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SYNTHESIS AND ION-EXCHANGE PROPERTIES OF NIOBIUM ARSENATE

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SUMMARY

Eight samples of niobium arsenate with different ratios of niobium to arsenic have been prepared, and their stabilities and compositions have been determined. The results of thermogravimetry and X-ray studies are reported and compared with those for niobium pentoxide. The separations of Mg^{2+} from Al^{3+} and Mn^{2+}, of Ga^{3+} from Al^{3+} and of Hg^{2+} from Cd^{2+} are achieved. A plot of $pK_{sp} \cdot r^0$ *vs.* K_d is a straight line.

INTRODUCTION

Of the various inorganic ion exchangers that have been studied, materials based on niobium and tantalum are probably the least investigated. Phillips and Kraus[1] prepared niobium vanadate, which exhibits ion-exchange capacity between 0.5 and 2.0 mequiv./g and has good selectivity towards Ce^{3+} and Eu^{3+}. Sukharev and co-workers have synthesized niobium phosphate[2,3] and hydrated niobium pentoxide[4–7], and, for niobium phosphate, have examined conditions under which it shows ion-exchange behaviour; they also studied its composition. Hydrated niobium pentoxide, which acts as an amphoteric ion-exchange material, was selective towards $Cr_2O_7^{2-}$, WO_4^{2-}, $[Fe(CN)_6]^{4-}$ and $Mo_2O_7^{2-}$. Thermodynamic and kinetic studies were also carried out for the exchange of OH^-, $Cr_2O_7^{2-}$ and $[Fe(CN)_6]^{4-}$.

A search of the literature has revealed no such studies on niobium arsenate; we have therefore synthesized this material, studied its ion-exchange properties, and demonstrated its analytical importance by achieving some difficult quantitative separations. The ion-exchange equilibria are discussed with regard to the solubilities of the arsenates of the metal ions involved.

EXPERIMENTAL

Reagents

Niobium pentoxide (Bhabha Atomic Research Centre, Bombay, India) and sodium arsenate (Riedel, G.F.R.) were used, the sodium arsenate solution being prepared in 2 *M* hydrochloric acid. All other reagents were of analytical-reagent grade.

TABLE I

SYNTHESIS AND PROPERTIES OF VARIOUS FORMS OF NIOBIUM ARSENATE

Sample No.	*Mixing ratio*		*pH*	*Refluxing time (h)*	*Capacity for Na^+ (mequiv./g)*	*Colour*	*Ratio of Nb to As in product*	*Solubility (mg/l)*					
	Nb	*As*						*Demineralized water*		*4 M HNO_3*		*4 M HCl*	
								Nb	*As*	*Nb*	*As*	*Nb*	*As*
1	1	9	0	—	1.06	Grey	1.96	1.25	58.00	2.18	76.48	2.58	132.60
2	2	8	0	—	0.90	White	2.75	1.25	32.24	3.75	37.48	4.60	118.20
3	3	7	0	—	0.72	White	2.46	0.00	12.48	1.00	67.48	3.75	195.00
4	4	6	0	—	0.68	Chalk	2.29	1.00	54.00	2.00	78.00	3.20	158.00
5	1	9	0	24	0.70	White	2.16	1.00	37.48	2.00	108.00	3.80	170.00
6	2	8	0	24	0.74	White	2.12	0.00	27.48	1.00	50.00	—	—
7	3	7	0	24	0.56	Chalk	2.03	0.00	52.50	1.40	50.00	3.75	160.80
8	4	6	0	24	0.66	Chalk	2.64	1.00	45.00	2.00	60.00	—	—

Niobium pentoxide (20.00 g) was heated with 500 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

An electric temperature-controlled Sico Shaker, Elico pH meter, Stanton thermobalance, Philips X-ray unit and Bausch and Lomb Spectronic 20 were used for shaking, pH measurement, thermogravimetric analysis, X-ray studies and spectrophotometric measurements, respectively.

Syntheses

The samples were prepared by mixing acid solutions of 0.1 *M* niobium and 0.1 *M* sodium arsenate in the desired ratio at room temperature; sodium hydroxide solution was then added to the mixture with constant shaking until the pH was zero. The resulting precipitate was allowed to stand for 24 h in the mother liquor and was then washed by decantation with distilled water and filtered by suction; it was then dried at 40°. This dried product broke into small granules when it was immersed in water, and these granules were converted into the H^+ form with 2–3 *M* nitric acid.

Synthesis of hydrated niobium pentoxide

A concentrated solution of sodium hydroxide was added dropwise to the 0.1 *M* niobium solution until the pH was zero; the resulting precipitate was allowed to stand for 24 h.

Ion-exchange capacity

The ion-exchange capacities of the various samples of niobium arsenate were determined by the column method, the ion-exchanger (H^+ form) being placed in a column with a glass-wool support. The results are summarized in Table I. The ion-exchange capacities of the hydrated niobium pentoxide synthesised as described above and of that obtained from the manufacturers were 0.65 and 0.12 mequiv./g, respectively. The ion-exchange capacity of sample No. 1 of the niobium arsenate for different cations is shown in Table II.

Composition

A 200-mg portion of the well-powdered niobium arsenate was dissolved in 10 ml of hot concentrated sulphuric acid, and arsenic in the resulting solution was determined volumetrically[8]; niobium was determined gravimetrically by precipitation with cupferron[9] from the exchanger solution adjusted to contain 5% of tartaric acid and 10% of sulphuric acid[10]. The results are summarized in Table I.

Dissolution of niobium arsenate

To determine the solubility of this material, a 0.2-g portion was heated under reflux with 25 ml of the appropriate solvent for 1 h, and after removal of the undissolved material, niobium and arsenic were determined in the filtrate by the potassium thiocyanate–diethyl ether extraction[11] and the molybdenum blue[12] methods, respectively. The results are shown in Table I.

TABLE II

ION-EXCHANGE CAPACITY OF A SAMPLE OF NIOBIUM ARSENATE TOWARDS VARIOUS IONS

Eluting cation	*Concentrations of cation (M)*	*Ion-exchange capacity (mequiv./g)*
Na^+	1.0	1.06
K^+	1.0	1.44
Mg^{2+}	0.5	0.90
	1.0	0.98
Ba^{2+}	0.5	1.58
	1.0	1.88

Distribution studies

The distribution coefficients for 30 metal ions in demineralized water and 0.1 *M* nitric acid were determined by using a loading of the cation equal to 3% of the total ion-exchange capacity; the total volume of solution was 50 ml and the amount of

TABLE III

DISTRIBUTION COEFFICIENTS FOR 30 METAL IONS USING A LOADING OF 3% OF THE TOTAL CAPACITY

K_{sp} = solubility product.

Cation	*Radius (r^0) of non-hydrated ion (Å)*	*pK_{sp} of arsenate of metal ion*	*$pK_{sp} \cdot r^0$*	*K_d value (ml/g)*	
				Demineralized water	*0.1 M HNO_3*
Mg^{2+}	0.65	19.67	12.78	171	7
Ca^{2+}	0.99	18.17	17.98	298	22
Co^{2+}	0.74	28.12	20.80	387	15
Sr^{2+}	1.13	18.09	21.26	553	55
Cd^{2+}	0.97	32.66	31.04	950	110
Cu^{2+}	0.96	35.11	33.70	1600	65
Pb^{2+}	1.20	35.38	42.45	1850	557
Ba^{2+}	1.35	50.11	67.64	2980	85
Ni^{2+}	0.72	25.50	18.36	1005	13
Zn^{2+}	0.74	27.88	2.63	1100	71
Mn^{2+}	0 80	28.72	22.97	1930	11
Al^{3+}	0.50	—	—	1930	133
Fe^{3+}	0.64	20.24	12.93	115	72
Hg^{2+}	1.10	—	—	31	12
V^{4+}	0.60	—	—	540	469
Zr^{4+}	0.80	—	—	109	193
In^{3+}	0.81	—	—	779	51
Pr^{3+}	—	—	—	9460	47
Nd^{3+}	—	—	—	8460	55
Sm^{3+}	—	—	—	9260	20
Eu^{3+}	1.03	—	—	2110	79
Gd^{3+}	-	—	—	2313	10
Tb^{3+}	—	—	—	7820	28
Ho^{3+}	—	—	—	8660	266
Er^{3+}	—	—	—	8020	31
Tm^{3+}	—	—	—	3420	41
Yb^{3+}	—	—	—	4820	70
Y^{3+}	—	—	—	9460	14
Ti^{4+}	—	—	—	1900	1002
Hf^{4+}	—	—	—	183	77

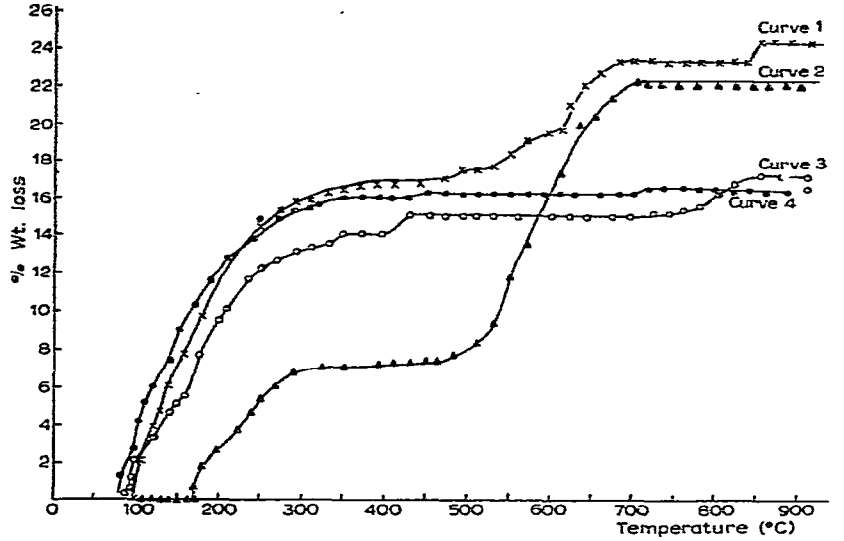

Fig. 1. Thermogravimetric curves for samples of niobium arsenate. Curve 1 = sample 1 in H^+ form; curve 2 = sample 1 in K^+ form; curve 3 = sample 5 in H^+ form; curve 4 = sample 5 in K^+ form.

exchanger used was 0.5 g. Titanium was determined spectrophotometrically[13], and all other cations by titration with 2 *mM* EDTA. The results are shown in Table III.

Thermogravimetric analysis

Samples 1, 2 and 5 (see Table I), and hydrated niobium pentoxide, in H^+ and K^+ forms, and sample 4 (in H^+ form) were subjected to thermogravimetric analysis over the range 50° to 900°; the results are summarized in Figs. 1 and 2.

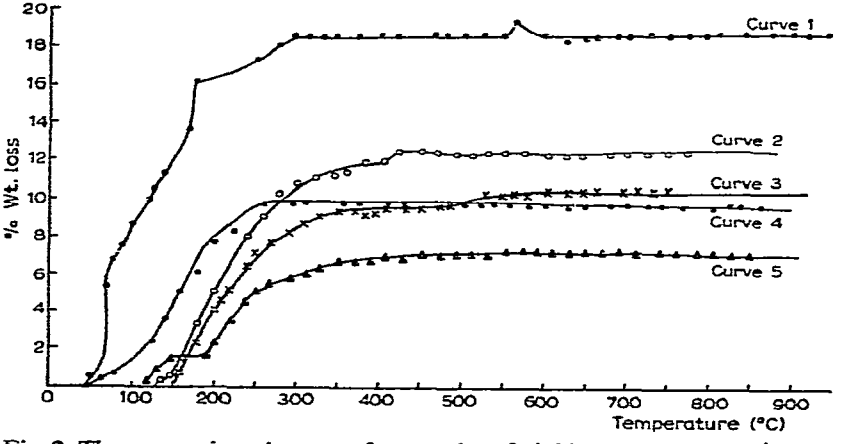

Fig. 2. Thermogravimetric curves for samples of niobium arsenate and hydrated niobium pentoxide. Curve 1 = Hydrated niobium pentoxide in H^+ form; curve 2 = sample 4 in H^+ form, curve 3 = sample 2 in H^+ form; curve 4 = hydrated niobium pentoxide in K^+ form; curve 5 = sample 2 in K^+ form.

Separation studies

For these experiments, a glass column was filled with 2 g of niobium arsenate (H^+ form) on a glass-wool support. The flow-rate in all separations was 0.6 to 0.8 ml/min. The ions of magnesium, gallium and bivalent mercury were eluted with 0.2% ammonium nitrate solution; other ions retained on the column were eluted with 2.5 *M* nitric acid–5% ammonium nitrate solution. The results are shown in Fig. 3 and Table IV.

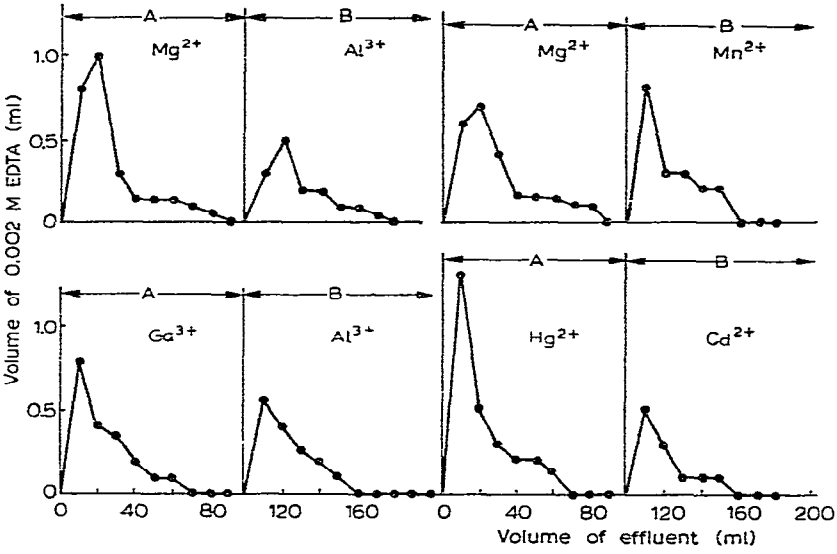

Fig. 3. Separation of some metal ions on niobium arsenate. A = 0.2% ammonium nitrate solution as eluent; B = 2.5 *M* nitric acid + 5% ammonium nitrate solution as eluent.

TABLE IV

SEPARATIONS ACHIEVED ON NIOBIUM ARSENATE COLUMN

Experiment No.	*Mixture loaded*	*Cation eluted*	*Eluent*	*Total volume of effluent collected (ml)*	*Amount loaded (μg)*	*Amount found (μg)*	*Error (%)*
1	Mg^{2+}–Al^{3+}	Mg^{2+}	0.2% NH_4NO_3	100	126.46	131.33	+ 3.57
		Al^{3+}	5% NH_4NO_3 + 2.5 *M* HNO_3	90	81.98	78.98	− 4.58
2	Mg^{2+}–Mn^{2+}	Mg^{2+}	0.2% NH_4NO_3	100	126.46	128.80	+ 1.84
		Mn^{2+}	5% NH_4NO_3 + 2.5 *M* HNO_3	70	203.24	197.84	− 2.65
3	Ga^{3+}–Al^{3+}	Ga^{3+}	0.2% NH_4NO_3	80	264.94	271.90	+ 2.56
		Al^{3+}	5% NH_4NO_3 + 2.5 *M* HNO_3	70	81.98	80.91	− 1.23
4	Hg^{2+}–Cd^{2+}	Hg^{2+}	0.2% NH_4NO_3	90	543.29	533.23	− 1.85
		Cd^{2+}	5% NH_4NO_3 + 2.5 *M* HNO_3	70	123.65	123.65	0.0

DISCUSSION

The chemical stability of niobium arsenate in the solvents tested increases in the order demineralized water, 4 *M* nitric acid, 4 *M* hydrochloric acid. Thermo-

gravimetric studies show that the thermal stabilities of the various samples increases in the order sample 2, sample 4, sample 5, hydrated niobium pentoxide, sample 1. With samples 2, 4 and 5 there is no weight loss above 500°, and none for the hydrated niobium pentoxide above 300°; with sample 1, weight loss is continuous up to 850°. The higher weight loss with sample 1 is probably due to its higher content of arsenic (see Table I).

Thermogravimetric analysis shows that the weight loss from the H^+ form of the exchanger is greater than that for the K^+ form; this is because, in the latter form, removal of water molecules by condensation is not possible. It appears that external water molecules are removed at temperatures up to 450°, after which condensation probably starts in niobium arsenate. As the niobium content of the material decreases, the thermal stability (as shown by the weight loss) also decreases, as is clear from Table I. The hydrated niobium pentoxide has more hydroxyl groups, which are easier to condense than arsenate groups, and its thermal stability is thus smaller than that of the arsenate.

Nickel filtered Cu K_α X-ray diffractograms of sample 1 and of hydrated niobium pentoxide show that both materials are amorphous.

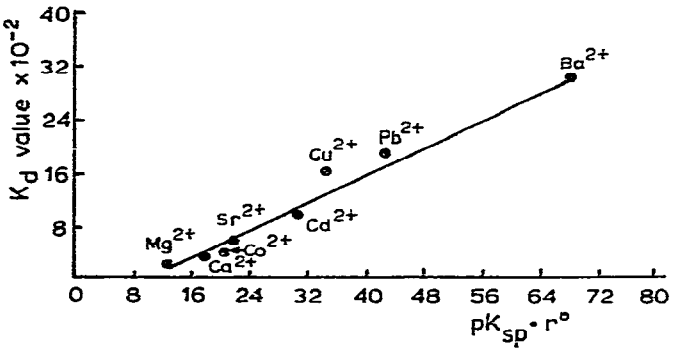

Fig. 4. Graph of values of K_d against $pK_{sp} \cdot r^0$ for the metals studied.

The analytical importance of niobium arsenate has been illustrated by achieving four binary separations on columns of the material (see Fig. 3), and Fig. 4 shows that a graph of $pK_{sp} \cdot r^0$ against K_d is a straight line. This follows from the well-known fact that insoluble substances (having high values of pK_{sp}) have large K_d values. A large value of r^0 indicates little hydration and hence a larger attraction for the matrix.

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