CRYSTALLINE INSOLUBLE SALTS OF POLYBASIC METALS

V. ION-EXCHANGE PROPERTIES OF CRYSTALLINE AND AMORPHOUS ZIRCONIUM ARSENATE*

E. TORRACCA, U. COSTANTINO AND M. A. MASSUCCI

Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N. and Istituto di Chimica Generale ed Inorganica dell'Università di Roma, Rome (Italy)

(Received July 11th, 1967)

In the previous papers of this series, the preparation and the ion-exchange properties of crystalline titanium phosphate[1] and cerium(IV) phosphate of various crystallinities[2] were reported. Continuing the systematic investigation on new crystalline ion exchange materials, we report in this paper the preparation and the ion-exchange properties of crystalline zirconium arsenate; ion-exchange properties of amorphous zirconium arsenate are also reported for comparison.

While this work was in progress similar material had been prepared independently by CLEARFIELD et al.[3].

EXPERIMENTAL

Chemicals

$ZrOCl_2 \cdot 8 \ H_2O$ and $3As_2O_5 \cdot 5 \ H_2O$ were Merck "pro analysi" products. All other reagents were Erba RP products. Thallium, caesium and rubidium hydroxide solutions were prepared by adding the corresponding sulfate to a hot barium hydroxide solution, in a closed system filled with nitrogen.

Preparation of amorphous zirconium arsenate

One liter of $1 \ M$ HCl solution containing 200 g of $ZrOCl_2 \cdot 8 \ H_2O$ was added dropwise at room temperature to 1.86 l of $1 \ M$ HCl solution containing 235 g of $3As_2O_5 \cdot 5 \ H_2O$. The precipitate was allowed to stand overnight, was filtered and washed with a 0.2 M arsenic acid solution until free of chloride ions; this product was then washed with distilled water until the pH was about 3.5, and dried over P_2O_5.

Analytical procedures

The As/Zr ratio of zirconium arsenate was determined as follows. Three hundred milligrammes of material were dissolved in 10 ml of 1 M hydrofluoric acid and the solution diluted to 25 ml. Zirconium was determined as described previously[4] in a 10 ml aliquot of this solution; arsenic was determined iodometrically in the remaining solution. Titration and ion-uptake curves were obtained by equilibrating several samples of zirconium arsenate in the H+- or Na+-form (0.250 g) with 50 ml of 0.1 N (MCl + MOH) or (MCl + HCl) solution. After shaking for two days at 25°, samples

---

of the supernatant liquid were analyzed for their metal and arsenate content and their pH was measured. 0.1 N $TlNO_3$ and 0.1 N $BaCl_2$ solutions were used in the ion-uptake curves with Tl^+ and Ba^{2+}. The Ba^{2+} curve was established in a nitrogen atmosphere to prevent precipitation of barium carbonate.

Alkali metals were determined with a Beckman model DU flame spectrophotometer. Thallium was titrated at $60°$ with standard potassium bromate[5]; barium was determined by standard EDTA titration[6].

Arsenate was determined colorimetrically following the same procedure as that adopted in a previous paper[4] for the determination of orthophosphate; when thallium was present, it was precipitated as chloride before developing the colour. In the presence of Ba^{2+} ions, arsenate was determined iodometrically.

The X-ray diffraction patterns were taken using $CuK\alpha$ radiation.

RESULTS AND DISCUSSION

Amorphous zirconium arsenate $(AsO_4/Zr = 1.78)$

Ion-exchange properties. Since very little experimental work has been reported on amorphous zirconium arsenate as an ion-exchanger[7,8], some ion exchange properties of this material were determined in order to compare it with crystalline zirconium arsenate.

In Fig. 1 the titration curves of amorphous zirconium arsenate dried over P_2O_5 to constant weight are reported for Na^+, K^+ and Cs^+ ions. The ion uptakes (mequiv./g) and the millimoles of arsenate released to the solution by 1 g of material are plotted in Fig. 2 at a function of pH.
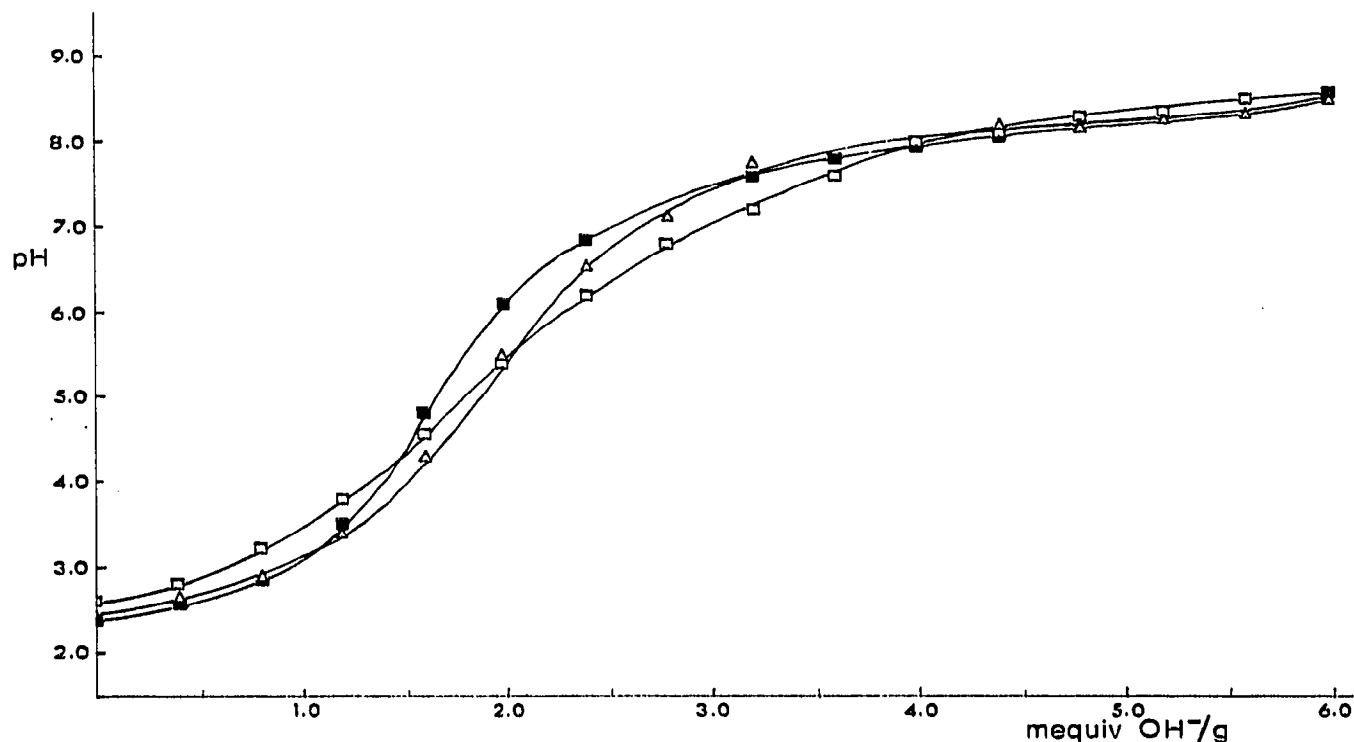

Fig. 1. Titration curves of amorphous zirconium arsenate dried over P_2O_5 to constant weight. (□) Na^+; (△) K^+; (■) Cs^+.
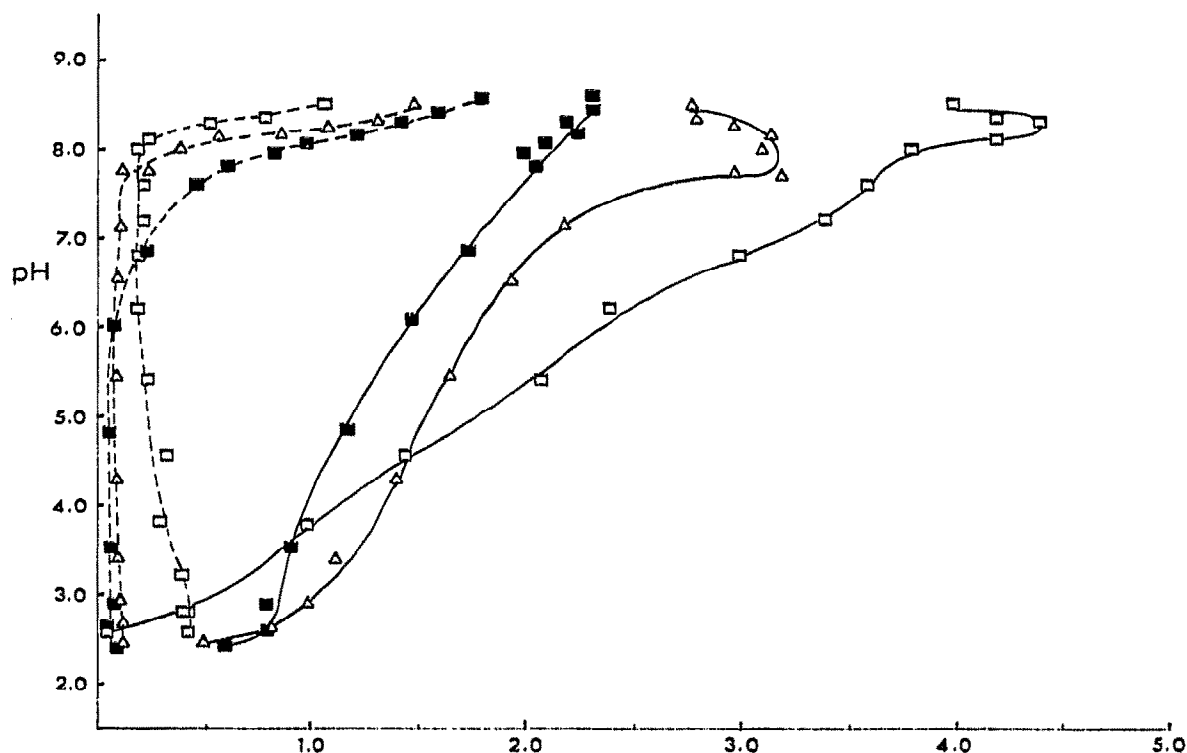
Fig. 2. Ion uptake and hydrolysis of amorphous zirconium arsenate dried over P_2O_5 to constant weight as function of pH. Abscissae: full curves, ion uptake (mequiv./g); dashed curves, arsenate released to the external solution (mmole/g). (□) Na⁺; (△) K⁺; (■) Cs⁺.

Fig. 1 shows that the titration curve with Cs⁺ lies below those with K⁺ and Na⁺ at low pH values, while the opposite is found at higher pH's. From Fig. 2, it can be seen that at pH values lower than 2.6, Cs⁺ is more strongly absorbed than K⁺ and Na⁺, the order of exchange affinities being Cs⁺ > K⁺ > Na⁺; between pH 2.6 and 3.8 the order becomes K⁺ > Cs⁺ > Na⁺, while between pH 3.8 and 4.65, it changes to K⁺ > Na⁺ > Cs⁺; finally above pH 4.65, the order is completely reversed to Na⁺ > K⁺ > Cs⁺. This reversal in selectivity observed for amorphous zirconium arsenate as the conversion to salt form proceeds could be due to the same steric effects that have been found to reverse the mobility sequence of the alkali metal ions in amorphous zirconium phosphate[9]. Representing both the exchangers with the same model, we suppose that amorphous zirconium arsenate, due to its disordered structure, exchanges hydrogen with other counterions through channels or cavities widely differing in size. Larger cavities may have enough room for ions to be hydrated, but more and more dehydrated ions must be exchanged with hydrogen as the size of the cavities decreases. In the course of the titration, larger cavities are involved at first and the exchanger will prefer the counterion with the smallest hydrated volume; since smaller and smaller cavities have to be involved as conversion proceeds, the affinity order will gradually change and the exchanger will finally prefer the ion with the smallest crystalline radius.

When considering each ion exchange process separately, this pattern indicates also that it must become more and more difficult to substitute hydrogen by other counterions as the extent of the exchange increases, thus accounting for the fact that the pH of the solution has to be raised progressively when converting to the salt form.

Fig. 2 shows, however, that beyond a certain pH value, amorphous zirconium arsenate is severely hydrolysed and the counterion content inside the exchanger can even decrease.

Crystalline zirconium arsenate

Preparation and composition. On refluxing amorphous zirconium arsenate with fairly concentrated arsenic acid, a crystalline product is obtained. After 1 h of refluxing in 4 M arsenic acid, the AsO_4/Zr ratio of the material becomes 1.91 and the crystallization is nearly complete; the product is completely crystalline after 10 h of refluxing. All the data reported in the present paper on crystalline zirconium arsenate concern the product obtained by refluxing 54 g of amorphous material for 90 h in 1.5 l of 4 M arsenic acid. This material was washed until neutral and dried over P_2O_5 under vacuum to constant weight. Its AsO_4/Zr ratio was 1.98. When dried at 115° under vacuum it loses 4.7 % water, while 9.3 % water is lost at 750°. Taking into account its AsO_4/Zr ratio, this compound can be represented by the empirical formula $ZrO_2 \cdot As_2O_5 \cdot 2H_2O$. Since X-ray analysis indicates that this material does not undergo any appreciable change in structure when heated at 115°, we believe that crystalline zirconium arsenate dried over P_2O_5 can be represented by the formula $Zr(HAsO_4)_2 \cdot H_2O$[*] which corresponds to a total ion-exchange capacity of 5.1 mequiv./g.

Ion-exchange with alkali metal ions. In Fig. 3 the Li^+, Na^+, K^+, Rb^+ and Cs^+ uptakes (mequiv./g) on crystalline zirconium arsenate dried over P_2O_5 to constant
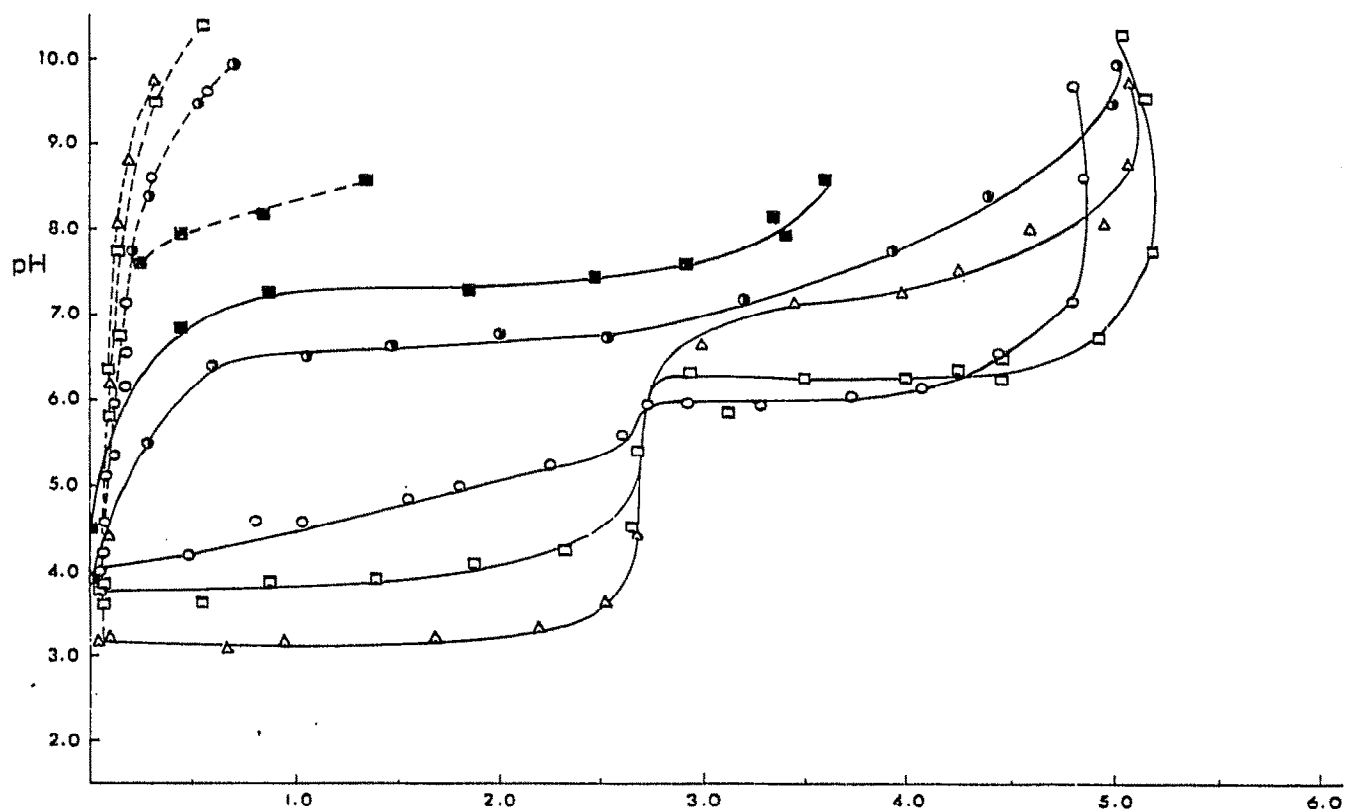

Fig. 3. Ion uptake and hydrolysis of crystalline zirconium arsenate dried over P_2O_5 to constant weight as function of pH. Abscissae: full curves, ion uptake (mequiv./g); dashed curves, arsenate released to the external solution (mmole/g). (O) Li^+; (□) Na^+; (△) K^+; (◑) Rb^+; (■) Cs^+.

[*] CLEARFIELD *et al.*[3] have recently arrived at the same conclusion independently.

weight are reported as a function of the pH. The number of millimoles of arsenate released to the solution by 1 g of material are plotted in the same figure. From Fig. 3 it can be seen that the shape of the ion uptake curves of crystalline zirconium arsenate is very much affected by the nature of the ion: Rb^+ and Cs^+ are not appreciably exchanged in acid media, while Li^+, Na^+ and K^+ curves show two plateaus at different pH's. This behaviour is very close to that observed for crystalline zirconium phosphate [10] and could be accounted for by assuming that the structure of both exchangers is very similar.

According to CLEARFIELD[3], this structure is a layered one, each layer consisting of zirconium atoms sandwiched between phosphate (or arsenate) groups above and below the plane of metal atoms; this arrangement of the zirconium with the phosphate (or arsenate) groups, produces zeolitic cavities within the crystal (one for zirconium atom). Thus the ion exchange process is assumed to proceed as follows: during the replacement of the first hydrogen, cavities are occupied by the exchanging ions and the interlayer distance remains unchanged; when one mole of hydrogen per formula weight of exchanger has been replaced, the incoming cations must insert themselves between layers, as demonstrated by the increase in the value of interlayer distance[3]. The two different mechanisms involved in the ion exchange process could thus account for the fact that hydrogen is exchanged at two different pH values.

Concerning the ion uptake curves of crystalline zirconium arsenate, Fig. 3 shows that at the same counterion content, the equilibrium pH's below half conversion of the exchanger are in the order $Cs^+ > Rb^+ > Li^+ > Na^+ > K^+$. This could be due to the fact that Li^+, Na^+ and K^+ are small enough to enter cavities according to their decreasing hydrated volume, while Rb^+ and Cs^+ are sufficiently large to undergo steric hindrance and pH must be raised to allow these ions to exchange. Cs^+ cannot substitute hydrogen completely, as can be seen from Fig. 3; beyond an uptake of about 3 mequiv./g, the exchanger is extensively hydrolysed and its crystal structure, as demonstrated by X-ray analysis, is almost completely destroyed.

Above half conversion of the exchanger, the equilibrium pH's, as shown in Fig. 3, are in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. This could indicate that the cations insert themselves between the layers completely or almost completely dehydrated; the larger the counterion, the larger the energy required for the exchange of the second hydrogen, i.e. the equilibrium pH.

As regards the ion exchange capacity of crystalline zirconium arsenate, the endpoint of the curves obtained for Li^+, Na^+, K^+ and Rb^+ corresponds to the uptake of about 5 mequiv./g, thus supporting the formula $Zr(HAsO_4)_2 \cdot H_2O$ given above.

To get a better insight into the ion exchange process, the water content of crystalline zirconium arsenate when titrated with 0.1 N (LiCl + LiOH), (NaCl + NaOH), (KCl + KOH) and (RbCl + RbOH) solutions was determined. Assuming that the composition of the exchanger during the titration could be represented by the formula $Zr(H_{2-a}M_a)(AsO_4)_2 \cdot nH_2O$, where a represents the moles of the counterion per formula weight, the water content of the sample has been derived from the percent weight loss by means of the following relation:

$$\frac{n \times 18}{\text{mol. wt.} + n \times 18} \times 100 = \% \text{ wt. loss}$$

The mol.wt. is the molecular weight of the anhydrous exchanger at different stages of the titration. The samples were dried in a desiccator over saturated lithium chloride (about 11 % relative humidity) before being dehydrated at 200° under vacuum, since X-ray analysis has shown that the salt forms of crystalline zirconium arsenate change their structure when dried over P_2O_5*.
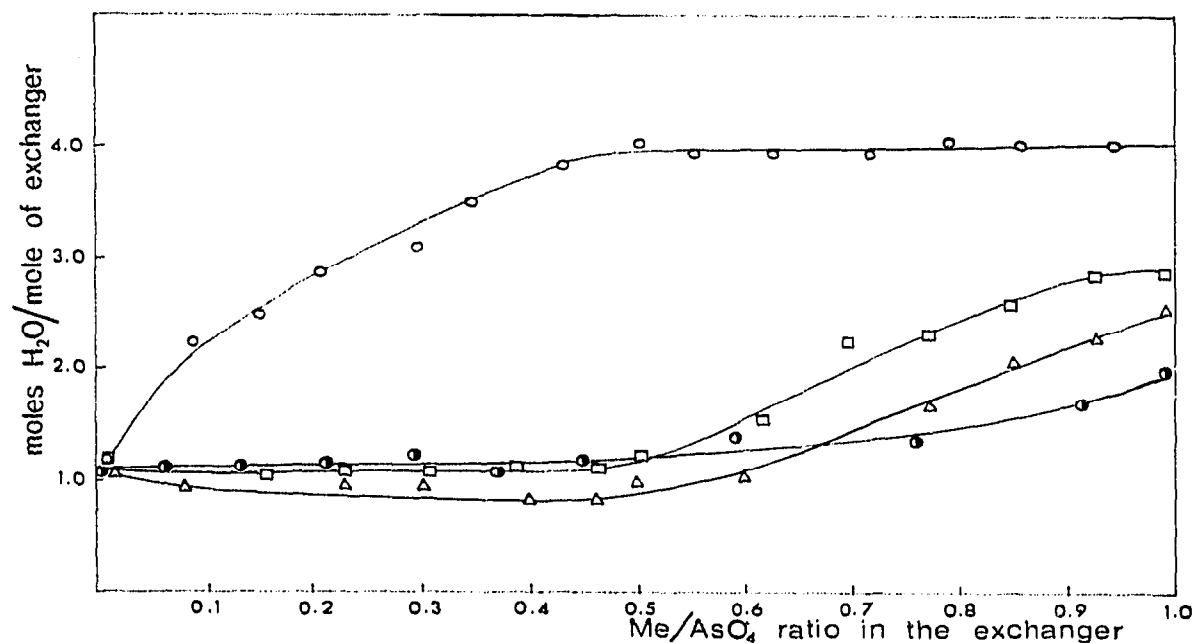

Fig. 4. Water content of crystalline zirconium arsenate at various stages of the titration with alkali metals. (O) Li+; (□) Na+; (△) K+; (◑) Rb+.

In Fig. 4 the water content of the exchanger is reported as a function of the Me/AsO_4 ratio. This figure shows that:

(1) The slope of the curves changes more, or less, markedly at the half conversion stage of the exchanger. This is in agreement with the fact that two different mechanisms are involved whether the first or the second hydrogen is exchanged.

(2) The water content of the exchanger below half conversion increases for Li+, remains nearly constant for Na+ and Rb+, and slightly decreases for K+. This could be explained assuming that H_3O^+ is displaced from the cavities as the first hydrogen is substituted; the water content of the exchanger must then increase or decrease depending on whether the incoming cation brings more or less than one water molecule respectively.

The slopes of the curves thus seem to indicate that Li+ enters cavities more hydrated than Na+ and K+, in agreement with the selectivity sequence below half conversion discussed above. The fact that the water content of the exchanger does not decrease when titrated with Rb+, could be explained by assuming that cavities become slightly larger to accomodate this ion.

(3) The water content above half conversion remains constant for Li+, while it increases for Na+, K+ and Rb+.

---

* The samples of the titration with 0.1 N (LiCl + LiOH) were dried over lithium nitrate saturated solution (47 %r.h.), since the Li+-form of crystalline zirconium arsenate changes its structure even when dried at 11 % r.h.

These differences between the Li+ and other alkali ions cannot be explained easily at present on the basis of the data at our disposal; the mechanism of the water sorption during the second stage of the titration would seem to be worth investigating further to get a clear picture of the whole ion exchange process.

Ion-exchange with thallium(I) and barium. To extend our investigation to ions other than alkali metals, Tl+ and Ba^{2+} exchange on crystalline zirconium arsenate has been studied. In Fig. 5 Tl+ and Ba^{2+} uptakes (mequiv./g) and arsenate released to the solution by 1 g of material are reported as a function of pH. As it can be seen from Fig. 5, Tl+ uptake increases as the pH of the solution is raised, while Ba^{2+} is exchanged at a lower constant pH. Only 4.1 mequiv. of Ba^{2+} are absorbed by 1 g of exchanger at pH 2.6, while at higher pH values, Ba^{2+} seems to be exchanged beyond the theoretical ion exchange capacity and hydrolysis decreases. This is very likely due to precipitation of barium arsenate on the exchanger.
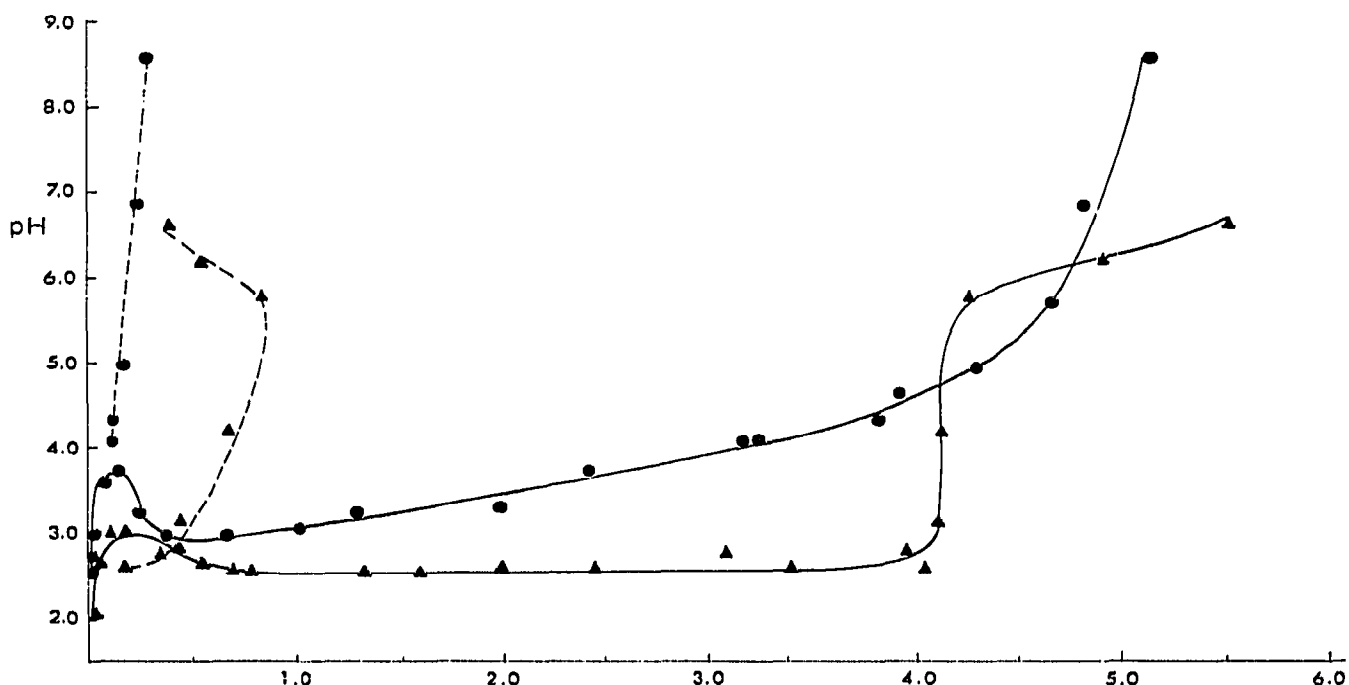

Fig. 5. Ion uptake and hydrolysis of crystalline zirconium arsenate dried over P$_2$O$_5$ to constant weight as a function of pH. Abscissae: full curves, ion uptake (mequiv./g); dashed curves, arsenate released to the external solution (mmole/g). (●) Tl+; (▲) Ba^{2+}.

In Fig. 5 it can be seen that at low uptake values, the equilibrium pH increases up to about 0.1 mequiv./g, while it decreases more or less markedly above this value.

This is rather unusual and difficult to explain: probably it has something to do with an increase in selectivity of the exchanger for Tl+ and Ba^{2+} when the ion uptake exceeds a certain value. Furthermore, Fig. 5 shows that the exchanger can exhibit different compositions at the same pH value: this seems to indicate an irreversibility of this phenomenon.

Reversibility of the ion exchange process. Direct and reverse titrations of crystalline zirconium arsenate with 0.1 *N* (NaCl + NaOH) and 0.1 *N* (NaCl + HCl) respectively were performed. In Fig. 6 the composition of the exchanger is reported as function of pH and it can be seen that the exchanger exhibits the same composition
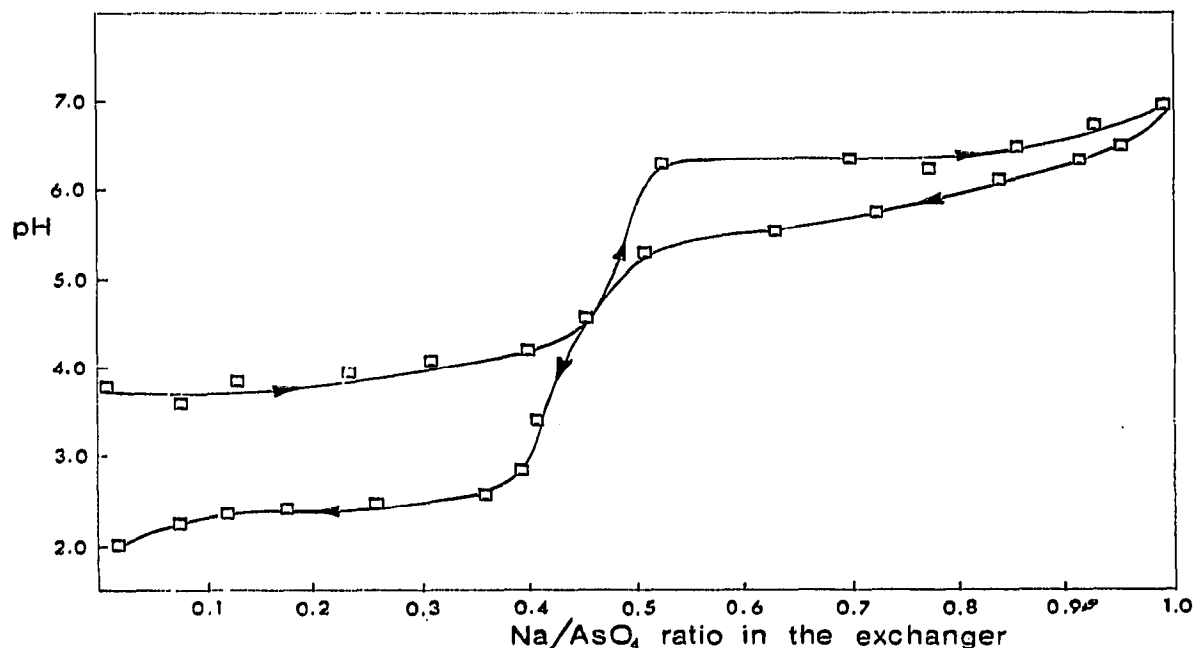
Fig. 6. Irreversibility of the Na^+/H^+ exchange on crystalline zirconium arsenate.

at different pH's. Moreover, samples equilibrated at the same pH show very different X-ray diffraction patterns depending on the initial composition of the exchanger.

Crystalline zirconium phosphate behaves in a very similar manner: irreversibility has been found in the Na^+/H^+ exchange and in Na^+/K^+, Na^+/Li^+ and Li^+/K^+ systems[11].

This, together with the reported data, confirms that crystalline zirconium arsenate and crystalline zirconium phosphate are very similar materials. An increase in the ion exchange capacity and resistance to hydrolysis is found when amorphous materials become crystalline, steric effects became more important and large ions can be excluded in acid media. Rearrangement in the structure occurs and irreversibility in ion exchange is found when converting to the salt form.

ACKNOWLEDGEMENT

Our most sincere thanks are due to Prof. G. ALBERTI for many valuable discussions and helpful suggestions.

SUMMARY

On refluxing amorphous zirconium arsenate in fairly concentrated arsenic acid, a crystalline product, with the formula $Zr(HAsO_4)_2 \cdot H_2O$, is obtained. Titration curves of amorphous and crystalline materials were performed for several ions and results are discussed. Steric effects were found to play an important role in the ion exchange process of both materials.

REFERENCES

1 G. ALBERTI, P. CARDINI-GALLI, U. COSTANTINO AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 29 (1967) 571.
2 G. ALBERTI, U. COSTANTINO, F. DI GREGORIO, P. GALLI AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, in press.
3 A. CLEARFIELD, G. D. SMITH AND B. HAMMOND, private communication.
4 G. ALBERTI, A. CONTE AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 28 (1966) 225.
5 I. M. KOLTHOFF AND R. BELCHER, *Volumetric Analysis*, Vol. III, Interscience, New York, London, 1957.
6 L. MEITES, *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963.
7 K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON AND J. S. JOHNSON, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 2nd, 1958*, United Nations, Vol. 28, p. 3.
8 C. B. AMPHLETT, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 2nd, 1958*, United Nations, Vol. 28, p. 17.
9 G. ALBERTI AND E. TORRACCA, to be published.
10 A. CLEARFIELD AND J. A. STYNES, *J. Inorg. Nucl. Chem.*, 26 (1964) 117.
11 E. TORRACCA, to be published.