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## SYNTHESIS OF TIN(IV) ANTIMONATE OF HIGH THERMAL AND CHEMICAL STABILITY

SEPARATION OF  $Mg^{2+}$  FROM  $Sr^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Al^{3+}$  AND  $La^{3+}$ 

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## SUMMARY

Seven samples of antimonates of tin(IV), iron(III) and thorium(IV) have been synthesized under various conditions. The chemical stabilities of these antimonates were determined in dilute solutions of mineral acids. The distribution coefficients of metal ions were determined at different pH values on tin(IV) antimonate. The analytical importance of this exchanger was demonstrated by achieving the separations of some important pairs of metal ions.

## INTRODUCTION

During the last five years we have synthesized new inorganic ion exchangers and studied their ion-exchange potentialities. Titanium antimonate<sup>1</sup> was found to be unique regarding selectivity towards inorganic ions. Preliminary studies regarding the synthesis and adsorption of alkali metals on tin(IV) antimonate have also been reported by ABE *et al.*<sup>2</sup> This paper summarizes the results obtained on the chemical stabilities of the antimonates of thorium(IV), tin(IV) and iron(III) in dilute mineral acids and the selectivity of tin(IV) antimonate for a number of metal ions other than alkali metal ions. Some important pairs of ions have been separated on columns of tin(IV) antimonate.

## EXPERIMENTAL

*Reagents*

Antimony pentachloride of density 2.3 g/ml, ferric chloride and thorium nitrate (B.D.H.), and stannic chloride (B & A) were used. All other reagents were of AnalaR grade.

*Apparatus*

Spectrophotometric, pH, X-ray, shaking and IR studies were performed by

TABLE I

CONDITIONS OF PREPARATION AND PROPERTIES OF ANTIMONATES OF TIN(IV), THORIUM(IV) AND IRON(III)

Thorium(IV) antimonate					Iron(III) antimonate					Tin(IV) antimonate					
Mixing ratio, Th:Sb	Concentration (M)	pH	Ion-exchange capacity (mequiv./g)	Colour	Mixing ratio, Fe:Sb	Concentration (M)	pH	Ion-exchange capacity (mequiv./g)	Colour	Mixing ratio, Sn:Sb	Concentration (M)	pH	Ion-exchange capacity (mequiv./g)	Chemical composition, Sn:Sb	Colour
1:1	0.05	2.8	0.15	Glassy white	1:1	0.1	8.6	0.25	Dark brown	1:1	0.1	-ve	1.30	1:5.83	Yellowish white
2:1	0.1	2.8	0.16	Glassy white	1:1	0.1	1.6	0.10	Dark brown	1:1	0.1	1	0.63	1:1.72	Yellowish white
3:1	0.05	2.8	0.01	Glassy white	1:1	0.1	5-6	0.30	Dark brown	1:1	0.1	6-7	0.85	1:0.88	Bright yellow
1:2	0.1	2.8	0.22	Chalk-like	2:1	0.1	8-9	0.10	Dark brown	1:1	0.1	7-8	0.40	1:0.34	Light brown
1:1	0.01	8.5	0.01	White	1:2	0.1	8-9	0.30	Dark brown	1:2	0.1	2-3	1.90	1:10.4	White
1:1	0.1	2.8	0.01	White	1:1	0.4	8-9	0.15	Dark brown	2:1	0.1	2-3	0.75	1:0.99	Greenish yellow
1:2	0.05	8.5	0.03	White	—	—	—	—	—	1:1	0.05	2-3	0.95	1:1.4	Yellow

using a Bausch & Lomb Spectronic-20 colorimeter, an Elico pH meter, Model LI-10, a Philips X-ray unit with a camera, a 'Sico' shaker and a Perkin-Elmer spectrophotometer, Model-137, respectively.

### Preparation

Conditions of preparation for different antimonates are summarized in Table I. The reagents of different concentrations were mixed in different volume ratios and concentrated ammonia solution was added to the clear reaction mixture so obtained until the required pH was attained. Further treatments of the precipitates obtained were similar to those reported earlier<sup>1</sup>.

### Ion-exchange properties

The saturation cation-exchange capacity for  $\text{Na}^+$  and  $\text{Ba}^{2+}$ , pH titration curves and distribution coefficients were determined in the same manner as earlier<sup>1</sup>. 1 g of tin(IV) antimonate was loaded into a glass column containing a glass-wool support for chromatographic studies.

### Physical measurements

X-ray photographs of tin(IV) antimonate dried at  $40^\circ$  were taken by the powder method. IR spectra (Fig. 1) for tin(IV) antimonate dried at  $40^\circ$ ,  $200^\circ$  and  $500^\circ$  in the  $\text{H}^+$ ,  $\text{K}^+$  and  $\text{Ba}^{2+}$  forms were obtained by the potassium bromide disk method.

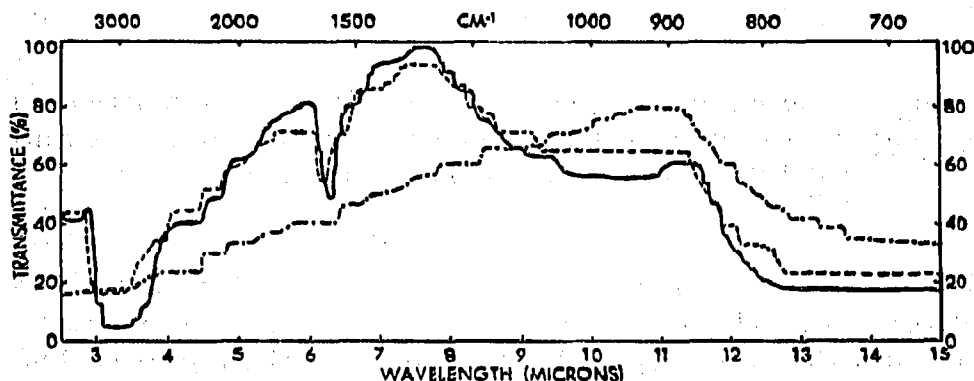


Fig. 1. Infrared absorption spectra of tin(IV) antimonate at different temperatures by the potassium bromide disk method. Drying temperature ( $^\circ\text{C}$ ): —, 40; ---, 200; - · - · -, 500.

### Analytical procedures

To determine the chemical composition of tin(IV) antimonate, 200 mg of the sample were dissolved in concentrated hydrochloric acid. Antimony was precipitated as sulphide in the presence of oxalic acid and determined titrimetrically<sup>3</sup>. Tin in the filtrate was also determined titrimetrically<sup>4</sup>. For chemical stability, 0.50 g of the exchanger was shaken in 50 ml of solvent for 6–7 h in a temperature-controlled shaker. The undissolved portion of the ion exchanger was removed by filtration and the antimony in thorium(IV) and tin(IV) antimonates was determined directly by the spectrophotometric method<sup>5</sup>. To determine the tin content of tin(IV) antimonate, antimony was first removed as sulphide and the phenylfluorone method<sup>6</sup>

TABLE II

DISTRIBUTION COEFFICIENTS ( $K_d$ ) OF METAL IONS AT DIFFERENT pH VALUES ON TIN(IV) ANTIMONATE

Cation	pH			
	0	1	2	3
Mg <sup>2+</sup>	0	1.81	243	294
Ca <sup>2+</sup>	0	0	476	600
Sr <sup>2+</sup>	8.8	95	580	1391
Ba <sup>2+</sup>	60	660	1420	1600
Zn <sup>2+</sup>	0	29.58	1126	1740
Cd <sup>2+</sup>	457	1542	3244	4080
Hg <sup>2+</sup>	14.3	30.9	30.9	3090
Cu <sup>2+</sup>	0	0	7500	15100
Ni <sup>2+</sup>	0	4	1460	15500
Co <sup>2+</sup>	0	14.4	2865	14700
Fe <sup>3+</sup>	0	8.8	444	580
Al <sup>3+</sup>	0	0	700	7900
Mn <sup>2+</sup>	7	10.85	592.8	1452
VO <sup>2+</sup>	0	0	1246	16060

was used. Thorium and iron in thorium(IV) and iron(III) antimonates were determined spectrophotometrically by the thoron<sup>7</sup> and 1,10-phenanthroline<sup>8</sup> methods, respectively.

## RESULTS

Some of the properties of the ion exchangers under study are summarized in Table I. The ion-exchange capacities, distribution coefficients of inorganic ions and chemical stability data are recorded in Tables I, II and III, respectively.

*Sorption studies*

Distribution coefficients ( $K_d$ ) for 24 metal ions were determined on tin(IV) antimonate (sample 6) at different pH values. The cations Zr<sup>4+</sup>, Hf<sup>4+</sup>, Th<sup>4+</sup>, La<sup>3+</sup>, Ce<sup>3+</sup>, Y<sup>3+</sup>, Sc<sup>3+</sup>, Sm<sup>3+</sup>, Nd<sup>3+</sup> and Pr<sup>3+</sup> are adsorbed totally in the pH range 0-6. The  $K_d$  values for the remaining 14 ions are given in Table II. To illustrate the ion-

TABLE III

CHEMICAL STABILITY SEQUENCES FOR DIFFERENT ION EXCHANGERS IN DILUTE MINERAL ACIDS AND WATER

Abbreviations: Sn:Sb = tin(IV) antimonate; Sn:As = tin(IV) arsenate; Sn:Mo = tin(IV) molybdate; Ti:Sb = titanium(IV) antimonate; Ti:Mo = titanium(IV) molybdate; Ti:W = titanium(IV) tungstate; Th:Mo = thorium(IV) molybdate; Th:W = thorium(IV) tungstate.

Solvent	Stability sequence						
4 M nitric acid	Sn:Sb	>	Ti:W	>	Ti:Sb	>	Sn:Mo > Th:W > Sn:As >
	Th:Mo	>	Ti:Mo				
4 M sulphuric acid	Sn:Sb	>	Ti:Sb	—	—	—	—
4 M hydrochloric acid	Sn:As	>	Ti:Sb	>	Sn:Sb	—	—
Water	Sn:Sb	>	Ti:Sb	>	Sn:As	>	Sn:Mo > Ti:Mo > Th:Mo

TABLE IV

SEPARATION FACTORS OF SOME IMPORTANT PAIRS OF IONS ON SOME SYNTHETIC INORGANIC ION EXCHANGERS

Separation factors	Tin(IV) antimonate	Titanium(IV) antimonate	Tin(IV) arsenate	Tin(IV) molybdate	Tin(IV) tungstate
$K_{\text{La}}^{\text{Mg}}$	Very large	$\frac{1600}{248} = 6.5$	$\frac{158}{40} = 3.95$	—	—
$K_{\text{Sr}}^{\text{Mg}}$	$\frac{1391}{294} = 4.7$	$\frac{900}{248} = 3.6$	$\frac{393}{40} = 9.70$	$\frac{25.7}{8.1} = 3.17$	$\frac{114}{94.4} = 1.2$
$K_{\text{Al}}^{\text{Mg}}$	$\frac{7900}{294} = 26.8$	$\frac{212}{248} = 10.3$	$\frac{47.80}{40} = 1.17$	$\frac{8.1}{8.1} = 1.00$	—
$K_{\text{Cu}}^{\text{Mg}}$	$\frac{15100}{294} = 51.3$	$\frac{3400}{248} = 0.86$	$\frac{652}{40} = 16.3$	$\frac{21.8}{8.1} = 2.7$	$\frac{116}{94.4} = 1.2$
$K_{\text{Cu}}^{\text{Cd}}$	$\frac{15100}{4080} = 3.7$	$\frac{3400}{2266} = 1.05$	$\frac{652}{633} = 1.02$	$\frac{21.8}{11.3} = 1.93$	$\frac{116}{77.8} = 1.5$
$K_{\text{Ca}}^{\text{La}}$	Very large	$\frac{1600}{5000} = 0.32$	$\frac{158}{247} = 0.54$	—	—

exchange potentialities of tin(IV) antimonate in chemical analysis, separation factors for some metal ions were calculated and are compared for the exchangers based on either antimony(V) or tin(IV). Results are given in Table IV.

#### X-ray and IR studies

X-ray analysis shows that all the samples of tin(IV) antimonate in the  $\text{H}^+$  form are amorphous. IR spectra (Fig. 1) are similar to those reported for thorium(IV) tungstate<sup>9</sup> and tin(IV) arsenate<sup>10</sup>. However, the peak with a maximum at  $1390\text{ cm}^{-1}$  corresponding to the deformation vibration of OH groups obtained in the case of antimonic acid<sup>11</sup> and titanium(IV) antimonate<sup>12</sup> is absent.

#### DISCUSSION

Tin(IV) antimonate shows some unusual features as an ion exchanger. It has high chemical and thermal stabilities (Tables III and V, respectively). It shows a

TABLE V

PERCENTAGE LOSS IN ION-EXCHANGE CAPACITY ON HEATING

Exchanger	Temperature ( $^{\circ}\text{C}$ )			
	40	100	200	500
Tin(IV) phosphate	0.00	20	40	100
Tin(IV) tungstate	0.00	77	82.5	100
Tin(IV) molybdate	0.00	90	93.0	99.00
Titanium(IV) tungstate	0.00	4.70	18	99.3
Tin(IV) antimonate	0.00	21.60	44	50

TABLE VI

COMPARISON OF  $K_d$  VALUES AT pH = 2

Metal ion	Titanium(IV) antimonate	Tin(IV) antimonate	Metal ion	Titanium(IV) antimonate	Tin(IV) antimonate
Zn <sup>2+</sup>	105	1126	Ga <sup>3+</sup>	210	—
Cd <sup>2+</sup>	51.1	3244	In <sup>3+</sup>	506	—
Hg <sup>2+</sup>	1.42	30.9	VO <sup>2+</sup>	350	592
Mg <sup>2+</sup>	2.5	243	Sc <sup>3+</sup>	86.66	Complete adsorption
Ca <sup>2+</sup>	22.85	476	Y <sup>3+</sup>	40	Complete adsorption
Sr <sup>2+</sup>	46.1	580	Ce <sup>3+</sup>	180	Complete adsorption
Ba <sup>2+</sup>	108.61	1420	La <sup>3+</sup>	140	Complete adsorption
Pb <sup>2+</sup>	700	—	Pr <sup>3+</sup>	68	Complete adsorption
Fe <sup>3+</sup>	5700	444	Nd <sup>3+</sup>	86	Complete adsorption
Co <sup>2+</sup>	37.77	2865	Sm <sup>3+</sup>	108	Complete adsorption
Ni <sup>2+</sup>	21.33	1460	Hf <sup>4+</sup>	7000	Complete adsorption
Cu <sup>2+</sup>	453	7500	Zr <sup>4+</sup>	6200	Complete adsorption
Mn <sup>2+</sup>	8	592	Th <sup>4+</sup>	5800	Complete adsorption
Al <sup>3+</sup>	0	700	Mo <sup>3+</sup>	85	Complete adsorption

very high uptake of cations. The  $K_d$  values on tin(IV) antimonate are much higher than on titanium(IV) antimonate (Table VI). The ion-exchange capacity increases with the ratio of the anion (Fig. 2), as noticed by SZIRTES *et al.*<sup>13</sup>. We also synthesized the antimonates of iron, thorium, aluminium and lead under similar conditions, but none of them showed any ion-exchange capacity. It is obvious from Table I that the antimonates are very sensitive to the mixing ratios of the starting materials and to the acid concentration at which they are synthesized. Sample I, synthesized at low pH, contains more antimony, while sample 4, synthesized at a pH greater than 8, contains more tin. Samples 5 and 6, synthesized at constant pH but with the parent reagents mixed in the reverse volume ratio, have different chemical composition. Thus sample 5 contains more antimony while sample 6 contains more tin. Hence it seems that antimonates are formed as a result of condensation between the two hydroxides. X-ray analysis shows that tin(IV) antimonate samples do not contain free antimonous acid or tin(IV) oxide, but these are new amorphous products. On the basis of the above conclusions and chemical composition, a tentative structure for tin(IV)

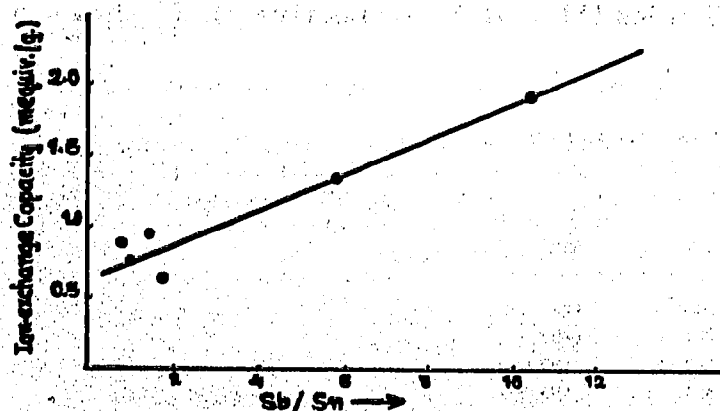
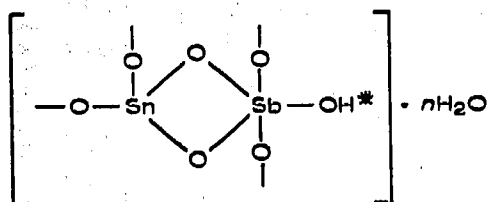


Fig. 2. Graph of ion-exchange capacity against composition for tin(IV) antimonate.

antimonate (sample 6), similar to that of titanium(IV) antimonate, can be postulated as follows:



The hydrogen marked with an asterisk is responsible for the cation-exchange capacity.

In order to compare the ion-exchange properties of tin(IV) antimonate with those reported for titanium(IV) antimonate, fairly stable tin(IV) antimonate (sample 6) was chosen for detailed studies. pH titrations (Fig. 3) show monofunctional behaviour similar to that reported for titanium(IV) antimonate. Samples 1 and 5, containing more antimony, have greater ion-exchange capacities than samples 4 and 6, which contain more tin. Hence it appears that OH groups linked to antimony are more acidic in nature and are responsible for the cation-exchange capacity at neutral pH. The saturation cation-exchange capacity for divalent ions is double that for monovalent ions, as expected. IR spectra confirm the presence of water and OH groups and also show that the intensity of the peak decreases as the heating temperature increases. Tin(IV) antimonate can be used up to 500° without an appreciable change in the ion-exchange capacity (Table V). Table VII shows that tin(IV) antimonate is more stable than the corresponding antimonates of thorium(IV) and iron(III) in dilute mineral acids. Thorium(IV) and iron(III) antimonates show negligible ion-exchange capacities. This may be due to the formation of simple salts such as  $\text{FeSbO}_4 \cdot 3/4\text{H}_2\text{O}$  (ref. 14), contrary to the antimonates of tin(IV) and titanium(IV). They do not have ionisable OH groups, which are responsible for cation-exchange capacity.

Chemical stability sequences are shown in Table III. It is clear that tin(IV) antimonate is more stable in dilute nitric and sulphuric acids than in dilute hydrochloric acid. Tin(IV) antimonate is highly selective because it absorbs  $\text{Zr}^{4+}$ ,  $\text{Th}^{4+}$ ,

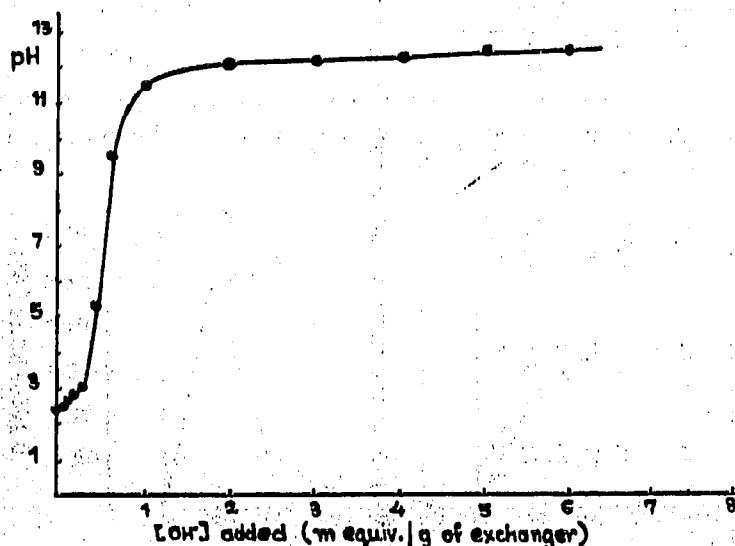


Fig. 3. pH titration curve for tin(IV) antimonate.

TABLE VII

SOLUBILITIES OF ANTIMONATES OF IRON(III) THORIUM(IV) AND TIN(IV) IN MINERAL ACIDS (mg/50 ml)

4 M nitric acid				4 M sulphuric acid				4 M hydrochloric acid			
Fe-A <sup>a</sup>	Th-A <sup>a</sup>	Sn-A <sup>a</sup>		Fe-A	Th-A	Sn-A		Fe-A	Th-A	Sn-A	Fe-A
Fe	Th	Sn	Sb	Fe	Th	Sn	Sb	Fe	Th	Sn	Sb
0.50	34	0.23	0.05	14.50	48.00	4.50	0.72	—	—	—	—
0.80	35	0.30	0.03	14.00	60.00	7.00	0.50	—	—	—	—
0.50	87	0.40	0.04	22.75	80.00	5.50	0.05	—	—	—	—
2.20	46	0.12	0.03	29.00	48.00	1.75	0.04	—	—	—	—
8.00	74	0.08	0.10	17.50	67.00	4.50	0.40	—	—	—	—
17.00	132.0	0.15	0.05	21.00	62.00	4.50	0.03	—	—	—	—
—	—	—	0.07	—	—	—	0.14	—	—	—	—



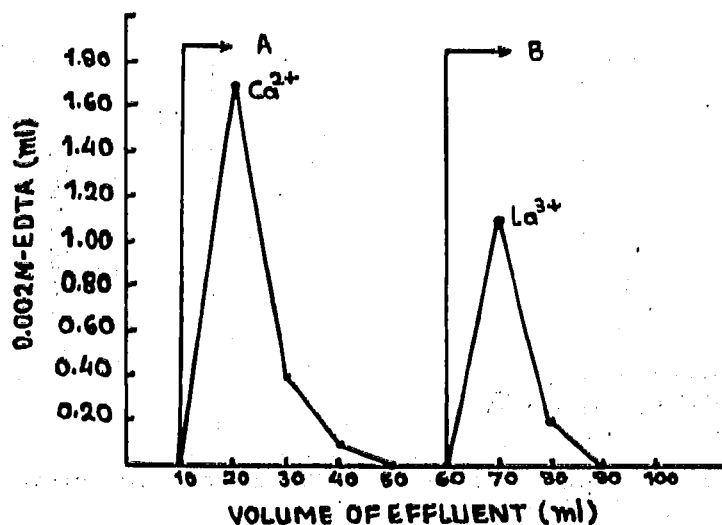
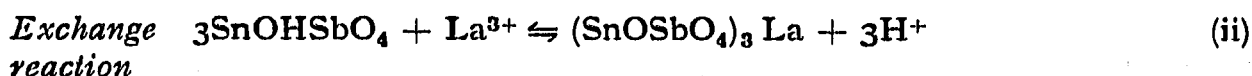
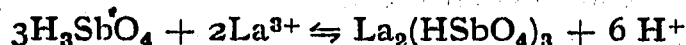
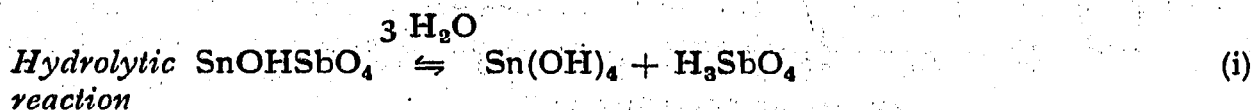


Fig. 4. Separation of  $\text{Ca}^{2+}$  from  $\text{La}^{3+}$ . A, 0.40 *M* ammonium nitrate + 0.10 *M* nitric acid; B, 1.50 *M* nitric acid.

$\text{Hf}^{4+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Pr}^{3+}$  ions completely even at zero pH. There are appreciably low  $K_d$  values for other cations (Table II), and therefore a number of separations can be achieved. It is also obvious from Table IV that tin(IV) antimonate has greater separation factors than other exchangers. The plot of  $\log K_d$  against pH for the cations listed in Table II have been drawn and the slopes were found to be much less than expected. Hence it appears that hydrolysis occurs in addition to the exchange reaction. Hydrolytic and ion-exchange reactions may be written as:



The more hydrolysing nature and the higher uptake of inorganic ions by amorphous substances, compared to these properties for the corresponding crystalline materials<sup>15</sup>, also support the above conclusion.

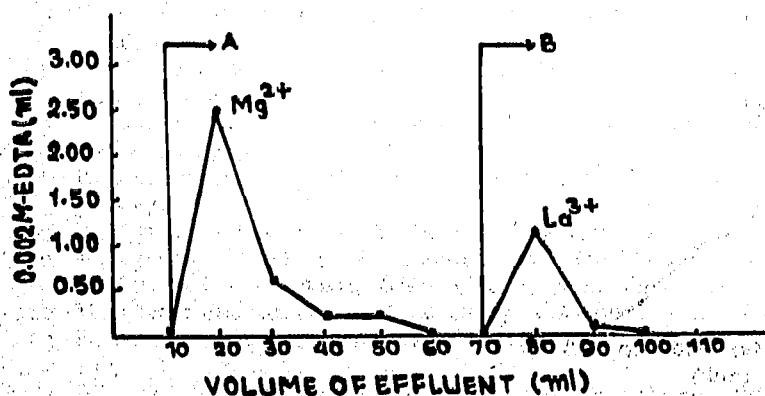


Fig. 5. Separation of  $\text{Mg}^{2+}$  from  $\text{La}^{3+}$ . A, 0.40 *M* ammonium nitrate; B, 1.50 *M* nitric acid.

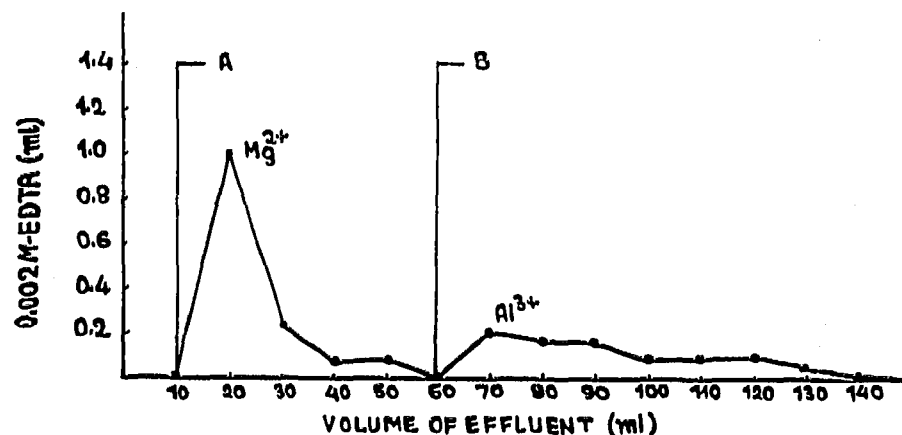


Fig. 6. Separation of  $Mg^{2+}$  from  $Al^{3+}$ . A, 0.4 *M* ammonium nitrate; B, 0.4 *M* ammonium nitrate + 0.2 *M* nitric acid.

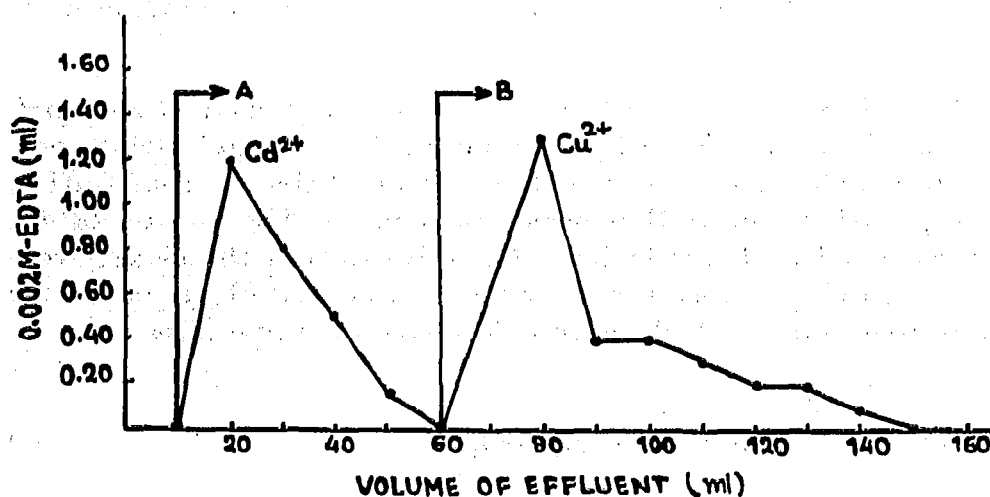


Fig. 7. Separation of  $Cd^{2+}$  from  $Cu^{2+}$ . A, 0.10 *M* nitric acid; B, 1.00 *M* nitric acid.

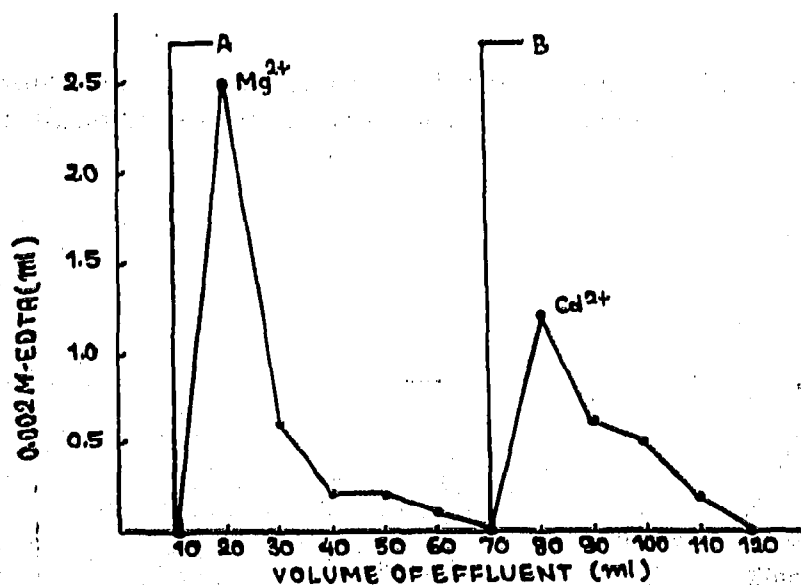


Fig. 8. Separation of  $Mg^{2+}$  from  $Cd^{2+}$ . A, 0.40 *M* ammonium nitrate; B, 0.10 *M* nitric acid.

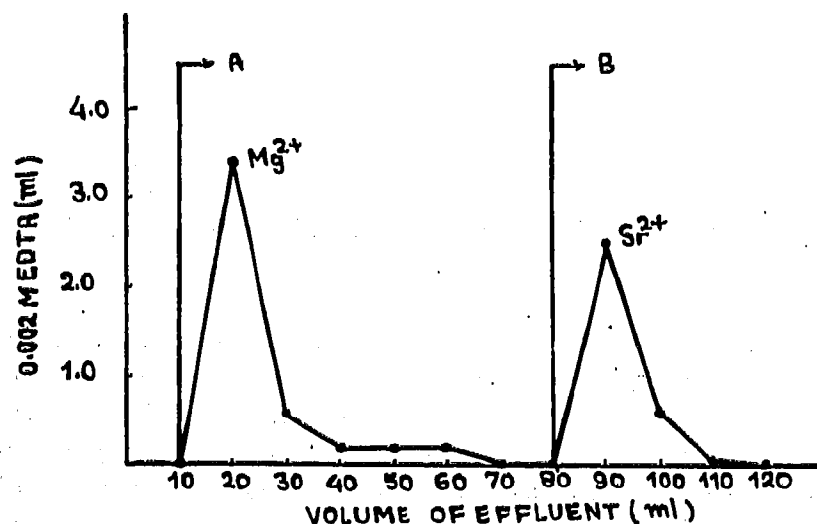


Fig. 9. Separation of  $Mg^{2+}$  from  $Sr^{2+}$ . A, 0.40% ammonium nitrate; B, 3% ammonium chloride + 0.10 *M* nitric acid.

On the basis of chemical stabilities and selectivities for the cations studied, it can be concluded that tin(IV) antimonate is a better cation exchanger than other exchangers based on antimony, titanium and thorium. Its analytical utility has been illustrated by achieving six binary separations on its columns (Figs. 4-9).

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