Studies of the Synthetic Inorganic Ion Exchanger. II.[1] *The Properties of Stannic Phosphate*

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(Received May 25, 1963)

The stannic phosphates, a group of synthetic inorganic ion exchangers which would be expected to have radiation and thermal stability, have been prepared by various methods and their compositions, ion exchange capacities and chemical stabilities have been investigated, as the preceding report describes.[1]

The exchanger, precipitated from a slightly acidic solution by mixing phosphate with stannic in the ratio of over two to one, has the stoichiometric composition of $PO_4^{3-}/Sn^{4+}=5/4$. It is in the form of white, hard and semitransparant granules and can be used for column operation. The neutral salt decomposition capacity is about 1.3~1.4 meq./g., considerably higher than that of natural inorganic ion exchangers. As to chemical stability, stannic phosphate is comparatively stable in mineral acid, except in concentrated hydrochloric acid, but in alkaline solutions it is unstable, even in a 0.1 N sodium hydroxide solution.

For the purpose of evaluating the availability for a typical ion exchanger like an ion exchange resin, the mutual separation of the alkali metal has been conducted. By using various concentrations of ammonium chloride as eluants, the complete separation of sodium, potassium and cesium from one other has been achieved with a relatively small column. The object of this report is to contribute to the knowledge concerning such fundamental properties of this exchanger as its ion exchange characteristics, its thermal stability and its radiation stability. Moreover, the recommended preparation method and the structure of the exchanger are suggested.

Experimental

Preparation. — The synthetic method has been outlined in the previous report, but the procedure was not detailed.[1] From the evidence which is to be presented later, the following procedure is most recommended. This method corresponds to that used for No. 7 in the first report of this series.

Two hundred and ten grams of stannic chloride pentahydrate were dissolved in 600 ml. of distilled water while it was being heated, and it was then filtered to remove the suspended materials. Into this solution 1.2 l. of a 1.2 N sodium hydroxide solution containing 187 g. of sodium dihydrogen phosphate dihydrate was added rapidly, stirring vigorously at room temperature. At first, the flocculent precipitate was formed, then the gel structure grew from one minute to the next, and finally the solution completely coagulated as a gelatinous mass. After the solution had thus stood for several hours, distilled water was added, and it was stirred to obtain a homogeneous suspension. After the gelatinous suspension had settled down, the supernatant liquid was decanted. This procedure was repeated

1) Y. Inoue, *J. Inorg. Nucl. Chem.*, in press.

several times till the pH of the washings (nearly 3) remained constant. At the last stage of washing, the precipitate was filtered through fine filter paper under suction, washed twice or three times by distilled water, removed from the funnel, and dried at room temperature till it shrank. The gel thus obtained broke down easily to small particles with cracking and with slight evolution of heat when it was immersed in water. If the gel did not break down to the desired particle size, it was ground in a porcelain mortar and sized by sieving. To convert it thoroughly to the hydrogen form, it was then immersed in 1 N nitric acid or 1 N hydrochloric acid for two or three days (the solution was sometimes renewed in the course of immersion), washed several times by distilled water, filtered, and dried in air. In the present work, an exchanger of a 100~200 mesh size was used unless otherwise stated, except in the K_d determination, in which a 200~350 mesh was used.

Titration Curves.—These were determined by the standard technique.[2] A half gram of stannic phosphate was equilibrated with 75 ml. of a solution containing sodium chloride and sodium hydroxide, the total sodium concentration being 0.1 M. After the mixture had stood for three days with intermittent shaking, the pH of the supernatant liquid was measured on a Toa Dempa pH meter. As will be described later, the titration curves were different from batch to batch, therefore, the samples of the same batch were used throughout one set of experiments.

Distribution Coefficients. — Batch distribution coefficients were determined by equilibrating weighed amounts (usually 500 mg.) of the ion exchanger with 50 ml. of suitable solutions for two or three days in a thermostat at 25°C. The acidities of solutions containing 10^{-3} M of the cation in question were adjusted by dilute nitric acid. This was followed by filtration of the mixture, and analysis and pH measurement of the filtrate were then made. The metallic ion content of the exchanger after equilibrium was estimated from the difference between the total initial and final concentrations of metal present in the solutions.

Distribution coefficients were calculated by means of the usual relationship.

$$K_d = \frac{\text{meq. of cation in exchanger/g. of exchanger}}{\text{meq. of cation in solution/ml. of solution}}$$

The analyses of sodium, potassium, rubidium, cesium, copper, gallium, zinc, strontium, calcium, iron and cobalt were carried out radiometrically using ^{24}Na, ^{42}K, ^{86}Rb, ^{137}Cs, ^{64}Cu, ^{72}Ga, ^{65}Zn, ^{89}Sr, ^{45}Ca, ^{59}Fe and ^{60}Co respectively as tracers. The analysis of lithium was made by flame photometry; manganese, by the persulfate oxidation-permanganate photometric method; chromium, by the diphenyl carbazide photometric method; and ammonium, by the extraction-photometric method.

Rate of Exchange.—This was measured by almost the same method as K_d determination. The temperature employed was 25°C or 80°C, and exchangers of a 100~200 mesh or a 200~350 mesh were used. From the analytical results of an aliquot of the supernatant liquid taken every suitable time interval, the rate of exchange was determined. In this case, 500 mg. of the exchanger was used with 100 ml. of the solution.

Gamma-ray Irradiation.—The samples, sealed in a hard glass tube, were irradiated by a 10000 curies cobalt-60 gamma-ray irradiation facility of The Japan Atomic Energy Research Institute at the dose rate of 1.11×10^6 r./hr. for a definite period. After this irradiation, the samples were conditioned as described before; then the titration curves, exchange capacities, selectivity and so on were measured. When irradiation was done in an aqueous solution, 8 g. of the exchangers were immersed in 8 ml. of the solutions.

Treatment of the Exchanger with High Temperature Water. — Ten grams of exchanger were immersed in 50 ml. of distilled water; this was treated for eight days in static autoclaves up to 300°C. The samples were then taken out of the autoclaves and conditioned as described above; then the titration curves, exchange capacities, selectivities and so on were measured.

Another Experimental Method. — The densities of the exchangers were measured by the usual manner, using a 5 ml. pycnometer. The column operation and the measurement of the exchange capacity were carried out as described in the first report. The exchange capacity is the "hydrogen liberation capacity" as defined in the previous report.

Thermogravimetry was performed with Shimadzu Model T-1A thermal analysis equipment, employing an TB-1 thermal balance as additional equipment. Measurement was carried out in air at a heating rate of 10°C/min. over the temperature range from 20°C to 800°C.

In the X-ray diffraction experiments, copper K_α radiation was employed.

Results

The Recommended Method for the Synthesis of Stannic Phosphate.—The yields and densities of the stannic phosphates obtained by six typical preparation methods are presented in Table I. Densities are about 2.0~2.4 g./cm^3, and no differences among the methods of preparation were observed. From the exchange capacities and physical properties described in the first report, the mixing ratio of stannic to phosphate of 2 to 1 is the most appropriate. As to yield, from the economical point of view, that for stannic chloride would be most important. The No. 7 sample shows the highest yield per unit amount of stannic chloride. Putting the above results together, the synthetic method of No. 7 is most recommended.

Titration Curves.—The titration curves of stannic phosphates prepared by various methods are represented in Fig. 1. The curves show that the stannic phosphates are weakly acidic

2) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, **1949**, 3299.

TABLE I. VARIOUS PROPERTIES OF STANNIC PHOSPHATE

Sample No.	Synthetic method			Yield g.	PO_4^{3-}/Sn^{4+}*	Hydrogen* liberation capacity meq./g.	Density g./cm³
	$NaH_2PO_4 \cdot 2H_2O$, g.	NaOH g.	$SnCl_4 \cdot 5H_2O$ g.				
3	94	72	210	159	0.912	1.21	2.06
6	94	76	210	161	0.565	0.98	2.40
7	187	48	210	200	1.28	1.35	2.17
9	187	96	210	90	1.04	1.26	2.22
13	187	36	105	76	1.25	1.41	2.26
20	108	48	210	140	0.56	0.78	2.29

* From the data of the first report.

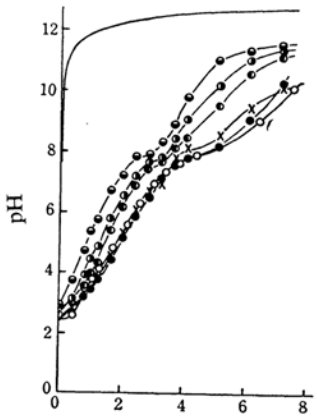

Fig. 1. Titration curves of stannic phosphate. Legend: -◑- No. 3; -◐- No. 6; -○- No. 7; -●- No. 9; -×- No. 13; -◒- No. 20; — In the absence of exchanger

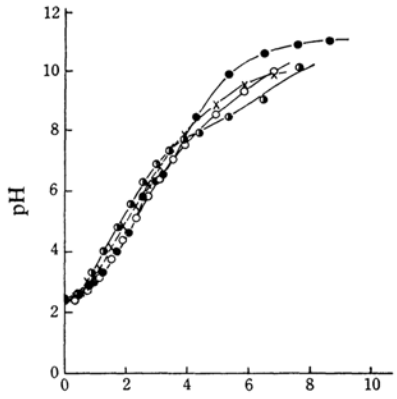

Fig. 2. Titration curves of stannic phosphate prepared by the recommended procedure.
Legend: -○- Batch No. 1; 200~350 mesh exchanger; conditioning solution HCl
-×- Batch No. 1; 200~350 mesh exchanger; conditioning solution HNO_3
-●- Batch No. 2; 100~200 mesh exchanger; conditioning solution HCl
-◑- Batch No. 3; 100~200 mesh exchanger; conditioning solution HNO_3

cation exchangers and possess several dissociable hydrogen atoms over a range of pK_a values. The lack of sharpness of the inflection points suggests that there may be somewhat overlapping values of pK_a. However, it seems that the most acidic exchange group has a pK_a value of approximately three. This value probably corresponds to the pK_a value of the second hydrogen ion of the activated phosphoric acid group. In an acidic solution this dissociable hydrogen is most important, and it is considered that the neutral salt decomposition capacities result from one hydrogen ion of the $H_2PO_4^-$. From the practical point of view, it is sufficient to pay special attention to this exchanging group.

The reproducibility of the preparation was fairly good from the point of view of exchange capacity, as has been discussed in the preceding report, but variations in the titration curves have been observed between different batches; these variations are usually most marked in the high pH region (above 8) of the curve. This is perhaps attributable to the unstability in the face of an alkaline medium. The general pattern is, however, fairly constant in the pH range of less than 8, as Fig. 2 shows. The influence on the shape of the titration curves

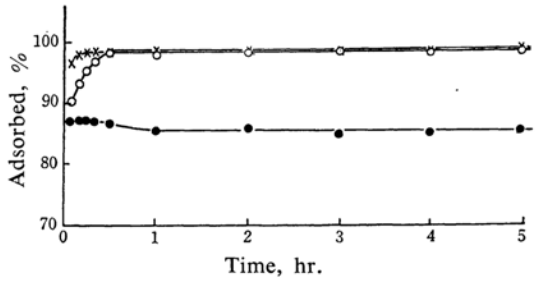

Fig. 3 a). Rate of exchange of cesium (temperature 25°C).
Legend: -○- Conc. of Cs C. F.; 100~200 mesh of exchanger
-×- Conc. of Cs C. F.; 200~350 mesh of exchanger
-●- Conc. of Cs 10^{-3} M; 200~350 mesh of exchanger

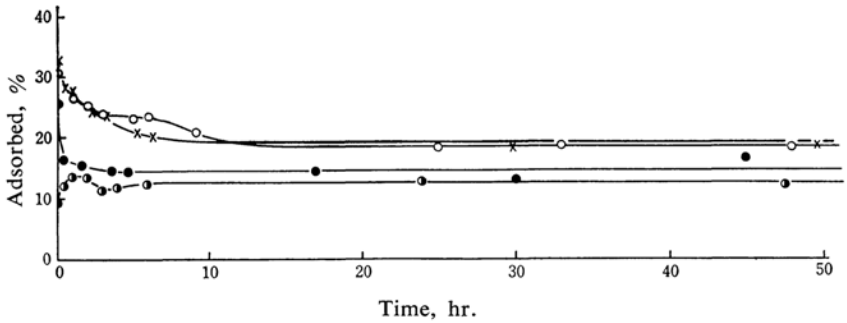

Fig. 3 b). Rate of exchange of sodium.
Legend: -×- Conc. of Na 10^{-3} M; 100~200 mesh of exchanger; 25°C
-○- Conc. of Na 10^{-3} M; 200~350 mesh of exchanger; 25°C
-◑- Conc. of Na 10^{-2} M; 200~350 mesh of exchanger; 25°C
-●- Conc. of Na 10^{-3} M; 200~350 mesh of exchanger; 80°C

of the different acids by which the exchangers are converted to the hydrogen form, has been investigated, hydrochloric acid gives titration curves more acidic than nitric acid, but this effect is not very great. No effect of particle size on the titration curves was recognized.

Rate of Exchange.—To evaluate the time of standing indispensable for batch experiments, the rate of exchange was investigated using a 100~200 mesh or a 200~350 mesh exchanger at 25°C and 80°C (cf. Fig. 3). Carrier-free ^{137}Cs, 10^{-3} M cesium, 10^{-2} M sodium and 10^{-3} M sodium ion were used as the exchanging cations.

When the concentration of the exchanging cation was 10^{-3} M, the maximum adsorption was attained immediately after the exchangers were immersed in a solution; thereafter the amount of exchange gradually decreased with the lapse of time. After ten or twenty four hours, equilibrium was reached. On the contrary, when the concentration was 10^{-2} M or a tracer concentration, the amount of adsorbed cation gradually increased and then reached constant. In the case of 80°C, equilibrium was attained within two hours, and it was apparent that the exchange rate was accerelated by a high temperature. As a result of the above investigation, to be on the safe side, a standing period for two or three days is recommended for batch equilibrium experiments.

Distribution Coefficients. — The distribution coefficients of various cations are tabulated in Table II. They were measured using nearly neutral solutions of the cations in question. The pH of the solution in equilibrium with the exchanger was also measured, as the table shows.

The affinity series for alkali metal follows the pattern shown by many organic exchangers, viz.

$$Li < Na < NH_4 < K < Rb < Cs$$

Table II. Distribution coefficients of cations
500 mg. of exchanger/50 ml. of solution, at 25°C, 10^{-3} M/l.

Cation	Compound used	pH	K_d, ml./g.
Li^+	Chloride	2.70	11.4±0.6
Na^+	Chloride	2.53	28.9±0.3
NH_4^+	Chloride	2.70	147±4
K^+	Chloride	2.49	356±13
Rb^+	Chloride	2.57	735±6
Cs^+	Chloride	2.57	1343±12
Ca^{2+}	Chloride	2.48	2247±121
Sr^{2+}	Nitrate	2.40	602.8±11.2
Zn^{2+}	Nitrate	2.03	315.0±6.6
Cu^{2+}	Nitrate	2.59	$(5.87\pm0.38)\times10^3$
Mn^{2+}	Sulfate	2.60	2090±122
Fe^{2+}	Sulfate	1.00	7.6
Co^{2+}	Chloride	1.97	96.70±2.00
Fe^{3+}	Sulfate	0.91	4207±172
Ga^{3+}	Nitrate	2.20	$(1.35\pm0.07)\times10^4$
Cr^{3+}	Sulfate	2.48	3595±318

There are, however, differences between the behavior of ion exchange resins and stannic phosphates. For example, it is interesting to note that calcium is adsorbed more selectively than strontium and that ferric ions show an exceptionally high distribution coefficient. The reason for this is not clear, although it might be due to a specific chemical interaction other than a simple ionic reaction.

Thermal Stability.—*Heat Treatment in Air.*—In order to obtain a rough idea of the thermal stability of the stannic phosphate, a thermogravimetric analysis was conducted on material which had been dried at room temperature (cf. Fig. 4). Also, the weight losses and exchange capacities of the exchangers dried to a constant weight at temperatures ranging from 110 to 410°C are shown in Table III.

Figure 4 shows a step-by-step decomposition

curve. It is assumed that the weight loss observed from room temperature to 200°C mainly corresponds to the desorption of water retained in the gel structure and that structural water is lost at the inflection point near 350°C. The weight loss obtained from the thermal analysis curve is generally identical with that obtained by heating to a constant weight, but at 110°C these values differ from one other. This difference is perhaps due to the non-equilibrium condition of the thermal analysis. This is clear from the fact that the thermal analysis curve shows a steep slope near 110°C.

The exchange capacity does not change upon heat treatment at 110°C, provided the correction due to the weight loss is performed. However, it is reduced to half when it is heated to 210°C. If stannic phosphate is treated at 410°C to a constant weight, the cation exchange capacity completely diminishes. The

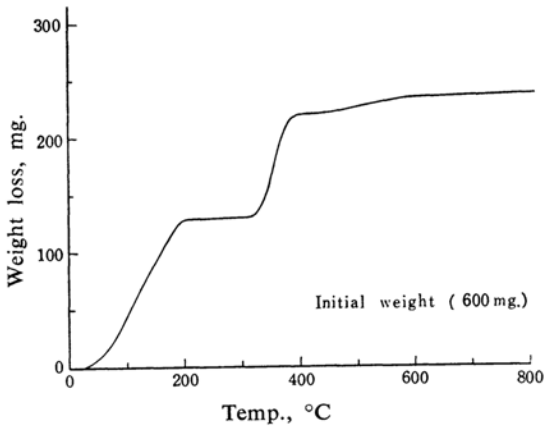

Fig. 4. Thermogram for stannic phosphate.

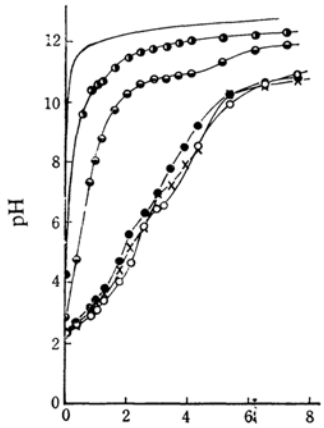

Fig. 5. Titration curves of stannic phosphate as a function of drying temperature.
Legend : -○- Room temperature ; -×- 110°C; -●- 210°C ; -◒- 320°C ; -◑- 410°C ;— In the absence of exchanger

TABLE III. EFFECT OF HEAT TREATMENT IN AIR

Temp.	Exchange capacity, meq./g.		Weight, mg.	
°C	Calculated value	Experimental value	Calculated value	Experimental value
Room temp.	1.28	1.35	600	600
110	1.62	1.62	475	475
210	0.81	0.82	468	469
320	—	0.23	461	460
410	—	0.02	392	392

titration curves obtained by the samples dried at various temperatures give support to this observation ; that is to say, the titration curve of stannic phosphate dried at 320°C shows a considerable decrease in the most acidic exchange group. At 410°C, the inflection point originating from the most acidic hydrogen ions completely disappears (Fig. 5).

To evaluate the separation abilities of the stannic phosphates dried at temperatures higher than room temperature, the separation of sodium and cesium was conducted by the same method as in the preceding paper. Even in the sample dried at 110°C one can not separate these ions, presumably because of the tailing of the elution curve. Thus, the stannic phosphates dried at temperatures 110°C or higher cannot be used as cation exchangers.

Heat Treatment in an Aqueous Solution.—As has been mentioned above, the stannic phosphate is not stable against heat treatment in air. To know whether or not this is also true in an aqueous solution, an examination was conducted of the ion exchange properties of a stannic phosphate refluxed with distilled water or 7 N nitric acid for five hours and then treated with distilled water in a static autoclave up to 300°C for eight days. The results are summarized in Table IV and Fig. 6. When stannic phosphate is treated both in water and 7 N nitric acid at their boiling points, its external appearance does not change, but at 200°C it slightly loses its transparency. At 250°C the particles break down to some extent. If the temperature of water rises to 300°C, the particles completely break down and disperse into

TABLE IV. EFFECT OF HEAT TREATMENT IN AQUEOUS SOLUTIONS

Solution	Temp. °C	Time	Exchange capacity meq./g.
—	—	—	1.23
7 N HNO_3	100	5 hr.	1.17
H_2O	100	5 hr.	1.22
H_2O	100	8 days	1.22
H_2O	200	8 days	1.27
H_2O	250	8 days	1.10

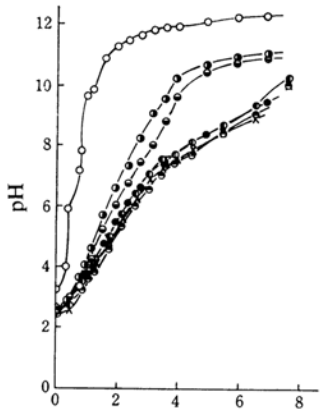

Fig. 6. Effect of heat treatment in aqueous solution on the titration curves of stannic phosphate.
Legend: -◐- In 7 N HNO_3, at boiling point, 5 hr.; -◓- In H_2O, at boiling point, 5 hr.; -●- In H_2O, 100°C, 8 days; -◒- In H_2O, 200°C 8 days; -◑- In H_2O, 250°C, 8 days; -○- In H_2O, 300°C, 8 days

the water as a suspension and, therefore, the exchanger cannot be used.

The exchange capacity does not change up to 200°C, but it slightly decreases upon treatment at 250°C; the titration curves show a similar trend. Samples treated at 300°C do not only break down physically, but they also completely lose their cation exchange capacity, as Fig. 6 shows. Moreover, in the same way as in the preceding section, the separation of sodium and cesium was carried out. These separations go well using stannic phosphate treated in water at temperatures up to 250°C.

It is apparent from the above results that stannic phosphate can be used in pressurized, high-temperature water or in boiling concentrated nitric acid.

Radiation Stability.—The exchange capacities and titration curves of the irradiated samples are shown in Table V and Fig. 7 respectively. These coincide with those of reference runs within the range of experimental error. The separation of sodium and cesium gose as well as before, and it is concluded that stannic phosphate is stable against irradiation of about 10^9 r.

X-Ray Diffraction.—The results are shown in Fig. 8. Stannic phosphate dried at room temperature shows a weak line at d=4.14 Å, and one more line appears at d=3.73 Å when the sample dried at 110°C is used. When the drying temperature is 410°C, it shows 7 lines; however, the spacings of these lines do not coincide at all with that of the lines which appear in the diffraction patterns of exchangers

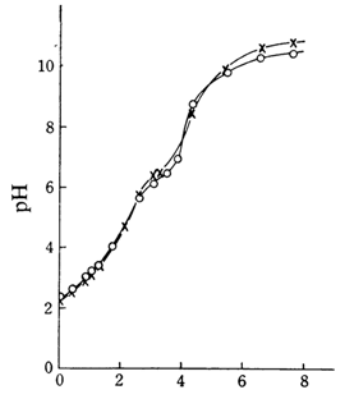

Fig. 7. Effect of irradiation on the titration curve of stannic phosphate.
Legend: -×- Reference; -○- 10^9 r

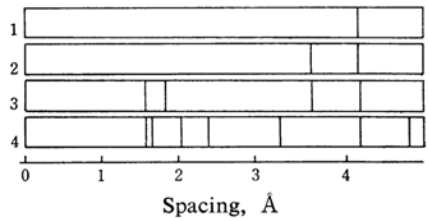

Fig. 8. X-Ray diffraction.
1: Dried at room temperature
2: Dried at 110°C
3: Dried at 210°C
4: Dried at 410°C

Table V. Effect of radiation

Environment	Dose, r	Exchange capacity meq./g.
Reference	—	1.44
Air	1.10×10^8	1.40
Air	1.13×10^9	1.40
H_2O	1.02×10^9	1.45
7 N HNO_3	1.02×10^9	1.45

dried at 210°C or a lower temperature. This suggests that some remarkable changes in structure may occur between 210°C and 410°C. There are only a small number of diffraction lines, and the intensities of these lines are so weak that the relative intensity can not be determined. Consequently, the stannic phosphate has a nearly amorphous structure, and, therefore, a detailed analysis of the results is impossible.

Discussion

Structure.—On the basis of the results concerning the properties of the exchanger hitherto obtained, one can put forward the following assumptions.

a) When the air-dried exchanger is heated at 110°C to a constant weight, the weight loss measured is due to water retained in the gel structure; this water completely volatilizes off at this temperature. (About 20.8% of this water is contained in an air-dried exchanger.)

b) The neutral salt decomposition capacity results from one hydrogen ion of the H_2PO_4-group. The strongly dissociable hydrogen ions due to one-half of the H_2PO_4-groups disappear at 210°C, and the other half, at 320°C with the condensation of the H_2PO_4-groups. The titration curves support this assumption.

c) The weight loss near 350°C is due to the loss of structual water. This assumption is supported by the evidence of X-ray diffraction study and by the marked change in appearance.

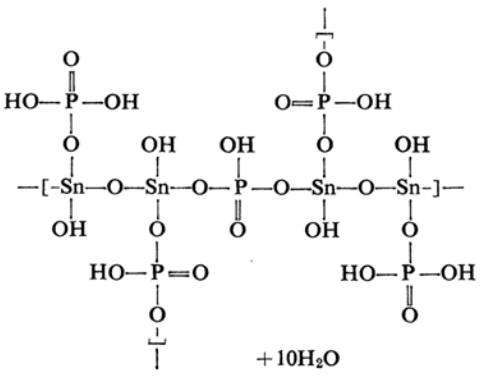

Fig. 9. Structure of stannic phosphate.

Taking the composition of stannic phosphate (P/Sn=5/4) and the above assumptions into consideration, the structure represented in Fig. 9 may be inferred.

The neutral salt decomposition capacities and weight losses calculated on the basis of the above assumptions are presented in Table III. These values and experimental results agree fairly well.

It seems that the arrangement of such a unit structure is not very regular because the X-ray diffraction patterns display a nearly amorphous structure.

Rate of Exchange.—The separation of sodium and cesium did not go well when stannic phosphate dried at 110°C was used, even though the exchange capacity was unchanged. This is mainly due to prolonged tailing, and it is perhaps also attributable to the slow rate of exchange. On the other hand, this phenomenon does not occur when stannic phosphate treated in water even at so high a temperature as 250°C is used. If one thinks of the rate-determining step as particle diffusion, as has been made clear in the case of zirconium phosphate,[3] and if one considers that ions migrate through adsorbed water, the above phenomenon may be explained well.

The findings of Fig. 3 can be illustrated as follows. When the concentration of exchanging cations is 10^{-3} M, which corresponds to about one-seventh of the exchange capacity, the cations are adsorbed in a high distribution coefficient immediately after the exchanger comes in contact with the solution. Part of the cations, once adsorbed on the exchanger, are liberated into the solution at a finite rate in consequence of the decrease in the distribution coefficient, which is accompanied by the drop of the pH of the solution; then equilibrium is attained. The adsorption curve when a 10^{-2} M solution is used, differs from that obtained when the concentration is 10^{-3} M. In this case the exchanging cations added are not adsorbed rapidly in so high a distribution coefficient as when the pH of the solution is high. As a result of this fact and of the pH change of the solution during the exchange step, such a curve as represented in Fig. 3 is obtained. On the other hand, in the case of infinite dilution, no pH change of the solution occurs during the adsorption process and the exchange occurs in a simple adsorption process.

Ion Exchange Equilibria.—Assuming that the exchanging ion is a simple cation, which does not undergo complexing, polymerization or hydrolytic reaction in the media of interest, and assuming that only one type of exchanging group contributes to the ion exchange reaction, the ion exchange equilibria may be written in the form:

$$M^{n+} + nHR = MR_n + nH^+ \quad (1)$$

with the equilibrium constant:

$$K = \frac{(MR_n)\,[H^+]^n \gamma_{MR_n} \gamma_{H^+}^n}{[M^{n+}]\,(HR)^n \gamma_{M^{n+}} \cdot \gamma_{HR}^n} \quad (2)$$

where brackets is the concentration of the ion in the aqueous phase, parentheses is the concentration in the exchanger phase, and γ is the activity coefficient. K is the equilibrium constant. Equation 2 is useful as an ion exchange equation, at least under some limiting conditions, if the activity coefficients in the exchanger phase do not vary rapidly.

With organic exchangers, the activity coefficient ratio, $\gamma_{MR_n}/\gamma_{HR}^n$, for the exchanger phase is essentially constant if exchange reactions are carried out in moderately dilute electrolyte solutions, if one of the adsorbed ions occurs at dilute concentrations, and if no complexing or hydrolytic reactions occur. The composition of the exchanger is, therefore,

3) G. H. Nancollas and R. Paterson, *J. Inorg. Nucl. Chem.*, 22, 259 (1961).

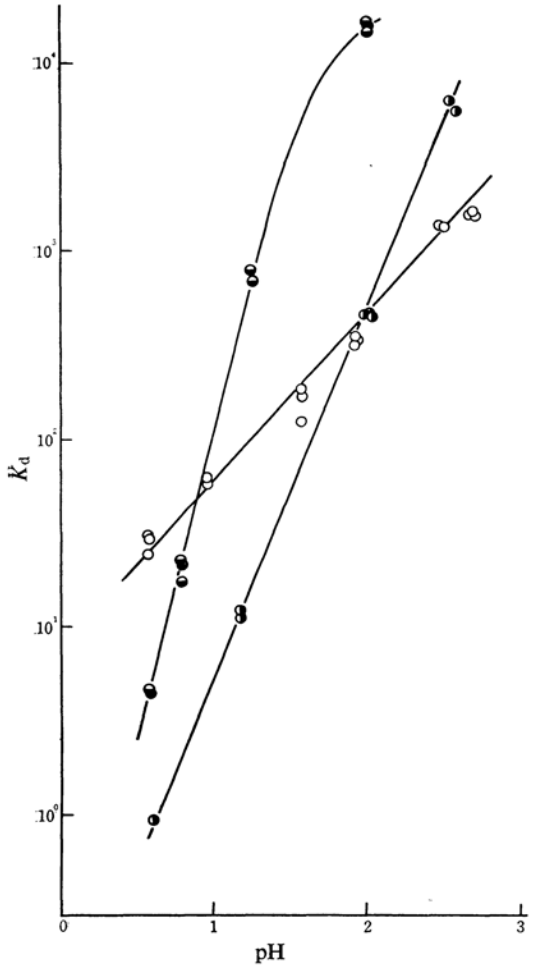

Fig. 10. Distribution coefficients for Cs(I), Cu(II) and Ga(III) on stannic phosphate at different pH.
Legend: -○- Cs(I); -◑- Cu(II); -◒- Ga(III)

essentially independent of the concentration of the adsorbed ions and Eq. 2 simplifies to:

$$K_d [H^+]^n \frac{\gamma_{H^+}^n}{\gamma_{M^{n+}}} = \text{const.} \quad (3)$$

where the distribution coefficient, K_d, is defined by:

$$K_d = \frac{(MR_n)}{[M^{n+}]} \quad (4)$$

If the ionic strength of the solution is low, the activity coefficient, $\gamma_{M^{n+}}$, will be unity. Equation 3 can, therefore, be rewritten to:

$$\log K_d = \text{const.} + n \times \text{pH} \quad (5)$$

According to Eq. 5, a plot of log K_d vs. pH should be a straight line with a slope of n.

This relationship has been verified for cesium(I), copper(II) and gallium(III) ions, as illustrated in Fig. 10. This relationship shows that only one type of exchange reaction contributes to the reaction in such a low pH as less than 3.

Summary

A recommended procedure for the preparation of stannic phosphate and a discussion of its ion exchange properties have been presented.

Some of the results obtained are as follows.

1) The density of the stannic phosphate is 2.17 g./cm^3.

2) Stannic phosphate is a weakly acidic cation exchanger and possesses several dissociable hydrogen atoms in the range of pK_a values. In a weakly acidic solution, in which the exchanger is useful, the exchange group having the pK_a value of approximately three is most important.

3) The ion exchange equilibrium can be elucidated by the mass action law.

4) The affinity series for alkali metal coincides with the usual relationship observed in the ion exchange resin.

5) The rate-determining step is assumed to be the migration of ions through the water retained in the gel structure.

6) Stannic phosphate is unstable against heat treatment in air; that is, the separation of alkali metal does not go well with the exchanger dried at 110°C due to the slow rate of exchange.

7) It is fairly stable against heat treatment in water; that is, it undergoes only a slight decrease in ion exchange capacity even when it is treated in water at 250°C for 8 days.

8) It is stable against irradiation of about 10^9 r.

9) The structure of stannic phosphate has been suggested on the basis of its thermal decomposition curve, its exchange capacity, its titration curves, and its X-ray diffraction patterns.

The author wishes to thank Dr. Hidehiro Goto and Dr. Shin Suzuki of Tohoku University for their guidance, discussion and continuous encouragement.

This project was partly financed by a grant-in-aid for Fundamental Scientific Research provided by the Ministry of Education, to which the authors' gratitude is due.

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