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Studies on Stannic Selenoarsenate. II. Separation of Uranium from Numerous Metal Ions

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Abstract

Stannic selenoarsenate has been synthesized by adding 0.05 *M* sodium selenite and 0.05 *M* sodium arsenate to a 0.05 *M* solution of stannic chloride in a volume ratio of 1:1:1 at pH 1. A tentative structure has been proposed on the basis of chemical composition, pH titrations, and infrared and thermogravimetric analyses. Distribution coefficients of several metal ions have been studied in hydrochloric acid, citric acid, ammonium citrate–citric acid, and water–dioxane systems. The unusual adsorption behavior of uranium has been utilized for its quantitative separation from several metal ions.

INTRODUCTION

We have reported some of our results in an earlier paper regarding the synthesis, ion exchange properties and few applications of stannic selenoarsenate (*1*). The differential selectivity of metal ions and separation potential for pairs of metal ions has prompted us to explore the utility of the material in the field of separation science in detail. Keeping these views in mind, distribution coefficients of important metal ions have been determined in diverse solvent systems. As a result, a number of binary, ternary, and quaternary separations of metal ions have been achieved on columns of stannic selenoarsenate. Uranium has been selectively separated from a number of metal ions. Infrared and thermogravimetric studies have been performed to characterize the ion-exchange material. The following pages summarize our results in this direction.

EXPERIMENTAL

Reagents. Stannic chloride pentahydrate (Reachim), sodium selenite (B.D.H.), and sodium arsenate (E. Merck) were used for the synthesis. All other chemicals were of reagent grade.

Apparatus. Spectrophotometric studies were performed using a Bausch and Lomb Spectronic 20 colorimeter. Perkin Elmer model 137 spectrophotometer and Stanton thermobalance type H_4 were used for IR and thermogravimetric studies.

Synthesis. Stannic selenoarsenate was synthesized by adding an aqueous solution which was 0.05 *M* in sodium arsenate and 0.05 *M* in sodium selenite to a 0.05 *M* aqueous solution of stannic chloride at pH 1 as described in our earlier paper (*1*).

IR Studies. IR spectra of stannic selenoarsenate in the H^+ form, dried at different temperatures, were recorded using the KBr disk method.

Thermal Treatment. Thermogravimetric analysis of the material in the H^+ form was performed at a heating rate of 10°C/min. 0.3510 g of the exchanger was taken for this purpose (Fig. 1).

Distribution Coefficients. The distribution coefficients of several metal ions were determined in different solvent systems by the method described earlier (*1*). The results are reported in Table 1.

Quantitative Separations. 2.0 g of the exchanger in the H^+ form (150–200 mesh) was filled in the column (0.60 cm i.d.) with glass wool support. The mixture of the metal ions was poured into the column and allowed to be adsorbed. The metal ions adsorbed by the exchanger were then eluted with appropriate eluting agents. The flow rate of the effluent was maintained at 1.0 mL/min throughout the elution process. The metal ions in 10 mL fractions of the effluent were collected and determined by standard methods. The separation of metal ions achieved on the columns are reported in Table 2.

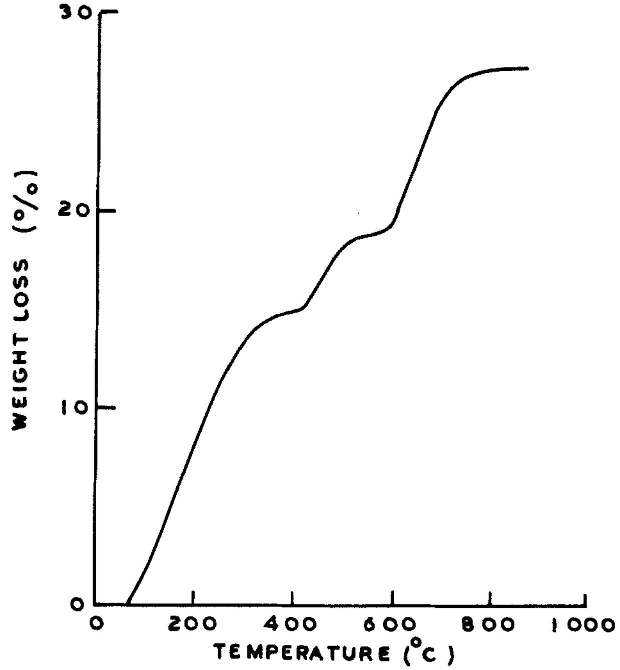

FIG. 1. Thermogram of stannic selenoarsenate in H^+ form.

DISCUSSION

A comparison of the IR spectra of stannic selenoarsenate in the H^+ form (dried at different temperatures) with stannic arsenate (*2*) and stannic selenite (*3*) shows three strong peaks in the 800–900, 1600–1650, and 3000–3600 cm^{-1} regions. The broad peak in the 3000–3600 cm^{-1} region with a maximum at 3500 cm^{-1} is characteristic of water of coordination and OH groups. The second sharp peak in the 1600–1650 cm^{-1} region with a maximum at 1620 cm^{-1} may be due to water of crystallization. The third peak in the 800–900 cm^{-1} region may be attributed to selenite and arsenate groups (*4*). However, the drying temperature has no effect on the nature of the spectra of stannic selenoarsenate up to 500°C.

The thermogram (Fig. 1) of stannic selenoarsenate when compared with stannic arsenate (5) a shows continuous loss in weight (7.5%) up to 200°C which may be due to the elimination of external water molecules. The loss in weight from 200 to 350°C may be assigned to the removal of water molecules by condensation of OH groups. This process is complete at

TABLE 1

Distribution Coefficients of Metal Ions on Stannic Selenoarsenate at Room Temperature

K_d (mL/g)

Metal/solvent	Water[a]	0.001 *M* HCl	0.01 *M* HCl	0.05 *M* HCl	Dioxane:water		0.001 *M* citric acid, pH = 3.1	0.01 *M* citric acid, pH = 2.6	0.05 *M* citric acid, pH = 2.2	0.01 *M* citric acid + 0.01 *M* ammonium citrate (1:1), pH = 3.1
					1:4	7:3				
Mg^{2+}	308	65	32	2	109	169	73	32	10	32,900
Ca^{2+}	308	182	72	2	300	336	60	1,100	3,900	23,900
Sr^{2+}	900	586	66	2	242	336	85	5,900	5,900	23,900
Ba^{2+}	500	14,900	400	20	300	500	150	2,400	3,650	14,900
Fe^{3+}	860	530	215	125	800	2,000	293	293	500	91
Al^{3+}	4,900	333	73	24	6,400	8,566	3,150	3,150	4,233	550
Co^{2+}	3,233	126	51	13	—	—	100	395	7,400	2,590
Ni^{2+}	1,386	105	38	350	5,875	5,875	291	114	38	95
Cu^{2+}	5,100	378	173	19	1,550	1,100	1,100	1,100	20	112
Zn^{2+}	3,630	121	43	1	32	21	228	120	70	143
Hg^{2+}	113	6,275	25,400	25,400	900	460	66	2,733	4,266	25,400
Pb^{2+}	473	25,900	25,900	25,900	480	2,788	333	4,233	6,400	25,900
Cd^{2+}	900	26,400	26,400	26,400	4,300	60	230	2,844	2,844	26,400
Zr^{4+}	1,011	70	308	192	920	1,600	76	466	4,150	1,175
Th^{4+}	5,100	489	253	136	4,316	4,316	1,000	2,844	2,844	2,108
UO_2^{2+}	—	3,900	566	253	1,100	900	1,400	900	823	1,400
Pr^{3+}	4,900	207	78	36	131	67	57,650	57,650	57,650	57,650
Nd^{3+}	10,700	214	125	50	117	80	33,650	33,650	33,650	33,650
Sm^{3+}	12,900	304	146	32	118	91	53,400	53,400	53,400	53,400
Gd^{3+}	—	290	113	30	109	75	58,400	58,400	58,400	58,400
Tb^{3+}	—	217	116	28	90	90	47,400	47,400	47,400	47,400
Yb^{3+}	—	715	102	21	169	79	46,900	46,900	46,900	46,900

[a] Data taken from earlier paper.

TABLE 2

Separations of Metal Ions on Stannic Selenoarsenate Columns at Room Temperature

Sample	Metal ions separated	Amount loaded (μg)	Amount found (μg)	Total elution volume (mL)	Eluent used
1	Ni^{2+}	211.3	220	60	0.05 *M* citric acid
	Mg^{2+}	320.7	320.2	70	0.01 *M* citric acid + 0.05 *M* HCl
	Cu^{2+}	609	673	80	0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
2	Ni^{2+}	211.03	215.5	60	0.05 *M* citric acid
	Mg^{2+}	320	320.5	70	0.01 *M* citric acid + 0.05 *M* HCl
	Hg^{2+}	1203	1111	60	0.05 *M* HCl
	UO_2^{2+}	2000	2030	40	0.5 *M* HCl
3	Ni^{2+}	211.3	219.6	60	0.05 *M* citric acid
	Mg^{2+}	320	320.2	70	0.01 *M* citric acid + 0.01 *M* HCl
	Pb^{2+}	2152.8	2082	50	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2000	40	0.5 *M* HCl
4	Ni^{2+}	211.3	220.2	60	0.05 *M* citric acid
	Ba^{2+}	823.8	905	40	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
5	Ni^{2+}	211.3	219.8	60	0.05 *M* citric acid
	Ca^{2+}	384	388	30	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
6	Ni^{2+}	211.3	220	60	0.05 *M* citric acid
	Zn^{2+}	1587	1640	60	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
7	Ni^{2+}	211.3	219	60	0.05 *M* citric acid
	Cd^{2+}	1775	1585	60	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
8	Ni^{2+}	211.3	219.6	60	0.05 *M* citric acid
	Mn^{2+}	638	620	30	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
9	Ni^{2+}	211.3	221.2	60	0.05 *M* citric acid
	Sr^{2+}	841	860	30	0.01 *M* citric acid + 0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
10	Th^{4+}	1531	1387	40	0.05 *M* citric acid
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
11	Al^{3+}	280	251	60	0.05 *M* HCl
	UO_2^{2+}	2000	2100	40	0.5 *M* HCl
12	VO^{2+}	510	494	80	0.05 *M* HCl
	UO_2^{2+}	3000	2600	40	0.5 *M* HCl

400°C, and the weight becomes constant in the 350 to 400°C region. A weight loss is again observed in the 400 to 550°C region which may be attributed to the loss of selenium by vaporization along with the removal of water molecules due to condensation of the second type of OH groups. The weight again becomes constant in the 550 to 600°C region indicating complete vaporization of selenium. The capacity of the material at 550°C almost coincides (0.50 meq/g) with that of stannic arsenate (0.52 meq/g dried at 600°C) (*2*). The further loss in weight above 600°C may be due to the loss of water molecules by condensation of the third type of OH groups along with the loss of arsenic by vaporization. A similar behavior was observed by Costantino in the case of stannic arsenate where arsenic is lost as arsenic pentaoxide (*5*).

On the basis of chemical composition, pH titration curves (reported in an earlier paper), and thermogravimetric and IR studies, the following formula is proposed for stannic selenoarsenate:

$$[SnO_2 \cdot H_2ASO_4 \cdot HSeO_3]_n \cdot 2nH_2O$$

if it is assumed that the weight loss (7.5%) up to 200°C is due to the removal of external water molecules. The number of water molecules per molecule of the exchanger corresponding to this weight loss is 2 as calculated by the method given by Alberti et al. (*6*). Further, if it is assumed that only one H^+ ion is exchanged at pH 6.5, then the theoretical ion-exchange capacity calculated from the above formula is found to be 2.0 meq/g, which is in good agreement with the observed values (1.8 meq/g from pH titration curves and 1.44 meq/g by column operation).

The values of distribution coefficients of metal ions in several solvents are shown in Table 1. K_d values in general are lower in 0.01 *M* HCl compared to those determined in 0.01 *M* HNO_3 (*1*). This effect is quite prominent in the case of rare earth metals. On comparing K_d values of rare earth metals in pure water and in dioxane–water, one can conclude that K_d values are significantly decreased in the mixed solvents. A comparison of K_d values in pure water and aqueous solutions of citric acid reveals that K_d values for alkaline earth metals and rare earth metals are generally higher in citric acid systems. However, K_d values for transition metals are found to be higher in pure water. It is also observed that with an increase in citric acid concentration, K_d values increase in general. It is interesting to observe the adsorption behavior of metal ions in 0.01 *M* citric acid and in a mixture of 0.01 *M* citric acid and 0.01 *M* ammonium citrate. The presence of ammonium citrate in the system increase the K_d values of the metal ions with the exception of Al^{3+}, Fe^{3+}, Cu^{2+}, and Th^{4+} which show the reverse behavior. However, the uptake of rare earth remains unaffected.

The utility of the material has been demonstrated by achieving a number of binary, ternary, and quaternary separations of some important metal ions as listed in Table 2. Stannic selenoarsenate shows exceptional behavior toward the UO_2^{2+} ion. The unusual selectivity for the UO_2^{2+} ion can be advantageously utilized for its selective separation from a large number of metal ions. The minimum amount of UO_2^{2+} ion that can be recovered from the stannic selenoarsenate column was found to be 200 μg. The amount of uranium in many uranium-containing ores varies from 0.002 to 0.013% with an average of 0.008%. This low amount of the uranium in ores can be determined using stannic selenoarsenate columns. The separation of uranium from aluminum and nickel can be used for the determination of uranium in nuclear fuel alloys; for example, uranium–aluminum alloy and uranium stainless steel alloys.

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