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Synthetic Inorganic Ion-exchange Materials. XXXX. Ion Exchange Properties of Tin(IV) Antimonate for Alkaline Earth and Transition Metal Ions and Its Application to Metal Separations

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Ion-exchange selectivities of alkaline earth and transition metal ions on tin(IV) antimonate cation exchanger were investigated in nitric acid media. The selectivity sequences were found to be; $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$ for alkaline earth metal ions and $Ni^{2+}<Mn^{2+}<Cd^{2+}<Co^{2+}<Cu^{2+}<Zn^{2+}$ for transition metal ions. The separation factors for neighboring pairs on the exchanger gave larger values than those on the ion-exchange resin of a strong acid type. The effective separations of Mg^{2+}-Ca^{2+}, Sr^{2+}-Ba^{2+}, and Na^{+}-Cs^{+}, Sr^{2+} have been achieved with a small column (5cm×0.5 cm i.d.).

The synthesis and ion-exchange properties of inorganic materials have been studied extensively by many workers.[1—4] Some inorganic ion-exchangers showed an excellent selectivity for a certain element or group of elements in the presence of large amounts of other components.

Phosphates of quadrivalent metals, such as zirconium and titanium, have been studied extensively by several workers.[5] Quadrivalent metal antimonate ion-exchangers were studied by Abe and Ito.[6] Tin(IV) and titanium(IV) antimonates (SnSbA and TiSbA) behaved as cation exchangers with relatively high capacities, and showed unusual selectivities for alkali metal ions in the order: $Na^{+}<K^{+}<Rb^{+}<Cs^{+}\ll Li^{+}$ on SnSbA,[7] and $Na^{+}<K^{+}<Rb^{+}<Li^{+}<Cs^{+}$ on TiSbA,[8] which are not included in Eisenman's selectivity series.[9] Thermal and chemical stabilities, and the selectivities of various metal antimonates for a number of metal ions have also been reported by Qureshi and co-workers.[10] The ion-exchange behavior of tin(IV) antimonate prepared by metathesis of $SnCl_4$ and $H[Sb(OH)_6]$, has been studied by Mathew and Tandon.[11] It has been known that the ion-exchange properties including the selectivities of inorganic ion-exchangers depend much on their preparative conditions. Especially, SnSbA with relatively high molar ratio of Sb/Sn up to 2.0 showed an excellent selectivity for lithium ions and could be applied to the removal of lithium ions from a large amount of sodium ions in solutions, such as seawater and hydrothermal water.[12]

This paper describes the ion-exchange properties of SnSbA for alkaline earth metal ions and its applications to chromatographic separations.

Experimental

Preparation of SnSbA. Suitable conditions were chosen so that the highest selectivity for lithium ions may be obtained.[7] The preparation procedure is as follows. A 62 cm³ of liquid antimony(V) chloride was prehydrolyzed with an equal amount of demineralized water in order to prevent fractional precipitation of antimonic acid during the further procedures. The resultant 4 M (M=mol/dm³) antimony (V) chloride solution was mixed with a 4 M tin(IV) chloride solution of 80 cm³ at 80 °C. The mixed solution was hydrolyzed immediately in a 50-fold volume of demineralized water at 60 °C. The white precipitate obtained was kept in the mother solution at 60 °C overnight, then filtered and washed with water using a centrifuge (10000 min⁻¹) until the pH value of the supernatant solution was higher than 1.5. After drying at 60 °C, the product was ground and sieved to 100—200 mesh size. The collected samples were rewashed with water to remove adherent fine particle of SnSbA, and finally dried at 60 °C.

The characterization and identification of the SnSbA were carried out by powdered X-ray diffraction analysis with Ni-filtered Cu-*Kα* radiation with a JEOL Model JDX-7, by IR spectra using a KBr technique with a Nihon Bunko Model 701G spectrometer, and by thermal analysis with a Rigaku Denki Thermoflex Model 8001.

Chemical Composition of the SnSbA. The composition was determined as reported previously.[7]

pH Titration Curves. The pH titration curve of the ion exchanger is one of its important characteristic properties. The character of the ion exchanging groups can be estimated from the pH titration curve as well as the ion-exchange capacity. A weighed amount (0.10 g) of the sample was immersed in 10.0 cm³ of a mixed solution of varying ratio of $\{M(NO_3)_n+KOH\}$ or $\{M(NO_3)_n+HNO_3\}$ adjusted to an ionic strength of 0.1 with intermittent shaking at 30±0.5 °C. After the attainment of equilibrium, the pH of the supernatant solution was measured with a Toa model HM-5B pH meter. The amounts of the uptake of the metal ions were calculated from the difference in the metal ion concentration relative to the initial concentration in the solution.

Distribution Coefficient, K_d. The equilibrium K_d values of the metal ions were determined by a batch technique. The SnSbA was immersed in 10.0 cm³ of a solution containing the metal ions of 10^{-4} M and nitric acid of different concentrations. The concentration of the metal ions in the exchanger and solution was deduced from the concentration relative to the initial concentration in the solution. The concentrations of metal ions were determined by flame photometry or atomic absorption spectrometry with a Varian Techtron 1100. The K_d values were calculated as follows:

$$K_d=\frac{\text{amount of metal ions in exchanger}}{\text{amount of metal ions in solution}}\times\frac{\text{cm}^3\text{ of solution}}{\text{g of exchanger}}$$

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Reagents. Antimony(V) chloride (>99.9% as metal, Yotsuhata Chemical Co. Ltd.) and tin(IV) chloride (Wako Chemical Co. Ltd.) were used without purification. The solutions of transition metal ions were prepared by dissolving the pure metals (>99.99%) in a nitric acid solution at a suitable concentration. Other reagents used were all of analytical grade.

Results and Discussion

Preparation of the SnSbA. The SnSbA obtained was identified by X-ray diffraction analysis, thermal analysis and IR spectra. The results showed a good agreement with those of our previous work.[7] The crystallite size of the SnSbA was found to be 41 Å by using the Scherrer's equation from a plane (110).[13]

Chemical Composition of the SnSbA. The Sb/Sn molar ratio in the SnSbA was found to be 1.88, which is similar to the previous results.[7]

The water content was determined from the weight loss of the heated sample at 950 °C, by assuming that the sample is finaly transformed to a mixture of α- and β-Sb_2O_4, and SnO_2 (cassiterite).[14]

The empirical formula of SnSbA can be given as;

$$SnO_2\ 0.94Sb_2O_5\ 4.95H_2O.$$

pH Titration Curves. A typical example of the pH titration curves is illustrated in Fig. 1. The pH titration curve of the SnSbA showed weak dibasic acid behavior, which is almost the same as reported in the previous work for alkali metal ions.[7] The uptake of strontium ions increased on increasing the pH of the solution, and is higher than that of lithium or potassium ions in the entire range studied. The ion-exchange sites in the SnSbA may be overlapping with different strength of the acidic sites. The uptakes of lithium and potassium ions on the exchangers were consistent to the amount of hydrogen ions liberated from the exchangers (Fig. 1), indicating that the dissolution of the exchangers was negligible within experimental error.

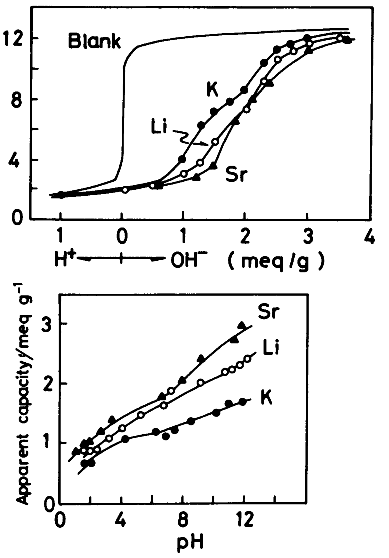

Fig. 1. pH Titration curves and apparent capacities of SnSbA.
Soln; $\{M(NO_3)_n+HNO_3\}$ or $\{M(NO_3)_n+M(OH)_n\}$ with ionic strength of 0.1, total voume; 10.0 cm^3, ion-exchanger; 0.10 g, temp; 30±0.5 °C.

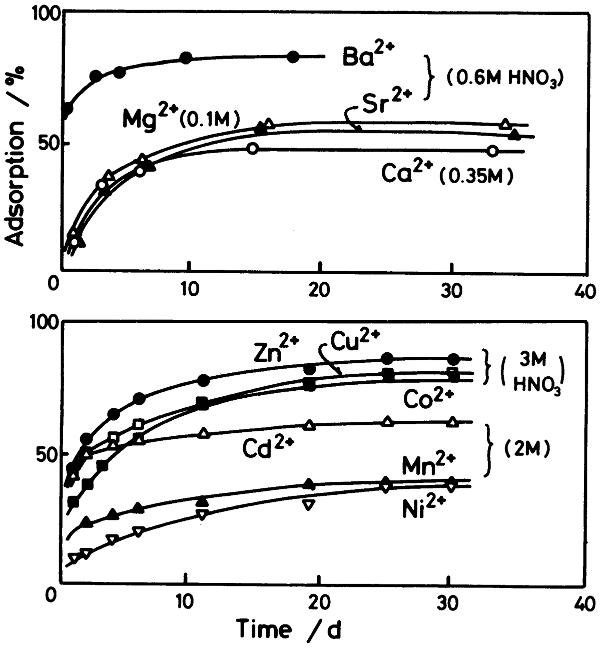

Fig. 2. Time dependence of adsorption of different metal ions on SnSbA.
Initial concn. of metal ions; 10^{-4} M, ion-exchanger; 0.10 g, total volume; 10.0 cm^3, temp; 30±0.5 °C.

Distribution Coefficient, K$_d$. The time dependence on adsorption of the different metal ions was studied in order to determine the equilibrium distribution coefficient (Fig. 2). The ion-exchange equilibrium of alkali metal ions-H^+ (except Li^+–H^+) on SnSbA was attained within 24 h, while that of Li^+–H^+ was about 10 d as reported previously. The reaction with alkaline

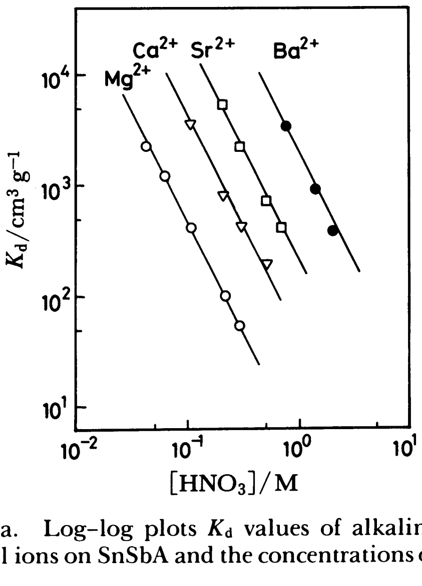

Fig. 3-a. Log-log plots K_d values of alkaline earth metal ions on SnSbA and the concentrations of nitric acid.
Initial concn. of metal ions; 10^{-4} M, ion-exchanger; 0.250 g, total volume; 25.0 cm^3, temp; 30±0.5 °C.

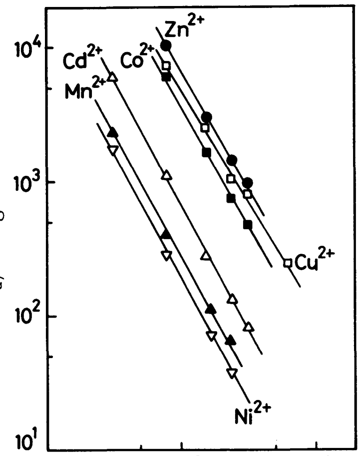

Fig. 3-b. Log-log plots of K_d values of transition metal ions on SnSbA *vs.* concentration of nitric acid. Initial concn. of metal ions; 10^{-4} M, exchanger; 0.250 g, total volume; 25.0 cm^3, temp; 30±0.5 °C.

earth or transition metal ion /H^+ was extremely slow, about 20—30 d being required for equilibrium.

The K_d values of alkali metal ions on the SnSbA showed almost the same values (except Li^+) as those on the sample (Sb/Sn ratio of 1.6) hydrolyzed at 100 °C, while the K_d values (2.2×10^4 in 0.1 M HCl) of Li^+ was lower than that (6.6×10^4) reported previously.[7] However, the selectivity sequence of alkali metal ions, $Na^+<K^+<Rb^+<Cs^+\ll Li^+$, agreed with the previous results.[7] The K_d values of alkaline earth and transition metal ions on a SnSbA are given in Figs. 3-a and 3-b, as log-log plots of K_d *vs.* [HNO$_3$]. The slope, d log K_d/d log [HNO$_3$], was about −2, indicating ideal "1:2" ion-exchange reaction. The selectivity sequence showed: $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$, giving the same sequence of increasing crystal ionic radii of alkaline earth metals, as is obtained on organic ion-exchange resins of strong acid type. The K_d values and separation factors ($\alpha=K_{dB}/K_{dA}$), for a neigboring pair, are summarized in Table 1, where values from other ion-exchangers are shown for comparison. The sequence on the SnSbA is the same as that reported by Qureshi *et al.*[10] However, the separation factors for neigboring pairs of alkaline earth metal on the SnSbA are much larger than those obtained on strong acid type resins or the tin antimonate obtained by Qureshi *et al.*[10] The sequence, $Mg^{2+}<Ba^{2+}<Ca^{2+}<Sr^{2+}$, on tin antimonate prepared by Mathew and Tandon.[11] is the same as that obtained on the crystalline antimonic(V) acid which shows extremely high K_d values for Ca^{2+}, Sr^{2+} and Cd^{2+}.[14] The selectivity sequence for transition metal ions on the SnSbA, $Ni^{2+}<Mn^{2+}<Cd^{2+}<Co^{2+}<Cu^{2+}<Zn^{2+}$, is different from those on the tin antimontate prepared by Qureshi *et al.*[10] From data reported by Qureshi *et al.*, the slopes of d log K_d/d pH for transition metal ions, calculated by this author, do not show 2, even in a range of pH 0—1. In general, the K_d values also depend on the metal ion loading on the exchanger. The difference in the selectivity may be due to the difference of the loading and preparation of two exchangers. From data reported by Mathew and Tandon[11] and Qureshi *et al.*,[10] the extrapolated K_d values of bivalent metal ions to 1.0 M HNO$_3$ concentration were smaller

TABLE 1. K_d VALUES AND SEPARATION FACTORS(α) OF ALKALINE EARTH AND TRANSITION METAL IONS ON DIFFERENT EXCHANGERS

Exchanger	ions											
		Mg		Ca		Sr		Ba				
SnSbA	K_d	1.9×10^1		1.9×10^2		7.0×10^2		2.1×10^4				
(1M HNO$_3$)	α		10		3.7		30					
AG 50W-X8[a]	K_d	7.1×10^1		1.13×10^2		1.46×10^2		2.71×10^2				
(1M HNO$_3$)	α		1.6		1.3		1.9					
Tin antimonate[b]	K_d	2.43×10^2		4.76×10^2		5.8×10^2		1.42×10^3				
(pH=2)	α		2.0		1.2		2.4					
		Ni		Mn		Cd		Co		Cu		Zn
SnSbA	K_d	2.0×10^2		3.0×10^2		7.0×10^2		3.7×10^3		5.0×10^3		7.0×10^3
(1M HNO$_3$)	α		1.5		2.3		5.3		1.4		1.4	
		Zn		Cu		Ni		Mn		Co		Cd
AG 50W-X8[a]	K_d	25.2		26.8		28.1		28.4		28.8		32.8
(1M HNO$_3$)	α		1.1		1.0		1.0		1.0		1.1	
		Mn		Zn		Ni		Co		Cd		Cu
Tin antimonate[b]	K_d	5.9×10^2		1.1×10^3		1.5×10^3		2.9×10^3		3.2×10^3		7.5×10^4
(pH=2)	α		1.9		1.3		2.0		1.1		2.3	

a) F. W. E. Strelow *et al.*, *Anal. Chem.*, **37**, 106 (1965). b) M. Qureshi *et al.*, *J. Chromatogr.*, **67**, 351 (1972).

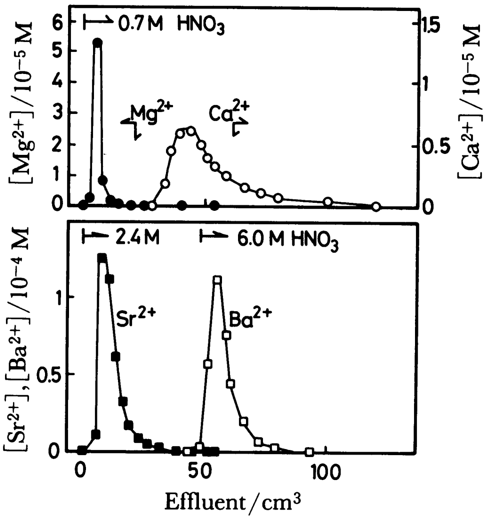

Fig. 4. Separation of alkaline earth metal ions with SnSbA column.
Column; 5.0 cm×0.5 cm i.d. (2.0 g of SnSbA), metal ion loading; 0.2 µmol for Mg^{2+} and Ca^{2+}, and 1.0 µmol for Sr^{2+} and Ba^{2+}, flow rate; 0.2 cm^3 min^{-1}.

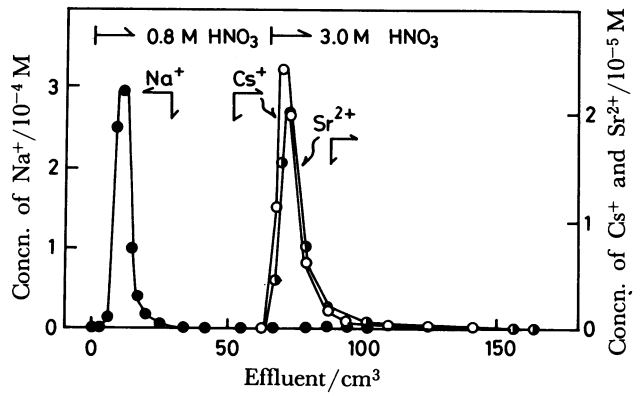

Fig. 5. Separation of Sr^{2+} and Cs^+ from Na^+ with SnSbA column.
Column; 5.0 cm×0.5 cm i.d. (2.0 g of SnSbA), metal ion loading; 2.0 µmol for Na^+, and 0.2 µmol each for Sr^{2+} and Cs^+, flow rate; 0.2 cm^3 min^{-1}.

than those obtained on the SnSbA. This indicates that the number of the strongly acid sites in the SnSbA are larger than those in the tin antimonate prepared by Mathew and Tandon,[11] or Qureshi *et al.*[10]

Ion Exchange Separation. It is evident from studies of the separation factors on the SnSbA that some selective separation is feasible for various metal ions including alkali metal ions. Separations of Mg^{2+}-Ca^{2+} and Sr^{2+}-Ba^{2+} have been achieved by using a small column (5.0 cm×0.5 cm i.d.) containing 2.0 g of SnSbA with nitric acid solutions of different concentrations as eluents. The quantitative separations of Mg^{2+} from Ca^{2+} and of Sr^{2+} from Ba^{2+} were performed with 99—100% recovery with relatively short time (Fig. 4). From studies of the K_d values of alkali metal ions and bivalent metal ions, small amounts of Cs^+ and Sr^{2+} can be separated effectively from a relatively large amount of sodium. A satisfactory separation of Cs^+ and Sr^{2+} was performed from 10 fold (in mmol) of Na^+ with 98% recovery (Fig. 5).

The use of SnSbA is promising for the separation of radioactive ^{90}Sr and ^{137}Cs from natural water and seawater.

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