CHROM. 9183

CRYSTALLINE INSOLUBLE ACID SALTS OF TETRAVALENT METALS

XXIV. ION-EXCHANGE BEHAVIOUR OF FIBROUS CERIUM(IV) PHOSPHATE

G. ALBERTI, M. CASCIOLA, U. COSTANTINO and M. L. LUCIANI

Istituto di Chimica Inorganica, Università di Perugia, Via Elce di Sotto, 06100 Perugia (Italy)

(Received March 15th, 1976)

SUMMARY

Titration curves of fibrous cerium(IV) phosphate with alkali and alkaline earth metal ions show that the ion-exchange processes occur without phase transition. The exchanger displays a wide range of acidities like an amorphous or semi-crystalline material. About 30% of exchangeable protons are much more acidic than the others. In these sites, the exchanger prefers counter ions that have a large ionic radius, while several inversions occur at high metal ion loadings. Furthermore, the shapes of the Na^+/K^+ and Na^+/Cs^+ isotherms also indicate that there are about 30% of sites where the counter ions that have the largest ionic radius are preferred.

Separations factors and K_d values for various cations at different concentrations have been determined and a marked selectivity for Pb^{2+}, Ba^{2+}, Ag^+ and Tl^+ has been found. The selectivity for Pb^{2+} was investigated for the full range of composition of the exchanger and the H^+/Pb^{2+} isotherm was obtained.

The unusual selectivity of fibrous cerium(IV) phosphate for certain cations should lead to some useful practical applications. The batch analytical separation of Ca^{2+}–Pb^{2+} at low pH values has shown that Pb^{2+} is selectively exchanged also in presence of large amounts of Ca^{2+}.

INTRODUCTION

In a previous paper in this series[1], the syntheses, chemical composition, X-ray powder diffraction patterns and some ion-exchange properties of cerium(IV) phosphates of various crystallinities were described. One of these materials was found to have a definite chemical composition ($CeO_2 \cdot P_2O_5 \cdot 4H_2O$), and a fibrous structure. The chemical formula of the anhydrous product is $Ce(HPO_4)_2$, while the formula $Ce(HPO_4)_2 \cdot 3H_2O$ was suggested for the hydrated product. This formula has recently been supported by infrared spectroscopy[2,3] and is in good agreement with the experimental ion-exchange capacity (5.2 mequiv./g, that is, two exchangeable protons per formula weight). Herman and Clearfield[4] recently reported the synthesis of a sim-

ilar product. Another exchanger having a fibrous structure, thorium phosphate, was subsequently prepared[5].

Fibrous inorganic ion exchangers are very interesting because they can be used to prepare inorganic ion-exchange papers suitable for chromatographic cation separations, or inorganic membranes without a binder[6-8]. It therefore seemed of interest to investigate in greater detail the ion-exchange properties of fibrous exchangers in order to obtain additional information on their ion-exchange mechanism and possible practical uses.

In this paper, some chemical and physical properties, and also the ion-exchange behaviour of fibrous cerium(IV) phosphate (CeP_f) towards alkali and alkaline earth metal ions and Pb^{2+}, are reported and discussed. Separation factors and K_d values for some other cations have also been determined.

EXPERIMENTAL

Chemicals

Carlo Erba (Milan, Italy) R.P.E. reagents were used, except for $Ce(SO_4)_2 \cdot 4H_2O$, which was a Merck (Darmstadt, G.F.R.) pro analysi product.

Ion-exchange material

CeP_f in the hydrogen form was precipitated as previously described.[1] The precipitate was filtered and washed with distilled water until free from sulphate ions. In order to facilitate this washing, it is advisable to use a large Buchner funnel (*ca.* 50 cm² per gram of exchanger). After air drying, the CeP_f sheet was detached from the Buchner funnel and cut into small pieces (*ca.* 0.2 cm²).

The disodium form was obtained by percolating 0.1 *N* disodium hydrogen orthophosphate solution through a column containing CeP_f in the hydrogen form. Both hydrogen and sodium forms were stored in a vacuum desiccator over saturated sodium chloride solution.

Ion-exchange experiments

Each point on the titration curves was obtained by equilibrating, with shaking at 25°, 0.5 g of CeP_f with 100 ml of 0.1 *N* (MCl + MOH) or [MCl₂ + M(OH)₂] solution. For calcium and magnesium ions, titration curves were operated as previously described for crystalline zirconium phosphate[9].

The reversibility of the H^+–Na^+ exchange was tested using a Mettler automatic titrimeter. A 0.5-g amount of CeP_f was equilibrated with 100 ml of 0.1 *N* sodium chloride and titrated with a 0.5 *N* sodium hydroxide–0.1 *N* sodium chloride solution. In the reverse exchange, the titration was performed with 0.5 *N* hydrochloric acid–0.1 *N* sodium chloride solution.

Na^+/K^+ and Na^+/Cs^+ ion-exchange isotherms at 25° were obtained by equilibrating, with shaking for 4 days, 0.5 g of CeP_f in the disodium form with 100 ml of 0.1 *N* (MCl + M'Cl) solutions. For the H^+/Pb^{2+} ion-exchange isotherms, 0.1 *N* [perchloric acid + lead(II) nitrate] solutions were used. High conversions were achieved with large volumes of a 0.1 *N* solution of the in-going ion. After equilibration, both for titration and ion-exchange isotherms, the pH values of the solutions were determined and their metal cation and phosphate contents were measured. Distri-

bution coefficients were determined by equilibrating 0.5 g of CeP_f with 100 ml of 10^{-3} N salt solution. Separation factors (α_H^M) were obtained by equilibrating 0.5 g of CeP_f with 100 ml of 10^{-1} or 10^{-3} N salt solution at an initial pH of 1.5 or 3.0. During the equilibration, the composition of the solution was maintained constant at the initial value by adding a solution that was 0.1 N in the corresponding metal hydroxide and 0.1 N (or 10^{-3} N) in its salt, by means of the Mettler automatic titrimeter operating in the pH-stat mode.

Analytical procedure

The phosphate released into the solution and the PO_4:Ce(IV) molar ratio in the exchanger were determined as previously described[1].

The cations examined were determined using a Perkin-Elmer 305 atomic-absorption spectrophotometer or by standard EDTA titrations. The water content of the exchanger at various stages of exchange was obtained by measuring the weight loss at 180°. The X-ray powder patterns of the samples were obtained with Ni-filtered Cu Kα radiation, using a General Electric diffractometer.

RESULTS AND DISCUSSION

Alkali metal ions

Titration curves of fibrous cerium(IV) phosphate for Li^+, Na^+, K^+ and Cs^+ ions are shown in Fig. 1, which also indicates the amount of phosphate released into
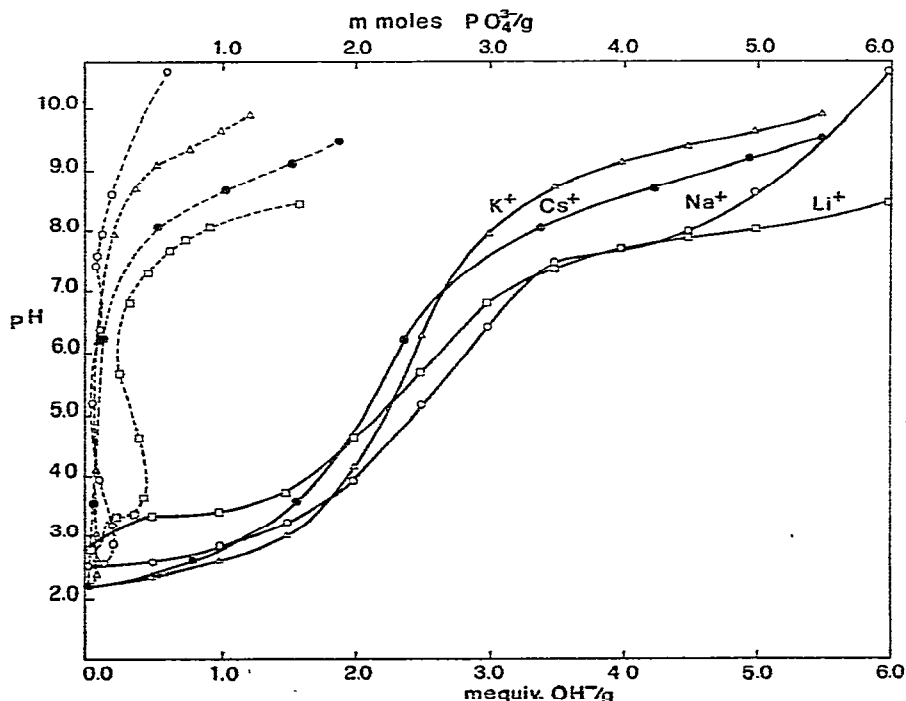

Fig. 1. Titration curves of CeP_f with alkali metal ion hydroxides. The number of millimoles of phosphate released into the solution by 1 g of CeP_f, at different pH values is also reported (dashed curves).
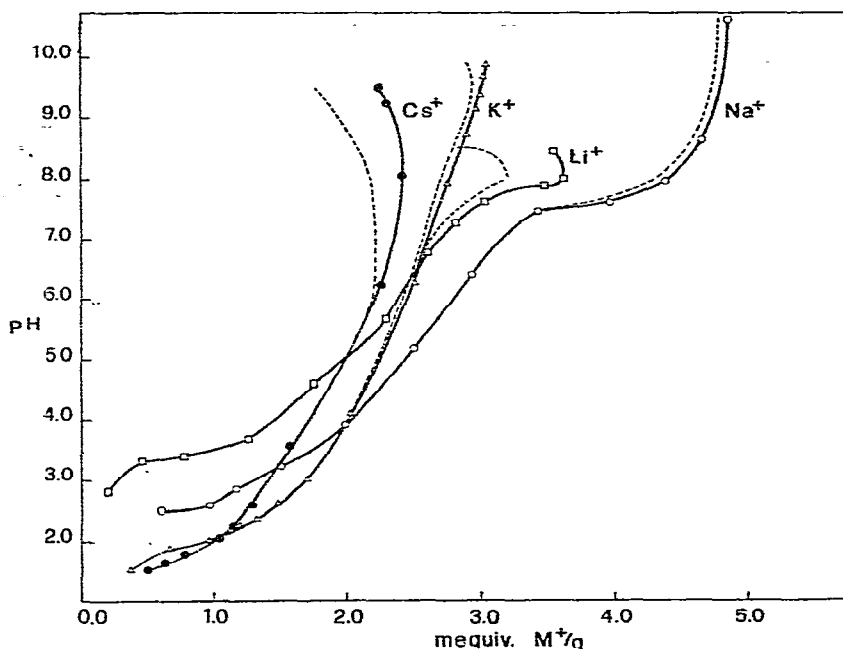
Fig. 2. Comparison between experimental (full lines) and calculated (dashed lines) uptake curves obtained from the titration curves of $CePf$ with alkali metal ion hydroxides. The dotted lines refer to uptake values obtained in the presence of added $HClO_4$.

the solution by 1 g of the material at different equilibrium pH values (dashed curves).

As $CePf$ loses an appreciable amount of phosphate groups, especially in alkaline medium, then in order to obtain the uptake values from the titration curves they must be corrected for the milliequivalents of OH^- consumed by the hydrolytic process. Calculated uptake curves can be obtained assuming that one OH^- ion is consumed for each phosphate group released into the solution and taking into account the equilibrium pH as well as the titration curve of the phosphoric acid with 0.1 N MOH solutions.

In Fig. 2, calculated and experimental uptake curves are compared. It can be seen that there is a reasonable correspondence among these curves. However, at high pH values, the experimental are higher than the calculated uptakes, probably owing to some cation exchange on the hydroxyl groups produced for hydrolysis of the exchanger.

From the shape of the uptake curves, the following conclusions can be drawn:

(a) In contrast to the corresponding uptake curves for layered exchangers such as zirconium phosphate, where there are definite plateaux indicating phase transitions[3], the uptake curves for fibrous cerium(IV) phosphate show that the exchangeable hydrogen ions display a wide range of acidities like amorphous or semi-crystalline inorganic ion exchangers.

(b) The nature of the alkali metal ions strongly affects the shape of the titration curve. At low metal ion loading (less than 25 % conversion, that is, 1.3 mequiv./g), the sequence of decreasing cation preference is that of the lyotropic series $Cs^+ > K^+ >$
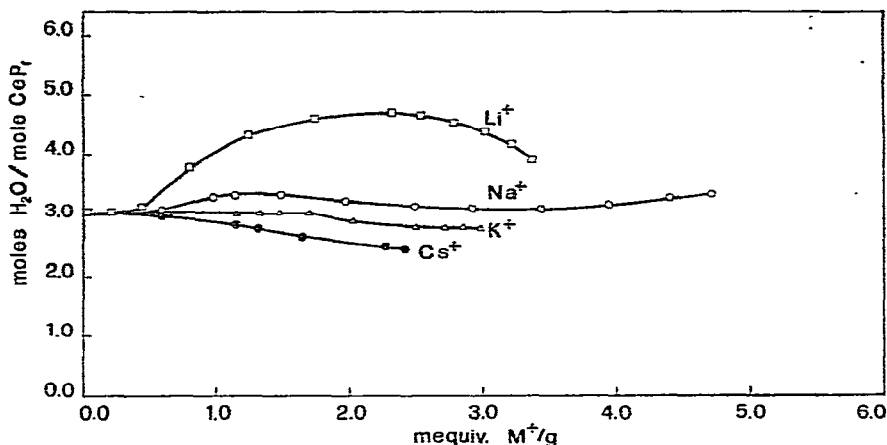
Fig. 3. Water content of CeP_f at various stages of the titration with alkali metal ions.

$Na^+ > Li^+$, while several inversions occur at higher loading, probably due to steric factors.

(c) With cations that have a large crystalline radius, such as K^+ and Cs^+, conversions higher than 50% could not been obtained in acidic medium, whereas when the pH was increased to alkaline values, the exchanger hydrolyzed appreciably.

The water content of some samples at different level of exchange (conditioned over saturated sodium chloride solution) are shown in Fig. 3. It can be seen that the water content increases appreciably, for Li^+ exchange, at conversions in the range 0–30%, but decreases again at higher Li^+ conversion. The water content does not

TABLE I

FIRST d VALUE IN THE X-RAY POWDER PATTERNS OF HYDRATED AND ANHYDROUS SAMPLES OF CeP_t EXCHANGED AT VARIOUS LOADINGS WITH ALKALI METAL IONS
The d values of the hydrogen form are also reported for comparison.

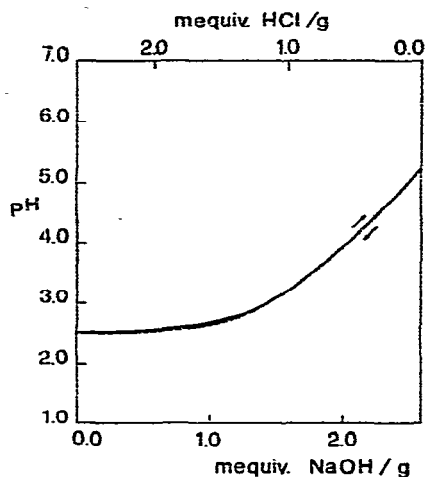| Cation	Conversion (mequiv. M^+/g)	d value (Å)		
		Wet	Dried over P_4O_{10}	Dried at 180°
H^+		11.2	10.9	7.9
Li^+	1.3	12.6	Amorphous	Amorphous
	2.3	12.8	Amorphous	Amorphous
Na^+	1.2	11.9	—	9.7
	2.5	11.9	—	9.8
	3.9	11.9	—	—
	4.8	11.9	—	10.1
K^+	1.3	11.6	10.1	9.9
	2.5	11.7	—	—
	3.0	11.6	10.6	10.2
Cs^+	1.6	11.9	10.8	10.1
	2.4	—	—	10.6

Fig. 4. Reversibility of H⁺/Na⁺ ion exchange on CePᵣ. Forward titration: full line. Backward titration: dashed line.

change appreciably during the exchange of Na⁺ and K⁺ ions, and even decreases during Cs⁺ exchange. The lower tendency of large cations to hydrate and steric factors may be responsible for such behaviour.

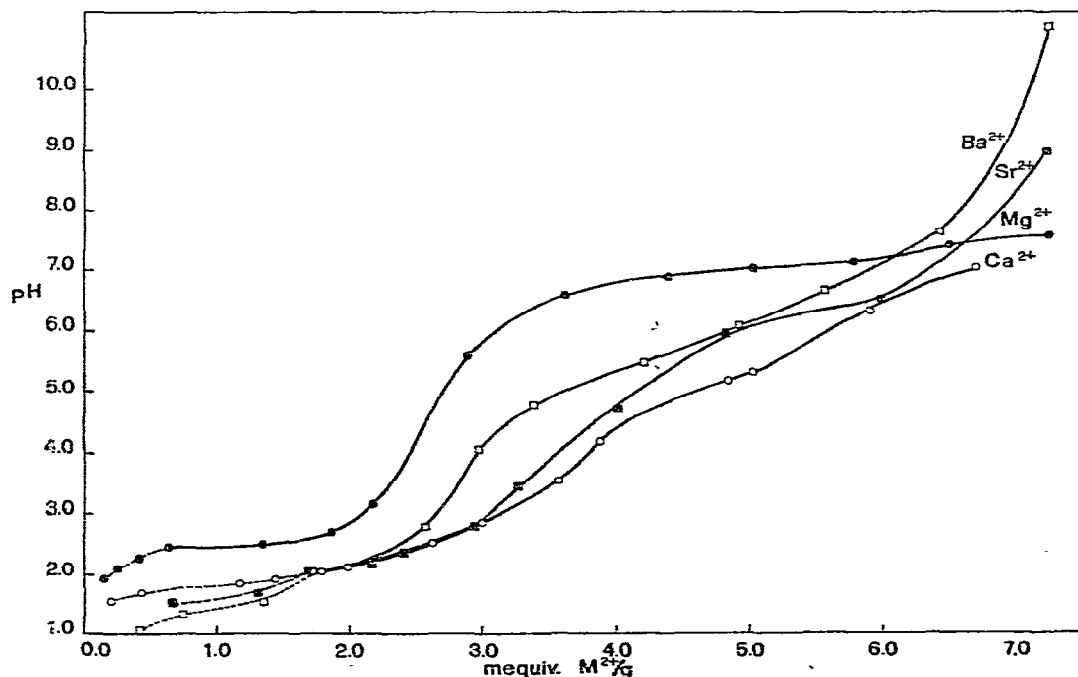It is interesting that, from the measurements of the concentration potentials

Fig. 5. Uptake curves of alkaline earth metal ions on CePᵣ. Dotted lines refer to uptake values obtained in the presence of added HClO₄.

($\Delta\psi_{Na+}$ and $\Delta\psi_{H+}$) and from the electrical conductance of a cerium(IV) phosphate membrane as a function of the conversion in the Na^+ form[7], it was found that only 25–30% of the counter ions were active for ionic transport. It was further found that, when 30% of H^+ was replaced with Na^+ ions, the transport number (t_{H+}) of the remaining protons was practically zero, indicating that the exchanger possesses about 25–30% of sites that have more dissociable protons.

Taking into account that (a) about 30% of cations are exchanged at low pH values, (b) large cations are preferred at conversions lower than 25% and (c) the water content of Li^+ ions increases appreciably in the range 0–30% of Li^+ conversion, we suggest that the exchanger possesses about 25–30% of sites where the steric factors are considerably lower than at the remaining sites. The X-ray powder pattern of $Ce(HPO_4)_2 \cdot 3H_2O$ exhibits only a few lines, the first being much more intense than the others. Its value (11.2 Å) increases slightly with increasing water content of the exchanger and, for anhydrous samples, increases slightly with increasing crystalline ionic radius of the counter ions (Table I).

The reversibility of the ion exchange was tested for Na^+ ions at conversions in the range 0–50%. Fig. 4 shows that the exchange is reversible, within experimental error.

Alkaline earth metal ions

Titration curves of $Ce(HPO_4)_2 \cdot 3H_2O$ with alkaline earth metal ions are shown in Fig. 5.

TABLE II

FIRST d VALUE IN THE X-RAY POWDER PATTERNS OF HYDRATED AND ANHYDROUS SAMPLES OF CeP_t EXCHANGED AT VARIOUS LOADINGS WITH DIVALENT CATIONS
The water content of these samples, conditioned over saturated NaCl solution, is also reported.

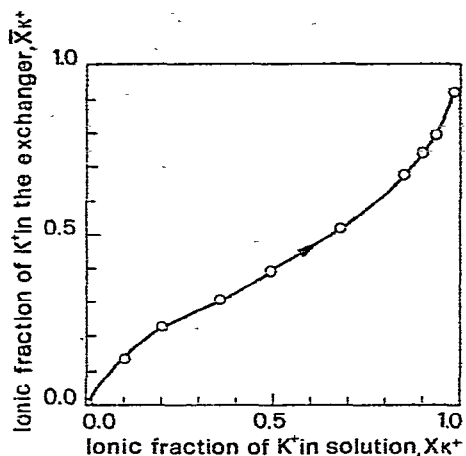| Cation	Conversion (mequiv. M^{2+}/g)	Water content (moles H_2O/formula weight	d value (Å)		
			Wet	Dried over P_4O_{10}	Dried at 180°
Mg^{2+}	1.3	4.7	12.6	12.1	9.7
	2.9	5.0	12.8	12.1	9.7
	3.6	5.4	12.8	11.3	9.7
	5.1	5.4	12.6	11.3	9.7
Ca^{2+}	1.7	3.5	12.6	11.9	—
	2.6	3.5	13.0	11.6	9.8
	3.6	3.7	13.0	12.2	—
	4.9	3.8	13.0	12.4	9.7
Sr^{2+}	1.7	3.3	12.4	11.5	—
	2.4	3.6	12.4	11.3	—
	4.0	3.7	12.8	—	9.7
	4.8	3.7	13 0	—	—
Ba^{2+}	1.9	3.1	11.9	11.2	—
	2.6	3.3	11.8	11.3	9.7
	3.4	3.5	11.6	11.3	9.7
	4.9	3.2	11.9	11.4	9.8
Pb^{2+}	2.2	—	11.4	11.2	—
	3.6	—	11.9	11.8	—

Fig. 6. Na$^+$/K$^+$ ion-exchange isotherm on CePr. Concentration, 0.1 N; temperature, 25°.

In this case also the sequence of decreasing preference, at metal ion loadings less than 30%, is that of the lyotropic series Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}, while several inversions occur at higher metal ion loadings. The water content increases appreciably only for the Mg^{2+} exchange at conversions in the range 0–30%. X-ray powder patterns show only small modifications as the exchanging ion or the degree of exchange is changed (Table II). Dehydration at 180° decreases the first d value to 9.7–9.8 Å for all of the samples examined. It can be seen from Fig. 4 that uptakes higher than 5.2 mequiv./g are obtained at high pH values. By following a procedure similar to that already described for the exchange of alkaline earth metal ions on crystalline zirconium phosphate[9], it was found that apparent conversions higher than 100% were due to the hydrolysis of the phosphate groups and to the precipitation of insoluble alkaline earth metal ion phosphates.
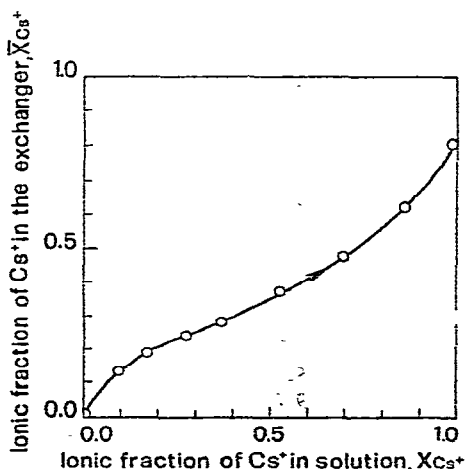

Fig. 7. Na$^+$/Cs$^+$ ion-exchange isotherm on CePr. Concentration, 0.1 N; temperature, 25°.

TABLE III

SEPARATION FACTOR (α_H^M) OF SOME CATIONS ON CeP_f AT DIFFERENT CONCENTRATION AND pH VALUES

$$\alpha_H^M = \frac{\bar{X}_M}{\bar{X}_H} \cdot \frac{X_H}{X_M}$$

Cation	$\alpha_H^M \cdot 10^3$		
	$C = 10^{-3} N,$ $pH = 3.0$	$C = 10^{-1} N,$ $pH = 3.0$	$C = 10^{-1} N,$ $pH = 1.5$
Li^+	24	0.6	—
Na^+	62	3.7	—
NH_4^+	110	4.2	—
$(CH_3)_4N^+$	125	2.2	—
K^+	150	5.5	27
Cs^+	680	4.1	40
Tl^+	—	7.8	150
Mg^{2+}	—	6.7	7.2
Ca^{2+}	690	15	14
Sr^{2+}	870	17	60
Ba^{2+}	950	12	140
Pb^{2+}	—	500	920

Na^+/K^+ and Na^+/Cs^+ ion-exchange isotherms

The Na^+/K^+ ion-exchange isotherm is shown in Fig. 6. The K^+ ion is preferred to Na^+ ion at low K^+ loadings, while the opposite occurs at high K^+ loadings. The shape of the isotherm is in good agreement with our previous suggestion that there are about 25–30% of sites where the steric hindrance is low and consequently the counter ions that have the largest crystalline ionic radius are preferred.

The Na^+/Cs^+ ion-exchange isotherm (Fig. 7) is very similar to that for Na^+/K^+.

Separation factors and distribution coefficients

A very high selectivity of CeP_f for certain cations, such as Pb^{2+}, Ag^+, Tl^+ and K^+, has already been established by ascending chromatography on cerium(IV) phosphate paper[6]. In order to obtain more quantitative data, separation factors and

TABLE IV

DISTRIBUTION COEFFICIENTS (K_d) OF SOME CATIONS ON CeP_f

Experimental conditions: 0.5 g of exchanger equilibrated with 100 ml of 10^{-3} N solution.

Cation	K_d (mequiv. M/g:mequiv. M/ml)
Li^+	11
Ni^{2+}	50
Co^{2+}	$1.0 \cdot 10^2$
Na^+	$1.2 \cdot 10^2$
Ag^+	$5.5 \cdot 10^2$
Cu^{2+}	$1.3 \cdot 10^3$
K^+	$3.5 \cdot 10^3$
Pb^{2+}	$>5 \cdot 10^4$

TABLE V

BATCH EXPERIMENTS FOR Ca^{2+}–Pb^{2+} SEPARATION ON CeP_f

Conditions: 1 g of $Ce(HPO_4)_2 \cdot 3H_2O$ equilibrated with solutions at initial pH 0.95.

Composition of initial solution (mequiv./ml)		Volume of solution (ml)	Uptake (mequiv./g)		$\dfrac{[Pb^{2+}]}{[Ca^{2+}]} \cdot \dfrac{[Ca^{2+}]_{eq.}}{[Pb^{2+}]_{eq.}}$
$[Pb^{2+}]$	$[Ca^{2+}]$		$[Pb^{2+}]$	$[Ca^{2+}]$	
$1.0 \cdot 10^{-1}$	$2.05 \cdot 10^{-1}$	200	2.6	$9 \cdot 10^{-2}$	68
$1.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	400	2.2	$8 \cdot 10^{-2}$	$1.2 \cdot 10^2$
$1.0 \cdot 10^{-2}$	$2.05 \cdot 10^{-1}$	200	1.6	$1.1 \cdot 10^{-1}$	$1.5 \cdot 10^3$

K_d values on CeP_f for some inorganic cations were determined. The results reported in Table III and Table IV, respectively, show that the chromatographic results have been substantially confirmed and that some interesting separations are possible.

Batch experiments for Ca^{2+}–Pb^{2+} separation at low pH values and different Pb^{2+}–Ca^{2+} compositions (Table V) showed that Pb^{2+} is taken up selectively by fibrous cerium(IV) phosphate even in the presence of high Ca^{2+} concentrations.

H^+/Pb^{2+} ion-exchange isotherm

Owing to the high selectivity of fibrous cerium(IV) phosphate towards Pb^{2+}, it was thought to be of interest to study the H^+/Pb^{2+} exchange over the full range of composition.

The isotherm in Fig. 8 shows that, although fibrous cerium(IV) phosphate can be considered a weak exchanger, Pb^{2+} is preferred to H^+ up to a Pb^{2+} loading of about 70%.

Redox reactions

Owing to the presence of Ce(IV) in the exchanger, redox reactions may accompany the exchange of highly reducing ions. This behaviour, already found for Mn^{2+}
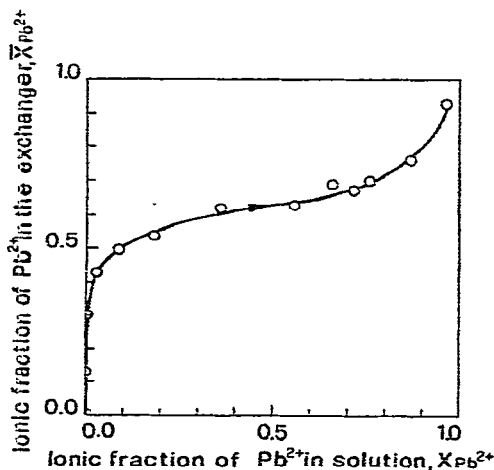

Fig. 8. H^+/Pb^{2+} ion-exchange isotherm on CeP_f. Concentration, 0.1 N; temperature, 25°.

in amorphous cerium(IV) phosphate[10], has also been confirmed for the exchange of Mn^{2+}, Fe^{2+} and Cr^{3+} in CeP_f. These redox reactions are irreversible in so far as when Ce(III) is again oxidized to Ce(IV), the fibrous structure is lost and an amorphous cerium(IV) phosphate is obtained.

Fibrous cerium(IV) phosphate is sufficiently stable in hydrochloric acid at concentrations less than 0.1 N; for more concentrated acid, non-complexing and non-reducing acids such as perchloric acid have to be used.

It can be pointed out that fibrous thorium phosphate is stable towards reducing agents and therefore it can replace fibrous cerium(IV) phosphate for some particular uses. However, as the radioactivity of thorium is usually undesirable, efforts are being made to obtain a fibrous exchanger with a non-radioactive and non-reducible tetravalent metal such as titanium or zirconium.

CONCLUSION

Although a more correct interpretation of the ion-exchange mechanism of fibrous cerium(IV) phosphate will be possible only when its crystalline structure is krown, the results obtained here give a fairly good idea of its ion-exchange behaviour towards several inorganic cations.

The very high selectivity towards certain cations such as Pb^{2+} and Ag^+ increases the possible practical applications of this fibrous inorganic exchanger.

ACKNOWLEDGEMENTS

REFERENCES

1 G. Alberti, U. Costantino, F. di Gregorio, P. Galli and E. Torracca, *J. Inorg. Nucl. Chem.*, 30 (1968) 295.
2 R. Cataliotti, U. Costantino, M. L. Luciani and G. Paliani, *VII Convegno Nazionale di Chimica Inorganica, B₁, Pesaro, 1974*, A.I.C.I., 1974.
3 G. Alberti and U. Costantino, *J. Chromatogr.*, 102 (1974) 5.
4 R. G. Herman and A. Clearfield, *J. Inorg. Nucl. Chem.*, 37 (1975) 1697.
5 G. Alberti and U. Costantino, *J. Chromatogr.*, 50 (1970) 482.
6 G. Alberti, M. A. Massucci and E. Torracca, *J. Chromatogr.*, 30 (1967) 579.
7 G. Alberti, *Study Week on Biological and Artificial Membranes and Desalination of Water, Pontificia Academia Scientiarum, Vatican, Rome, 14–19 April, 1975*, in press.
8 K. Anil De and K. Chowdhury, *Separ. Sci.*, 10 (1975) 39.
9 G. Alberti, U. Costantino and M. Pelliccioni, *J. Inorg. Nucl. Chem.*, 35 (1973) 1327.
10 E. M. Larsen and W. A. Cilley, *J. Inorg. Nucl. Chem.*, 30 (1968) 287.