Mechanism of Cadmium and Lead Ion Exchange by α-Zirconium Bis(monohydrogenorthophosphate) Monohydrate

By **Jai P. Gupta** and **Derek V. Nowell,*** School of Natural Sciences, The Hatfield Polytechnic, P.O. Box 109, Hatfield, Herts. AL10 9AB

An investigation of the ion-exchange processes between Cd^{2+} or Pb^{2+} and α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), at 18, 50 ± 2, 75 ± 2, and 98 ± 1 °C has been carried out. The uptake of these ions was found to increase with increase in temperature. The fully ion-exchanged phases were obtained at the highest temperature. The exchanged samples have been characterised by *X*-ray diffraction and thermogravimetric analysis. The addition of small amounts of sodium chloride to the systems at room temperature increased the Cd^{2+}–H^+ exchange from 15% to 80% but the Pb^{2+}–H^+ exchange by only 30%. The effect of $Na[NO_3]$ and $Na[O_2CMe]$ on the Pb^{2+}–H^+ system was also studied. Ion-exchange isotherms and distribution coefficients have been calculated. A particularly high separation factor for Cd^{2+} and Pb^{2+} was observed in the experiment with added NaCl at room temperature.

IN recent years, zirconium phosphates have received considerable attention as ion exchangers owing to their excellent chemical, thermal, and radiation stabilities.[1-3] Since the introduction of kidney machines, zirconium phosphate has been employed for the removal of ammonium ion from the hydrolysis of urea dialyzed from blood,[4] but nothing has been reported concerning ion-exchange reactions between α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), and toxic metal ions such as cadmium and lead, which can cause kidney and brain damage even at micro levels.[5-7]

To carry out exchange with highly crystalline α-ZrP compared to the amorphous product generally requires the addition of bases together with metal salts, but cadmium and lead form insoluble hydroxides making exchange difficult. Recent investigations carried out by Clearfield and Hagiwara [8] have suggested that the use of acetates may overcome the problem. The uptake of cadmium and lead in acetate form by α-ZrP has therefore been examined at different temperatures, as well as the effect of sodium ion upon the equilibria at room temperature.

EXPERIMENTAL

Preparation of Exchanger, Analytical Methods, and Reagents.—Crystalline α-ZrP was prepared by our direct precipitation method.[9] The cadmium and lead were estimated by atomic absorption and sodium by emission spectroscopy. Zirconium, phosphate, and thermogravimetric analyses were carried out as described earlier.[9] *X*-Ray diffraction patterns were obtained on a Philips *X*-ray unit using nickel-filtered Cu-K_α radiation, while the pH measurements were made with a Pye model 79 pH meter. Deionized water was used throughout the exchange experiments. Infrared studies were carried out on a Perkin-Elmer 257 grating i.r. spectrophotometer by the KBr disc method.

Equilibrium Procedure.—A series of ion-exchange experiments were performed as follows. (*a*) At 18 °C, each point on the titration curve was obtained by mixing α-ZrP (500 mg) in deionised water with a known amount of cadmium or lead acetate solution so that the total volume of the mixture was 100 dm^3. The mixtures were shaken in stoppered conical flasks. The amount of cadmium or lead salt added per gram of exchanger varied from 0 to 8 milliequivalents. (*b*) The experiments were repeated with the addition in each case of 1 milliequivalent of sodium salt per gram of exchanger; NaCl was tested with both metals, and $Na[NO_3]$ and $Na[O_2CMe]$ only in the case of lead. (*c*) At 50 ± 2 °C and 75 ± 2 °C, the procedure was as in (*a*). (*d*) At 98 ± 1 °C, the mixture was as in (*a*) but contained in a two-necked flask fitted with a condenser and thermometer and stirred magnetically. Clearfield and Hagiwara reported [8] that the exchange of alkaline-earth metals from acetate solutions was not reversible at higher temperature, but becomes reversible at lower temperature. Therefore, the solids were filtered from the liquids, while hot, which took less than 45 s. They were then washed thoroughly with deionised water and dried over saturated sodium chloride solution under vacuum. The cationic content was determined in the solution, after cooling to room temperature.

Column Operation.—A column of crystalline α-ZrP was prepared, and heated to 100 °C by an external steam jacket. Either $Cd[O_2CMe]$ or $Pb[O_2CMe]$ (0.05 mol dm^{-3}) was then passed through the column until the exit concentration was identical with that of the solution entering the column. The exchanged α-ZrP was then washed with deionised water and dried as above.

Definitions.—The ionic fraction of M^{2+} (Cd^{2+} or Pb^{2+}) in the solution is defined by equation (1) and there is a

$$X_A = 2m_M/(2m_M + m_H) \qquad (1)$$

corresponding expression for the exchanger (m = molarity of species in question). The distribution coefficient (K_d) is given by equation (2) where $m_M{}^i$ and $m_M{}^f$ are the molarities

$$K_d = (m_M{}^i - m_M{}^f)V/m_M{}^f W \qquad (2)$$

of M in the solution before and after the equilibrium, V is the total volume of the solution in contact with ion exchanger, and W is the mass of ion exchanger. Quantities referring to the exchanger phase will be indicated by a bar, *e.g.* $\bar{m}$, $\bar{X}$.

RESULTS

The potentiometric ion-exchange titration curves of α-ZrP against Cd^{2+} and Pb^{2+} are given in Figures 1 and 2 respectively. The fall in pH is a measure of the uptake of heavy-metal ion. The uptake increases with temperature in both cases, with little uptake at room temperature.

Figures 3 and 4 show the actual measured uptake of M^{2+} (Cd^{2+} or Pb^{2+}) from acetate solutions against milliequivalents

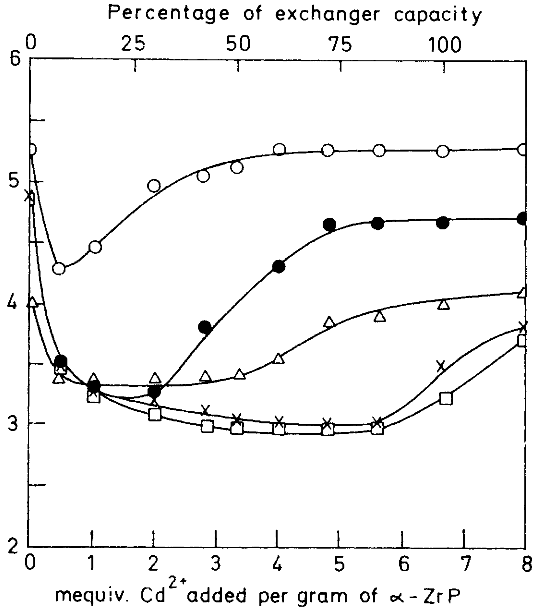

FIGURE 1 Ion-exchange potentiometric titration of α-ZrP for cadmium at various temperatures: 18 (○); 50 (●); 75 (×); 98 ± 1 °C (□); and in the presence of NaCl at 18 °C (△)

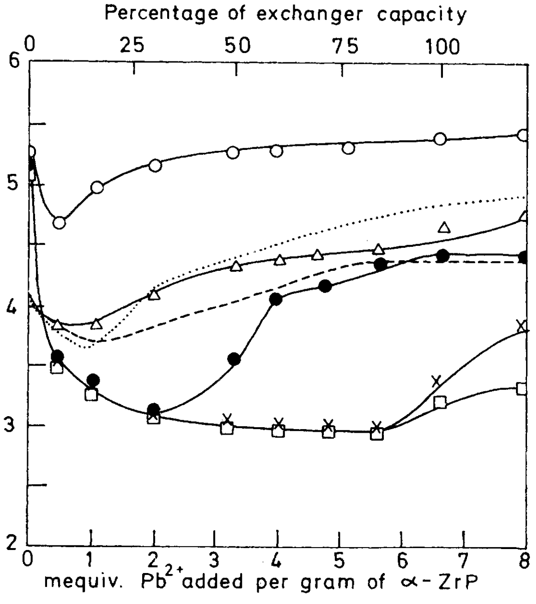

FIGURE 2 Ion-exchange potentiometric titration of α-ZrP for lead at various temperatures: 18 (○); 50 (●); 75 (×); 98 ± 1 °C (□); in the presence of NaCl at 18 °C (△); in the presence of $Na[NO_3]$ at 18 °C (· · · ·); and in the presence of $Na[O_2CMe]$ at 18 °C (– – – –)

of M^{2+} added to the system. It can be seen that at 98 °C and 75 °C most of the points indicate essentially total uptake, except at the highest values. At 50 °C, the Pb^{2+} curve follows the trend indicated by the titration curve (Figure 2), but with Cd^{2+} this is not the case throughout. The ions Pb^{2+} and Cd^{2+} show identical behaviour at room temperature where a maximum of 15% uptake was found.

The *X*-ray diffraction patterns of the loaded solids at 18 °C indicate solid solutions throughout the experiment. However, in the experiments at 98 °C, after M^{2+} addition amounting to *ca.* 15% of the exchanger capacity, the *X*-ray patterns show a mixture of two phases for both cations until complete conversion to the M^{2+} form has occurred. The crystalline nature of this material is enhanced as more M^{2+} is added. The two-phase mixture also occurred in experiments at 50 °C and 75 °C. At 98 °C when the amount of added M^{2+} exceeded the ion-exchange capacity by 20%, only a single phase, $ZrM(PO_4)_2 \cdot nH_2O$ ($n = 3.5$ for Cd^{2+} and 1.5 for Pb^{2+}), was obtained, and the same single phase was observed at 75 °C in the presence of a large excess of M^{2+}. The *X*-ray diffraction patterns are reported in Tables 1 and 2. For the reaction at 50 °C a single phase was never obtained.

Figures 1 and 2 also show the effect of the addition of small amounts of Na^+ on the exchange equilibria. The results indicate that the extent of exchange of H^+ by M^{2+} has increased from 15% to 80% in the case of Cd^{2+} but only from 15% to 30% in the case of Pb^{2+}. At the end of the exchange all the Na^+ was found to be in the solution and

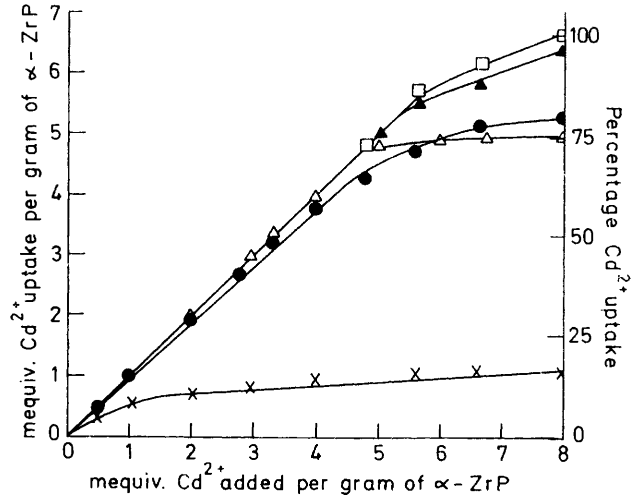

FIGURE 3 Plot of uptake of cadmium ion by α-ZrP against milliequivalents of cadmium added to the system: at 18 °C (×); in the presence of NaCl at 18 °C (●); at 50 (△); 75 (▲); and 98 ± 1 °C (□)

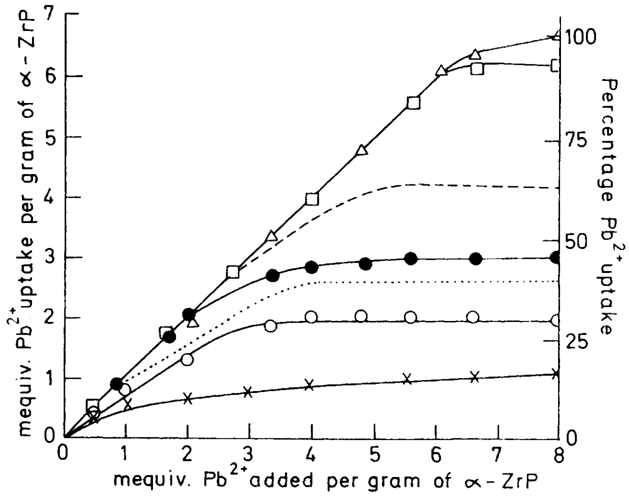

FIGURE 4 Plot of uptake of lead ion by α-ZrP against milliequivalents of lead added to the system: at 18 (×); 50 (●); 75 (□); 98 ± 1 °C (△); in the presence of NaCl at 18 °C (○); in the presence of $Na[NO_3]$ at 18 °C (· · · ·); and in the presence of $Na[O_2CMe]$ at 18 °C (– – – –)

TABLE 1

X-Ray diffraction powder pattern of $ZrCd(PO_4)_2{\cdot}3.5H_2O$

d/Å	I/I_0 (%)	d/Å	I/I_0 (%)
9.5	6.8	2.33	5.3
7.3	4.4	2.12 (br) *	7.3
6.65	4.4	2.08	8.3
6.5	4.4	2.05	9.2
4.92	4.4	2.01	7.28
4.79	100.0	1.93	7.20
4.57	7.3	1.87	5.3
4.43	7.8	1.86	6.3
4.12	29.6	1.78	11.2
3.75	7.3	1.76	8.3
3.70	10.2	1.72 (br)	6.8
3.34	5.3	1.67	8.5
3.29	11.2	1.65	8.3
3.19	10.6	1.62	3.4
2.97	12.6	1.60	10.2
2.92	8.3	1.56	3.4
2.64	15.0	1.54	2.9
2.61	18.5	1.51 (br)	2.9
2.35	5.3		

* br = Broad.

none in the exchanger. Furthermore, in these experiments equilibrium was achieved in *ca.* 150 min, in contrast to those in which Na^+ was absent, when equilibrium was not achieved until 120 h had elapsed.

Figures 2 and 4 illustrate the effect of various sodium salts on the Pb^{2+}/H^+ equilibria. The Pb^{2+} uptake increases in the order $Na[O_2CMe] > Na[NO_3] > NaCl$.

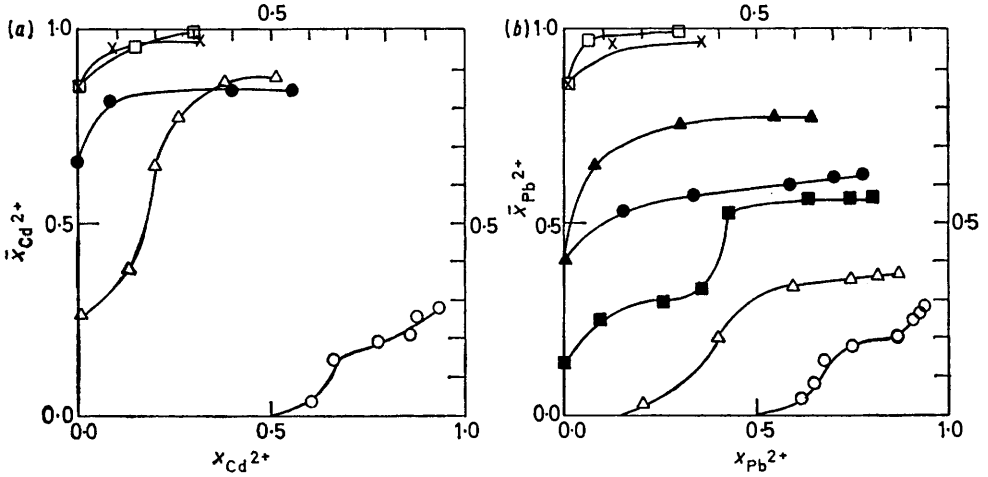

FIGURE 5 Ion-exchange isotherms for Cd^{2+}/H^+ (*a*) and Pb^{2+}/H (*b*): at 18 (○); 50 (●); 75 (×); 98 °C (□); in the presence of NaCl at 18 °C (△); in the presence of $Na[NO_3]$ at 18 °C (■); and in the presence of $Na[O_2CMe]$ at 18 °C (▲)

The results of column operation gave fully converted phases, whose X-ray diffraction patterns were identical with those from the batch equilibrium studies (Tables 1 and 2).

Figure 5(*a*) and 5(*b*) are derived from Figures 3 and 4 and show the ionic fraction of M^{2+} in the exchanger plotted against that in solution. Comparing the two diagrams we see that the selectivity increased from 18 to 50 °C, and that complete conversion took place at 98 °C at an ionic fraction in solution as low as 0.3. Nevertheless, the separation factor at 18 °C, when NaCl was used, was very high and this offers a possibility of separating Cd^{2+} from Pb^{2+} in acetate solution.

TABLE 2

X-Ray diffraction powder pattern of $ZrPb(PO_4)_2{\cdot}1.5H_2O$

d/Å	I/I_0 (%)	d/Å	I/I_0 (%)
8.92	7.6	2.61	9.0
8.03	17.5	2.47	2.8
6.75	2.8	2.31	3.8
5.50	3.6	2.25	14.7
5.15	2.8	2.19	6.2
4.48	48.4	2.13	3.3
4.37	100.0	2.09	2.8
4.03	1.9	2.02	5.7
3.83	4.3	1.97	1.0
3.58	6.6	1.90	3.8
3.53	11.4	1.83	9.5
3.39	5.2	1.80	10.9
3.24	12.8	1.75	2.8
2.96	41.2	1.69	7.1
2.85	18.5	1.62	2.8
2.82	15.2	1.54	4.7
2.79	16.6	1.49	3.3
2.66	20.9	1.41	1.0

The distribution coefficients of Pb^{2+} and Cd^{2+} under various conditions are given in Tables 3 and 4. They are very high (approaching infinity) for small M^{2+} additions in almost all cases.

TABLE 3

Distribution coefficients of cadmium

System temp. (θ_c/°C)	Added Cd^{2+} as a percentage of exchanger capacity							
	4	8	15	25	50	75	100	120
18	300	200	200	120	68	49	36	30
18 (NaCl)	∞	∞	3 800	1 875	5 333	1 800	662	382
50	∞	∞	∞	∞	∞	3 800	586	325
75	∞	∞	∞	∞	∞	∞	1 380	866
100	∞	∞	∞	∞	∞	∞	2 259	977

TABLE 4

Distribution coefficients of lead

System temp. (θ_c/°C)	Added Pb^{2+} as a percentage of exchanger capacity							
	4	8	15	25	50	75	100	120
18	300	200	200	132	58	47	35	30
18 (NaCl)	300	466	800	418	267	134	86	60
18 ($Na[NO_3]$)	∞	1 800	3 800	722	510	219	129	96
18 ($Na[O_2CMe]$)	∞	∞	∞	∞	5 333	931	344	221
50	∞	∞	∞	∞	3 666	279	165	120
75	∞	∞	∞	∞	∞	4 130	2 456	689
100	∞	∞	∞	∞	∞	4 130	3 729	976

DISCUSSION

The main feature of the present studies is that the uptake of cadmium and lead by α-ZrP increased with temperature (Figures 1—4), like that of the alkaline earths and certain other bivalent transition-metal ions from acetate solution.[10] Attempts to reach such high temperatures with organic exchange resins would lead to degradation of the resin.[11]

The reported high uptake of copper by α-ZrP [10] compared with cadmium or lead ions at room temperature in the present studies requires comment. Four points may be considered. (*i*) If the process involved not only M^{2+} but also CH_3COOM^+, then acetate would be present in the exchanged solids. However, no indication of acetate groups was found by i.r. or thermogravimetric analysis. (*ii*) The stability constants of the mono-acetate complexes in aqueous solution fall in the order $Cu^{2+} > Pb^{2+} > Cd^{2+}$.[12] This exchange does not follow this order. (*iii*) The ionic radii of the bivalent species under investigation follow the sequence $Cu^{2+} < Cd^{2+} < Pb^{2+}$, which explains at least the high uptake of Cu^{2+} by α-ZrP on steric grounds. It follows that the uptake of Cd^{2+} should be greater than that of Pb^{2+}. (*iv*) In general the selectivity of α-ZrP for metal ions decreases with increase in crystallinity, the latter depending on the method of preparation.[13] The ion-exchange material for the Cu^{2+}–H^+ system was prepared by a reflux method, in contrast to that used in the present study, and gave a less crystalline material. The steric effect would therefore be less marked and a high uptake of metal ion would be expected.

The effect of the addition of low concentrations of sodium ion is considerable (see Figures 1 and 2). The mechanism proposed is as follows.[14] Initially Na^+ diffuses into the host lattice producing $ZrNaH(PO_4)_2\cdot5H_2O$ and increasing the interlayer distance to 11.8 Å. This phase can accommodate larger ions which now enter and displace the Na^+ again. A programme on the exchange behaviour of $ZrNaH(PO_4)_2\cdot5H_2O$ and $Zr(NaPO_4)_2\cdot3H_2O$ towards Cd^{2+} and Pb^{2+} is in progress,[15] and the initial results suggest that not only are they selective for such ions at room temperature, but that complete displacement of the Na^+ takes place at a very low M^{2+} ionic fraction in the solution.

The uptake of lead in the presence of NaCl was much lower than that of cadmium. This cannot be explained by the formation of insoluble lead chloride, because the concentration of chloride ion is much too low to have a sufficient effect on the ion-exchange capacity. A difference in anion complexing is a possibility, and it may be noted that Cd^{2+} and Pb^{2+} form chloroacetate complexes with stability constants of 6.9 and 32.0 respectively.

The effect of the other two sodium salts, whose anions do not form insoluble lead compounds, is shown in Figure 4. It can be seen that the uptake of Pb^{2+} decreases from acetate to nitrate to chloride.

From the batch and column experiments reported here, it has been demonstrated that α-ZrP may be useful for removal of cadmium and lead over a range of concentrations.

The results of the investigations may be summarised by equations (3)—(6) for the reaction between the exchanger and the cations in solution where x and y are

$$Zr(HPO_4)_2\cdot H_2O + M^{2+} \xrightarrow{98^\circ C} ZrM(PO_4)_2\cdot nH_2O + H^+ \tag{3}$$

$$Zr(HPO_4)_2\cdot H_2O + M^{2+} \xrightarrow{75^\circ, 50^\circ C} \left\{\begin{array}{c} x[ZrM(PO_4)_2\cdot nH_2O] \\ + \\ y[Zr(HPO_4)_2\cdot H_2O] \end{array}\right\} + H^+ \tag{4}$$

$$Zr(HPO_4)_2\cdot H_2O + Na^+ \xrightarrow{18^\circ C} ZrHNa(PO_4)_2\cdot 5H_2O + H^+ \tag{5}$$

$$ZrHNa(PO_4)_2\cdot 5H_2O + M^{2+} \xrightarrow{18^\circ C} \left\{\begin{array}{c} x[ZrM(PO_4)_2\cdot nH_2O] \\ + \\ y[Zr(HPO_4)_2\cdot H_2O] \end{array}\right\} + Na^+ \tag{6}$$

variables depending upon the cation uptake and $n = 3.5$ and 1.5 for Cd^{2+} and Pb^{2+} respectively.

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