CHAPTER V
The analytical importance of synthetic inorganic ion exchangers is now firmly established due to their high selectivity, thermal stability and resistance to radiations. They are finding increasing use in the fields of medicine, energy resources recovery and pollution abatement. Therefore, the investigation of these materials has become a current field of research. A large number of insoluble salts of polybasic acids have been investigated as inorganic ion exchangers and have proved to be an excellent alternative to organic resins.

Unfortunately it is not yet possible to predict the properties of inorganic ion exchangers. An interesting attempt has been made to find an empirical relation between the chemical stability and the chemical structure of an ion exchanger[1]. According to this study the chemical stability of an inorganic ion exchanger depends upon the anion present and is in the following order,

molybdate < arsenate < selenate < antimonate < phosphate < tungstate.
Another important characteristic of an ion exchanger is its ion exchange capacity. It is therefore worthwhile to synthesize new inorganic ion exchangers and to determine their ion exchange capacities. For this purpose Fe(II) antimonate, Hg₂(II) antimonate, Ag(I) antimonate, Uranyl tungstate, basic tantalum sulphate and niobium tungstoarsenate were synthesized and their ion exchange capacities determined. The first three exchangers are based on common cations and may prove to be inexpensive. Uranyl phosphates have been systematically studied[2-4] but very little work has been done on Uranyl tungstates as ion exchange materials.

Oxides of tantalum and niobium are noted for their chemical inertness and hence their salts are expected to have good thermal and chemical stabilities. While reporting a detailed investigation on tantalum tungstate, Qureshi et. al. reported[5] some preliminary studies on basic tantalum sulphate as an ion exchange material. We have synthesized basic tantalum sulphate. It's anion exchange properties were found to be more interesting than its cation exchange properties.

The cation exchange behaviour of the salts of heteropoly acids and their derivatives is well known. It is an interesting feature of the heteropoly acid derivatives that their properties are different from those of the simple salts from which they are derived. Heteropoly tungstates have been used as catalysts for
the photochemical reduction of oxygen and water recently[6]. Various molybdophosphates, tungstophosphates and other heteropoly acid salts used as ion exchangers were reviewed by Pekarek and Vesely[7].

While studying the ion exchange properties of a variety of heteropoly acid salts the Van R. Smits group reported[8] the synthesis of ammonium-12-tungsto arsenate, \((\text{NH}_4)_3(\text{As} \cdot \text{W}_{12} \text{O}_{40}) \cdot \text{X H}_2\text{O}\) but found that it either dissolved or it formed a colloidal solution when used for absorption studies. Later on with some improvements the same material was reported to have a high cation exchange capacity and was found suitable for the separation of \(\text{Rb}^+, \text{Cs}^+, \text{K}^+, \text{Tl}^+\) and \(\text{Ag}^+[9]\). Tungsto arsenate salts were further improved by replacing the ammonium ions with organic base anions such as the pyridinium ion[10].

The exchanger pyridinium tungstoarsenate was found to be highly selective for \(\text{Ag}^+\) and \(\text{Cs}^+\). Heterogenous membranes of salts of tungsto arsenates of Rb(I) and Cu(II)[11] and Cs(I) and Tl(I) [12] were used as ion selective electrodes.

Extensive literature survey reveals that less attention has been paid to the development of niobium based exchangers and even lesser attention to its heteropoly acid derivatives. Woven and Ghizdov[13] synthesized heteropoly acid compounds of niobium such as niobio tungstosilicate, \(\text{H}_6(\text{Si} \cdot \text{W}_{10} \text{Nb}_2 \text{O}_{40})\) and the structure of the phase was established on the basis of its composition, IR and polarographic studies. Kato et. al[14] reported the synthesis of
niobium molybdophosphate and found that it was a suitable catalyst for the oxidation of unsaturated aldehydes. Though a considerable work has been reported on the polybasic acid salts of niobium such as phosphate, tungstate, arsenate, molybdate, antimonate and niobium hydroxide none of its heteropoly acid salts have been explored for its ion exchange properties so far. Niobium tungstoarsenate is expected to be a stable and selective ion exchange and hence these samples were synthesized under a variety of experimental conditions and their ion exchange capacities were determined.

Our studies on the synthesis and ion exchange properties of ferrous antimonate, silver antimonate, uranyl tungstate, basic tantalum sulphate and niobium tungstoarsenate are presented in this Chapter.

**EXPERIMENTAL**

**Synthesis of Ferrous antimonate:**

**Reagents:**

Ferrous ammonium sulphate (Sarabhai Chemicals, India), potassium pyroantimonate (Riedel, Germany), Dowex 50 WX8 (Na⁺), antimony pentachloride (BLH, Poole). All other reagents used were of AnalaR grade.
Procedure:

Antimonic acid was prepared as described earlier. 0.01M solutions ferrous ammonium sulphate and antimony pentachloride were prepared in 0.01M sulfuric acid and 4M hydrochloric acid respectively. Samples of ferrous antimonate were prepared using both antimonic acid and antimony pentachloride. Formic acid was added to prevent the oxidation of Fe$^{+2}$ ion during precipitation. The samples were then refluxed and were converted to H$^+$ form as described previously. The ion exchange capacities, determined as described earlier, are summarised in Table 20.

Synthesis of Silver Antimonate:

Reagents:

Silver nitrate (E Merck), Potassium pyroantimonate (Riedel, Germany), Dowex 50 W X8(Na$^+$ form). All other reagents used were of AnalaR grade.

Procedure:

0.01M antimonic acid was prepared as before. 0.1M solution of silver nitrate was prepared in 0.01M nitric acid.
Silver antimonate samples were obtained by mixing the two solutions in 1:2 ratio (silver nitrate : antimonic acid) at different pH values. The precipitate so obtained was allowed to stand for 24 hrs at room temperature. It was then refluxed with the mother liquor, filtered, washed and then dried at 40° - 50°C. The material was converted to the hydrogen form as before. Silver antimonate thus obtained was in the form of powder and was unsuitable for column operation.

**Synthesis of Uranyl tungstate:**

**Reagents:**

Uranyl nitrate (BDH, Poole), Sodium tungstate(BDH).

All other reagents used were of AnalaR grade.

**Procedure:**

0.05M, 0.1M and 0.3M solutions of Uranyl nitrate (were prepared in the corresponding concentrations of nitric acid) and Sodium tungstate were prepared. The solutions were mixed in different ratios at various pH values. The precipitates were then filtered and washed several times with distilled water. The samples were dried and were then converted to the hydrogen form as described earlier. The ion exchange capacities of the samples, determined as described before, are summarised in Table 20.
Synthesis of Basic tantalum sulphate:

Reagents:

Tantalum pentoxide (BnH, Poole), Potassium carbonate, Potassium nitrate and Sulfuric acid were of E. Merck. All other reagents used were of Analy grade.

Apparatus:

Real electric furnace (Real Scientific Corporation, Calcutta, India) to maintain the required temperature, platinum crucible for fusion purpose.

Procedure:

A new procedure for the dissolution of tantalum pentoxide was devised by Qureshi et al. [15] and is adopted here for the purpose. A mixture of well powdered tantalum pentoxide (1g), potassium nitrate (2.5 g) and potassium carbonate (2.5 g) in 15 ml platinum crucible was heated in a furnace at 740-760°C for 15 min. The temperature was carefully controlled as at higher temperature e.g. 840°C it gives a product insoluble in concentrated \( \text{H}_2\text{SO}_4 \). The cooled melt was then transferred to a borosilicate glass beaker with not more than 25 ml of concentrated \( \text{H}_2\text{SO}_4 \) and the contents of the beaker were heated on an electric
heater for 30 min. During this treatment brown fumes were evolved with vigorous effervescence. A clear solution was obtained in sulfuric acid. Following this procedure 10g of tantalum pentoxide was dissolved in 500 ml of concentrated sulfuric acid and diluted to 5 litres with distilled water, 50 ml of concentrated nitric acid was added and the solution was boiled for two hours. The precipitate so obtained was allowed to stand for 24 hrs at room temperature. It was then washed repeatedly with distilled water and dried at 60°C. The material broke down to small particles on immersion in water.

**Ion Exchange Capacity:**

For the determination of Ion exchange capacity 100 ml of 1M HCl was passed through a column packed with 0.5 g of the exchanger in sulphate form. The effluent was then collected and the sulphate ion concentration in it was determined volumetrically[16]. The anion exchange capacity was found to be 0.88 meq/g for Cl⁻.
Synthesis of Niobium tunstoarsenate:

Reagents:

Niobium pentoxide (BDH, Poole), Sodium tungstate (BDH), Sodium arsenate (J.T. Baker, USA) and Ammonium sulphate (BDH). All other reagents used were of AnalR grade.

Procedure:

13.291 g of Niobium pentoxide was heated with 400 ml of concentrated H₂SO₄ containing 135 g of Ammonium sulphate until a clear solution was obtained. The solution was then cooled and 200 ml of concentrated H₂SO₄ was added to make a 60% acid concentration. The solution was then diluted to 1 lit. with distilled water to give a 0.01M niobium solution. 0.1M solutions of sodium tungstate and sodium arsenate were prepared in distilled water. The solutions of sodium tungstate and sodium arsenate were mixed before adding them to niobium solution. The samples were prepared by mixing the solutions in different ratios and the pH was adjusted to 1 with Ammonia. The precipitates were then kept for 24 hrs. at room temperature, filtered and washed several times with distilled water. They were then dried at 60°C. Conversion to the H⁺ form was carried out as described earlier. Their ion exchange capacities are given in Table 20.
During the last fifteen years many new inorganic ion exchangers have been synthesized and their ion exchange properties have been studied. They have been found to be selective for some inorganic ions. It has also been observed that the selectivity of an ion exchanger can be varied by changing the conditions of preparation. In continuation of our systematic work on some new inorganic ion exchange materials a few preliminary studies have been carried out on the synthesis and ion exchange properties of Fe(II) antimonate, Ag(I) antimonate Uranyl tungstate, Basic tantalum sulphate and Niobium tungsto arsenate. The conditions for the synthesis of these ion exchangers are summarised in Table 20.

A study of the different factors such as the nature of the starting materials(e.g., substitution of antimonic acid for potassium pyroantimonate as a source of the antimonate ions) for the synthesis, the concentration of the solution of the starting materials, mixing ratios of the solutions, order of mixing of the parent reagents, precipitation pH, the chemicals used to maintain the precipitation pH(e.g. NH₄OH or NaOH) and refluxing the precipitates on the ion exchange capacity of the inorganic ion exchangers makes an interesting study.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Concentration of Reagents</th>
<th>Volume ratio (v/v)</th>
<th>Precipitation pH</th>
<th>Refluxing conditions</th>
<th>Appearance</th>
<th>I.E.C. (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>0.01M Ferrous ammonium-sulphate + 0.01M Antimonic acid</td>
<td>1:2</td>
<td>0</td>
<td>Unrefluxed</td>
<td>Greenish yellow particles</td>
<td>0.76</td>
</tr>
<tr>
<td>F-2</td>
<td>0.01M Ferrous ammonium sulphate + 0.01M Antimonic acid</td>
<td>1:2</td>
<td>0</td>
<td>Refluxed for 10 hrs. in mother liquor</td>
<td>Grey coloured</td>
<td>0.54</td>
</tr>
<tr>
<td>F-3</td>
<td>0.01M Ferrous ammonium sulphate + 0.01M Antimonic acid</td>
<td>1:2</td>
<td>3</td>
<td>Unrefluxed</td>
<td>Brown coloured</td>
<td>1.05</td>
</tr>
<tr>
<td>F-4</td>
<td>0.01M Ferrous ammonium sulphate + 0.01M Antimonic acid</td>
<td>1:2</td>
<td>3</td>
<td>Refluxed for 10 hrs. in mother liquor</td>
<td>Dark brown</td>
<td>0.96</td>
</tr>
<tr>
<td>F-5</td>
<td>0.01M Ferrous ammonium sulphate + 0.01M Antimony pentachloride</td>
<td>1:2</td>
<td>3</td>
<td>Unrefluxed</td>
<td>Brownish yellow</td>
<td>0.52</td>
</tr>
<tr>
<td>F-6</td>
<td>0.01M Ferrous ammonium sulphate + 0.01M Antimony pentachloride</td>
<td>1:2</td>
<td>3</td>
<td>Refluxed for 10 hrs. in mother liquor</td>
<td>Orange</td>
<td>0.44</td>
</tr>
<tr>
<td>S.No.</td>
<td>Concentration of Reagents</td>
<td>Volume ratio (v/v)</td>
<td>Precipitation pH</td>
<td>Refluxing conditions</td>
<td>Appearance</td>
<td>I.E.C. (meq/g)</td>
</tr>
<tr>
<td>-------</td>
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</tr>
<tr>
<td>S-1</td>
<td>0.01M Silver nitrate+ 0.01M antimonic acid</td>
<td>1:2</td>
<td>0</td>
<td>Refluxed for 10 hrs in mother liquor</td>
<td>Grey powder</td>
<td>-</td>
</tr>
<tr>
<td>S-2</td>
<td>0.01M Silver nitrate+ 0.01M antimonic acid</td>
<td>1:2</td>
<td>4</td>
<td>Refluxed for 10 hrs in mother liquor</td>
<td>Grey powder</td>
<td>-</td>
</tr>
<tr>
<td>S-3</td>
<td>0.01M Silver nitrate+ 0.01M Antimony pentachloride</td>
<td>1:2</td>
<td>2</td>
<td>Refluxed for 10 hrs in mother liquor</td>
<td>Grey powder</td>
<td>-</td>
</tr>
<tr>
<td>S-4</td>
<td>0.01M Silver nitrate+ 0.01M Antimony pentachloride</td>
<td>2:1</td>
<td>2</td>
<td>Refluxed for 10 hrs in mother liquor</td>
<td>Grey powder</td>
<td>-</td>
</tr>
</tbody>
</table>

F-1 - F-6 Ferrous antimonate samples; S-1 - S-4 Silver antimonate samples
(Table 20 contd.) **EXPERIMENTAL CONDITIONS FOR THE SYNTHESIS OF URANYL TUNGSTATE**

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>U-1</td>
<td>0.05M</td>
<td>0.05M</td>
<td>1:1</td>
<td>1</td>
<td>Yellow</td>
<td>0.30</td>
</tr>
<tr>
<td>U-2</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1:1</td>
<td>1</td>
<td>Yellow</td>
<td>0.20</td>
</tr>
<tr>
<td>U-3</td>
<td>0.1M</td>
<td>0.1M</td>
<td>2:1</td>
<td>1</td>
<td>Yellow</td>
<td>0.23</td>
</tr>
<tr>
<td>U-4</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1:2</td>
<td>1</td>
<td>Yellow</td>
<td>0.20</td>
</tr>
<tr>
<td>U-5</td>
<td>0.1M</td>
<td>0.1M</td>
<td>2:1</td>
<td>2</td>
<td>Yellow</td>
<td>0.22</td>
</tr>
<tr>
<td>U-6</td>
<td>0.1M</td>
<td>0.1M</td>
<td>2:1</td>
<td>3</td>
<td>Yellow</td>
<td>0.40</td>
</tr>
<tr>
<td>U-7</td>
<td>0.1M</td>
<td>0.1M</td>
<td>2:1</td>
<td>4</td>
<td>Yellow</td>
<td>0.44</td>
</tr>
<tr>
<td>U-8</td>
<td>0.3M</td>
<td>0.3M</td>
<td>1:1</td>
<td>1</td>
<td>Yellow</td>
<td>0.16</td>
</tr>
<tr>
<td>U-9</td>
<td>0.3M</td>
<td>0.3M</td>
<td>1:1</td>
<td>2</td>
<td>Yellow</td>
<td>0.42</td>
</tr>
<tr>
<td>U-10</td>
<td>0.3M</td>
<td>0.3M</td>
<td>1:1</td>
<td>3</td>
<td>Yellow</td>
<td>0.46</td>
</tr>
<tr>
<td>U-11</td>
<td>0.3M</td>
<td>0.3M</td>
<td>1:1</td>
<td>4</td>
<td>Yellow</td>
<td>0.48</td>
</tr>
</tbody>
</table>

(\(\text{\textit{w}}\) added to \(\text{\textit{U}}\))

| U-12 | 0.3M              | 0.3M                 | 1:1               | 4                | Yellow     | 0.25          |

(\(\text{\textit{U}}\) added to \(\text{\textit{w}}\))
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N-111</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1 : 1 : 1</td>
<td>1</td>
<td>1.04</td>
<td>0.98</td>
</tr>
<tr>
<td>N-112</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1 : 1 : 2</td>
<td>1</td>
<td>1.17</td>
<td>1.24</td>
</tr>
<tr>
<td>N-121</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1 : 2 : 1</td>
<td>1</td>
<td>1.16</td>
<td>1.23</td>
</tr>
<tr>
<td>N-122</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1 : 2 : 2</td>
<td>1</td>
<td>1.21</td>
<td>1.76</td>
</tr>
<tr>
<td>N-144</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1 : 4 : 4</td>
<td>1</td>
<td>1.41</td>
<td>-</td>
</tr>
<tr>
<td>N-211</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>2 : 1 : 1</td>
<td>1</td>
<td>0.99</td>
<td>0.94</td>
</tr>
<tr>
<td>N-411</td>
<td>0.1M</td>
<td>0.1M</td>
<td>0.1M</td>
<td>4 : 1 : 1</td>
<td>1</td>
<td>1.02</td>
<td>0.75</td>
</tr>
<tr>
<td>NTA*</td>
<td>0.1M Niobium pentachloride</td>
<td>0.1M</td>
<td>0.1M</td>
<td>1 : 1 : 1</td>
<td>1</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

(a) Samples whose pH was adjusted with Ammonia
(b) Samples whose pH was adjusted with sodium hydroxide
Effect of the nature of the starting materials:

The conventional method of precipitation with potassium pyroantimonate for the preparation of antimonates of various metals gave products which were unsuitable for column operation. During systematic studies on the ion exchange properties of antimonates prepared with antimononic acid it was found that the materials exhibit better mechanical strengths, attain a larger particle size and show an increase in the ion exchange capacity as compared to the materials obtained from potassium pyroantimonate. Such an investigation was extended to Fe(li) antimonate. It yielded samples with higher ion exchange capacities compared to the samples prepared by using potassium pyroantimonate and antimony pentachloride. We have attempted to synthesize niobium tungstoarsenate samples using tungstooarsenic acid in place of sodium tungstoarsenate. However, there was little success in our efforts to synthesise tungstooarsenic acid by traditional methods. Further investigations are to be carried out to find an alternative method for the synthesis of tungstooarsenic acid and use it as one of the parent reagents for the synthesis of niobium tungstoarsenate.

Effect of the Concentrations of the mixing solutions:

In the case of Uranyl tungstate the samples obtained from 0.05M and 0.1M solutions of the parent reagents were in the form of greenish yellow opaque particles with low ion exchange
capacities. As the concentration of the reagents was increased to 0.3M the samples obtained were yellow shiny particles with higher ion exchange capacities. 0.01M concentration of Fe(II), Ag(I) and antimonic acid solutions were used for the preparation of all the samples of Fe(II) and Ag(I) antimonates. Our previous experience on antimonates showed that the samples obtained are more suitable for column operations when the concentrations of the mixing reagents are lowered. 0.1M concentrations of niobium, tungstate and arsenate solutions were used for the preparation of all the samples of niobium tungsto arsenate. While synthesizing the insoluble salts of niobium (e.g., Niobium phosphate) it was observed that the samples obtained with 0.1M concentrations of the reagents exhibited better ion exchange properties compared to the samples prepared with higher concentrations of the reagents.

Effect of the mixing ratios and the order of mixing of the parent reagents:

In the case of uranyl tungstate and Niobium tungsto arsenate there was a gradual improvement in the physical properties (e.g., cracking) and the ion exchange capacity of the samples with increase in the metal-anion ratio. An increase in the volume ratio of sodium tungstate and sodium arsenate
solutions resulted in either colloidal solutions or gave a material which dissolved at pH 1. There was not much difference in the ion exchange capacities however.

It is interesting to note the variability exhibited by the samples following the order of mixing of the parent reagents. The samples prepared by adding the solution of sodium tungstate dropwise to a solution of uranyl nitrate showed higher capacities while the samples prepared by adding uranyl nitrate solution dropwise to a solution of sodium tungstate showed lower capacities. Mixing ratios of 1:2(M:Sb) for Fe(II) antimonate, 1:1 (M:W) for uranyl tungstate and 1:2:2 (Nb:W:As) for Niobium tungsto arsenate were found to give good samples with higher ion exchange capacities.

**Effect of precipitation pH and the nature of the bases used to maintain the precipitation pH:**

The ion exchange capacity of Fe(II) antimonate increases with increase in the precipitation pH for the samples prepared with antimonial acid. In the case of Uranyl tungstate the samples obtained were greenish yellow opaque materials at low precipitation pH values and exhibited little cracking on immersion in water. The samples showed improved physical properties and mechanical strengths with an increase in the precipitation pH. When precipitated at higher pH values shiny particles were obtained.
which cracked significantly on immersion in water. Ion exchange capacities are higher for these samples. A precipitation pH of 4 was found to be suitable for the Uranyl tungstate synthesis. Two types of niobium tungstenarsenate samples were prepared. The conditions for the synthesis of the two types were identical in all respects except that in one case NH₄OH was used to maintain the precipitation pH at 1 while in the other case sodium hydroxide was used for this purpose. The precipitates obtained by adjusting the precipitation pH with sodium hydroxide were difficult to filter and produced samples with very small particle size. Sample S-144 dissolved when the pH was adjusted with NaOH to 1. The samples were grey in colour and opaque. They showed little cracking on immersion in water. However there was a remarkable improvement in the physical properties and mechanical strengths of the samples when the precipitation pH was adjusted with ammonium hydroxide. The samples were white shiny particles which broke down vigorously on immersion in water. The precipitate of sample S-144 could also be obtained when the precipitation pH was adjusted with ammonium hydroxide whereas it dissolved with the addition of sodium hydroxide.

Inspite of the fact that there exists a drastic difference in physical properties of the two types of the samples there is little difference in their ion exchange capacities.
Effect of refluxing the precipitates:

The ion exchange capacities of the refluxed samples were always less in the case of Fe(II) antimonate samples compared to the unrefluxed ones. This was attributed to the surface area of the unrefluxed samples. Ag(I) antimonate was obtained in the form of a powder and remained in the powder form even after refluxing the precipitates with the mother liquor. Hence no further studies could be carried out on this material.

Basic tantalum sulphate is a white hard glassy material and possesses an anion exchange capacity of 0.88 meq/g. It hydrolyses in water and may show anion exchange properties in acidic and nonaqueous media. Infact in concentrated nitric acid and concentrated sulphuric acid it dissolves to a very small extent. Further refluxing this material with nitric acid may prove to be useful and this aspect is to be studied.

Detailed studies are to be carried out on all these ion exchange materials synthesized above to make a full use of their ion exchange potentialities.
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