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Intercalation of *n*-alkylamines into layered materials: a method for the recognition of isomorphism in semicrystalline compounds

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n-Alkylamines were intercalated into $Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$ (TiOAs) and $Zr_2O_3(HAsO_4)\cdot 3H_2O$ (ZrOAs) by exposing the solids to the amine vapour. The formulae of the intercalation compounds are $Ti_2O_3(H_2AsO_4)_2\cdot 1.7C_nH_{2n+1}NH_2\cdot 2H_2O$ and $Zr_2O_3(HAsO_4)\cdot 0.6C_nH_{2n+1}NH_2\cdot 2H_2O$ ($n = 3$–6), respectively. The intercalated amines form bimolecular layers in the interlayer space of the polyvalent metal arsenates. The changes in the basal spacing of the intercalation compounds as a function of the length of the alkyl chain were used for evaluation of the free area associated with each active centre in the arsenate layers: 11.8 (TiOAs) and 10.8 Å^2 (ZrOAs). The comparison of these data with analogous data reported for *n*-alkylamine intercalation into other metal(IV) arsenates and metal(IV) phosphates resulted in the formulation of a procedure for the recognition of isomorphism in semicrystalline compounds.

Introduction

The synthesis and characterisation of layered tetravalent metal phosphates has extensively been studied over the past three decades. α-$Zr(HPO_4)_2\cdot H_2O$ (α-ZrP) and γ-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ (γ-ZrP), in addition to their isomorphic titanium(IV) phosphates, are typical representatives of such layered compounds.[1,2] The structural features, physical and chemical properties, applications as selective ion exchangers, acid catalysts, proton conductors and novel functionalised materials of different layered polyvalent metal phosphates have been reported and discussed in books and reviews.[3–8]

Recent implementations of *soft chemistry* approaches to the synthesis of layered compounds have resulted in the discovery of several novel metastable phases of metal(IV) phosphates and arsenates.[9–13] For example, a new layered titanium(IV) phosphate, $Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$ (TiOP), was synthesized in 1996.[14] Crystalline sodium titanium oxides, $Na_2Ti_3O_7$ and $Na_4Ti_9O_{20}$, were used as initial titanium-containing reagents for the preparation of these layered compounds. Titanium(IV) arsenate, $Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$ (TiOAs), possessing a similar formula was prepared by acid treatment of $NH_4TiOAsO_4$ at ambient temperature.[15] Alkaline leaching of α-ZrP, carried out under mild hydrothermal conditions, resulted in the formation of new Zr-rich layered compounds (ψ phases), $Zr_2O_3(MPO_4)\cdot nH_2O$ (M = Na or K).[16] ψ-Zirconium phosphates exhibit unique chemical stability in alkaline media, possess ion-exchange properties and show a distinct preference for the uptake of large cations. It has recently been found that ψ-ZrP-type compounds may be prepared by a direct reaction between zirconium- and phosphorus-containing reagents in alkaline media under mild hydrothermal conditions.[17] Zirconium(IV) arsenates, $Zr_2O_3(MAsO_4)\cdot nH_2O$ (M = Na or K; $n = 1$–3), were also prepared by this route.[18] ψ-ZrP and ψ-ZrAs could easily be converted into the proton phases, $Zr_2O_3(HPO_4)\cdot 1.5H_2O$ (ZrOP) and $Zr_2O_3(HAsO_4)\cdot 3H_2O$ (ZrOAs), by treatment with mineral acids. Unfortunately, all these new compounds have relatively low crystallinity and as a result their structures are still unknown.

The intercalation behaviour of layered titanium and zirconium phosphates has been studied extensively.[1,4,19,20] However, the intercalation data have, until now, never been used as an indirect probe for characterisation of the polyvalent metal phosphate layer structure. This paper is an attempt to show the validity of such an approach. In doing this the intercalation reactions of *n*-alkylamines with two layered metal(IV) arsenates of unknown structure, $Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$ and $Zr_2O_3(HAsO_4)\cdot 3H_2O$, were studied. The data obtained are compared to previously reported data for the intercalation of *n*-alkylamine into the analogous phosphates, $Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$[14] and $Zr_2O_3(HPO_4)\cdot 1.5H_2O$.[16]

Results and discussion

Intercalation into $Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$ (TiOAs)

The intercalation of *n*-alkylamines into layered acid phosphates may be considered as an acid–base topotactic solid-state reaction between an acid host and Brönsted-base guests.[21] The process is controlled by diffusion of the amine molecules in the solid, and the rate of the intercalation reaction decreases with increase in the length of the alkylamine chain.[22] Two particular behaviours should be distinguished.

In the case of methyl- and ethyl-amine intercalation layered organo-inorganic materials are formed at the beginning. However, further contact of the solids with the amine vapours transforms the former into amorphous gels and the percentage of amine in the solid phase increases dramatically. Fig. 1(a) shows the SEM image of the starting material (TiOAs). This layered compound (basal spacing 10.2 Å) is made up of pseudo-globular particles formed by non-ordered thin flakes. The intercalation of small amounts of methylamine does not appreciably change the morphology of the solid (Fig. 1(b)), which retains its layered structure. The amorphisation process leads to the formation of inter-particle aggregates containing a high amount of non-protonated methylamine (Fig. 1(c)).

The intercalation of $C_nH_{2n+1}NH_2$ ($n = 3$–6) originates only layered materials. The equilibrium time strongly depends on the length of the alkylamine used and varies from 3 days contact in the case of propylamine to more than 40 days in the case of hexylamine. The elemental analysis data and tentative formulae

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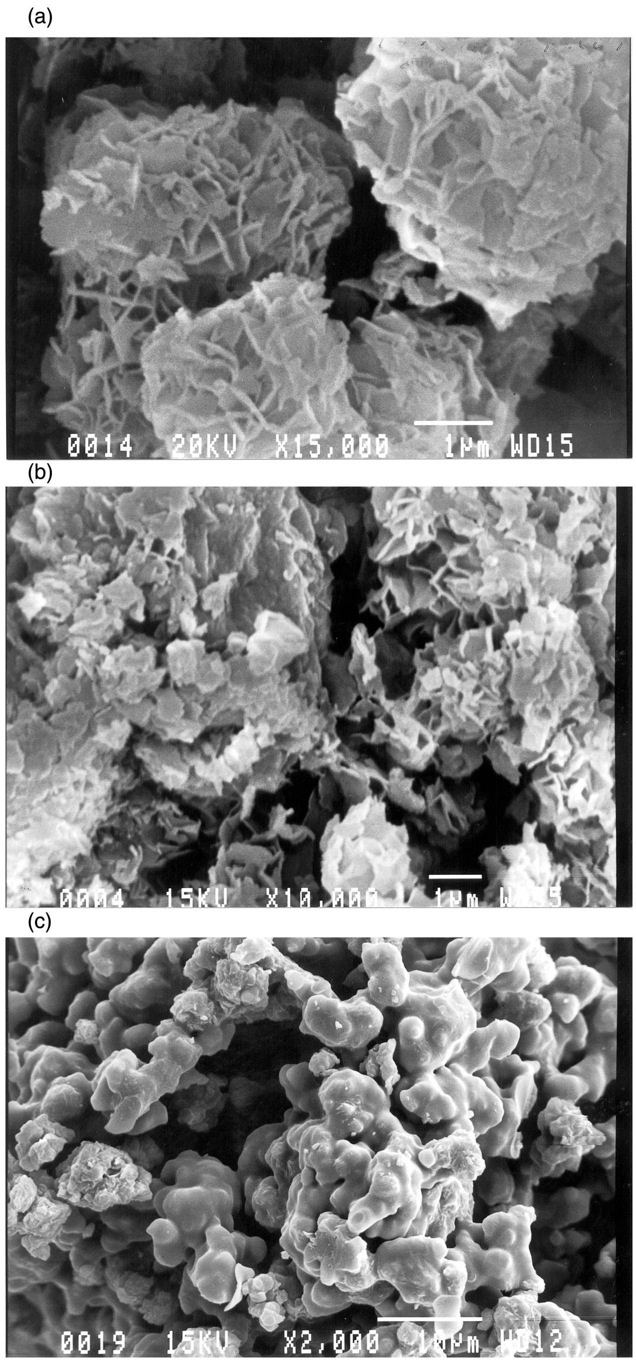

Fig. 1 SEM images of: (a) TiOAs, (b) TiOAs contacted with methylamine 7 h, and (c) (b) after 2 days.

Table 1 Microanalytical data for the $Ti_2O_3(H_2AsO_4)_2\cdot 1.7C_nH_{2n+1}$-$NH_2\cdot 2H_2O$ intercalation compounds

	Experimental			Calculated		
Amine	% C	% H	% N	% C	% H	% N
Propylamine	10.01	4.60	4.72	10.89	4.15	4.24
n-Butylamine	13.68	4.66	4.07	13.93	4.56	4.06
n-Pentylamine	15.97	4.97	3.89	16.73	4.94	3.90
n-Hexylamine	20.08	5.85	4.05	19.33	5.29	3.76

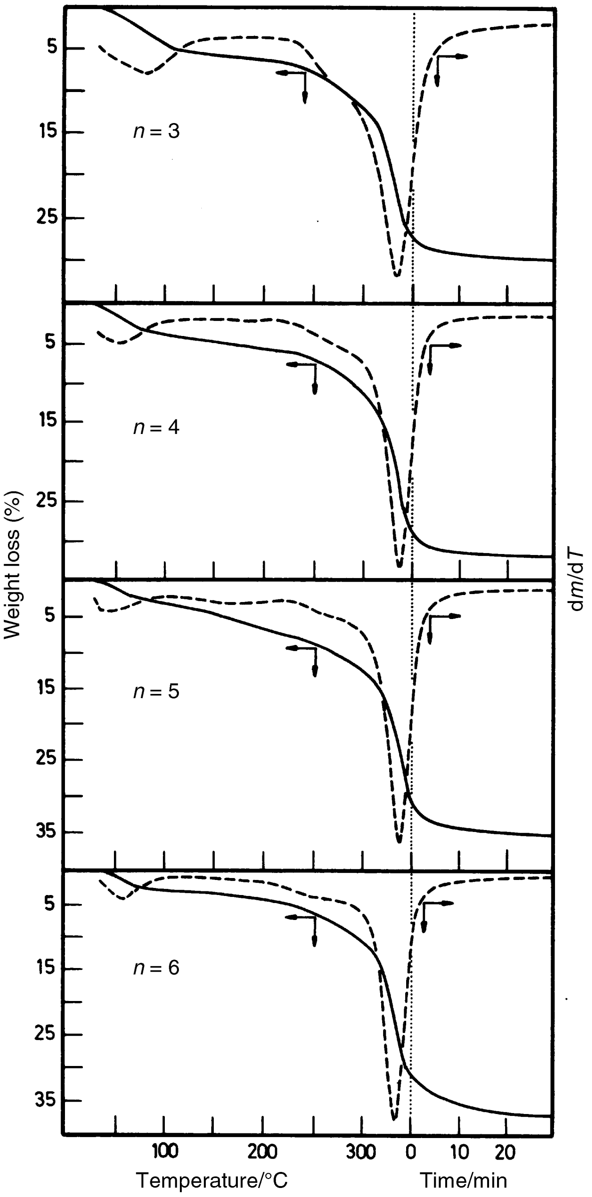

Fig. 2 TG (—) and DTG (---) curves of $Ti_2O_3(H_2AsO_4)_2\cdot 1.7C_nH_{2n+1}$-$NH_2\cdot 2H_2O$ compounds.

assigned to the intercalation compounds are reported in Table 1 and their interlayer distances are summarised in Table 2. It is worth noting that all the alkylamine intercalates have the same stoichiometrical composition, $Ti_2O_3(H_2AsO_4)_2\cdot 1.7C_nH_{2n+1}$-$NH_2\cdot 2H_2O$. Their interlayer distances increase linearly with increase in number of carbon atoms in the amine alkyl chain, n_c. The straight line determined can be defined by eqn. (1).

$$d = 11.6 + 1.7\, n_c \tag{1}$$

Considering that the increment of alkyl chain length (*trans-trans* conformation) for each additional carbon atom is 1.27 Å,[23] it is reasonable to assume that the amines in these compounds form a bimolecular layer of extended molecules with their longitudinal axes tilted on average by 42° with respect to the plane of the sheet.

Fig. 2 shows the TG and DTG curves of $Ti_2O_3(H_2AsO_4)_2\cdot 1.7C_nH_{2n+1}NH_2\cdot 2H_2O$ ($n = 3$–6) intercalation compounds. Considering that the release of As_2O_5 starts at 400–450 °C, the samples were heated up to only 350 °C and then kept below this temperature isothermally for 30 minutes. In all cases the weight loss occurs in two or more steps. The first takes place at a temperature below 200 °C and we associate it with the loss of crystallisation water. At a higher temperature desorption of *n*-alkylamine and loss of condensation water takes place. It is difficult to separate desorption and condensation processes by the TG method, mainly because there is an unidentified overlap between the beginning of the water condensation and the end of the amine desorption processes.

Table 2 Interlayer distances (*d*, in Å) and amine content of the *n*-alkylamine intercalates

	$Ti_2O_3(H_2AsO_4)_2\cdot xRNH_2\cdot 2H_2O$[a]		$Ti_2O_3(H_2PO_4)_2\cdot xRNH_2\cdot 2H_2O$[b]		$Zr_2O_3(HAsO_4)\cdot xRNH_2\cdot 2H_2O$[a]		$Zr_2O_3(HPO_4)\cdot xRNH_2\cdot 3H_2O$[c]	
Amine	*d*	*x*	*d*	*x*	*d*	*x*	*d*	*x*
Propylamine	16.7	1.7	18.8	1.37	17.8	0.6	19.0	0.4
n-Butylamine	18.1	1.7	20.8	1.00	21.5	0.6	21.2	0.4
n-Pentylamine	20.5	1.7	22.6	1.06	23.2	0.6	23.3	0.4
n-Hexylamine	21.8	1.7	24.8	1.18	26.5	0.6	25.2	0.4

Data taken from this work ([a]) and references 14 ([b]) and 16 ([c]).

Table 3 Microanalytical data for the $Zr_2O_3(HAsO_4)\cdot 0.6C_nH_{2n+1}NH_2\cdot 2H_2O$ intercalation compounds

	Experimental			Calculated		
Amine	% C	% H	% N	% C	% H	% N
Propylamine	4.80	2.18	1.77	4.88	2.35	1.90
n-Butylamine	6.74	2.50	1.78	6.39	2.57	1.86
n-Pentylamine	7.79	2.94	1.83	7.85	2.79	1.83
n-Hexylamine	9.75	3.55	1.93	9.25	3.00	1.79

Intercalation into $Zr_2O_3(HAsO_4)\cdot 3H_2O$ (ZrOAs)

In a similar way to that described in the previous section, the adsorption of *n*-alkylamine vapour gives rise to stable layered intercalation compounds if the number of carbon atoms of the alkyl chain is equal or superior to three. The interlayer distances of these materials (Table 2) also increase linearly with the number of carbon atoms of the amine intercalated. The straight line obtained follows eqn. (2). Hence, the amine

$$d = 10.4 + 2.6\, n_c \qquad (2)$$

molecules in these compounds must be arranged in a bilaminar disposition and placed almost perpendicularly to the arsenate layer.

Analytical data (Table 3) show that all intercalation compounds have the formula $Zr_2O_3(HAsO_4)\cdot 0.6C_nH_{2n+1}NH_2\cdot 2H_2O$ ($n = 3$–6). The thermal behaviour of these materials is similar to that of the titanium arsenate intercalates. In all cases, two well defined mass losses are clearly seen. The crystallisation water is released at $T < 200$ °C, and amine desorption and loss of condensation water take place at $T > 200$ °C.

Intercalation into metal(IV) phosphates

The compositions and interlayer distances of all the compounds obtained by intercalation of *n*-alkylamines into $Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$ and $Zr_2O_3(HPO_4)\cdot 1.5H_2O$ are given in Table 2. It can be seen that the interlayer distances of $Ti_2O_3(H_2AsO_4)_2\cdot 1.7C_nH_{2n+1}NH_2\cdot 2H_2O$ intercalates are lower than those for the analogous phosphate-based compounds, despite the fact that the amine content in titanium arsenate intercalates is higher. The intercalation data strongly indicate that, despite similar stoichiometry of the phosphate and arsenate compounds, their layered structures are different.

For Zr-based compounds it is also difficult to establish a clear relationship among the basal spacings of amine intercalates. In both cases, ZrOP and ZrOAs, the interlayer distances increase linearly with increasing number of carbon atoms in the alkyl chain (Fig. 3). However, the fact that the two straight lines cross is unusual for isotypic compounds. The $Zr_2O_3(HPO_4)\cdot 0.4C_nH_{2n+1}NH_2\cdot 3H_2O$ intercalation phases are defined by eqn. (3).

$$d = 13.4 + 2.0\, n_c \qquad (3)$$

The slope value indicates that the amines in the ZrOP are present as a bimolecular layer of extended molecules with their longitudinal axes inclined at an average of about 52° with respect to the plane of the sheet.

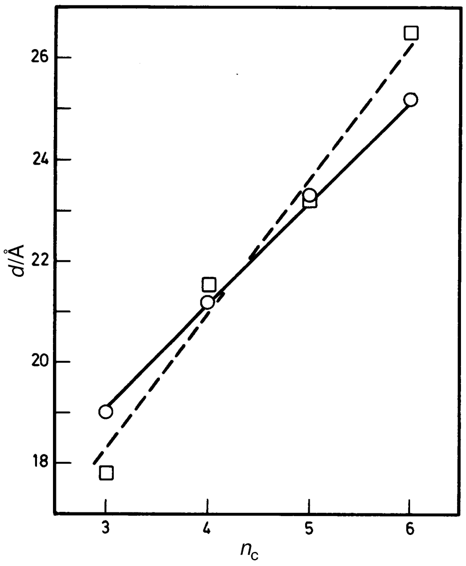

Fig. 3 Interlayer distances in *n*-alkylamine intercalate compounds as a function of the number of carbon atoms in the alkyl chain: ZrOAs (□), and ZrOP (○).

Amine interlayer packing

The structures of these metastable titanium (and zirconium) phosphates (and arsenates) have not yet been resolved, therefore their cell parameters and surface areas associated with the active centres are not known. However, the surface area can be calculated by assuming that the packing parameter is equal to one and following the procedure previously described in ref. 23. The packing parameter V_p can be defined by eqn. (4), where V_c

$$V_p = V_c / V_t \qquad (4)$$

is the volume occupied by the alkyl chains and V_t that available in the interlayer region. V_t can be calculated by subtracting from the interlayer distance (d) the space occupied by the layer itself, crystalline water and terminal NH_3^+ groups (d'). Referring to 1 cm^2 of layer, V_t will be given by eqn. (5), where d' is the

$$V_t = d - d' \qquad (5)$$

value (in cm) of the interlayer distance when $n_c = 0$. Since the cross-section of an alkyl chain, in *trans-trans* conformation, can be calculated from the cell dimensions of solid paraffin ($a \times b/2 = 18.6 \times 10^{-16}$ cm^2),[24] it can be assumed that the volume of an alkyl chain containing n_c carbon atoms is defined by (6).

$$n_c\,(1.27 \times 10^{-8})\,(18.6 \times 10^{-16})\ \mathrm{cm}^3 \qquad (6)$$

On the other hand, the number of amine molecules contained in the volume V_t, as defined in eqn. (5), must be equal to two times the number of acid centres present on 1 cm^2 of surface of

Table 4 Associated area (in $Å^2$ per H atom) at each acid centre on the basal plane, assuming that $V_p = 1$

n-Alkylamine	$Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$	$Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$	$Zr_2O_3(HAsO_4)\cdot 3H_2O$	$Zr_2O_3(HPO_4)\cdot 1.5H_2O$	$Ti(HPO_4)_2\cdot H_2O$	$Zr(HPO_4)_2\cdot H_2O$
Propylamine	11.8	8.3	11.5	10.1	20.8	22.1
n-Butylamine	12.4	6.1	10.2	9.7	21.7	24.5
n-Pentylamine	11.3	6.5	11.1	9.5	21.5	23.0
n-Hexylamine	11.8	7.1	10.6	9.6	21.8	22.8
Average value	11.8	7.0	10.8	9.7	21.7	23.5

Table 5 Structural data of layered metal(IV) phosphates and arsenates: interlayer distance (*d*, in Å), associated free area (in $Å^2$ per H atom) at each acid centre and arsenate : phosphate free area ratio

Compound	*d*	Free area	Area ratio	Ref.
α-$Ti(HAsO_4)_2\cdot H_2O$	7.8	22.20	1.03	25
α-$Ti(HPO_4)_2\cdot H_2O$	7.6	21.60		26
α-$Zr(HAsO_4)_2\cdot H_2O$	7.8	24.68	1.03	27
α-$Zr(HPO_4)_2\cdot H_2O$	7.6	23.99		28
γ-$Zr(AsO_4)(H_2AsO_4)\cdot 2H_2O$	11.8	19.04	1.07	29
γ-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$	12.3	17.84		30

each side of a layer (n_a) multiplied by the ratio $n_A : n_H$, where n_A and n_H are the number of amines and the number of acid hydrogens per formula unit, respectively. By recalling that the "free area" of each acid centre (F_a) can be expressed as $1/n_a$, and assuming that $V_p = 1$, we can write expression (7). Thus, the

$$V_c = V_t = d - d' = n_c\,(1.27 \times 10^{-8})\,(18.6 \times 10^{-16})\,2\,n_A/F_a\,n_H \quad (7)$$

"free area" associated with each acid centre can be calculated. Table 4 lists the associated area values for the active centres in $Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$ and $Zr_2O_3(HAsO_4)\cdot 3H_2O$, as well as in the phosphates of similar composition, $Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$ and $Zr_2O_3(HPO_4)\cdot 1.5H_2O$. Additionally, Table 4 contains values calculated for α-$Ti(HPO_4)_2\cdot H_2O$ and α-$Zr(HPO_4)_2\cdot H_2O$ by means of a similar technique. Associated areas for α-TiP and α-ZrP determined from structural data are shown in Table 5. It can be seen that the agreement between the two methods of associated area calculations for the α-type layered phosphates is very good. This means that the *n*-alkylamine intercalation gives a reliable indirect method for determining the area associated with active centres in layered solid acids.

Structural data

Table 5 lists the free area associated with each acid centre, calculated on the basis of structural data, for three phosphate/arsenate pairs. These values are mainly a function of the structure type. In all the α-type compounds the free area values are from 21.6 to 24.7 $Å^2$ per H atom. In γ-compounds they are smaller: 17.8–19.0 $Å^2$ per H atom. In addition, the differences within each structural type can be explained on the basis of differences in the phase composition. In this way the higher values of the free area for arsenates could be related to the As : P atom size ratio. The free area ratio between arsenates and phosphates is 1.03 : 1 for the α phases and 1.07 : 1 for the γ phases (Table 5). These values are directly related to the interlayer distances in the metal(IV) phosphates (Fig. 4).

The data obtained for $Zr_2O_3(HAsO_4)\cdot 3H_2O$ and $Zr_2O_3(HPO_4)\cdot 1.5H_2O$ (10.8 and 9.7 $Å^2$ per H atom, respectively) and for $Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$ and $Ti_2O_3(H_2PO_4)_2\cdot 2H_2O$ (11.8 and 7.0 $Å^2$ per H atom, respectively) can be used as an indicator of the isomorphism among these compounds. Fig. 4 shows that for ZrOP/ZrOAs the experimental data concur with those found for α- and γ-type compounds. The representation of the arsenate : phosphate free area ratio *vs.* the interlayer distance of the phosphate is a straight line. ZrOP and ZrOAs are isomorphic compounds. In agreement with previous reports,[16–18] this layered structure is noted as ψ type. In contrast, the experimental data (Table 4 and Fig. 4) cannot justify the isomorphism of TiOP and TiOAs.

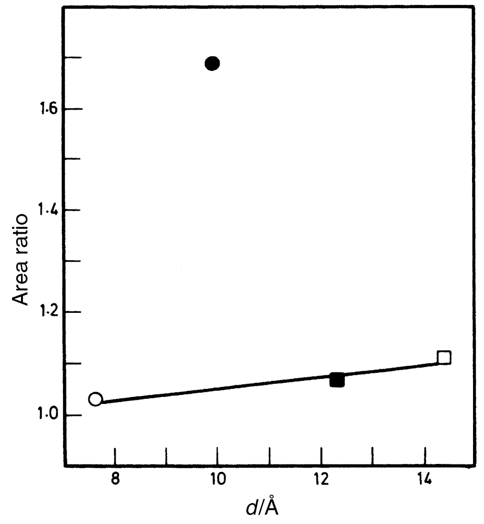

Fig. 4 Arsenate : phosphate free area ratio as a function of the interlayer distance of the metal(IV) phosphate: α-TiP and α-ZrP (○), γ-ZrP (□), ZrOP (■), and TiOP (●).

Conclusion

New layered acid phosphates and arsenates are materials with interesting and valuable properties. The behavior of these compounds is related closely to their structures. However, the structure of only a limited number of known phases has been characterised completely. The *n*-alkylamine intercalation can be used to determine the free area of interlayer space associated with each active centre.

Experimental

$Ti_2O_3(H_2AsO_4)_2\cdot 2H_2O$[15] and $Zr_2O_3(HAsO_4)\cdot 3H_2O$[18] were synthesized as previously described. The intercalation compounds were obtained by placing the starting materials in an atmosphere saturated with amine vapour, $C_nH_{2n+1}NH_2$ (n = 1–6), for 3–40 days at room temperature.

Microanalytical data (C, N, H) were obtained with a Perkin-Elmer model 2400B elemental analyser. The diffractometer used was a Philips PW 1729/1720 model with Cu-Kα radiation. Thermal analysis was performed with a Mettler TA 4000-TG 50 instrument (under nitrogen, heating rate 10 °C min^{-1}). Micrographs were recorded with a JEOL JSM-6100 scanning electron microscope operating at 20 kV.

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