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Antimony(V) Arsenatophosphate as a Thermally Stable Cation Exchanger: Selective Adsorption of Alkaline Earth and Transition Metal Ions on Its Column

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A new inorganic ion exchanger based on antimony has been prepared viz. antimony(V) arsenatophosphate, which has shown a peculiarly high thermal stability and selectivity for alkaline earth and transition metal ions. As a result, its column use has been demonstrated for the separation of mercury from magnesium and zinc and of iron from other transition metals. A tentative formula has also been proposed for the material, on the basis of its chemical analysis and other characterization studies.

Antimony(V) salts have received attention because of their exceedingly good reproducible characteristics[1-4] and analytical potential[5,6] as inorganic ion exchangers. Antimony(V) silicate, synthesized in these laboratories,[7] has shown excellent stability and ion-exchange behavior. Since the mixed salts are found to show enhanced ion exchange properties over the single salts[8-10] it is important to study the properties of double salts based on antimony. In continuation of our such an effort the present paper deals with the synthesis, characterization and column applications of a thermally stable phase of the new inorganic ion exchanger viz. antimony(V) arsenatophosphate, exceptionally selective for some alkaline earths and transition metals.

Experimental

Reagents. Antimony pentachloride used in this study was of the 95% purity obtained from Fluka Switzerland. Trisodium orthophosphate and disodium hydrogenarsenate were of AnalaR grade (98.5—99%) obtained from B. D. H. Poole (England) and E. Merck (Darmstadt) respectively. All other reagents and chemicals were also of AnalaR grade.

Instruments Used. The following instruments were used for the various studies: A Philips X-ray diffraction unit with Cu*Kα* target, an Elico (India) pH-meter Model LI-10, a Bausch and Lomb Spectronic-20 spectrophotometer, a Beckman IR-20 spectrophotometer, a Pye Unicam Model Sp-2900 atomic absorption spectrophotometer, a Systronics (India) flame photometer and a water bath incubator shaker with a temperature variation of ±0.5 °C.

Preparation of the Reagent Solutions. A stock solution (1M[†]) of antimony pentachloride ($SbCl_5$) was prepared in 4 M HCl. Further dilutions to the desired concentration were also made by 4 M HCl. Disodium hydrogenarsenate and trisodium phosphate were dissolved directly in demineralized water (DMW).

Synthesis of the Ion Exchange Material. Various samples of antimony(V) arsenatophosphate were prepared by mixing 0.05 M solutions of $SbCl_5$, disodium hydrogenarsenate and trisodium orthophosphate in different volume ratios and adjusting the pH of the mother liquor at 0 to 1 by adding aqueous ammonia with constant stirring. The gels thus obtained were conditioned for 24 h at room temperature before being separated with suction. The excess acid was washed off with DMW and the material was dried in an air oven at 40 °C before cracking in DMW to obtain granules of uniform size suitable for column operation. They were converted into the H^+-form by putting in 1M HNO_3 at least for 24 h with intermittently replacing the supernatant liquid. After washing off the excess acid the material was dried at 40 °C and passed through different sieves to obtain the various mesh sized particles. On the basis of the appearance and Na^+-ion exchange capacity (i.e.c.) determined by the column process, a sample obtained by mixing the Sb, arsenate and phosphate solutions in the volume ratio 3 : 1 : 1 was selected for all the studies. Its i.e.c. was found to be 2.2 meq $(\text{g dry})^{-1}$.

Chemical Stability. The solubility of antimony(V) arsenatophosphate in various solvents was determined as given below:

250 mg portions of the material were kept with 25 ml of the solvent for 24 h at room temperature with intermittent shaking. 5 ml of the supernatant liquid was evaporated to dryness and the residue was dissolved in 10 ml DMW. Antimony, arsenic and phosphorus were then determined separately using the standard methods given below.

(1) Determination of Antimony. To the 2 ml portion of the above solution were added 1.6 ml of 18 M H_2SO_4 and 5 ml of KI reagent (11.2 g of KI+2 g of ascorbic acid in 100 ml water). The colored solution thus obtained was diluted to 10 ml with water in a standard volumetric flask and the absorbance was measured after 2—3 minutes at 420 nm against a reagent blank.[11]

(2) Determination of Arsenic. It was done by the molybdenum blue method.[12] The reagent solution was prepared by mixing 10 ml of solution A (1 g ammonium molybdate in 100 ml of 2.5M H_2SO_4) with 1 ml of solution B (0.15 g of hydrazine sulfate in 100 ml DMW) and diluting the mixture to 100 ml. Fresh reagent solution was prepared every time. 10 ml of this reagent solution was added to the sample solution (2 ml) and the mixture was heated on a steam bath for 15 min. After cooling to the room temperature, it was transferred to a 25 ml volumetric flask and diluted to the mark with DMW. The absorbance was taken at 840 nm.

Determination of Phosphorus. A teaspoonful carbon black was added to the sample solution (10 ml) followed by 100 ml of 0.5 M $NaHCO_3$. The contents of the flask were shaken for 30 min on a mechanical shaker and filtered through a Whatman No.42 filter paper. 15 ml of the filtrate

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[†] $1M=1\ \text{mol dm}^{-3}$.

Table 1. Chemical Stability of Antimony(V) Arsenatophosphate in Various Solvents

Solvent (25ml)	Amount dissolved in mg		
	Antimony (Sb)	Arsenic (As)	Phosphorus (P)
1M HNO_3	0.58	0.79	0.03
2M HNO_3	0.85	1.7	0.05
4M HNO_3	1.2	1.7	0.06
1M HCl	0.83	1.6	0.05
2M HCl	1.0	1.8	0.01
4M HCl	2.3	1.9	0.06
1M H_2SO_4	1.2	1.6	0.03
2M H_2SO_4	1.3	1.7	0.04
1M $HClO_4$	0.58	1.9	0.02
1M $NaNO_3$	0.00	0.21	0.00
2M $NaNO_3$	0.23	0.24	0.00
0.05M NaOH	0.69	0.23	0.01
0.1M NaOH	1.1	1.7	0.04
0.1M aq. NH_3	1.4	1.5	0.02
0.5M aq. NH_3	1.5	2.2	0.03
1M CH_3COOH	1.5	1.5	0.02
0.1M KOH	1.4	0.30	0.59

Amount of the material taken=250 mg.

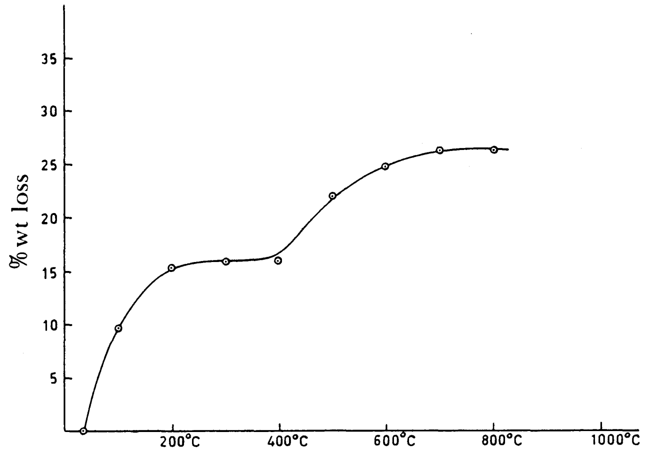

Fig. 1. % wt loss of the exchanger on heating to various temperatures.

was taken in a 25 ml volumetric flask followed by 5 ml of ammonium molybdate solution (1.5 g ammonium molybdate+100 ml of 3.2 M HCl+5 ml concd HCl). The sides of the flask were washed with distilled water and the solution was shaken thoroughly. 1 ml of $SnCl_2$ solution (10 g $SnCl_2 \cdot 2H_2O$ dissolved in 25 ml concd HCl diluted to 1320 ml with DMW) was then added to it and the volume was made up to the mark. The absorbance was taken at 660 nm, against a blank prepared in the similar manner.[13] Table 1 summarized the results.

Thermal Stability. Several 1 g portions of the exchanger were heated at various temperatures in a muffle furnace for 1 h each, and the i.e.c. was determined by the column process as usual after cooling them to room temperature. Percent weight loss was also recorded, the results of which are shown in Table 2 and Fig. 1.

Table 2. Effect of Heating on the Ion Exchange Capacity, Weight and Appearance of Antimony(V) Arsenatophosphate

Heating temperature °C	Appearance	Percent retention in i.e.c.	Percent weight loss
45	White	100	0.0
100	White	100	9.9
200	Light brown	100	15.5
400	Light brown	60	16.0
600	Pale yellow	18.2	25.0
800	Pale yellow	0.0	25.0

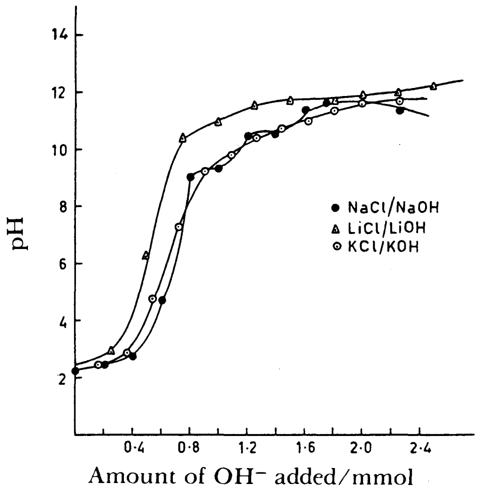

Fig. 2. pH titration curve for antimony(V) arsenatophosphate.

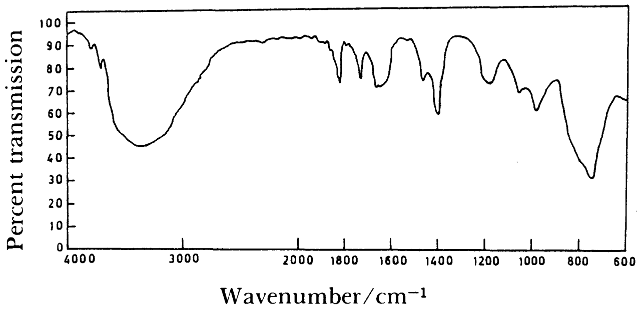

Fig. 3. Infrared spectra of antimony(V) arsenatophosphate in H^+ form.

Characterization of the Material. (A) Chemical Composition: 500 mg of the exchanger was dissolved in 20 ml concd HCl in a beaker by heating. The solution was further diluted to 50 ml by adding 4 M HCl. The amounts of antimony, arsenic and phosphorus were determined by the methods described above. The determinations were further confirmed by atomic absorption spectrophotometry. The mole ratio was found to be 6 : 1 : 5 for Sb, As, and P.

(B) pH Titrations: 500 mg of the exchanger in H^+-form was placed in each of the several 250 ml conical flasks, followed by the equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml to maintain the ionic strength constant. The pH of the solution was recorded after equilibrium (attained on keeping them for overnight) and plotted against the milliequivalents of the OH^- ions added as shown in Fig. 2.

(C) IR and X-Ray Studies: The IR spectrum of the exchanger in H^+-form was taken by the KBr disc method and is shown in Fig. 3. The X-ray diffraction patterns show the amorphous nature of the material.

Distribution Studies. 250 mg of the exchanger in H^+-form was shaken in an electric shaker at 30±2 °C for 4 h with 25 ml of the metal solution, adjusting the initial metal ion concentration less than 3% of the total ion-exchange capacity of the material. The metal ion concentrations in the solution before and after the equilibrium were determined by the standard volumetric methods using EDTA as the titrant.[14] The distribution coefficient (K_d) for alkaline earth and transition metal ions in DMW, $HClO_4$, and HNO_3 systems are summarized in Table 3.

The following formula was used for the calculation of the K_d values:

$$K_d = \frac{I-F}{F} \times \frac{V}{M}\ \mathrm{ml\,g^{-1}}$$

where

I = initial volume of the EDTA used,
F = final volume of the EDTA used,
V = total volume of the solution (ml),
M = mass of the exchanger (g).

Elution Behavior. 250 ml of the various $NaNO_3$ solutions (0.2, 0.4, 0.5, 0.8, 1.0, 1.2 M) were passed through the several columns (i.d. ca. 1 cm), each containing one gram of the exchanger in H^+-form with a flow rate ca. 0.5 ml min^{-1}. The H^+-ion thus eluted out was titrated against a standard (0.1M) NaOH solution. Maximum elution was observed with a 1M NaOH solution. Then, a similar column in H^+-form was eluted with a 1M $NaNO_3$ solution and the effluent collected in several 10 ml fractions, the total volume being again 250 ml. It was observed that the majority of the H^+-ion was released in the first 60 ml of the effluent.

Column Applications. Since the material appears to be highly selective for some transition metals such as Cu, Cd, Mn, and Zn, adsorption of these metal ions can be achieved on columns from a solution containing several other metal ions. Iron and mercury are not adsorbed appreciably and are excluded from the column of antimony(V) arsenatophosphate. Thus, the material can be used for exclusion of mercury, a chief pollutant, from an aqueous system by a simple column chromatographic method. Similarly, the method is applicable for some separations of analytical importance such as Fe(III) from Mn(II), Zn(II), Cu(II), Mg(II), Co(II), and Ba(II). Table 4 summarized the results of such separations on a column of i.d. ca. 0.6 cm containing 2 g of the 50—70 mesh size exchanger beads in H^+-form.

Results and Discussion

The main feature of this study has been to synthesize a chemically and thermally stable cation exchanger selective for certain heavy metals. As the results point out antimony(V) arsenatophosphate appears to have a high chemical stability in acids and alkalies (Table 1) and ion-exchange behavior. The most striking feature is, however, its extraordinary thermal stability (Table 2). It shows its original i.e.c. (2.20 meq (g dry)$^{-1}$) up to 200 °C and then loses slowly retaining 60% on heating upto 400 °C and 18% up to 600 °C. It is a peculiar behavior of this exchanger when compared with other materials of this class (Fig. 4).

Chemical analysis of the material points to the following emperical formula:

$$(Sb_2O_5)_3 \cdot H_3AsO_4 \cdot (H_3PO_4)_5 \cdot nH_2O$$

If it is assumed that whole of the external water is lost at 200 °C, then on the basis of the thermal studies (Table 2) we have the following expression for the number of external water molecules per molecule of the material, n

$$\frac{1800n}{M+18n} = x$$

where x is the percent weight loss at 200 °C and M is the molecular weight of the exchanger excluding the

Table 3. K_d Values of Some Metal Ions on Antimony(V) Arsenatophosphate in DMW, $HClO_4$, and HNO_3 Systems

Sl. No.	Metal ion	K_d values				
		DMW	0.01M $HClO_4$	0.1M $HClO_4$	0.01M HNO_3	0.1M HNO_3
1	Na(I)	150	55	15	80	34
2	K(I)	935	225	43	225	62
3	Mg(II)	3880	3800	469	T.A.[a]	342
4	Ca(II)	1980	1286	940	494	420
5	Ba(II)	2900	1400	650	500	400
6	Sr(II)	3700	3700	1800	1800	1166
7	Cu(II)	T.A.[a]	T.A.[a]	1540	3180	720
8	Fe(II)	202	113	90	126	101
9	Cd(II)	T.A.[a]	3640	523	1770	434
10	Pb(II)	1860	684	460	790	684
11	Mn(II)	T.A.[a]	T.A.[a]	672	T.A.[a]	451
12	Zn(II)	T.A.[a]	3600	1750	1133	825
13	Hg(II)	400	178	108	78	56
14	Ni(II)	1166	442	375	322	192

a) T.A.=Total adsorption.

Table 4. Some Binary Separations of Metal Ions Achieved on Antimony(V) Arsenatophosphate Columns

Sl No.	Separation achieved	Amount loaded μg	Amount found μg	% Error	Eluent used	Volume of the eluent used/ml
1	Hg(II)-Mg(II)	1404 Hg(II)	1383 Hg(II)	−1.4%	0.01M HNO_3	100
		268 Mg(II)	266 Mg(II)	−0.6%	1M NH_4NO_3	50
2	Hg(II)-Zn(II)	1404 Hg(II)	1393 Hg(II)	−0.8%	0.01M HNO_3	100
		670 Zn(II)	654 Zn(II)	−2.4%	1M NH_4NO_3	80
3	Fe(III)-Mn(II)	408 Fe(III)	402 Fe(III)	−1.4%	0.01M $HClO_4$	100
		538 Mn(II)	541 Mn(II)	+0.5%	1M NH_4NO_3	80
4	Fe(III)-Zn(II)	407 Fe(III)	388 Fe(III)	−4.8%	0.01M $HClO_4$	100
		654 Zn(II)	644 Zn(II)	−1.5%	1M NH_4NO_3	100
5	Fe(III)-Cu(II)	396 Fe(III)	388 Fe(III)	−2.1%	0.01M $HClO_4$	100
		540 Cu(II)	543 Cu(II)	+0.6%	1M NH_4NO_3	50
6	Fe(III)-Mg(II)	408 Fe(III)	399 Fe(III)	−2.0%	0.01M HNO_3	100
		249 Mg(II)	251 Mg(II)	+1.0%	1M NH_4NO_3	80
7	Fe(III)-Ca(II)	382 Fe(III)	371 Fe(III)	−2.9%	0.01M $HClO_4$	100
		309 Ca(II)	309 Ca(II)	0%	1M NH_4NO_3	80
8	Fe(III)-Ba(II)	413 Fe(III)	408 Fe(III)	−1.4%	0.01M $HClO_4$	100
		1071 Ba(II)	1078 Ba(II)	+0.6%	1M NH_4NO_3	90

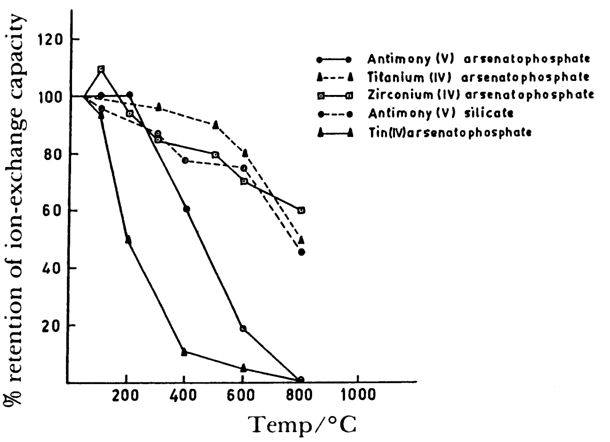

Fig. 4. Percent retention in the i.e.c. of antimony(V) arsenatophosphate and some other ion-exchangers on heating.

external water molecules. It gives the value of n as 16.

The pH-titration curves for alkali metals (Fig. 2) illustrate the maximum adsorption for Li^+ ions, which is obvious because of its highest hydrated radii ($Li^+_{(aq)}$=3.4 Å, $Na^+_{(aq)}$=2.76 Å, $K^+_{(aq)}$=2.32 Å). However, there is no appreciable difference in the adsorption behavior for Na^+ and K^+. It is also clear from the figure that the adsorption is a single step process. It is possible because the two acids, H_3AsO_4 and H_3PO_4 which provide the protogenic sites to the material, ionize almost to the same extent (pK_a for H_3PO_4=2.15 and pK_a for H_3AsO_4=2.3) thus releasing the H^+ ions simultaneously.

Infrared spectrum (Fig. 3) shows the peaks at wavenumbers 750, 950, 1100, 1200, 1400, 1700, 1750, 1800, and 3300 cm^{-1} representing the Sb–O stretchings (750), arsenate group (950), phosphate group (1100 and 1200) and the external water molecules (rest peaks) respectively.[15]

The most important aspect of an ion-exchange material is its analytical applications. Antimony(V) arsenatophosphate prepared in these studies has shown a maximum selectivity for Cu(II), Cd(II), Mg(II), Mn(II), and Zn(II) and a minimum selectivity for Hg(II), Ni(II), Fe(III). On the basis of these observations the following separations have been successfully achieved.

Hg(II)-Mg(II), Hg(II)-Zn(II), Fe(III)-Mg(II),
Fe(III)-Ba(II), Fe(III)-Cu(II), Fe(III)-Zn(II),
Fe(III)-Mn(II), Fe(III)-Ca(II).

Table 4 gives the salient features of these separations. Thus the material is useful for the separation of mercury from magnesium and zinc and of iron from magnesium, barium, copper, zinc manganese, and calcium.

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