On the Synthesis of Crystalline and Semicrystalline Tin(IV) Selenophosphate

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Synopsis. Samples of tin(IV) selenophosphate have been synthesized by mixing 0.05 M (1 M=1 mol dm^{-3}) aqueous solutions of tin(IV) chloride, sodium selenite, and sodium dihydrogenphoshate in different volume ratios and at different pH. A crystalline and a semicrystalline products are obtained when the precipitates are refluxed. Ion-exchange behavior of refluxed product is compared with the unrefluxed one.

Despite a large amount of work done on synthetic inorganic ion-exchangers only a little effort has been made to develop crystalline materials. In order to understand the mechanism of ion-exchange phenomenon in a systematic manner the crystallinity of the product is very important.[1] It is with this view in mind we have made an effort to synthesize tin(IV) selenophosphate in different sets of conditions. This report summarizes our findings in this direction.

Experimental

Reagents. Tin(IV) chloride (Baker Analyzed; U. S. A.), sodium selenite (BDH, England), and sodium dihydrogenphosphate (BDH, India) were used for the synthesis of tin(IV) selenophosphate. All other chemicals were of AnalarR grade.

Apparatus. The X-ray diffractometer PW 1140/90 was used for X-ray study.

Table 1. Synthesis and Properties of Tin(IV) Selenophosphate

Sample No.[a]	Conditions of synthesis					Appearance of bead after drying at 40°C	Ion-exchange capacity for K^+ ions (meq/dry g)	X-Ray Results
	$SnCl_4 \cdot 5H_2O$ M	Na_2SeO_3 M	NaH_2PO_4 M	Mixing ratio (v/v/v)	pH			
P_1	0.05	0.05	0.05	1:1:2	−ve	White, shiny	1.55	Amorphous
R_1	0.05	0.05	0.05	1:1:2	−ve	White, shiny	1.60	Amorphous
P_2	0.05	0.05	0.05	1:1:2	0.0	Brownish, shiny	1.32	Amorphous
P_3	0.05	0.05	0.05	1:1:1	0.0	Light brown, shiny	1.35	Amorphous
P_4	0.05	0.05	0.05	3:1:2	0.0	White opaque	1.10	Amorphous
R_2	0.05	0.05	0.05	1:1:2	0.0	White, shiny	1.21	Amorphous
R_3	0.05	0.05	0.05	1:1:2	0.0	Brownish, shiny	1.60	Semicrystalline
R_4	0.05	0.05	0.05	1:1:2	0.0	White, fine powder	—	Crystalline
P_5	0.05	0.05	0.05	1:1:2	1.0	Brownish, shiny	1.21	Amorphous
P_6	0.05	0.05	0.05	1:1:2	2.0	Brownish, shiny	1.07	Amorphous
P_7	0.05	0.05	0.05	1:1:2	3.0	Brownish, shiny	0.72	Amorphous

a) R_1=Refluxed in concd HNO_3 for 6 h; R_2=Refluxed in 2M H_3PO_4 for 6 h; R_3=Refluxed in 2M H_3PO_4+2M selenious acid (1:1); R_4=Refluxed in 2M selenious acid.

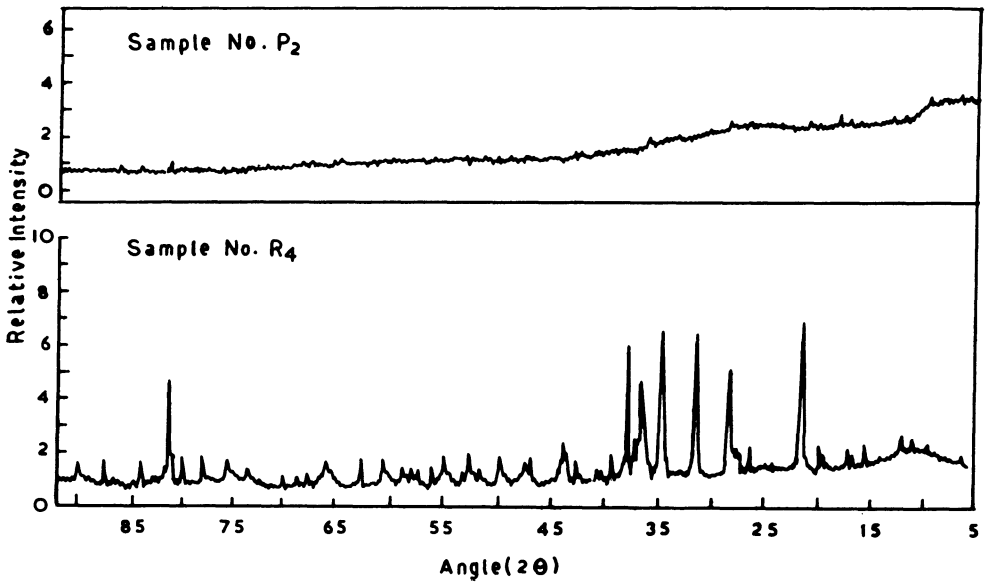

Fig. 1. X-Ray diffraction pattern of tin(IV) selenophosphate.

Table 2. Ion-Exchange Capacity (pH=6) of Tin(IV) Selenophosphates with Different Metal Ions at 25±1 °C

Ion	Salt used	Capacity (meq/g)	
		P_2 (Unrefluxed)	R_3 (Refluxed)
NH_4^+	NH_4Cl	0.87	1.1
Li^+	LiCl	0.83	0.84
Na^+	NaCl	0.91	0.65
K^+	KCl	1.32	1.60
Ca^{2+}	$Ca(NO_3)_2$	2.39	2.66
Sr^{2+}	$Sr(NO_3)_2$	0.97	1.36
Ba^{2+}	$Ba(NO_3)_2$	1.23	1.75

Table 3. X-Ray Data of Tin(IV) Selenophosphate (sample R_4)

θ/degree	d/Å	Intensity of the peak[a]
10.7	5.2136	S
13.1	4.2708	S
14.1	3.9734	S
15.7	3.5772	S
17.3	3.2551	S
18.3	3.0828	S
18.55	3.0427	M
19.0	2.9732	S
21.9	2.5952	M
23.75	2.4034	M
24.8	2.3077	M
26.25	2.1886	M
27.5	2.0963	M
30.3	1.9186	M
33.0	1.7773	M
37.6	1.5863	M
40.6	1.4874	M

a) S: sharp, M: medium.

Synthesis. Samples of tin(IV) selenophosphate were prepared by mixing 0.05M sodium dihydrogenphosphate and 0.05M sodium selenite solutions to 0.05M solution of tin(IV) chloride as described earlier.[2] The pH of mixture was adjusted by adding dilute sodium hydroxide or dilute hydrochloric acid solutions. The precipitate so formed was allowed to settle down for 24 h with mother liquor and then filtered, washed several times with distilled water, and then dried at 40 °C. The precipitate as obtained above was also refluxed for 6 h in various solutions. The refluxed precipitates (R_1, R_2, R_3, and R_4) were then filtered, washed with distilled water, dried at 40 °C, and converted into H^+ form by earlier method.[2] Conditions of synthesis, ion-exchange capacities and appearance of samples of tin(IV) selenophosphate are summarized in Table 1.

Ion-Exchange Capacity. The hydrogen-ion-liberation capacities of samples P_2 and R_3 with different metal ions were determined by column operations as reported earlier.[3] The results are given in Table 2.

X-Ray Diffraction Analysis. Manganese filtered Fe $K\alpha$ radiation was used for X-ray diffraction analyses of all samples. The results are reported in Table 3 and Fig. 1.

Discussion

It is clear from Table 1 that in general the ion-exchange capacity decreases by increasing the pH of solution at constant mixing ratio. It is also observed that there is no significant change in ion-exchange capacity of the material when the precipitate is refluxed for 6 h either in 2M nitric acid or in 2M phosphoric acid. The exchange capacity of tin(IV) selenophosphate (sample R_3) increases when the precipitate of sample P_2 is refluxed in a mixture of selenious acid and phosphoric acid. However, the product (sample R_4) becomes unstable when the precipitate is refluxed with selenious acid alone.

On comparing ion-exchange properties of refluxed product with unrefluxed material it is noted that the former has higher capacities with different metal ions (Table 2). The X-ray analysis of tin(IV) selenophosphate samples indicates that all samples are amorphous except samples R_4 and R_3 which appear to crystalline and semicrystalline. The diffraction pattern of R_4 is more pronounced and well defined (Fig. 1). It is interesting to note that amorphous tin(IV) selenophosphate (sample P_2) becomes crystalline when the precipitate is refluxed in 2M selenious acid for 6 h. The d-values of crystalline product of tin(IV) selenophosphate were calculated by Bragg's equation and are given in Table 3.

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