Studies on Synthetic Inorganic Ion Exchangers: Part VII—Quantitative Separations of Binary Mixtures of Manganese(II) with Magnesium(II), Barium(II) & Cadmium(II) & of Binary Mixture Nickel(II)-Copper(II) on Stannic Arsenoantimonate Columns

PRITAM S THIND* & SUSHEEL K MITTAL
Department of Chemistry, Guru Nanak Dev University, Amritsar 145005

Received 15 December 1982; accepted 7 February 1983

Stannic arsenoantimonate, having Sn:As:Sb ratio of 5:5:1 and cation-exchange capacity of 0.90 meq/g is being introduced as a new inorganic ion exchanger. It is fairly stable in water and dilute solutions of acids and bases. Ion distribution studies on sixteen metal ions have been carried out on this gel in aqueous and non-aqueous systems. The following mixtures have been separated: Mg\(^{2+}\) & Mn\(^{2+}\), Ba\(^{2+}\) & Mn\(^{2+}\), Cd\(^{2+}\) & Mn\(^{2+}\) and Ni\(^{2+}\) & Cu\(^{2+}\).

Recently heteropoly acid salts have received much attention as synthetic inorganic ion exchangers as these show different ion exchange properties and selectivity in comparison to simple salts. The good performance of stannic arsenate\(^9\) and stannic antimonate at elevated temperatures and their thermal stability make them promising for the ion exchange work at higher temperatures. Inspired by this, we report in this note our successful efforts to synthesize thermally stable stannic arsenoantimonate, which has been used in the separations of title binary mixtures of bivalent metal ions.

All the reagents used were of AR grade.

Five samples of stannic arsenoantimonate were prepared by mixing 0.1 \(M\) solutions of sodium arsenate (J.T. Baker) and potassium pyroantimonate (BDH) with 0.1 \(M\) solution of stannic chloride pentahydrate (POCH, Poland) in the volume ratio 1:1.2. The required \(pH\) of the solution was adjusted by adding either nitric acid or sodium hydroxide solution. The hot gel was stirred for 30 min. The precipitate obtained filtered off, washed with demineralized water of \(pH\) 6 and dried at 60 C. The dried product broke down into small granules when immersed in water. The material was converted into \(H^+\)-form by treatment with 0.1 \(M\) nitric acid for 24 hr with occasional shaking and intermittently changing the acid. The product was washed free of acid with demineralized water and dried at 60 C.

The ion exchange capacities of the samples of stannic arsenoantimonate were determined as follows:

The \(H^+\)-form ion exchanger (1 g) was taken in a glass column having glass wool support. Column after washing with demineralized water was eluted with 1.0 \(M\) sodium nitrate solution, collecting the effluent (400 ml) at a rate of 10-12 drops/min. Liberated \(H^+\) ions were titrated against standard sodium hydroxide solution. On the basis of its better exchange capacity, lower solubility and higher yield as compared to other samples prepared, sample-2 was selected for a detailed study.

The sample-2 was dissolved in conc. hydrochloric acid (A R). Tin was estimated: in acidic solution gravimetrically by cupferron\(^1\), and antimony and arsenic in the filtrate were estimated gravimetrically as antimonous pyrogallate\(^1\) and iodimetrically\(^1\), respectively. The results of chemical analysis show the ratio of Sn:As:Sb in sample-2 as 5:5:1.

It is observed that the exchangers prepared at different \(pH\) values have different exchange capacities varying from 0.84 to 1.3 meq/g. The ion exchange capacity increases from 0.84 to 1.06 meq g as the \(pH\) changes from 0 to 2. The sample prepared at high temperature of mother liquor has low capacity compared to the one prepared at room temperature. This is probably due to the fact that initially a number of phases are present in ion exchange material and on heating, this material becomes homogeneous. All the five samples are chemically stable in water as well as in dilute acids and bases.

Ion exchange capacity (meq/g) of sample-2 for different metal ions was found to be as follows: Li\(^+\) 0.50; Na\(^+\) 0.90; K\(^+\) 0.69; Mg\(^{2+}\) 0.97; Ca\(^{2+}\) 0.92; Sr\(^{2+}\) 0.89; and Ba\(^{2+}\) 0.79, indicating decrease in exchange capacity with increase in ionic radii of the alkaline earth cations. Further the exchange capacity with bivalent cations is comparatively more than that with monovalent cations. Stannic arsenoantimonate can be regenerated and used again without suffering much decrease in capacity.

Ion exchange capacity of stannic arsenoantimonate increases with increase in temperature from 60 to 200 C and thereafter it decreases. Exchange capacity of stannic arsenate increases only upto 100 C and thereafter it decreases while the exchange capacity of stannic antimonate decreases with increase in temperature.

Sample-2 exhibited in its IR spectrum bands at 3300, 1600 and 1100 cm\(^{-1}\) assignable to \(v_1(H_2O\) or OH), \(\delta_1(H_2O)\) and \(\delta_2(OH)\) respectively. Sample-2 changes its colour on heating and becomes hard, probably due to the loss of interstitial water molecules. This fact is
further supported by the infrared studies. The bands at 3300 and 1600 cm\(^{-1}\) start diminishing as the drying temperature is increased and completely disappear at 800 \(^\circ\)C.

Potentiometric titrations performed by added salt method\(^1\)\(^4\), indicate that stannic arsenoantimonate exhibits monofunctional behaviour for sodium and potassium while bifunctional behaviour for lithium (Fig. 1). Lithium having smaller ionic radius as compared to potassium and sodium is able to enter the exchanger matrix, thus easily replacing both the protons.

On the basis of chemical analysis, TG and IR studies, the following formula may be tentatively proposed for the material: \((\text{SnO}_2)\_x(\text{H}_3\text{AsO}_4)\_y(\text{H}_3\text{SbO}_4)\_z\cdot n\text{H}_2\text{O}\). The number of water molecules \((n)\) was determined from the thermogram of the sample-2 using Alberti formula: \(18n = x(M + 18n)/100\), where \(x\) = per cent mass loss in exchanger. \(n\) is the number of external water molecules and \(M\) is the molecular weight of the exchanger without water molecules. If it is assumed that all external water is removed at 200 \(^\circ\)C, which corresponds to a mass loss of \(\sim 21\%\), the value of \(n\) comes out to be \(\sim 22\).

The distribution coefficients \((K_d)\) of 16 metal ions for sample-2 were determined as usual by batch process in demineralized water (DMW), acetic acid, DMSO and dioxane. The metal ions were determined in the solution volumetrically using EDTA\(^1\)\(^5\). The following formula was used for determining \(K_d\) values:

\[
K_d = \frac{I - F}{F} \times \frac{v}{M} \text{ ml g}^{-1}
\]

where \(I\) = initial concentration of the metal ion in solution, \(F\) = final concentration of the metal after equilibrium, \(v\) = the total volume of the solution (ml) and \(M\) = the weight of the exchanger (g). The order of selectivities of various cations in different solvents is:

- DMW: \(\text{Th}^{4+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}\)
- Acetic acid: \(\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Al}^{3+} > \text{Mn}^{2+} > \text{Nd}^{3+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{La}^{3+} \approx \text{Mg}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Hg}^{2+} > \text{Sr}^{2+}\)
- DMSO: \(\text{Al}^{3+} > \text{Cu}^{2+} > \text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+} > \text{Th}^{4+} > \text{Zn}^{2+} > \text{La}^{3+} > \text{Nd}^{3+} > \text{ZrO}^{2+} = \text{UO}_2^{2+}\)
- Dioxane: \(\text{Sr}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Th}^{4+} > \text{La}^{3+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}\)

On the basis of selectivity sequence in aqueous medium, a series of separations can be achieved. Table 1 shows the binary separations achieved using glass column (0.69 cm int. diam.) and 1.0 cm of exchanger bed, with details of amount of the metal ions loaded and recovered alongwith % error in each case. These separations are quantitative and rapid as compared to organic ion exchange resins. All the cations involved in separation are recovered in less than 20 ml of effluent in each case.

### Table 1 - Separations of Some Binary Mixtures of Bivalent Metal Cations on Stannic Arsenoantimonate (Sample-2)

<table>
<thead>
<tr>
<th>Binary</th>
<th>Eluents</th>
<th>Vol. of effluent (ml)</th>
<th>Cations ((\mu)g)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixtures</td>
<td></td>
<td></td>
<td>Taken</td>
<td>Found</td>
</tr>
<tr>
<td>Mg(^{2+}) + Mn(^{2+})</td>
<td>0.005 M NaNO(_3)</td>
<td>10</td>
<td>565</td>
<td>581</td>
</tr>
<tr>
<td>0.01 N HNO(_3)</td>
<td>20</td>
<td>2060</td>
<td>1950</td>
<td>-5.3</td>
</tr>
<tr>
<td>Ba(^{2+}) + Mn(^{2+})</td>
<td>0.025 M NaNO(_3)</td>
<td>18</td>
<td>4807</td>
<td>4464</td>
</tr>
<tr>
<td>0.1 N HNO(_3)</td>
<td>10</td>
<td>2060</td>
<td>2019</td>
<td>-2.0</td>
</tr>
<tr>
<td>Cd(^{2+}) + Mn(^{2+})</td>
<td>0.025 M NaNO(_3)</td>
<td>12</td>
<td>3653</td>
<td>3821</td>
</tr>
<tr>
<td>0.1 N HNO(_3)</td>
<td>12</td>
<td>2403</td>
<td>2280</td>
<td>-5.1</td>
</tr>
<tr>
<td>Cu(^{2+}) + Ni(^{2+})</td>
<td>0.1 N HNO(_3)</td>
<td>12</td>
<td>1382</td>
<td>1461</td>
</tr>
<tr>
<td>0.025 M NaNO(_3)</td>
<td>10</td>
<td>1100</td>
<td>998</td>
<td>-9.3</td>
</tr>
</tbody>
</table>

### References
6 Pekarek V & Vesely V, Talanta, 19 (1972) 1245.