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Stability and Distribution Studies on Semicrystalline Tin(IV) Selenophosphate. Separation of Metal Ions

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Tin(IV) selenophosphate has been synthesized by mixing 0.05 mol dm^{-3} aqueous solutions of tin(IV) chloride, sodium selenite and sodium dihydrogenphosphate in 1:1:2 ratio at pH=0. The chemical and thermal stabilities are investigated. A tentative formula has been proposed for tin(IV) selenophosphate on the basis of chemical composition, pH titration, IR spectrum and thermogravimetric anslysis. The distribution coefficients of metal ions have been determined in DMF, DMSO, DMF-HNO_3, and DMSO-HNO_3 media. A number of binary, ternary, and quaternary separations of metal ions have been achieved on the columns of tin(IV) selenophosphate.

Studies on amorphous tin(IV) selenophosphate have been reported.[1] Crystalline products as an ion exchanger are being developed because of its many advantages over amorphous products.[2] Recently semicrystalline tin(IV) selenophosphate has been synthesized in our laboratory.[3] The present paper deals with the studies on semicrystalline tin(IV) selenophosphate beyond its synthesis.

Experimental

Reagents. Tin(IV) chloride (Baker Analyzed; USA), dihydrogenphosphate (BDH, England) and sodium dihydrogenphosphate (BDH, India) were used for the synthesis of tin(IV) selenophosphate. Other chemicals were of analytical reagent grade.

Apparatus. The spectrophotometry and pH measurements were performed using EC spectrophotometer GS 866D and Elico LI-10 pH-meter respectively. Perkin Elmer model 137 spectrophotometer and stanton thermobalance type H_4 were used for Infrared and thermogravimetric analyses.

Synthesis. Two samples of tin(IV) selenophosphate were prepared by earlier method.[3] The condition of synthesis and their few properties are shown in Table 1.

Ion Exchange Capacity. The hydrogen libration capacities of sample P_2 and R_3 with potassium ions were determined by column operations as reported earlier.[3]

Chemical Stability. The chemical stabilities of samples

Table 1. Synthesis and properties of tin(IV) selenophosphate[3]

Sample No	Condition of synthesis					Appearance of beads after drying at 40 °C	Ion-exchange capacity for K^+ ions meq (dry g)$^{-1}$	X-ray results
	$SnCl_4\cdot5H_2O$ mol dm^{-3}	Na_2SeO_3 mol dm^{-3}	$Na_2H_2PO_4$ mol dm^{-3}	Mixing ratio v/v/v	pH			
P_2[a)]	0.05	0.05	0.05	1:1:2	0	Brownish shiny	1.32	Amorphous
R_3[b)]	0.05	0.05	0.05	1:1:2	0	*ditto*	1.60	Semi crystalline

a) Sample P_2 is unrefluxed product. b) Sample R_3 is refluxed product in 2 mol dm^{-3} H_3PO_4+2 mol dm^{-3} selenious acid (1:1).

Table 2. Comparison of the chemical stability of various samples of tin(IV) selenophosphate

Solvent	SSP_2[1] (mg 50^{-1} cm^{-3})			P_2(unrefluxed) (mg 50^{-1} cm^{-3})			R_3(refluxed) (mg 50^{-1} cm^{-3})		
	Sn released	Se released	PO_4 released	Sn released	Se released	PO_4 released	Sn released	Se released	PO_4 released
H_2O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2 mol dm^{-3} HNO_3	2.2	1.02	0.0	3.6	3.8	0.0	2.5	0.2	0.0
2 mol dm^{-3} HCl	8.2	6.2	5.1	1.8	10.2	0.15	1.0	0.02	0.13
2 mol dm^{-3} H_2SO_4	0.0	0.22	0.1	0.9	1.0	0.0	0.78	0.01	0.0
4 mol dm^{-3} CH_3COOH	0.0	0.2	0.0	0.0	0.1	0.0	0.0	0.0	0.0
4 mol dm^{-3} HCOOH	0.92	0.10	0.0	0.0	0.2	0.0	0.0	0.02	0.0
4 mol dm^{-3} DMF	—	—	—	0.0	0.0	0.0	0.0	0.0	0.0
8 mol dm^{-3} DMF	—	—	—	0.02	0.1	0.01	0.0	0.0	0.0
4 mol dm^{-3} DMSO	—	—	—	0.0	0.0	0.0	0.0	0.0	0.0
8 mol dm^{-3} DMSO	—	—	—	0.01	0.01	0.0	0.0	0.0	0.0

P_2 and R_3 were determined in several solvents at room temperature. A 0.5 g of the material was equilibrated with 50 cm^3 of the solvent and kept for 24 h with intermittent shaking. Tin(IV), selenium and phosphate ion released in the solution were then determined by standard spectrophotometric methods.[4–6] The results are summarized in Table 2.

Composition. For determination of chemical composition of tin(IV) selenophosphate, 0.5 g of the sample was dissolved in hot concentrated hydrochloric acid. Tin(IV) and selenium were determined spectrophotometrically using hematoxylin and potassium iodide reagents.[4,5] Phosphate ion was determined titrimetrically.[7]

pH-Titrations. pH Titrations for NaCl–NaOH system have been performed on sample R_3. A 0.25 g of the exchanger in hydrogen form was equilibrated with 25 cm^3 of the solution at room temperature. pH-titration curve is shown in Fig. 1.

Thermal Treatment. Thermogravimetric analysis (Fig. 2) of the sample R_3 in hydrogen form was performed at a heating rate of 10 °C min^{-1}. To examine the effect of temperature on the ion-exchange capacity, the material (Sample R_3) was heated at different temperatures in a muffle furnace for 1 h. The results are reported in Table 3.

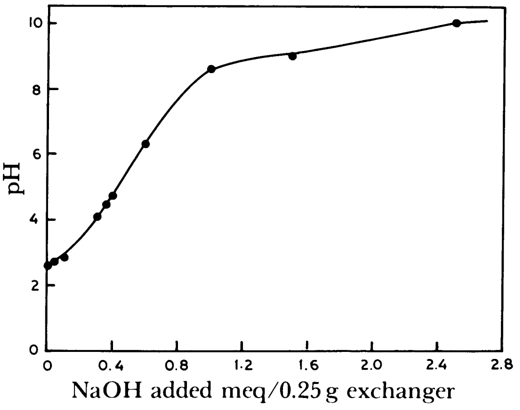

Fig. 1. pH Titration curve of tin(IV) selenophosphate.

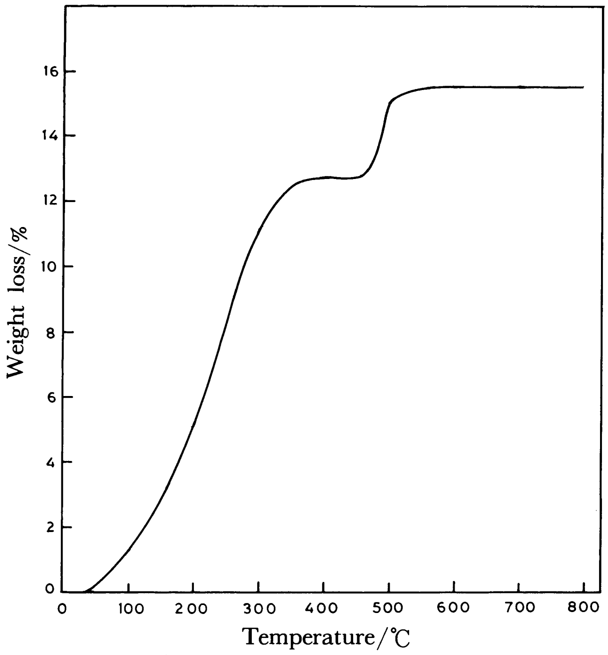

Fig. 2. Thermogram of tin(IV) selenophophate(in H$^+$ form).

Table 3. Effect of drying temperature on the ion-exchange capacity of different materials

Drying temperature	Ion-exchange Capacity (meq g^{-1})		
°C	Tin(IV) phosphate[12]	Tin(IV) Selenite[11]	Tin(IV) Seleno-phosphate
40	1.35	0.75	1.60
100	1.62	0.75	1.63
200	0.82	0.75	1.0
300	0.23	0.75	0.88
400	0.02	0.75	0.70
500	—	0.70	0.64
600	—	0.20	0.38
800	—	—	0.20

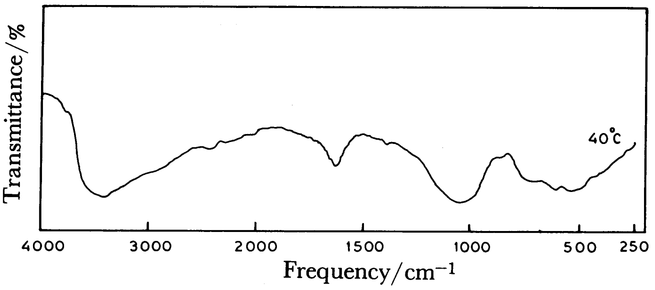

Fig. 3. Infrared spectrum of tin(IV) selenophosphate-(in H$^+$ form).

IR Analysis. The IR spectrum of sample R_3 dried at 40 °C was obtained by KBr disc method (Fig. 3).

Distribution Coefficients. Distribution coefficients (K_d) of some important metal ions were determined in *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and in mixtures of nitric acid–DMF and nitric acid–DMSO systems as described earlier.[9] The K_d value is defined as following,

$$K_d = \frac{I-F}{F \times W} \times 50$$

where, I is the volume of EDTA consumed by the original solution, F is the volume of EDTA consumed after equilibrium and W is the weight of ion-exchanger in g. The ionic strengths of various metal ion solutions lies between 0.0006 to 0.02. Four mol dm^{-3} DMSO, 4 mol dm^{-3} DMF, and 0.5 mol dm^{-3} HNO_3 were used for distribution studies. The results are given in Tables 4 and 5.

Quantitative Separations. The ion-exchange column was prepared using an earlier method.[10] A 2.0 g of the exchanger (50—100 mesh size) in hydrogen form was taken into a glass column of internal diameter 0.60 cm. Mixture of metal ions was then applied and allowed to pass through the column with a slow rate. The metal ions adsorbed on the exchanger were then eluted with suitable eluting reagent. The flow rate of the effluent was maintained 1 cm^3 min^{-1}, until the metal ions were completely eluted from the column. The metal ions in 10 cm^3 fractions of the effluent were collected and determined either titrimetrically or by standard photometric method.[8] Table 6 describes the separations of metal ions which have been actually achieved on tin(IV) selenophosphate columns.

Results and Discussion

The results of Table 2 show that the samples of

TABLE 4. DISTRIBUTION COEFFICIENTS FOR SOME CATIONS ON TIN(IV) SELENOPHOSPHATE IN *N*,*N*-DIMETHYLFORMAMIDE AND MIXED SOLVENT SYSTEMS

Metal ions	K_d/cm^3 g^{-1}						
	DMF	DMF:HNO_3 (8:2)	DMF:HNO_3 (6:4)	DMF:HNO_3 (4:6)	DMF:HNO_3 (2:8)	HNO_3	H_2O
Mn^{2+}	46±6	25±2	2±1	2±1	2±1	2±1	70±5
Ni^{2+}	28±2	33±5	6±1	2±1	2±1	2±1	1020±30
Cu^{2+}	133±5	101±5	75±2	25±2	2±1	2±1	940±20
VO^{2+}	133±5	250±5	176±5	138±5	43±2	2±1	3900±30
Pb^{2+}	72400±500	72400±500	72400±500	72400±500	72400±500	26±2	8500±50
UO_2^{2+}	500±15	500±15	300±10	200±5	33±2	6±1	9980±100
Fe^{3+}	54±2	145±5	66±5	54±5	44±2	29±2	900±20
Cr^{3+}	900±20	900±20	900±20	900±20	900±20	900±20	—
Th^{4+}	75±5	12±2	9±2	6±2	6±1	4±1	4900±35
Zr^{4+}	7±2	733±16	733±15	341±5	328±5	27±2	9900±100
Cr^{6+}	25±2	25±2	25±2	8±2	00	00	—

TABLE 5. DISTRIBUTION COEFFICIENTS FOR SOME CATIONS ON TIN(IV) SELENOPHOSPHATE IN DIMETHYL SULFOXIDE AND MIXED SOLVENT SYSTEMS

Metal ions	K_d/cm^3 g^{-1}				
	DMSO	DMSO:HNO_3 (8:2)	DMSO:HNO_3 (6:4)	DMSO:HNO_3 (4:6)	DMSO:HNO_3 (2:8)
Mn^{2+}	12±2	2±1	2±1	2±1	2±1
Ni^{2+}	17±2	4±1	3±1	2±1	2±1
Cu^{2+}	69±2	10±2	5±2	5±2	5±2
VO^{2+}	69±2	25±2	12±2	9±2	5±2
Pb^{2+}	79900±500	79900±500	79900±500	79900±500	79900±500
UO_2^{2+}	33±2	33±2	60±2	77±2	77±5
Fe^{3+}	16±2	145±5	116±5	22±2	17±2
Cr^{3+}	650±5	650±5	650±5	650±5	650±5
Th^{4+}	7±2	31±2	21±2	16±2	12±2
Zr^{4+}	47±2	40±2	36±2	29±2	23±2

TABLE 6. SEPARATIONS OF METAL IONS ACHIEVED ON THE COLUMNS OF TIN(IV) SELENOPHOSPHATE

S.No.	Separation achieved	Amount loaded	Amount found	Total elution volume	Eluent used[a]
		μg	μg	cm^3	
1	Cr^{6+}	40	32	30	Water
	Cr^{3+}	500	440	30	1 mol dm^{-3} HNO_3
2	Ni^{2+}	1056	575	70	B
	Fe^{3+}	669	558	60	1 mol dm^{-3} HNO_3
3	Mn^{2+}	682	748	50	A
	Fe^{3+}	669	558	60	1 mol dm^{-3} HNO_3
4	Cr^{6+}	40	38	30	Water
	Cu^{2+}	305	295	40	0.1 mol dm^{-3} HNO_3
	Fe^{3+}	335	357	60	1 mol dm^{-3} HNO_3
5	Mn^{2+}	682	792	50	A
	Cu^{2+}	292	213	40	0.1 mol dm^{-3} HNO_3
	Fe^{3+}	669	570	60	1 mol dm^{-3} HNO_3
6	Ni^{2+}	1056	567	70	B
	Cu^{2+}	292	302	40	0.1 mol dm^{-3} HNO_3
	Fe^{3+}	669	560	60	1 mol dm^{-3} HNO_3
7	Cr^{6+}	40	38	30	Water
	Mn^{2+}	330	294	50	A
	Cu^{2+}	292	343	40	0.1 mol dm^{-3} HNO_3
	Fe^{3+}	669	569	60	1 mol dm^{-3} HNO_3
8	Cr^{6+}	40	38	30	Water
	Ni^{2+}	528	340	70	B
	Cu^{2+}	292	352	40	0.1 mol dm^{-3} HNO_3
	Fe^{3+}	335	312	60	1 mol dm^{-3} HNO_3

A=4 mol dm^{-3} DMF+0.5 mol dm^{-3} HNO_3 (8:2). B=4 mol dm^{-3} DMF+0.5 mol dm^{-3} HNO_3 (2:8).

tin(IV) selenophosphate prepared by these methods are more chemically stable than those prepared earlier.[1] The material becomes more stable when it was refluxed in a mixture of phosphoric acid and selenious acid (sample R_3). Tin (IV) selenophosphate is not affected at all by DMSO and DMF. The pH titration curve however shows bifunctional behaviour of tin(IV) selenophosphate.

A comparison of the ion-exchange capacities of tin(IV) selenophosphate, tin(IV) selenite[11] and tin(IV) phosphate[12] after drying the material at different temperatures are shown in Table 3. Tin(IV) selenophosphate appears to be thermally more stable than tin(IV) phosphate and tin(IV) selenite as it retains reasonable capacity (0.38 meq g^{-1}) upto 600 °C.

The molar composition of tin(IV) selenophosphate shows that tin(IV), selenium and phosphate ion are present in the ratio of 4:1:6.

The thermogram of tin(IV) selenophosphate (Fig. 2) in H^+ form shows continuous loss in weight upto 350 °C. The weight loss upto 200 °C (5%) may be due to the loss of external water molecules. The weight loss from 200 to 350 °C may be due to the loss of water molecules by condensation of OH groups and the conversion of phosphate into pyrophosphate. This process is completed at 450 °C and the ion-exchange capacity of the material coincides with the ion-exchange capacity of tin(IV) selenite (0.70 meq g^{-1}) dried at 500 °C (Table 3). The ion exchange capacity of tin(IV) phosphate is completely lost at this temperature (Table 3). The loss in weight is again observed at about 450 °C. This loss may be referred to the loss of water molecules by condensation of more OH groups and the ion-exchange capacity gradually decreases. After 600 °C the weigt becomes constant due to the formation of oxides and the ion-exchange capacity drops to a negligible value at 800 °C.

IR spectrum of sample R_3 (Fig. 3) in H^+ form shows three strong peaks in the regions of 3500—3000 cm^{-1}, 1700—1500 cm^{-1}, and 1100—900 cm^{-1}. The broad peak in the region 3500—3000 cm^{-1} may be due to presence of water molecules and OH groups. A sharp peak in the region 1700—1500 cm^{-1} with a maximum at 1650 cm^{-1} is characteristics of interstitial water molecules. A third broad peak in the region 1100—900 cm^{-1} may be attributed to HPO_4^{2-} ion.

On the basis of the ion-exchange capacity, pH titration curve, chemical composition and thermogravimetric analysis, the following tentative formula for the tin(IV) selenophosphate may be proposed.

$$[(SnO)_4(OH)(HSeO_3)(H_2PO_4)_6]_n \cdot 4nH_2O \qquad (1)$$

If it is assumed that the weight loss (5%) upto 200 °C is due to the removal of external water molecules then the number of water molecules per molecule of exchanger, calculated from the formula given by Alberti[13] are 4. If two hydrogen ions are exchanged at pH 6.5, the ion-exchange capacity calculated from the above formula is 1.48 meq g^{-1} which is in good agreement with the experimental value (1.60 meq g^{-1}). The weight in the temperature range 350—450 °C remains constant (Fig. 2) which is supposed to be due to the conversion of hydrogen phosphate to pyrophosphate. The above formula then can be modified to

$$(SnO)_4(HSeO_3)(P_2O_7)_3 \qquad (2)$$

The transformation in this temperature range corresponds to 13.4% loss in weight of the sample. This theoretical value is very close to the weight loss calculated from TGA curve (13% at 400 °C). The ion-exchange capacity therefore at 400 °C should only be due to $HSeO_3$ group of the material. The ion-exchange capacity calculated from formula 2 is 0.80 meq g^{-1} which resembles the experimental ion-exchange capacity (0.70 meq g^{-1} at 400 °C).

The potentiality of tin(IV) selenophosphate has been further investigated for the separation of metal ions. The distribution coefficients (K_d) for some important metal ions have been determined in nitric acid and in some more prospective solvents such as DMF, DMSO, DMF–HNO_3, and DMSO–HNO_3 media. It has been observed that these organic solvents have pronounced effect on the adsorption ability of the material. It is observed that the adsorption of almost all metal ions is very low in DMF and DMSO as compared to water. The K_d values increases as the nitric acid concentration increases in the mixture of DMF and DMSO (Tables 4 and 5). However this effect is more pronounced in the cases of Ni^{2+}, Cu^{2+}, and Mn^{2+}. K_d values become almost negligible with the increased concentration of nitric acid in the mixture. However Pb^{2+} has been found to behave in different manner. The metal ion is strongly adsorbed on tin(IV) selenophosphate in DMSO–HNO_3 and DMF–HNO_3 mixtures. In 0.5 mol dm^{-3} HNO_3 solution the K_d value drops to a negligible value. The peculiar behaviour of Pb^{2+} permits the selective separations of Pb^{2+} from other metal ions in a mixture. A very unique feature which has been noticed regarding this exchanger is that the adsorptions of Cr^{VI} is very low in almost all these media as compared to Cr^{III}. The differential uptake of metal ions in these solvents have been utilized for the separations of some important and valuable metal ions. A number of binary, ternary and quaternary separations have been achieved on the columns of tin(IV) selenophosphate (Table 6).

Tin(IV) selenophosphate may be utilized in the determination of Cr^{VI}/Cr^{III} ratio in sea water which is one of the most important subjects in chemical oceanography.[14] The separations of chromium, nickel, manganese, copper, and iron from one another on columns of tin(IV) selenophosphate suggest the possibility of determination and separation of metal ions in steel, alloys, ores, rocks, and related materials.

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