Ion-exchange Mechanism of some Bivalent Transition-metal Ions on Half-converted Sodium and Lithium Forms of Crystalline Zirconium Phosphate[1]

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The ion-exchange processes of Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+} on half-converted sodium and lithium (M^I) forms of crystalline zirconium phosphate, $ZrHM^I(PO_4)_2{\cdot}nH_2O$, occur in two steps from 0 to 80% and 80 to 100% conversion of the exchanger. Different ion-exchange mechanisms operate for the first step of exchange, depending on the proton activity in solution. Measurements on mixtures of transition-metal ions and fully converted metal(II) forms of zirconium phosphate, $ZrM^{II}(PO_4)_2{\cdot}nH_2O$, show that the exchange is a non-equilibrium process.

PRELIMINARY experiments on the ion-exchange properties of $ZrHNa(PO_4)_2{\cdot}5H_2O$ towards bivalent transition-metal ions [2] showed that this exchanger (in close agreement with data obtained by Alberti *et al.*[3] on alkaline-earth metal ions) gave high loading values when contacted with 0.05 mol dm^{-3} $M[NO_3]_2$ solutions. The high affinity of the half-converted form of crystalline zirconium phosphate towards transition-metal ions compares very favourably with that of both semi- and highly crystalline zirconium phosphate [4,5] in dihydrogen forms loaded to *ca.* 1—2%. Very recently,[6] Clearfield and Kalnins were able to fully convert also $Zr(HPO_4)_2{\cdot}H_2O$ (α-ZP) (prepared by the refluxing procedure) into the transition-metal ion forms by equilibrating the exchanger and solutions of the appropriate metal(II) at *ca.* 100 °C.

This paper reports the ion-exchange behaviour, at room temperature, of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} on crystalline $ZrHNa(PO_4)_2{\cdot}5H_2O$ and $ZrHLi(PO_4)_2{\cdot}4H_2O$. It seemed of interest to study this latter form also in the light of the possible applications of synthetic inorganic ion exchangers in nuclear technology (on-line decontamination of power reactors) since lithium ion cannot be activated by nuclear radiation.

EXPERIMENTAL

All the reagents were E. Merck ' pro-analysi ' products. Crystalline $Zr(HPO_4)_2{\cdot}H_2O$ was prepared according to the direct-precipitation method.[7] The compounds $ZrHNa(PO_4)_2{\cdot}5H_2O$, $ZrHLi(PO_4)_2{\cdot}4H_2O$, and $ZrHK(PO_4)_2{\cdot}H_2O$ were obtained by titrating the dihydrogen form until half-conversion and then drying over a saturated solution of $BaCl_2$ (relative humidity *ca.* 90%).

Equilibrium Experiments.—Several samples (1 g) of half-exchanged forms were equilibrated by shaking with different volumes of 0.005 mol dm^{-3} solutions of $Cu[O_2CMe]_2$ or $Cu[NO_3]_2$ for 4 d at 25 ± 1 °C. Measurements of distribution coefficients and separation factors were made by equilibrating fixed amounts (6 milliequiv.) of $ZrHNa(PO_4)_2{\cdot}5H_2O$ with a 0.005 mol dm^{-3} solution (600 cm^3) of $M[O_2CMe]_2$ (M = Cu, Ni, Mn, Co, or Zn). This method was used in order to obtain transition-metal concentrations in solution corresponding to two or three times the fixed charges on the exchangers. The solid was filtered off and the supernatant solutions were analysed for pH and contents of alkali- and transition-metal ions. *X*-Ray diffractograms were determined both for wet and conditioned (r.h. 90%) samples.

Analytical Procedures.—Alkali- and transition-metal ions were determined with a Varian Techtron A.A. 120 flame spectrophotometer. Phosphates were determined colorimetrically.[8] pH Measurements were made with a Beckman Research model 1019 pH meter. The water content was determined with a Stanton model T.G. 750 thermobalance (heating rate, 2 °C min^{-1}). *X*-Ray diffraction patterns were taken on a Philips diffractometer using nickel-filtered Cu-K_α radiation.

RESULTS

Figure 1(*a*) and (*b*) shows the amount of Cu^{2+} (in milliequiv.) taken up by 1 g (5.1 milliequiv.) of $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å),† as well as the amount of Na^+ and H^+ released to the supernatant solutions, plotted against the amount of Cu^{2+} initially present in the added 0.005 mol dm^{-3} solution of (*a*) $Cu[O_2CMe]_2$ and (*b*) $Cu[NO_3]_2$. The influence of the anion on the ion-exchange behaviour of Cu^{2+} is immediately obvious on comparing Figure 1(*a*) with (*b*). The two cases will now be described separately.

$ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) + 0.05 mol dm^{-3} $Cu[O_2CMe]_2$

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† The interlayer distances are in parentheses.

[1] Presented in part at the 12th Congresso Nazionale della Società Chimica Italiana, S. Margherita di Pula (Cagliari), Italy, Septemper 1975.

[2] S. Allulli, A. La Ginestra, M. A. Massucci, M. Pelliccioni, and N. Tomassini, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 337.

[3] G. Alberti, R. Bertrami, M. Casciola, U. Costantino, and J. P. Gupta, *J. Inorg. Nuclear Chem.*, 1976, **38**, 843.

[4] S. Ahrland, N. Bjork, R. H. Blessing, and R. G. Herman, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2377.

[5] Y. Saito and I. Tomita, *J. Chromatog.*, 1972, **71**, 538.

[6] A. Clearfield and J. M. Kalnins, *J. Inorg. Nuclear Chem.*, 1976, **38**, 849.

[7] G. Alberti and E. Torracca, *J. Inorg. Nuclear Chem.*, 1968, **30**, 317.

[8] G. Alberti, A. Conte, and E. Torracca, *J. Inorg. Nuclear Chem.*, 1966, **28**, 225.

Solutions.—Figure 1(a) shows that, up to *ca.* 80% loading of Cu^{2+}, the exchanger picks up all the Cu^{2+} from the solution and, at the same time, releases both Na^+ and H^+ ions with a molar ratio $Na : H > 1 : 1$. After 80% conversion the entering Cu^{2+} exchange the remaining H^+ until the fully converted $ZrCu(PO_4)_2\cdot4H_2O$ (9.6 Å) phase is obtained (by a column technique).

X-Ray diffraction patterns of samples at various loadings of Cu^{2+} (Figure 2) show that, in the range x_{Cu} 0.0—0.15,* zirconium layers keep their original distance of 11.8 Å, so that the exchanged copper ions presumably give rise to a solid solution. After x_{Cu} 0.15, a reflection at 2θ 9.2 (9.6 Å) appears and its intensity continuously increases with x_{Cu}, whilst the intensity of the $ZrHNa(PO_4)_2\cdot5H_2O$ (11.8 Å) phase decreases. At x_{Cu} 0.80 only one first diffraction maximum is observed at 2θ 9.2. Thus, in the range x_{Cu} 0.15—0.80, the exchange occurs *via* a two-phase transition mechanism. In the range 80—100% loading of Cu^{2+}, the *X*-ray patterns suggest the occurrence of a solid solution, since only small variations in the peak intensities are found.

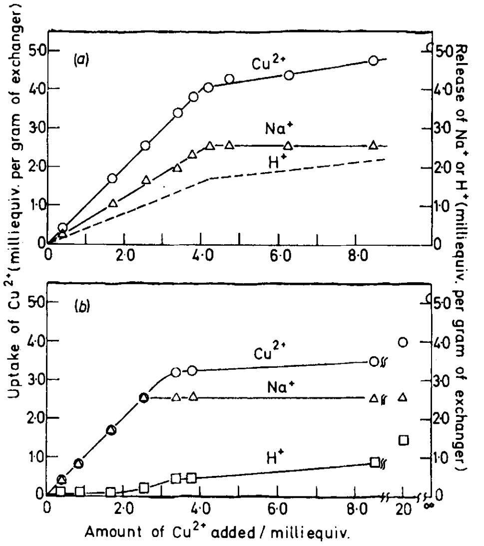

FIGURE 1 Ion exchange of Cu^{2+} on $ZrHNa(PO_4)_2\cdot5H_2O$ (11.8 Å). The exchanger (1 g) was equilibrated with different volumes of (*a*) 0.005 mol dm^{-3} $Cu[O_2CMe]_2$ and (*b*) 0.005 mol dm^{-3} $Cu[NO_3]_2$ at 25 °C. The broken line in (*a*) was calculated from the difference between the Cu^{2+} and Na^+ values

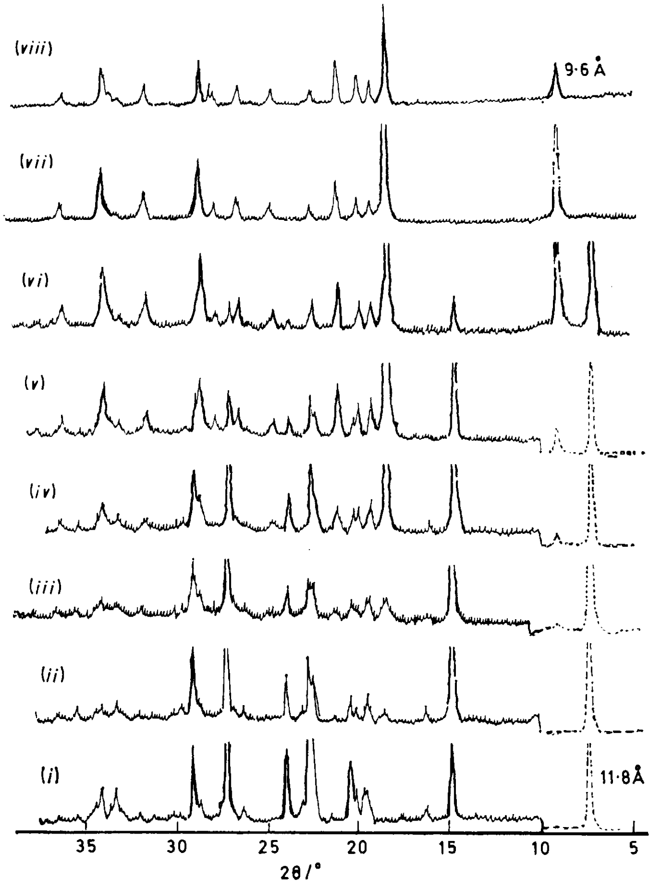

FIGURE 2 *X*-Ray diffraction patterns of several samples from the $ZrHNa(PO_4)_2\cdot5H_2O$ (11.8 Å) + $Cu[O_2CMe]_2$ process. Sensitivity, 2×10^3 count s^{-1}; broken line, 4×10^3 count s^{-1}. x_{Cu} = 0.0 (*i*), 0.08 (*ii*), 0.16 (*iii*), 0.33 (*iv*), 0.50 (*v*), 0.75 (*vi*), 0.80 (*vii*), and 1.0 (*viii*)

It is noteworthy that this behaviour closely parallels that reported by Clearfield and Kalnins[6] for exchange of Cu^{2+} ion (as the acetate) on the $Zr(HPO_4)_2\cdot H_2O$ (7.6 Å) phase at *ca.* 100 °C. Thus, the overall ion-exchange process can be written as in (1).

$$\underset{(11.8\ \text{Å})}{ZrHNa(PO_4)_2\cdot5H_2O} \xrightarrow[+0.8\,Cu^{2+}]{-H_2O-Na^+-0.6\,H^+} \underset{(9.6\ \text{Å})}{ZrH_{0.4}Cu_{0.8}(PO_4)_2\cdot4H_2O} \xrightarrow[+0.2\,Cu^{2+}]{-0.4\,H^+} \underset{(9.6\ \text{Å})}{ZrCu(PO_4)_2\cdot4H_2O} \qquad (1)$$

From the equilibrium data in Figure 1(*a*) it was possible to calculate the Cu : Na : H molar ratio in the solid up to 80% loading of Cu^{2+}. Assuming that before disappearing the starting form $ZrHNa(PO_4)_2\cdot5H_2O$ maintains the ratio Na : H = 1 : 1, the entering Cu^{2+} ions exchange Na^+ and H^+ in such a ratio that a molar ratio Cu : H ranging from 0.75 : 0.5 to 0.85 : 0.3 in the exchanged solid is found (see also the next section). At the same time (*i.e.* up to 80% loading of Cu^{2+}) the distribution coefficients of Cu^{2+} approach infinity. After 80% conversion, the affinity of the exchanger (a copper–hydrogen form) for Cu^{2+} ions decreases, so that higher chemical potentials are required to allow a further loading of the zirconium phosphate and the K_d^{Cu} values markedly decrease.

$ZrHNa(PO_4)_2\cdot5H_2O$ (11.8 Å) + 0.05 mol dm^{-3} $Cu[NO_3]_2$ *Solution.*—Figure 1(*b*) shows that when $ZrHNa(PO_4)_2\cdot5H_2O$ (11.8 Å) is equilibrated with various volumes of 0.005 mol dm^{-3} $Cu[NO_3]_2$ solution the exchanger picks up all the Cu^{2+} ions in solution, only up to 50% of its theoretical ion-exchange capacity. Furthermore, in the range 0—50% loading of Cu^{2+} the entering Cu^{2+} ions seem to replace only the Na^+ of the exchanger. This is confirmed by the *X*-ray diffraction patterns of the sample at 50% loading of Cu^{2+} (Figure 3), where the reflections of the $ZrHNa(PO_4)_2\cdot5H_2O$ (11.8 Å) phase completely disappear.

A careful examination of the *X*-ray diffraction patterns of samples at various loadings of Cu^{2+} (Figure 3) shows that

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* x_{Cu} = mole fraction of Cu^{2+} in the exchanger.

in the region x_{Cu} 0.0—0.50 the ion-exchange process in nitrate solutions is not restricted to exchange between Na^+ and Cu^{2+} ions. In fact samples having x_{Cu} 0.16 and 0.32 display four first diffraction maxima at 2θ 7.5 (11.8), 8.4 (10.4), 9.2 (9.6), and 11.6° (7.6 Å) and an evident shoulder at 8.8° (10.0 Å). At x_{Cu} 0.50, only two first diffraction maxima, at 2θ 9.2 (9.6) and 11.6° (7.6 Å) are found. This finding can be explained on the basis of the ion-exchange behaviour of alkaline-earth metal ions with $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) described by Alberti *et al.*,[3] especially that of Ba^{2+} ions. These workers found that a number of consecutive reactions take place involving several solid phases, *i.e.* $ZrHM_{0.5}(PO_4)_2{\cdot}nH_2O$, $ZrH_{2-2x}M_x(PO_4)_2{\cdot}mH_2O$ ($x > 0.5$), $Zr(HPO_4)_2{\cdot}H_2O$, and $Zr(HPO_4)_2{\cdot}6H_2O$.[9] Following their arguments, the overall reactions involved in the exchange of Cu^{2+} in nitrate solutions up to 50% loading can be schematized as in equation (2) and (3).

$$\underset{(11.8\ \text{Å})}{ZrHNa(PO_4)_2{\cdot}5H_2O} + 0.5\ Cu^{2+} \longrightarrow \underset{(10.0\ \text{Å})}{ZrHCu_{0.5}(PO_4)_2{\cdot}nH_2O} + Na^+ \qquad (2)$$

$$\underset{(10.0\ \text{Å})}{ZrHCu_{0.5}(PO_4)_2{\cdot}nH_2O} + x\ Cu^{2+} \longrightarrow \underset{(9.6\ \text{Å})}{ZrH_{(1-2x)}Cu_{(0.5+x)}(PO_4)_2{\cdot}mH_2O} + 2x\ H^+ \qquad (2a)$$

$$\underset{(11.8\ \text{Å})}{ZrHNa(PO_4)_2{\cdot}5H_2O} + H^+ \longrightarrow a\ \underset{(10.4\ \text{Å})}{Zr(HPO_4)_2{\cdot}6H_2O} + b\ \underset{(7.6\ \text{Å})}{Zr(HPO_4)_2{\cdot}H_2O} \qquad (3)$$

It must be borne in mind that the set of reactions (2) and (3) is by no means complete since: (*a*) the $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) phase can release both the Na^+ and H^+ ions simultaneously to the solution, thus causing sufficient lowering of the external pH values to give rise immediately to reaction (3); (*b*) other solid phases, such as $Zr(HPO_4)_2{\cdot}6H_2O$ (10.4 Å),[9] may, in turn, exchange Cu^{2+}. Furthermore, the numerical order does not represent the sequence of the reactions, which is strongly dependent on the equilibration time and pH. (For a more detailed assessment of these equilibria see ref. 3.) At 50% loading of Cu^{2+} only two phases, $Zr(HPO_4)_2{\cdot}H_2O$ (7.6 Å) and $ZrH_{(1-2x)}Cu_{(0.5+x)}(PO_4)_2{\cdot}mH_2O$ (9.6 Å), exist. Figures 1(*b*) and 3 show that by contacting the $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) phase with larger amounts of Cu^{2+}, the $Zr(HPO_4)_2{\cdot}H_2O$ (7.6 Å) phase is loaded by Cu^{2+} until it disappears at 80% loading. This behaviour, which seems in contrast to that previously observed for α–ZP,[5] may be explained by taking into account the fact that the Na^+ ions released in the first 50% exchange catalyse the exchange of the hydrogen ion by Cu^{2+} through the formation (when allowed by the external pH) of the sodium–hydrogen phase.[10]

$$\underset{(11.8\ \text{Å})}{ZrHNa(PO_4)_2{\cdot}5H_2O} \xrightarrow[0.5\ Cu^{2+}]{-Na^+ - 2H_2O} 0.62\ \underset{(9.6\ \text{Å})}{ZrH_{0.4}Cu_{0.8}(PO_4)_2{\cdot}4H_2O} + 0.38\ \underset{(7.6\ \text{Å})}{Zr(HPO_4)_2{\cdot}H_2O}$$

$$(Na^+\ \text{catalysed}) \xrightarrow[+\,0.3\ Cu^{2+} + H_2O]{-0.6\ H^+} \underset{(9.6\ \text{Å})}{ZrH_{0.4}Cu_{0.8}(PO_4)_2{\cdot}4H_2O}(Na^+\ \text{catalysed}) \xrightarrow[0.2\ Cu^{2+}]{-0.4\ H^+} \underset{(9.6\ \text{Å})}{ZrCu(PO_4)_2{\cdot}4H_2O} \qquad (4)$$

Also taking into account data from the acetate solution as well as the similarity between *X*-ray diffraction patterns of the 80% loaded materials (Figures 2 and 3), the composition of $ZrH_{0.4}Cu_{0.8}(PO_4)_2{\cdot}4H_2O$ (9.6 Å) has been assigned to the phase previously reported as $ZrH_{(1-2x)}Cu_{(0.5+x)}(PO_4)_2{\cdot}nH_2O$ (9.6 Å). Thus, the ion-exchange process can be synthesized in three steps [equation (4)].

To support this suggestion, a known amount of 50% Cu^{2+}-loaded exchanger (see Figure 3) was suspended in 0.01 mol dm^{-3} NaCl and titrated with 0.01 mol dm^{-3} Na[OH]. Figure 4 shows that H^+ ions are exchanged by the Na^+ in three steps. The two plateaux correspond to the titration of the assumed 38% of $Zr(HPO_4)_2{\cdot}H_2O$ (7.6 Å) whilst the third step corresponds to the exchange of H^+ belonging to the $ZrH_{0.4}Cu_{0.8}(PO_4)_2{\cdot}4H_2O$ (9.6 Å) phase, which occurs *via* a solid–solution mechanism. *X*-Ray diffraction patterns of the titrated sample (conditioned at r.h. 90%) show two first diffraction maxima corresponding to d_{002} 9.9 [$Zr(NaPO_4)_2{\cdot}3H_2O$] [11] and 9.6 Å [$ZrCu(PO_4)_2{\cdot}4H_2O$].

Column experiments further support the proposed mechanism. By eluting $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) with a 0.005 mol dm^{-3} solution of $Cu[NO_3]_2$, only 50% loading of Cu^{2+} was achieved, since, in contrast to the batch procedure, Na^+ ions are completely removed by the effluent; thus the catalytic mechanism cannot hold in this case. In fact, full conversion of the exchanger was achieved by adding Na^+ ions (0.01 mol dm^{-3}) to the percolating copper solution.

Influence of the Alkali-metal Counter Ion on the Exchange of the Transition-metal Ions.—In order to test the influence of the alkali-metal counter ion on the exchange behaviour of Cu^{2+}, 0.005 mol dm^{-3} solutions of $Cu[O_2CMe]_2$ and $Cu[NO_3]_2$ were equilibrated with the $ZrHLi(PO_4)_2{\cdot}4H_2O$ (10.0 Å) phase. In both cases the results coincide with those on $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å), thus showing that the exchange of Cu^{2+} on zirconium phosphate does not depend on the presence of Li^+ or Na^+ in the starting materials.

To ascertain if the same behaviour holds for other transition-metal ions, $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) and $ZrHLi(PO_4)_2{\cdot}4H_2O$ (10.0 Å) were contacted with 0.005 mol dm^{-3} solutions of the acetates and nitrates of Mn^{II}, Ni^{II}, Co^{II}, and Zn^{II}. The liquid : solid ratio was chosen in order to have 3 milliequiv. of metal ions in solution and 6 milliequiv. of counter ions in the solid (maximum loading allowed, 50%) and the results are shown in Table 1, those for Cu^{2+} being reported for comparison. The data obtained show that

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[9] G. Alberti, U. Costantino, and J. S. Gill, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1733.

[10] G. Alberti, U. Costantino, and J. P. Gupta, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2109.

[11] G. Alberti and U. Costantino, *J. Chromatog.*, 1974, **102**, 5.

on $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) all the cations investigated behave in a similar way. Furthermore, by eluting this phase with 0.005 mol dm^{-3} solutions of $M[O_2CMe]_2$, zirconium phosphate was fully converted into the several transition-metal ion forms $ZrM(PO_4)_2{\cdot}4H_2O$ (9.6 Å).*

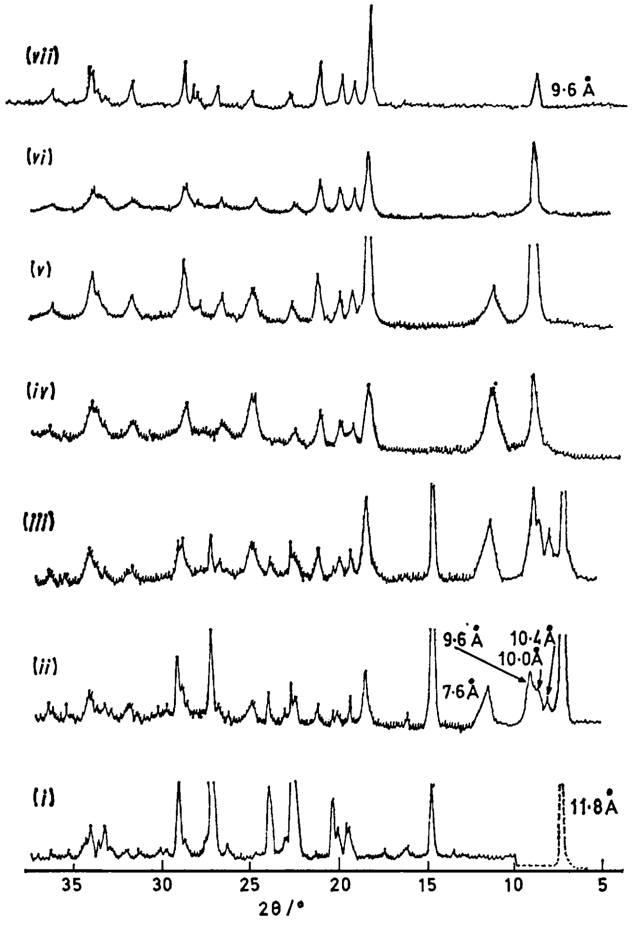

FIGURE 3 X-Ray diffraction patterns of several samples from the $ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å) + $Cu[NO_3]_2$ process. Sensitivity, 2×10^3 count s^{-1}; broken line, 4×10^3 count s^{-1}. x_{Cu} = 0.0 (*i*), 0.16 (*ii*), 0.33 (*iii*), 0.50 (*iv*), 0.68 (*v*), 0.80 (*vi*), and 1.0 (*vii*)

TABLE 1

Loading (milliequiv.) of M^+ and M^{2+} of half-converted sodium and lithium forms of zirconium phosphate equilibrated with 0.005 mol dm^{-3} $M[O_2CMe]_2$ or 0.005 mol dm^{-3} $M[NO_3]_2$ at 25 °C

	$ZrHNa(PO_4)_2{\cdot}5H_2O$ (11.8 Å)				$ZrHLi(PO_4)_2{\cdot}4H_2O$ (10.0 Å)			
	$M[O_2CMe]_2$		$M[NO_3]_2$		$M[O_2CMe]_2$		$M[NO_3]_2$	
Ion	M^{2+}	Na^+	M^{2+}	Na^+	M^{2+}	Li^+	M^{2+}	Li^+
Mn^{2+}	1.5	0.4	1.5	<0.1	1.5	0.5	1.5	<0.1
Co^{2+}	1.5	0.5	1.5	<0.1	0.7	1.05	0.7	1.05
Ni^{2+}	1.5	0.5	1.5	<0.1	0.3	1.25	1.5	<0.1
Cu^{2+}	1.5	0.5	1.5	<0.1	1.5	0.6	1.5	<0.1
Zn^{2+}	1.5	0.5	1.5	<0.1	1.5	0.6	1.5	<0.1

In contrast, differences were found when $ZrHLi(PO_4)_2{\cdot}4H_2O$ (10.0 Å) was employed. Particularly surprising is the ion-exchange behaviour of Ni^{2+}, which gives higher loading values in nitrate than in acetate solution, even after equilibration for 30 d. Given the buffering properties of the acetate anion, an easier release of H^+ from the exchanger might have been expected. In order to investigate how the equilibrium pH might influence the ion-exchange behaviour of Ni^{2+} ions, acetate solutions were reinvestigated by adding acetic acid up to pH 3.5, *i.e.* very near to the equilibrium pH reached in nitrate solutions. Under these conditions, all the Ni^{2+} was exchanged and a final molar composition of Ni : Li : H = 1.5 : 0.6 : 2.4 in the solid was achieved. In this case, as for Co^{2+}, complete removal of the metal ions from the solutions may occur through the formation, by decreasing the external pH value, of the $Zr(HPO_4)_2{\cdot}6H_2O$ (10.4 Å) phase,† which also easily undergoes exchange with transition-metal ions.[9]

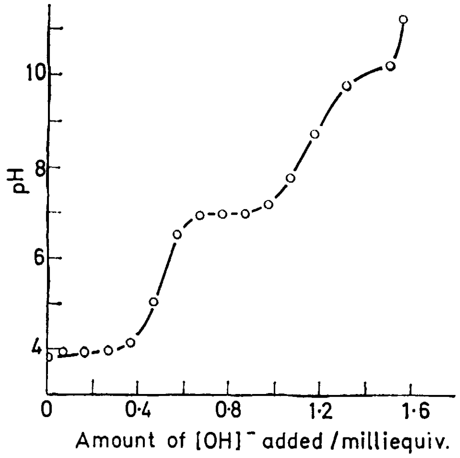

FIGURE 4 Titration curve of half-exchanged copper zirconium phosphate sample, containing 1.5 milliequiv. of hydrogen ion. Titrant: 0.01 mol dm^{-3} Na[OH] + 0.01 mol dm^{-3} NaCl

Further confirmation of the influence of the initial counter ion was achieved by measurements of copper(II) acetate and nitrate solutions on $ZrHK(PO_4)_2{\cdot}H_2O$ (7.95 Å) (under the same conditions as in Table 1): in both cases only *ca.* 7—10% loading of the exchanger by Cu^{2+} was obtained.

Distribution Coefficients of some Mixtures of Transition-metal Ions.—Beside the ion-exchange behaviour of a single transition-metal ion, it was thought of interest to study the mutual influence such ions may have on the ion-exchange process. Thus Table 2 reports some distribution coefficients and separation factors obtained by contacting several

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* The stereochemistries of the exchanged Co^{2+}, Cu^{2+}, and Ni^{2+} ions and their variation with temperature have been discussed elsewhere.[12]

† This was confirmed by contacting $ZrHLi(PO_4)_2{\cdot}4H_2O$ (10.0 Å) with a solution of $MeCO_2H$ at pH 3.5.

[12] S. Allulli, C. Ferragina, A. La Ginestra, M. A. Massucci, N. Tomassini, and A. A. G. Tomlinson, *J.C.S. Dalton*, 1976, 2115.

TABLE 2

Distribution coefficients and separation factors (α) of some mixtures of transition-metal ions on half-converted sodium form of crystalline zirconium phosphate

	Mixture					
	Cu^{2+}–Mn^{2+}	Cu^{2+}–Co^{2+}	Cu^{2+}–Ni^{2+}	Cu^{2+}–Zn^{2+}	Mn^{2+}–Ni^{2+}	Cu^{2+}–Ni^{2+}–Mn^{2+}
K_d^{Cu}	8×10^2	1.5×10^3	2.5×10^3	1×10^3		2×10^3
K_d^{Mn}	2.5×10^2				1×10^3	1×10^2
K_d^{Co}		2×10^2				
K_d^{Ni}			8×10^1		5×10^1	5×10^1
K_d^{Zn}				3×10^2		
$\alpha = \bar{m}_A m_B / \bar{m}_B m_A$	3	8	3×10^1	3	2×10^1	$\alpha^{Cu}{}_{Mn} = 2 \times 10^1$ $\alpha^{Cu}{}_{Ni} = 4 \times 10^1$, $\alpha^{Mn}{}_{Ni} = 3$

mixtures of 0.01 mol dm^{-3} solutions of $M[O_2CMe]_2$ with $ZrHNa(PO_4)_2 \cdot 5H_2O$ (11.8 Å). Except for the Mn^{2+}–Ni^{2+} case, 90—100% loadings of M^{2+} were obtained and the *X*-ray diffraction patterns were very similar. From the data obtained a selectivity order of Cu > Zn ⩾ Mn > Co > Ni can be derived.

Finally, Table 3 lists the distribution coefficients of some transition-metal ions on the $ZrCo(PO_4)_2 \cdot 4H_2O$ (9.6 Å), $ZrNi(PO_4)_2 \cdot 4H_2O$ (9.6 Å), and $ZrZn(PO_4)_2 \cdot 4H_2O$ (9.6 Å) forms of crystalline zirconium phosphate. These data indicate the strong preference of the exchanger for the initial counter ion, and suggest that the ion-exchange processes of the transition-metal ions are related to non-equilibrium processes, in good agreement with high-temperature data.[6]

TABLE 3

Distribution coefficients of some transition-metal ions on crystalline zirconium phosphate fully converted into cobalt(II), nickel(II), and zinc(II) forms

Process *	K_d^{Co}	K_d^{Ni}	K_d^{Cu}	K_d^{Zn}
Ni^{2+}, Co^{2+}	2×10^4	5×10^1		
Cu^{2+}, Co^{2+}	1×10^4		5×10^1	
Zn^{2+}, Co^{2+}	1×10^4			5×10^1
Co^{2+}, Ni^{2+}	2×10^2	3×10^3		
Cu^{2+}, Ni^{2+}		2×10^3	2×10^2	
Zn^{2+}, Ni^{2+}		3×10^4		5×10^1
Co^{2+}, Zn^{2+}	10^{-5}			10^5
Ni^{2+}, Zn^{2+}		10^{-5}		10^5
Cu^{2+}, Zn^{2+}			5×10^1	1×10^4

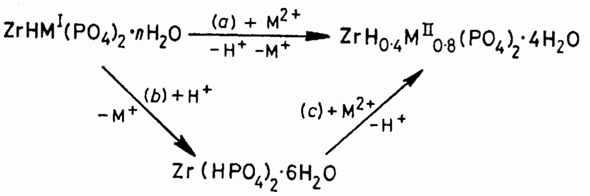
* Replacement in crystalline phase of second ion by the first quoted.

DISCUSSION

Data collected on the ion-exchange processes of some transition-metal ions on crystalline zirconium phosphate confirm, as observed previously, the enormous difficulty in fully describing the ion-exchange mechanism (also for parent ions) by simply investigating the ion-exchange behaviour of a single cation. In addition to differences in crystallinity,[13] factors such as the nature of the initial counter ions in the exchanger, the inter-layer spacing, and the characteristics of the equilibrating solutions must be taken into account (especially when cations other than alkali-metal ions are considered) since these may give rise to different ion-exchange mechanisms, even for the same exchanging cation.

The inability of crystalline zirconium phosphate compounds with narrow interlayer spacing to exchange highly hydrated cations may be related to the high activation energy required for diffusion of the entering cations through the layers. This hindrance may be overcome by means of a M^+-catalysed mechanism [10] and high temperatures,[6] or by employing materials with larger interlayer spacings such as the highly hydrated dihydrogen form [9] or the alkali-metal half-converted forms of crystalline zirconium phosphate, as our previous results [2] and the present data confirm.

When half-converted alkali-metal forms of zirconium phosphate $ZrHM(PO_4)_2 \cdot nH_2O$ ($M = Li^+, Na^+, K^+$, *etc.*) are employed the overall ion-exchange reaction may be represented by a two-step process ($0.0 \leqslant x_{M^{2+}} \leqslant 0.8$, $0.8 \leqslant x_{M^{2+}} \leqslant 1.0$) which takes place through a two-phase transition between the $ZrHM^{I}(PO_4)_2 \cdot nH_2O$ and $ZrH_{0.4}M^{II}{}_{0.8}(PO_4)_2 \cdot 4H_2O$ phases and the subsequent transformation of the latter into $ZrM^{II}(PO_4)_2 \cdot 4H_2O$ *via* a solid–solution mechanism. Nevertheless, this general scheme does not always hold for the first step of exchange, which, depending on the experimental conditions, may give rise to a more complicated three-ion exchange mechanism:



(5)

Both the occurrence and relative contribution of the given mechanism (see above) to the final loading values are related to the activities of the ions in solution and to the activation energies [which decrease in the order $ZrHK(PO_4)_2 \cdot H_2O$ (7.9 Å), $ZrHLi(PO_4)_2 \cdot 4H_2O$ (10.0 Å), $ZrHNa(PO_4)_2 \cdot 5H_2O$ (11.8 Å)] [14] required for ionic diffusion into the exchanger lattice. Thus when acetate solutions are employed, the reaction proceeds through path (*a*) owing to the buffering power of the acetate anion. For nitrate and/or acetate containing acetic acid, as soon as the pH values reach those for back titration of the half-converted forms [9] paths (*b*) and (*c*) are involved for the loading of the exchanger.

Additional information on the ion-exchange mechanism can be derived by considering the selectivity order for the transition-metal ions on zirconium phosphate found under our experimental conditions (see Tables 2

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[13] G. Alberti, U. Costantino, S. Allulli, M. A. Massucci, and M. Pelliccioni, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1347.

[14] G. Alberti, R. Bertrami, and U. Costantino, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1729.

and 3). The trend $Cu^{2+} > Zn^{2+} \geqslant Mn^{2+} > Co^{2+} > Ni^{2+}$ cannot be directly related to the stability of complex species with the various ligands present nor to the stereochemistry adopted in the lattice, which is approximately the same for all the transition-metal ions investigated.[12] A rationalization is possible if it is remembered that all the transition-metal ions in solution are six-co-ordinate and, in order to interact with the fixed groups of the exchanger (abbreviated O^-), keeping this co-ordination, two of the original ligands must be replaced through a first-order S_N1 reaction (6) which can be divided into two steps (6a) and (6b).

$$[ML_6]^{2+} + 2O^- \longrightarrow [ML_4O_2] + 2L \qquad (6)$$

$$[ML_6]^{2+} \longrightarrow [ML_4]^{2+} + 2L \qquad (6a)$$

$$[ML_4]^{2+} + 2O^- \longrightarrow [ML_4O_2] \qquad (6b)$$

The half-lives, $t_{\frac{1}{2}}$, for dissociation processes such as (6a) have been calculated[15] for $L = H_2O$, and the sequence obtained is $Cu^{2+} < Zn^{2+} \simeq Mn^{2+} < Co^{2+} < Ni^{2+}$ with the ratio for Ni^{2+} and Cu^{2+} being $\simeq 10^4 : 1$. Also, taking into account the remarkable hysteresis found in the M^{2+} ion-exchange process (see Table 3), the correspondence between the $t_{\frac{1}{2}}$ and selectivity scales may be accounted for by non-equilibrium phenomena. In fact, the exchanger will be initially loaded by that cation which more readily gives rise to the species able to diffuse into the lattice; further equilibrium with the other transition-metal ions in solution is drastically slowed by the inertness of the lattice counter ions. Therefore, the selectivity of the exchanger when contacted with a mixture of transition-metal ions should depend on the time required by the cations considered to give rise to the species which diffuse into the zirconium phosphate lattice.

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[15] M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 105.