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CRYSTALLINE INSOLUBLE ACID SALTS OF TETRAVALENT METALS

X. FIBROUS THORIUM PHOSPHATE, A NEW INORGANIC ION-EXCHANGE MATERIAL SUITABLE FOR MAKING (SUPPORT-FREE) INORGANIC SHEETS

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SUMMARY

Some investigations on the preparative procedure of fibrous thorium phosphate are reported. This new inorganic ion exchanger has been characterized on the basis of chemical analysis, thermal stability and ion-exchange properties with alkali metal ions. The ion-exchange capacity for Na^+ is 3.7 mequiv./g.

Fibrous thorium phosphate has been employed to prepare porous, support-free, inorganic ion-exchange sheets suitable for chromatographic experiments.

INTRODUCTION

In a previous paper[1] the preparation and some ion-exchange properties of a fibrous cerium(IV) phosphate were reported. This compound, besides possessing good ion-exchange capacity, has the property of giving flexible sheets similar to cellulose paper[2]. Since these inorganic ion-exchange sheets are very interesting both for theoretical studies and for their potential practical applications in chromatography[3], electrophoresis, ion-exchange membranes, etc., research was carried out to obtain other fibrous inorganic ion exchangers of the cerium(IV) phosphate type. In the present study the synthesis and some ion-exchange properties of a fibrous thorium phosphate are reported.

EXPERIMENTAL

All reagents were C. Erba R.P. products. The molar ratio of PO_4 to Th was determined as follows: 100–200 mg of sample were dissolved in 6 ml of hot concentrated HNO_3. The solution was then diluted to 100 ml with distilled water. Phosphates were determined colorimetrically in 2 ml of this solution, as previously described[1], while thorium was precipitated in the remaining solution as oxalate and determined as ThO_2. X-ray analysis, titration and weight-loss curves were obtained as described in previous papers of this series[1,4,5].

RESULTS AND DISCUSSION

It is known that when an acidic solution of a thorium salt is mixed (at room temperature) with a solution of phosphoric acid, amorphous thorium phosphate is obtained. This material shows a variable PO_4/Th ratio (depending on the preparative conditions) and a poor ion-exchange capacity (about 1 mequiv. of Na^+ per g) (ref. 6).

To obtain a fibrous material we have studied the effect of the concentration of the reagents, temperature and digestion time on the formation of the precipitate. It was found that the formation of fibrous thorium phosphate is favoured by a high PO_4/Th ratio, high temperature and a long digestion. Temperature and digestion time are interdependent; the lower the temperature the longer the digestion must be to obtain a good fibrous material for the preparation of inorganic sheets (Table I). A low yield or no precipitate is obtained (depending on the temperature) when the

TABLE I

PO_4/Th RATIO OF VARIOUS SAMPLES OF FIBROUS THORIUM PHOSPHATE PREPARED AT DIFFERENT TEMPERATURES, PO_4/Th RATIOS IN SOLUTION AND DIGESTION TIMES

$Th(NO_3)_4$ solution is 0.1 *M* in 1 *M* HNO_3.

H_3PO_4 (molarity)	PO_4/Th (in solution)	Temperature (°C)	Digestion time (h)	PO_4/Th (in solid)	Remarks
1	10	25		1.5[a]	No sheets obtained
1	10	60	3	1.6	Friable sheets obtained
1	10	60	20	1.8	Friable sheets obtained
1	10	90	3	—	Friable sheets obtained
1	10	90	10		Not very flexible sheets obtained
1	10	90	40	1.9[b]	Flexible sheets obtained
1	10	100	3		Friable sheets obtained
1	10	100	10		Not very flexible sheets obtained
1	10	100	20	1.9[b]	Flexible sheets obtained
2	20	90	10		Not very flexible sheets obtained
2	20	90	40	2.1[b]	Flexible sheets obtained
2	20	100	24		Flexible sheets obtained
2	20	100	40	2.0[b]	Flexible sheets obtained
3	30	100	—	—	No precipitation occurs

[a] Amorphous material.
[b] Fibrous material.

phosphoric acid concentration is higher than 2 *M* and the PO_4/Th ratio is higher than 30. This fact is most likely concerned with the well-known formation of soluble thorium complexes with phosphoric acid.

The fibrous phosphate employed in this work was prepared as follows. A volume of a 0.1 *M* thorium nitrate solution in 1 *M* HNO_3 was added dropwise (~1 ml/min) to a well-stirred volume of 2 *M* phosphoric acid. The temperature was maintained at about 100°. The precipitate so obtained was stirred for about 40 h at this temperature, then filtered, washed with distilled water until reaching pH 3–4 and dried in a desiccator over saturated sodium chloride. By filtering the precipitate under the same conditions described for cerium(IV) phosphate flexible inorganic

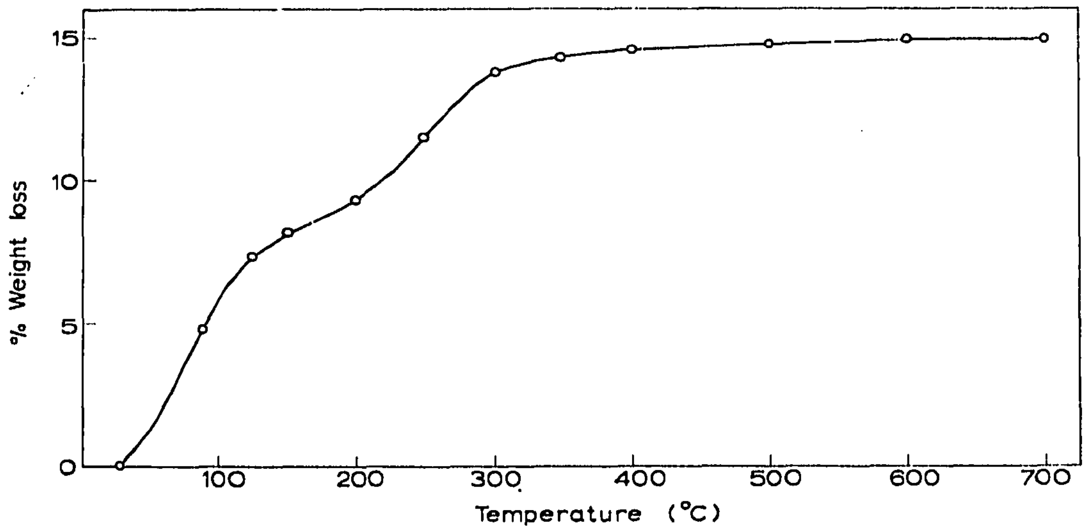

Fig. 1. Percentage weight loss of fibrous thorium phosphate, dried over a saturated NaCl solution at different temperatures.

sheets were obtained and it could be seen under the microscope that thorium phosphate is a fibrous material of cerium(IV) phosphate type[7].

As regards its chemical composition solid fibrous thorium phosphate has a PO_4/Th ratio of about 2, and when it is heated to 800° it loses 4 moles of water for each gramatom of thorium. Two moles of water are lost at 120° (or when dried over P_4O_{10} under vacuum); the third is lost between 120 and 240°, while the material is practically anhydrous at 500° (Fig. 1). Fibrous thorium phosphate can thus be represented as $ThO_2 \cdot P_2O_5 \cdot 4H_2O$. Its X-ray diffraction pattern is reported in Table II.

TABLE II

d VALUES FROM X-RAY POWDER PATTERN OF FIBROUS THORIUM PHOSPHATE IN H^+ FORM

d (*Å*)	*I*
11.47	s
5.38	w
4.95	vw
3.79	vw
3.54	vw
2.91	vw
2.80	vw
2.05	vw
1.56	w

We have investigated the ion-exchange properties of fibrous thorium phosphate with alkali metal ions. Fig. 2 shows the uptake curve of Na^+ and the phosphate loss curve at different pH values. From the sodium uptake and the mmoles of phosphate released to the solution at pH 11, one can derive an experimental ion-exchange capacity of 3.68 + 0.17 = 3.85 mequiv./g; a value close to 4.18 mequiv./g is calculated assuming two exchangeable hydrogen ions per formula weight of exchanger.

In Table III the saturation capacity and the phosphate loss, obtained with

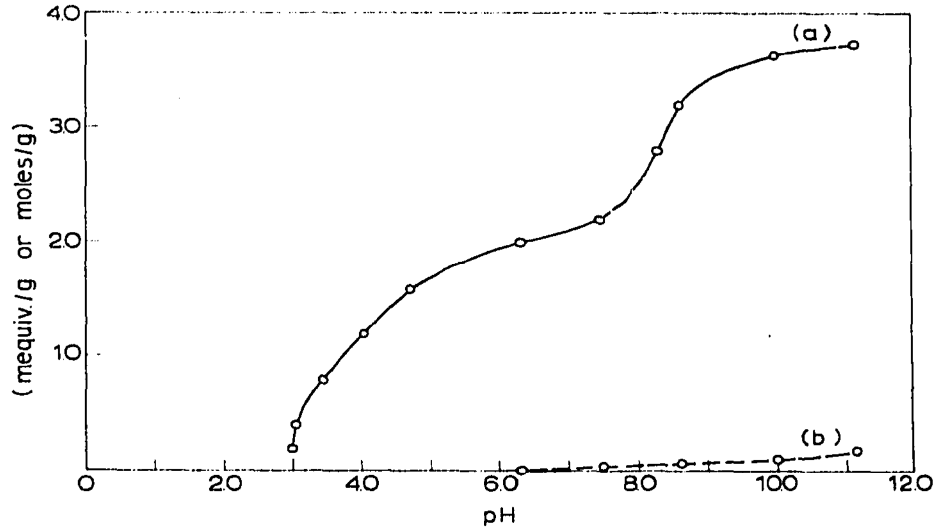

Fig. 2. Sodium uptake (a) and hydrolysis (b) curves of fibrous thorium phosphate titrated with 0.1 *M* (NaCl + NaOH).

batch experiments, are reported for the alkali metal ions. For Na^+, K^+ and Cs^+, the saturation capacity decreases with increasing crystalline ionic radius, while the reverse occurs for the phosphate loss. This fact can be accounted for by considering steric effects or electrostatic interactions in the exchanger. The relatively high phosphate loss in the Li^+–H^+ process can be explained by the macroscopic swelling observed in the material when converted into the Li^+ form.

As already mentioned, fibrous thorium phosphate can be employed to prepare inorganic ion-exchange sheets similar to those obtained with fibrous cerium(IV) phosphate. Because of their practical applications, it seems convenient to compare these inorganic ion-exchange sheets. Thorium phosphate sheets compare favorably with those of cerium(IV) phosphate as regards stability to strong reducing agents.

TABLE III

CAPACITY AND PHOSPHATE LOSS OF FIBROUS THORIUM PHOSPHATE (DRIED OVER SATURATED NaCl SOLUTION) FOR VARIOUS ALKALI METAL IONS

Ion	*Equilibrium pH*	*Capacity (mequiv./g)*	*Phosphate loss (mmoles/g)*
Li^+	10.7	3.2	0.7
Na^+	10.8	3.7	0.2
K^+	10.9	3.1	0.4
Cs^+	11.3	1.9	0.6

This property may be important in chromatography where reducing agents are often used as eluents or spot-test reagents. Furthermore, cerium(IV) phosphate decomposes at temperatures higher than 500° (for the Ce(IV)–Ce(III) reduction), while this does not occur for fibrous thorium phosphate. On the other hand, thorium phosphate sheets are radioactive and have a lower flexibility than cerium(IV) phosphate sheets. For these reasons, work is being pursued in our laboratory to obtain non-radioactive but chemically stable new inorganic ion-exchange sheets.

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