CHAPTER V

COMPARISON OF THE ION-EXCHANGE BEHAVIOUR OF ZIRCONIUM, THORIUM, VANADIUM, URANIUM, STANNIC AND TITANIUM TUNGSTATES

Titanium tungstate (TiW) and its ion-exchange properties have been described previously\(^1\)-\(^3\), Amphlett\(^4\) has observed that the composition and the ion-exchange properties of amorphous zirconium phosphate depend on the conditions of preparation. We have therefore synthesized zirconium, uranium, stannic, thorium, and vanadium tungstates under conditions identical to those for titanium tungstate\(^2\). In this chapter we have made a comparative study of their properties.
EXPERIMENTAL

Reagents - Stannic chloride pentahydrate (Poland) was used. All other reagents were of 'AnalaR' grade.

Apparatus - Electric temperature controlled SICO shaker, Bausch and Lomb Spectronic 20 colorimeter, and Elico pH meter model LI-10 (India) were used for shaking, spectrophotometry and pH measurements.

Preparation of Ion-Exchange materials - The tungstates were synthesized under conditions given in Table XXI. The reagents were mixed at room temperature with continuous stirring and were allowed to stand for 24 hr at room temperature. The supernatant liquid was decanted, the gel filtered off, and washed with distilled water. The product so obtained was dried at 80°C. The dried product (≈ 40 g) was immersed in 100 ml of 1.0M nitric acid to remove the foreign ions adsorbed during the preparation. Very little exchanger dissolved during this process. Finally the exchangers were washed with demineralized water to remove excess acid and again dried at 80°C.
Ion-Exchange capacity - Ion-exchange capacity was determined by column operations as usual as given in Chapter II.

Composition - A 100 mg portion of the exchanger was dissolved in 25 ml of concentrated sulphuric acid. Tungsten was separated from tin, zirconium or uranium with benzoinoxime and estimated. Tin(IV) in the filtrate was determined volumetrically with dichromate. Zirconium and uranium were determined gravimetrically. The results are summarized in Table XXI.

Dissolution of Exchangers - The components of ion-exchange materials dissolved by water and 6M nitric acid were determined by the methods used earlier. Titanium and tungsten, tin, zirconium and uranium were estimated spectrophotometrically. The results are given in Table XXI.

pH-Titrations' - pH titrations were carried out by the method of Topp and Pepper. There is only one break in the titration curves so the exchangers are monofunctional.

Determination of Distribution Coefficients - Some distribution coefficients were determined by the method used before. The results are summarized in Table XXII.
<table>
<thead>
<tr>
<th>Ion-exchange material</th>
<th>Metal salt* M</th>
<th>Sodium-tungstate M</th>
<th>Volume ratio</th>
<th>Precipitation pH</th>
<th>Chemical composition W/M</th>
<th>Solubility g/l Water</th>
<th>Appearance of the dried material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium tungstate (ZrW)</td>
<td>0.3 ZrC</td>
<td>0.3</td>
<td>1:1</td>
<td>3.8</td>
<td>0.4</td>
<td>0.36 0.0 0.0 0.33 0.28</td>
<td>White opaque particles</td>
</tr>
<tr>
<td>Thorium tungstate (ThW)</td>
<td>0.3 ThN</td>
<td>0.3</td>
<td>1:1</td>
<td>0.8</td>
<td>-</td>
<td>- - - - -</td>
<td>Precipitate does not form. White opaque particles</td>
</tr>
<tr>
<td>Vanadium tungstate (VW)</td>
<td>0.3 VS</td>
<td>0.3</td>
<td>1:1</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>Dissolved completely</td>
</tr>
<tr>
<td>Uranium tungstate (UN)</td>
<td>0.3 UN</td>
<td>0.3</td>
<td>1:1</td>
<td>2.6</td>
<td>1.1</td>
<td>0.82 0.0 0.0 0.25 0.010</td>
<td>Yellow opaque particles</td>
</tr>
<tr>
<td>Stannic tungstate (SnW)</td>
<td>0.3Sn(IV)C</td>
<td>0.3</td>
<td>1:1</td>
<td>0.3</td>
<td>0.3</td>
<td>1.00 0.006 0.006 0.050 0.010</td>
<td>White shiny particles</td>
</tr>
<tr>
<td>Titanium tungstate (TiW)</td>
<td>0.3Ti(IV)C</td>
<td>0.3</td>
<td>1:1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.80 0.0 0.0 0.0 0.0</td>
<td>Lemon yellow shiny particles</td>
</tr>
</tbody>
</table>

*Zr = zirconyl; V = Vanadyl; U = Uranyl; C = Chloride; S = Sulphate; N = Nitrate
TABLE - XXII

Distribution coefficients for some metal ions on various tungstates in water (pH 5.3)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$10^{-2} x K_d$ value, ml/g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrW</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>3.0</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>13.0</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>7.0</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2.5</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>6.2</td>
</tr>
</tbody>
</table>
DISCUSSION

The thorium tungstate showed no ion-exchange behaviour and vanadyl tungstate dissolved when immersed in water, so only zirconium, uranium, stannic and titanium tungstates were examined in detail. The solubility in water and 6M nitric acid was found to increase with the difference in electronegativities between the two components of the exchanger.

Fig. 15 shows the effect of precipitation pH on the ion-exchange capacity of numerous ion-exchangers synthesized in our laboratory, both in earlier studies\textsuperscript{12-16} and in the present work. The precipitation pH is the pH of the reagent mixture before precipitation starts. In our earlier studies it varied from 0 to 10, and was adjusted in the case of titanium molybdate by adding sulphuric acid, of thorium tungstate by adding nitric acid, of tin hexacyanoferrate by adding sodium hydroxide, and of titanium antimonate and tungstate by adding ammonia solution. The precipitation pH of ion-exchangers which were synthesized for this work was 0.2.4, and was simply that of the mixture without further addition of acid or base. The amorphous gels obtained in this way do not show reproducible properties. It is therefore
Fig. 15 The effect of precipitation pH on the ion exchange capacity
Fig. 16 The effect of precipitation PH on the composition of ion exchangers.
surprising that even so there is the general trend that ion-exchange capacity increases with decrease in precipitation pH, exceptions probably being due to the non-reproducible nature of the gels formed.

Fig. 16 shows the effect of precipitation pH on the composition of the six exchangers. Only three of the 22 points plotted are against the general trend that as the precipitation pH increases the cation/anion ratio also increase. This appears understandable since at higher pH the cation is precipitated as a hydroxide while the anion remains in solution. The same explanation holds for stability in nitric acid increasing with increase in precipitation pH. The solubility behaviour in water is different from that in nitric acid because in the former case hydrolysis becomes the predominant factor. The apparently anomalous behaviour of titanium molybdate may be due to complex formation by titanium with the sulphuric acid used to adjust the pH.

An unusual and interesting feature of titanium tungstate is the negligible adsorption of tervalent ions such as Fe$^{3+}$, Al$^{3+}$ and In$^{3+}$. Other tungstates show complete adsorption of these ions. In view of this characteristic property and its high stability it can be more useful than other tungstate ion-exchange materials for the separation of tervalent from univalent and bivalent ions. Stannic tungstate has a very high capacity for Zn and therefore it can be used to separate Zn from numerous metal ions.
LITERATURE CITED