characterization and application of a derivatized acidic salt of tetravalent metal: pyridine anchored onto tin (IV) tungstoselenate
INTRODUCTION

Among the various inorganic ion exchange materials of current importance, insoluble acidic salts of tetravalent metals (Zr, Ti, Sn) occupies a pivotal position. There is increasing interest in the improvement of ion exchange capacities and molecular specificities with higher selectivities towards various metal ions of this kind of materials. This can be achieved by the derivatization of ion exchange material with organic moieties bearing inorganic groups such -OH, -COOH, -SO3H, H2NR, HNR2 etc. which also act as an ion exchanger. These compounds are known as inorgano-organic ion exchangers or derivatized tetravalent metal acid salts (1-4). Interest in these materials stems from the fact that the inorganic matrix provides a stable and relatively inert anchor for the organic moiety. It will have advantages of both the counterparts in terms of thermal and chemical stability, ion exchange capacity and selectivity for certain metal ions. In layered materials the organic molecules are incorporated within the layers by increasing the inter layer distance so that large complexes could be exchanged whereas in non-layered materials the organic moieties get anchored, sorbed on the surface or get encapsulated within the pores of matrix. Intercalated materials prove to be vary useful in pillaring reaction (5-7), modification of the host’s optical properties, superconducting critical temperature, inter layer magnetic coupling and material design (8-10). Some recent and very interesting applications involve the use of these materials to modify electrode surfaces, in the preparation of low-dimensional conducting polymers and to assemble molecular multilayers at solid/liquid interfaces (11). A variety of non-bridged organic derivatives of tetravalent metals having general composition $\text{Zr(O}_3\text{PC}_5\text{H}_4\text{SO}_3\text{H})_x (\text{HPO}_3)_{2-x}$ have been reported (12). Zirconium phosphate is the most explored in organic molecule intercalation processes and various features of intercalation of n-alkyl mono-(13-15) di-(11,16) and aromatic (17,18) amines have been studied. The γ-titanium phosphate (19), α-titanium hydrogen phosphate (20) and titanium arsenate (21) have been selected for intercalation of amines. Recently o-chlorophenol has been anchored onto amorphous zirconium tungstate (22).
The present work has undertaken to study the derivatization of ion exchange material tin (IV) tungstoselenate by pyridine. The inorgo-organic material has been characterized in terms of SEM, FTIR, DTA and TGA. The utility has been explored by studying the uptake of some transition metal ions on this material.
EXPERIMENTAL

Materials

Tin (IV) chloride pentahydrate (Baker analyzed, USA), sodium selenite (BDH), sodium tungstate dihydrate (BDH) and pyridine (E.Merck) and all other chemicals were of analytical reagent grade. Demineralized water (DMW) was used throughout the experiment.

Synthesis of tin (IV) tungstoselenate (TTS)

The ion exchange material TTS was synthesized as described previously (23). A mixture of 0.05 M aqueous solution sodium selenite and sodium tungstate was gradually added to an aqueous solution of tin (IV) chloride (0.05M) in a ratio of 1:1:4. The pH was adjusted to zero by adding HCl and kept for 12 h at 25±2°C. The white gel was filtered off, washed several times with DMW and dried at 40±1°C. The material was broken down into small particles by immersing in DMW and converted to H⁺ form by treating it with 1M HNO₃ for 24 h at 25±2°C with intermittent shaking. The excess acid and nitrate ion was removed by repeated washing with DMW and finally dried at 40±1°C.

Preparation of pyridine derivative (TTS-Py)

The TTS-Py was prepared by shaking 2.5 g TTS in H⁺ form with 10 mmoles of aqueous solution of pyridine (0.1 M) in a temperature controlled shaker for 6 h at 30±1°C. It has been found experimentally that the extent of sorption does not increase beyond 6h at this temperature. The solid was filtered off, washed with DMW and air dried. The clear solution was titrated with standard HCl. The amount of pyridine sorbed onto TTS was determined as the difference between initial and final concentration of pyridine.
**Distribution studies**

The ion exchange behaviour of both TTS and TTS-Py for some transition metal ions was studied in DMW by batch method. The 0.2 g ion exchange material was equilibrated with 20ml of solution containing 0.02 mmoles of metal nitrate for 6 h of constant shaking at 30±1°C. the metal ion concentration in the residual solution was analysed using EDTA as a titrant. Distribution coefficient (Kd) were determined using the formula

\[ K_d = \frac{\text{mmoles of metal ions / g of exchanger}}{\text{mmoles of metal ions / ml of solution}} (\text{ml / g}) \]

**Uptake of metal ions on TTS-Py**

The uptake of some metal ions onto TTS-Py was attempted following the some procedure (batch method) as in distribution studies. The 0.2g of STS-Py was equilibrated with 20ml of aqueous solution of varying concentration (5×10^{-4}-5×10^{-3}M) of metal nitrate for 6h at 30±1°C.

Effect of pH on the uptake of metal ions was also studied by equilibrating 0.2g of TTS-Py with a constant amount (0.03mmoles) of each metal ion in acetate buffer solutions (20 ml) of varying pH values (3.0-5.5) for 6h at 30±1°C.

**Analytical procedure**

Electron microscopy (SEM) were performed on ground samples by LEO 435 VP microscope with attached imaging device. FTIR spectrum was recorded on samples pressed into KBr disc using Perkin Elmer 1730 spectrometer. The loss of mass determination and thermal behaviour of powdered TTS-Py upto temperature of 1000°C were obtain at a heating rate of 10°C min-1 in flowing N2 using a General V4.1C DuPont 2100 thermoanalyzer.
RESULTS AND DISCUSSION

TTS was prepared by the procedure described earlier (23) wherein the formula of this material was suggested as \([(\text{SnO}_2)_7 \ \text{HSeO}_3 (\text{HWO}_4)_{18}]_{45} \ \text{H}_2\text{O}\). TTS-Py compound was obtained by equilibrating 0.1M aqueous solution of pyridine with powdered TTS for 6h at 30±1°C. The amount of pyridine sorbed was estimated as 1.24 mmoles per g of TTS. On the basis of its chemical composition the mole ratio of TTS to pyridine was found to be 806.5:1.0, indicating a weak sorption onto the surface of TTS. The schematic representation of the sorption of the pyridine onto the surface of TTS can be shown as.

\[
\begin{array}{c}
\text{OH} + \text{N} \\
\text{TTS} \quad \text{Pyridine} \quad \text{TTS-Py}
\end{array}
\]

Pyridine has an excellent coordinating ability since the nitrogen atom is incorporated into a conjugated \(\pi\)-system hence a position is available for metal ions to coordinate easily. Thus a high selectivity TTS-Py for some transition metal ions is likely to be expected.

SEM photographs of TTS and TTS-Py at 440x and 120x magnifications are presented in fig 5.1. It has revealed the fact that TTS shows a plate like morphology. Upon the sorption of pyridine on TTS the morphology has been somewhat changed.

The IR spectra of TTS and TTS-Py samples have been shown in figs 5.2 and 5.3 respectively. A strong and broad peak appearing in the region 3500-3200 cm\(^{-1}\) ascribed to asymmetric and symmetric stretching vibration of water. A sharp peak in the region 1650-1600 cm\(^{-1}\) with a maximum at 1637 cm\(^{-1}\) was assigned to interstitial water. The peaks at 1176 cm\(^{-1}\), 1850 cm\(^{-1}\), and 709 cm\(^{-1}\) where assigned to metal oxygen bond (24). In the fig 5.3, the aromatic C-H vibrations are expected in the region 3100-2950 cm\(^{-1}\).
Fig. 5.1 SEM images (a) tin (IV) tungstoselenate (440 x magnification) (b) tin (IV) tungstoselenate-pyridine (120 x magnification)
Fig. 5.3 FTIR spectrum of tin (IV) tungstoselenate-pyridine
which were assumed to be overlapped with the band at 3500-3200 cm\(^{-1}\). The peaks at 1485 cm\(^{-1}\) and 1575 cm\(^{-1}\) may be due to C=C and C=N stretching vibrations while C-H deformation vibration occurs at 959 cm\(^{-1}\) (25). These confirmed the presence of pyridine in TTS-Py sample.

The thermogravimetry (TG) curve for TTS-Py (Fig 5.4) shows some distinct steps. In the first step, the mass loss of 4% was observed up to 90°-110°C that can be assigned to hydration water. This loss is indicated by a weak endothermic peak in the DTA curve (Fig 5.5). This is followed by a gradual loss of mass up to 400°C owing to the removal of water molecules formed by the condensation of OH groups and dissociation of -HSeO\(_3\) (26). In the third step pyridine was eliminated at the temperature ranges from 400°-490°C (27), accompanying a mass loss of 14.35%. It has been supported by a sharp exothermic peak with a maximum at 486°C in DTA curve. However, the last traces of pyridine were not removed until around 700°C. Actually some of pyridine carbonizes and deposits on the surface of TTS and therefore, a higher temperature was required to remove this carbon. The weight becomes constant beyond 700°C due to the formation of stable oxides of metal. Overall weight loss was observed 19.0%.

A comparison of distribution coefficient (K\(_d\)) values of Cu\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Fe\(^{3+}\) and Fe\(^{2+}\) on TTS and TTS-Py in DMW has been shown in table 5.1. It is interesting to note that a remarkable enhancement in K\(_d\) values of these transition metal ions on TTS-Py are observed. The high uptake may be due to the formation of coordination complexes with these transition metal ions by back-donation of non-bonding metal electrons into vacant acceptor antibonding \(\pi\) orbitals of pyridine ring TTS-Py (28).

The adsorption isotherm of Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{3+}\) and Fe\(^{2+}\) on TTS-Py was shown in Fig 5.5. It is evident from the table 5.2 and figure 5.6 that TTS-Py takes up Cu\(^{2+}\) more readily followed by Co\(^{2+}\), Ni\(^{2+}\), Fe\(^{2+}\) and Fe\(^{3+}\). The uptake of metal ions increase initially with the increase in loading and becomes constant beyond 8.0\(\times\)10\(^{-2}\) mmoles of loading except for Fe\(^{3+}\) in which uptake becomes constant at 6.0\(\times\)10\(^{-2}\) mmoles of loading. The pyridine was not eluted from TTS-Py during the uptake of metal ions. This provides evidence for insitu coordination of metal ions with the ligand (pyridine).
Fig. 5.4 TGA curve of tin (IV) tungsten selenate-pyridine
Fig. 5.5 DTA curve of In(IV) tungstoselenate-pyridine
Table 5.1  
K<sub>d</sub> values of metal ions on TTS and TTS-Py

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>TTS</th>
<th>TTS-Py</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>466.67</td>
<td>9900.00</td>
</tr>
<tr>
<td>Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>145.78</td>
<td>19900.00</td>
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<tr>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>114.74</td>
<td>19900.00</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>200.00</td>
<td>376.19</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>178.38</td>
<td>6566.67</td>
</tr>
</tbody>
</table>

Table 5.2  
Uptake of metal ions as a function of loading by TTS-Py

<table>
<thead>
<tr>
<th>Metal ions Loaded (m moles × 10&lt;sup&gt;-2&lt;/sup&gt; /0.2 g)</th>
<th>Uptake of metal ions (m moles × 10&lt;sup&gt;-2&lt;/sup&gt; /0.2 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2.00</td>
<td>1.98</td>
</tr>
<tr>
<td>3.00</td>
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</tr>
<tr>
<td>4.00</td>
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<td>6.00</td>
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<td>7.00</td>
<td>4.99</td>
</tr>
<tr>
<td>8.00</td>
<td>5.20</td>
</tr>
</tbody>
</table>
Fig. 5.6 Uptake of metal ions on as a function of loading by tin (IV) tungstoselenate-pyridine.
Table 5.3 Uptake of metal ions as a function of pH by TTS-Py

<table>
<thead>
<tr>
<th>pH of the solution</th>
<th>Metal ions loaded (mmoles × 10^{-2} /0.2 g)</th>
<th>Uptake of metal ions (mmoles × 10^{-2} /0.2 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu^{2+}</td>
</tr>
<tr>
<td>3.0</td>
<td>3.00</td>
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</tr>
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<td>3.5</td>
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<td>5.5</td>
<td>3.00</td>
<td>2.45</td>
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</table>
Fig. 5.7 Uptake of metal ions as a function of pH by tin (IV) tungstoselenate-pyridine
The uptake of $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ on TTS-Py was also studied as a function of pH and the results are presented in table 5.3 and fig 5.7. It was observed that the uptake of $\text{Cu}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$ and $\text{Fe}^{2+}$ is maximum in the pH range 3.5 to 4.5, beyond this pH it starts decreasing, whereas for $\text{Fe}^{3+}$ it increases sharply with increasing pH and attained a maximum value at pH 5.
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12. L.H. Kullberg, A. Clearfield, Solvent Extraction and Ion Exchange, 1989, 1, 527