Mechanism of Some Alkylammonium-ion Exchanges by α-Zirconium Bis(monohydrogenorthophosphate) Monohydrate

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Crystalline zirconium phosphate, α-ZrP, has been investigated as an ion exchanger for the systems ($NEtH_2$ + $[NEtH_3]^+$)–H^+, (NEt_2H + $[NEt_2H_2]^+$)–H^+, and (NEt_3 + $[NEt_3H]^+$)–H^+ by potentiometric titrations. The exchange process in the case of ethylammonium ions occurs *via* phase transitions in four equal stages with the formation of pure phases. However, the ion exchange between α-ZrP and diethylammonium ions goes through three equal steps, again with phase transition. Two coexisting phases are observed throughout the exchange process of triethylammonium ions with α-ZrP. The maximum of uptake of ethyl-, diethyl-, and triethyl-ammonium ions is 100, 50, and 25% of the proton-exchange capacity of α-ZrP, respectively. *X*-Ray diffraction and thermal analysis methods have been used to characterize the products at different steps of the process.

CRYSTALLINE zirconium phosphate (α-ZrP) possesses a layer lattice structure.[1] Because of some steric impediments, α-ZrP is considered to be a poor ion-exchange material for removing larger ions, in spite of its excellent chemical, thermal, and radiation stabilities.[2,3] However, if these hindrances are reduced by enlarging its lattice by employing the Na^+ or Li^+ half-exchanged forms and/or by accelerating the ion-exchange process using elevated temperatures, ions such as Rb^+ and Cs^+,[3,4] alkaline-earth metal ions,[5] and transition-metal ions [6,7] can enter the crystals very easily.

α-ZrP can easily exchange potassium for hydrogen ions at room temperature but it excludes ammonium ions, even though the ionic size is almost identical. A mechanism, different from that of potassium-ion exchange has been suggested by us based on the removal of ammonia from solutions following a process involving hydrogen bonding.[8,9]

Very little is known of the reactions between α-ZrP and organic molecules.[10,11] Michel and Weiss [10] reported in brief on ion exchange between α-ZrP and organic cations. γ-ZrP, $Zr(HPO_4)_2{\cdot}2H_2O$, contains an additional water molecule whose first interlayer distance is 12.1 Å compared with α-ZrP where this distance is 7.56 Å. The P–O–C ester bond formation due to an intercalation process between γ-ZrP and ethylene oxide in an aqueous medium has been recently reported in detail by Yamanaka.[12] The present paper deals with the uptake mechanism (at room temperature) of ethyl-, diethyl-, and triethyl-ammonium ions by α-ZrP.

EXPERIMENTAL

All the chemicals were of reagent grade and were used without further purification. The amine solutions were made in a cold room (4 °C) to avoid any amine loss by evaporation. Carbon dioxide-free demineralized water was used throughout the course of ion-exchange experiments. Crystalline zirconium phosphate was prepared by our direct-precipitation method using zirconia.[9]

Ion-exchange Experiments.—Potentiometric ion-exchange titrations. Several samples (500 mg) of α-ZrP were equilibrated with a mixture (100 dm^3) of alkylamines and alkylammonium chlorides. The ionic strength was constant at 0.1 mol dm^{-3}. The amount of amine was varied from 0 to 8 milliequivalents per gram of α-ZrP. This slurry was shaken in a temperature-controlled room (25 ± 0.5 °C) and the equilibrium time was decided by measuring pH values of the supernatant liquids at different intervals of time. The solids [after filtering, washing, and drying (relative humidity 90%)] were examined by *X*-ray diffraction and analyzed for their C, H, and N contents.

Column and batch ion-exchange experiments. (*a*) Ethylammonium chloride (0.1 mol dm^{-3}) solution was percolated through columns of $\overline{ZrNaH(PO_4)_2{\cdot}5H_2O}$ $(\overline{NaH})$ and of $\overline{Zr(NaPO_4)_2{\cdot}3H_2O}$ $(\overline{2Na})$ until the effluent gave a negative test for sodium ion. The preparation of $\overline{NaH}$ and $\overline{2Na}$ has been reported previously.[4] The exchanged samples obtained after saturation with ethylammonium ion (on the columns) were washed and dried as usual. This experiment was also done by the batch process. $\overline{NaH}$ and $\overline{2Na}$ (500 mg) were separately equilibrated with 0.1 mol dm^{-3} $[NEtH_3]Cl$ solution (200 cm^3) for 100 h. The solids were washed and dried as usual. Solid samples from column and batch experiments were characterized by *X*-ray diffraction, chemical analysis, and thermal methods.

(*b*) Various pure phases (obtained at the end-points in the ethylamine potentiometric titrations), called $\overline{2NEtH_3}$, $\overline{H_{0.5}(NEtH_3)_{1.5}}$, $\overline{H(NEtH_3)}$, and $\overline{H_{1.5}(NEtH_3)_{0.5}}$, and of 1 mol dm^{-3} HCl (1 l) were shaken separately for *ca.* 100 h. The solids were separated by centrifuging, washed, and dried in air. They were then characterized by their PO_4 : Zr ratio, *X*-ray diffraction, and thermal methods.

Analytical Procedures.—The Zr and PO_4 contents were determined as previously reported. The pH measurements were made on a Pye model 79 pH meter. Thermogravimetric and *X*-ray analyses were obtained by a Dupont 900 linked to a 950 TG unit, and a Philips *X*-ray unit (nickel-filtered Cu-K_α radiation) respectively.

RESULTS

The potentiometric ion-exchange titration curves of α-ZrP with ethyl-, diethyl-, and triethyl-ammonium ions are shown in Figure 1. The three cases will now be dealt with separately.

Ion-exchange Behaviour of α-ZrP *with Ethylammonium Ion.*—The pH-titration curve for ethylammonium ion indicates a process occurring in four stages, showing four end-points corresponding to 25, 50, 75, and 100% of the total ion-exchange capacity of α-ZrP [6.64 mequiv. (g α-ZrP)$^{-1}$]. This, in contrast to alkali-metal ions, produces four pK values, calculated to be pK_1 3.1, pK_2 6.3, pK_3 6.8, and pK_4 8.7. Comparative *X*-ray diffraction patterns of

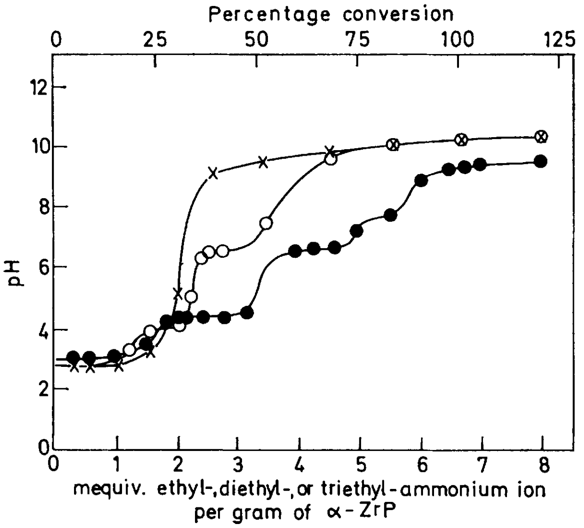


FIGURE 1 Ion-exchange potentiometric titration curves for α-ZrP. Titrants (0.1 mol dm^{-3}): ethylamine (●); diethylamine (○); and triethylamine (×)

some ethylammonium ion-exchanged samples of α-ZrP revealed that two phases of interlayer spacings 7.56 and 10.04 Å were present, until the loading of ethylamine exceeded the first end-point [1.66 mequiv. (g α-ZrP)$^{-1}$]. The peak intensities of phase at 10.04 Å gradually increased, while the phase at 7.56 Å decreased in intensity with increasing loading of ethylammonium ion. At a loading of 1.66 mequiv. ethylamine per gram α-ZrP the phase of interlayer distance 7.56 Å was no longer seen and a single phase (10.04 Å) was detected. Upon analysis this pure phase gave the composition $Zr(HPO_4)_{1.5}(NEtH_3PO_4)_{0.5}\cdot 1.5H_2O$ [Found: C, 3.60; H, 2.70; N, 1.95. Calc.: C, 3.55; H, 2.65; N, 2.00%. Weight loss due to interstitial water molecules: 9.07 (calc.: 9%)]. This phase will be termed as $\overline{H_{1.5}(NEtH_3)_{0.5}}$ elsewhere.

Along the second plateau of the pH titration curve the *X*-ray diffraction patterns again showed the existence of two phases of interlayer distances 10.04 and 10.64 Å; the intensities of the two peaks varied as before. At a loading of 3.32 mequiv. of ethylamine per gram α-ZrP (the vertical portion of the curve) a single phase of basal spacing 10.64 Å was observed. This phase has the composition $Zr(HPO_4)(NEtH_3PO_4)\cdot H_2O$ (Found: C, 6.80; H, 3.35; N, 3.80. Calc.: C, 6.90; H, 3.15; N, 4.00%) and will be referred to as $\overline{H(NEtH_3)}$. The phase transition continued, with the formation of solid solutions along the horizontal portions followed by a single phase at the vertical sections of the titration curve in the regions of 50—75, 75, 75—100, and 100% of the total ion-exchange capacity of α-ZrP. The pure phases obtained by loading 4.98 mequiv. ethylammonium ion (75% conversion) and 6.64 mequiv. ethylammonium ion per gram of α-ZrP (100% conversion) gave first interlayer distances of 14.7 and 16.35 Å respectively. Their compositions $Zr(HPO_4)_{0.5}(NEtH_3PO_4)_{1.5}\cdot 3.5H_2O$ and $Zr(NEtH_3PO_4)_2\cdot H_2O$ were very close to those determined by C, H, and N element analyses and thermogravimetry. These phases will be termed $\overline{H_{0.5}(NEtH_3)_{1.5}}$ and $\overline{2NEtH_3}$ respectively.

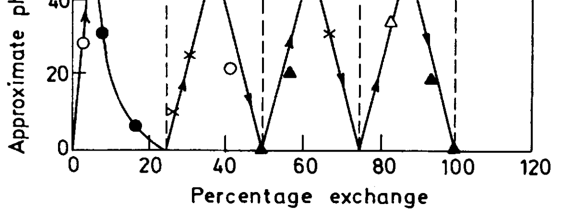


FIGURE 2 Phase composition as a function of ethylamine loading. (●) Phase A = α-ZrP, *d* = 7.56 Å; (○) phase B = $Zr(HPO_4)_{1.5}(NEtH_3PO_4)_{0.5}\cdot 1.5H_2O$, *d* = 10.04 Å; (×) phase C = $Zr(HPO_4)(NEtH_3PO_4)\cdot H_2O$, *d* = 10.64 Å; (▲) phase D = $Zr(HPO_4)_{0.5}(NEtH_3PO_4)_{1.5}\cdot 3.5H_2O$, *d* = 14.7 Å; and (△) phase E = $Zr(NEtH_3PO_4)_2\cdot H_2O$, *d* = 16.35 Å

Figure 2 shows the linear relationship between phase composition and the percentage of loading of ethylammonium ion. The phase composition was derived by measuring the peak height of the phases in the *X*-ray diffractogram at their half-width [*i.e.* percentage phase 1 = $10^2 dH^1/(dH^1 + dH^2)$; percentage phase 2 = 100 − percentage phase 1, where dH^1 and dH^2 are the peak heights at their half-width of phases 1 and 2 respectively]. This Figure also clearly illustrates the existence of pure phases which occurred at 25, 50, 75, and 100% of the total ion-exchange capacity of α-ZrP. Figure 3 shows the rate of exchange of various alkylammonium ions with α-ZrP. It can be seen that the exchange between ethylammonium ion and α-ZrP is fast in comparison with other cations and the equilibrium is established in 1 h. Thus the overall ion-exchange process can be written as in Scheme 1.

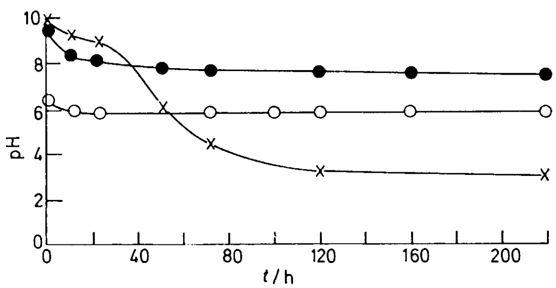
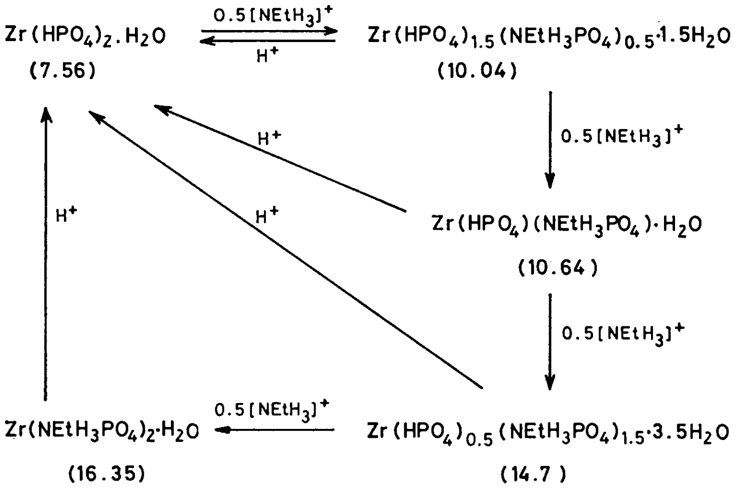


FIGURE 3 Kinetics of alkylammonium-ion exchange of α-ZrP. (○) 3.32 mequiv. ethylamine per gram α-ZrP; (●) 3.32 mequiv. diethylamine per gram α-ZrP; and (×) 1.66 mequiv. triethylamine per gram α-ZrP

The thermal analyses of the pure phases show that the decomposition of these products took place in three stages: dehydration, removal of amine, and condensation of P–OH groups to pyrophosphate groups respectively. An experiment on the thermal decomposition of these products using a differential thermal analysis (d.t.a.) system interfaced with a quadrupole mass spectrometer also confirmed the decomposition products.

The analytical data of the products obtained in the batch experiments (*a*) (see Experimental section) were similar to those for phases $\overline{H(NEtH_3)}$ and $\overline{2NEtH_3}$ respectively. Also experiment (*b*) produced α-ZrP, although crystallinity was not maintained. The evidence from these experiments leads to the conclusion that α-ZrP did not complex with ethylamine *via* intercalation of a P–OH group with amine as in the case of γ-ZrP,[12] but exchanges ethylammonium for hydrogen ion and *vice versa*. Recent investigations by Clearfield [13] have shown that if amines only (as distinct from our experiments) are combined with α-ZrP then the process appears to be one of intercalation. It was also noted in the same experiments that the titration curves did not exhibit any clear plateau; also the intercalation process took place at considerably higher pH values. The behaviour of α-ZrP with alkylamines is therefore not parallel to that with ammonia.[8,9]



SCHEME 1 Numerals in parentheses are the first interlayer distances (Å) of the ion-exchanged materials

Ion-exchange Behaviour of α-ZrP *with Diethylammonium Ion.*—The isotherms representing pH and uptake of diethylammonium ion are shown in Figure 1. The maximum uptake of diethylammonium ion by 1 g of α-ZrP was 3.32 mequiv., which corresponds to 50% of the total ion-exchange capacity. However, this isotherm exhibited three inflection points, and is supported by *X*-ray diffraction patterns of the exchanged solids. Up to *ca.* 1.11 mequiv. per gram the *X*-ray patterns have shown a mixture of α-ZrP (7.56 Å) and a phase with a first basal spacing of 10.04 Å. At 1.11 mequiv. the pattern becomes that of the latter phase. Between 1.11 and 2.20 mequiv. per gram there were two phases of first interlayer distances 10.04 and 11.47 Å, with the formation of a pure phase at 2.21 mequiv. per gram. This is consistent with the sharp upturn in the isotherm. At higher loads (2.22—3.30 mequiv. per gram) a mixture of two phases having interlayer distances of 11.47 and 12.61 Å was obtained. Finally, at a loading greater than 3.32 mequiv. per gram only a single phase having a first interlayer distance of 12.61 Å was observed.

The phase diagram was drawn from the *X*-ray diffraction patterns of the exchanged solids (see Figure 4). This Figure shows the linear relationship between phase composition and uptake. Pure phases occur at 16.7, 33.4, and 50% of the total ion-exchange capacity of α-ZrP. Thus the various steps of the ion-exchange process can be represented by Scheme 2. The compositions of the pure phases were in good agreement with those from C, H, and N analyses [Found: C, 5.40; H, 2.60; N, 1.55. Calc. for $Zr(HPO_4)_{1.67}(NEt_2H_2PO_4)_{0.33}{\cdot}H_2O$: C, 4.85; H, 2.45; N, 1.40. Found: C, 8.95; H, 3.40; N, 2.45. Calc. for $Zr(HPO_4)_{1.33}(NEt_2H_2PO_4)_{0.67}{\cdot}H_2O$: C, 8.95; H, 3.35; N, 2.60. Found: C, 12.1; H, 3.85; N, 3.40. Calc. for $Zr(HPO_4)(NEt_2H_2PO_4){\cdot}2.5H_2O$: C, 11.95; H, 4.40; N, 3.40%].

Ion-exchange Behaviour of α-ZrP *with Trimethylammonium Ion.*—The titration curve of α-ZrP with triethylamine is given in Figure 1. It indicates only one inflection point at 1.66 mequiv. triethylamine per gram of α-ZrP. The *X*-ray diffraction analysis revealed that a solid solution of two phases was present until the end-point, the intensities of the phase at d = 12.61 Å increasing linearly as that of the phase at d = 7.56 Å decreases (*cf.* Figure 5). Between 23 and 120% triethylamine loadings, a mixture of two phases remained with 90% $Zr(NEt_3HPO_4)_{0.46}(HPO_4)_{1.56}{\cdot}2H_2O$ and 10% $Zr(HPO_4)_2{\cdot}H_2O$. It can be seen from Figure 3 that the equilibrium was not reached even after a mixture was shaken for as long as 10 d. Longer equilibration periods may produce a pure phase at 25% loading, if this is

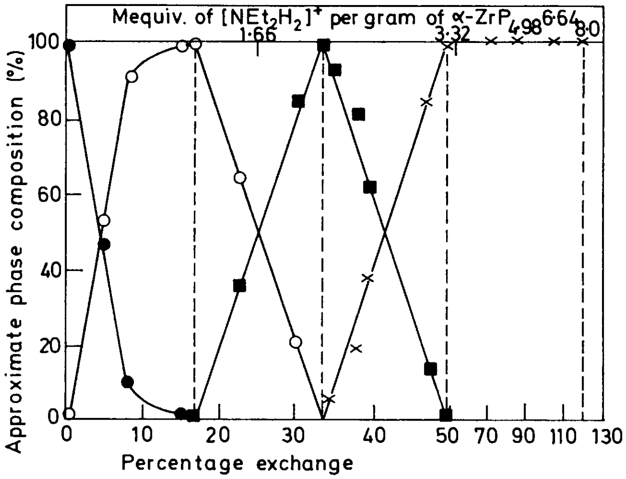


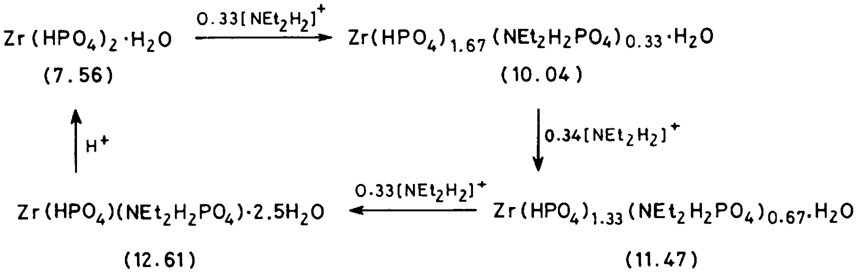
FIGURE 4 Phase composition as a function of diethylamine loading. (●) Phase A = α-ZrP, d = 7.56 Å; (○) phase B = $Zr(HPO_4)_{1.67}(NEt_2H_2PO_4)_{0.33}{\cdot}H_2O$, d = 10.04 Å; (■) phase C = $Zr(HPO_4)_{1.33}(NEt_2H_2PO_4)_{0.67}{\cdot}1.5H_2O$, d = 11.47 Å; and (×) phase D = $Zr(HPO_4)(NEt_2H_2PO_4){\cdot}2.5H_2O$, d = 12.61 Å

purely a kinetic effect. The exchange process can therefore be represented as in Scheme 3(a). At equilibrium, however, it would be likely to follow Scheme 3(b).

Upon analysis the product of Scheme 3(a), which is a solid solution, gave the following analytical data (%):

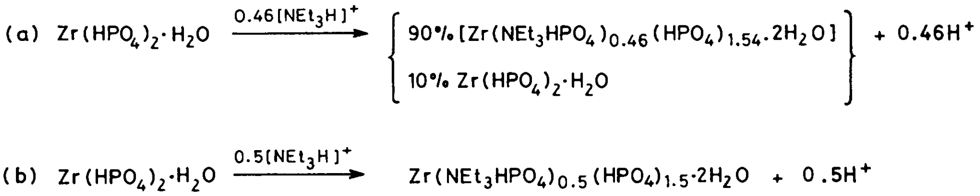
	C	H	N
Found:	7.20	3.35	1.70
Calc.:	8.25	3.20	1.60

This sample was also analyzed for C, H, and N after heating at 800 °C; less than 0.2% of each element was present. This indicates that the possibility of triethylamine being retained by intercalation with the lattice is unlikely.



$$\begin{tikzcd} \underset{(7.56)}{Zr(HPO_4)_2\cdot H_2O} \arrow[r, "0.33[NEt_2H_2]^+"] & \underset{(10.04)}{Zr(HPO_4)_{1.67}(NEt_2H_2PO_4)_{0.33}\cdot H_2O} \arrow[d, "0.34[NEt_2H_2]^+"] \\ \underset{(12.61)}{Zr(HPO_4)(NEt_2H_2PO_4)\cdot 2.5H_2O} \arrow[u, "H^+"] & \underset{(11.47)}{Zr(HPO_4)_{1.33}(NEt_2H_2PO_4)_{0.67}\cdot H_2O} \arrow[l, "0.33[NEt_2H_2]^+"'] \end{tikzcd}$$

Scheme 2



$$(a)\quad Zr(HPO_4)_2\cdot H_2O \xrightarrow{0.46[NEt_3H]^+} \left\{\begin{array}{l} 90\%\,[Zr(NEt_3HPO_4)_{0.46}(HPO_4)_{1.54}\cdot 2H_2O] \\ 10\%\,Zr(HPO_4)_2\cdot H_2O \end{array}\right\} + 0.46H^+$$

$$(b)\quad Zr(HPO_4)_2\cdot H_2O \xrightarrow{0.5[NEt_3H]^+} Zr(NEt_3HPO_4)_{0.5}(HPO_4)_{1.5}\cdot 2H_2O + 0.5H^+$$

Scheme 3

α-ZrP has been shown to be catalytically active.[14] A catalytic reduction of triethylamine to diethylamine by α-ZrP is possible. Thus the sample was subjected to thermogravimetry and mass spectrometry. It can be seen from the Table that this compound decomposed in three stages, namely dehydration, removal of amine, and condensation of orthophosphate groups to pyrophosphate. The weight loss in the second stage, considered to be the evolution of triethylamine, is almost identical to the theoretical amount of triethylamine present in the zirconium phosphate lattice. The evidence for the presence of triethylamine can be seen from the mass-spectral results (Table). The major *m/e* peaks not only correspond to the NEt_3 entity but also agree with their $I : I_0$ ratio.[15] Thus, on this evidence, α-ZrP is not behaving as a catalyst.

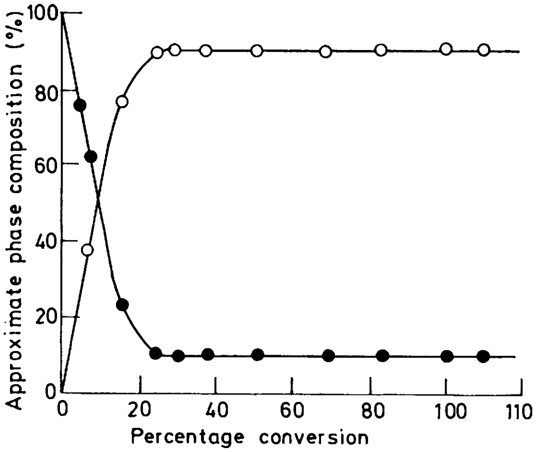


FIGURE 5 Phase composition as a function of triethylamine loading. (●) Phase A = α-ZrP, $d = 7.56$ Å; and (○) phase B = $Zr(HPO_4)_{1.5}(NEt_3HPO_4)_{0.5}\cdot 2H_2O$, $d = 12.61$ Å

DISCUSSION

Figure 1 shows that at the start of the titration curves (at zero points) where the α-ZrP was equilibrated solely with aqueous salts only a very small uptake of any ion was noted (*ca.* 5% of the total ion-exchange capacity of α-ZrP). If the base was added together with its salt the reaction took place with the exchangeable hydrogen ions. This observation is consistent with the recent conclusions drawn by Albertson *et al.*[16] and Troup and Clearfield [17] whilst investigating the crystal structure of α-ZrP. Zirconium phosphate having a high degree of crystallinity must require appreciable energy to sustain exchange. This can be supplied by adding a base (amines in the present studies) together with the salts through reaction with the exchangeable hydrogen ions.

Michel and Weiss have reported [10] the exchange of primary, secondary, and tertiary amines by α-ZrP, the carbon chain length of the amines varying from 4 to 18. They noted large increases in the basal spacing of the layer lattice with increasing chain length and generalized that the hydrogen-ion exchange was 100, 40, and 15% for the primary, secondary, and tertiary amines respectively. Yamanaka *et al.*[11] have also studied complex formation of n-butylamine with α-ZrP. They concluded that the process was purely ion exchange. Similar observations based on ammonium-ion exchange by α-ZrP were reported by Hasegawa and Aoki; [18] they noted that all the hydrogen ions were exchanged for n-butylamine, and obtained two pure phases of composition $Zr(NBuH_3PO_4)_{1.34}(HPO_4)_{0.67}\cdot H_2O$ and Zr(NBu-

$H_3PO_4)_2 \cdot H_2O$ at 67 and 100% exchange respectively. No sharp upturn in the ion-exchange isotherm was seen at 67% exchange. This may be due to their poorly crystalline material; the latter would have cavities of different sizes rather than a relatively constant set of dimensions as in the fully crystalline exchanger, which may not effect the ion-exchange capacity but would certainly have an effect on the sharpness of the plateau in the titration curve.

A most interesting feature of the present studies is the fact that the hydrogen ions of α-ZrP undergo 100% exchange for ethylamine, 50% for diethylamine, and 25% for triethylamine respectively, in contrast to the results of Michel and Weiss.[10] Secondly, ethylamine exchange goes through four steps with the formation of four new phases and the diethylamine exchange produces three plateaux in the ion-exchange isotherm. The plateaux may be due to the fact that the hydrogen ions of α-ZrP present different acid sites towards various alkylammonium ions. To explain the former observation the following points may be considered: (*a*) the basicity of various amines; (*b*) the chain length of the amines; and (*c*) the action of amines either as proton acceptors (Brønsted base), or as a Brønsted acid, acting as an ammonium ion which exchanges the hydrogen ion.

Thermogravimetric and mass-spectral analyses of 23% triethylammonium ion-exchanged α-ZrP

Thermogravimetry					Mass spectrum
		Weight loss (%)			
Stage of decomposition	Temperature range (θ_c/°C)	Found	Calc.	Evolved species	Major *m/e* peaks *
First	40—150	10.16	10.00	$2H_2O$ (interstitial)	16, 17, 18
Second	210—300	11.53	11.60	90% $(NEt_3)_{0.46}$	30 (41), 58 (32), 86 (100), 87 (7), 100 (8), 101 (16)
Third	450—600	5.02	5.00	H_2O (condensation)	16, 17, 18

* Numerals in parentheses are the $I : I_0$ ratios in percentages.

If (*a*) was predominant in the ion exchange of α-ZrP with primary, secondary, and tertiary amines then the exchange should follow the basicity sequence. The order is $NEt_3 > NEtH_2 > NEt_2H$. Clearly our results do not follow this sequence. The increase in chain length of the alkylammonium ions explains at least in part the orientation and space requirement of the organic molecules in the zirconium phosphate interlayers. The conclusion that the amine is acting as a Brønsted acid again supports our results. As we have noted, various amines presented to the α-ZrP as their aqueous salt solutions enter the interlayer space as a corresponding ethylammonium ion replacing the counter ion initially present. By inspection of Figures 1, 2, 4, and 5 the exchange reaction between α-ZrP and alkylammonium ions can be seen to cease at *ca.* pH 9. At higher pH the amines may exist as uncharged species and thus no ion exchange took place due to unavailability of counter ions. It is envisaged that such enlarged cavities of zirconium phosphates could lead to exchange of larger ions which were excluded by the α-ZrP host lattice at room temperature. Thus the exchange of Rb^+, Cs^+, transition-metal ions, and lanthanoid ions with these new phases is expected.

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