CHAPTER IV
Most of the work on inorganic ion exchangers has been done on zirconium phosphate type materials. The antimonates, arsenates, oxides and other insoluble salts of multivalent metal ions have been found useful for many difficult separations. It was first recognised by Kraus that the sulphides of Cd(II), Ag(I), Fe(II), Cu(II), Zn(II), Pb(II) and As(III) have favourable adsorption properties and they can be used as adsorbents for metal ions which form more insoluble sulphides\([1,2]\). The reactions of various heavy metal ions with cadmium sulphide showed that when dilute (e.g., tracer) or concentrated (e.g., 1M) solutions of silver, copper or mercury nitrates with or without supporting electrolyte (\(\text{NaNO}_3, \text{HNO}_3\)) were passed through columns of cadmium sulphide quantitative removal of the ions from the solution was obtained\([2]\).

A survey of the literature shows that prior to the systematic work of Kraus some preliminary studies were reported on the adsorption properties of Zirconium sulphide\([3]\). Sulphides of Ag(I), Fe(II), Cu(II), Zn(II), Pb(II), Cd(II), Ni(II), As(III) and Sb(V) have also been studied as ion exchange materials\([4-11]\). Later on Qureshi and coworkers studied the adsorption properties of Sn(IV)
sulphide[12]. However as far as could be ascertained from the literature no systematic work has been reported on antimony sulphide. In this chapter are given the results of the studies on antimony sulphide as an inorganic ion exchanger.
**EXPERIMENTAL**

**Reagents:**

Antimony pentachloride (BDH, Poole, England), Sodium sulphide (Flakes, India) and all other reagents used were of reagent grade.

**Apparatus:**

Bausch & Lomb Spectronic-20 spectrophotometer, Phillips pH meter, Perkin-Elmer spectrophotometer were used.

**Synthesis of Hydrous Antimony Sulphide:**

Hydrous antimony sulphide (HAS) was prepared by mixing 0.1M SbCl$_5$ in 4M HCl and 0.5M sodium sulphide solutions in volume ratio 1:2 respectively. HAS was precipitated in an orange-reddish colour from the highly acidic mixture. It was then allowed to settle down and was subjected to refluxing in the mother liquor for 6 hours. The precipitate was filtered under a reduced pressure of 25-30 Kg/Cm$^2$ and washed with different concentrations of hydrochloric acid and finally with demineralised water. The washed precipitate was dried at 40-60°C. It broke down into small granules with immersion of the dried sample in water. The antimony sulphide was thus obtained in two phases. The $\gamma$-phase which was
in white colour and in the form of fine powder was removed with continuous washing with DMW. The \( \beta \)-phase was orange in colour with a particle size of 50-200 mesh. It was then converted to the \( \text{H}^+ \) form using 0.1M HNO\(_3\).

**Ion Exchange Capacity:**

The ion exchange capacity was determined by the column method \[13\]. 0.5g of the exchanger in the hydrogen form was packed in a column with a glass wool support. The packed column was washed with distilled water. The hydrogen ions were then eluted with 1M solution of sodium nitrate. The effluent was collected at a rate of 15-20 drops/min. It was about 200 ml. The liberated \( \text{H}^+ \) ions were titrated against a standard sodium hydroxide solution. The ion exchange capacity was found to be 0.66 meq/g for Na\(^+\) ions.

**Chemical Composition:**

0.5 g of the sample was heated with the fusion mixture (1.5 g of \( \text{NaNO}_3 \) and 1.5 g \( \text{Na}_2\text{CO}_3 \)) and the melt was dissolved in water. After reduction antimony was determined using the pyrogallol method\[14\]. The sulphur was oxidized with HNO\(_3\) and was determined as \( \text{BaSO}_4 \) gravimetrically\[15\]. The mole ratio of Sb to S was found to be 1.86.
Chemical Stability:

0.2 g of the sample was shaken in a number of mineral acid solutions for 6 hours and the antimony was determined spectrophotometrically[16]. Sulphur was determined titrimetrically[17].

IR Spectrum:

It was recorded by the KBr disc method, and the data are given in Table 17.

Distribution Coefficients:

The distribution coefficients (Kd) for some of the cations were determined by the batch process in DMW. Kd values were calculated using the equation,

\[
Kd = \frac{I - F}{F} \times \frac{50}{0.2} \text{ ml/g.}
\]

where I is the initial volume of EDTA consumed by the solution, \( F \) the final volume of EDTA consumed after equilibration. All the cations were estimated by titrations with EDTA[18]. The results are given in Table 18.
Separations:

For separation studies a 50 cm glass column with a 0.6 cm diameter was used. 1.5 g of the exchanger in the $H^+$ form was packed in the column with a glass wool support. A solution of metal ions was then transferred to the column and was passed through at a slow rate and the process of recycling was carried out. The elution of metal ions was started after 30 minutes of loading. The flow rate was maintained at 1 ml/min. throughout the elution process. Metal ions in 10 ml fractions were then collected and determined titrimetrically with EDTA. The results are summarised in Table 19.
RESULTS AND DISCUSSION

A number of samples were prepared with different mixing ratios of antimony pentachloride and sodium sulphide. However, the sample of HAS under study was found best regarding the mechanical stability, particle size and other column operation qualities. The composition results indicate that the mole ratio of Sb in the material is higher than that of S. This may be due to the hydrolysis of antimony pentachloride besides the formation of the sulphide because the acidity of antimony solution changes upon the addition of sodium sulphide solution. The change in acidity leads to the formation of hydrolysed antimony sulphide and therefore the precipitate so obtained is designated as hydrous antimony sulphide.

The Infrared data (Table 17) of HAS show maxima at 3100 cm⁻¹, 1580 cm⁻¹, 1230 cm⁻¹ and at 940 cm⁻¹ which correspond to the deformation vibration of the coordinated water ((H₂O) Co-ord), deformation vibration of interstitial water and of hydroxyl groups [δ₂(H₂O) int and (OH)], deformation vibration of M-OH groups [δ₃(Sb-OH)] and stretching vibrations of M-S [γ₁(Sb-S)] respectively. A very small peak appears at 780 cm⁻¹ which corresponds to the stretching vibration of M-O[γ₂(Sb-O)] bonds. This study supports the contention that the material is not only the sulphide of antimony but it is hydrous antimony sulphide.
<table>
<thead>
<tr>
<th>Band (cm(^{-1}))</th>
<th>Intensity</th>
<th>Specific group vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100</td>
<td>S, B</td>
<td>(\delta_1) (\text{H}_2\text{O}) (deformation vibration of Co-ord. (\text{H}_2\text{O}))</td>
</tr>
<tr>
<td>1580</td>
<td>S, B</td>
<td>(\delta_2) (\text{H}_2\text{O}) and OH (deformation vibration of interstitial (\text{H}_2\text{O}) and OH).</td>
</tr>
<tr>
<td>1230</td>
<td>S, Shp</td>
<td>(\delta_2) M-OH (deformation vibration of M-OH)</td>
</tr>
<tr>
<td>940</td>
<td>M, Shp</td>
<td>(\gamma_1) Sb-S (Stretching vibration of Sb-SO)</td>
</tr>
<tr>
<td>780</td>
<td>W, B</td>
<td>(\gamma_2) Sb-O (Stretching vibration of Sb-O)</td>
</tr>
</tbody>
</table>

S : Strong; M : Medium; W : Weak; B : Broad; Shp : Sharp
Heat treatment of the samples at various temperatures shows that HAS loses its total ion exchange capacity at 350°C.

The distribution coefficients for some metal ions in DMW were determined and are presented in Table 18. The $pK_{sp} (-\log K_{sp}, K_{sp} = solubility\ product)$ of the corresponding metal sulphides are also shown in the same table and a plot of $pK_{sp}$ vs log Kd in Fig. 17 is also given. Kd values in DMW vary with the $pK_{sp}$ values i.e. the Kd value increases with increase in the $pK_{sp}$ value. Mg(II), Ca(II), Sr(II) and Ba(II) have low Kd values because they form water soluble sulphides. This behaviour of HAS reveals that the uptake of the ion from water is mainly through adsorption. Therefore the ions whose sulphides have high $pK_{sp}$ values form highly stable precipitates during adsorption over the surface of HAS. The low uptake of the ions whose sulphides are soluble is mainly due to the ion exchange process.

It is clear from Table 18 that the material shows the highest preference for the Hg(II) ion. The separation factors ($Q_{M}^{Hg}$) for Hg(II) with respect to other ions have been calculated and listed in Table 19. A number of metal ion pairs with Hg(II) have been separated successfully.

It is clear from the above that hydrous antimony sulphide can be used for the removal of an important pollutant i.e. Hg(II) from polluted water. Further work is necessary for the characteri-
Fig. 17 - A plot of $\log kd$ vs $pk_{sp}$ for metal ions on Hydrous Antimony Sulphide
Table 18 DISTRIBUTION COEFFICIENTS FOR SOME METAL IONS IN DMSO ON HAS AND $pK_{sp}$ VALUES OF THEIR CORRESPONDING SULPHIDES

<table>
<thead>
<tr>
<th>Cation</th>
<th>$K_d$ value (ml/g)</th>
<th>$pK_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>55.20</td>
<td>-</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>68.00</td>
<td>-</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>92.00</td>
<td>-</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>88.60</td>
<td>-</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>160.00</td>
<td>15.15</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>182.00</td>
<td>18.40</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>194.80</td>
<td>26.72</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>208.00</td>
<td>27.00</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>264.60</td>
<td>28.29</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>10917.00</td>
<td>53.00</td>
</tr>
</tbody>
</table>
Table 19  
**SEPARATION FACTOR ($q_{Hg}^{Hg}$) OF Hg$^{2+}$ ION WITH RESPECT TO OTHER METAL IONS ON HAS IN DM**

<table>
<thead>
<tr>
<th>Separated pair</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{Mg}^{Hg}$</td>
<td>197.90</td>
</tr>
<tr>
<td>$q_{Ca}^{Hg}$</td>
<td>160.40</td>
</tr>
<tr>
<td>$q_{Sr}^{Hg}$</td>
<td>118.60</td>
</tr>
<tr>
<td>$q_{Ba}^{Hg}$</td>
<td>124.00</td>
</tr>
<tr>
<td>$q_{Mn}^{Hg}$</td>
<td>68.19</td>
</tr>
<tr>
<td>$q_{Fe}^{Hg}$</td>
<td>59.94</td>
</tr>
<tr>
<td>$q_{Co}^{Hg}$</td>
<td>56.02</td>
</tr>
<tr>
<td>$q_{Ni}^{Hg}$</td>
<td>52.44</td>
</tr>
<tr>
<td>$q_{Cd}^{Hg}$</td>
<td>41.32</td>
</tr>
</tbody>
</table>
zation of HAS and for studying the mechanism of adsorption of the various ions.
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