Crystalline Zirconium(IV) Hydrogenarsenate Hydrogenphosphate Monohydrate: Synthesis, Ion-exchange Properties, and Thermal Behaviour

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A new crystalline layered inorganic ion-exchanger with formula $Zr(HAsO_4)(HPO_4)\cdot H_2O$ has been prepared by refluxing the amorphous product. Its ion-exchange properties towards sodium ions and its thermal behaviour, together with that of the pure sodium phases obtained, are reported and discussed. The exchanger is very stable to hydrolysis and has a high exchange capacity. Its general behaviour is intermediate between that of $Zr(HPO_4)_2\cdot H_2O$ and $Zr(HAsO_4)_2\cdot H_2O$.

In recent years synthetic inorganic ion-exchangers of the class of acid phosphates or arsenates of tetravalent metals, with general formula $M(HEO_4)_2\cdot nH_2O$ (M = Ge, Ti, Zr, or Sn; E = P or As; n = 1, 2, *etc.*) have received increasing attention because of their potential employment in catalysis.[1-4]

In our investigation on the catalytic properties of zirconium(IV) hydrogenphosphate and other members of the class of crystalline layered materials, we have observed that for a given test reaction, their activity depends on the chemical compound, the degree of crystallinity, the structure of the phase present during the catalytic process, the thermal pre-treatment, surface area, *etc.*[5]

Since until now only 'single' salts have been investigated in this field, we were interested in studying the catalytic behaviour of 'mixed' materials [*i.e.* compounds containing two different tetravalent metals and a given anion (phosphate or arsenate) or two different anions and a given tetravalent metal], in order to determine how the gradual substitution of one tetravalent metal with another or one pentavalent element with another affects the catalytic activity of these materials.

Examples of mixed compounds are the crystalline zirconium–titanium phosphates with different compositions[6] and the amorphous arsenate phosphates of tetravalent metals,[7,8] studied merely as ion-exchangers.

The mixed zirconium–titanium acid phosphates were prepared by Clearfield and Frianeza[6] in an attempt to obtain pure phases with a controlled ion-sieve efficiency and to improve the poor stability towards hydrolysis of the single α-titanium acid phosphate, α-$Ti(HPO_4)_2\cdot H_2O$.

The amorphous arsenate phosphates of Ti, Zr, Sn, and Ce proved to be interesting for their selective ion-exchange properties. For the amorphous zirconium arsenate phosphate, with molar ratio Zr:As:P = 1:1:1, Varshney and co-workers[7,8] found that its ion-exchange capacity, rather low if compared to those of the layered crystalline acid phosphates, is maintained to some extent after ignition at 800 °C. The material is severely hydrolyzed in slightly alkaline media.[7]

In this paper we report the preparation, the ion-exchange behaviour towards sodium ions, and the chemical stability of the crystalline zirconium arsenate phosphate of formula $Zr(HAsO_4)(HPO_4)\cdot H_2O$, together with phase changes with temperature, with a view to its subsequent employment in catalysis. Comparisons with the single salts α-$Zr(HPO_4)_2\cdot H_2O$ and α-$Zr(HAsO_4)_2\cdot H_2O$ are also made.

Table 1. Analytical data for crystalline zirconium(IV) hydrogenarsenate hydrogenphosphate monohydrate

	Analysis (%)			
	ZrO_2	P_2O_5	As_2O_5	H_2O
Found for four representative preparations	35.65	20.65	33.30	10.40
	35.70	20.65	33.45	10.20
	35.70	20.50	33.30	10.50
	35.60	20.50	33.30	10.60
Calculated[a]	35.65	20.60	33.35	10.45

[a] Calculated for $ZrO_2(As_2O_5)_{0.5}(P_2O_5)_{0.5}\cdot 2H_2O$.

Experimental

Chemicals.—All reagents were Erba RPE-ACS products except $ZrOCl_2\cdot 8H_2O$, which was a Merck 'pro analysi' product.

Preparation of α-$Zr(HAsO_4)_2\cdot H_2O$ *and* α-$Zr(HPO_4)_2\cdot H_2O$. Crystalline zirconium(IV) hydrogenphosphate, $Zr(HPO_4)_2\cdot H_2O$, and hydrogenarsenate, $Zr(HAsO_4)_2\cdot H_2O$, were prepared as described[9,10] by refluxing the amorphous product in 10 mol dm^{-3} H_3PO_4 and 4 mol dm^{-3} H_3AsO_4 respectively, for 100 h. These preparations will be referred to throughout as (10,100) and (4,100) respectively, the first number in each case indicating the acid concentration and the second the reflux time.

Preparation of Crystalline Zirconium(IV) *Hydrogenarsenate Hydrogenphosphate.*—A solution (volume 500 cm^3) containing $ZrOCl_2\cdot 8H_2O$ (50 g) was added under stirring at room temperature to a 500-cm^3 solution containing 14.5 mol dm^{-3} H_3PO_4 (12 cm^3) and $3As_2O_5\cdot 5H_2O$ (40 g): a white gel immediately formed. The slurry to which was added 14 mol dm^{-3} HNO_3 (88 cm^3) was refluxed for 50 h; then, to help the crystallization process, the suspension was made 4 mol dm^{-3} in HNO_3 and refluxed for a further 50 h. After cooling, the solid was filtered off, washed with water till pH 4.5, and dried over P_4O_{10} under vacuum to constant weight.

Analytical data for four preparations of this crystalline product are summarized in Table 1 and show it to have the stoicheiometry $ZrO_2(As_2O_5)_{0.5}(P_2O_5)_{0.5}\cdot 2H_2O$. The first mole of water is lost by 150 °C, the second after heating at 700 °C.

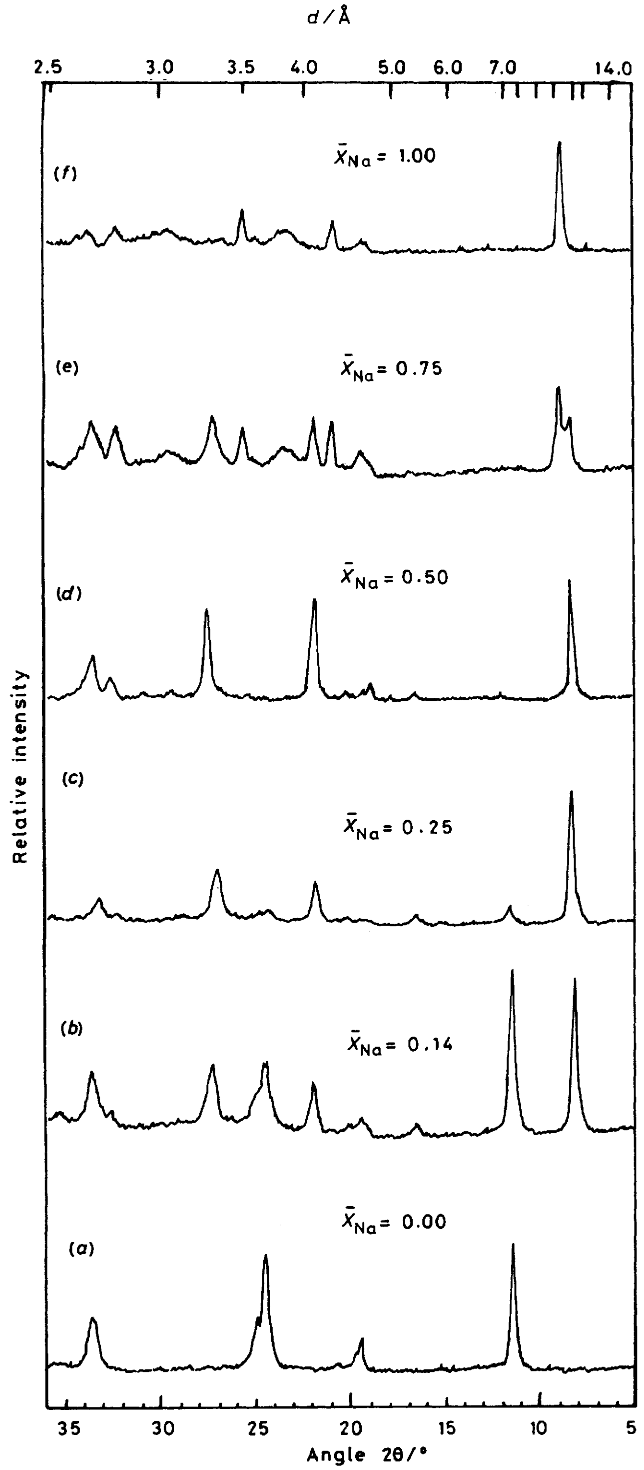

Figure 1. X-Ray diffraction patterns of samples at different Na^+ loadings, expressed in molar fraction of sodium content in the solid ($\bar{X}_{Na}$)

Titration Curve.—The titration of $Zr(HAsO_4)(HPO_4){\cdot}H_2O$ was carried out by the batch procedure, equilibrating several samples of exchanger (0.5 g) with 100 cm^3 of a 0.1 mol dm^{-3} (NaCl + NaOH) solution. In the range 70—100% conversion, the last amounts of titrant were added at intervals to prevent hydrolysis. After shaking at 20 °C for 3 d, the supernatant liquids were filtered off, analyzed for their arsenate and phosphate content, and their pH measured.

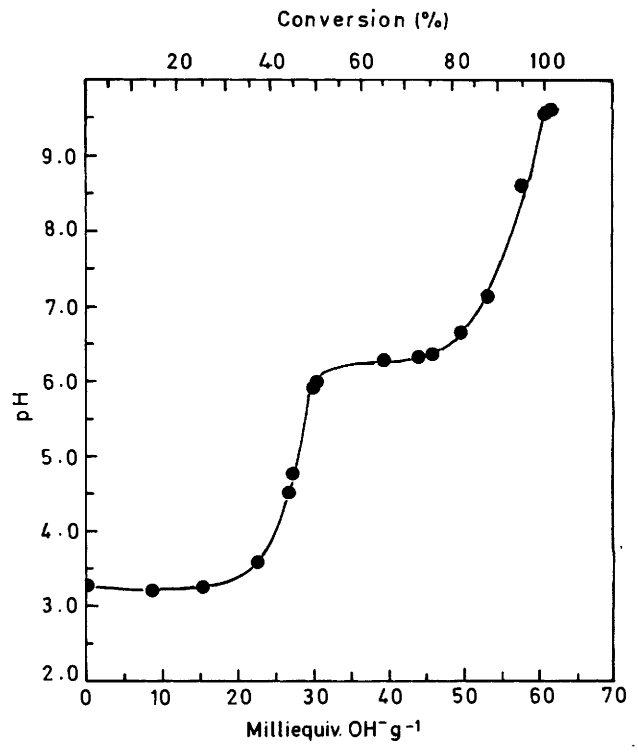

Figure 2. Titration-uptake curve for $Zr(HAsO_4)(HPO_4){\cdot}H_2O$: titrant 0.1 N NaOH + 0.1 N NaCl

Analytical Procedures and Physical Measurements.—The Zr:As:P ratio of crystalline $Zr(HAsO_4)(HPO_4){\cdot}H_2O$ was determined as follows: 300 mg of material were dissolved in 1 mol dm^{-3} HF (10 cm^3) and the solution diluted to 50 cm^3. Zirconium was determined gravimetrically as described,[11] in 10 cm^3 of this solution. Arsenate was determined iodometrically in 10 cm^3 of solution. Phosphate was determined colorimetrically as described,[12] in 2 cm^3 of solution. Since the method is also valid for the determination of arsenate, in order to subtract the unavoidable positive interference of this ion, the measurements were made against a reference solution containing the amount of arsenate present in the same volume, previously determined. A photoelectron DL spectrophotometer was used.

The same methods were employed for the determination of arsenate and phosphate present in the supernatant liquids of the batch-titration.

The solids (at various degrees of exchange) obtained from the titration were washed and conditioned over saturated $BaCl_2$ solution at 20 °C ($p/p_0 \simeq 0.9$).

X-Ray diffraction patterns were taken on a Philips PW 1130 diffractometer using nickel-filtered Cu-K_α radiation.

The water content of $Zr(HAsO_4)(HPO_4){\cdot}H_2O$, and of the pure phases formed during the titration, was determined from the weight losses during heating up to 900 °C.

Thermogravimetric (t.g.) and differential thermal analysis (d.t.a.) measurements were carried out on a Stanton simultaneous thermoanalyzer, model STA 781, with a heating rate of 5 °C min^{-1}, Pt/Pt–Rh (87 : 13) thermocouples, and platinum crucibles.

Results and Discussion

Although the structure of the new compound is not known, its X-ray powder diffraction pattern shown in Figure 1(*a*) (the corresponding *d* values are listed in Table 2) shows a great similarity with those of α-$Zr(HPO_4)_2{\cdot}H_2O$[13] and α-Zr(HAs-

Table 2. *X*-Ray powder diffraction spectra of the $\mathrm{ZrH_2(AsO_4)(PO_4)}$ forms and their dehydration products

$\mathrm{ZrH_2(AsO_4)(PO_4){\cdot}H_2O}$[a]		Layered $\mathrm{ZrAsPO_7}$[b]		Cubic $\mathrm{ZrAsPO_7}$[c]		$\mathrm{ZrH_2(AsO_4)(PO_4){\cdot}}n\mathrm{H_2O}$[d]	
d/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%
7.73	100	6.23	46	4.83	14	10.64	100
4.56	25	4.52	31	4.19	100	5.52	8
4.50	14	4.36	77	3.74	50	5.37	5
4.30	5	3.70	100	3.41	43	4.78	13
3.62	89	3.14	23	2.96	27	4.50	15
3.56	42	2.68	54	2.52	45	4.30	30
2.67	44	2.60	31	2.31	13	4.21	28
2.53	5					3.81	37
2.43	11					3.49	45
2.37	5					3.40	37
2.13	7					3.07	18
2.06	5					2.90	7
1.90	11					2.81	8
1.89	10					2.77	23
1.80	7					2.71	18
						2.67	28
						2.52	8
						2.41	5
						2.36	5

[a] Dried over $\mathrm{P_4O_{10}}$. [b] After heating at 650 °C. [c] After heating at 800 °C. [d] As prepared.

Table 3. *X*-Ray powder diffraction spectra of sodium half-exchanged $\mathrm{ZrH_2(AsO_4)(PO_4){\cdot}H_2O}$ and its dehydration products

$\mathrm{ZrHNa(AsO_4)(PO_4){\cdot}4H_2O}$[a]		$\mathrm{ZrHNa(AsO_4)(PO_4){\cdot}H_2O}$[b]		$\mathrm{ZrHNa(AsO_4)(PO_4)}$[c]		$\mathrm{NaZr_2(As_{0.5}P_{0.5}O_4)_3}$[d]	
d/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%
10.71	100	8.00	80	7.19	50	6.46	48
5.30	8	4.40	43	4.64	10	4.63	44
4.65	16	4.21	100	4.41	10	4.49	46
4.55	10	3.86	8	4.03	25	3.87	100
4.36	8	3.55	71	3.95	37	3.22	47
4.23	5	3.33	26	3.85	100	2.91	100
4.03	86	3.19	91	3.26	15	2.60	21
3.52	5	2.97	18	2.85	37	2.59	46
3.25	78	2.86	14	2.79	37	2.31	5
3.03	5	2.81	14	2.59	25	2.21	12
2.74	17	2.73	48			2.14	5
2.66	35	2.59	51			2.11	5
2.46	5					2.05	21
2.40	8					2.01	10
2.17	8					1.97	7
2.10	8					1.95	3
						1.93	31

[a] Conditioned at 90% relative humidity. [b] Dried over $\mathrm{P_4O_{10}}$. [c] After heating at 300 °C. [d] After heating at 700 °C.

$\mathrm{O_4)_2{\cdot}H_2O}$.[14] These data together with the ion-exchange and thermal behaviour given below, strongly support the hypothesis that the material possesses an α-type layered structure. As a consequence, we assign the new compound the formula $\mathrm{Zr(HAsO_4)(HPO_4){\cdot}H_2O}$ and assume the first *d* value of 7.73 Å as the distance between two adjacent planes of zirconium atoms (d_{002}).

Ion-exchange Properties of Crystalline $\mathrm{Zr(HAsO_4)(HPO_4){\cdot}H_2O}$ *towards Sodium Ions.*—Figure 2 shows the titration and uptake curves for the $\mathrm{Na^+ \longrightarrow \bar{H}^+}$ process.* The curves are practically coincident since only negligible amounts of arsenate and phosphate ions were found in the solutions below pH 10. All data refer to 1 g of exchanger.

The titration process occurs in two stages, each stage requiring *ca.* 2.95 milliequiv. of $\mathrm{OH^-}$ ions. The total amount of NaOH employed (5.85 milliequiv.) is in good agreement with the theoretical ion-exchange capacity of the exchanger (5.80 milliequiv. $\mathrm{g^{-1}}$) calculated by considering two exchangeable hydrogens per mole formula.

X-Ray patterns of the samples at various degrees of $\mathrm{Na^+}$ uptake (Figure 1) completely agree with the shape of the titration curve. In the plateaux (constant pH 3.3 and 6.3 respectively) two phases are present, while along the slopes only one phase is found, in agreement with the phase rule.[15] Up to 3% $\mathrm{Na^+}$ uptake, the solid maintains the structure of the dihydrogen form, then, in the range of 4—30% $\mathrm{Na^+}$ loading, a new phase with an interlayer distance of 10.64 Å co-exists with the phase at d_{002} = 7.73 Å, the former increasing and the latter decreasing in intensity with $\mathrm{Na^+}$ uptake [Figure 1(*b*) and (*c*)]. At the end of the plateau ($\simeq$30% of $\mathrm{Na^+}$ exchanged) only the '10.64 Å' phase is present. The subsequent sodium uptake up to 50% occurs with the formation of a solid solution since no other phases appear: the interlayer distance of the phase present gradually shifts from 10.64 to 10.71 Å.

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* $\mathrm{Na^+ \longrightarrow \bar{H}^+}$ represents $\mathrm{Na^+}$ replacing $\mathrm{H^+}$ in the exchanger.

Table 4. *X*-Ray powder diffraction spectra of sodium full-exchanged $ZrH_2(AsO_4)(PO_4)\cdot H_2O$ and its dehydration products

$ZrNa_2(AsO_4)(PO_4)\cdot 3H_2O$ [a]		$ZrNa_2(AsO_4)(PO_4)\cdot H_2O$ [b]		$ZrNa_2(AsO_4)(PO_4)$ [c]	
d/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%
9.93	100	9.76	100	7.10	20
4.52	9	7.89	7	4.60	15
4.20	29	4.50	15	4.48	14
3.76	13	4.18	47	4.38	22
3.53	9	3.74	20	3.95	100
3.44	38	3.52	4	3.86	30
3.30	7	3.42	38	3.21	15
2.96	13	3.27	4	3.16	22
2.74	20	3.21	4	2.97	90
2.63	13	2.97	20	2.91	35
2.59	9	2.72	23	2.64	45
		2.61	25	2.60	17
				2.27	7
				1.97	35

[a] Conditioned at 90% relative humidity. [b] Dried over P_4O_{10}. [c] After heating at 700 °C.

At 50% Na^+ conversion the phase has the composition $ZrHNa(AsO_4)(PO_4)\cdot 4H_2O$. Its *X*-ray pattern is shown in Figure 1(*d*), while the *d* values are reported in Table 3.

The same reasoning applies between 50 and 100% of exchange. Here the new phase, possessing an interlayer distance of 9.93 Å, co-exists with the half-sodium form until at *ca.* 85% Na^+ loading [Figure 1(*e*)]; after this point it is the only one present. At the end of the process the new phase, still with d_{002} = 9.93 Å, has a composition $ZrNa_2(AsO_4)(PO_4)\cdot 3H_2O$ since the degree of hydrolysis is negligible. Its *X*-ray diffraction pattern is shown in Figure 1(*f*) and the corresponding *d* values are reported in Table 4.

The ion-exchange behaviour of $Zr(HAsO_4)(HPO_4)\cdot H_2O$ towards sodium ions is very similar to that found on titrating α-$Zr(HAsO_4)_2\cdot H_2O$ (4,100)[10] and α-$Zr(HPO_4)_2\cdot H_2O$(10,100),[16] the only difference is that the new exchanger exhibits shorter plateaux and wider slopes.

It is known that, for a given exchanged cation, the shape of the titration curve for these layered materials depends on the degree of crystallinity:[17,18] the lower the degree of crystallinity, the shorter is the plateau and therefore the wider is the step involving the solid solution formation (slope).[18,19]

In order to obtain information on the degree of crystallinity of $Zr(HAsO_4)(HPO_4)\cdot H_2O$, the procedure of Alberti *et al.*[20] was employed. These authors found that the back-titration of the half-sodium form of the α-$Zr(HPO_4)_2\cdot H_2O$ with the highest degree of crystallinity restores the monohydrated dihydrogen form, $Zr(HPO_4)_2\cdot H_2O$ (d_{002} = 7.56 Å), while zirconium(IV) hydrogenphosphates with gradually decreasing crystallinities give mixtures of a '7.56 Å phase,' and $Zr(HPO_4)_2\cdot 6H_2O$ (d_{002} = 10.4 Å) (termed θ-ZP by Clearfield *et al.*[21]), or $Zr(HPO_4)_2\cdot 6H_2O$ and a hydrogen phase with d_{002} = 11.5 Å. Pure $Zr(HPO_4)_2\cdot 6H_2O$ was obtained from the half-sodium form of α-$Zr(HPO_4)\cdot H_2O$ (10,100), which has a medium-to-low degree of crystallinity. This procedure applied on $Zr(HAsO_4)(HPO_4)\cdot H_2O$ and α-$Zr(HAsO_4)_2\cdot H_2O$ (4,100) gave pure dihydrogen forms $Zr(HAsO_4)(HPO_4)\cdot nH_2O$ and $Zr(HAsO_4)_2\cdot nH_2O$ ($n \gg 1$) respectively. Left in air, the materials lose water and the monohydrated dihydrogen forms are rapidly re-obtained as for $Zr(HPO_4)_2\cdot 6H_2O$. The *d* values of the highly hydrated $Zr(HAsO_4)(HPO_4)$ are given in Table 2.

From these experiments, it can be supposed that $Zr(HAsO_4)(HPO_4)\cdot H_2O$, prepared by refluxing the amorphous product for 100 h, should possess a degree of crystallinity comparable to that of α-$Zr(HPO_4)_2\cdot H_2O$ (10,100) and α-$Zr(HAsO_4)_2\cdot H_2O$ (4,100).

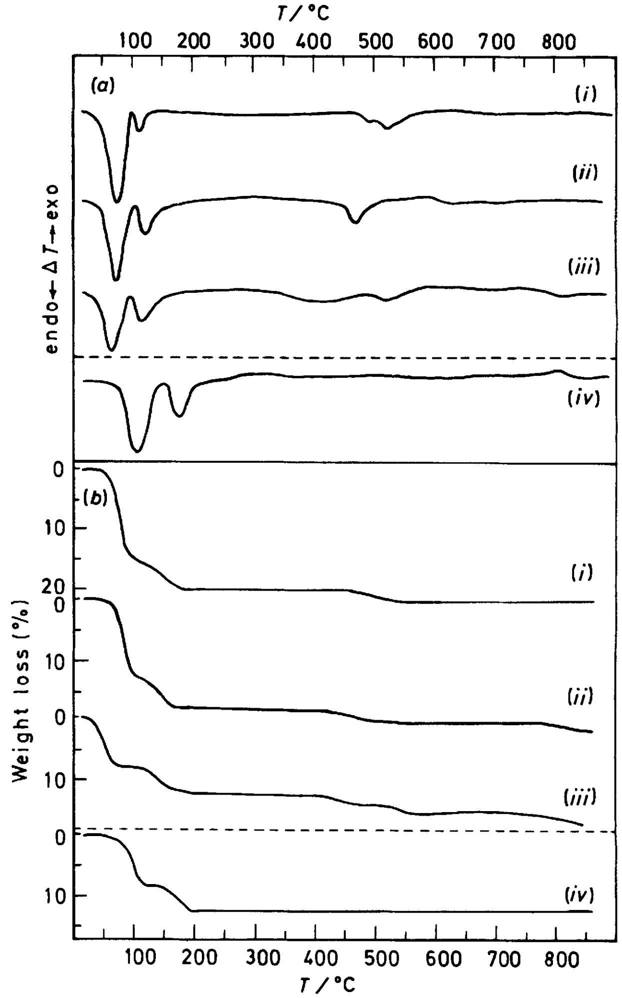

Figure 3. (*a*) D.t.a. and (*b*) t.g. curves of (*i*) $ZrH_2(PO_4)_2\cdot H_2O$, (*ii*) $ZrH_2(AsO_4)(PO_4)\cdot H_2O$, (*iii*) $ZrH_2(AsO_4)_2\cdot H_2O$, and (*iv*) $ZrH_2(AsO_4)(PO_4)\cdot nH_2O$ (regenerated)

Thus the shorter plateaux and wider slopes observed in the titration curve of $Zr(HAsO_4)(HPO_4)\cdot H_2O$ could be due either to the low degree of crystallinity or to a greater tendency of the mixed exchanger to give solid solutions because of the presence

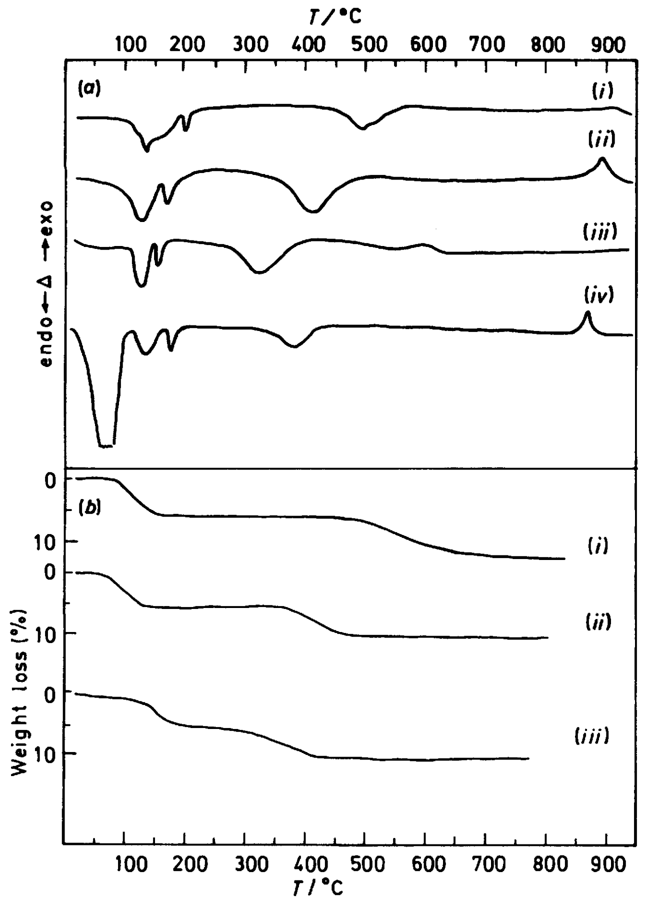

Figure 4. (a) D.t.a. and (b) t.g. curves of (i) $ZrHNa(PO_4)_2·5H_2O$, (ii) $ZrHNa(AsO_4)(PO_4)·4H_2O$, (iii) $ZrHNa(AsO_4)_2·3H_2O$, and (iv) $ZrNa_2(AsO_4)(PO_4)·3H_2O$

in the lattice layer of atoms (P and As) with analogous chemical characteristics but different dimensions.

Thermal behaviour of $Zr(HAsO_4)(HPO_4)·H_2O$ *and the Sodium-exchanged Phases.*—In order more completely to characterize the new ion-exchanger, the thermal behaviour of the dihydrogen and sodium forms of $Zr(HAsO_4)(HPO_4)·H_2O$ was studied and the results compared with those for the corresponding α-$Zr(HPO_4)_2·H_2O$ and α-$Zr(HAsO_4)_2·H_2O$ phases.

Figure 3 shows the t.g. and d.t.a. curves obtained from $ZrH_2(AsO_4)(PO_4)·H_2O$, $ZrH_2(AsO_4)_2·H_2O$, and $ZrH_2(PO_4)_2·H_2O$. $ZrH_2(AsO_4)(PO_4)·H_2O$ loses the mole of hydration water in the range 40—150 °C, and the related endothermic effect is narrower than those of $ZrH_2(AsO_4)_2·H_2O$ and $ZrH_2(PO_4)_2·H_2O$. The second endothermic effect (which is connected with a reversible phase transition) is thus better resolved than in the case of the other two exchangers.[22] It must be pointed out that in the case of $ZrH_2(AsO_4)(PO_4)·H_2O$ the phase transition occurs on the anhydrous phase, whilst for the other two materials it occurs on not completely dehydrated phases.

The third endothermic effect is related to the condensation of the ≡As–OH and ≡P–OH groups and the process takes place in the range 340—470 °C. The analogous processes for $ZrH_2(AsO_4)_2$ and $ZrH_2(PO_4)_2$ occur in the ranges 300—370 and 450—600 °C, respectively. Therefore, the thermal stability of these dihydrogen phases decreases as the phosphate groups are substituted with the arsenate ones.

After the condensation process, a layered zirconium pyroarsenophosphate is formed; above 800 °C, this transforms into a cubic pyro-compound (Table 2) behaving in exactly the same fashion as do $ZrH_2(PO_4)_2·H_2O$ and the other layered exchangers of this class.[23]

Figure 4 shows the t.g. and d.t.a. curves of $ZrHNa(AsO_4)(PO_4)·4H_2O$, together with those of $ZrHNa(AsO_4)_2·3H_2O$ and $ZrHNa(PO_4)_2·5H_2O$ for comparison.

The three half-exchanged materials lose their hydration water between 40 and 200 °C. The process occurs in two steps. The first weight loss leads to monohydrated phases, the second to anhydrous phases. Each monohydrated or anhydrous phase possesses a well defined interlayer spacing, which decreases with the decreasing water content.

The *X*-ray diffraction analysis shows that below 400 °C, all the materials maintain the layered structure. For the $ZrHNa(AsO_4)(PO_4)$ forms, d_{002} varies from 10.71 Å for the tetrahydrated compound, to 7.19 Å for the anhydrous phase heated at 300 °C.

In the range 400—500 °C, $ZrHNa(AsO_4)(PO_4)$ undergoes the condensation process. At 500 °C the solid is amorphous, then, at *ca.* 600 °C (after the occurrence of the exothermic peak in the d.t.a. curve) a recrystallization takes place with the formation of a new phase, isostructural with $NaZr_2(PO_4)_3$ and $NaZr_2(AsO_4)_3$ obtained by heating $ZrHNa(PO_4)_2$[24] and $ZrHNa(AsO_4)_2$[25] at 650 °C. The new phase should correspond to a sodium dizirconium tris(arsenate phosphate) with formula $NaZr_2(As_{0.5}P_{0.5}O_4)_3$.

The *X*-ray patterns of the various phases obtained from $ZrHNa(AsO_4)(PO_4)·4H_2O$ are reported in Table 3.

The t.g. and d.t.a. curves of $ZrNa_2(AsO_4)(PO_4)·3H_2O$ are also shown in Figure 4. The dehydration process is quite similar to that observed in the case of $ZrNa_2(PO_4)_2·3H_2O$.[24] The three moles of water are lost in two steps: two moles between 50 and 150 °C and the last mole between 150 and 200 °C. From 200 up to 780 °C, neither weight losses nor other phenomena are observed and the solid maintains the layered structure. At *ca.* 850 °C, after the occurrence of an exothermic peak in the d.t.a. curve, besides the layered phase, a new phase begins to form, the evolution of which cannot be followed because the material decomposes after 950 °C, with gradual elimination of As_2O_5.

The *X*-ray patterns of the various phases obtained from $ZrNa_2(AsO_4)(PO_4)·3H_2O$ are given in Table 4.

Conclusions

It is possible to prepare reproducibly, as a single crystalline phase, a layered mixed inorganic ion-exchanger containing two anions in a 1:1 ratio, *i.e.* $Zr(HAsO_4)(HPO_4)·H_2O$, which is isostructural with $Zr(HPO_4)_2·H_2O$ and $Zr(HAsO_4)_2·H_2O$, and posseses an interlayer spacing of 7.73 Å, intermediate between those of the last two compounds.

We believe that obtaining a single phase with the least favourable molar ratio (As:P = 1:1) presumably indicates that the Zr arsenate phosphate system shows a wide, if not complete, miscibility.

The substitution of P with As allows not only the variations in the ion-exchange and thermal properties of these materials to be gradually followed, but also the strength of their acidic sites when employed as acid catalysts. A study in this area is in progress.[5]

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