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SYNTHESIS AND ION-EXCHANGE PROPERTIES OF TIN(IV) TUNGSTO-ARSENATE

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SUMMARY

The inorganic ion exchanger tin(IV) tungstoarsenate with a tin:tungsten:arsenic ratio of 12:5:2 has been synthesized by mixing solutions of tin(IV) chloride, sodium tungstate and sodium arsenate in the volume ratio 2:1:1 at pH ≈ 1. A comparison of the ion-exchange properties of tin(IV) tungstoarsenate with those of tin(IV) tungstate and tin(IV) arsenate has been made. It was found that tin(IV) tungstoarsenate has a high thermal stability, showing high K_d values after heating at 500°. This ion exchanger is chemically more stable than the corresponding molybdoarsenate. Quantitative separations of Cu^{2+} from Ni^{2+} and Mg^{2+} and of Ba^{2+} from Mg^{2+} have been obtained.

INTRODUCTION

Many inorganic ion exchangers have been prepared in the past 5 years, most of them being amorphous, prepared by precipitation. The usual practice was to use different proportions of reactants and different treatments and then to study the distribution ratios for many cations in the hope of finding special selectivities. Some exchangers were studied by thermal analysis.

The heteropolyacid salts[1,2] of some metal ions can be used as ion exchangers. Various molybdophosphate, tungstophosphate and other heteropolyacid salts have been used as ion exchangers and were reviewed by Pekarek and Vesely[3] and Walton[4]. Titanium phosphate silicate has been prepared by Naqvi *et al.*[5]. Zirconium phosphate silicate[6,7] and phosphomolybdate have been synthesized[8] and cerium phosphate sulphate was prepared by Koenig and Graf[9]. A number of papers have been published on ammonium phosphomolybdate[10–12]. Lead strontium phosphate was prepared by Fedoroff *et al.*[13]. The ammonium salt of tungstoarsenic heteropolyacid[14] was applied as a high-capacity cation exchanger to Rb^+–Cs^+, K^+, Tl^+ and Ag^+ separations.

No such studies have been reported on tin(IV) tungstoarsenate, and it was therefore decided to synthesize this material at different pH values and to study its ion-exchange behaviour.

EXPERIMENTAL

Reagents

Tin(IV) chloride pentahydrate (pure; Polskie Odczynniki Chemiczne, Gliwice, Poland), sodium arsenate heptahydrate (Riedel, G.F.R.) and sodium tungstate (AnalaR) were used. All other reagents were of analytical-reagent grade.

Apparatus

Titrimetric and spectrophotometric studies were carried out with an Elico Model LI-10 pH meter and a Bausch and Lomb Spectronic 20 colorimeter, shaking was performed with a Sico temperature-controlled shaker.

Synthesis of tin(IV) tungstoarsenate

Tin(IV) tungstoarsenate was prepared by adding 0.25 *M* tin(IV) chloride solution to a mixture of 0.25 *M* sodium arsenate and 0.25 *M* sodium tungstate in the volume ratio 2:1:1. The pH of the mixture was adjusted to the values given in Table I and the precipitate obtained was allowed to stand for 24 h at room temperature. It was then washed by decantation, filtered off and washed with 2 *M* nitric acid. The gel was dried at 40°. The dry product broke down into small particles when immersed in water. Approximately 40 g of the exchanger were converted into the hydrogen form by the treatment with 100 ml of 1.0 *M* nitric acid and finally washed with demineralized water. The exchanger dissolved to some extent during this process. Finally, the exchanger was washed with demineralized water in order to remove the excess of acid and was again dried at 40°.

TABLE I

CONDITIONS OF PREPARATION AND THE ION EXCHANGE CAPACITY OF TIN(IV) TUNGSTOARSENATE SAMPLES

The reagents used were 0.25 *M* tin(IV) chloride +0.25 *M* sodium arsenate +0.25 *M* sodium tungstate in the ratio 2:1:1.

Sample No.	*pH*	*Ion-exchange capacity (mequiv./g)*
1	1.0	1.06
2	3.9	1.12
3	6.8	1.10
4	11.0	No ppt. obtained

Chemical composition

A 0.3-g amount of the exchanger was dissolved in sodium hydroxide solution. Tin, after reduction with lead, was determined by the potassium dichromate method[15], arsenic was determined titrimetrically by the potassium thiocyanate method[16] and tungsten was determined gravimetrically as tungsten(VI) oxide with α-benzoin oxime[17]. The ratio Sn:W:As was found to be 12:5:2.

Dissolution of tin(IV) tungstoarsenate ion exchanger

A 0.5-g portion of the exchanger was shaken in a flask with 50 ml of the solution concerned in a temperature-controlled shaker for 6 h until equilibrium was

TABLE II

CHEMICAL DISSOLUTION OF TIN(IV) TUNGSTOARSENATE AND MOLYBDOARSENATE

Solvent	*Tungstoarsenate (mg per 50 ml)*			*Molybdoarsenate (mg per 50 ml)*		
	Sn	*W*	*As*	*Sn*	*Mo*	*As*
4 *M* Nitric acid	8.0	0.60	1.0	3.6	20.0	17.5
4 *M* Hydrochloric acid	145.0	11.0	47.5	Dissolved completely		
4 *M* Sulphuric acid	29.0	0.4	20.0	22.50	62.5	30.0
0.1 *N* Sodium hydroxide	Dissolved completely					
1.0 *M* Ammonia	64.0	2.0	18.0	Dissolved completely		
1 *M* Acetic acid	0.38	0.16	14.0	0.03	10.0	7.5
1 *M* Ammonium nitrate	0.63	2.0	1.60	4.88	25.0	5.0
1 *M* Sodium acetate	2.75	3.30	9.0	0.02	0.6	5.25
1 *M* Formic acid	0.38	0.60	5.40	0.25	30.0	8.75
1 *M* Oxalic acid	56.25	5.40	10.0	Dissolved completely		
1 *M* Tartaric acid	47.50	0.20	0.20	8.75	30.0	15.0
1 *M* Citric acid	32.5	0.60	0.40	2.88	30.0	8.75
n Butanol	0.09	0.0	0.18	0.0	0.0	0.0
Dimethyl sulphoxide	0.07	0.0	0.20	0.0	0.0	0.5
Water	0.65	1.0	1.80	0.0	6.6	3.8

reached. The undissolved portion of the exchanger was removed by filtration. Tin, arsenic and tungsten were determined spectrophotometrically in the filtrate. The results are given in Table II.

RESULTS

Ion-exchange capacity

The ion-exchange capacity of various samples, determined by the standard method, are given in Table I.

Distribution coefficient studies

The distribution coefficients (K_d) of 24 cations were determined in nitric acid and ammonium nitrate + nitric acid systems. For this purpose, 0.5 g of the exchanger were shaken with 50 ml of the solution for 6 h. The amount of the cation in the solution was determined by titration with EDTA and the K_d values were calculated from the equation

$$K_d\,(\text{ml/g}) = \frac{I-F}{F}\cdot\frac{50}{0.5} \tag{1}$$

where I is the volume of EDTA consumed by the original solution and F is the volume of EDTA consumed after equilibrium. The results are given in Tables III–V.

Heat treatment

The ion-exchange material in the potassium form dried at 40° was heated at different temperatures in a muffle furnace for 2 h and the ion-exchange capacity was determined. The results are given in Table VI.

TABLE III

K_d VALUES (ml/g) OF METAL IONS ON TIN(IV) TUNGSTOARSENATE (SAMPLE No. 1) DRIED AT 50° IN NITRIC ACID

Metal ion	*0.1 N HNO_3*	*0.01 N HNO_3*	*0.001 N HNO_3*
Mg^{2+}	39	9.0	96
Ca^{2+}	267	60	462
Sr^{2+}	0	204	226
Ba^{2+}	31	251	—
Zn^{2+}	0	0	181
Cd^{2+}	45	262	2753
Cu^{2+}	62	401	944
Ni^{2+}	33	68	50
Mn^{2+}	160	116	620
Fe^{3+}	82	2.0	97
Al^{3+}	34	0.0	54
Y^{3+}	31	4160	1320
La^{3+}	99	850	79
Pr^{3+}	84	408	3286
Nd^{3+}	109	225	4400
Sm^{3+}	199	948	1064
Eu^{3+}	87	3696	366
Gd^{3+}	53	5260	1113
Tb^{3+}	276	2250	1780
Dy^{3+}	282	−507	2480
Ho^{3+}	405	5200	13150
Er^{3+}	509	5080	763
Tm^{3+}	67	2300	1271
Cr^{3+}	140	—	420

TABLE IV

K_d VALUES (ml/g) OF METAL IONS ON TIN(IV) TUNGSTOARSENATE (SAMPLE No. 1) IN AMMONIUM NITRATE + NITRIC ACID

Metal ion	*0.1 N HNO_3 + 0.1 N NH_4NO_3 (1:1)*	*0.1 N HNO_3 + 0.1 N NH_4NO_3 (1:2)*
Mg^{2+}	0	0
Ca^{2+}	13	3
Sr^{2+}	15	15
Ba^{2+}	95	111
Zn^{2+}	5	12
Cd^{2+}	8	7
Cu^{2+}	30	8
Ni^{2+}	0	0
Mn^{2+}	4	0
Fe^{3+}	57	—
Al^{3+}	0	6
Y^3	124	25
La^{3+}	198	54
Pr^{3+}	45	54
Nd^{3+}	125	—
Sm^{3+}	80	31
Eu^{3+}	100	328
Gd^{3+}	106	61
Tb^{3+}	104	306
Dy^{3+}	224	102
Ho^{3+}	76	311
Er^{3+}	210	85
Tm^{3+}	1.0	45
Cr^{3+}	218	84

TABLE V

K_d VALUES (ml/g) OF METAL IONS ON TIN(IV) TUNGSTOARSENATE (SAMPLE No. 1) WASHED WITH DEMINERALIZED WATER AND DRIED AT DIFFERENT TEMPERATURES

Metal ion	*50°*	*150°*	*300°*	*500°*	*800°*
Mg^{2+}	52	77	253	549	11
Ca^{2+}	718	650	1700	900	14
Sr^{2+}	1000	700	2100	115	13
Ba^{2+}	1676	1000	4300	2830	31
Zn^{2+}	1260	3980	2620	2620	31
Cd^{2+}	435	7033	2040	7033	27
Cu^{2+}	11650	11650	4600	4600	38
Ni^{2+}	92	92	100	191	15
Mn^{2+}	134	1240	1333	1333	17
Fe^{3+}	2460	753	509	540	30
Al^{3+}	1440	516	516	516	150
Y^{3+}	4160	965	674	674	10
La^{3+}	>11100	2140	851	—	16
Pr^{3+}	8366	913	361	313	10
Nd^{3+}	>24400	4400	800	592	18
Sm^{3+}	1640	336	319	217	0
Eu^{3+}	2610	269	167	230	8
Gd^{3+}	3540	201	241	304	10
Tb^{3+}	2250	754	276	248	10
Dy^{3+}	10220	218	203	164	9
Ho^{3+}	1413	178	98	165	10
Er^{3+}	2353	841	270	371	54
Tm^{3+}	1271	181	117	—	9

TABLE VI

PROPERTIES OF TIN(IV) TUNGSTOARSENATE HEATED AT DIFFERENT TEMPERATURES

Temperature (°C)	*Colour*	*Ion-exchange capacity (mequiv./g)*
50	White	1.18
150	White	1.24
300	White	0.51
500	Dirty white	0.31
800	Blackish brown	0.04

pH titration

Titrations were carried out by the method of Topp and Pepper[19]. The results are given in Fig. 1.

Column preparation

For separation studies, a 30 × 0.39 cm I.D. glass column was used and 2 g of tin(IV) tungstoarsenate were placed in the column with a glass-wool support. The column was washed with demineralized water and the amount of cation added to the column was less than 3% of the experimental ion-exchange capacity of the ion exchanger.

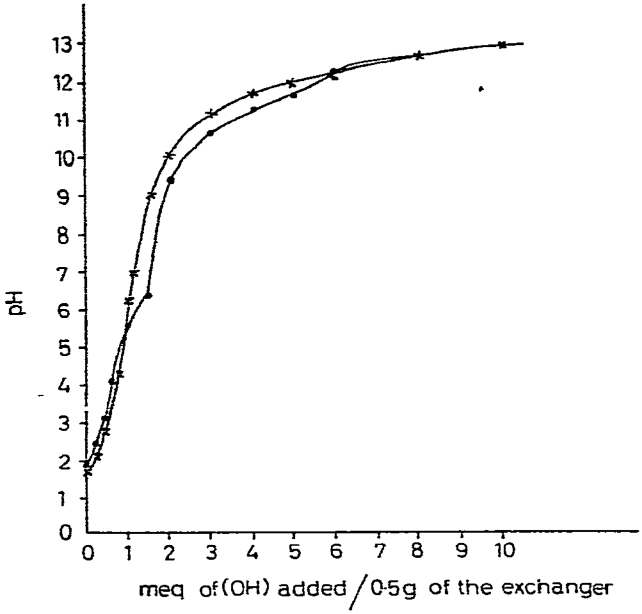

Fig. 1. Titration curves for tin(IV) tungstoarsenate. Titrant: ●—●, 0.1 *N* NaOH + 0.1 *N* NaCl; ×—×, 0.1 *N* KOH + 0.1 *N* KCl.

The flow-rate of the effluent was 8–9 drops/min. The cations were determined by EDTA titration and no interference due to dissolved anions was observed.

Separation

Quantitative separations of Mg^{2+} from Ba^{2+} and Cu^{2+} and of Cu^{2+} from Ni^{2+} were achieved on the tin(IV) tungstoarsenate column. The results are given in Table VII.

TABLE VII

SEPARATIONS ACHIEVED ON TIN(IV) TUNGSTOARSENATE COLUMN

Metal ion	*Eluent*	*Amount taken (μg)*	*Amount found (μg)*	*Error (%)*
Mg^{2+}	0.001 *M* HNO_3	1016	1013	−0.2
Ba^{2+}	1% NH_4NO_3 in 1.0 *M* HNO_3	1170	1200	+2.5
Mg^{2+}	0.001 *M* HNO_3	1016	1013	−0.2
Cu^{2+}	1% NH_4NO_3 in 1.0 *M* HNO_3	1008	1007	+0.1
Ni^{2+}	0.01 *M* HNO_3	1350	1360	+0.8
Cu^{2+}	1% NH_4NO_3 in 1.0 *M* HNO_3	1008	1010	+0.2

DISCUSSION

A comparison of tin(IV) tungstoarsenate and tin(IV) molybdoarsenate which were prepared under identical conditions shows that the chemical dissolution (Table

TABLE VIII

COMPARISON OF THE PREPARATION AND PROPERTIES OF (A) TIN(IV) TUNGSTOARSENATE WITH THOSE OF (B) TIN(IV) MOLYBDOARSENATE

Ion-exchange material	*Reagents*	*Mixing ratio*	*pH*	*Ion-exchange capacity (mequiv./g)*	*Sn:W:As ratio*
A	0.25 *M* tin(IV) chloride + 0.25 *M* sodium tungstate + 0.25 *M* sodium arsenate	2:1:1	1.0	1.06	12:5:2
B	0.25 *M* tin(IV) chloride + 0.25 *M* sodium molybdate + 0.25 *M* sodium arsenate	2:1:1	1.0	1.40	5:2:3

TABLE IX

COMPARISON OF PREPARATION AND PROPERTIES OF (A) TIN(IV) TUNGSTOARSENATE WITH THOSE OF (B) TIN(IV) TUNGSTATE AND (C) TIN(IV) ARSENATE

Ion-exchange material	*Reagents*	*Mixing ratio*	*pH*	*Ion-exchange capacity (mequiv./g)*
A	0.25 *M* tin(IV) chloride + 0.25 *M* sodium tungstate + 0.25 *M* sodium arsenate	2:1:1	1.0	1.06
B	0.25 *M* tin(IV) chloride + 0.25 *M* sodium tungstate	1:1	1.0	1.30
C	0.25 *M* tin(IV) chloride + 0.25 *M* sodium arsenate	1:1	1.0	1.40

TABLE X

COMPARISON OF K_d VALUES OF (A) TIN(IV) TUNGSTOARSENATE WITH THOSE OF (B) TIN(IV) TUNGSTATE AND (C) TIN(IV) ARSENATE

Cation	*A*	*B*	*C*
Mg^{2+}	52	530	66
Ca^{2+}	718	>22400	158
Sr^{2+}	1000	>21900	104
Ba^{2+}	1676	>21900	1276
Zn^{2+}	1260	2620	920
Cd^{2+}	435	6866	403
Cu^{2+}	11650	>23400	>23400
Ni^{2+}	92	>23900	292
Mn^{2+}	134	1500	>23900
Fe^{3+}	2460	265	>12700
Al^{3+}	1440	> 7600	> 7600
Y^{3+}	4160	>21206	>21200
La^{3+}	11100	258	851

II) and the ion-exchange capacity (Table VIII) of the latter are higher than those of the former. It has also been observed in our earlier work[18] that molybdate is the least stable and tungstate is the most stable.

The results in Table I show that the ion-exchange capacity is almost independent of pH (it varies from 1.06 to 1.12 when the pH varies from 1.0 to 6.8). This is a great advantage which had not been found with any other exchanger studied in this laboratory.

The results in Table II show that this exchanger is very stable in nitric acid, ammonium nitrate, formic acid, *n*-butanol, dimethyl sulphoxide and water. Therefore, the K_d values of metal ions were determined in nitric acid plus ammonium nitrate solution. On the basis of these K_d values, some interesting separations were obtained, *e.g.*, Mg^{2+}–Ba^{2+}, Mg^{2+}–Cu^{2+} and Ni^{2+}–Cu^{2+}; in addition, some other separations are possible, *e.g.*, Sr^{2+}–Y^{3+}, Al^{3+}–Fe^{3+}.

In order to study the effect of temperature, the K_d values of various cations were determined on samples heated to different temperatures. It was found that the ion exchanger has a high thermal stability up to 500°. Table IX shows that tin(IV) tungstoarsenate has a higher ion-exchange capacity than tin(IV) tungstate and tin(IV) arsenate. K_d values of cations on these exchangers are given in Table X.

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