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Synthesis and Ion-Exchange Properties of Reproducible Stannic Molybdoarsenate. Separations of Ba^{2} -La^{3} , Mg^{2} -La^{3} , Sr^{2} -Y^{3} , and Sr^{2} -La^{3}

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NOTE

Synthesis and Ion-Exchange Properties of Reproducible Stannic Molybdoarsenate. Separations of Ba^{2+}–La^{3+}, Mg^{2+}–La^{3+}, Sr^{2+}–Y^{3+}, and Sr^{2+}–La^{3+}

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Abstract

A new inorganic ion exchanger, stannic molybdoarsenate, has been prepared by treating a 0.25 *M* solution of stannic chloride with a mixture of a 0.25 *M* solution of sodium arsenate and sodium molybdate in the volume ratio Sn:Mo:As 2:1:1 at different pH values (0, 1, and 2). It may be used for the binary separation of Ba^{2+}–La^{3+}, Mg^{2+}–La^{3+}, Sr^{2+}–Y^{3+}, and Sr^{2+}–La^{3+}.

INTRODUCTION

Synthetic inorganic ion exchangers are resistant to heat and radiation. They have high selectivity for certain cations and can be easily impregnated on papers. They have, therefore, an established place in cation exchange (*1–7*) chromatography as column materials and for the impregnation of papers.

Some heteropolyacid salts (*7*, *8*) can be used as ion exchangers. The ion-exchange properties of ammonium molybdophosphate (*9–13*), ammonium tungstophosphate (*12*, *14*, *15*) and ammonium molybdoarsenate

(*16*) have been studied. The ion-exchange behavior of molybdophosphates and tungstophosphates has been reviewed (*8*). Ferrocyanomolybdates and mixed ferrocyanides of light and heavy metal elements have also been used as ion exchangers (*17*, *18*).

As no studies have been reported on tin(IV) molybdoarsenate, it was decided to synthesize this material at different pH values and to study its ion-exchange behavior. The exchanger prepared at pH = 0 and refluxed for 24 hr with the mother liquor was studied in detail. The ion-exchange capacity, stability in different systems, pH titrations, x-ray diffraction patterns, and K_d values have been determined for this material. Four important separations have been achieved.

EXPERIMENTAL AND RESULTS

Apparatus

A Bausch and Lomb Spectronic 20 colorimeter, an Elico pH meter model LI-10 (India), an electric temperature-controlled SICO shaker, and a Philips x-ray unit were used for spectrophotometry, pH measurement, shaking, and x-ray studies, respectively.

Reagents

Stannic chloride pentahydrate (pure, Poland), sodium arsenate (Reidel), and sodium molybdate (May and Baker) were used. All other chemicals were of analytical grade. Nitrates of rare-earth metals were prepared by dissolving oxides (B.D.H.) in nitric acid.

Method of Preparation

The stannic molybdoarsenate samples were prepared by mixing 0.25 *M* solutions of sodium molybdate, sodium arsenate, and stannic chloride in the volume ratio of 1:1:2 at pH = 0, 1, and 2. Ammonia solution (d 0.88) was used for adjusting the pH wherever necessary. The precipitate so obtained was divided in two parts in each case. One part was allowed to stand for 24 hr at room temperature and the other part was refluxed for 24 hr after attaining room temperature. The samples obtained by the former procedures at pH = 0, 1, and 2 have been labeled as Samples 1, 2, and 3, respectively, and those obtained by the latter procedure as Samples 4, 5, and 6. The yellowish white precipitate was washed by decan-

TABLE 1

Ion-Exchange Capacity of Stannic Molybdoarsenate Samples Dried at Different Temperatures

Drying temperature (°C)	Ion-exchange capacity (meq/g)
40	1.20
100	0.90
200	0.60
300	0.51
400	0.35
600	0.28
700	0.04

tation, filtered off, and washed with 0.1 *M* HCl and then with acetone. The gel was dried at 40°C. The dried product broke down into small particles when immersed in water. This dried product was immersed in 1 *M* nitric acid (approximately 50 g of the exchanger in 200 ml of 1 *M* nitric acid) to remove the foreign ions adsorbed during the preparation. The exchanger dissolved to some extent during this treatment. Finally, the exchanger was washed with demineralized water to remove excess acid and again dried at 40°C. In order to study the effect of drying temperature, the material so obtained was dried in a muffle furnace at different temperatures, as shown in Table 1.

Chemical Composition

A 0.20-g portion of the exchanger was dissolved in hydrochloric acid. The tin of the exchanger was precipitated with cupferron. The organic matter was removed by wet oxidation, and tin was determined titrimetrically by the potassium dichromate method after reduction with lead. The molybdenum was separated with α-benzoin oxime and determined gravimetrically as MoO_3. After removing the organic matter as above, the arsenic was separated as silver arsenate and determined volumetrically by Volhard's thiocyanate method (*3*).

Dissolution

To determine the chemical dissolution of stannic molybdoarsenate, 0.50 g of the exchanger was taken in a conical flask with 50 ml of the solution concerned for 6 hr in a temperature-controlled shaker. The undissolved exchanger was filtered off, and tin, arsenic, and molybdenum in the filtrate were determined spectrophotometrically by phenylfluorone, molybdenum blue, and potassium thiocyanate methods, respectively.

Ion-Exchange Studies

The ion-exchange capacity of stannic molybdoarsenate samples dried at different temperatures was determined by the standard method using 1 *M* electrolyte solutions. pH titration curves for Li^+, Na^+, K^+, and NH_4^+ were performed by the method described earlier (*19*).

The distribution coefficients (K_d) for inorganic ions have been determined on stannic molybdoarsenate samples dried at different temperatures after shaking for 6 hr. The K_d values have also been determined on Sample 4 in nitric acid solutions of varying pH and in HNO_3–NH_4NO_3 buffer systems. The loading of cations for the system was less than 3% of the experimental ion-exchange capacity. The equation used for the calculation was

$$K_d = \frac{I - F}{F} \times \frac{50}{0.5} \text{ ml/g}$$

where I is the volume of 0.002 *M* EDTA needed to titrate the original cation solution and F is the volume of 0.002 *M* EDTA needed for titration after equilibrium. The total volume of the equilibrating solution was 50 ml and the amount of the exchanger taken was 0.50 g.

Column Operation

For separation studies a 30 × 0.39 cm bore glass column was used,

TABLE 2

Synthesis and Chemical Composition of Stannic Molybdoarsenate Samples

Sample no.	Sample[a]	pH	Ion-exchange capacity (meq/g)	Analytical ratios, Sn: Mo: As
1	Sn–Mo–As (UR)	0.0	1.7	6:2:3
2	Sn–Mo–As (UR)	1.0	1.4	6:2:3
3	Sn–Mo–As (UR)	2.0	1.2	6:2:3
4	Sn–Mo–As (R)	0.0	1.4	4:2:2
5	Sn–Mo–As (R)	1.0	1.2	11:5:5
6	Sn–Mo–As (R)	2.0	1.3	5:2:2

[a] Sn–Mo–As = stannic molybdoarsenate, UR = unrefluxed, and R = refluxed.

TABLE 3

Solubility of Stannic Molybdoarsenate (Sample 4) in Water and Ammonium Nitrate

Solvent	Solubility (mg/50 ml)		
	Sn	Mo	As
Distilled water	0.00	6.6	3.80
0.1 *M* Ammonium nitrate	0.02	0.6	5.25

TABLE 4

Distribution Coefficient of Metal Ions on Stannic Molybdoarsenate (Sample 4) at Different pH Values

Metal ion	K_d values $\times 10^{-2}$ at different pH values			
	1	2	3	5
Mg^2	0.0	1.1	2.9	9.0
Ca^{2+}	0.0	1.1	8.4	10.8
Sr^{2+}	0.0	3.8	11.0	22.0
Ba^{2+}	0.1	4.4	15.3	23.0
Zn^{2+}	0.0	1.4	7.7	106.5
Cd^{2+}	0.1	1.4	9.2	21.5
Cu^{2+}	0.0	5.1	14.2	75.0
Ni^{2+}	0.2	0.8	6.8	10.5
Fe^{3+}	0.3	0.7	1.4	1.5
Mn^{2+}	0.6	3.4	9.0	109.0
Al^{3+}	1.2	2.4	4.6	7.4
Y^{3+}	7.5	27.4	84.0	212.0
La^{3+}	1.3	1.6	114.0	114.0
Pr^{3+}	4.1	11.6	251.0	251.0
Nd^{3+}	3.5	8.0	8.0	13.9
Sm^{3+}	2.3	7.8	12.2	16.6
Eu^{3+}	6.0	17.7	36.5	281.0
Gd^{3+}	4.9	4.9	34.0	34.0
Tb^{3+}	4.2	6.8	22.5	225.0
Dy^{3+}	7.5	11.7	16.0	50.0
Ho^{3+}	5.6	7.8	15.5	264.0
Er^{3+}	2.6	8.4	11.7	224.4
Tm^{3+}	3.8	7.0	31.0	239.0

and 1.50 g of ion exchanger was kept in the column with a glass wool support. The rate of flow was 9 to 10 drops/min. The effluent was titrated with 0.002 *M* EDTA. The separation of Ba^{2+}, Mg^{2+}, and Sr^{2+} from La^{3+}, and Sr^{2+} from Y^{3+} was achieved on this column.

Heat Treatment

The exchanger was heated at different temperatures in the muffle furnace for 1 hr and quenched to room temperature. The ion-exchange capacity and K_d values were determined from these heated samples (Tables 1, 4, 5, and 6).

pH Titration

pH titration were carried out by the method of Topp and Pepper (*20*). The more important results obtained are summarized in Tables 1–6.

Separations Achieved

La^{3+} (1284 μg) was separated from Ba^{2+} (1234 μg), Mg^{2+} (2178 μg), and Sr^{2+} (828 μg), and Sr^{2+} (828 μg) from Y^{3+} (4135 μg) on a stannic molybdoarsenate column. Ba^{2+}, Mg^{2+} and Sr^{2+}, were first eluted with

TABLE 5

Distribution Coefficients at pH = 5 on Stannic Molybdoarsenate Samples Dried at Different Temperatures

Metal ion	K_d value $\times 10^{-2}$ at temperatures (°C) of						
	40	100	200	300	400	600	700
Y^{3+}	212.0	3.4	0.3	0.2	0.1	0.0	0.00
La^{3+}	114.0	56.5	1.4	1.0	0.6	0.3	0.1
Pr^{3+}	251.0	251.0	0.5	0.5	0.2	0.1	0.1
Nd^{3+}	13.9	6.5	0.4	0.1	0.0	0.0	0.0
Sm^{3+}	16.6	2.9	0.3	0.2	0.1	0.1	0.1
Eu^{3+}	280.0	7.6	0.8	0.3	0.2	0.1	0.1
Gd^{3+}	34.5	4.6	0.2	0.1	0.1	0.1	0.0
Tb^{3+}	225.0	225.0	0.5	0.4	0.2	0.1	0.1
Dy^{3+}	50.0	11.8	0.2	0.1	0.1	0.1	0.0
Ho^{3+}	264.0	4.3	0.4	0.3	0.1	0.1	0.1
Er^{3+}	24.4	4.6	0.3	0.1	0.1	0.1	0.0
Tm^{3+}	239.0	3.8	0.2	0.1	0.1	0.1	0.0

TABLE 6

Distribution Coefficients of Metal Ions on Stannic Molybdoarsenate (Sample 4) in HNO_3-NH_4NO_3 Systems

	K_d value $\times 10^{-1}$ at 0.1 N HNO_3–0.1 N NH_4NO_3 ratios of				
Metal ion	3:1	2:1	1:1	1:2	1:3
Mg^{2+}	0.0	0.0	1.2	0.1	4.6
Ca^{2+}	0.1	0.1	0.1	0.1	1.0
Sr^{2+}	0.1	0.2	0.3	0.3	0.6
Ba^{2+}	0.1	0.2	0.3	0.8	0.5
Zn^{2+}	0.0	0.1	0.2	0.2	0.2
Ca^{2+}	0.0	0.1	0.1	0.3	0.2
Cu^{2+}	0.0	0.1	0.2	0.2	0.3
Ni^{2+}	0.0	0.0	0.2	0.3	0.3
Fe^{3+}	0.3	0.6	0.9	0.9	1.4
Mn^{2+}	0.0	0.0	0.0	0.1	0.1
Al^{3+}	0.0	0.1	0.2	0.3	0.6
Y^{3+}	1.1	1.8	2.0	3.3	4.3
La^{3+}	1.9	2.3	2.5	2.8	4.0
Pr^{3+}	4.0	9.1	0.4	1.7	2.1
Nd^{3+}	2.3	2.5	2.6	2.7	3.5
Sm^{3+}	2.5	3.1	3.4	4.3	10.8
Eu^{3+}	3.7	1.7	0.7	1.8	1.1
Ga^{3+}	2.8	1.5	3.1	7.8	9.6
Tb^{3+}	3.7	3.7	1.2	2.8	2.7
Dy^{3+}	1.3	1.4	2.0	2.3	2.7
Ho^{3+}	7.8	12.3	1.9	2.1	2.3
Er^{3+}	1.6	1.1	1.8	8.2	10.3
Tm^{3+}	2.0	1.6	0.8	2.0	2.2

1% NH_4NO_3, and La^{3+} and Y^{3+} were eluted with 4% NH_4NO_3 in 1.5 M HNO_3.

DISCUSSION

Stannic molybdoarsenate is a useful exchanger which behaves as a weak monoprotic acid (details omitted to save space). It should not be dried at a high temperature because its exchange capacity decreases with a rise in temperature and becomes 0.04 meq/g at 700°C (Table 1). The order of ion-exchange capacity for alkali metal ions is $Li^+ < Na^+ < K^+$. The ionic radii of these metal ions are also in the same sequence. This shows that Li^+ ions, and to a lesser extent sodium ions, are slow to move in and out of the exchanger compared to K^+ ions. X-ray studies of

Sample 4 dried at different temperatures show that the products are amorphous except the one heated to 600°C. The product heated at 600°C shows a crystalline character. This may be due to its decomposition into the corresponding metal oxides.

Table 2 shows that Samples 1, 2, and 3 have the same composition, while Samples 4, 5, and 6 have different Sn: Mo: As ratios. This shows that refluxing but not precipitation at different pH values is responsible for the change in composition.

Stannic molybdoarsenate is stable in some organic and inorganic systems. The ion exchanger is completely insoluble in dimethylsulfoxide (DMSO). A very small amount of arsenic was found in butan-1-ol. The solubility in oxalic acid may be due to complex formation. However, the stability of this material in ammonium nitrate is quite high (Table 3). Therefore the K_d values have been determined in its solution.

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