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Synthesis, Composition, and Ion-Exchange Behavior of Thermally Stable Zr(IV) and Ti(IV) Arsenophosphates: Separation of Metal Ions

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Abstract

Two new inorganic ion-exchange materials, Zr(IV) and Ti(IV) arsenophosphates, have been synthesized. They are reproducible in behavior and possess excellent thermal stability. Their tentative structures have been proposed based on pH titrations, thermogravimetry, chemical analysis, IR studies, and other ion-exchange properties. Distribution studies of some metal ions have also been made on the basis of which several useful binary separations have been achieved such as Fe(III) from VO(II), Cu(II), and Zn(II); Pb(II) from Cu(II), Hg(II), and Zn(II); Ti(IV) from UO_2(II) and Ce(IV); and Mg(II) from Sr(II) and Ba(II).

INTRODUCTION

Inorganic ion exchange materials (*1*) are important for metal separations. Double salts show some peculiar characteristics over their single salt counterparts. Zirconium phosphosilicate (*2*), for example, has successfully been used for plutonium isolation, and titanium phosphosilicate (*3*) for the separation of radionuclides. Stannic vanadophosphate (*4*) and stannic arsenophosphate (*5–7*) possess appreciable ion-exchange capacity even at elevated temperatures. The present work is in continuation of our studies on the double salts as inorganic ion exchangers. Two new arsenophosphates of zirconium and titanium have been synthesized which possess high thermal and chemical stability. Also, some important binary metal separations have been achieved on their columns.

EXPERIMENTAL

Reagents

Zirconyl chloride used in this study was a product of J. T. Baker Chemical Co. (Phillipsburg, New Jersey). Titanic chloride (sp. gr. 1.73), ammonium ceric sulfate, and trisodium orthophosphate were obtained from the B.D.H. Poole (England), while disodium arsenate was an E. Merck (Darmstadt) product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH measurements were made on an Elico (India) model LI-10, while IR studies were performed on a Perkin-Elmer 621 Grating Infrared Spectrophotometer using a nujol phase. A temperature-controlled Sico (India) shaker was used for shaking purposes, and the TGA apparatus was from FCI (India). A Bausch and Lomb spectronic 20 colorimeter was used for the spectrophotometric studies.

Preparation of Reagent Solutions

A stock solution (1 *M*) of titanic chloride was prepared in a 30% HCl solution which was diluted to the desired concentration with demineralized water (DMW). Zirconyl chloride, ceric ammonium sulfate, disodium arsenate, and trisodium orthophosphate were dissolved in DMW directly. The metal ion solutions for the distribution studies were also prepared in DMW except for trivalent and tetravalent metals for which 2–3 drops of the corresponding acids were added to prevent hydrolysis.

Synthesis of the Ion-Exchange Materials

Different samples of zirconium, titanium, and ceric arsenophosphates were prepared by varying the concentration and mixing ratios as mentioned in Table 1. The pH of the mixture was fixed in the pH range 0–1 by adding nitric acid or ammonium hydroxide as appropriate with constant stirring. The gels thus obtained were kept at room temperature (30°C) overnight and filtered, washed with DMW, and dried at 40°C in an air oven. The dried products were immersed in DMW and the granules were converted into the H^+ form as usual (5). On the basis of their stability and ion-exchange capacity, Samples S-3 and S-8 were selected for further studies. The reproducibility was checked by preparing the samples and observing their ion-exchange properties several times.

TABLE 1

Preparation of Zr(IV), Ti(IV), and Ce(IV) Arsenophosphates

Sample no.	Sample	Concentration of mixing solutions (*M*)	Mixing ratio by volumes M:As:P	i.e.c. (meq/dry g for Na^+)
S-1	Zirconium arsenophosphate	0.1	1:1:1	0.82
S-2	Zirconium arsenophosphate	0.1	1:2:1	0.84
S-3	Zirconium arsenophosphate	0.05	1:1:1	0.94
S-4	Titanium arsenophosphate	0.1	2:1:1	1.0
S-5	Titanium arsenophosphate	0.1	1:1:2	1.2
S-7	Titanium arsenophosphate	0.1	1:1:1	1.27
S-8	Titanium arsenophosphate	0.05	1:1:1	1.31
S-9	Ceric arsenophosphate	0.05	1:1:1	0.60

Composition

Zirconium Aresenophosphate. 500 mg of the powdered exchanger was fused with a mixture of powdered potassium carbonate (3 g) and powdered potassium nitrate (1 g) in a platinum crucible. After fusion the product was boiled with DMW, and the insoluble material was filtered and ignited to ZrO_2 (*8*) and weighed. The filtrate was analyzed for the arsenic and phosphorous content as before (*5*).

Titanium Arsenophosphate. 500 mg of the powdered exchanger was dissolved in 20 mL of 8 *M* H_2SO_4 by heating. Titanium was precipitated as its hydroxide by using NH_4OH, filtered, ignited to TiO_2 (*9*), and weighed. Arsenic and phosphorous were determined in the filtrate as above.

The Zr:As:P and Ti:As:P ratios in the two samples were found to be 2:1:1 and 3:1:1, respectively.

Ion-Exchange Capacity (i.e.c.)

The i.e.c. of Samples S-3 and S-8 was determined as usual by the column process (*5*). The values in meq/dry g for different metals were:

ZrAsP:Na(I)(0.94), K(I)(1.35), Mg(II)(0.83), Ca(II)(0.91)
TiAsP:Na(I)(1.31), K(I)(1.82), Mg(II)(1.17), Ca(II)(1.24)

Thermal Stability

The samples were heated at various temperatures in a muffle furnace for 1 h each and the i.e.c. was determined as usual after cooling them to room

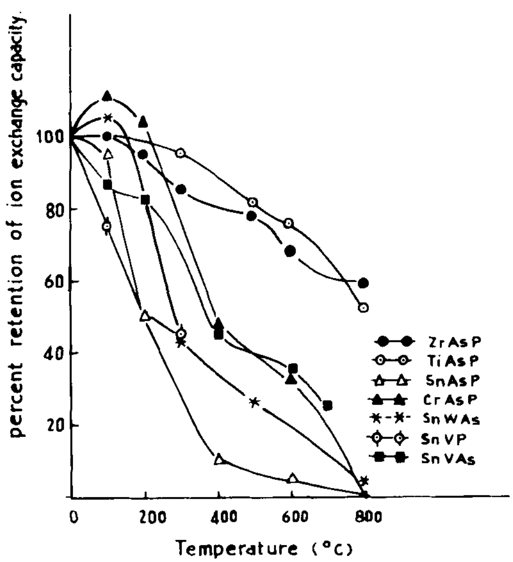

FIG. 1. Effect of temperature on the i.e.c. of different double salts.

temperature. Figure 1 shows the percent retention in the i.e.c. of some double salts such as Sn(IV) and Cr(III) arsenophosphates (5), Sn(IV) vandophosphate (*4*), Sn(IV) tungstoarsenate (*10*), and Sn(IV) vanadoarsenate (*11*), including those under study.

Chemical Stability

250 mg of the material was placed in a 25 mL solution of an acid or a base, with intermittent shaking for 24 h. The solution was then analyzed for the zirconium, titanium, phosphorous, and arsenic content by using standard spectrophotometric methods (*12–15*). Table 2 summarizes the results.

pH Titrations

500 mg of the exchanger was taken in each of several 250 mL conical flasks followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios (*16*), the final volume being 50 mL. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of OH^- added (Figs. 2 and 3).

TABLE 2

Chemical Stability of Zr(IV) and Ti(IV) Arsenophosphates

	Amount dissolved (mg)					
	Zr(IV) arsenophosphate			Ti(IV) arsenophosphate		
Solution	Zr	P	As	Ti	P	As
2 *M* HNO_3	0.06	0.13	0.20	10.5	0.9	0.84
4 *M* HNO_3	0.15	0.30	0.32	13.5	1.4	1.12
2 *M* HCl	0.06	0.38	0.42	7.2	1.75	1.60
4 *M* HCl	0.13	0.50	0.66	8.4	2.40	2.10
1 *M* H_2SO_4	0.56	0.45	0.60	11.2	2.70	2.50
2 *M* H_2SO_4	1.44	0.60	1.10	19.5	3.10	2.90
0.1 *M* KOH	0.12	6.80	7.10	0.0	5.30	4.40

Distribution Studies

These were performed in DMW and nitric acid (0.01 and 0.1 *M*) media for some common metal ions. 250 mg of the exchanger in the H^+ form was dipped in 25 mL of the solution containing the metal ion, not exceeding 3% of the total i.e.c. of the exchanger. The contents were shaken for 4 h at 30°C

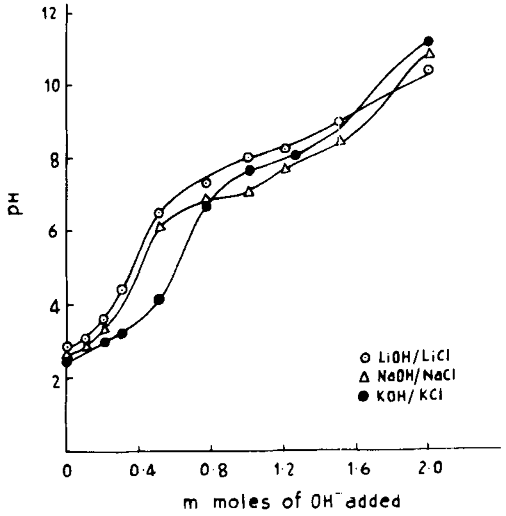

FIG. 2. pH titration curves for Zr(IV) arsenophosphate by added salt, batch method.

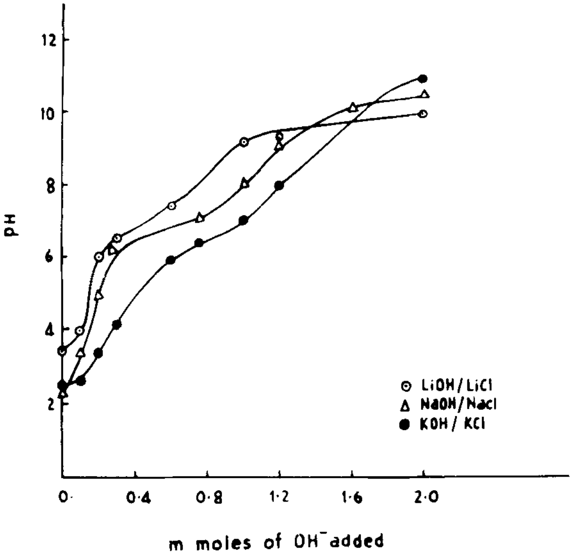

FIG. 3. pH titration curves for Ti(IV) arsenophosphate by added salt, batch method.

to achieve equilibrium, and the metal ions left in the solution were determined with EDTA as usual (*17*) except for Ti(IV), UO_2(II), and Ce(IV) which were determined spectrophotometrically (*13*, *18*, *19*). The K_d values were calculated by the usual expression (*6*). The distribution coefficients (K_d in mL/g) are summarized in Table 3.

Separations Achieved

Several binary separations were tried using a column containing 2 g of the sized (35–100 mesh) exchanger particles taken in a glass tube having an i.d. of ~0.6 cm. The metal ions were eluted at a flow rate of ~0.5 mL/min using eluants selected on the basis of the K_d values obtained. The metal ions in the effluent were determined as described above, and the results are summarized in Table 4.

DISCUSSION

The two ion-exchange materials prepared in these studies show a high thermal stability. They possess an appreciable i.e.c. (0.6–0.7 meq/dry g) even after heating to 800°C, a peculiar and unusual characteristic of an inorganic ion exchanger. A comparison with similar salts (Fig. 1) indicates

TABLE 3

K_d Values of Metal Ions on Zr(IV) and Ti(IV) Arsenophosphates in Different Media[a]

	ZrAsP			TiAsP		
Metal ion	DMW	0.01 *M* HNO_3	0.1 *M* HNO_3	DMW	0.01 *M* HNO_3	0.1 *M* HNO_3
Mg(II)	134	0	0	48	0	0
Ca(II)	188	0	0	95	12	8
Ba(II)	390	46	32	1560	21	19
Sr(II)	170	0	0	6500	181	181
Zn(II)	255	11	0	227	35	0
Cd(II)	860	6	0	291	15	0
Hg(II)	800	4	0	—	—	—
Pb(II)	TA	644	16	9500	1100	1100
Co(II)	360	40	1	—	—	—
Cu(II)	804	61	1	131	30	0
VO(II)	480	220	0	700	38	5
Ni(II)	217	10	9	48	0	0
Fe(III)	TA	TA	330	TA	2900	500
U(VI)	713	290	20	95	0	0
Y(III)	TA	2520	8	TA	160	4
Ce(III)	TA	124	35	TA	76	6
La(III)	TA	260	40	—	—	—
Al(III)	TA	860	0	TA	TA	0
Th(IV)	TA	460	89	TA	240	0
Ti(IV)	TA	TA	550	—	—	—
Ce(IV)	TA	525	440	550	525	400

[a] TA = total adsorption; (—) = metal ions not studied.

that the percent retention in the i.e.c. of zirconium and titanium arsenophosphates is higher than of any other compound of this type heated at temperatures ranging from 100 to 800°C. They can therefore be used for metal separations even after they have been heat treated. The solubilities of these materials in different acid and basic media indicate that they are fairly stable in 1 *M* mineral acids. Zirconium arsenophosphate appears to be more stable than the titanium salts in all the media used (Table 2). In alkali solutions above 0.1 *M*, both salts hydrolyze slowly. The elution of the H^- ions from the column of the ion-exchange material depends on the concentration of the eluant used. When a fixed volume (120 mL) of $NaNO_3$ solutions of varying concentrations (0.1 to 1 *M*) was used as eluant, the maximum i.e.c. was observed at a concentration of 0.5 *M* and above. The nature of the elution curves was similar to the one obtained for Sn(IV) arsenophosphate (5).

TABLE 4

Binary Separations of Metal Ions Achieved on Zr(IV) and Ti(IV) Arsenophosphates

Sample no.	Separation	Material used	Amount taken (μg)		Amount found (μg)		Error (%)		Eluant and its volume used for different metals
			M_1 (μg)	M_2 (μg)	M_1 (μg)	M_2 (μg)	M_1	M_2	
1	Mg–Sr	TiAsP	218 Mg	823 Sr	223 Mg	823 Sr	+2.3	0	Mg: 0.001 M HNO_3, 60 mL Sr: 0.1 M HNO_3, 60 mL
2	Mg–Ba	TiAsP	218 Mg	645 Ba	218 mg	631 Ba	0	−1.2	Mg: 0.001 M HNO_3, 60 mL Ba: 0.1 M HNO_3, 60 mL
3	Pb–Cu	TiAsP	597 Cu	1947 Pb	609 Cu	1906 Pb	+2.1	−2.2	Cu: 0.1 M HNO_3, 50 mL Pb: 1 M HNO_3 + 0.5 M NH_4NO_3, 60 mL
4	Pb–Hg	TiAsP	1925 Hg	1947 Pb	1925 Hg	1926 Pb	0	−1.1	Hg: 0.1 M HNO_3, 65 mL Pb: 1 M HNO_3 + 0.5 M NH_4NO_3, 60 mL
5	Pb–Zn	TiAsP	313 Zn	1947 Pb	320 Zn	1947 Pb	+2.1	0	Zn: 0.1 M HNO_3, 30 mL Pb: 1 M HNO_3 + 0.5 M NH_4NO_3, 60 mL
6	Fe–Zn	ZrAsP	339 Zn	491 Fe	339 Zn	502 Fe	0	+1	Zn: 0.1 M HNO_3, 40 mL Fe: 2 M HNO_3, 80 mL
7	Fe–VO	ZrAsP	575 VO	491 Fe	586 VO	480 Fe	−1.2	−2.2	VO: 0.1 M HNO_3, 40 mL Fe: 2 M HNO_3, 85 mL
8	Fe–Cu	ZrAsP	584 Cu	491 Fe	584 Cu	491 Fe	0	0	Cu: 0.1 M HNO_3, 30 mL Fe: 2 M HNO_3, 80 mL
9	Ti–UO	ZrAsP	480 Ti	1270 UO	474 Ti	1280 UO	−1.2	−0.8	UO_2: 0.1 M HNO_3, 40 mL Ti: 0.5 M H_2SO_4 + 3% H_2O_2, 40 mL
10	Ti–Ce	ZrAsP	480 Ti	1400 Ce	475 Ti	1390 Ce	−1.1	−0.8	Ce: 0.5 M H_2SO_4 + 1 M $(NH_4)_2SO_4$, 50 mL Ti: 0.5 M H_2SO_4 + 3% H_2O_2, 40 mL

These ion exchangers are probably bifunctional in behavior as indicated by their pH–titration curves (Figs. 2 and 3). The curves also reveal that the materials have a higher affinity for K(I) than for Na(I) or Li(I), which may be due to a smaller hydrated radius of the K(I) ion (γ_hK(I) = 2.32 Å, γ_hNa(I) = 2.76 Å, γ_hLi(I) = 3.40 Å). The i.e.c. values observed in the column process also point to the same conclusion. In the KOH/KCl system the first inflection point is obtained at pH ~ 4.3 for ZrAsP and at pH ~ 5.3 for TiAsP. However, the second inflection is not very sharp, probably due to a slow ion-exchange process or a wide spread of effective pK_a values. The pH–titration curves indicate a higher i.e.c. than obtained in the column process. Less acidic protons might also be removed in the former case.

The IR spectra show a number of strong and sharp peaks at frequencies of ~800, ~1000, ~1400, ~1500, ~1600, and ~2900 cm^{-1}. The first peak is indicative of the M-O stretching vibrations (*20*), while the next three are due to the presence of HPO_4^{2-}, $HAsO_4^{2-}$, PO_4^{3-}, and AsO_4^{3-} in the structure. The presence of water of crystallization is shown by the peaks at ~1600 and ~2900 cm^{-1}. The peak at ~1600 cm^{-1} is also indicative of a strongly hydrogen bonded OH or an extremely strongly coordinated H_2O. On heating the exchanger up to 300°C, the peaks at ~1600 cm^{-1} are broadened and become less intensive, perhaps due to a decrease in the interstitial water molecules in the structure. The same peaks were also observed in the IR spectra of Sn(IV) and Cr(III) arsenophosphates (5).

On the basis of chemical composition, TGA (Fig. 4), and IR studies, the following tentative formula is proposed for these materials: $[(TiO_2)_3(H_3AsO_4)(H_3PO_4)]\cdot nH_2O$ and $[(ZrO_2)_2(H_3AsO_4)(H_3PO_4)]\cdot nH_2O$. The value of n, the external water molecules, has been obtained using Alberti's equation (*21*).

$$18n = \frac{X(M + 18n)}{100}$$

where X = % weight loss in the material, M = molecular weight minus the external water molecules, and n = number of external water molecules.

From the TGA curves we find that the maximum weight loss is ~30% for both zirconium and titanium arsenophosphates. The weight loss observed at ~200°C is 12.5% for ZrAsP and 13% for TiAsP. If it is assumed that at this temperature only the external water molecules are removed from the exchanger, then the value of n, as obtained from the above equation, comes out to be ~4.

The potential of these ion exchangers has been demonstrated by achieving some important binary separations. For example, ZrAsP has shown the separation of Fe(III)–VO(II), Fe(III)–Cu(II), Fe(III)–Zn(II), Ti(IV)–

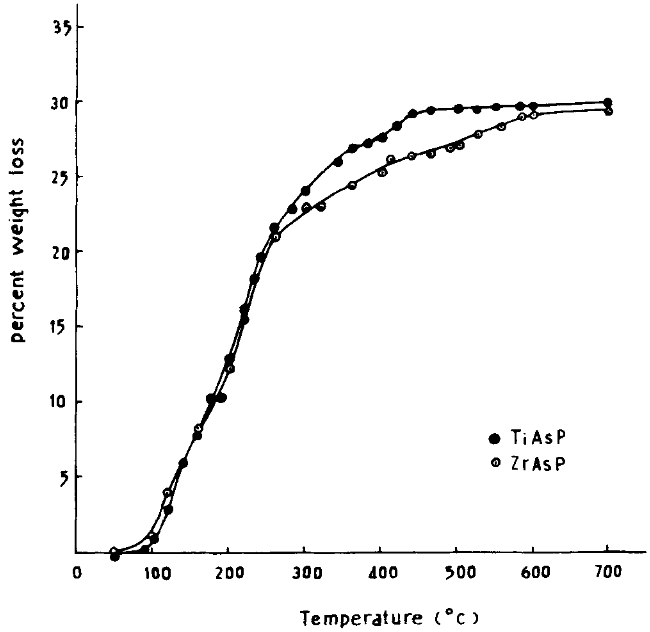

FIG. 4. TGA curves for Zr(IV) and Ti(IV) arsenophosphates in the H^+ form.

UO_2(II), and Ti(IV)-Ce(IV) on its column, which are important from the industrial point of view. The exchanger may therefore be useful in the analysis of ferrous alloys. Similarly, TiAsP gives such separations as Pb(II)-Hg(II), Pb(II)-Cu(II), Pb(II)-Zn(II), Mg(II)-Sr(II), and Mg(II)-Ba(II) which are of analytical importance. It is also highly selective for Pb(II), indicating a possibility of adsorbing lead selectively from its alloy solutions. The elutions are quick and sharp, and the results are fairly precise and reproducible as summarized in Table 4.

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