724 © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 724—730 (1985) [Vol. 58, No. 2

Preparation, Properties, and Analytical Applications of Crystalline Tin(IV) Tungstoselenate

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(Received January 5, 1984)

Synthesis of tin(IV) tungstoselenate has been done under a variety of conditions. The effects of mixing ratio of reagents and the pH of the mixture on the properties of the material have been studied. The crystalline sample of tin(IV) tungstoselenate has been chosen for detailed studies, such as chemical and thermal stabilities, chemical composition, pH-titrations, IR and X-ray analyses. On the basis of above studies a tentative formula has been proposed for tin(IV) tungstoselenate. The adsorption behaviour of metal ions in different concentrations of perchloric acid has been studied. On the basis of K_d values few analytically important separations of metal ions have been achieved on small columns of tin(IV) tungstoselenate.

It has been observed that double salts often exhibit much better ion-exchange properties than simple salts.[1–5] Most of the ion-exchange studies reported in the area of synthetic inorganic ion-exchangers are based on amorphous products. Zirconium phosphate is probably the most widely studied crystalline ion-exchange material.[6–12] Recently, synthesis and ion-exchange properties of crystalline tin(IV) selenophosphate have been reported by Nabi *et al.*[13] Crystalline inorganic ion-exchanger shows superiority over amorphous products in many respects. Amorphous materials are restricted in their application as they undergo extensive hydrolysis even in weakly alkaline or neutral solutions. Moreover, the crystalline products are rigid in their structure and reversible in nature. Synthesis of crystalline inorganic ion-exchangers is also important in order to understand the mechanism of exchange.

The present paper deals with the synthesis, ion-exchange properties, and analytical applications of tin(IV) tungstoselenate as a new inorganic ion-exchanger.

Experimental

Reagents. Tin(IV) chloride (Baker analyzed, U.S.A.), sodium selenite (BDH), and sodium tungstate (BDH) were used for the synthesis of tin(IV) tungstoselenate. All other chemicals were of analytical reagent grade.

Apparatus. EC Spectrophotometer GS 866D for spectrophotometry, Elico LI-10 pH-meter for pH measurements, Perkin Elmer model 137 spectrophotometer for IR studies, X-ray diffractometer PW 1140/90 for X-ray analysis and stanton thermobalance type H_4 for TGA, were used. A temperature controlled shaker 'SICO' was used for shaking purposes.

Synthesis. Tin(IV) tungstoselenate samples were prepared by adding an aqueous mixture which was 0.05 mol dm^{-3} in sodium selenite and 0.05 mol dm^{-3} in sodium tungstate to 0.05 mol dm^{-3} aqueous solution of tin(IV) chloride in varying volume ratios and at different pH values as indicated in Tables 1 and 2. The pH of the mixture was adjusted by adding either an acid or a base and was then kept for one day at room temperature. The white product was filtered, washed several times with demineralized water to remove excess reagents and then dried at 40 °C. The particles of 50—100 mesh size were obtained when the product was immersed in demineralized water. The material was converted to H^+ form by treating it with 1 mol dm^{-3} nitric acid for 24 h at 25 ± 2 °C. The excess acid was removed after several washings with demineralized water. The material was finally dried at 40 °C in an oven. Tables 1 and 2 describe the conditions of synthesis and few properties of the ion-exchange material.

Ion-exchange Capacity. Ion-exchange capacities for some uni and bivalent cations are reported in Table 3. A 0.5 g exchanger in the hydrogen form was taken in the column. The hydrogen ions were then eluted by applying 1 mol dm^{-3} solutions (pH=6) of cations. The hydrogen ions in the effluent were determined after titrating against standard sodium hydroxide solution.

Chemical Stability. A 0.5 g of the material (sample SSW_4 in Table 1) was shaken with 50 cm^3 of the solvent of interest for 6 h at room temperature. Tin(IV), selenium, and tungsten in the aqueous phase were determined spectrophotometrically using hematoxylin,[14] potassium iodide[15] and potassium thiocynate[16] as colouring reagents, respectively. The results are given in Table 4.

Thermal Stability. The thermogravimetric analysis of the ion-exchanger in the hydrogen form was performed at a heating rate of 10 °C/min. The thermogram of the material is shown in Fig. 1. The effect of heating on the ion-exchange capacity of the material was also examined. The ion-exchange capacity for potassium ions is given in Table 5. The material in the hydrogen form was heated at the desired temperature for 1 h in a muffle furnace.

Chemical Composition. A 0.5 g of the sample was dissolved in hot concentrated hydrochloric acid. The solution was cooled and diluted. Tin[14] and selenium[15] were then estimated spectrophotometrically. Tungsten content was determined by gravimetric analysis.[17]

pH-Titrations. Topp and Peppers' method[18] was used for pH titrations using NaCl–NaOH system. For this purpose 0.5 g of the exchange material was treated with 50 cm^3 of the solution. Figure 2 represents the pH-titration curve of tin(IV) tungstoselenate.

IR Analysis. The infrared spectra of crystalline sample (SSW_4) dried at different temperatures were obtained by potassium bromide disc method (Fig. 3).

X-Ray Analysis. For X-ray diffraction analysis, manganese filtered Fe-$K\alpha$ radiation was used. The sample SSW_4 (dried at 40 °C) in the hydrogen form was used. Table 6 and Fig. 4 show the X-ray results.

Distribution Coefficients. Distribution coefficients for various metal ions in perchloric acid medium were determined by a published method.[19] The ion-exchange material (50—100 mesh size) was equilibrated with cation solutions at 25 ± 1 °C. The ionic strength of Ce(IV) and Th(IV) ion solutions was 0.0041 and 0.0175 respectively whereas the

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Table 1. Synthesis and ion-exchange properties of tin(IV) tungstoselenate

Sample	Conditions of synthesis					Appearance of precipitate	Appearance after drying the material at 40 °C	Ion-exchange capacity by K^+ ions
	$SnCl_4\cdot5H_2O$ mol dm^{-3}	Na_2SeO_3 mol dm^{-3}	$Na_2WO_4\cdot2H_2O$ mol dm^{-3}	Mixing ratio (v/v/v)	pH			meq/dry g
SSW_1	0.05	0.05	0.05	1:1:1	0.0	White Upper layer-gelatinous Lower layer-granular	White opaque	0.80
SSW_2	0.05	0.05	0.05	2:1:1	0.0	White granular	White opaque	0.73
SSW_3	0.05	0.05	0.05	3:1:1	0.0	White gelatinous	Brownish shiny	0.72
SSW_4	0.05	0.05	0.05	4:1:1	0.0	White gelatinous	White shiny	0.88
SSW_5	0.05	0.05	0.05	1:1:2	0.0	White Upper layer-gelatinous Lower layer-granular	White Powdery opaque	0.91
SSW_6	0.05	0.05	0.05	1:2:1	0.0	White Upper layer-gelatinous Lower layer-granular	White powdery opaque	1.07
SSW_7	0.05	0.05	0.05	2:1:2	0.0	White Upper layer-gelatinous Lower layer-granular	Brownish opaque	0.84
SSW_8	0.05	0.05	0.05	2:2:1	0.0	White Upper layer-gelatinous Lower layer-granular	White powdery opaque	1.07

Table 2. Effect of pH on the synthesis and ion-exchange properties of tin(IV) tungstoselenate

Sample	Conditions of synthesis					Appearance of precipitate	Appearance of beads after drying at 40 °C	Ion-exchange capacity by K^+
	$SnCl_4\cdot5H_2O$ mol dm^{-3}	Na_2SeO_3 mol dm^{-3}	$Na_2WO_4\cdot2H_2O$ mol dm^{-3}	Mixing ratio (v/v/v)	pH			meq/g
SSW_4	0.05	0.05	0.05	4:1:1	0.0	White gelatinous	White shiny	0.88
SSW_9	0.05	0.05	0.05	4:1:1	1.0	White gelatinous	White shiny	0.85
SSW_{10}	0.05	0.05	0.05	4:1:1	2.0	White gelatinous	White powdery	0.84
SSW_{11}	0.05	0.05	0.05	4:1:1	3.0	White gelatinous	White powdery	0.77

Table 3. Ion-exchange capacity (Meq/g) of various ion-exchange materials with different metals ions at 25±2 °C

Metal ions	Salt used	Tin(IV) selenite[20)]	Tin(IV) tungstate[21)]	Tin(IV) tungsto-selenate
Li^+	LiCl	1.15	—	0.71
Na^+	NaCl	0.96	0.50	0.77
K^+	KCl	0.75	0.57	0.88
Ca^{2+}	$Ca(NO_3)_2$	—	—	1.43
Sr^{2+}	$Sr(NO_3)_2$	—	0.59	1.36
Ba^{2+}	$Ba(NO_3)_2$	1.0	—	1.36

ionic strength of other ion solutions lie between 0.0006 to 0.006. The results are given in Table 7. The metal ions in the solution after and before treatment with the exchanger were determined by EDTA titrations.

Quantitative Separations. Important separations of metal ions were achieved on the columns of tin(IV) tungstoselenate. The elution curves for each set of separations are shown in Figs. 5a—5c. For each separation, 1.5 g of the exchanger (50—100 mesh size) in the hydrogen form was taken in a column of i.d. 0.6 cm with glass wool support. The mixture of the metal ions solution was adsorbed on the exchanger beads. The exchange bed was washed with demineralized water. The all metal ions loaded were eluted with suitable reagent and collected in 10 cm^3 fractions at the flow rate

TABLE 4. CHEMICAL STABILITY OF SOME TIN(IV) BASED ION-EXCHANGERS

Solvent	Tin(IV) selenite[20] (mg/50 cm^3)		Tin(IV) tungstate[21] (mg/50 cm^3)		Tin(IV) tungstoselenate (mg/50 cm^3)		
	Sn released	Se released	Sn released	WO_4 released	Sn released	Se released	WO_4 released
Demineralized Water	0.0	0.03	0.065	0.00	0.00	0.0	0.0
4 mol dm^{-3} Nitric acid	1.1	5.0	—	0.0	0.54	0.25	0.0
1 mol dm^{-3} Sulfuric acid	—	—	—	4.26	0.39	0.15	2.5
1 mol dm^{-3} Hydrochloric acid	—	—	—	14.0	2.46	0.20	4.2
1% Perchloric acid	—	—	—	1.0	0.06	0.0	0.0
0.1 mol dm^{-3} Oxalic acid	—	—	—	Dissolved	0.02	0.1	1.6
0.01 mol dm^{-3} Sodium hydroxide	—	—	—	20.00	0.0	0.40	0.45
4 mol dm^{-3} Acetic acid	—	—	—	—	0.0	0.0	0.0
4 mol dm^{-3} Formic acid	—	—	—	—	0.0	0.0	0.0

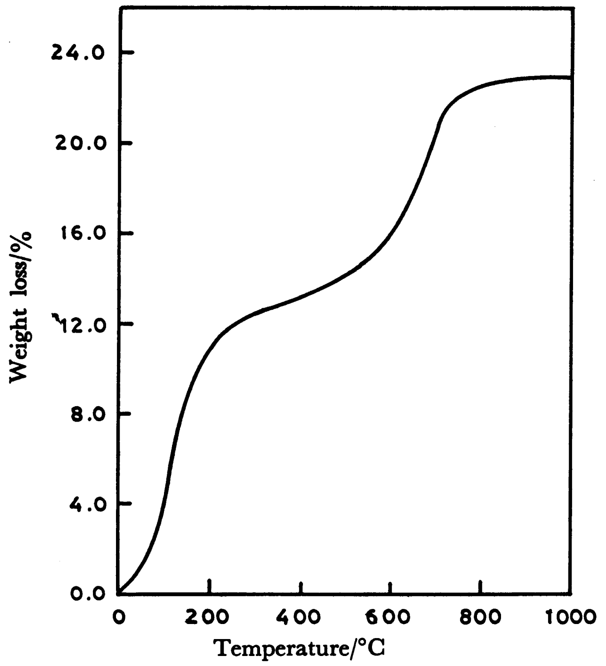

Fig. 1. Thermogram of tin(IV)tungstoselenate in H$^+$ form.

of 15 drops/min. The metal ions were then titrated against 0.002 mol dm^{-3} EDTA solution.

Discussion

It is apparent from Table 1 that the mixing ratio of reagents in the preparation of tin(IV) tungstoselenate is found to affect the ion-exchange capacity to some extent. The capacity is found higher for those samples which have been prepared with higher concentrations of either selenite or tungstate in the reaction mixtures. Table 2 shows the effect of pH on the mixing solutions. Between 0—2 pH the capacity remains almost constant but it reduces to 0.77 meq/g when the sample is prepared at pH 3. However, it has been observed that the capacity significantly increased (1.8 meq/g) when the preparation of tin(IV) tungstoselenate is done in highly acidic medium (negative pH).

TABLE 5. EFFECT OF DRYING TEMPERATURE ON THE ION-EXCHANGE CAPACITY (Meq/g) OF DIFFERENT MATERIAL

Temperature/°C	Tin(IV) selenite[20]	Tin(IV) tungstate[21]	Tin(IV) tungstoselenate
40	0.75	0.57	0.88
100	0.75	0.13	0.62
200	0.75	0.10	0.58
300	0.75	0.10	0.48
400	0.75	0.10	0.45
500	0.70	0.10	0.34
600	0.20	0.10	0.22
700	—	0.10	0.20
800	—	—	0.00

The tin(IV) tungstoselenate sample (SSW_4) has been found to possess an ion-exchange capacity higher than tin(IV) selenite[20] and tin(IV) tungstate.[21]

It is interesting to note that tin(IV) tungstoselenate (SSW_4), prepared by mixing tin(IV) chloride sodium selenite and sodium tungstate in the ratio of 4 : 1 : 1 at pH=0, shows the crystalline character. Therefore, this sample has been chosen for detailed studies.

The data in Table 3 show that ion-exchange capacities for alkaline earths are higher than for alkali metals as expected. This is in accordance with the size of the hydrated radii of the metal. In the case of alkali metals, the capacity increases with the decrease in size of the hydrated radius of the ions. However, the capacity for alkaline earth metals remains almost constant as there is little difference in the size of hydrated radii of these metals.

Tin(IV) tungstoselenate is highly stable in water and appreciable concentrations of sulfuric acid, nitric acid, oxalic acid, perchloric acid, and low concentrations of hydrochloric acid and sodium hydroxide. A comparison of the chemical stability of tin(IV) based ion-exchangers shows that tin(IV) tungstoeslenate is more stable than tin(IV) selenite and tin(IV) tungstate (Table 4). The order of chemical stability of various ion-exchangers are as follows: Tin(IV) tungstoeslenate >tin(IV) tungstoarsenate[22]>tin(IV) molybdoarsenate.[3]

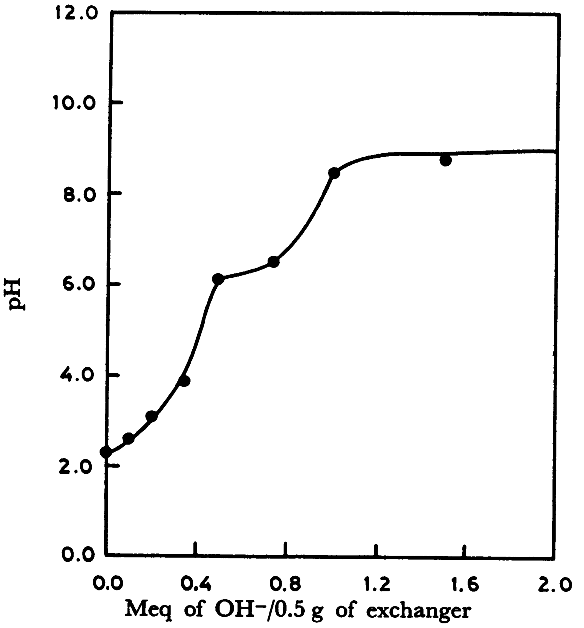

Fig. 2. pH Titration curve of tin(IV)tungstoselenate.

The ion-exchange capacity is also affected by drying temperatures of the material. The data in Table 5 indicate that tin(IV) tungstoselenate is thermally more stable than tin(IV) tungstate. Tin(IV) tungstoselenate shows considerable ion-exchange capacity (0.34 meq/g) even when the drying temperature is raised to 500 °C and can thus safely used as an ion-exchanger. On the other hand tin(IV) tungstate loses its ion-exchange capacity almost completely when a drying temperature is 100 °C.

The thermogram of tin(IV) tungstoselenate (Fig. 1) may be interpreted as follows. The material experiences a continuous loss in weight (11%) upto 200 °C which can be attributed to the loss of external water

Table 6. X-ray data of tin(IV) tungstoselenate (sample SSW_4)

Angle (θ/°)	d-Values	Intensity of peak
6.4	9.6451	S
8.3	7.457	W
16.45	3.7882	S
17.82	3.5037	W
20.5	3.0586	M
22.0	2.8576	W
23.95	2.6347	W
24.65	2.5635	W
26.05	2.4329	W
26.95	2.3563	M

S=Sharp. M=Medium. W=Weak

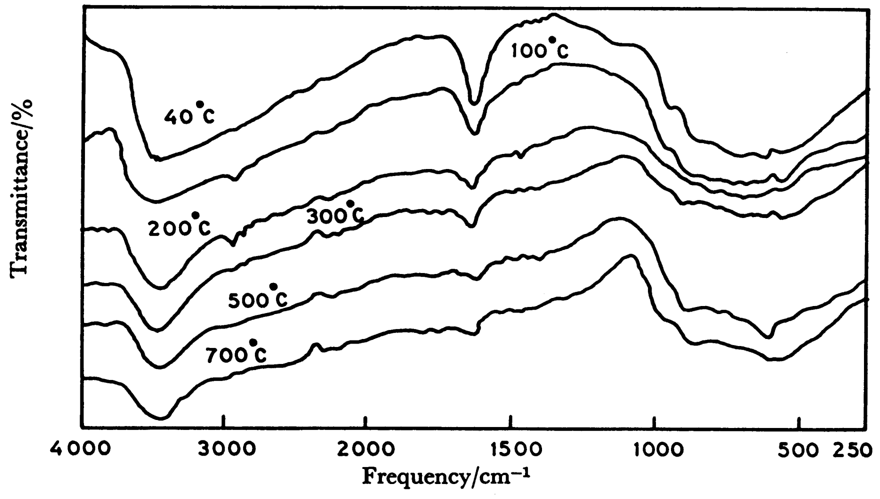

Fig. 3. Infrared spectra of tin(IV)tungstoselenate dried at different temperatures.

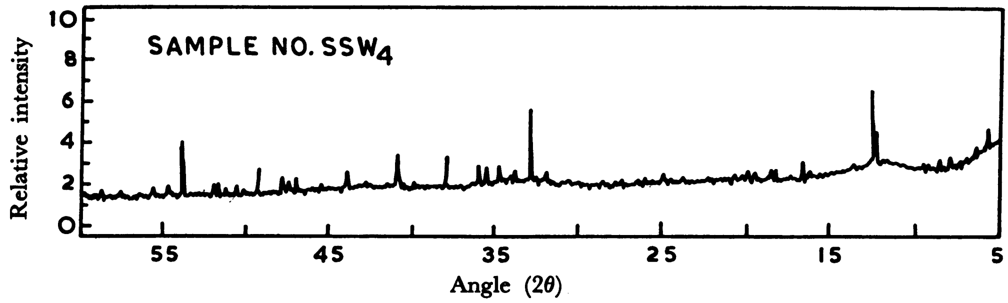

Fig. 4. X-Ray diffraction pattern of tin(IV)tungstoselenate.

molecules. The weight loss in the region 200—350 °C may be due to the removal of water molecules due to condensation of OH groups and is accompanied by loss of selenium by vaporization. No prominent weight loss is found in the small temperature range 350 °C to 400 °C which probably indicates the gradual loss of selenium by vaporization. This conclusion is also supported by the exchange capacity data at these temperatures. As the temperature is raised beyond 400 °C, decomposition of the material starts which continues upto 800 °C. The loss in weight in this region may be referred to the loss of water molecules by the condensation of the other type of OH groups and loss of tungsten. This is in good agreement of the capacity data at 400—600 °C. The capacity reduces gradually after 600 °C and vanishes completely at 800 °C. The weight becomes constant after 800 °C due to the formation of stable oxides of metals.

Table 7. Distribution coefficients of some metal ion tin(IV) tungstoselenate

Metal ion	K_d/ml/g			
	Water	$HClO_4$ 0.01 mol dm^{-3}	$HClO_4$ 0.05 mol dm^{-3}	$HClO_4$ 0.1 mol dm^{-3}
Ba^{2+}	1500±35	888±25	197±6	80±2
Ca^{2+}	1720±50	185±5	125±5	125±2
Sr^{2+}	923±30	174±5	15±2	2±1
Mg^{2+}	194±5	26±2	5±1	2±1
Zn^{2+}	3260±62	804±8	222±10	32±2
Mn^{2+}	504±8	412±6	43±2	15±2
Co^{2+}	2900±60	102±2	97±2	3±1
Hg^{2+}	2235±55	918±20	152±2	10±1
Pb^{2+}	8582±180	1011±24	404±2	84±2
Cd^{2+}	9900±200	985±20	138±2	98±2
Ni^{2+}	1724±50	560±5	89±2	8±2
Cu^{2+}	2335±52	608±6	66±2	10±2
Th^{4+}	9980±200	8906±100	989±5	722±5
Ce^{4+}	3800±64	3665±66	2742±50	909±5

The molar composition of tin(IV) tungstoselenate shows that tin(IV) selenium and tungsten are present in the ratio of 7 : 1 : 18. The pH-titration curve shows bifunctional character of tin(IV) tungstoselenate (Fig. 2) whereas tin(IV) tungstate and tin(IV) selenite are found to be mono and bifunctional respectively.[20,21)]

The IR spectra of tin(IV) tungstoselenate dried up to 600 °C resemble each other and show three absorption peaks (Fig. 3). A strong and broad peak in the region 3600—3200 cm^{-1} represents the interstitial water, free water, and OH groups. Another sharp peak in the region 1700—1500 cm^{-1} with a maximum at 1620 cm^{-1} is characteristic of interstitial water. The third peak in the region 1100—250 cm^{-1} may be due to metaloxygen bonds. There is no difference in the IR spectra between hydrogen form and patassium form of the sample dried at 40 °C.

The X-ray diffraction pattern suggests that tin(IV)

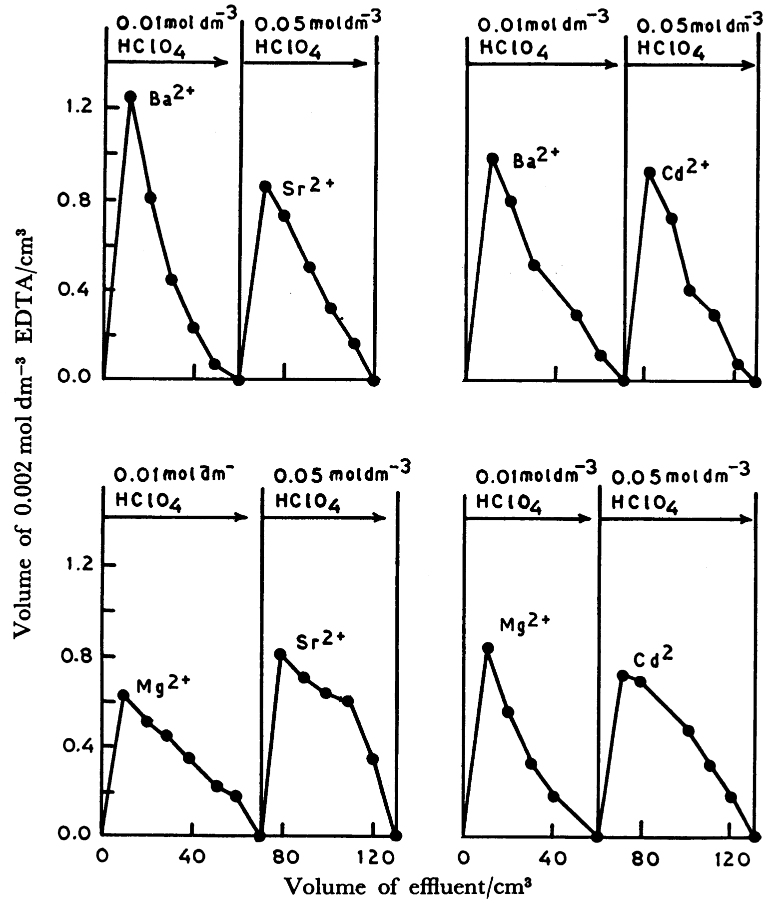

Fig. 5A Separations of Ba^{2+}–Sr^{2+}, Ba^{2+}–Cd^{2+}, Mg^{2+}–Sr^{2+}, and Mg^{2+}–Cd^{2+}.

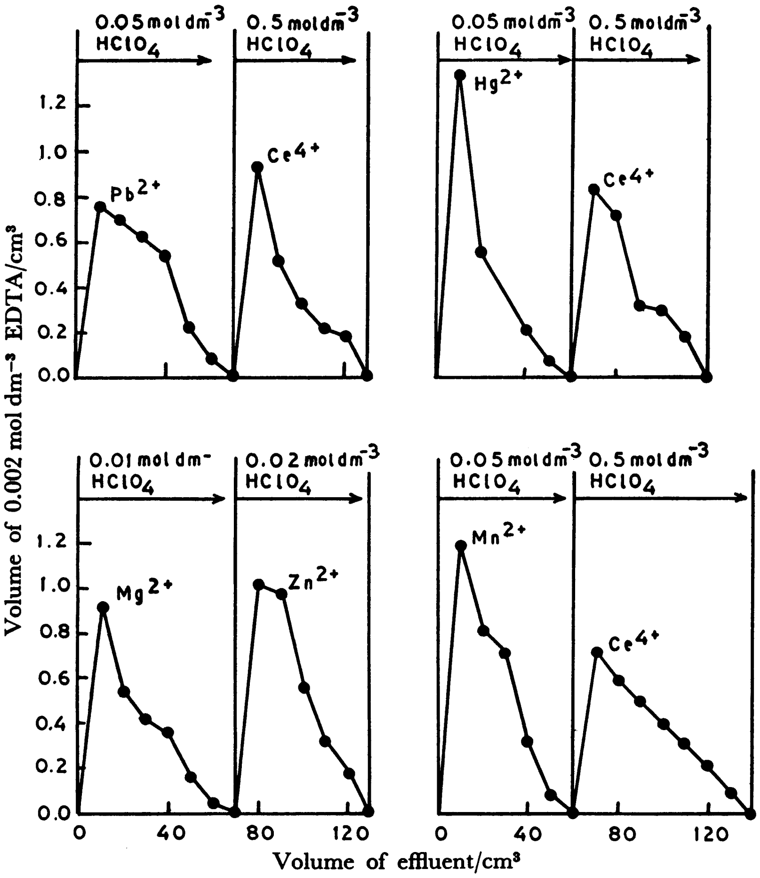

Fig. 5B Separations of Pd^{2+}–Ce^{4+}, Hg^{2+}–Ce^{4+}, Mn^{2+}–Ce^{4+}, and Mg^{2+}–Zn^{2+}.

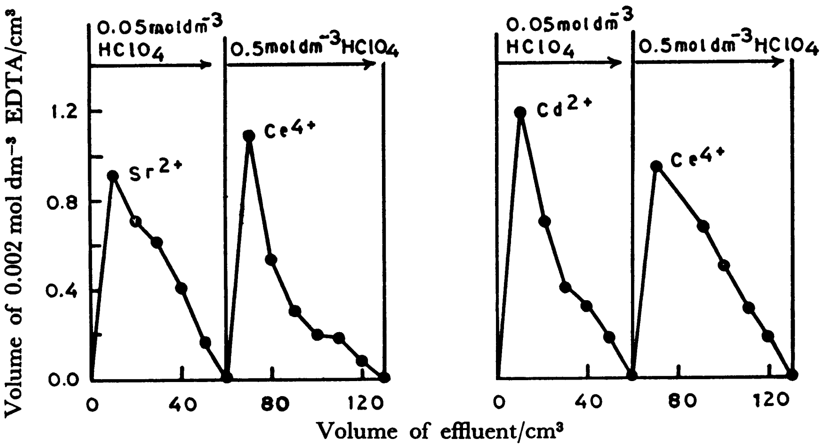

Fig. 5C Separations of Sr^{2+}–Ce^{4+} and Cd^{2+}–Ce^{4+}.

tungstoselenate (sample SSW_4) is crystalline in character. The *d*-values and other results of tin(IV) tungstoselenate are given in Table 6 and Fig. 4.

On the basis of chemical composition, pH-titration, thermogravimetric and IR studies, the following tentative formula may be assigned to tin(IV) tungstoselenate.

$$[(SnO_2)_7 \cdot HSeO_3(HWO_4)_{18}] \qquad (1)$$

If all the external water molecules are lost upto 200 °C, the percentage weight loss is 11%. The number of water molecules then calculated by the method of Alberti *et al.*[23] The number of external water molecules per molecule of the exchanger is found to be 45. The formula therefore can be rewritten as

$$[(SnO_2)_7 \cdot HSeO_3(HWO_4)_{18}] \cdot 45H_2O \qquad (2)$$

The molecule contains nineteen replaceable hydrogen atoms according to the above formula. If it is assumed that only $7H^+$ ions are exchanged at pH=6, then the ion-exchange capacity calculated from formula 2 is 0.91 meq/g which is very close to the experimental value (1.0 meq/g from pH-titration curve). When the pH of the mixture is increased upto 8.5, the capacity as indicated by pH-titration curve becomes 2.4 meq/g and supports the theoretical ion-exchange capacity of the material (2.5 meq/g) when all the replaceable hydrogen ions are taken into consideration.

The data in Table 7 show that K_d values for metal ions decrease in general with the increase in the concentration of perchloric acid. K_d values of Th(IV), and Ce(IV) are exceptionally high in all concentrations of perchloric acid, whereas negligible adsorption of almost all metal ions occurs in 0.5 mol dm^{-3} $HClO_4$. The behavior of barium(II) is quite different from other alkaline earth metals and therefore can be selectively separated from a mixture of these metal ions on tin(IV) tungstoselenate.

On the basis of differential selectivity of metal ions in various concentrations of perchloric acid, a number of important separations have been achieved quantitatively using tin(IV) tungstoselenate columns. The elution curves of metal ions separated from one another are shown in Figs. 5A-5C.

The authors are thankful to Prof. W. Rahman, Chairman, for providing research facilities and to C.S. I.R. New Delhi for financial assistance.

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