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SYNTHESIS AND ION-EXCHANGE PROPERTIES OF A SEMICRYSTALLINE, MAGNESIUM-SELECTIVE NIOBIUM ANTIMONATE

M. QURESHI, ANEK P. GUPTA and (Mrs) T. KHAN

Chemical Laboratories, Aligarh Muslim University, Aligarh 202001 (India)

and

JAI P. GUPTA

Chemical Sciences, The Hatfield Polytechnic, Hatfield, Herts. (Great Britain)

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SUMMARY

Semicrystalline niobium antimonate is shown to be suitable for use as an ion exchanger from 40° to 300°. It has high chemical stability and can be used to separate Mg²⁺ quantitatively from Sr²⁺, Ba²⁺, Hg²⁺, Al³⁺, Ga³⁺, Fe³⁺, La³⁺ and Th⁴⁺. Mg²⁺ is eluted with 0.01 M nitric acid and the other ions are eluted with a solution of 2 M in nitric acid and 0.25 M in ammonium nitrate. The results of X-ray, infrared thermogravimetric and differential-scanning calorimetric studies of the crystalline sample are presented and discussed.

INTRODUCTION

Synthetic inorganic ion exchangers are being increasingly used in the field of inorganic, nuclear and organic chemistry owing to their resistance to heat and to radiation, and may prove to be important in biological and medicinal chemistry because of their high selectivity. Although considerable work has been done on these materials, some aspects of them need elucidation; for example, amorphous materials sometimes show a lack of reproducibility of composition, dissolve significantly in the eluents and are unstable at high temperatures.

The oxides of niobium and tantalum are noted for their chemical and thermal inertness, and their salts may also prove to be superior in these respects. We have therefore attempted to make a systematic study of the ion-exchange behaviour of these substances; our work on niobium arsenate¹, tantalum antimonate² and tantalum arsenate^{3,4} has been published. Here, we describe the ion-exchange behaviour of semicrystalline niobium antimonate, with particular regard to its reproducibility, chemical dissolution, thermal stability and analytical utility.

EXPERIMENTAL

Reagents

Niobium pentoxide and antimony pentachloride were obtained from BDH (Poole, Great Britain); all other reagents were of AnalaR grade. Niobium pentoxide (20.00 g) was heated with 400 ml of concentrated sulphuric acid containing 200 g of ammonium sulphate, and the clear solution was diluted with water to 750 ml to give a solution 0.1 *M* in niobium.

Apparatus

The following instruments were used: a Bausch & Lomb Spectronic 20 colorimeter, an Elico pH meter (model Li-10), a Philips X-ray unit, a Perkin-Elmer spectrophotometer, Dupont 900 and 950 thermal analyzers, and an electric Sico shaker.

Syntheses of niobium antimonate

The samples were prepared by mixing acid solutions of 0.1 *M* niobium and 0.1 *M* antimony in the volume ratio 1:2 at room temperature; sodium hydroxide solution was added to the mixture, with constant shaking, until the pH was nearly 1. The resulting precipitate was divided into two parts; one part was set aside at room temperature for 24 h (sample AT₁), and the other part was boiled under reflux with the mother liquor for 20 h (sample AT₂). Sample AT₁ was dried at 40°, then boiled under reflux in 3 *M* sulphuric acid for 24 to 30 h (sample AT₃); sample AT₄ was prepared by similarly refluxing sample AT₁ (dried at 40°) with 3 *M* sulphuric acid for *ca.* 100 h. To prepare sample AT₅, the precipitate of niobium antimonate was washed with water until

TABLE I

SYNTHESIS, ION-EXCHANGE CAPACITY, COMPOSITION AND REPRODUCIBILITY OF NIOBIUM ANTIMONATE

All samples were white in colour.

Sample No.	Ion-exchange capacity for Na ⁺ (mequiv./g)	Ratio of Nb to Sb in product	Distribution coeff. in demineralized water		
			Mg ²⁺	Al ³⁺	Th ⁴⁺
AT ₁	0.86	1.836	1067	1400	4400
	0.84	1.845	1078	1420	4400
	0.86	1.839	1076	1400	4400
AT ₂	0.76	0.892	800	550	4250
	0.74	0.889	810	550	4250
	0.78	0.881	800	550	4250
AT ₃	1.10	1.408	20	272	900
	1.10	1.410	20	275	870
	1.12	1.406	24	275	870
AT ₄	1.16	1.234	2.85	62	385
	1.16	1.228	2.80	62	390
	1.14	1.232	2.85	62	390
AT ₅	1.20	1.469	180	173	125
	1.20	1.438	186	173	125
	1.16	1.452	184	173	138

the pH of the washings was 6, then the material was heated under reflux in 3 *M* sulphuric acid for 24 to 30 h. Samples AT₃, AT₄ and AT₅ were successively washed with 1 *M* and 0.25 *M* sulphuric acid and with demineralized water, then dried at 40° and converted into the H⁺ form with dilute nitric acid.

Synthesis of hydrated antimony pentoxide

A concentrated solution of sodium hydroxide was added to 0.1 *M* antimony pentachloride solution to bring the pH to 1, and the precipitate so obtained was washed, filtered and dried at 40°. The dried product was heated under reflux with 3 *M* sulphuric acid for 24 to 30 h, then washed successively with 1 *M* and 0.25 *M* sulphuric acid and demineralized water.

Synthesis of hydrated niobium pentoxide

Concentrated sodium hydroxide solution was added to the 0.1 *M* niobium solution until the pH was 1; the subsequent treatment was as in the synthesis of hydrated antimony pentoxide.

Ion-exchange capacity

The ion-exchange capacities of the various samples of niobium antimonate were determined by the column method; the results are summarized in Tables I and II. The capacities of hydrated antimony pentoxide and hydrated niobium pentoxide were 1.80 and 0.68 mequiv./g, respectively.

TABLE II
ION-EXCHANGE CAPACITIES FOR VARIOUS CATIONS

Cation	Capacity (mequiv./g) of sample		
	AT ₁	AT ₃	AT ₅
Li ⁺	0.36	0.44	0.50
Na ⁺	0.84	1.10	1.20
K ⁺	0.96	1.66	1.20
Mg ²⁺	0.44	0.46	0.40
Ca ²⁺	0.66	0.70	0.56
Sr ²⁺	0.86	0.76	0.80
Ba ²⁺	1.10	1.00	1.20

Composition

A 200-mg portion of well-powdered niobium antimonate was dissolved in 25 ml of hot concentrated sulphuric acid, and antimony was precipitated from the solution as sulphide and estimated volumetrically⁵; the niobium was determined gravimetrically with cupferron⁶ as described previously¹. The results are presented in Table I.

Dissolution

To study its chemical stability, 200 mg of the material was shaken with 25 ml of the appropriate solution for 6 h; after removal of undissolved material, niobium and antimony were determined in the filtrate by methods involving use of potassium thiocyanate (with diethyl ether extraction)⁷ and Rhodamine B⁸, respectively. The results are shown in Table III.

Drying of the sample

The sample was dried in an electric furnace in air for 1 h at each selected temperature.

X-ray studies

X-Ray diffractograms were taken with use of Cu K_{α} radiation (nickel filter); the results are shown in Table IV.

TABLE IV

COMPARISON OF d° SPACINGS (Å) I/I_0 = percent transmittance.

Sample AT ₃ *		Sample AT ₂ *		Antimony pentoxide**		Antimonic acid***		Antimonic acid [§]	
d°	I/I_0	d°	I/I_0	d°	I/I_0	d°	I/I_0	d°	I/I_0
5.97	42	5.975	45	6.00	100	6.00	100	5.83	100
3.13	55	3.13	36	3.10	80	3.128	80	3.09	62-70
3.01	54	3.01	37	2.97	80	2.995	75	2.957	62-70
2.60	16	2.59	11	—	—	2.594	15	2.569	14-17
2.40	17	2.40	8	—	—	—	—	—	—
2.04	16	—	—	—	—	1.998	17	1.981	14-18
1.84	24	1.76	12	1.82	50	1.835	31	1.822	31-36
1.76	19	—	—	—	—	1.754	22	1.741	22-23
1.57	18	1.57	12	1.550	36	1.565	14	1.565	22-29
1.50	18	—	—	—	—	—	—	—	—
1.467	12	1.467	8	—	—	—	—	—	—
1.350	10	—	—	1.15	4	—	—	—	—

* This work on niobium antimonate, with Cu radiation.

** With Mo radiation (see ref. 9).

*** With Cu radiation (see ref. 10).

§ With Cu radiation (see ref. 11).

Infrared studies

The infrared (IR) spectra were recorded by the Nujol method and are shown in Figs. 1 and 2.

Thermogravimetric and differential-calorimetric analysis

Thermogravimetric analysis (TGA) was performed under an atmosphere of

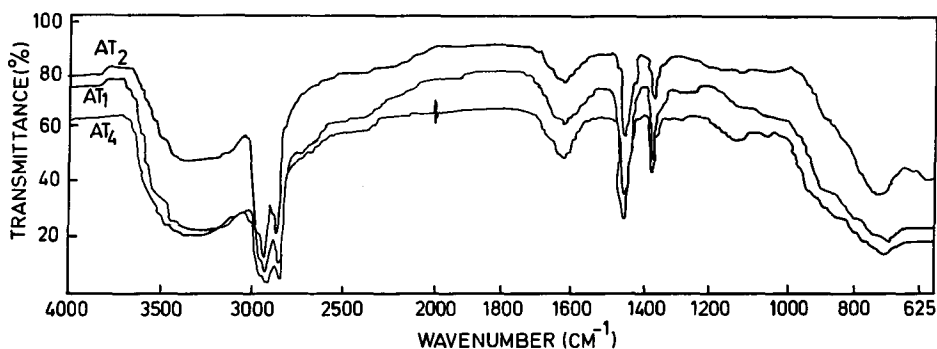


Fig. 1. IR spectra of niobium antimonate samples.

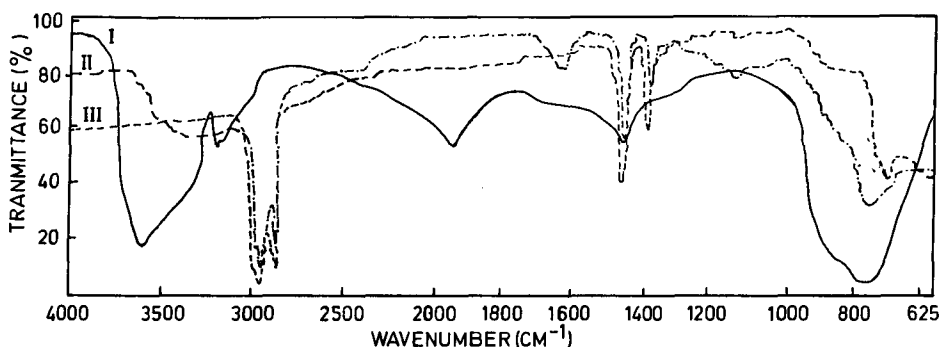


Fig. 2. IR spectra of niobium antimonate samples and antimonitic acid. I = Antimonitic acid (crystalline); II = NbSb (sample AT₃); III = NbSb (sample AT₃) heated at 1000°.

nitrogen flowing at 400 ml/min; the heating rate was 5°/min and the time constant was 1 sec. Differential scanning calorimetry was carried out in an atmosphere of nitrogen as well as in air; the results are shown in Figs. 3–5.

Determination of distribution coefficients

A 250-mg portion of the exchanger (H⁺ form) was allowed to stand in 25 ml of the cation solution in the appropriate solvent, the amount of cation being 3% of the total ion-exchange capacity of the exchanger. The mixture was shaken intermittently, and portions of the supernatant liquid were withdrawn and titrated with 2 mM EDTA. The results are shown in Figs. 6–8 and in Table V.

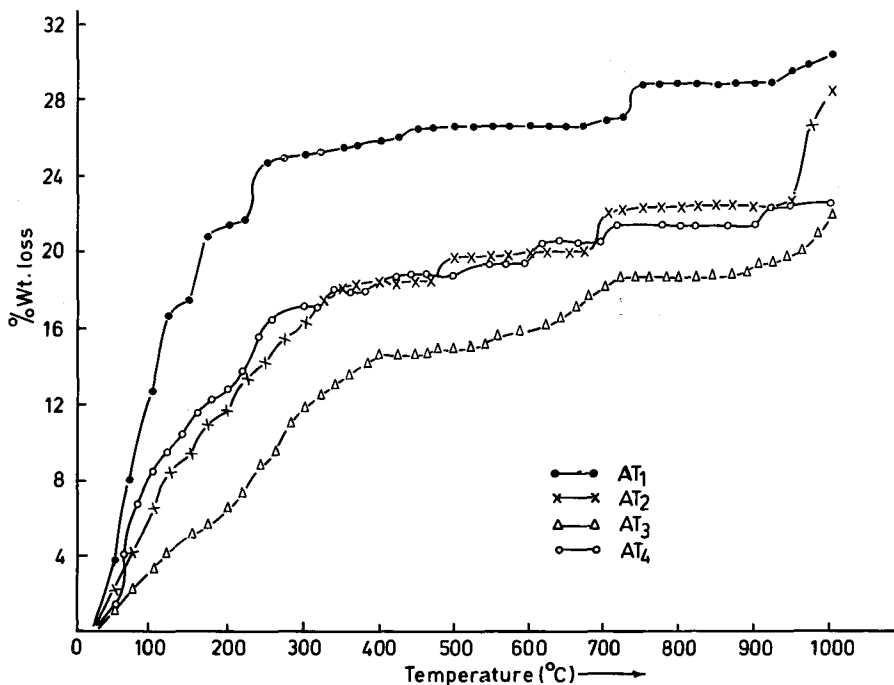


Fig. 3. TGA curves for niobium antimonate samples.

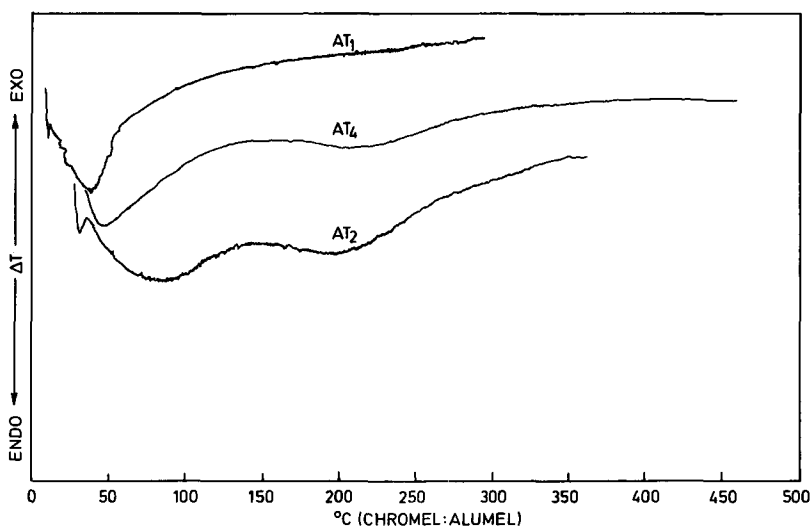


Fig. 4. Differential-scanning calorimetric curves for niobium antimonate samples.

Separation

For separation studies, a glass column was filled with 1.5 g of niobium antimonate (sample AT₃), in the H⁺ form, on a glass-wool support. The flow-rate in all the separations was 0.6–0.8 ml/min. Mg²⁺ was eluted with 0.01 M nitric acid and the other ions were eluted with a solution which is 2 M in nitric acid and 0.25 M in ammonium nitrate. The results are shown in Table VI.

For separation studies on sample AT₃ dried at 300°, Cd²⁺, Cu²⁺ and Ni²⁺ were

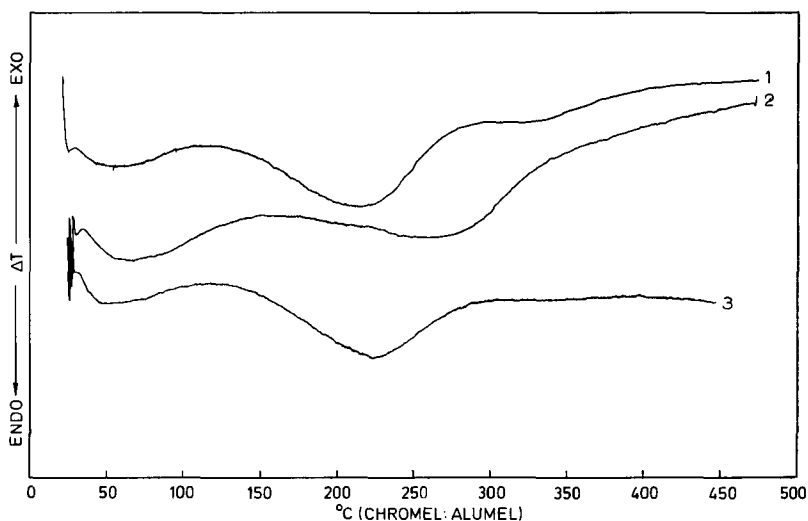


Fig. 5. Differential-scanning calorimetric curves for sample AT₃. 1 = Under nitrogen (400 ml/min); 2 = in static air; 3 = dynamic air (400 ml/min).

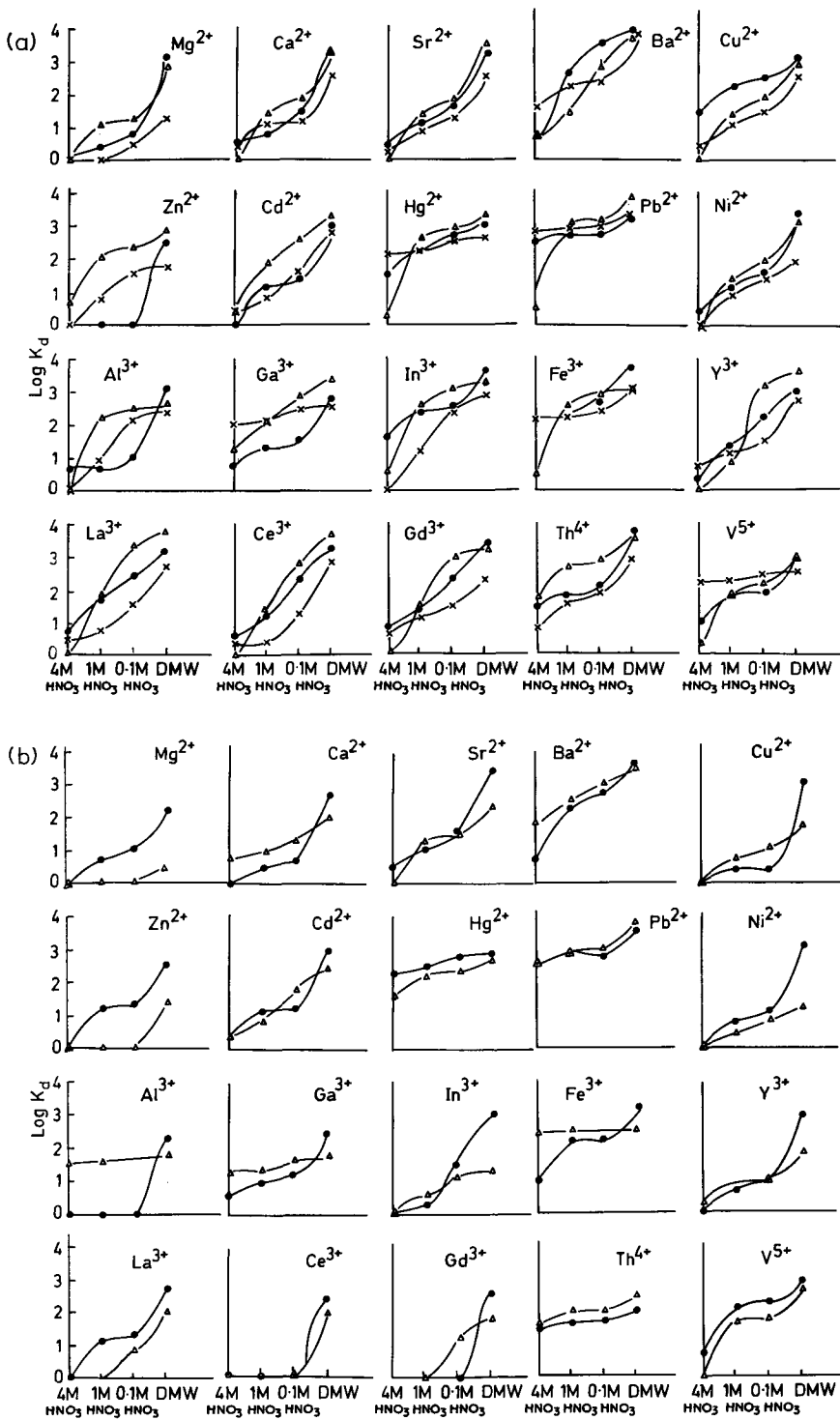


Fig. 6. K_d values on niobium antimonate samples. (a), ● = AT₁; △ = AT₂; × = AT₃. (b), △ = AT₄; ● = AT₅. DMW = Demineralized water.

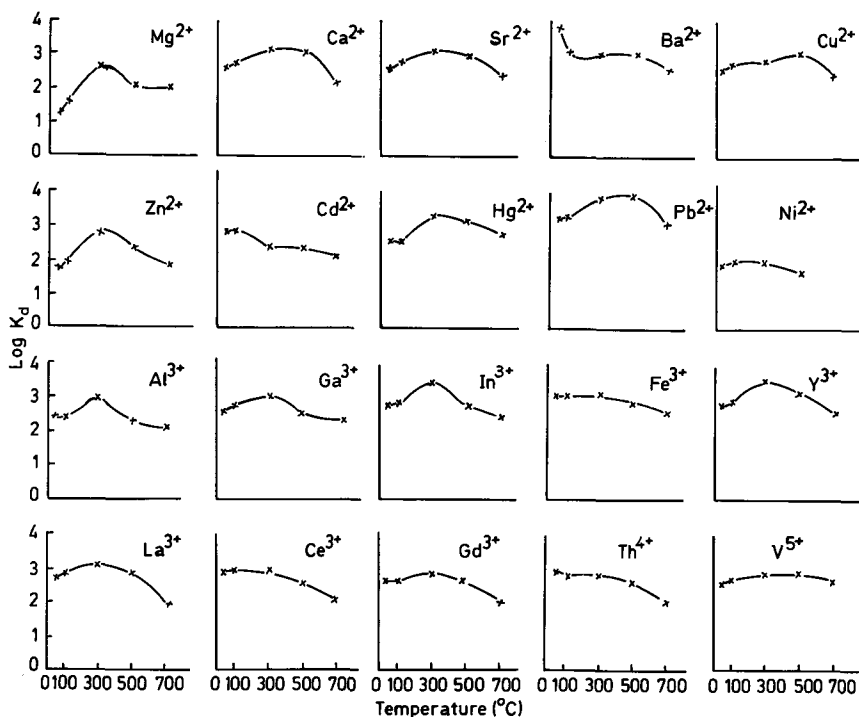


Fig. 7. K_d values on sample AT_3 at various temperatures.

eluted with a solution 0.1 M in nitric acid and 0.2% in ammonium nitrate, and Hg^{2+} and Pb^{2+} were eluted with a solution 2 M in nitric acid and 1.5 M in ammonium nitrate. The other conditions were the same. The results are shown in Table VII.

RESULTS AND DISCUSSION

It is clear from Table I that, even although the mixing ratio of the two reagents is the same for all five samples of niobium antimonate, the ratio of niobium to antimony ratio in the samples varies from 0.889 to 1.839; this is due to the different procedures used in the syntheses. Refluxing with 3 M sulphuric acid improves the reproducibility of the material (sample AT_3), probably because the material becomes more homogeneous. The reproducible behaviour of the samples was checked by determining the distribution coefficients of Mg^{2+} , Al^{3+} and Th^{4+} . The results, which showed that the deviation was within the limits of experimental error, are included in Table I.

The results of tests on the chemical dissolution of niobium antimonate are shown in Table III; all five samples were chemically stable. The stability in demineralized water and in mineral acids is decreased in the order AT_4 , AT_5 , AT_3 , AT_1 , AT_2 , which indicates that refluxing with sulphuric acid improves the stability. Niobium antimonate is less stable in alkaline medium due to its conversion into niobates and in 4 M hydrochloric acid due to formation of chloro-complexes of antimony.

The ion-exchange capacities of samples AT_1 , AT_3 and AT_5 for various cations are listed in Table II, from which it is apparent that the capacity for a cation increases

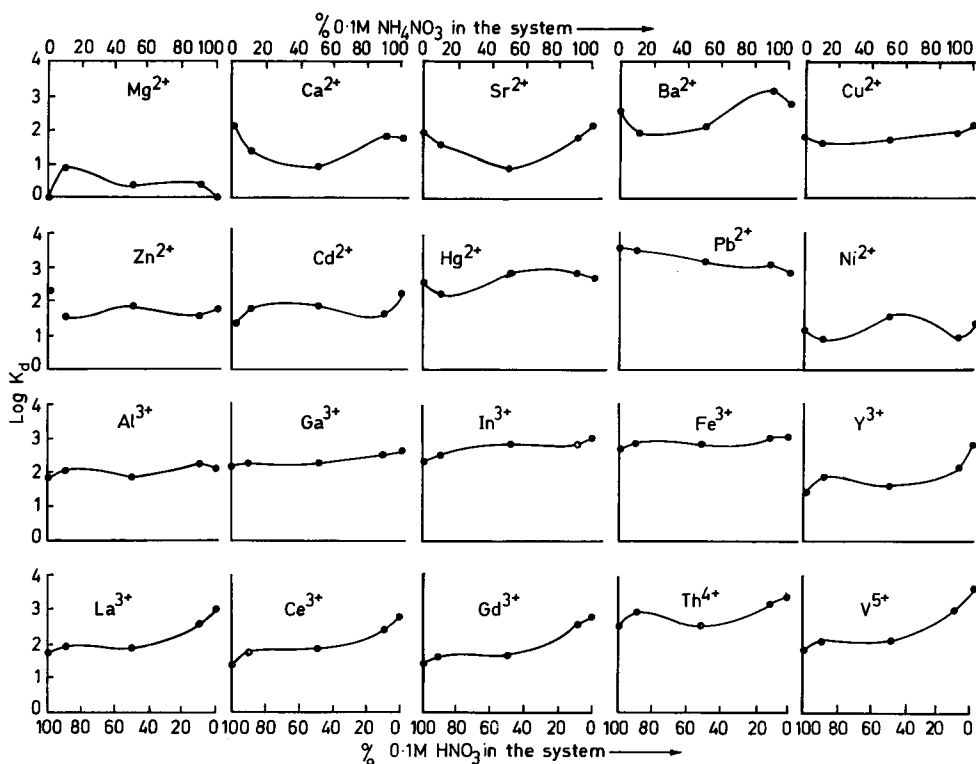


Fig. 8. K_d values on sample AT_3 dried at 300° .

TABLE V

K_d VALUES AT pH 1 (0.1 M NITRIC ACID)

Cation	Niobium antimonate (AT_3)	Hydrated Sb_2O_5	Hydrated Nb_2O_5
Mg^{2+}	2.85	1.40	0.00
Ca^{2+}	17.50	126.67	0.00
Sr^{2+}	23.30	196.00	4.62
Ba^{2+}	280.00	470.00	62.20
Cu^{2+}	25.86	—	2.88
Zn^{2+}	37.50	—	2.95
Cd^{2+}	39.24	—	0.00
Hg^{2+}	410.00	683.34	370.00
Pb^{2+}	1066.67	1450.00	425.00
Ni^{2+}	26.67	218.20	12.90
Al^{3+}	160.00	140.00	0.00
Ga^{3+}	325.00	—	17.50
In^{3+}	271.45	—	4.45
Fe^{3+}	285.72	308.00	22.08
Y^{3+}	30.00	—	10.76
La^{3+}	50.00	—	2.04
Ce^{3+}	20.00	176.80	0.00
Gd^{3+}	34.48	—	0.00
Th^{4+}	95.00	350.00	50.00
V^{5+}	260.00	50.11	142.86

TABLE VI
SEPARATIONS ACHIEVED ON NIOBIUM ANTIMONATE SAMPLE AT₃

Experiment No.	Mixture loaded	Cation eluted	Eluent*	Total volume of effluent (ml)	Amount loaded (μg)	Amount found (μg)	Error (%)
1	Mg ²⁺ -Sr ²⁺	Mg ²⁺	A	120	172.80	174.72	+1.10
		Sr ²⁺	B	60	319.20	319.20	+0.18
2	Mg ²⁺ -Ba ²⁺	Mg ²⁺	A	120	172.80	173.76	+0.55
		Ba ²⁺	B	60	414.00	397.44	-4.00
3	Mg ²⁺ -Al ³⁺	Mg ²⁺	A	120	172.80	173.76	+0.55
		Al ³⁺	B	70	135.20	132.60	-1.924
4	Mg ²⁺ -Hg ²⁺	Mg ²⁺	A	120	172.80	168.96	-2.22
		Hg ²⁺	B	80	800.00	784.00	-2.00
5	Mg ²⁺ -Ga ³⁺	Mg ²⁺	A	120	172.80	168.96	-2.22
		Ga ³⁺	B	40	154.00	157.60	+1.92
6	Mg ²⁺ -Fe ³⁺	Mg ²⁺	A	120	172.80	173.76	+0.55
		Fe ³⁺	B	80	296.80	280.00	-5.67
7	Mg ²⁺ -La ³⁺	Mg ²⁺	A	120	172.80	174.68	+2.20
		La ³⁺	B	60	583.80	583.80	0.00
8	Mg ²⁺ -Th ⁴⁺	Mg ²⁺	A	120	172.80	173.76	+0.55
		Th ⁴⁺	B	80	881.60	844.48	-4.21

* A = 0.01 M nitric acid; B = 2 M nitric acid-0.25 M ammonium nitrate.

as the radius of the hydrated ion decreases. This shows that ion exchange takes place with the hydrated form of the cation.

X-Ray diffractograms (not shown) of samples AT₁, AT₂ and AT₃ showed that AT₂ and AT₃ were semicrystalline, whereas AT₁ was amorphous. Hydrated niobium pentoxide is also amorphous, but hydrated antimony pentoxide⁹ shows some *d* spacing (*d*, spacing between adjacent planes in the crystal). Antimonic acid samples prepared by Ito and Abe¹⁰ and by Baetsle and Huys¹¹ also showed crystalline characteristics. A comparison of the *d* values of niobium antimonate, hydrated antimony pentoxide and different antimonic acids is made in Table IV. The *d* spacings of niobium anti-

TABLE VII
SEPARATIONS ACHIEVED ON NIOBIUM ANTIMONATE SAMPLE AT₃ DRIED AT 300°

Experiment No.	Mixture loaded	Cation eluted	Eluent*	Total volume of effluent (ml)	Amount loaded (μg)	Amount found (μg)	Error (%)
1	Cd ²⁺ -Hg ²⁺	Cd ²⁺	C	100	414.40	403.20	-2.70
		Hg ²⁺	D	60	262.60	272.70	+3.66
2	Cu ²⁺ -Pb ²⁺	Cu ²⁺	C	80	390.60	378.00	-3.01
		Pb ²⁺	D	60	724.50	701.28	-2.94
3	Ni ²⁺ -Pb ²⁺	Ni ²⁺	C	90	318.60	323.50	+1.84
		Pb ²⁺	D	60	724.50	701.28	-2.94

* C = 0.1 M nitric acid-0.2% ammonium nitrate; D = 2 M nitric acid-1.5% ammonium nitrate.

monate resemble those reported for hydrated antimony pentoxide and antimonite acid. The maximum inter-layer distances in AT_2 and AT_3 are 5.95 and 5.97 Å, respectively.

The IR spectra of samples AT_1 , AT_2 , AT_3 and AT_4 are shown in Figs. 1 and 2; all four samples have peaks at *ca.* 1600 cm^{-1} and 750 cm^{-1} , and samples AT_3 and AT_4 show peaks at 1150 cm^{-1} . The other maxima in the spectra represent Nujol peaks. The maximum at 1600 cm^{-1} corresponds to the deformation vibrations of interstitial water and of the hydroxyl groups [$\delta_1(H_2O)$ and (OH)] and the maximum at *ca.* 750 cm^{-1} is due to the stretching vibration of the M–O bonds [$\nu_1(Nb-O, Sb-O)$]. Earlier IR studies on crystalline antimonite acid¹² showed that the maxima between 1100 and 1330 cm^{-1} corresponded to the deformation of Sb–OH groups [$\delta_2(Sb-OH)$]. Crystalline antimonite acid shows a peak at *ca.* 1280 cm^{-1} , but niobium antimonite (samples AT_3 and AT_4) shows one at *ca.* 1150 cm^{-1} . Thus, we interpret this maximum as arising only from deformation of Sb–OH groups. This also suggests that sample AT_3 is crystalline, the shift in band frequency may be due to differences in the crystal structures of the two materials.

The peak maxima at 1600 cm^{-1} and 1150 cm^{-1} are heat-sensitive and disappear when the material is heated for 30 min at 1000°. The peak at 1600 cm^{-1} is lost due to the removal of the interstitial water, and that at 1150 cm^{-1} due to conversion of $Sb(OH)_5$ into Sb_2O_5 and finally Sb_2O_3 .

The results of the thermogravimetric analysis are shown in Fig. 3, from which it can be seen that the thermal stability of the samples decreases in the order AT_3 , AT_4 , AT_2 , AT_1 . Sample AT_1 loses more weight up to 400°, and, after this, its weight remains constant up to 700°. Thus, this sample contains a greater number of external water molecules, and the weight loss is due to the removal of these molecules and to condensation of hydroxyl groups (the condensation takes place between 450° and 700°). The weight losses (%) between 450° and 700° as calculated from the curves are 0.42, 3.80, 3.30 and 1.68 for samples AT_1 , AT_2 , AT_3 and AT_4 , respectively. Of these samples, the total weight loss on heating to 400° is the least for AT_3 , so that this material can be safely used at temperatures up to 400°. There is one inflexion point on the TGA curves between 900° and 1000°. The weight loss in this range is due only to conversion of Sb_2O_5 into Sb_2O_3 , the optimum temperature for this reaction being 930°. The weight losses (%) in this range are 1.27, 4.05, 4.84 and 0.86 for AT_1 , AT_2 , AT_3 and AT_4 , respectively. Our contention that samples AT_2 and AT_3 lose more weight owing to conversion of Sb_2O_5 into Sb_2O_3 is supported by the fact that these samples contain more antimony than do samples AT_1 and AT_4 .

The results of differential scanning calorimetry are shown in Figs. 4 and 5 and suggest that sample AT_3 is probably the best of all the materials studied. Removal of water of crystallization begins at 45, 85, 75 and 50° for AT_1 , AT_2 , AT_3 and AT_4 , respectively, and condensation starts at 200, 250 and 200° for AT_2 , AT_3 and AT_4 , respectively. This confirms the greater stability of sample AT_3 with respect to condensation.

The ion-exchange capacity of AT_3 on drying in air decreases with increase in temperature. The results are plotted in Fig. 9; for comparison, data on other antimonates, *i.e.*, those of tin¹³, titanium¹⁴, tantalum², chromium¹⁵, cerium¹⁶, aluminium¹⁷ and iron¹⁸, are included. The curves show that sample AT_3 is second only to ferric antimonate in this respect. The fall in ion-exchange capacity is due to condensation of hydroxyl groups at higher temperatures.

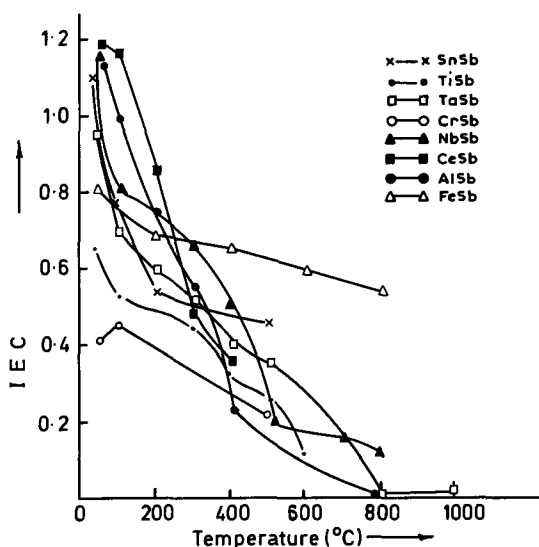


Fig. 9. Loss of ion-exchange capacity (IEC, mequiv./g) of various antimonates.

The distribution coefficients of metal ions in demineralised water are so high that one cannot decide whether or not niobium antimonate is selective for any cation. In order to investigate its selectivity for metal ions distribution coefficients (K_d) were determined in 0.1 *M*, 1 *M* and 4 *M* nitric acid; the results are shown in Fig. 6. The K_d values at pH 1 indicate the selectivity of the material. The selectivity sequence is almost the same for all samples, but the K_d values differ between samples. This difference is probably attributable to differences in composition and in the method of synthesis. The material having the greatest antimony content has the greatest uptake of ions. To find out whether niobium antimonate is a new phase or only a mixture of the oxides of niobium and antimony, the K_d values of some metal ions were determined on hydrated antimony pentoxide and hydrated niobium pentoxide at pH 1. The results for these materials and for sample AT₃ are given in Table V and show that the uptake of ions is different for the three materials; thus, AT₃ is not a mixture of oxides, but is a new phase. This conclusion is not confirmed by the X-ray data, since the d values for AT₃ are the same as those for antimononic acid.

The distribution coefficients for the dried samples of AT₃ show a regular trend, *i.e.*, the K_d values of most cations increase on drying the samples from 40° to 300°, and then decrease on drying to a higher temperature. The results are plotted in Fig. 7. This increase in K_d value may be due to a decrease in hydroxyl groups, as the oxides have a greater adsorptive power than the hydroxides. The dried material was selective towards Hg²⁺, Pb²⁺, Fe³⁺ and Th⁴⁺ throughout the temperature range studied. The K_d values on AT₃ dried at 300° were also determined in 0.1 *M* nitric acid, 0.1 *M* ammonium nitrate and a mixture of the two; the results are given in Fig. 8, which shows that the K_d values decrease as the content of 0.1 *M* nitric acid in the system increases.

Niobium antimonate sample AT₃ appears to be specific for separating Mg²⁺ from numerous metal ions; Mg²⁺ is only slightly adsorbed and hence can be separated

quantitatively from Sr^{2+} , Ba^{2+} , Hg^{2+} , Al^{3+} , Ga^{3+} , Fe^{3+} , La^{3+} and Th^{4+} (see Table VI). The K_d values of Hg^{2+} and Pb^{2+} differ from those of Cu^{2+} , Ni^{2+} and Cd^{2+} on sample AT_3 (dried at 300°) in 0.1 *M* nitric acid as well as in 0.1 *M* nitric acid–0.1 *M* ammonium nitrate (1:1) hence Cd^{2+} , Cu^{2+} and Ni^{2+} have been separated from Hg^{2+} and Pb^{2+} on columns of AT_3 so dried (see Table VII).

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