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Tin(IV) Antimonate as a Lead-Selective Cation Exchanger: Synthesis, Characterization, and Analytical Applications

K. G. VARSHNEY* and Upma GUPTA
Department of Applied Chemistry, Faculty of Engineering and Technology,
Aligarh Muslim University, Aligarh-202002, India
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A new phase of a lead-selective cation exchange material, tin(IV) antimonate has been prepared, which possesses a good column exchange capacity (2.4 mequiv g^{-1}). Its characterization has been done on the basis of its ion-exchange characteristics and some instrumental studies such as TGA, IR, and X-ray diffraction. The utility of the material has been demonstrated by achieving some binary separations of metal ions on its column, such as Al(III)–Pb(II), Mg(II)–Pb(II), Fe(III)–Pb(II), Al(III)–Fe(III), Mg(II)–Al(III), and Mg(II)–Fe(III). Maximum limits of the column's loading capacity have also been evaluated for all metal ions.

Although a large number of inorganic ion exchangers have been prepared and studied so far,[1] there is still need to obtain a material which may have a good ion-exchange capacity, reproducible properties, stability, and selectivity for a particular ion. These properties are important for a better utility of a material in separation science. Tin(IV)-based inorganic ion exchangers[2–10] generally possess a greater stability both chemical and thermal as compared to the other materials of this class. The present study was undertaken to obtain an ion exchanger, superior in ion-exchange properties and stability over other similar materials.

Tin(IV) antimonate has been found to have a satisfactory behavior in this regard. It has been found to have a high selectivity for lead which is a chief polluting metal in the atmosphere. The common source of lead poisoning is the exhaust fumes from cars. About ninety percent of the lead present in the atmosphere comes from petrol fumes. Its accumulation in body leads to the poisoning and produces chronic illness characterized by severe anaemia and changes in the kidneys and arteries.

The following pages summarize the synthesis, characterization and analytical applications of tin(IV) antimonate. Its utility has also been explored for the quantitative separation of lead(II) from some binary mixtures on its column. A tentative structure of the compound has also suggested on the basis of these studies and IR spectroscopy.

Experimental

Reagents. The tin(IV) chloride used in this study was a C. D. H. (A. R.) product, while the potassium antimonate was a Loba Chemie product. All other reagents and chemicals were of Analar grade.

Apparatus. Spectrophotometry, pH metry, X-ray diffraction, and IR studies were performed by using a Bausch and Lomb Spectronic-20, spectrophotometer, an Elico pH-meter, Model LI-10, a Philips X-ray diffraction unit with a Mo $K\alpha$ target, and a Perkin Elmer spectrophotometer, Model-783, respectively. Heating effect on the ion-exchange capacity and weight loss was studied manually in a muffle furnace.

Preparation of the Reagent Solutions. A solution (0.05 M; 1 M=1 mol dm^{-3}) of tin(IV) chloride ($SnCl_4 \cdot 5H_2O$) was prepared directly in deionized water, obtained by passing the tap water through a deionizer plant (CA-20/U and CA-60/U). Potassium antimonate [$KSb(OH)_6$] was dissolved in 5.8 M HCl solution to obtain a 0.05 M solution.

Synthesis of the Ion-Exchange Material. A number of samples of tin(IV) antimonate were prepared by mixing the solutions of tin(IV) chloride (0.05 M) and potassium antimonate (0.05 M) in different volume ratios, such as 1:1, 1:2, 1:3, and 2:1. The pH of the resulting gel was fixed in the range 0—1 by adding aqueous ammonia with constant stirring. The gel thus obtained was kept for 24 hours at room temperature (ca. 30 °C) and filtered by suction. The excess acid was removed by washing with deionized water and the material was dried in an air oven at 45 °C. It was then cracked into small granules by putting in deionized water. The granules so obtained were of the uniform size suitable for column operation. They were converted into the H^+-form by treating with 1 M HNO_3 for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with a fresh acid. The material thus obtained was finally washed to remove the excess acid and then dried at 45 °C. It was then sieved to obtain particles of uniform size (50—72 mesh) before using for further studies. Following four samples were obtained possessing different Na^+ ion-exchange capacity shown in parentheses corresponding to the four mixing volume ratios as indicated above:

TA-1 (1.2), TA-2 (2.4), TA-3 (2.19), TA-4 (0.90)

All these samples were powdery in nature and white in color except the TA-1 which was light yellow. On the basis of its capacity and apparent stability in acids and bases, sample TA-2 was selected for all the studies.

Ion Exchange Capacity (i.e.c.). The i.e.c. was determined as usual by the column process taking 1 g of the exchanger (H^+-form) in a glass tube of internal diameter (i.d.) ca. 1 cm, fitted with the glass wool at its bottom and passing through it the eluant (ca. 250 ml) and maintaining a very slow flow rate (ca. 0.5 ml min^{-1}). The effluent was titrated against a standard alkali solution to find out the total H^+ ions eluted. The values of the i.e.c. in mequiv g^{-1} for various metal ions are given below:

Li^+—2.17, Na^+—2.40, K^+—1.95, Mg^{2+}—2.2, Ca^{2+}—3.12, Sr^{2+}—3.44, Ba^{2+}—3.3, NH_4^+—4.93

Effect of Eluant Concentration on the i.e.c. The extent of elution was found to be dependent on the concentration of the eluant. Hence, a fixed volume (250 ml) of the $NaNO_3$ solution of varying concentrations was passed through a column containing 1 g of the exchanger keeping a standard (0.5 ml min^{-1}) flow rate and effluent was titrated against a standard alkali solution for the H^+ ions eluted out. The optimum concentration of the eluant for a complete elution of H^+ ions in 250 ml was found to be 1 M.

Elution Behavior. Since the optimum concentration for a complete elution was observed to be 1 M, a column containing 1 g exchanger was eluted with a $NaNO_3$ solution of 1 M concentration in different 10 ml fractions with a minimum flow rate as described above. This experiment was conducted to find out the minimum volume necessary for a complete elution of the H^+ ions, which reflects the efficiency of the column. The column required 110 ml of the eluant.

Composition. 100 mg of the powdered sample was dissolved in a minimum amount of concentrated HCl. The solution was then diluted to 250 ml with 4 M HCl and the amount of tin and antimony was determined as follows:

(a) Determination of Tin: Tin was precipitated with a freshly prepared 6% aqueous solution of cupferron from an acidic solution cooled at 10 °C. It was filtered through a lose texture paper containing a small amount of paper pulp. The paper and precipitates were thoroughly washed, first with a cold H_2SO_4 solution (1:9) containing 1 g of cupferron/litre and then with a cold dilute cupferron solution (1 g l^{-1}), ignited and weighed as SnO_2.[11]

(b) Determination of Antimony: The filtrate was analyzed for antimony after destroying cupferron with perchloric acid. It was evaporated to dryness and the residue was collected in a weighed crucible, blasted in a muffle furnace at 900 °C and weighed as Sb_2O_4.

These studies suggest a molar composition of the compound as Sn:Sb=2:11.

Chemical Stability. The solubility of tin(IV) antimonate in various solvents was determined by the method given below:

200 mg portions of the material were kept with 20 ml of the solvent for 24 hours at room temperature with intermittent shaking. Antimony was determined quantitatively in the supernatant liquid as follows:

To the 2 ml portion of the above solution were added 1.0 ml of 9 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 color so developed was diluted to 10 ml with water in a standard volumetric flask and the absorbance was measured after 2—3 minutes at 425 nm against a reagent blank.[12]

The amount in ppm of antimony found in the various solvents after the above treatment are given below in parentheses:

DMW (1.71), 1 M CH_3COOH (1.11), 2 M HCl (2.05), 4 M HCl (4.09), 1 M HNO_3 (0.77), 2 M HNO_3 (1.02), 4 M HNO_3 (1.37), 1 M H_2SO_4 (1.24), 2 M H_2SO_4 (2.44), 1 M $HClO_4$ (0.68), 2 M $HClO_4$ (0.94), 0.1 M NaOH (0.98), 1 M $NaNO_3$ (0.08), 1 M HNO_3 (0.21), 1 M NH_4NO_3 (0.21).

It dissolved appreciably in 0.1 M KOH solution.

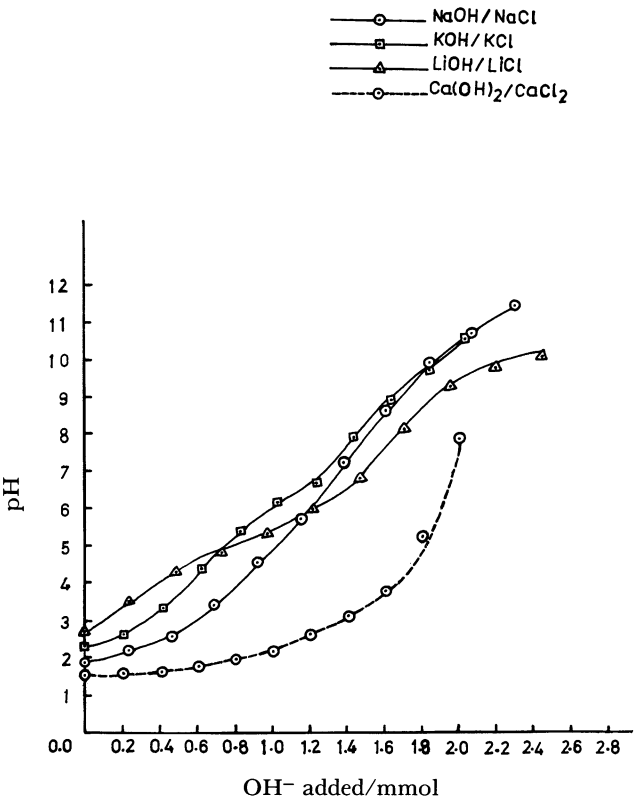

Fig. 1. Equilibrium pH titration curves of tin(IV) antimonate.

pH Titrations. pH titrations were performed by the method of Topp and Pepper[13] 500 mg of the exchanger were placed in each of the several 250 ml conical flasks, followed by the equimolar solutions of alkali and alkaline earth 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 solutions was recorded after 24 hours to find out the time required for equilibrium. It was observed that the equilibrium was achieved in 12 days. Figure 1 shows the pH-titration curves after keeping the mixtures for such a time period.

Thermal Analysis. For thermal stability several 1 g portions of the exchanger were heated for 1 hour each at various temperatures in a muffle furnace, and the Na^+ ion-exchange capacity in mequiv/dry g was determined as usual by the column process at room temperature. The results are summarized below:

45 °C—2.40; 100 °C—2.40; 200 °C—2.05; 400 °C—1.90; 600 °C—1.00; 800 °C—0.98.

The same sample was also heated at 400 and 800 °C for 4 hours each resulting to the i.e.c. as 1.50 and 0.55 mequiv/dry g respectively. No change in color was observed upto 200 °C. Above this temperature the color changed to light yellow, yellow, and dirty yellow at the temperatures mentioned above in that order.

For studying the weight loss in the material, 50 mg sample was heated as above at various temperatures for an hour each and weight loss recorded. It was repeated to assure the

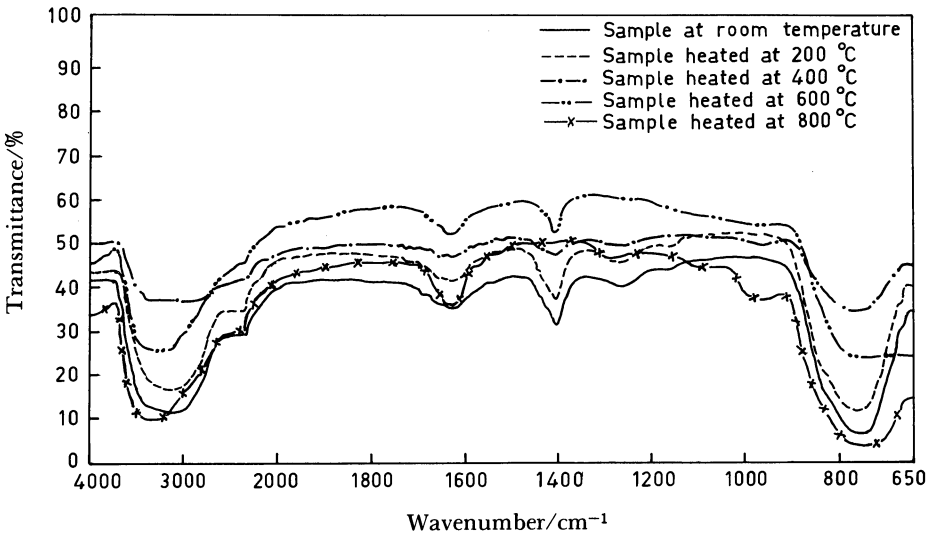

Fig. 2. IR spectra of normal and heated samples of tin(IV) antimonate cation exchanger.

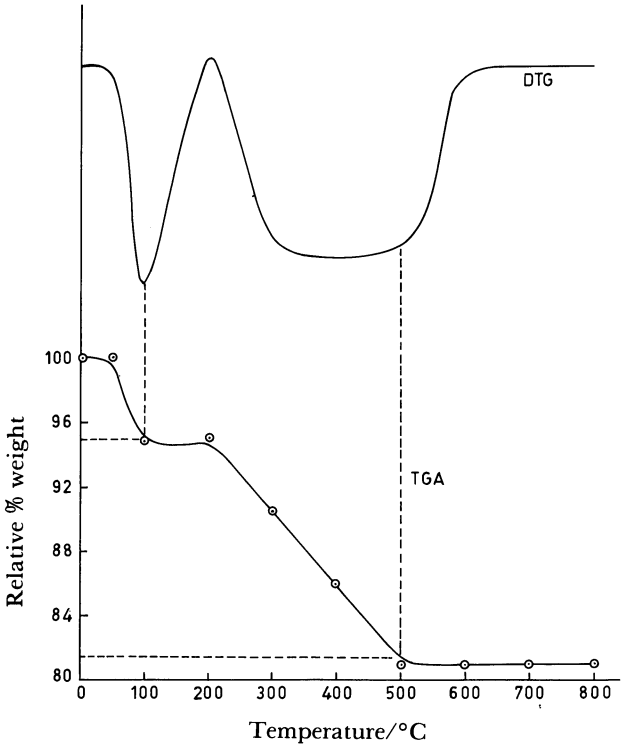

Fig. 3. Thermogravimetric (TGA) and differential thermogravimetric (DTG) curves of tin (IV) antimonate.

reproducibility. Figure 3 shows the thermogram and its differential (DTG).

IR Studies. The IR spectra of tin(IV) antimonate were taken by the KBr disc method and are shown in Fig. 2, for the various samples heated at different temperatures.

Distribution Studies. Distribution studies were performed on a sample of tin(IV) antimonate (TA-2) for different metal ions in various solvents as follows:

200 mg of the exchanger beads in H^+-form were equilibrated with the selected solvents (20 ml) by keeping it at room temperature for 24 hours. The initial metal ion concentration was so adjusted that it may not exceed 3% of the total ion-exchange capacity of the material and the determination was carried out volumetrically using EDTA as titrant,[14] while the concentration of alkali metal ions was determined by the flame photometer.

The K_d values, as summarized in Table 1, were obtained by the formula

$$K_d = \frac{I - F}{F} \times \frac{V}{A} \quad (\text{ml g}^{-1})$$

where

I=Initial amount of the metal ion in the solution phase.
F=Final amount of the metal ion in the solution phase.
V=Volume of the solution (ml).
A=Amount of the exchanger (g).

Separations Achieved. The 60—100 mesh sized particles of the exchanger (2 g) in H^+-form were used for the column separation in a glass tube having an internal diameter of ca. 0.6 cm. The column was washed thoroughly with deionized water and the mixture to be separated was loaded on it, maintaining a flow rate of ca. 2—3 drops/min. The separation was achieved by passing a suitable solvent through the column as eluent and ther metal ions in the effluent were determined quantitatively by EDTA titrations. The salient features of these separations are given in Table 2 and Fig. 4.

Discussion

The most exciting feature of these studies is the unusually high ion-exchange capacity of the material, prepared as an inorganic ion exchanger. It appears that the tin(IV) antimonate prepared in these studies is superior to the other tin(IV) based inorganic ion exchangers in terms of their i.e.c. and thermal stability[2-10] as a comparison shows. A study of the

Table 1. K_d Values of Some Common Metal Ions on Tin(IV) Antimonate in Various Media

Metal ion	$K_d \times 10^{-2}$								
	Solvent								
	Deionized water	0.01 M HNO_3	0.1 M HNO_3	1 M HNO_3	0.01 M $HClO_4$	0.1 M $HClO_4$	1 M $HClO_4$	1 M NH_4NO_3	1 M $NaNO_3$
Na(1)	69.0	13.0	6.8	4.0	13	6.8	4.0	2.5	0.0
K(I)	34.0	6.7	3.3	2.3	7.0	4.0	2.0	1.3	0.97
Mg(II)	7.1	3.1	1.0	1.0	1.7	1.0	0.62	0.62	0.62
Ca(II)	7.4	7.4	7.4	3.1	7.4	7.4	7.4	3.1	3.1
Sr(II)	7.0	7.0	7.0	7.0	7.0	7.0	7.0	3.0	3.0
Ba(II)	5.3	5.3	5.3	2.0	5.3	5.3	2.0	2.0	1.0
Al(III)	4.0	4.0	0.0	0.25	4.0	1.5	4.0	0.67	1.5
Mn(II)	7.0	7.0	3.0	1.7	7.0	3.0	1.0	1.7	1.0
Fe(III)	74.0	74.0	6.5	6.5	6.5	2.8	6.5	6.5	6.5
Co(II)	7.5	7.5	1.8	3.3	7.5	3.3	84.0	3.3	7.5
Ni(II)	80.0	7.1	1.0	1.7	7.1	1.0	80.0	1.0	1.7
Cu(II)	69.0	6.0	6.0	2.3	6.0	6.0	5.5	5.5	5.5
Zn(II)	8.9	8.9	4.0	2.3	8.9	8.9	8.9	4.0	4.0
Cd(II)	80.0	7.1	3.0	3.0	7.1	3.0	7.1	7.1	7.1
Hg(II)	4.0	4.0	1.5	1.5	4.0	0.67	0.67	4.0	1.5
Pb(II)	210.0	210.0	20.0	210.0	210.0	210.0	210.0	20.0	20.0
Bi(III)	—	—	89.0	8.0	—	89.0	89.0	—	—

(—)=Not detectable.

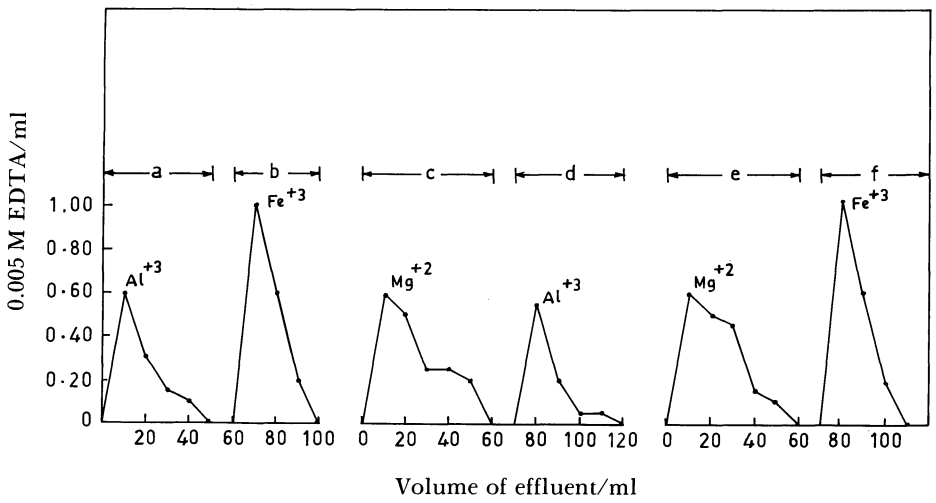

Fig. 4. Separation of Al^{3+} from Fe^{3+}, Mg^{2+} from Al^{3+}, and Mg^{2+} from Fe^{3+} on tin(IV) antimonate columns: (a) and (d), 1 M HNO_3; (b) and (f), 2 M HCl+2 M NH_4Cl; (c) and (e), 0.1 M $HClO_4$.

percent retention of the i.e.c. on heating to various temperatures indicates that the material (TA-2) does not lose its i.e.c. upto 100 °C. It retains about 41% of its i.e.c. even on heating upto 800 °C which is a remarkable feature. The mixed oxides produced on heating the material upto such a high temperature might be converted into their hydrated forms, when the material is treated with water, which may be responsible for the ion exchange behavior. Another important feature of this ion exchanger is its reproducible nature. It is observed that tin(IV) antimonate obtained in various batches does not show any appreciable deviation in its ion-exchange properties. Chemically, also the material appears to be highly stable. As the results indicate only a negligible amount of TA dissolved in various solvents out of the 200 mg taken for its chemical stability in each experiment. The tin(IV) antimonate prepared earlier by Qureshi et al.[2] seems to inferior in this regard. It appears that the starting material used for the preparation of the ion exchanger plays an important role in determining its properties. In the earlier studies antimony(V) chloride was used for synthesizing the material as against the potassium antimonate [$KSb(OH)_6$] used in the present study. No definite conclusion can, however, be drawn at the moment

Table 2. Some Binary Separations of Metal Ions Achieved on Tin(IV) Antimonate Columns

Sl. No.	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used	Volume of eluant (ml)	Maximum limit of the loading capacity of the column/μg
1	Al(III)–Pb(II)	155.3 (Al)	155.3 (Al)	0.00	1 M HNO_3	40	Pb —20721.00
		5698.2 (Pb)	Not leached (Pb)	—	—	—	Al — 809.40
2	Mg(II)–Pb(II)	224.96 (Mg)	218.88 (Mg)	−2.70	0.1 M $HClO_4$	50	Fe — 2513.25
		5698.2 (Pb)	Not leached (Pb)	—	—	—	Mg— 1216.00
3	Fe(III)–Pb(II)	558.5 (Fe)	572.46 (Fe)	+2.49	2 M HCl+2 M NH_4Cl	30	
		5698.2 (Pb)	Not leached (Pb)	—	—	—	
4	Al(III)–Fe(III)	155.3 (Al)	162.0 (Al)	+4.31	1 M HNO_3	50	
		544.5 (Fe)	530.6 (Fe)	−2.55	2 M HCl+2 M NH_4Cl	40	
5	Mg(II)–Al(III)	224.96 (Mg)	218.88 (Mg)	−2.70	0.1 M $HClO_4$	60	
		114.58 (Al)	114.58 (Al)	0.00	1 M HNO_3	50	
6	Mg(II)–Fe(III)	231.04 (Mg)	218.88 (Mg)	−5.26	0.1 M $HClO_4$	60	
		558.5 (Fe)	558.5 (Fe)	0.00	2 M HCl+2 M NH_4Cl	40	

because of the confusing and contradictory statements regarding the varying water contents in the antimonic acid produced on the surface of the material depending upon the starting antimony salt.[15]

The column elution experiments indicate a dependence of the concentration of the eluant on the rate of elution. The minimum molar concentration of $NaNO_3$ as eluant is 1 M for the maximum elution of H^+ ions from a column of 1 g of TA. The elution is quite fast as only 110 ml of the effluent is sufficient for almost complete elution of the H^+ ions from its column.

pH titration curves obtained under equilibrium conditions are shown in Fig. 1 for LiOH/LiCl, NaOH/NaCl, KOH/KCl, and $Ca(OH)_2/CaCl_2$ systems. These studies are different from others generally made on such materials. The normal practice has been to perform the pH-titration under a nonequilibrium process.[2] As it is clear from the figure, the inflection point for the exchange of alkali metals resemble with the i.e.c. obtained, i.e. 2.4 mequiv/dry g. The pH titration curve for Ca^{2+} however does not show any inflection. In this regard our product is similar to antimony(V) silicate[16] and hydrated antimony oxides.[17]

Thermogravimetry and IR studies point to the following tentative formula of the compound

$$Sn_2[Sb(OH)_6]_{11}\cdot nH_2O$$

Assuming that at 100 °C only the external water molecules are lost, the 5.2% loss represented by the TGA curve must be due to the loss of nH_2O from the above structure. The value of 'n', the external water molecules, can be calculated using Alberti's equation:[18]

$$18n = \frac{x(M + 18n)}{100}$$

where, x is the % weight loss (5.2%) in the exchanger on heating upto 100 °C. M=molecular weight of the material minus the external water molecules.

The above equation then gives the external water molecules per molecule of tin(IV) antimonate as ca. 8.

The differential thermogram (DTG) gives a better view of the changes corresponding to the two inflections in the TGA curve (Fig. 3). The sharp peak at ca. 100 °C represents the loss of external water molecules while the other broad one is due to the condensation process which continues upto ca. 500 °C. Beyond this temperature the material might have completely changed into the oxides that is why no further weight loss occurs.

The IR studies confirm the presence of –OH groups and external water molecules in addition to the metal oxides (SnO and Sb_2O_5) present in the material.[19] The

peaks at 1400—1500 cm^{-1} and ca. 3000 cm^{-1} are representative of the external water molecules, the former being also representative of the strongly bonded OH groups in the matrix. As Fig. 2 indicates these peaks are observed even when the material is heated at a much high temperature. It may be due to the absorption of water molecules from the atmosphere by the material during cooling. X-Ray studies point to the amorphous nature of the TA as no peaks are observed by the diffraction pattern.

The most promising property of the material is its extraordinary high selectivity for lead. When the separation of lead from other metal ions was tried on its column, it was observed that lead was totally adsorbed and its leaching was not possible even in an eluant consisting of 4 M HCl+4 M KCl. It may be due to the formation of an insoluble lead antimonate on the surface. Lead antimonate has been found to an inorganic ion exchanger.[20] The experimental details of some representative separations of Pb(II) from Al(III), Fe(III), and Mg(II) are given in Table 2. Thus, the material can be utilized for a quantitative separation of lead from the mixtures containing several metal ions. This property of TA may prove useful in the environmental studies. Other binary separations tried on the TA column have been Al(III)–Fe(III), Al(III)–Mg(II), and Mg(II)–Fe(III). Table 2 and Fig. 4 illustrate the salient features of these separations.

Conclusion

Tin(IV) antimonate, prepared in these studies as a new inorganic ion-exchange material has a good ion exchange capacity and is highly selective for Pb. This behavior of TA is promising in the field of pollution chemistry where an effective separation method is needed for lead from other pollutants. This material has been characterized on the basis of its chemical and thermal analysis, IR studies, and some ion-exchange characteristics such as ion-exchange capacity, elution and concentration behavior, pH-titrations and distribution studies. On the basis of distribution studies some binary metal separations have been achieved.

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