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Synthetic Inorganic Ion-Exchangers.* XIX. Preparation, Properties, and Ion-Exchange Behavior of Lanthanum Antimonate

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Abstract

Different samples of lanthanum(III) antimonate have been prepared under different conditions. The physicochemical properties, compositions, IR spectra, breakthrough capacity, cation exchange behavior, and distribution coefficients for several metals have been studied. The separations of some metal ions from Hg(II) and Mg(II) have been achieved.

INTRODUCTION

The importance of synthetic inorganic ion-exchangers has increased in recent years due to their selectivity and stability toward heat and ionizing radiation. Thorium-based exchangers have been reported earlier from our laboratory (*1–8*), but lanthanum-based exchangers have not been reported in the literature.

In the present paper the synthesis, composition, chemical and thermal stability, IR spectra, pH titration, and ion-exchange behavior of lanthanum antimonate, along with the breakthrough capacity and distribution coefficients of metal ions using lanthanum antimonate, are reported.

EXPERIMENTAL

Chemicals and Reagents

Lanthanum nitrate used was of analar grade (Indian Rare Earths Ltd.). Potassium pyroantimonate was of pro-analysi grade (E. Merck). EDTA was

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*For Part XVIII, see Ref. *1*.

of A.R. grade (BDH). All other chemicals and reagents were of analytical grade.

Apparatus

The following instruments were used: ELICO Model LI-10 pH Meter (Hyderabad, India), Single Pan Electric Balance, OWA Labour type 707-04 (Calcutta, India), ECIL Spectrophotometer Model G.S. 865B (Hyderabad, India).

Synthesis

0.05 mol/dm^3 potassium pyroantimonate solution (2 L) was taken in a 5-L flask fitted with a mechanical stirrer, and 0.1 mol/dm^3 lanthanum nitrate (1 L) solution in 0.1 mol/dm^3 nitric acid was added with constant stirring at room temperature. The addition was complete within 15 min. The mixture was stirred for different hours for different batches as shown in Table 1. It was allowed to settle, filtered, washed with deionized water, and dried in air. The product was then converted to H$^+$ form by treating with 1.0 mol/dm^3 HNO_3 and dried as before. Details of synthesis and composition are given in Table 1.

Composition

About 0.5 g of the powdered lanthanum antimonate was dissolved in conc HCl. The lanthanum content was determined as La_2O_3 via oxalate precipita-

TABLE 1

Details of Synthesis and Composition of Lanthanum Antimonate

Batch no.	Ratio of 0.1 mol/dm^3 $La(NO_3)_3$ in 0.1 mol/dm^3 HNO_3 and 0.05 mol/dm^3 $K[Sb(OH)_6]$	Digestion time and temperature	Composition	
			Sb:La	H_2O:La
1	1:2	Room temperature. Stirring time 2 h	4.35	—
2	1:2	Refluxing time 16 h	4.55	12.92
3	1:2	Refluxing time 4 h	4.98	—
4	1:2	Refluxing time 8 h	4.14	11.78
5	1:2	Room temperature. Stirring time 16 h	4.39	18.79
6	1:2	Room temperature. Stirring time 8 h	4.17	10.01

TABLE 2

Solubility of Lanthanum Antimonate in Different Solvents

	Antimony dissolved, mg/50 mL				Lanthanum dissolved, mg/50 mL			
Solvent	Batch no. 2	Batch no. 3	Batch no. 5	Batch no. 6	Batch no. 2	Batch no. 3	Batch no. 5	Batch no. 6
0.1 mol/dm^3 H_2SO_4	2.75	3.75	4.50	5.0	0.68	0.94	1.10	1.11
1.0 mol/dm^3 H_2SO_4	5.20	5.75	5.50	3.50	1.25	1.45	1.52	0.91
0.1 mol/dm^3 HNO_3	3.50	3.75	3.75	4.25	0.91	0.81	0.92	1.06
1.0 mol/dm^3 HNO_3	7.50	8.0	8.75	9.75	1.90	1.65	2.20	2.43
0.1 mol/dm^3 HCl	1.25	1.0	1.75	2.75	0.42	0.31	0.43	0.72
1.0 mol/dm^3 HCl	6.50	7.0	7.5	8.75	1.63	1.44	1.61	2.21
0.1 mol/dm^3 NaOH	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

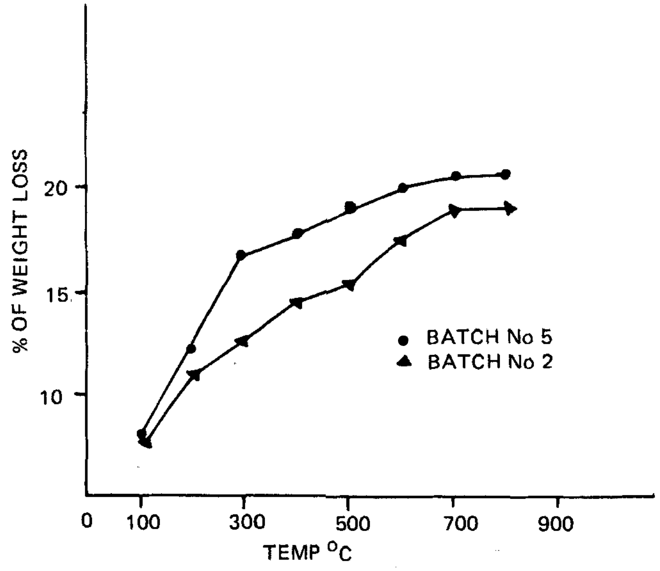


FIG. 1. Percentage of weight loss curve of lanthanum antimonate (batches No. 2 and 5) as a function of temperature.

tion (*9*) while antimony was determined volumetrically by iodometric titration (*10*). The compositions are given in Table 1.

Chemical Stability

0.05 g of the exchanger was shaken intermittently for 2 d with 1.0 mol/dm^3 HCl, HNO_3, H_2SO_4, NaOH, and 0.1 mol/dm^3 HCl, HNO_3, H_2SO_4, and NaOH. Lanthanum was determined spectrophotometrically using Alizarin-S indicator (*11*). Antimony was determined iodometrically using potassium iodate and ascorbic acid as reagents. The results are given in Table 2.

Heat Treatment

0.5 g of the exchanger was taken in a silica crucible and treated from 100 to 800°C in steps of 100°C. For each step of heating, a separate sample was taken. The heating time was 1 at the desired maximum temperature in each case. The percentage of water loss was plotted against the temperature of

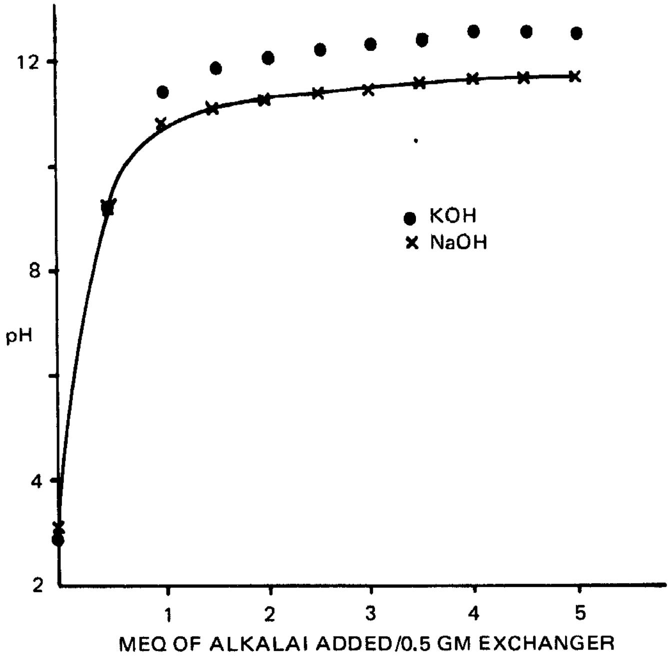


FIG. 2. pH titration curve for lanthanum antimonate with 2*M* (MCl + MOH) Batch No. 2.

heating and the curve is shown in Fig. 1. On the basis of weight loss the ratio of H_2O:La was calculated by using the formula of Alberti et al. (*12*).

Infrared Spectra

The IR spectra of the two batches (No. 2 and 5) of lanthanum antimonate were found to differ slightly from that of normal lanthanum antimonate (obtained just by addition of reagents, filtration, and drying) in respect to La—O (450 cm^{-1}) and Sb—O (600 cm^{-1}) bands.

pH Titration

For pH titration (Batches No. 2 and 5) the method of Topp and Peppers (*13*) was employed. 100 cm^3 solutions containing different amounts of MOH ($M = Na^+, K^+$) were added to 0.5 g of the exchanger. The mixture was shaken intermittently for 2 days. The equilibrium pH was noted. The experiment was repeated with a solution containing 1 mol/dm^3 (MOH + HCl) and the pH was noted as above. The pH titration curves are shown in Figs. 2–5.

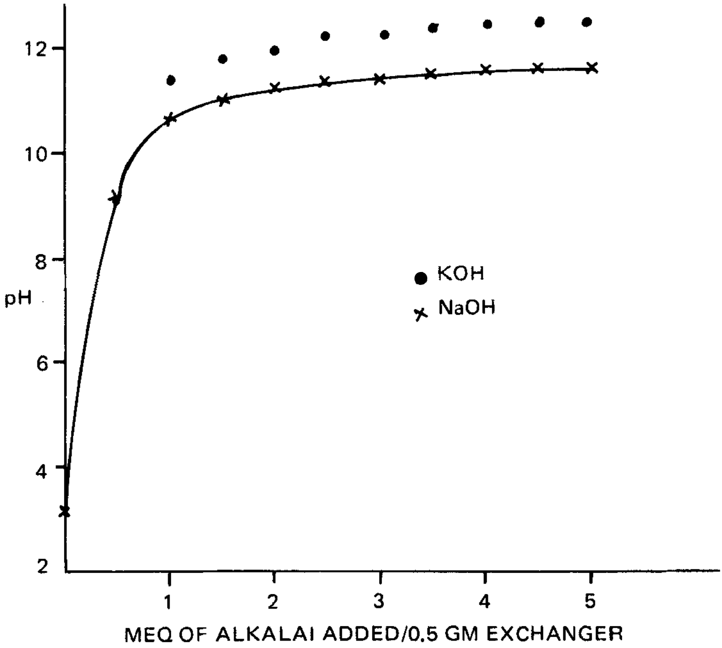


FIG. 3. pH titration curve for lanthanum antimonate (Batch No. 2).

Ion Exchange Capacity

Lanthanum antimonate exhibits cation exchange properties. It was first converted to the H^+ form as stated above. The exchange capacity was measured as the amount of hydrogen ion liberated by shaking lanthanum antimonate with the solution of a neutral salt such as sodium chloride. The exchange capacity of the different batches was determined by shaking 0.5 g of the exchanger with 100 cm^3 of 2 mol/dm^3 NaCl for about 24 h intermittently (Table 3).

The effect of salt concentration and time of equilibration on the exchange capacity of lanthanum antimonate were determined by batch operation. It was found that the optimum salt concentration was 1.5 mol/dm^3 NaCl solution and optimum equilibration time was 12 h.

Loss in Exchange Capacity on Heating

0.5 g of the exchanger was weighed in a silica crucible and ignited from 100 to 700°C in steps of 100°C. For each step of heating a separate sample was taken. The ignited sample was transferred to a bottle and the exchange

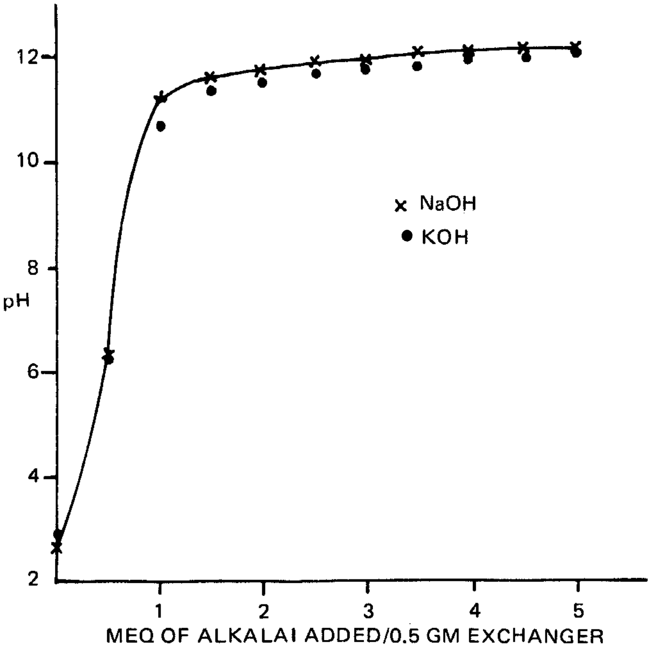


FIG. 4 pH titration curve for lanthanum antimonate with 2*M* (MCl + MOH) Batch No. 5.

TABLE 3

Ion-Exchange Capacity of Lanthanum Antimonate for Different Cations

Batch no.	Exchange capacity at pH 3.5 (meq/g)					Exchange capacity (Na^+) in acetate buffer (pH 6.5)
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	
1	0.34	0.50	0.28	0.51	0.62	1.3
2	0.36	0.56	0.30	0.54	0.72	1.0
5	0.48	0.66	0.36	0.60	0.66	1.5
6	0.41	0.80	0.36	0.78	0.80	1.4

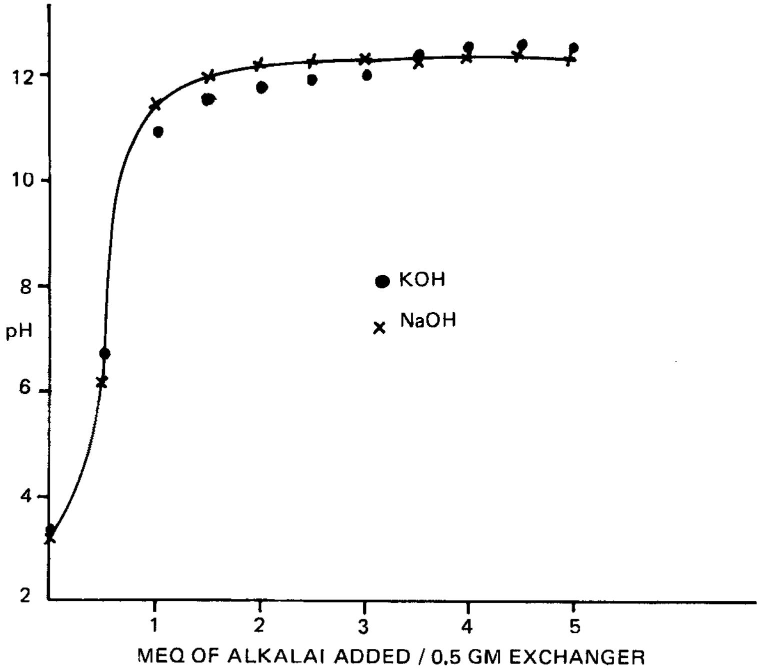


FIG. 5. pH titration curve for lanthanum antimonate Batch No. 5.

capacity was determined by shaking with 2 mol/dm^3 of NaCl solution as described above.

Breakthrough Capacity

The breakthrough capacity of lanthanum(III) antimonate (H^+ form) was determined for three divalent cations using 4 g of the exchanger in a column of 1.2 cm diameter and 3.2 cm length. The flow rate was 1 mL/min and particle size was 100–200 mesh. The strength of Hg^{2+} solution was 0.5 mg/cm^3, of Cd^{2+} was 0.52 mg/cm^3, and of Pb^{2+} was 0.41 mg/cm^3. The nature of the breakthrough curve is shown in Fig. 6.

Distribution Coefficients

The K_d values of 15 metal ions were determined by batch operation after equilibrium had been attained by shaking the metal ion solution with the

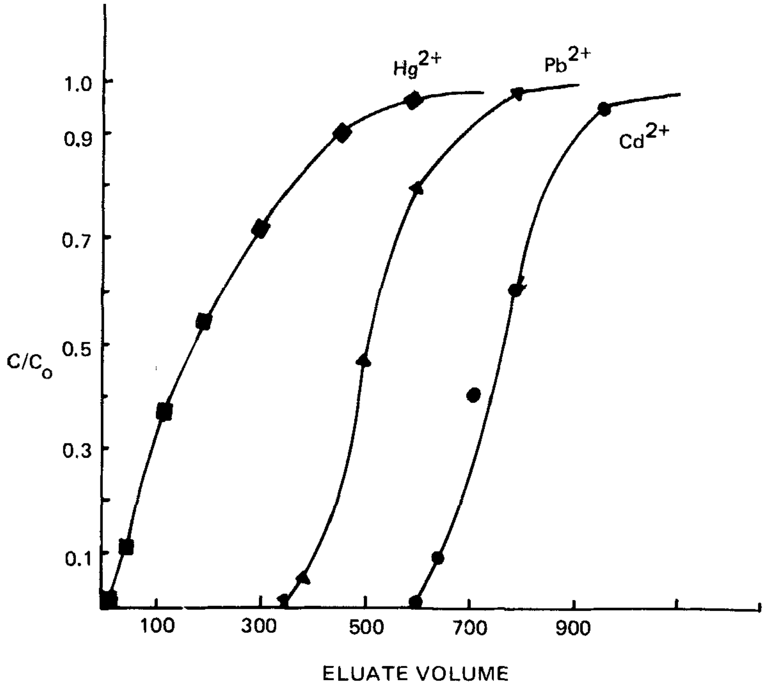


FIG. 6. Breakthrough curve of different cation solutions on lanthanum antimonate (Batch No. 5).

exchanger (H^+ form) for 2 days at room temperature. The cation in solution was determined by EDTA titration (*15*) and the K_d values were calculated. The total volume of equilibrating solution was 100 mL, and the amount of exchanger was 0.5 g. The equilibrium time was kept at 12 h. The K_d values were studied at different pH values and in presence of different electrolytes. The distribution coefficient data are tabulated in Table 4.

Ion Exchange Separations

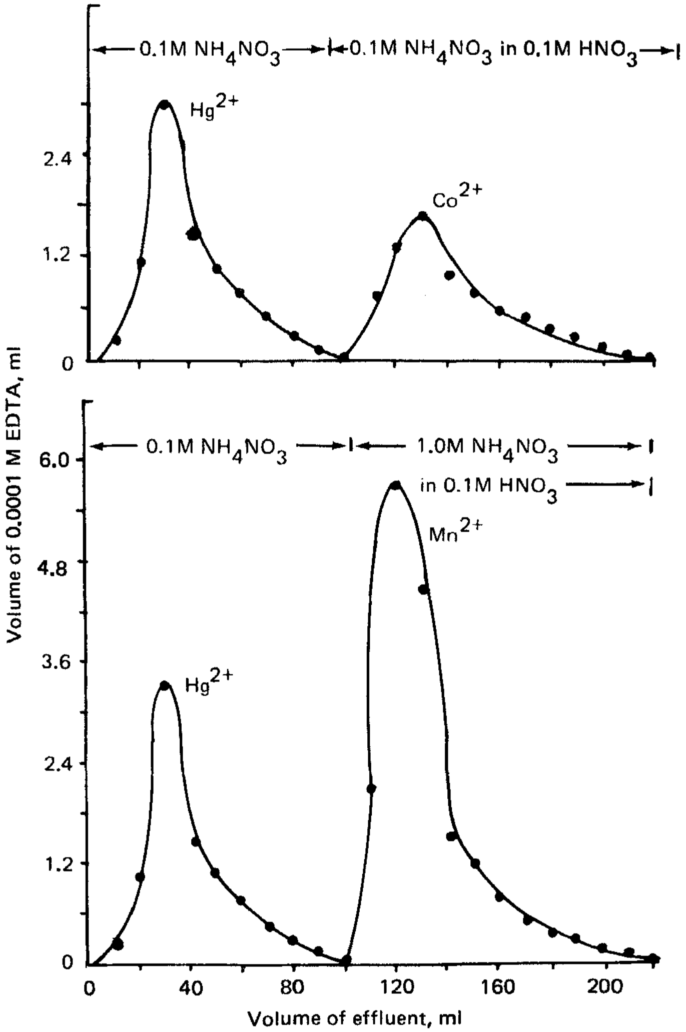
For column separations a column (1.2 cm) was filled with 5.0 g of exchanger (100–200 mesh size) supported at the bottom with glass wool. The column was washed with deionized water. The flow rate was maintained at 0.8 to 1 mL/min during column operation. Quantitative separations of 12 binary mixtures were carried out. Some of the elution curves are shown in Figs. 7 and 8.

TABLE 4

Distribution Coefficient Values of Lanthanum Antimonate (Batch No. 5)

	K_d values (mL/g)					
Metal ions	pH 6–7	0.1 mol/dm^3 NH_4NO_3 + 0.1 mol/dm^3 HNO_3	0.1 mol/dm^3 NH_4NO_3	1.0 mol/dm^3 NH_4NO_3	0.5 mol/dm^3 NH_4NO_3	0.1 mol/dm^3 HNO_3
Mg^{2+}	189.7	0	25.5	6.6	21.3	0
Co^{2+}	1479	41.9	142.8	66.6	94.5	51.8
Cu^{2+}	3070	13.11	121	41.67	53.84	46.15
Mn^{2+}	6889	20	621.3	115.1	544.4	45.5
Ba^{2+}	679.2	18.61	260	120.9	243.2	14.04
Sr^{2+}	574.1	16.21	127.2	110.0	811.7	22.68
Zn^{2+}	1294	10.42	92.53	41.97	51.16	26.37
Cd^{2+}	T.A.[a]	48.77	1199	367.7	908	94
Hg^{2+}	471	6.96	9.2	3.21	4.91	10.9
Ni^{2+}	2412	21.87	43.95	35.71	15.55	21.05
Pb^{2+}	3309	240	1964	894.5	2200	330.4
Th^{4+}	—	4548	5467	2500	2166	—
UO_2^{2+}	—	255.2	363.1	538.7	—	—

[a] Total absorption.


0.1M NH_4NO_3
0.1M NH_4NO_3 in 0.1M HNO_3
Hg^{2+}
Co^{2+}
2.4
1.2
0
0.1M NH_4NO_3
1.0M NH_4NO_3
in 0.1M HNO_3
Mn^{2+}
Hg^{2+}
6.0
4.8
3.6
2.4
1.2
0
0
40
80
120
160
200
Volume of 0.0001 M EDTA, ml
Volume of effluent, ml

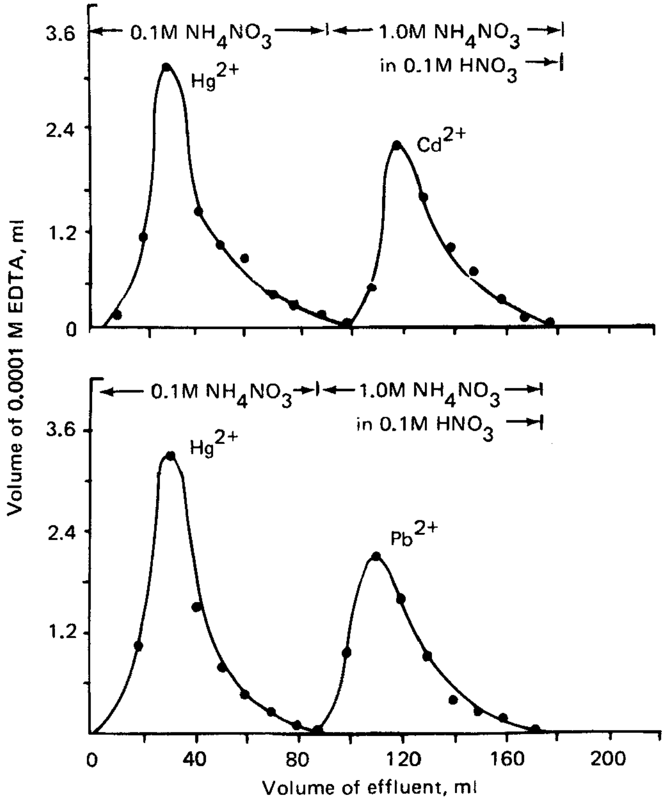
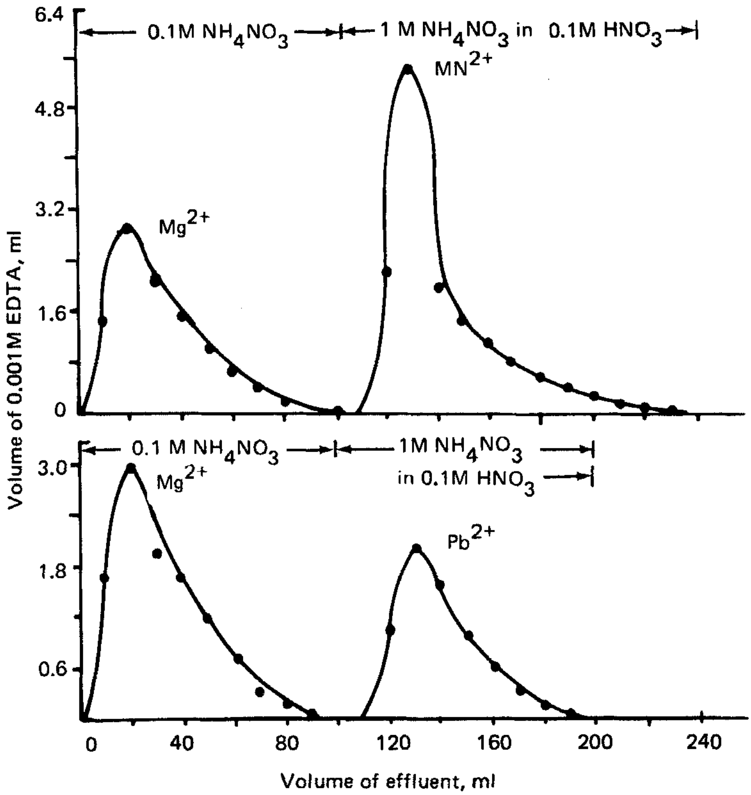


FIG. 7. Binary separations of Hg^{2+}–Pb^{2+}, Hg^{2+}–Cd^{2+}, Mg^{2+}–Mn^{2+}, and Hg^{2+}–Co^{2+} on lanthanum antimonate (Batch No. 5) column.



RESULTS AND DISCUSSION

It follows from Table 1 that although the mixing ratio of the reagents is the same for all six samples of lanthanum antimonate, the Sb:La ratio varies from 4.14 to 4.98. This is due to the different procedures used in the synthesis. Refluxing for a prolonged period does not improve the product materially. The products are all amorphous and fairly stable in acids and alkalies (up to 0.1 *N*). The reproducible behavior of the samples was checked by determining the composition and ion-exchange capacity of the samples prepared under identical conditions. The results were found to be within experimental error.

The ion-exchange capacity follows the normal trend: the values increase with a decrease of the radius of the hydrated ion (Table 3).

The exchange capacity decreases progressively with a gradual loss of

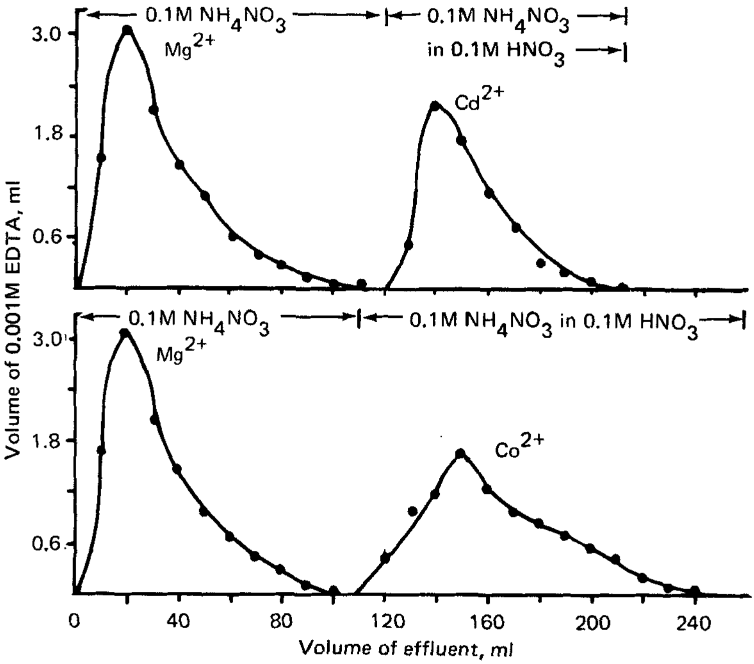


FIG. 8. Binary separations of Mg^{2+}–Co^{2+}, Mg^{2+}–Cd^{2+}, Mg^{2+}–Pb^{2+}, and Mg^{2+}–Mn^{2+} on lanthanum antimonate (Batch No. 5) column.

water on heating from 100 to 600° C. For Batch No. 5 the typical exchange capacity values (K^+) are 0.64 (100°C), 0.50 (300°C), and 0.30 (600°C).

The breakthrough capacity, as shown in Fig. 6, is related to the respective K_d values of the metal ions and indicates the possible separations of Hg^{2+} from Pb^{2+} and Cd^{2+}.

The distribution coefficient values in different electrolytes (Table 4) indicate that Mg^{2+} ($K_d = 0$) can be separated from numerous cations using by 0.1 mol/dm^3 NH_4NO_3 + 0.1 mol/dm^3 HNO_3. Hence Mg^{2+} has been quantitatively separated from Co^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, and Th^{4+}. Similarly, Hg^{2+} with a moderate K_d value in 0.1 mol/dm^3 NH_4NO_3 has been separated from Cd^{2+}, Pb^+, Mn^{2+}, Co^{2+}, Ni^{2+}, and Th^{4+} with high K_d values. In each case a column of lanthanum antimonate (Batch No. 5) was employed. In each case the results are accurate to within ±5%.

It may be concluded that, under optimum conditions, lanthanum antimonate is fairly selective toward Mg^{2+} and Hg^{2+}.

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REFERENCES

1. A. K. De, S. K. Das, and P. Chakraborty, *J. Inorg. Nucl. Chem.*, *43*, 1904 (1981).

2. A. K. De and S. K. Das, *Sep. Sci. Technol.*, *13*, 465 (1978).

3. A. K. De and S. K. Das, *Chromatographia*, *11*, 6 (1978).

4. H. Kaulsky and H. Wesslau, Z. Naturforsch., *B*, *9*, 559 (1954).

5. C. B. Amphlett, *Proceedings of the 2nd International Conference on the Peaceful Uses of Atomic Energy,* Vol. 28, United Nations, Geneva, 1958, p. 17.

6. G. Alberti and U. Costantino, *J. Chromatogr.*, *50*, 482 (1970).

7. A. K. De and K. Chowdhury, *Ibid.*, *101*, 63 (1974).

8. A. K. De and K. Chowdhury, *Sep. Sci. Technol.*, *10*, 639 (1975).

9. R. C. Vickery, *Analytical Chemistry of the Rare Earths,* Vol. 3, Pergamon, New York, 1961.

10. G. Charlot and D. Benzier, *Quantitative Inorganic Analysis,* 3rd ed., Longmans, London (1957).

11. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience, New York, 1959.

12. G. Alberti, U. Costantino, and L. Zsinka, *J. Inorg. Nucl. Chem.*, *34,* 3549 (1973).

13. N. E. Topp and K. W. Peppers, *J. Chem. Soc.*, p. 3299 (1949).

14. O. Samuelson, *Ion-Exchange Separation in Analytical Chemistry,* Wiley, New York, 1963.

15. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd ed., Longmans, London, 1962.

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