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Ion-Exchange and Selectivity Behavior of Thermally Treated and γ-Irradiated Phases of Zirconium(IV) Arsenophosphate Cation Exchanger: Separation of Al(III) from Some Metal Ions and Removal of Cations from Water

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Abstract

Ion-exchange and selectivity behavior of zirconium(IV) arsenophosphate (ZAP) has been studied systematically after thermal and irradiation treatments. As a result, an increase in the ion-exchange capacity and a complete reversal in the selectivity sequence for some common metal ions has been observed on heating. The modified phase of ZAP has been utilized successfully for the quantitative separation of aluminum from numerous metal ions and for the removal of cations from water.

INTRODUCTION

Zirconium(IV) arsenophosphate (ZAP), prepared earlier in these laboratories (*1*), has shown promising ion-exchange behavior for some common metal ions. It showed an increase in its ion-exchange capacity and an improvement in its chemical stability after thermal treatment. It was, therefore, decided to make a systematic study in this direction with the view of exploring the possibilities of some more useful applications of ZAP. The following pages summarize the ion-exchange behavior of the revised phases of this material after heat treatments and γ-irradiation, and its application in separation science.

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EXPERIMENTAL

Reagents

Zirconyl chloride, trisodium orthophosphate, and disodium arsenate used in this study were of AnalaR grade (98.5–99%) obtained either from the B.D.H. Poole (England) or from the E. Merck (Darmstadt).

Apparatus

pH measurements were made on an Elico (India) model LI-10 pH meter, and infrared studies were performed on a Beckman IR-20 spectrophotometer using KBr pellets. A Philips x-ray unit with a Mo-K_α target was used for x-ray studies, while a Bausch and Lomb spectronic-20 was used for colorimetry. Radiometric measurements were made in a well-type single channel analyzer with a NaI(Tl) detector obtained from the Electronic Corporation of India Ltd.

Synthesis of the Ion-Exchange Materials

ZAP was prepared (*1*) by the following method. Aqueous solutions (0.05 *M*) of zirconyl chloride, disodium arsenate, and trisodium orthophosphate were mixed in equal volumes and the pH of the mixture was fixed in the 0–1 range by adding nitric acid with constant stirring. The gel thus obtained was kept at room temperature (30°C) overnight and filtered, washed with demineralized water (DMW), and dried at 40°C in an air oven. The dried product was cracked in DMW to obtain granules which were converted into the H^+-form with 1 *M* HNO_3. It was then heated up to 200 and 400°C for 1 h each to get two separate phases, α-ZAP and β-ZAP, respectively, for further studies.

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

The Na^+-ion exchange capacity of the material was determined by the column process (*1*). It was found to be 1.03 and 0.94 meq/dry g for α-ZAP and β-ZAP, respectively, with a coefficient of variation <0.5 for 10 observations. Figure 1 shows the percent retention of the i.e.c. on heating the material up to various temperatures.

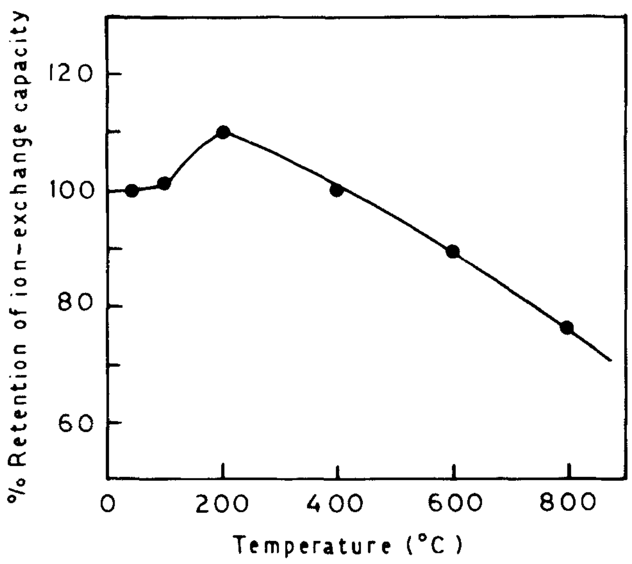

FIG. 1. Effect of temperature on the i.e.c. of Zr(IV) arsenophosphate.

γ-Irradiation

ZAP was exposed to γ-radiations obtained from a ^{60}Co-source for 96 h with a dose rate of 0.4 Mrd/h, $FeSO_4$ being the dosimeter. The sample thus obtained (γ-ZAP) showed an i.e.c. of 0.94 meq/dry g for Na^+.

Elution Behavior

250 mL $NaNO_3$ solutions of varying concentrations (0.1, 0.2, 0.5, and 1.0 *M*) were passed through several columns (internal diameter ~1 cm), each containing 1 g of α-ZAP in the H^+-form with a very slow flow rate (~0.5 mL/min). The H^+-ions thus eluted were titrated against a standard (0.1 *M*) NaOH solution and a maximum elution was observed with 1.0 *M* $NaNO_3$. To study the elution behavior, 100 mL of 1.0 *M* $NaNO_3$ solution was run through a column in the H^+-form and several 10 mL fractions of the effluent were collected at room temperature (30 ± 2°C). This was repeated at a working temperature of 95 ± 2°C by using a double-walled column, the outer part of which was surrounded by steam during the experiment. Figure 2

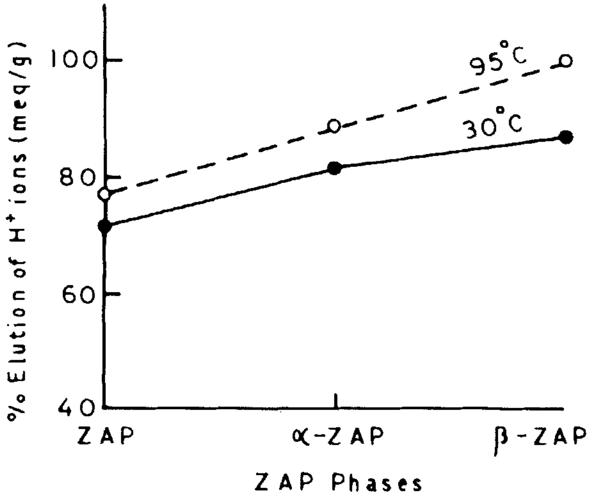

FIG. 2. Elution behavior of the various ZAP phases at 30 and 95°C as the working temperatures.

summarizes the percent elution of H^+-ions from the various phases studied, taking their original i.e.c. as the basis.

pH Titrations

pH titrations were performed by the method of Topp and Pepper (*2*) on the various phases. The curves are shown in Fig. 3.

Distribution Studies

250 mg of the sample was taken in a conical flask containing 25 mL of the solvent and shaken for 4 h at room temperature. Equilibrium was attained within 4 h as indicated by a concentration vs time curve. The metal ion concentration in the liquid phase was determined with EDTA (*3*). For alkali metals, however, the radiotracer technique was applied by taking the following isotopes (with their half-life periods shown in parentheses): ^{24}Na

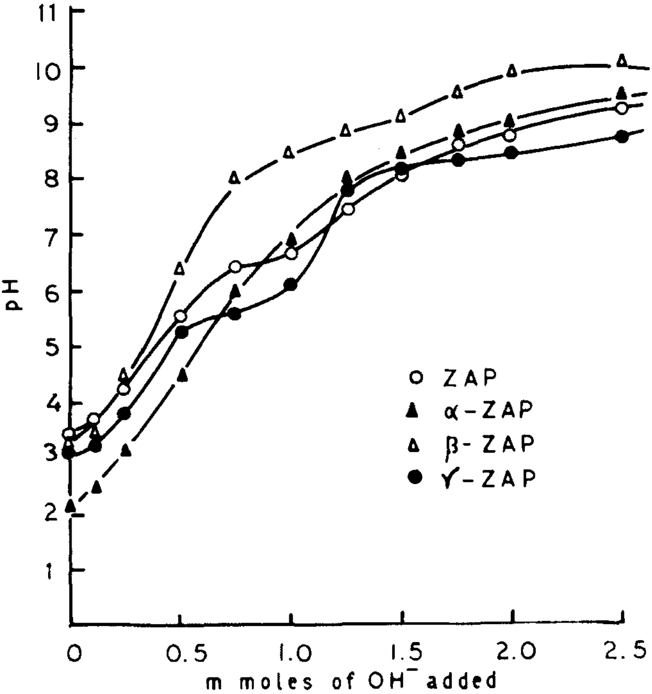

FIG. 3. pH titration curves for the various ZAP phases.

(15 h), ^{42}K (12.5 h), ^{86}Rb (18 days), ^{137}Cs (30.2 years). K_d values were calculated by

$$K_d = \left(\frac{1 - F}{F} \frac{V}{M}\right) \text{mL/g}$$

where F is the fraction of the total metal-ion concentration in the equilibrated solution phase, V is the volume of the solution (mL), and M is the mass of the exchanger (g). Table 1 summarizes the K_d values obtained on ZAP and α-ZAP samples in various solvents. Figure 4 shows the comparative distribution behavior of these two phases in DMW and 0.01 M HNO_3 solvent systems.

TABLE 1

K_d Values of Some Metal Ions on ZAP (*1*) and α-ZAP in Different Media

	$K_d \times 10^{-2}$									
	DMW		0.01 *M* HNO_3		0.10 *M* HNO_3		0.01 *M* $HClO_4$		0.10 *M* $HClO_4$	
Metal ion	ZAP	α-ZAP	ZAP	α-ZAP	ZAP	α-ZAP	ZAP	α-ZAP	ZAP	α-ZAP
Mg(II)	1.34	44.0	0.00	0.20	0.00	0.03	0.00	0.23	0.00	0.20
Al(III)	39.0	39.0	8.60	39.0	0.00	3.20	9.00	5.40	0.00	0.07
Ca(II)	1.88	37.0	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00
Mn(II)	5.25	35.3	0.36	0.52	0.00	0.45	0.20	0.16	0.00	0.06
Fe(III)	39.0	39.0	39.0	39.0	3.30	6.30	17.0	21.8	2.60	3.86
Co(II)	3.60	51.5	0.40	0.05	0.01	0.05	2.42	0.00	0.09	0.00
Ni(II)	2.17	51.5	0.10	0.68	0.09	0.20	0.12	0.05	0.08	0.00
Zn(II)	2.55	32.8	0.11	0.28	0.00	0.08	0.00	0.28	0.00	0.08
Sr(II)	1.70	31.5	0.00	0.00	0.00	0.00	0.12	1.40	0.00	0.97
Cd(II)	8.60	54.0	0.06	17.5	0.00	5.07	1.55	5.76	0.05	4.86
Ba(II)	3.90	19.0	0.46	0.83	0.32	0.65	0.58	1.31	0.36	1.06
Hg(II)	8.00	3.26	0.04	0.30	0.00	0.20	1.00	1.60	0.05	1.30
Pb(II)	56.5	56.5	6.44	3.60	0.16	2.68	5.66	2.68	0.18	0.67

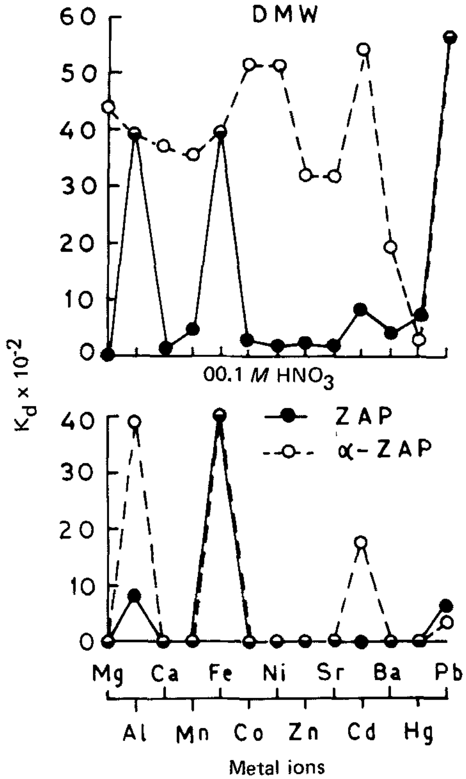

FIG. 4. Distribution behavior of ZAP and α-ZAP for various metal ions in DMW and 0.01 *M* HNO_3.

Separations Achieved

Two grams of the 60-100 mesh-sized particles of the exchanger (α-ZAP) in H^+-form were used for column operation in a glass tube having an internal diameter of ~0.6 cm. The column was then washed thoroughly with DMW and the mixture was loaded. After recycling 2 or 3 times to ensure complete adsorption of the mixture on the column bed, the elution of the metal ions other than Al(III) was done by 0.01 *M* HNO_3, selected on the basis of K_d values. Finally, aluminum(III) was removed with 0.1 *M* $HClO_4$. Table 2 summarizes the salient features of the separations achieved while Fig. 5 shows their elution curves.

TABLE 2
Some Salient Features of the Separations of Al(III) from Other Metal Ions on α-ZAP Columns

No.	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used and its volume (mL)	HETP (cm)
1.	Mn(II)–Al(III)	137.5 Mn	141.4 Mn	2.8	0.01 *M* HNO_3, 50	0.375
		67.50 Al	67.50 Al	0.0	0.10 *M* $HClO_4$, 40	—
2.	Mg(II)–Al(III)	60.00 Mg	60.00 Mg	0.0	0.01 *M* HNO_3, 40	0.135
		67.50 Al	67.50 Al	0.0	0.10 *M* $HClO_4$, 40	—
3.	Ni(II)–Al(III)	146.8 Ni	139.8 Ni	−4.9	0.01 *M* HNO_3, 30	0.960
		67.50 Al	67.50 Al	0.0	0.10 *M* $HClO_4$, 50	—
4.	Zn(II)–Al(III)	162.5 Zn	162.5 Zn	0.0	0.01 *M* HNO_3, 40	1.50
		67.50 Al	67.50 Al	0.0	0.10 *M* $HClO_4$, 40	—
5.	Pb(II)–Al(III)	520.0 Pb	508.7 Pb	−2.2	0.01 *M* HNO_3, 50	1.50
		67.50 Al	65.39 Al	−3.1	0.10 *M* $HClO_4$, 40	—
6.	Co(II)–Al(III)	147.3 Co	147.3 Co	0.0	0.01 *M* HNO_3, 50	0.735
		67.50 Al	67.50 Al	0.0	0.10 *M* $HClO_4$, 40	—
7.	Al(III) from a synthetic mixture	137.5 Mn 60.00 Mg 146.8 Ni 162.5 Zn 520.0 Pb 147.3 Co	—	—	0.01 *M* HNO_3, 150	—
		67.50 Al	67.50 Al	0.0	0.10 *M* $HClO_4$, 40	—

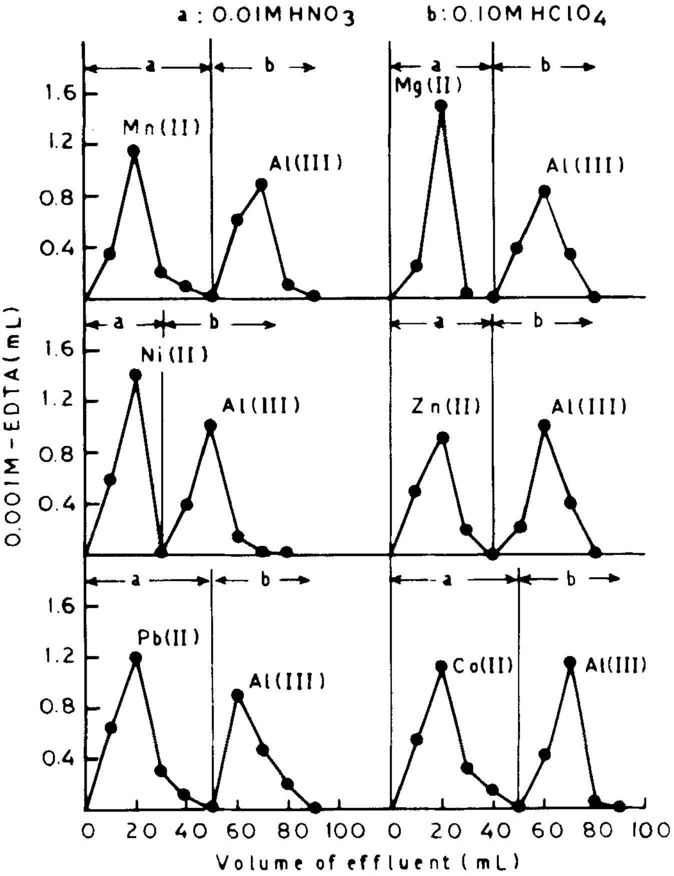

FIG. 5. Separation of Al(III) from other metal ions on α-ZAP columns.

DISCUSSION

This study highlights certain interesting features of zirconium(IV) arsenophosphate. As compared to the sample prepared after drying the gel at 40°C (ZAP), the sample obtained after heating it at 200°C for 1 h (α-ZAP) possesses a higher i.e.c. when determined at room temperature. Several repetitions invariably revealed that the increase in the i.e.c. is ~10% (Fig. 1). A higher working temperature (95 ± 2°C) further enhances this value. For example, the phase obtained after heating ZAP up to 400°C (β-ZAP) gives an i.e.c. almost equal to that of ZAP at room temperature. With 95°C as the working temperature, however, all three phases (ZAP, α-ZAP, and

β-ZAP) possess the same i.e.c. (1.2 meq/dry g). Thus a higher working temperature, preferably 95°C, appears to be more favorable for the exchange sites to become highly operative. A higher i.e.c. for α-ZAP as compared to ZAP is probably due to an irreversible removal of external water molecules on heating the material up to 200°C. This is substantiated by the thermogram of ZAP obtained in our earlier studies (*1*) which showed a weight loss equivalent to the net increase in the i.e.c. of ZAP on heating. The elution rate also appears to be affected by heating. It increases appreciably with an increase in the heating and working temperatures (Fig. 2). The pH-titration curve (Fig. 3) is, however, not affected significantly by the thermal treatment.

The effect of heating on the selectivity behavior of the material is summarized in Table 1. α-ZAP is highly selective for almost all the metal ions studied in DMW as against ZAP which is selective only for Al(III), Fe(III), Pb(II), and Cd(II) as Fig. 4 illustrates. In 0.01 *M* HNO_3, α-ZAP becomes selective only for Al(III), Fe(III), and Cd(II). These studies therefore reveal that α-ZAP has greater utility at elevated temperatures, which may be unsuitable for an ion-exchange resin. This material has also shown its potential for the quantitative separation of Al(III) from other metal ions, the results of which are shown in Table 2 and Fig. 5. The height equivalent to a theoretical plate (HETP) can be determined (*4*) by

$$\text{HETP} = \frac{Lb^2}{8V_{\text{max}}^2}$$

where L is the column height (12 cm), b is the peak width (mL) at a height of $0.368C_{\text{max}}$, and V_{max} is the eluant volume (mL) at peak. These values for the metals separated from Al(III) are summarized in Table 2.

Another important application of α-ZAP may be for the removal of metal ions from water. When a water sample containing metal impurities was passed through a small column (5 g) of α-ZAP, the impurities equivalent to 256 mg $CaCO_3$ were found removed from the sample. Since the ion exchanger is highly stable chemically, the effluant does not contain any amount of Zr(IV), P(V), or As(V) as determined by an atomic absorption spectrophotometer.

Table 3 summarizes the effect of γ-irradiation on some of the physical and ion-exchange properties of ZAP. As is clear from this table, an irradiation up to ~10^6 rads has a negligible effect. Only the pH titration is slightly affected. It shows bifunctional behavior after being irradiated as against the normal monofunctional behavior of the material (Fig. 3).

IR studies of these new phases reveal the presence of the same functional groups as observed in ZAP prepared earlier (*1*). These observations

TABLE 3
Effect of Irradiation on Some Physical and Ion-Exchange Properties of ZAP

No.	Ion-exchange property	Observations
1.	Appearance	No change
2.	Color	No change
3.	Ion-exchange capacity	No change
4.	pH titration	Very slight change (Fig. 3)
5.	Elution behavior	Becomes slightly sharper on irradiation
6.	Distribution behavior	Practically no change in the K_d values of alkali metals

supplement our experimental data about the persistance of i.e.c. in heated phases (α-ZAP and β-ZAP). X-ray diffractograms, however, do not show any peaks of appreciable intensity, thus indicating the amorphous nature of the material even on heating up to 400°C.

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