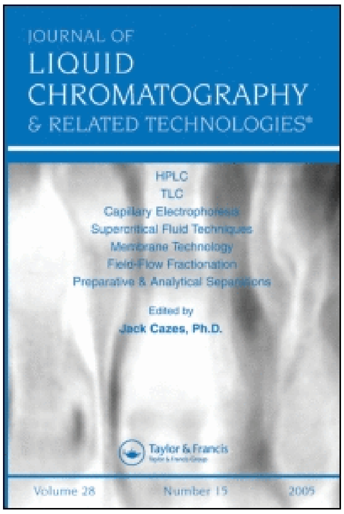

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STUDIES ON SYNTHETIC INORGANIC ION EXCHANGERS-III QUANTITATIVE SEPARATIONS OF Mg^{2+} -Pb^{2+}, Zn^{2+} - Pb^{2+} Cu^{2+} - Pb^{2+}, Al^{3+} - Pb^{2+}, Zn^{2+} - Cd^{2+}, AND Mg^{2+} - Cd^{2+} ON LEAD ANTIMONATE COLUMNS

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ABSTRACT

A new inorganic ion exchanger, lead antimonate has been synthesized having an Pb:Sb ratio of 1:5 and cation exchange capacity of 1.46 mequiv./g. It is fairly stable in water and dilute solutions of acids, bases and salts. Ion distribution studies on twenty metal ions have been determined on this gel at pH 1,2,3 and 5. The following mixtures have been separated: Mg^{2+} - Pb^{2+}, Zn^{2+} - Pb^{2+}, Zn^{2+} - Pb^{2+}, Cu^{2+} - Pb^{2+}, Al^{3+} - Pb^{2+}, Zn^{2+} - Cd^{2+} and Mg^{2+} - Cd^{2+}. Mg^{2+} and Al^{3+} were removed with 0.4 M ammonium nitrate, Cu^{2+} and Zn^{2+} with 0.4 M ammonium nitrate + 0.1M nitric acid (1:1), Pb^{2+} with 0.5M nitric acid and Cd^{2+} with 0.25M nitric acid. A tentative structure of this material is proposed on the basis of chemical analysis, pH titrations, thermogravimetry and IR spectrophotometry.

INTRODUCTION

Studies in the field of inorganic ion exchangers are increasing day by day due to their selectivity and stability under certain conditions. Analytical applications in the field of separation science have been reviewed by Inczedy (1) and Walton (2). Antimonates of zirconium (3), titanium (4), tin (5), cerium (6), thorium (7), tantalum (8), aluminium (9), and iron (10) have been synthesized and used for various separations in analytical chemistry. Of the various compounds studied, the lead compounds have received scant attention. A search of literature showed that no studies have been reported on lead antimonate (PbSb). We have, therefore, synthesized this exchanger under various conditions. The importance of this synthesis has been demonstrated by achieving some difficult quantitative separations on its columns.

EXPERIMENTAL

Reagents

Lead nitrate (BDH), potassium pyroantimonate (BDH) were used. All other reagents used were of AnalaR grade.

Apparatus

Digital pH meter (Toshniwal), Carlziess-Jena-VSU2-P spectrophotometer (DDR), Flame photometer (Photoelectric Instruments Jodhpur, India), Spectromom-2000 (Hungary) were used for pH determinations, spectrophotometric, flame photometric and IR studies. TG analysis was performed on the instrument from Fertilizer Corporation of India (Sindri).

Synthesis

Six samples of lead antimonate were prepared by mixing 0.2M solution of potassium pyroantimonate with 0.2M solution of lead nitrate under conditions given in Table 1. The required pH of the product was adjusted by adding either hydrochloric acid or ammonium hydroxide or potassium hydroxide. The precipitate so obtained was filtered and washed with demineralized water (pH 6). The gel was dried at 40°C. The dried product broke down into small granules when immersed in water. The material was converted into the H^+ form by treatment with 1.0M nitric acid for 24 hrs. with occasional shaking and intermittently changing the acid. The product was washed free of acid with demineralised water and dried at 40°C in a temperature controlled oven.

Ion-Exchange Capacity

The ion-exchange capacity of various samples of lead antimonate was determined by taking 1.0g of the exchanger in the hydrogen form in a glass column having glass wool support. Column after washing with demineralised water was eluted with 1.0M soldium nitrate solution. 300 ml of effluent was collected at a rate of 15-20 drops/min. each time. Liberated H^+ ions were titrated against standard sodium hydroxide solution.

Ion-exchange capacity for some monovalent and divalent cations on sample 4 was also determined.

Chemical Analysis

Lead in lead antimonate samples was determined by precipitating it as $PbSO_4$ 0.2g of the sample was heated with 4.1 ml conc. sulphuric acid on a low temperature hot plate until thick fumes are evolved freely. Cooled and diluted the solution carefully with about 100 ml of water. Precipitates were kept overnight and filtered through sintered glass crucible. The precipitate was washed with 3% H_2SO_4 and then with rectified spirit. Dried the precipitate at 130°C and weighed as $PbSO_4$.

Antimony was estimated from the filtrate spectrophotometrically by KI and ascorbic acid method (11).

Chemical Stability

Solubilities of lead antimonate samples in DMW and of the chosen sample in various solvents were determined. 0.2g of the sample was kept in contact with 20 ml of the solvent for 24 hrs. with intermittent shaking and then filtered. Spectrophotometric determination of lead by dithizone extraction method, and of antimony by KI-ascorbic acid method (11) were carried out from the filtrate.

Sorption Studies

The distribution coefficients (K_d values) for the cations have been determined at various pH values using the equation:

$$K_d = \frac{I-F}{F} \times \frac{50}{0.2} \text{ meq/g}$$

where I is the initial volume of 0.005M EDTA used for the cation and F is the volume of 0.500M EDTA used after equilibration. Total volume of the equilibrating solution was 50 ml and the amount of exchanger taken was 0.2g.

pH Titrations

pH titrations with the chosen sample were performed by the added salt method (12).

Column Preparation

For separation studies a glass column (50 x 0.60 cm) was used with a glass-wool support. 1.5g of the exchanger was placed in the column. Cation was loaded after washing the column with demineralised water. The flow-rate of effluent was 8-10 drops/min. Cations in the effluent were determined by EDTA (13).

Physical Measurements

Infrared studies were made in Nujol and KBr disc methods. Thermogravimetric analysis was done by heating the exchanger (0.4g) at a rate of 6°/min.

RESULTS

Physical Properties

The important properties of lead antimonate samples are recorded in Table I. The dried products crack when immersed in water.

TABLE I

Conditions of Preparation and Properties of Lead Antimonate Samples.

	Conditions of Synthesis				Properties						
Sample Number	Molarity of Reagents	Mixing Volume Ratio	pH	Color	Ion-Exchange Capacity $[Na^+]$ meq/g	Precipitation Temp°C	Chemical Composition (mole ratio) Pb		Sb	Solubility in DMW mg/lit Pb	Sb
1	0.2MLN+0.2MPA	1:1	1	White	0.65	38	1	:	4.406	68.00	80.00
2	0.2MLN+0.2MPA	1:1	2	White	0.35	38	1	:	3.449	36.00	88.00
3	0.2MLN+0.2MPA	1:1	3	White	0.20	38	1	:	2.400	28.00	20.00
4	0.2MLN+0.2MPA	1:2	1	White	1.46	100	1	:	5.437	0.00	15.00
5	0.2MLN+0.2MPA	1:2	2	White	0.95	100	1	:	3.549	0.00	32.00
6	0.2MLN+0.2MPA	1:2	3	White	0.35	100	1	:	0.836	0.00	40.00

NOTE: LN = Lead nitrate

PA = Potassium pyroantimonate

DMW = Demineralised water

TABLE II

Effect of Temperature and Regeneration Cycles on Cation Exchange Capacity of Lead Antimonate Sample (4).

	Effect of Temperature			Effect of Regeneration Cycles	
Temperature °C	Ion-Exchange Capacity meq/g[Na$^+$]	% Loss in IEC	Color	Regeneration Cycle	IEC Na$^+$ meq/g.
40	1.46	0.00	White	I	1.46
100	1.14	21.90	White	II	1.45
200	0.84	42.46	White	III	1.40
300	0.56	61.64	Brownish White	IV	1.38
400	0.36	75.34	Pale Yellow	-	-
600	0.05	96.57	Creamy White	-	

TABLE III

Ion Exchange Capacities of Lead Antimonate (Sample 4) With Some Monovalent and Divalent Cations.

Metal Ion	Salt Solution	Ion-Exchange Capacity (Meq/g)	Hydrated Radii (A°)	pH of Solution
Li^+	Lithium Nitrate (1M)	0.62	3.40	6.05
Na^+	Sodium Nitrate (1M)	1.46	2.76	5.05
K^+	Potassium Nitrate (1M)	1.55	2.32	6.90
Mg^{2+}	Magnesium Chloride (0.5M)	0.84	7.00	4.80
Ca^{2+}	Calcium Chloride (0.5M)	1.12	6.30	6.40
Sr^{2+}	Strontium Chloride (0.5M)	1.52	-	6.50
Ba^{2+}	Barium Chloride (0.5M)	1.60	5.90	6.95

Chemical Properties

Effect of drying temperature on the cation-exchange capacity and the change in color of the exchanger is given in Table II. A slight decrease in the exchange capacity, as observed in the four successive regeneration cycles was found to be 1.46, 1.45, 1.40, and 1.38 meq/g respectively. Chemical stability data is recorded in Table IV.

TABLE IV

Solubilities of Lead Antimonate (Sample 4) in Various Solvents.

Solvent	Solubility (mg/lit) at 38°C	
	Pb	Sb
DMW	0.0000	15.0000
0.1N-NaOH	0.0000	23.0000
0.1N-NaCl	0.0000	12.0000
0.1N-HNO_3	0.0000	76.0000
0.1N-CH_3OOOH	0.0000	16.0000
Methanol	0.0000	0.0000

TABLE V

Distribution Coefficients (K_d) of Cations on Lead Antimonate Sample (4).

	K_d Values (ml/g)				
		pH			
Cation	1.05 1	1.90 2	2.85 3	5.20 5	0.1M KNO_3
Na^+	-	-	-	62.50	-
K^+	-	-	-	97.22	-
Mg^{2+}	18.40	47.25	49.38	184.61	36.76
Zn^{2+}	20.45	24.05	49.38	40.90	39.06
Ba^{2+}	26.78	61.40	71.76	537.03	275.00
Sr^{2+}	21.75	50.92	131.79	6083.33	800.00
Ca^{2+}	6.66	43.80	76.53	737.50	191.66
Pb^{2+}	312.50	650.00	3750.00	C.A	C.A
Cu^{2+}	10.08	19.39	21.93	64.81	29.54
Co^{2+}	-	-	-	2250.00	125.00
Mn^{2+}	-	-	-	845.00	231.62
Hg^{2+}	-	-	-	431.25	382.81
Ni^{2+}	-	-	-	49.09	8.52
Cd^{2+}	-	-	-	C.A	C.A
Vo^{2+}	0.00	69.44	88.41	134.61	31.25
Al^{3+}	0.00	21.87	29.60	129.03	16.89
Cr^{3+}	59.21	63.57	125.00	C.A	C.A
La^{3+}	0.00	40.66	60.18	300.00	47.17
Nd^{3+}	-	-	-	194.91	16.31
Th^{4+}	24.20	40.19	147.06	554.34	166.66

NOTE: C.A = Complete Adsorption

TABLE VI

Separations of Some Binary Cation Mixtures on Lead Antimonate Sample (4) Columns.

Separation	Eluents	Volume of Effluent (ml)	Cations Taken µg	Cations Found µg	% Error
Mg^{2+} - Pb^{2+}	Mg^{2+}-0.4MNH$_4$NO$_3$	60	236	237	+ 0.4
	Pb^{2+}-0.5MHNO$_3$	40	6257	6260	+0.04
Zn^{2+} - Pb^{2+}	Zn^{2+}-0.MNH$_4$NO$_3$+ 0.1MHNO$_3$	70	1588	1588	0.00
	Pb^{2+}-0.5MHNO$_3$	40	6257	6263	+0.08
Cu^{2+} - Pb^{2+}	Cu^{2+}-0.4MNH$_4$NO$_3$+ 0.1MHNO$_3$	60	1366	1378	+0.90
	Pb^{2+}-0.25MHNO$_3$	70	6257	6250	-0.11
Zn^{2+} - Cd^{2+}	Zn^{2+}-0.4MNH$_4$NH$_3$+ 0.1MHNO$_3$	100	2020	2023	+0.07
	CD^{2+}-0.25MHNO$_3$	120	5339	5421	+1.58
Mg^{2+} - Cd^{2+}	Mg^{2+}-0.4MNH$_4$NO$_3$	80	225	225	0.00
	CD^{2+}-0.25MHNO$_3$	100	5339	5300	-0.74
Al^{3+} - Pb^{2+}	Al^{3+}-0.4MNH$_4$NO$_3$	60	266	266	0.00
	Pb^{2+}-0.25MHNO$_3$	60	6058	6057	-0.01

Sorption Studies

Distribution coefficients for 20 cations at different pH on lead antimonate (Sample 4) were determined. The cations Pb^{2+}, Cd^{2+} and Cr^{3+} were completely adsorbed at pH 5. Kd values for the various cations are listed in Table V. Separation factors being large enough with those cations. The exchange potentialities of lead antimonate (Sample 4) are used to achieve a number of separations. The results are given in Table VI and Figure 6.

TG and IR Studies

Results of TG analysis on lead antimonate (Sample 4) in Na^+ and H^+ form are presented in Figure 3.

Infrared spectra of sample 4 in H^+ form dried at 40°, 100°, 200°, 300°, 400°, and 600° are similar and resemble those reported for Tin (IV) antimonate (5). The bands with maxima at about 3300, 1380 and 1610 cm^{-1} are characteristic of the stretching vibration of interstitial water and OH groups ν_1 (H_2O or OH), the M-OH deformation vibration (δ_2 OH) and the deformation vibration of interstitial water (δ_1 H_2O) respectively (Figure 4).

DISCUSSION

Lead antimonate shows some unusual features as an ion exchanger. It has high chemical and thermal stabilities (Table IV and II, respectively). It shows a very high uptake of cations. The results of ion exchange capacities of various samples show that the ion exchange capacity of the samples prepared at 100°C are comparatively higher than those prepared at room temperature (Table 18, Figure 2). This is probably due to the fact that initially a number of phases are present in the ion exchange material and on heating this becomes more homogeneous. It is obvious from Table I that as the precipitating pH of various samples increases, the Pb/Sb ration increases ultimately there is decrease in ion exchange capacity as noticed by SZIRTES et. al. (14). In order to investigate the working capacity of the exchanger, ion exchange capacities with some mono- and divalent ions were determined (Table III). The exchange capacities for the divalent ions are found to be in the order Mg^{2+}, < Ca^{2+} < Sr^{2+} < Ba^{2+}, showing that the ions enter the exchanger phase as hydrated ions. Lead antimonate can be used up to 300°C with about 40% of its ion exchange capacity retained at this temperature (Table II). It can be regenerated and used over and over again for its cation exchange properties without suffering much decrease in ion exchange capacity.

Potentiometric titration curves (Figure 1) show one inflexion point, exhibiting monofunctional behavior of the exchanger analogous to antimonates of tin and titanium. It can be easily inferred from the curves that the exchanger is not appreciably hydrolysed in acid medium. The results of chemical stability of lead antimonate Sample 4 are given in Table IV. It was found that the material was fairly stable in inorganic as well as in organic solvents. On heating PbSb beyond 200°C, its color begins to change (Table II) and becomes hard. It is probably due to the loss of interestitial water molecules. Comparison of results of thermogravimetric analysis of the H^+ - form and Na^+ - form of exchanger makes it clear that the weight loss in the former is higher than in the later case. It is therefore, obvious that lead antimonate contains free water molecules as well as OH groups. This fact is further supported by the infrared spectra of the PbSb (Figure 4). The bands at 3300, 1610 and 1300 cm^{-1} also start diminishing as the drying temperature is increased.

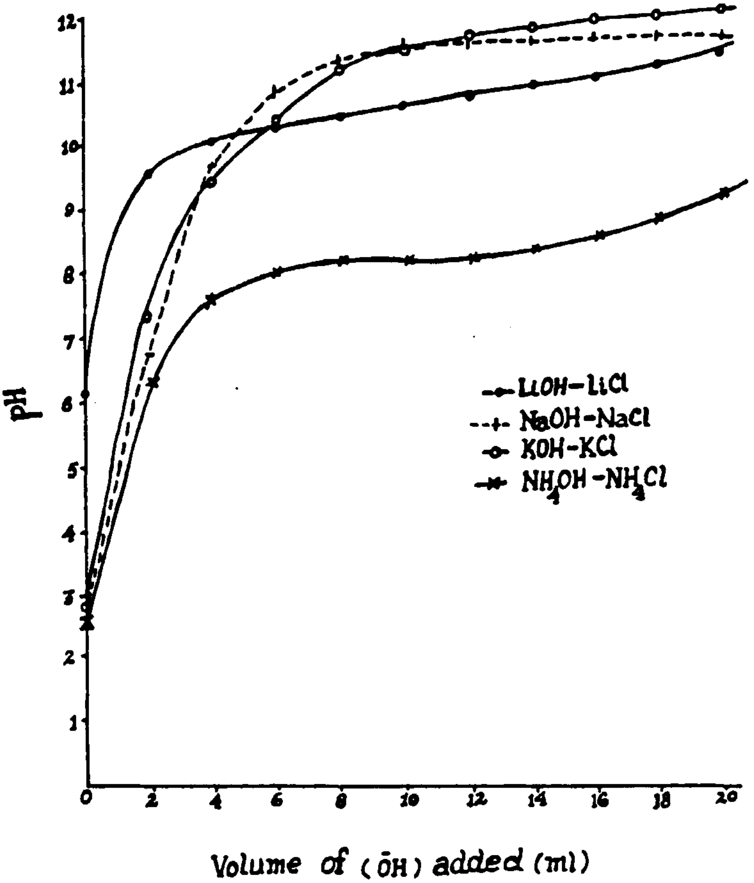


Fig. 1. pH Titrations of lead antimonate Sample-4.

The results of chemical analysis show Pb:Sb ration in PbSb Sample 4 as 1:5. Thermogravimetric analysis results show loss in weight due to water molecules to the extent of 18%. Since on heating, oxides of lead and antimony are formed, which should also be in the same mole ratio. Therefore, the empirical formula of the mixed oxide is $PbO.2.5Sb_2O_5$ having formula weight 1033. If "n" is the number of moles of water per mole of mixed oxide then

$$\frac{1800n}{(1033 + 18n)} = 18 \text{ or } n = 12.6 \approx 13$$

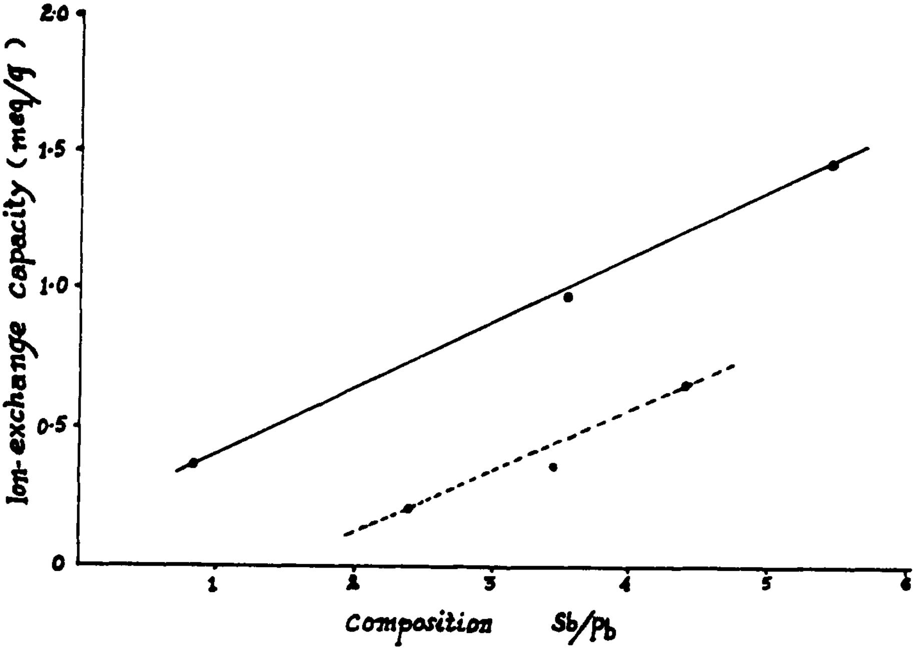
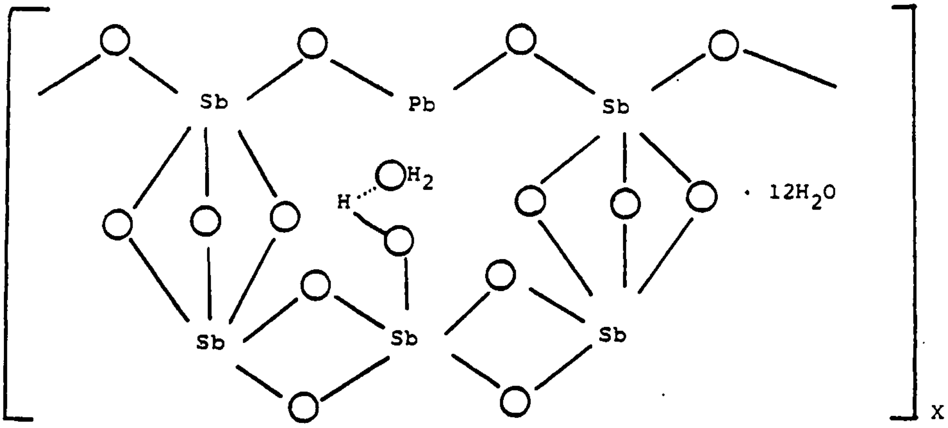


Fig. 2. Plots of ion-exchange capacity against composition; (i) Samples 1, 2, & 3 ------- (ii) Samples 4, 5, & 6 ———.

Molecular formula can therefore be written as $PbO.2.5Sb_2O_5.13H_2O$ having formula weight 1267. In the light of above discussion, a tentative structure of lead antimonate sample 4, can be written as



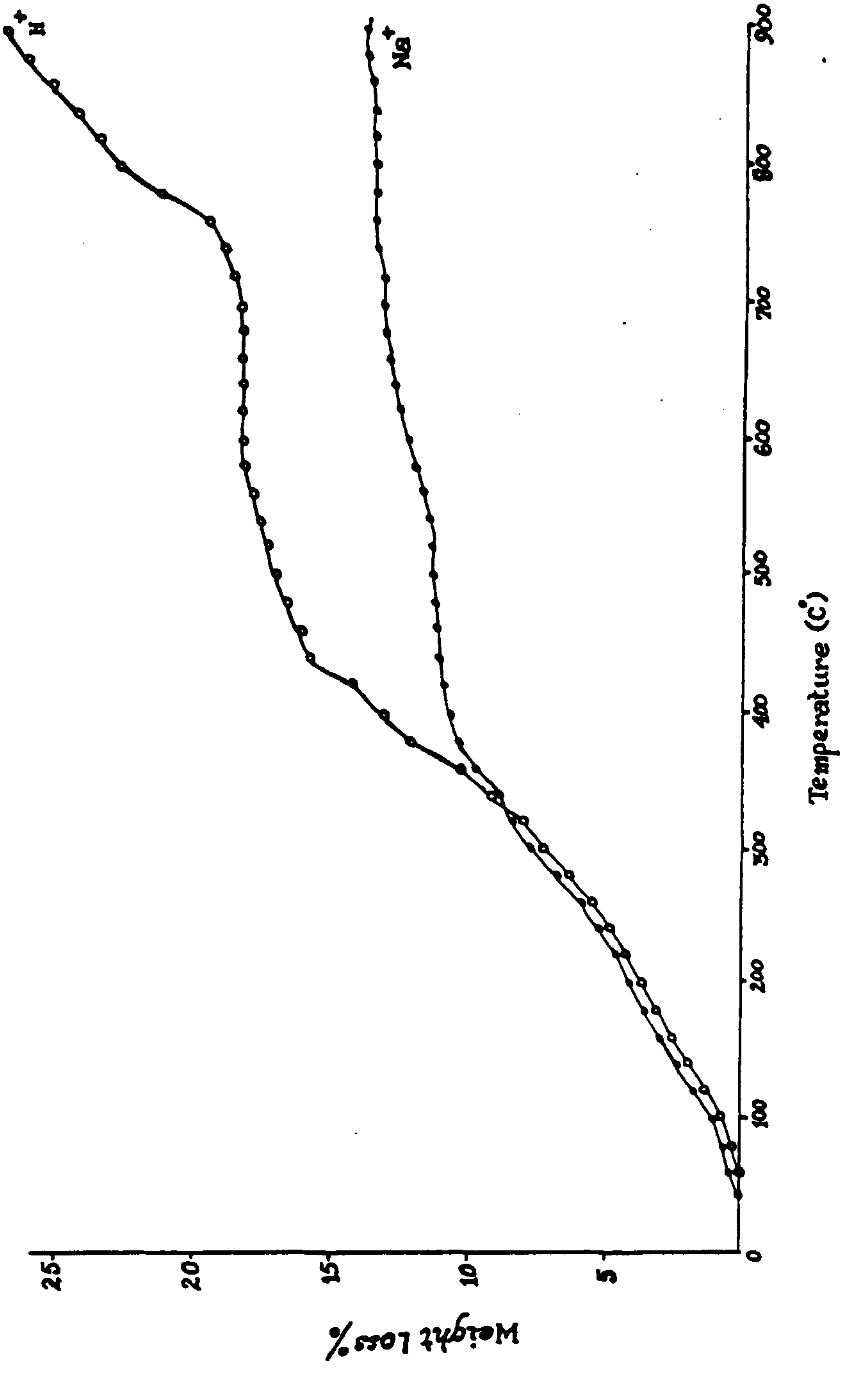


Fig. 3. TGA Graphs of lead antimonate (Sample-4).

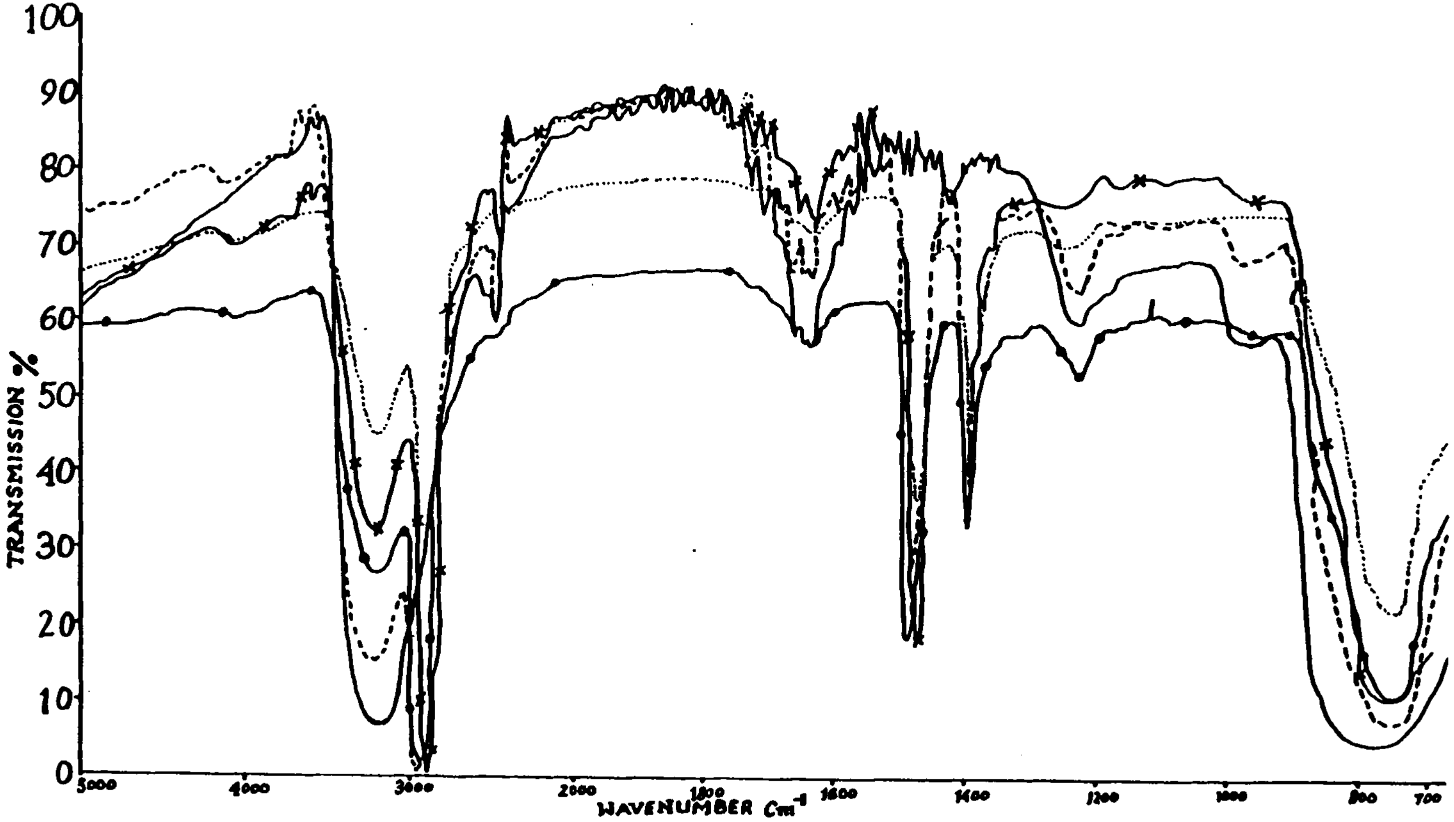


Fig. 4. IR Spectra of lead antimonate (Sample 4) dried at (i) 40° ——— (ii) 100° ----- (iii) 200° —·— (iv) 300° —x— and (v) ········ in nujol.

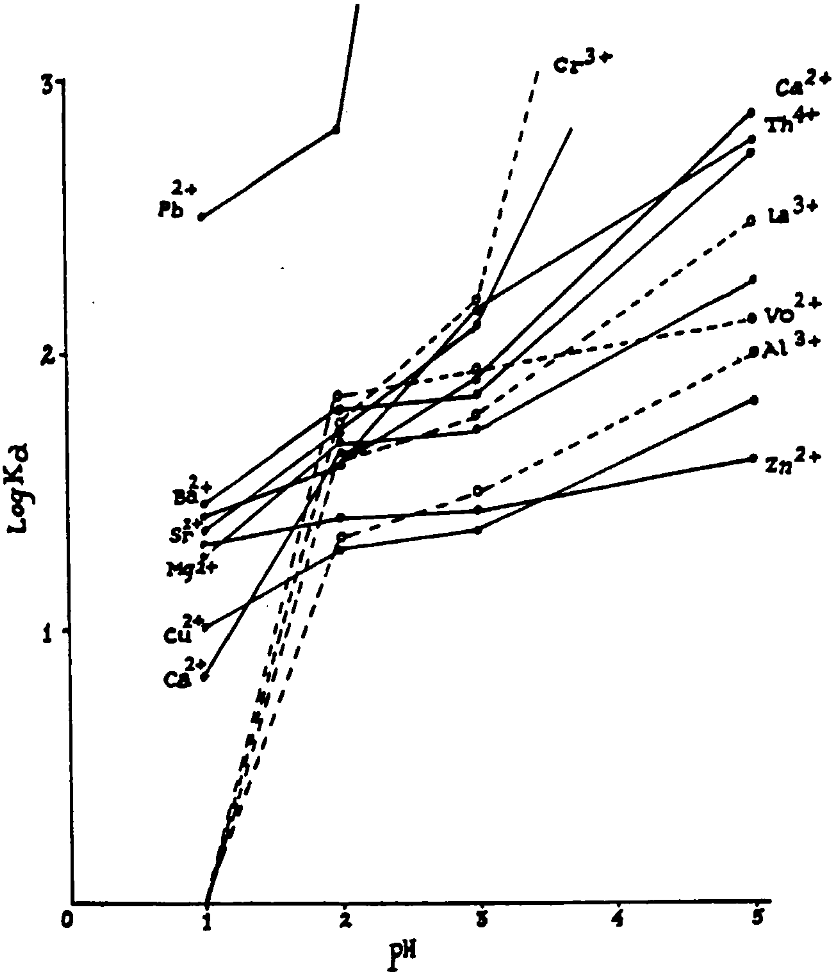


Fig. 5. K_a values on lead antimonate (Sample-4) as a function of pH.

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

Lead antimonate is highly selective for Pb^{2+}, Cd^{2+} and Cr^{3+} (Table V). This makes it possible to separate these ions from a large number of other ions without much difficulty. The plot of log Kd for various cations have been drawn (Figure 5) to study the effect of pH on Kd values. The plots make it clear that there occurs an appreciable decrease in the Kd values of cations as acid concentration is increased. It is quite obvious, as PbSb in H^+ - form acts as a weak acid and in the presence of high acid concentration its ionization is suppressed.

The order of selectivity for some cations on PbSb was found to be as follows:

At pH 1.0

$Pb^{2+} \gg Ba^{2+} > Th^{4+} > Sr^{2+} > Zn^{2+} > Mg^{2+} > Cu^{2+} > Ca^{2+} > Al^{2+} > La^{3+} > Vo^{2+}$.

At pH 2.0

$Pb^{2+} \gg Vo^{2+} > Ba^{2+} > Sr^{2+} > Mg^{2+} > Ca^{2+} > La^{3+} > Th^{4+} > Zn^{2+} > Al^{3+} > Cu^{2+}$.

At pH 3.0

$Pb^{2+} \gg Th^{2+} > Sr^{2+} > Vo^{2+} > Ca^{2+} > Ba^{2+} > La^{3+} > Mg^{2+} > Al^{3+} > Zn^{2+} > Cu^{2+}$.

At pH 5.0

Pb^{2+}, Cd^{2+}, $Cr^{3+} \gg Sr^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > Th^{4+} > Ba^{2+} > Hg^{2+} > La^{3+} > Nd^{3+} > Mg^{2+} > Vo^{2+} > Al^{3+} > K^{+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$.

Figure 6 also shows the specificity of PbSb. There is large difference in the distribution coefficients of Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Al^{3+}. Quantitative binary separation (Table VI) of Mg^{2+} - Pb^{2+}, Zn^{2+} - Pb^{2+}, Cu^{2+} - Pb^{2+}, Al^{3+} - Pb^{2+}, Zn^{2+} - Cd^{2+} and Mg^{2+} - Cd^{2+} were successfully achieved on a very small column of lead antimonate Sample 4. The amount of cations recovered are within the experimental error range.

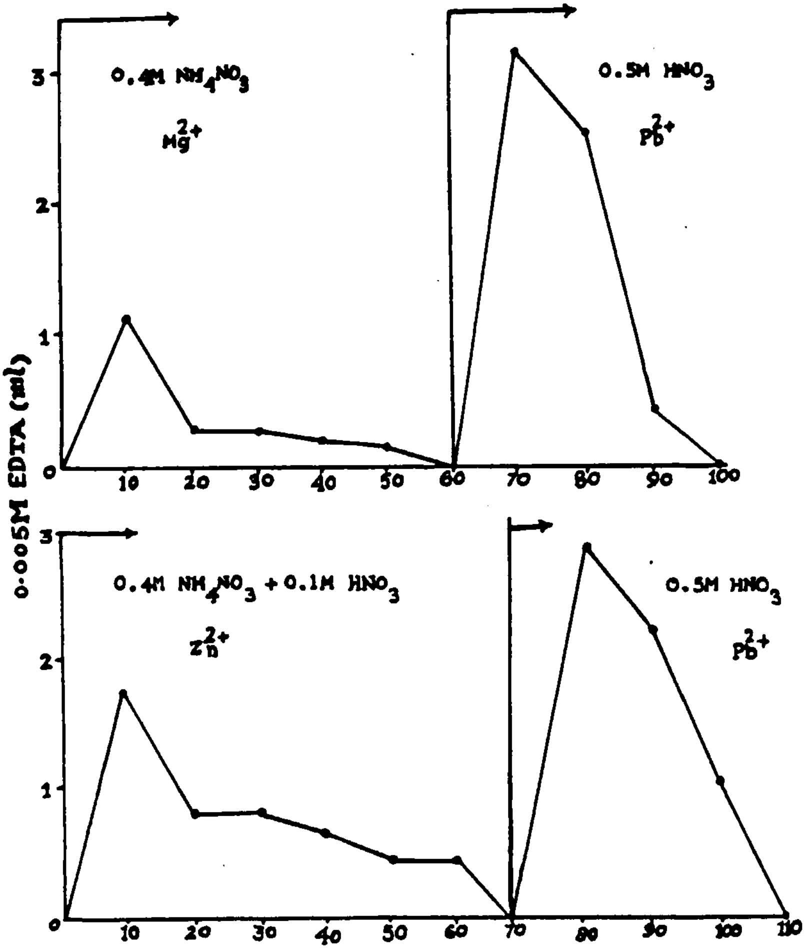


Fig. 6. Same binary Separations on lead antimonate (Sample 4) columns.

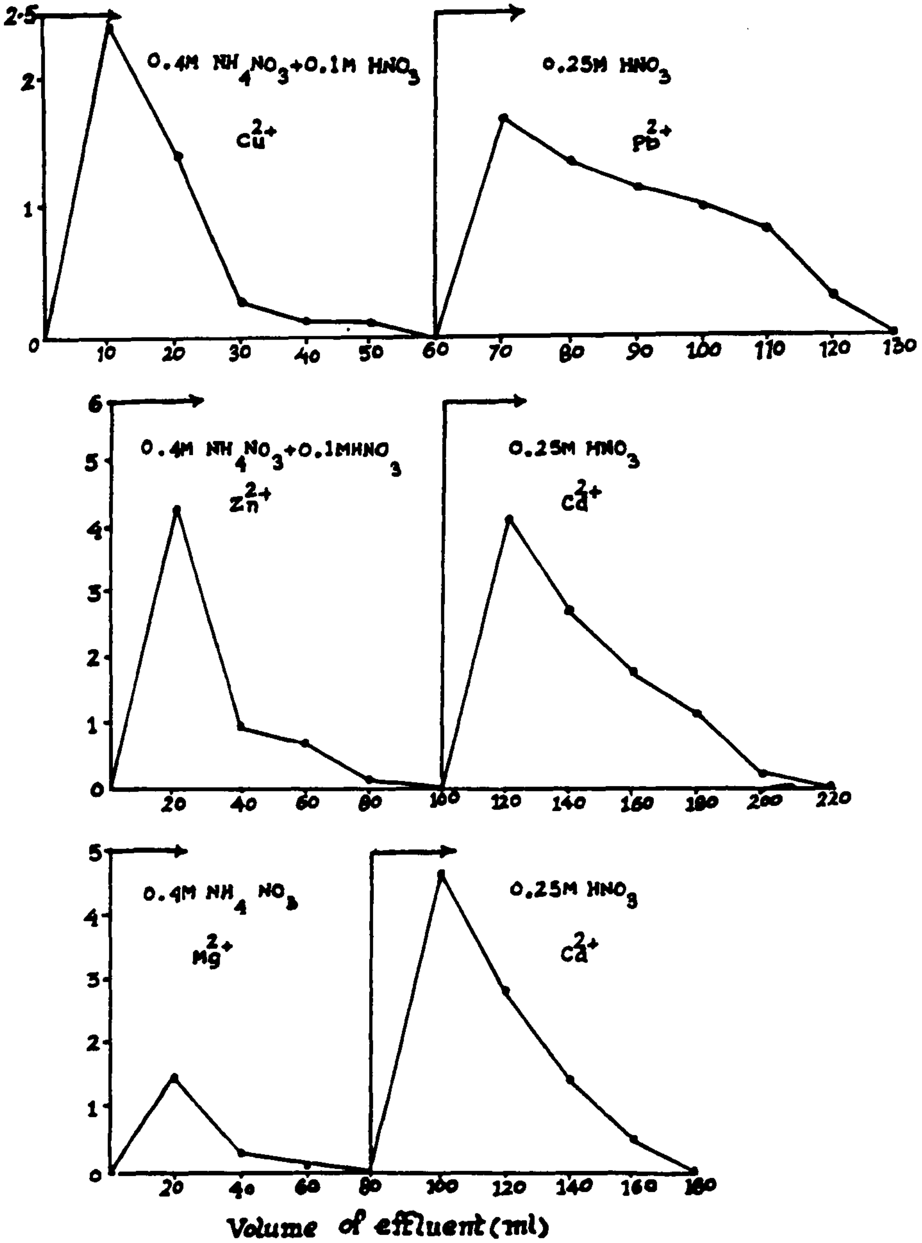


Fig. 6. (continued)

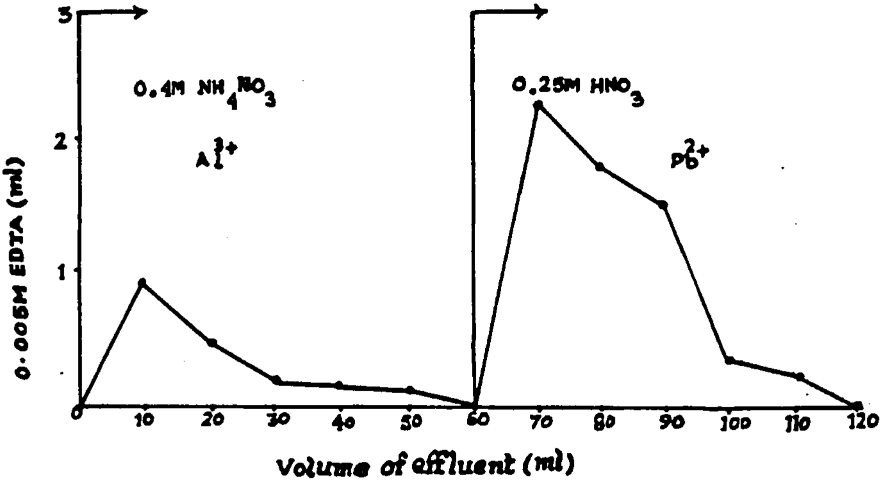


Fig. 6. (continued)

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