Synthesis and Ion Exchange Properties of Sodium Stannosilicate: A Silver Selective Inorganic Ion Exchanger

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(Received September 9, 1989)

An inorganic ion exchanger sodium stannosilicate has been synthesized. Its composition, chemical and thermal stabilities and ion exchange properties have been studied. This material is obtained as hard granules and is very stable at high temperatures. Its ion exchange capacity for Ag^+ is 2.25 mequiv g^{-1}. The material shows high selectivity towards Ag^+ which has been separated quantitatively from Pb^{2+}, Hg^{2+}, and Cu^{2+}. Recovery of Ag^+ from dilute solutions has also been studied.

The use of synthetic inorganic ion exchangers is successfully being developed for the selective separation of a number of metal ions. New materials are being synthesized[1—4] to solve such specific problems. There is a revived interest towards the ion exchange properties of silicates.[5—9] Zeolites have been extensively studied for its ion exchange properties particularly by Barrer.[10] Desai and Baxi have studied ion exchange properties of tin silicate.[6]

The present paper reports the synthesis, chemical composition, chemical and thermal stabilities, and ion exchange properties of sodium stannosilicate, an analogue of the zeolites. This material shows higher exchange capacity and is more stable at high temperatures than tin silicate prepared at pH 8.5. The distribution ratios for different metal ions have revealed that the exchanger is specific towards Ag^+. K_d values for other metal ions are also higher for sodium stannosilicate than those for tin silicate. The utility of this material has been studied for the separation of Ag^+ from other metal ions and its recovery from dilute solutions.

Experimental

Reagents: Tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) (Reachim) and sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) (Loba) were used. All other chemicals used were of A. R. grade.

Apparatus: An electric temperature controlled SICO shaker and Bausch and Lomb spectronic-20 (U.S.A.) were used for shaking and spectrophotometric determinations respectively. Elico pH meter model Li-10 (India) was used for pH measurements.

Preparation of Sodium Stannate Solution: Sodium stannate ($Na_2SnO_3 \cdot 3H_2O$) was prepared by mixing 0.5 M sodium hydroxide solution ($1 M = 1 mol dm^{-3}$) to 0.1 M tin(IV) chloride solution.[11] The pH was adjusted to 10 by adding sodium hydroxide solution. The solution initially turbid, turned into a clear solution of sodium stannate on heating at 60 °C.

Synthesis of Sodium Stannosilicate: Sodium stannosilicate was synthesized by mixing 0.1 M sodium metasilicate solution with 0.1 M sodium stannate solution in 1 : 1 volume ratio. The yield of sodium stannosilicate in other mixing volume ratios was very low. Therefore 1 : 1 volume ratio was chosen for synthesis. The resulting mixture was refluxed for 24 hours. The white precipitate obtained was allowed to settle overnight, washed with distilled water and dried at 60 °C. The dried product was immersed in distilled water when it broke down easily into small granules. It was washed several times with distilled water and then dried in an air oven at 60 °C.

Cation Exchange Capacity: Ion exchange capacity for H^+ ion was determined by taking sodium stannosilicate in H^+ form and then eluting with 1.0 M sodium nitrate solution. Metal ion capacity was determined by shaking 1.0 g of the exchanger with 50 ml 0.1 M aqueous solution of metal nitrate at 25 °C and titrating the metal ion left in the supernatant liquid.

Chemical Stability: The chemical stability of sodium stannosilicate was studied in different solvents. For this purpose 100 mg of the exchanger was shaken with 25 ml of the appropriate solvent for 6 hours at 25 °C. The amount of silica released in the supernatant liquid was determined by a standard colorimetric method.[12]

Chemical Composition: A 200 mg portion of sodium stannosilicate was dissolved in 200 ml solution containing 15 ml of sulfuric acid and 100 ml of hydrochloric acid. Tin in this sample was reduced by zinc powder and determined iodometrically.[13] For the determination of silicon a 200 mg portion of the exchanger was heated in 200 ml solution containing 100 ml of hydrochloric acid. Silicon was precipitated as silicic acid. It was ignited in a platinum crucible and weighed as SiO_2.[14]

Thermal Stability: Sodium stannosilicate (0.5 g) was weighed in different silica crucibles and dried at different temperatures in a muffle furnace for 2 hours. Exchange capacity for Ag^+ was determined for the products dried at 60, 100, 150, 200, and 250 °C. Weight loss was also calculated at the respective temperatures.

Hydrolysis: Sodium stannosilicate was taken in H^+ and Na^+ forms. The exchanger (0.5 g) was shaked with 25 ml of distilled water at 25 °C for different time intervals. The pH of the supernatant liquid was measured after each time-interval.

Water Sorption: Sodium stannosilicate (1.0 g) in different ionic forms was equilibrated with 20 ml of distilled water for 1 hour at 25 °C. Sodium stannosilicate was then separated from water and weighed in a stoppered weighing bottle. It was then dried over a dessicant in vaccum at 60 °C and reweighed. Amount of water sorbed by sodium stannosilicate was calculated from the difference between the wet weight and dry weight.

IR Analysis: IR spectrum of the material dried at 60 °C was obtained using KBr disc technique on an IR-20 spectrometer.

Distribution Coefficients: Sodium stannosilicate (0.5 g) was shaken with 50 ml of 0.02 M solution of the metal nitrate for 6 hours at 25 °C. The supernatant liquid was titrated for the determination of metal ion left. Silver was determined by titration with 0.02 M KSCN solution. All other cations were determined by titration with 0.02 M solution of EDTA. The K_d values of these ions were determined in aqueous solution.

Distribution coefficient values for a number of metal ions on sodium stannosilicate were calculated from the relationship

$$K_d = \frac{I-F}{F} \times \frac{V}{W}.$$

Where I and F are initial and final volumes of titrant before and after equilibration. V is volume of the metal ion solution and W is weight of the exchanger.

Column Separations: A glass column (length 45 cm, diameter 0.39 cm) was filled to a height of 14 cm with 2.0 g of the exchanger on a glass wool support. The column was washed with 10 bed volumes of distilled water. The aqueous mixture solution (10 ml) containing the metal ions to be separated was passed onto the column at a slow rate. The column was again washed with distilled water. The metal ions were then eluted by passing a suitable eluent. The eluent was passed at a flow rate of 0.2 ml min^{-1}. The metal ions in 10 ml fractions of effluent were collected and determined titrimetrically.

Recovery of Ag^+: Uptake of Ag^+ by sodium stannosilicate was studied from silver nitrate solution of different concentrations. Sodium stannosilicate (0.5 g) was shaked with 50 ml of silver nitrate solution at 25 °C for 6 hours. The supernatant liquid was titrated for the determination of Ag^+ left.

Uptake of Ag^+ from solutions containing sodium ion was also studied. Sodium stannosilicate (0.5 g) was added to 50 ml of 0.02 M silver nitrate solution containing equal amounts of sodium nitrate and shaked for 6 hours at 25 °C. The supernatant liquid was titrated for the determination of Ag^+ left.

Results and Discussion

From the results given in Table 1 it can be inferred that sodium stannosilicate works as an extremely weak cation exchanger and releases a small amount of hydrogen ions. The metal ion capacity is sufficiently high and varies from 0.8 to 2.25 mequiv g^{-1}.

Table 2 shows the stability of sodium stannosilicate in different solvents. The values in the table show that sodium stannosilicate can be used in nearly neutral media i.e. water, salt solutions, alcohols, dilute acids, and alkali without any appreciable loss. The results of thermal stability show that there is a slight (3.7%) weight loss at 100 °C and 8.12% weight loss at 150 °C; no further weight loss is observed up to 250 °C. The maximum capacity for Ag^+, however, remains contant throughout the temperature range studied. These

Table 1. Exchange Capacity of Sodium Stannosilicate

Serial No.	Cation	Exchange capacity mequiv g^{-1}
1	H^+	0.23
2	Ag^+	2.25
3	Mg^{2+}	0.80
4	Ca^{2+}	1.00
5	Cu^{2+}	1.20
6	Co^{2+}	0.90
7	Mn^{2+}	1.00
8	Hg^{2+}	1.44
9	Pb^{2+}	1.20
10	Cd^{2+}	1.10

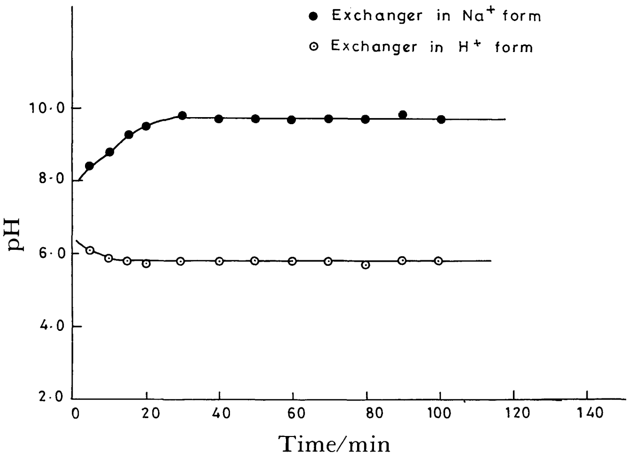

Fig. 1. Hydrolysis curves for sodium stannosilicate.

Table 2. Chemical Stability of Sodium Stannosilicate in Different Solvents[a)]

Serial No.	Solvent	Amount of silica released (mg/25 ml)
1	Distilled water	0.00
2	Nitric acid, 0.1 M	0.127
3	Hydrochloric acid, 0.1 M	0.127
4	Sulfuric acid, 0.1 M	0.165
5	Ethanol	0.00
6	Sodium acetate, 1 M	0.00
7	Sodium hydroxide, 0.1 M	0.185
8	Sodium nitrate, 1 M	0.00
9	Sodium citrate, 1 M	0.00

a) Amount of sodium stannosilicate taken=100 mg.

results suggest that only hydration water is released by heating up to 150 °C and no structural changes take place.

The chemical analysis of the exchanger sodium stannosilicate shows that the apparent ratio of Sn : Si is 1 : 1. The results of hydrolysis plotted in Fig. 1 show that sodium stannosilicate hydrolyses appreciably. When sodium stannosilicate is in Na^+ form there is a gradual increase in pH for up to 30 minutes, thereafter, pH remains almost constant. On the other hand, when sodium stannosilicate is in H^+ form there is very small, gradual decrease in pH for up to 15 minutes; no further change in pH is observed after 15 minutes. The results of water sorption presented in Table 3 show that water sorption of sodium stannosilicate decreases with increasing radius (crystallographic) of the counter ion.

It is quite evident from the IR spectrum plotted in Fig. 2 that the material contains water molecule and metal oxygen bond as is fully discussed below. The structure of sodium stannosilicate is a complicated one like some silicates with other metal ions. An indication of possible structure may be discussed in the light of IR spectrum of the compound. The IR spectrum of the material shows four bands at 3300, 1640, 990, and 700 cm^{-1} regions. In a sample of pure water a strong band is observed at 1630 cm^{-1} and two very strong bands around 3500 cm^{-1}. In the spectrum of the exchanger the band at 3300 cm^{-1} is very strong which can be attributed to O–H stretching frequency. A medium band around 1640 cm^{-1} can be attributed to H–O–H bending band. The O–H stretching bands merge together and is shifted to lower frequency in the spectrum of the exchanger. This is due to possiblity of hydrogen-bonding. In a neat sample of sodium metasilicate there is a very strong and very broad O–H stretching band around 3280 cm^{-1} region and a very strong band around 980 cm^{-1} region due to Si–O stretching frequency. In the spectrum of the exchanger the band around 990 cm^{-1} region can be attributed to Si–O stretching frequency. Since this band is much broader, it can be attributed to Si–O–Si continuous structure. In the spectrum of the exchanger the band around 700 cm^{-1} can be attributed to Sn–O–Sn bridging system.

On the basis of chemical composition and IR analysis the exchanger may be given an apparent formula

$$Na_x(SnO_2)_y(SiO_2)_y \cdot zH_2O$$

Table 3. Water Sorption on Sodium Stannosilicate in Different Ionic Forms

Serial No.	Counter ion	Ionic radius Å	Water sorbed (g/g)
1	Li^+	0.68	0.4910
2	Na^+	0.98	0.4700
3	K^+	1.33	0.4154
4	Rb^+	1.49	0.3240

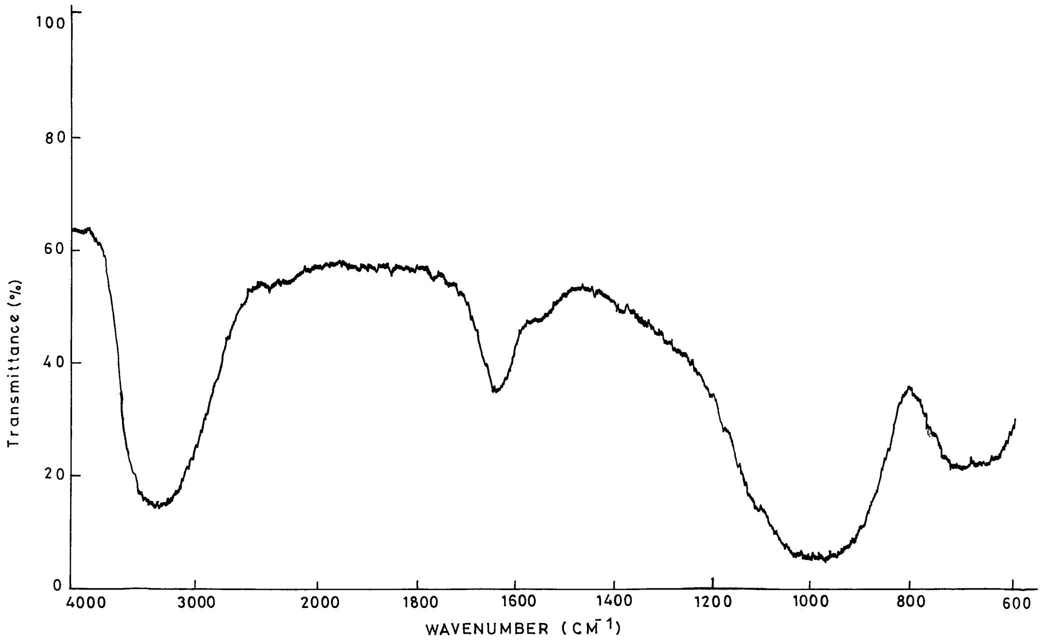

Fig. 2. IR Spectrum of sodium stannosilicate.

Table 4. K_d Values for Some Metal Ions on Sodium Stannosilicate

Serial No.	Metal ion	K_d Values ml g^{-1}	Serial No.	Metal ion	K_d Values ml g^{-1}
1	Mg^{2+}	57.14	6	Cu^{2+}	109.09
2	Ni^{2+}	61.54	7	Cd^{2+}	110.00
3	Co^{2+}	75.00	8	Pb^{2+}	133.33
4	Mn^{2+}	83.33	9	Hg^{2+}	400.00
5	Ca^{2+}	90.91	10	Ag^{2+}	3400.00

Table 5. Uptake of Ag^+ by Sodium Stannosilicate from Silver Nitrate Solution of Different Concentrations

Serial No.	Concentration of $AgNO_3$ solution	Volume of solution ml	mequiv of Ag^+	Uptake of Ag^+ mequiv/0.5 g
1	0.2 M	20	4.0	1.125
2	0.15 M	20	3.0	1.125
3	0.1 M	20	2.0	1.125
4	0.05 M	20	1.0	T.U.[a]
5	0.02 M	20	0.4	T.U.
6	0.01 M	20	0.2	T.U.

a) T.U.; Total uptake of Ag^+.

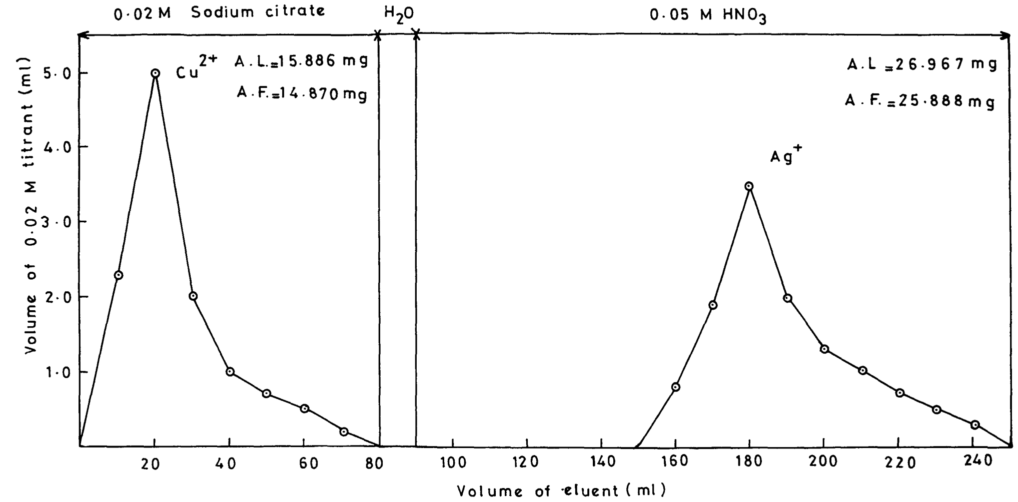

Fig. 3. Separation of Ag^+–Cu^{2+}.
A.L.=Amount loaded, A.F.=amount found.

where z is number of moles of water of hydration.

The distribution coefficient values given in Table 4 suggest the exchanger sodium stannosilicate to be specific for Ag^+. This substance may provide a good method for separation of Ag^+ from other metal ions. Based on K_d values the affinity of different metal ions for the exchanger is

$$Ag^+ > Hg^{2+} > Pb^{2+} > Cd^{2+} > Cu^{2+} > Ca^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+}.$$

Some quantitative separations were achieved on a column of sodium stannosilicate. The order and the eluents are presented in Figs. 3, 4, and 5. These results suggest sodium stannosilicate a useful means of separating Ag^+ from Cu^{2+}, Pb^{2+}, and Hg^{2+} and other fields where the removal of Ag^+ is important.

The results given in Table 5 show that from very dilute solutions, total uptake of Ag^+ is resulted provided that total Ag^+ content of the solution is less than the maximum capacity of sodium stannosilicate. The results of uptake of Ag^+ from solutions containing sodium ion show that the selectivity for Ag^+ is so high that uptake of Ag^+ is not affected by the presence of sodium. This shows the importance of sodium stannosilicate in the recovery of precious metals.

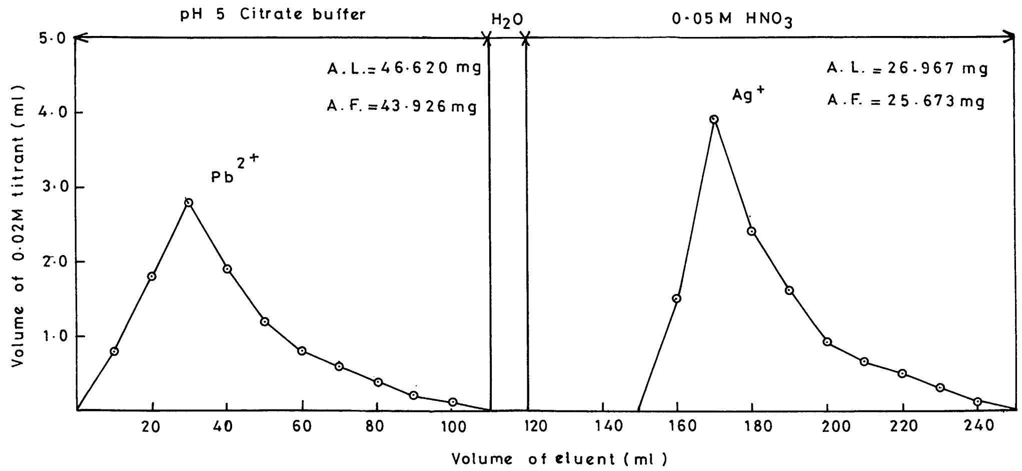

Fig. 4. Separation of Ag^+–Pb^{2+}.
A.L.=Amount loaded, A.F.=amount found.

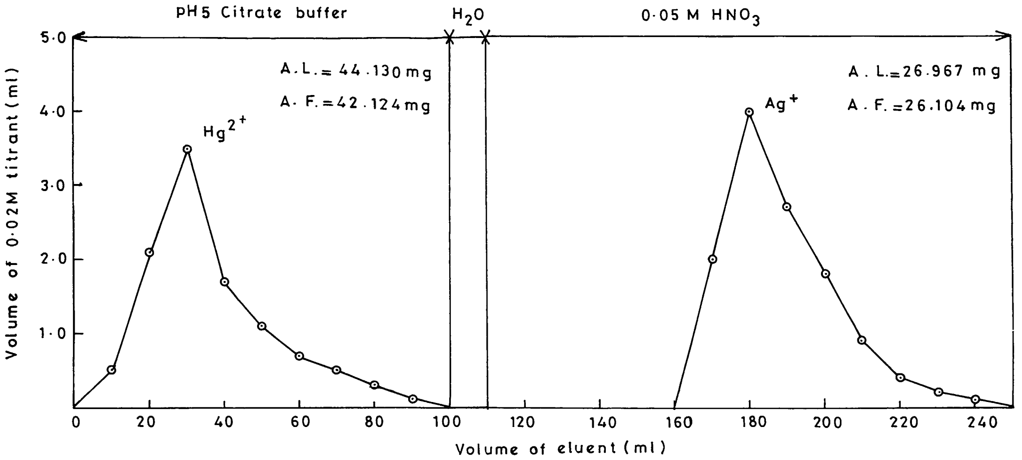

Fig. 5. Separation of Ag^+–Hg^{2+}.
A.L.=Amount loaded, A.F.=amount found.

The authors are thankful to Professor S. A. A. Zaidi, Chairman, Department of Chemistry, AMU, Aligarh for providing research facilities.

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