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Studies on New Inorganic Ion Exchangers Containing Phosphorus—Preparations and Properties of Stannic Selenopyrophosphate

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Abstract

A new inorganic ion exchanger, stannic selenopyrophosphate, was synthesized. Its chemical composition, ion-exchange capacity, thermal and chemical stabilities, pH titration curve, and distribution coefficients of 36 metal ions were studied systematically. It is a stable polyfunctional cation exchanger with a high ion-exchange capacity (2.29 meq/g for K^+). It has a high affinity for Ag(I), Pb(II), Ba(II), Bi(III), and Zr(IV). Its structure was studied by IR, Raman, and x-ray diffraction analyses. A chemical formula ($[(15SnO \cdot 8OH) \cdot 10H_2P_2O_7 \cdot 2HSeO_3]_n \cdot 5nH_2O$) for stannic selenopyrophosphate is proposed.

INTRODUCTION

Nabi et al. (*1*) reported an inorganic ion exchanger, stannic selenophosphate, which was more chemically and thermally stable than either stannic phosphate or stannic selenite. Our study (*2*) showed that stannic pyrophosphate had a much greater apparent ion-exchange capacity than stannic phosphate. By substituting the phosphate group in stannic selenophosphate with a pyrophosphate group, we expected to obtain a new ion exchanger which had both a large ion-exchange capacity and was chemically and thermally stable. On this basis, a new inorganic ion exchanger, stannic selenopyrophosphate, was synthesized. Studies on its physical and chemical properties showed that it is a highly stable amorphous polyfunctional cation exchanger with large ion-exchange capacity. It is very stable even in 4 *M* HNO_3 solution. The total weight loss at 900°C is only 17%. The ion-exchange capacity of stannic selenopyrophosphate is 40% greater than that of stannic selenophosphate and 30–200% greater than that of other heteropoly acidic salts. It has a high affinity for those ions with their bare radii near 1.25 Å such as Ag(I), Pb(II), and Ba(II). We will report the application of stannic selenopyrophosphate separately.

EXPERIMENTAL

1. Instruments and Reagents

Shimadzu DT-30B thermal analyzer, Shimadzu UV-3000 spectrometer, Nicolet 170-SX FTIR spectrometer, Shimadzu XD-3A x-ray diffraction spectrometer, Jobin U-1000 Raman spectrometer, WFD-Y2 atomic absorption spectrometer, and Raits 25 pH meter were used in the experiments.

Chemical reagents used were $SnCl_4 \cdot 5H_2O$, $K_4P_2O_7$, Na_2SeO_3, EDTA, and Arsenoazo III. They were all analytical reagent grade. Two sets of standard metal ion solutions (1 mg/mL and 10 μg/mL) were prepared by diluting appropriate metal ion solution in 0.1 *M* HNO_3.

2. Synthesis of the Exchanger

Stannic selenopyrophosphate was prepared by mixing solutions of stannic tetrachloride, potassium pyrophosphate, and sodium selenite in a volume ratio of 1:1:1 at 10–15°C. The concentration of all the solutions was 0.5 *M*. A solution of $K_4P_2O_7$ and Na_2SeO_3 was mixed first and then added to the $SnCl_4$ solution. The pH of the mixture was adjusted to 1.0 by adding a solution of 3 *M* HNO_3. Solid NaCl (about 0.2 *M*) was added to the mixture to help precipitate the stannic selenopyrophosphate. After keeping the gelatinous slurry at room temperature for 12 h, it was filtered under suction and washed to pH 3 with distilled water to remove the excess reagents present. It was dried at 40°C, then placed into water to crack into small granules. The exchanger was converted to the H^+ form by passing a 1 *M* HNO_3 solution through the exchanger in a column process (about 20 mL HNO_3/g exchanger). The exchanger was finally washed with distilled water until the pH value of the effluent was 5. The resulting exchanger was again dried at 40°C and meshed (100–200 mesh) for future use.

RESULTS AND DISCUSSION

1. Preparation Conditions and Chemical Compositions

The procedure for synthesizing stannic selenopyrophosphate (SSPP) was described in the above experimental section. The purpose of adding sodium chloride was to accelerate the precipitation of SSPP. The effect of different mixing ratios on the ion-exchange capacity (IEC) of stannic selenopyrophosphate is shown in Table 1. Since $SSPP_I$ was produced with both a high chemical yield and a high IEC value, it was selected for further studies.

The standard gravimetric, iodometric titration, and ammonium molybdate methods (*19*) were used to determine the stochiometric ratios of selenium, tin, and phosphorus. The results are presented in Table 2. It is apparent that the higher the P_2/Sn ratio, the higher the IEC value. Experiments showed there was no precipitation when the $K_4P_2O_7/SnCl_4$ ratio was larger than 2.

2. Ion-Exchange Capacity

The ion-exchange capacities of stannic selenopyrophosphate for alkali and alkaline earth metal ions were determined by column processes. One gram of the H^+ form exchanger (100–200 mesh) was packed into a column. It was washed with a 0.1 *M* solution of the corresponding metal ion listed in Table 3. The effluent was titrated with 0.1 *N* NaOH solution to determine the milliequivalents of H^+ ions released from the exchange process. The results are shown in Table 3.

The IEC value is one of the important parameters in assessing the properties of an inorganic ion exchanger. Table 4 lists the K^+ IEC values of stannic selenopyrophosphate and other reported heteropoly acidic salt-type inorganic ion exchangers. Stannic selenopyrophosphate has the highest IEC value. It is 40% higher than that of stannic selenophosphate and 30–200% higher than that of the others.

In a previous paper (*2*) we proposed a relationship between IEC values and the radii of metal ions:

TABLE 1
Preparation Conditions and IEC Values of SSPP

	Preparation conditions					IEC
Sample	$SnCl_4 \cdot 5H_2O$ (*M*)	Na_2SeO_3 (*M*)	$K_4P_2O_7 \cdot 3H_2O$ (*M*)		pH	(K^+, meq/g)
$SSPP_1$	0.5	0.5	0.5	1:1:1	1.0	2.29
$SSPP_2$	0.5	0.5	0.5	1:2:1	1.0	2.31
$SSPP_3$	0.5	0.5	0.5	2:2:1	1.0	1.70
$SSPP_4$	0.5	0.5	0.5	1:1:2	1.0	—[a]

[a] No precipitation.

TABLE 2
Chemical Compositions of SSPP

Sample	Sn (mmol/g)	Se (mmol/g)	P_2 (mmol/g)[a]	Sn:Se:P_2 (molar ratio)[a]
$SSPP_1$	3.23	0.43	2.13	1.52:0.20:1.00
$SSPP_2$	3.18	0.32	2.00	1.59:0.16:1.00
$SSPP_3$	4.67	1.13	1.36	3.43:0.83:1.00

[a] P_2 represents the pyrophosphate group.

$$\text{IEC (meq/g)} = a \log (r^2/|r_0 - r|) + b \qquad (1)$$

where a, b, and r_0 are constant for the exchanger, and r is the radius of a metal ion. The r_0 value is 1.0 Å for stannic pyrophosphate (SSP). We think that r_0 is a parameter which is connected to the selectivity of the exchanger, because SPP has a high affinity for ions with radii near 1.0 Å such as rare earth metal ions. The application of Eq. (1) to stannic selenopyrophosphate gives a r_0 value of 1.25 Å. Figure 1 shows a plot of log $(r^2/|r_0 - r|)$ vs IEC values for alkali (Curve 1) and alkaline earth (Curve 2) metal ions. The slope (a) of Curve 2 is twice that of Curve 1. This implies that the IEC value is also dependent on the charge (Z) of the metal ion. Assuming a and b are linear functions of Z, we fit the experimental IEC values listed in Table 3 to the following equation:

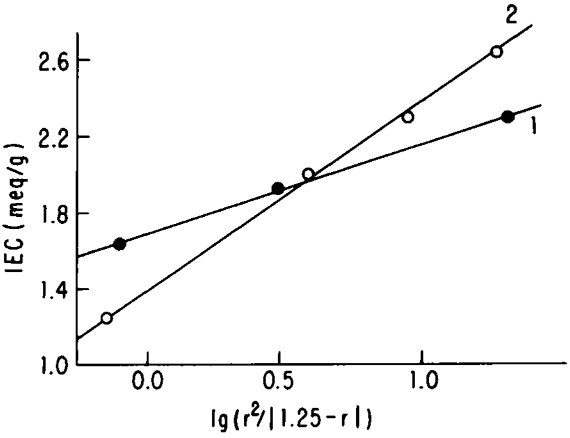

FIG. 1. A plot of IEC values vs log $(r^2/|1.25 - r|)$. 1: Alkali metal ions. 2: Alkaline earth metal ions.

TABLE 3
Experimental and Predicted IEC Values of Alkali and Alkaline Earth Metal Ions on SSPP

Metal Ion		Li^+	Na^+	K^+	Rb^+	Cs^+	Fr^+	Be^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
r (Å)		0.68	0.97	1.33	1.47	1.67	1.80	0.35	0.66	0.99	1.12	1.34	1.43
IEC (meq/g):	Experimental	1.67	1.95	2.29	—	—	—	—	1.24	2.01	2.22	2.60	—
	Predicted	1.64	1.92	2.30	1.88	1.84	1.83	1.01	1.24	1.91	2.29	2.61	1.78

TABLE 4

Comparison of the IEC (K^+) Values of Heteropoly Acidic-Salt-Type Exchangers[a]

Exchanger	SSPP	SSP	SAP	SVP	SBP	SIP	SBS	SBW	SBM	SVW	SBA
IEC (meq/g)	2.29	1.63	1.75	1.70	1.10	1.60	0.55	1.30	1.12	1.00	0.99
Exchanger	SWA	SMA	SSA	CAP	ZAP	ZIP	ZSA	TWP	FIP	CePS	SS
IEC (meq/g)	1.12	1.20	1.44	0.74	0.94	1.41	1.30	1.20	1.03	0.78	0.75

[a] SSP = stannic selenophosphate (*1*)
SAP = stannic arsenophosphate (*3*)
SVP = stannic phosphovanadate (*4–6*)
SBP = stannic borophosphate (*1*)
SIP = stannic phophoiodate (*7*)
SBW = stannic borosulfate (*1*)
SBM = stannic boromolybdate (*1*)
SVW = stannic vanadotunstate (*8*)
SBA = stannic boroarsenate (*1*)
SWA = stannic arsenotungstate (*9*)
SSA = stannic selenoarsenate (*7*)
CAP = Cr(III) arsenophosphate (*3*)
ZAP = zirconium arsenophosphate (*10, 11*)
ZIP = zirconium phosphoiodate (*7*)
ZSA = zirconium arsenosilicate (*10*)
TWP = titanium phosphotungstate (*12*)
FIP = Fe(III) phosphoiodate (*7*)
CePS = cerous phosphosulfate (*13*)
SS = stannic selenite (*7*)

$$\text{IEC (meq/g)} = AZ \log (r^2/|r_0 - r|) + BZ + C \qquad (2)$$

When $A = 0.2$, $B = -0.32$, and $C = 2.00$, the regression coefficient is 0.99. By using Eq. (2), we predicted the IEC values of other unmeasured alkali and alkaline earth metal ions (Table 3). Stannic selenopyrophosphate should have its highest selectivity for ions whose radii are near 1.25 Å.

3. Measurements of the Distribution Coefficients of Metal Ions

The distribution coefficients of 36 metal ions were measured by the static method used by Hamagrechi et al. (*14*) (Table 5). In accordance with our prediction, the results showed that stannic selenopyrophosphate has a high affinity for those ions with their bare radii near 1.25 Å [such as Ag(I), Pb(II), and Ba(II)]. The large distribution coefficients of Bi(III) and Zr(IV) may be due to the special properties of their aqueous ions.

4. pH Titration Curve

The titration curve of stannic selenopyrophosphate was carried out by the method described by Topp and Pepper (*15*). Figure 2 is a comparison of the titration curves of SSPP, SPP, and SS. SSPP has three breaks, showing it is a polyfunctional ion exchanger. It has a sharper and wider pH change at the first break compared to SPP and SS. Thus SSPP is a strong acidic cation exchanger which may have better ion-exchange kinetic properties than SPP or SS.

5. Thermal and Chemical Stabilities

The thermogravity curve (TGA) of SSPP is shown in Fig. 3. Compared with SPP and SP, it has the smallest weight loss in the temperature region from 0 to 900°C. The presence of the selenite group improves its thermal stability, as can be seen from Table 6. SSPP has a fairly high IEC value up to 300°C.

To measure the solubility of SSPP, 0.5 g of H^+-form SSPP was placed into 50 mL flasks, each containing one of the various solvents listed in Table 7. The undissolved exchanger was filtered after being placed on a vibrator for 24 h at 25 ± 2°C. The dissolved tin, selenium, and

TABLE 5
Distribution Coefficients of Metal Ions on SSPP (all in HNO_3 solution)

Metal ion		Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mn^{2+}	Co^{2+}	
Radius (Å)		0.66	0.99	1.12	1.34	0.80	0.72	
K_d (mL/g)	0.01 *N*	25.0	198	393	1,495	40.0	28.8	
	0.1 *N*	13.5	14.4	15.6	62.8	3.2	2.3	
	1.0 *N*	9.7	1.8	2.8	2.5	0.3	0.2	
Metal ion		Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}	
Radius (Å)		0.69	0.72	0.74	0.97	1.20	1.10	
K_d (mL/g)	0.01 *N*	13.8	625	450	688	CA[a]	17.1	
	0.1 *N*	5.7	21.4	12.3	35.4	1,450	10.8	
	1.0 *N*	3.1	0.7	0.5	0.7	23.9	0.0	
Metal ion		Fe^{3+}	Al^{3+}	Cr^{3+}	In^{3+}	Bi^{3+}	Th^{4+}	
Radius (Å)		0.64	0.51	0.62	0.81	0.96	1.02	
K_d (mL/g)	0.01 *N*	37.4	7.6	6.1	11.6	CA[a]	120	
	0.1 *N*	16.9	6.0	3.7	10.8	6,800	12.3	
	1.0 *N*	8.6	5.3	1.2	4.4	15.0	8.8	
Metal ion		UO_2^{2+}	Zr^{4+}	Sc^{3+}	Y^{3+}	La^{3+}	Ce^{3+}	
Radius (Å)		—	0.79	0.73	0.89	1.02	1.03	
K_d (mL/g)	0.01 *N*	9.9	1,386	6.3	20.6	92.9	64.0	
	0.1 *N*	6.5	84.0	5.8	13.2	17.4	15.1	
	1.0 *N*	4.4	41.0	5.6	3.9	0.9	0.9	
Metal ion		Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	
Radius (Å)		1.01	1.00	0.96	0.95	0.94	0.92	
K_d (mL/g)	0.01 *N*	28.6	53.0	26.7	28.3	45.2	27.6	
	0.1 *N*	9.6	16.3	10.7	10.0	20.0	11.4	
	1.0 *N*	0.8	0.9	0.9	0.8	0.0	0.3	
Metal ion		Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Ag^{+}
Radius (Å)		0.91	0.89	0.88	0.87	0.86	0.85	1.26
K_d (mL/g)	0.01 *N*	26.3	25.4	24.6	32.00	2.1	48.2	24,033
	0.1 *N*	9.9	9.2	8.8	12.1	8.3	10.6	1,074
	1.0 *N*	0.7	0.7	0.6	0.7	0.4	0.8	243

[a] Complete adsorption.

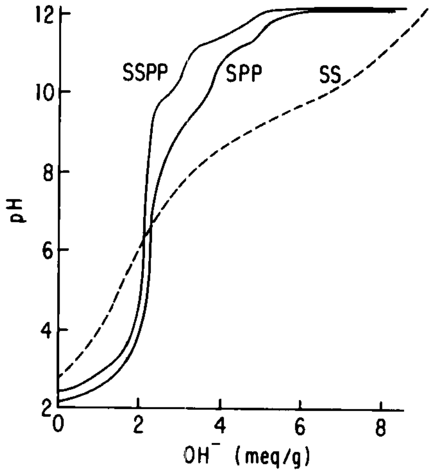

FIG. 2. pH titration curves. SSPP: stannic selenopyrophosphate. SPP: stannic pyrophophate. SS: stannic selenite.

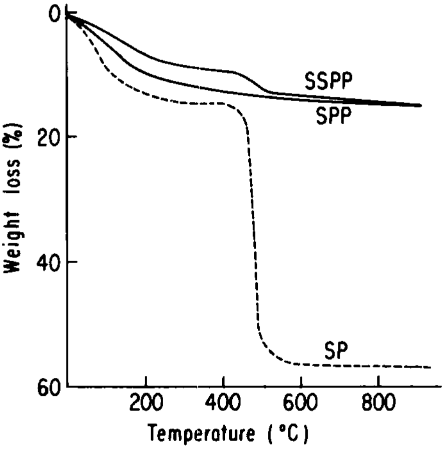

FIG. 3. TGA curves. SP: stannic phophate.

TABLE 6
Effect of Drying Temperature on the IEC (K^+) Values of SSPP

		Drying temperature (°C)				
		40	100	200	300	400
IEC (meq/g)	SSPP	2.29	2.06	0.73	0.72	0.07
	SPP	2.69	2.34	0.22	0.03	0.02

TABLE 7
Chemical Stability of SSPP in Various Solvents at 25 ± 2°C

Solubility (mg/50 mL)	H_2O	HNO_3 (*M*)				HCl (*M*)				H_2SO_4 (*M*)	
		0.1	1.0	2.0	4.0	0.1	1.0	2.0	4.0	1.0	2.0
Sn	0.00	0.02	0.03	0.04	0.08	0.16	0.43	1.03	10.33	0.03	0.04
Se	0.25	0.03	0.06	1.78	2.06	0.14	0.17	2.11	3.75	0.28	0.28
P	1.25	1.16	1.13	0.19	0.13	1.00	1.18	1.31	3.50	1.00	1.01

Solubility (mg/50 mL)	NaOH (*M*)	$HClO_4$ (*M*)		CH_3COOH (*M*)		Oxalic acid (*M*)		Citric acid (*M*)		$NaNO_3$ (*M*)	
	0.1	1.0	4.0	1.0	4.0	0.1	1.0	1.0	2.0	0.1	1.0
Sn	6.25	0.00	0.03	0.00	0.01	1.02	1.88	0.03	0.05	0.00	0.18
Se	0.73	0.75	1.30	0.18	0.21	1.39	1.66	1.03	1.48	0.22	0.35
P	2.25	1.19	0.94	0.80	0.76	1.10	1.65	0.50	0.30	0.76	0.30

phosphorus in various forms were measured by UV-visible spectrophotometric and atomic absorption methods. The results in Table 7 demonstrate that SSPP is very stable in water, salt, mineral acids, and organic acids. The sequences of stability of SSPP in mineral and organic acids are: $HNO_3 > H_2SO_4 > HClO_3 > HCl$; and acetic acid > citric acid > oxalic acid, respectively. Compared with some other tin-based inorganic ion exchangers (Table 8), SSPP shows very good chemical stability.

6. IR Studies

The IR spectra of SSPP heated at different temperatures are shown in Fig. 4. The peaks near 900-1200 cm^{-1} and 750 cm^{-1} were identified as vibration bands of $P_2O_7^{4-}$ and SeO_3^{2-}, respectively (*16*). The band in the 3000-3700 cm^{-1} region was identified as the OH stretching vibrations of structural water and hydroxyl groups in the exchanger. The band near 1650 cm^{-1} is the H—O—H bending motion of hydration water. With an increase in the drying temperature, these peaks gradually decreased, which could be correlated to the decrease in the IEC value of SSPP.

7. Laser Raman Studies

In order to get more information about the structure of SSPP, a Raman spectrum was taken in the region of 250 to 1250 cm^{-1} (Fig. 5). The peaks at

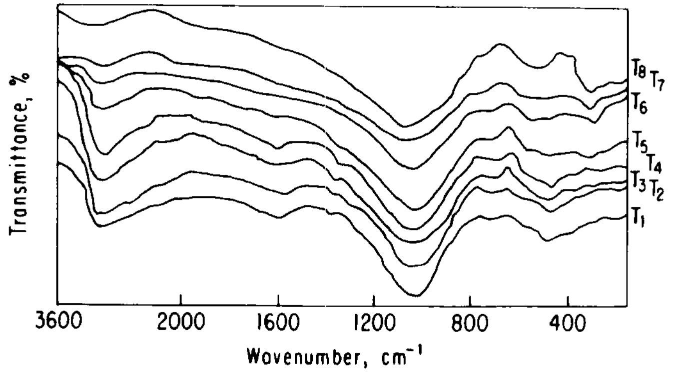

FIG. 4. IR spectra of SSPP dried at different temperatures (KBr disk). $T_1 = 40°C$, $T_2 = 100°C$, $T_3 = 200°C$, $T_4 = 300°C$, $T_5 = 400°C$, $T_6 = 500°C$, $T_7 = 600°C$, $T_8 = 800°C$.

TABLE 8
Comparisons of the Solubilities of Some Tin-Based Inorganic Ion Exchangers

		Solvent					
				HNO_3		HCl	
Exchanger		H_2O	NaOH, 0.1 *N*	2.0 *N*	4.0 *N*	2.0 *N*	4.0 *N*
SSPP (mg/50 mL)	Sn	0.00	6.25	0.03	0.04	0.43	10.33
	Se	0.25	0.73	0.06	1.78	0.17	3.75
	P	1.25	2.25	0.19	0.13	1.18	3.50
SPP (mg/50 mL)	Sn	0.00	22.50	0.07	0.12	3.55	35.00
	P	13.40	14.00	10.10	5.60	11.00	22.30
SS (mg/50 mL)	Sn	0.00	—	—	1.10	—	—
	Se	0.03	—	—	5.00	—	—
SSP (mg/50 mL)	Sn	0.00	0.00	2.20	—	8.20	—
	Se	0.00	6.80	1.02	—	6.20	—
	P	0.00	5.10	0.00	—	5.10	—
SWA (mg/50 mL)	Sn	0.65	CS[a]	—	8.00	—	145.00
	W	1.00	CS[a]	—	0.60	—	11.00
	As	1.80	CS[a]	—	1.00	—	47.50
SMA (mg/50 mL)	Sn	0.00	CS[a]	—	3.60	—	CS[a]
	Mo	6.60	CS[a]	—	20.00	—	CS[a]
	As	3.80	CS[a]	—	17.50	—	CS[a]

[a] Completely soluble.

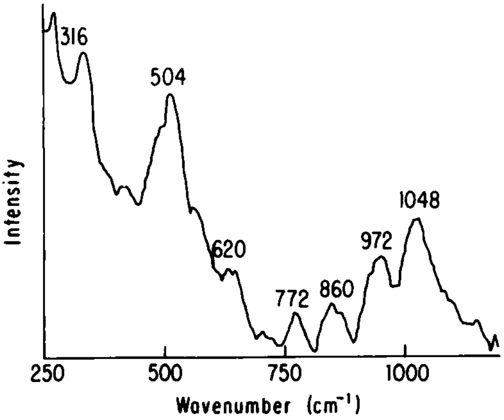

FIG. 5. Raman spectrum of SSPP.

972 and 1048 cm^{-1} are due to the asymmetric stretching vibrations of P−O−P and PO_3, respectively (*17*). The peaks at 860 and 620 cm^{-1} were identified as the ν_1 and ν_3 modes of $HSeO_3^-$ (or SeO_3^{2-}), respectively (*18*).

8. X-Ray Studies

Figure 6 is the x-ray diffraction patterns of SSPP after being heated at different temperatures. It shows that SSPP is an amorphous inorganic ion exchanger. The radial distribution function (RDF) and the pair correlation function *g*(*r*) of SSPP (Fig. 7) has also been measured and reported (*20*). Figure 7 shows that SSPP has short-range order or local structure. The first two peaks at 1.98 and 3.45 Å are due to the existence of Sn−O and Sn−O−Sn bonds in the exchanger. The valley near 2.75 Å implies that the probability of finding atoms near 2.75 Å from any arbitrary atom is very small. This could mean that the main cavity in the exchanger has a radius of 1.38 Å. It will be difficult for those ions with their radii larger than 1.38 Å to exchange with the H^+ inside the exchanger.

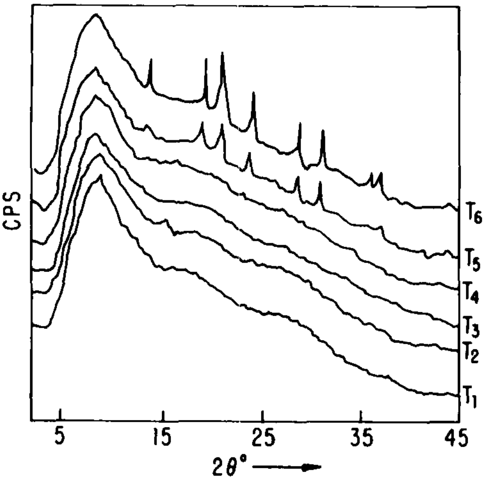

FIG. 6. X-ray diffraction patterns of SSPP dried at different temperatures. (Temperature notes are the same as in Fig. 4.)

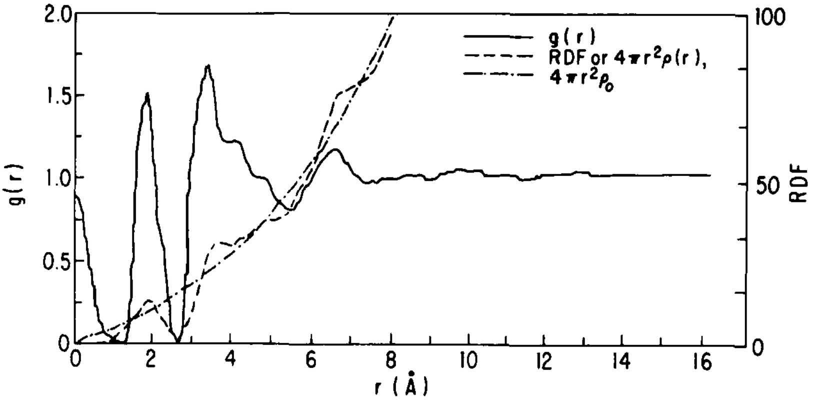

FIG. 7. The radial distribution function RDF and the pair correlation function $g(r)$ of SSPP.

9. Chemical Formula

As Table 2 shows, the molar ratio of $Sn/P_2/Se$ is 15/10/2. Analysis of the TGA curve shows that SSPP contains five H_2O molecules. The three breaks in the titration curve imply that SSPP has at least three exchangeable H^+ ions. The IR, Raman, and x-ray diffraction studies prove the existence of Sn—O, Sn—O—O, $P_2O_7^{2-}$, SeO_3^{2-}, —OH, and water of hydration. In reference to the structure of SPP (*2*), we propose a possible chemical formula for SSPP:

$$[(15SnO \cdot 8OH) \cdot 10H_2P_2O_7 \cdot 2HSeO_3]_n \cdot 5nH_2O$$

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