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Properties, Ion-Exchange Behavior, and Analytical Applications of Cerium Phosphate Cation Exchangers Suitable for Column Use

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ABSTRACT

Some investigations on the preparative procedure of cerium phosphate cation exchangers suitable for column use are reported. A number of novel forms of cerium phosphate compounds in the presence of different salts are synthesized. The properties of these inorganic ion exchangers have been characterized on the basis of chemical analysis, UV, thermal, IR and x-ray diffraction methods. Their ion-exchange properties, chemical stability, and selectivity for certain ions are investigated.

INTRODUCTION

During the last twenty-five years, ion exchange has firmly established itself as a technique for various unit operations. There has been a rapid and constantly increasing development of numerous applications of ion exchangers in various fields. Recovery of valuable products from industrial waste treatment of high temperature water, removal of corrosion products, and demineralization of water are some of the challenging tasks accomplished by the use of this technique. A number of applications in the nuclear industry have also been reported: purification of coolant and moderator water in pressurized water reactors, separation of reactor-produced isotopes, etc. Synthetic organic resins are often used for such applications because of their high exchange rates and chemical stability. However, their use on a large scale in the nuclear field has been limited by their instability in the presence of intense radiation doses and

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high temperature. A new type of compound known as synthetic inorganic exchangers, has received much notice and found ever-increasing applications in separation chemistry (1). In previous papers (2–10) fibrous thorium, cerium, and zirconium phosphate have produced compounds of acceptable cation-exchange capacities. A large number of new synthetic inorganic exchangers have been obtained and their ion-exchange properties investigated (11–13). Several of these exchangers were found to exhibit desirable chemical stability, and sometimes they proved to be highly selective for certain ions (2, 3). There is also great interest in relation to the treatment of contaminated water or coolant in reactors operating at high temperatures and pressures (14).

Recently, extensive studies have been undertaken in this laboratory to determine the ion-exchange properties of cerium(IV) phosphate toward several monovalent and divalent cations. However, the preparation of different salt forms of cerium phosphate is difficult because of its high hydrolysis rate. In the preliminary results of these studies, the mechanism of exchange seems to occur without phase transitions and the exchangeable hydrogen ions display a large range of acidities similar to amorphous or semicrystalline exchangers (2, 3, 8–10).

In the case of fibrous cerium(IV) phosphate at low loading, the sequence is $K^+ > Na^+ > Li^+$ while several reversals in selectivity occur upon increasing loading of the exchanger until the sequence is completely reversed (8).

The interest in inorganic ion exchangers is due primarily to their high resistance toward temperature and radiation. Other interests include the preparation of inorganic ion-exchangers suitable for chromatographic cation separations, high selectivities, and comparable exchange behaviors (3, 8). Therefore, it would be interesting to investigate, how the ion-exchange properties of fibrous exchangers interrelate with these new cation exchangers and how their mechanisms differ. It should be pointed out that as with all phosphate materials, the synergistic relationship between ion exchange and hydrolytic damage has not yet been determined. Hence, it is important to note that the bright yellow color of the hydrogen form of CeP fades as the ion-exchange capacity is exhausted but returns on regeneration.

This is a useful property which suggests that the Ce^{2+}/Ce^{3+} couple is involved in the “exchange” reactions on CeP(H). Furthermore, the exchangeable hydrogen ions in fibrous cerium(IV) phosphate display a wide range of acidities (15).

EXPERIMENTAL

All preparation were carried out in 3-neck round-bottom flasks fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. All reagents and chemicals used were of Analar grade obtained from Merck or Aldrich.

Synthesis of Novel Types of Cerium Phosphate

Different salt solutions of NaCl (2.98 g), $SrCl_2$ (13.46 g), $LiNO_3 \cdot H_2O$ (3.52 g), KCl (3.75 g), and $ZnCl_2$ (6.95 g) were made in 100 mL of deionized water and heated to 80°C. To these solutions, 7.2 g of orthophosphoric acid was added. After a few minutes of stirring, 2.77 g of cerium ammonium nitrate was added and the solution made up to 125 mL with deionized water. This was refluxed with stirring for 24 hours at 80°C. The precipitate was then cooled to about 60°C, filtered, and dried at 80°C for several hours. The solid was then ground and sieved to less than 350 μm, washed with deionized water, and equilibrated with HCl solutions of different molarities or eluted in a column with 0.5 M HCl solution.

The H^+ form of the ion-exchange material was prepared from CeP(Na) by elution with 0.5 M HCl.

Synthesis of Disodium, Dilithium, Dipotassium, and Distrontium Forms of Cerium Phosphate

These materials were synthesized by equilibrating 1 g of cerium phosphate (sodium, lithium, and potassium) with 100 mL of 0.1 N alkaline solutions of NaOH, LiOH, and KOH for 24 hours. The solutions were then filtered, washed and dried at 60°C for 2 hours, and kept in a desiccator over a saturated solution of NaCl.

The distrontium form was synthesized by refluxing 1 g of $SrCO_3$ with 500 mL of deionized water for 2 hours. The procedure was repeated until the final pH was about 8. The solution was then filtered and the precipitate washed with hot deionized water and dried at 60°C.

Chemical and Instrumental Analysis

Cerium was measured by ultraviolet spectrophotometry by means of a Cary 1E model. The exchanger was first dissolved in hot sulfuric acid and then a few crystals of oxalic acid were added to reduce Ce^{4+} to Ce^{3+}. The Ce^{3+} formed was complexed with molybdate using acetone to intensify the color, which could then be measured by its ultraviolet absorption peak at 253.5 mμ.

Phosphate concentrations were also determined by UV, using the absorption peak at 430 mμ, and following the same procedure as above.

The amount of sodium in the solids was determined using a Perkin-Elmer model 52C flame photometer; and the ammonium ion concentration was determined using a Kjeldhal autoanalyzer.

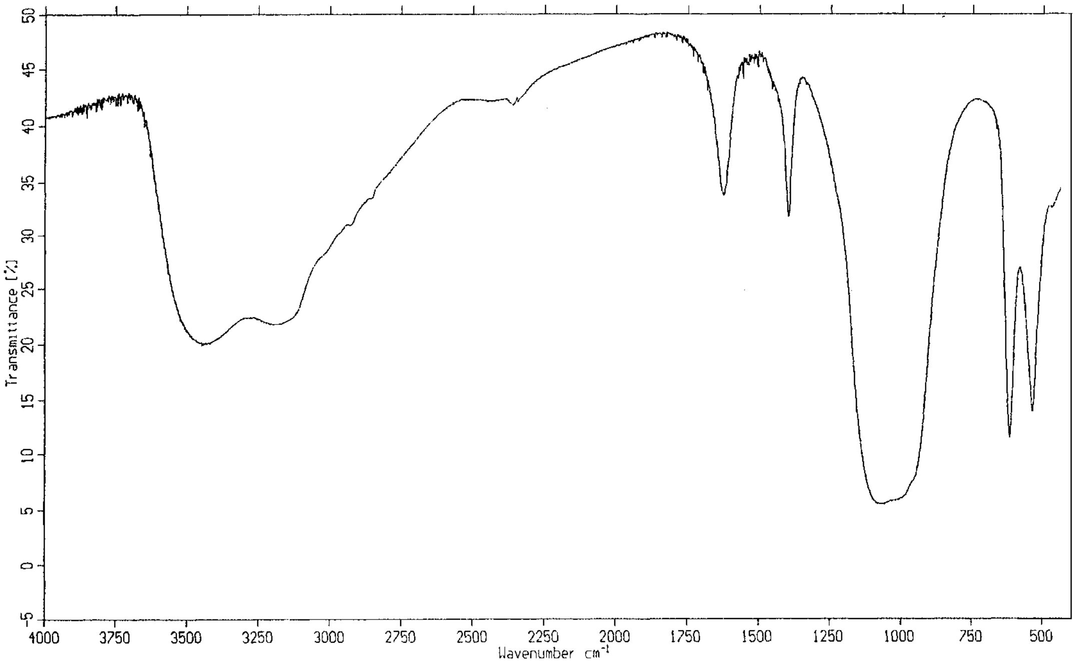

FIG. 1 Infrared spectrum of CeP(Na).

Infrared runs were carried out for each exchanger. A Perkin-Elmer spectrophotometer was used for IR studies. The IR spectrum of CeP(Na) is shown in Fig. 1.

X-ray powder diffractometry with a CuKα beam showed all the products to be amorphous.

Thermogravemetric analysis were carried out using a Dupont thermobalance model 951 which yielded the water contents to 800°C. The analyses for cerium phosphates were performed at a heating rate of 10°C/min. The thermogram for CeP(Na) is recorded in Fig. 2.

The Ion-Exchange Capacity Measurement

The Na^+ ion-exchange capacity was determined by the column process as follows: One gram of the ion-exchange material in its H^+ form was packed in a glass tube fitted with glass wool at its bottom. 250 mL of 1 M $NaNO_3$ was then passed through this column at the low flow rate of 0.4 mL/min, and the effluent was titrated with a 0.1 N NaOH solution. The strong acid capacities were expressed in terms of milliequivalents per dry gram of the different samples.

The hydrolysis of cerium phosphate was measured by means of weight loss observed after treatment with NaOH or NH_4OH. 0.2 g samples were equilibrated with 20 mL total volume of a solution of pH between 3 and 11 for 24 hours. The weights before and after equilibration were measured, and the de-

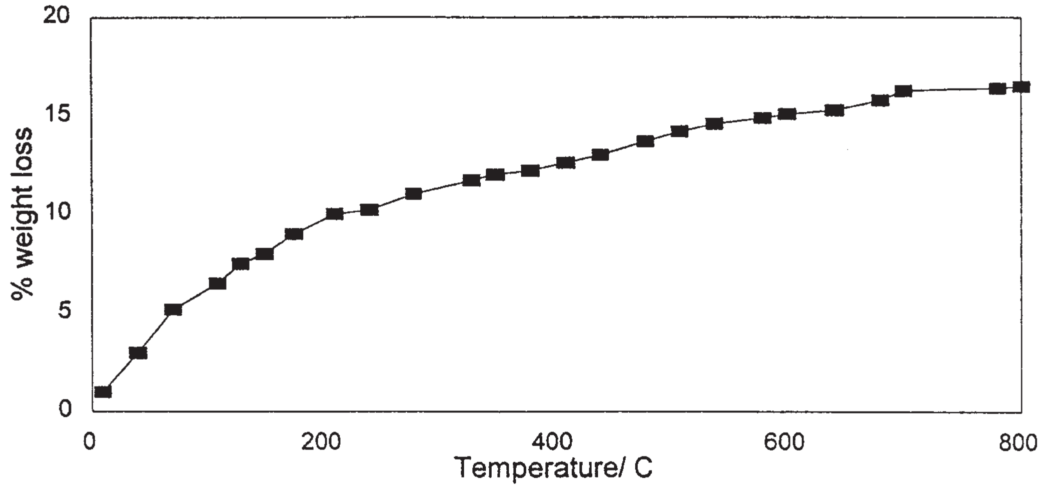

FIG. 2 Thermogram of CeP(Na).

gree of hydrolysis was calculated. The amount of hydrolysis was confirmed by measuring the amount of phosphate released to the solution after equilibration.

RESULTS AND DISCUSSION

The IR spectrum of cerium phosphate (Fig. 1) shows an interesting absorption pattern. Based on the analysis of literature data for phosphates (16), it can be concluded that the first peak at 3410 cm^{-1} is due to interstitial water and hydroxyl groups, and the second peak at 1620 cm^{-1} is due to deformation vibration of the free water molecules. The bands in the 1000–1100 cm^{-1} region are due to symmetric and antisymmetric stretching of P—O bonds in the highly symmetric PO_4 group, and the two bands in the 500–600 cm^{-1} region are connected to Ce—O bond vibrations.

The thermogram for CeP(Na) suggests that the weight loss of the ion exchanger up to 150°C is due to the removal of free external water molecules. At higher temperatures up to 300°C, condensation of exchangeable hydroxyl groups take place, which is characteristic of synthetic inorganic ion exchangers. Above 300°C the gradual loss in weight is due to the removal of structural water. The curve pattern suggests that the ion exchanger is stable up to 800°C (Fig. 2).

Table 1 shows that cerium phosphate in the presence of various inorganic salts gave robust materials which were green/yellow in color with densities in the 2.5–3.1 $kg\cdot dm^{-3}$ range and cation exchange capacities in the 4–5.35

TABLE 1
Properties of Cerium Phosphates Synthesized in the Presence of Different Salts

Cations present	Density ($kg \cdot dm^{-3}$)	PO_4/Ce ratio	Na^+ capacity ($meq \cdot g^{-1}$)	Color
Lithium	2.90	1.21	5.35	Bright yellow
Sodium	2.85	1.74	4.71	Greenish/yellow
Potassium	3.00	1.25	4.20	Yellow
Strontium	3.12	1.78	4.00	Greenish/yellow
Zinc	2.55	1.40	4.90	Green

$meq \cdot g^{-1}$ range. Their respective PO_4/Ce ratios varied from 1.21 to 1.78. The concentrations of the salts used had a direct relation with the particle size and its hardness (12).

Tomota and Ichiro (17, 18) found the maximum capacity of cerium phosphate to be 2.9 $meq \cdot g^{-1}$; however, Alberti et al. (19) found that fibrous crystalline cerium phosphate $Ce(HPO_4)_2 \cdot H_2O$ has a capacity of 5.2 $meq \cdot g^{-1}$. The capacity decreased as the pH value decreased (20).

Aly (21) reported that the rate of ion exchange is independent of the concentration of sodium or potassium ions in the range studied and increased with a decrease of particle size, indicating a particle diffusion-control mechanism.

It can be seen from Table 2 that treatment of cerium phosphates with 0.5 M HCl reduced the phosphate concentration. This is probably due to hydrolysis and hence the cations present are reduced. Alberti et al. (19) concluded that amorphous cerium phosphates are unstable toward hydrolysis and are readily hydrolyzed.

TABLE 2
Molar Ratios of Cerium Phosphates Synthesized with Respect to Cerium Prepared Before and After Treatment with 0.5 M HCl

0.5 M HCl treatment[a]	Cations	PO_4/Ce	NH_4/Ce	OH/Ce	H_2O/Ce
Li: Before	0.23	2.55	—	0.81	2.96
After	0.19	1.21	0.01	0.79	1.75
Na: Before	0.35	3.08	—	0.94	3.35
After	0.30	1.74	0.01	0.96	2.15
K: Before	0.24	2.59	—	0.83	3.00
After	0.19	1.25	0.01	0.80	1.92
Sr: Before	0.36	3.12	—	0.95	3.41
After	0.31	1.78	0.01	0.97	2.20
Zn/Ce: Before	0.26	2.74	—	0.85	3.15
After	0.21	1.40	0.01	0.83	2.00

TABLE 3

Capacity and Phosphate Loss Measurement of CeP(Na), CeP(Li), CeP(K), and CeP(Sr) at Different pH Values

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
CeP(Na):																
pH	12.1	11.7	10.7	9.37	7.78	6.91	6.13	5.64	4.43	3.81	3.26	3.0	2.7	2.5	2.4	2.3
meq. OH^-/g	6.4	4.8	3.6	3.0	2.6	2.2	1.8	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2	0
mmol PO_4^{3-}/g	0.70	0.52	0.38	0.20	0.11	0.12	0.12	0.18	0.20	0.21	0.22	0.1	0.1	0.1	0.1	0
CeP(Li):																
pH	8.1	7.7	7.5	7.4	7.2	6.2	5.1	3.8	3.1	2.8	2.6	2.3				
meq. OH^-/g	6.0	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5	0				
mmol PO_4^{3-}/g	1.5	0.85	0.70	0.66	0.49	0.40	0.30	0.49	0.51	0.45	0.30	0.1				
CeP(K):																
pH	9.8	9.2	9.0	8.8	8.4	7.7	6.0	4.0	2.8	2.5	2.3	2.1				
meq. OH^-/g	5.5	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5	0				
mmol PO_4^{3-}/g	1.2	1.0	0.75	0.55	0.45	0.30	0.20	0.20	0.12	0.12	0.12	0.12				
CeP(Sr):																
pH	8.8	6.2	5.8	4.5	3.2	2.8	2.2	2.1	1.9							
meq. OH^-/g	7.2	6.0	4.9	4.0	3.2	2.9	2.4	2.2	1.8							
mmol PO_4^{3-}/g								N/A								

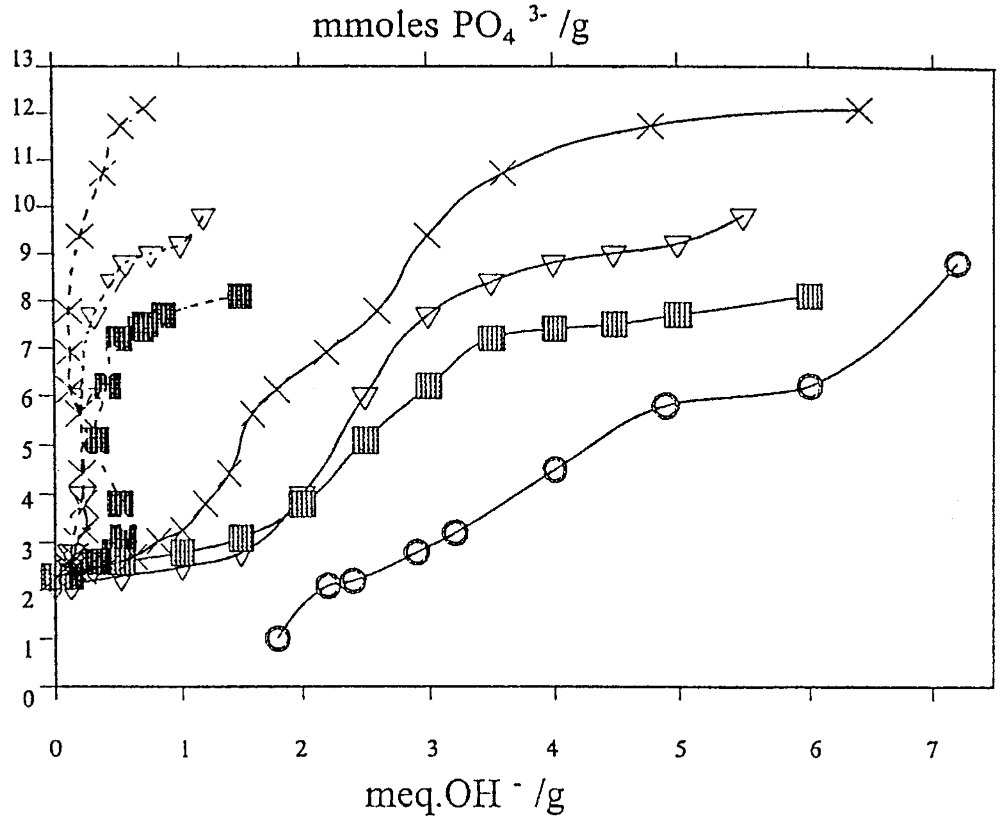

FIG. 3 Ion-exchange properties of cerium(IV) phosphate for lithium, sodium, potassium, and strontium ions, titrated with 0.1 N (NaCl + NaOH). (——) Milliequivalents OH^-/g of exchange. (- - -) Phosphate released to the external solution (mmol/g). CeP(Na) (×), CeP(Li) ▥, CeP(Sr) (○), CeP(K) (▽).

It is interesting to note that strontium, sodium, and to a lesser extent zinc forms of cerium phosphate are hard enough for column use. Their respective PO_4/Ce ratios were 1.78, 1.74, and 1.40, which are much higher than the others. It can also be concluded that all the cerium phosphates prepared had the same OH^- molar content, and this contributed to the weight loss by dehy-

TABLE 4

Distribution Coefficients (K_d)of Some Cations on CeP(Na)

Cation	Be^{II}	Mg^{II}	Ca^{II}	Sr^{II}	Ba^{II}	Ra^{II}	UO_2^{II}	Co^{II}	Ni^{II}	Cu^{II}	Cd^{II}	Hg^{II}
K_d ($mL \cdot g^{-1}$)	330	84	284	405	$>5^3 \times 10^3$	37	82	19	8	245	355	660
Cation	Pb^{II}	Cr^{III}	As^{III}	Se^{IV}	Th^{IV}	Te^{IV}	Zr^{IV}	Ti^{IV}	Sb^{V}	V^{V}	Mo^{VI}	W^{VI}
K_d ($mL \cdot g^{-1}$)	$>5 \times 10^3$	52	2	24	1.6×10^3	1.2×10^3	$>5 \times 10^3$	$>5 \times 10^3$	163	76	1.2×10^3	480

droxylation at high temperatures. Dyer (12) reported that OH^- content is independent of the salts concentration and its subsequent HCl treatment. This phenomenon is broadly similar to the findings of this work.

The titration curves of cerium phosphates for lithium, sodium, potassium, and strontium are shown in Fig. 3 which also indicates the amount of phosphate released into the solution at different pH values (Table 3).

Because the cerium phosphates for lithium, sodium, and potassium ions lose a large amount of their phosphate groups, in particular in alkaline medium, they must be corrected for milliequivalents of OH^- consumed by the hydrolytic process to obtain the uptake values from the titration curves. By assuming that one OH^- ion is consumed for each phosphate group released into the solution, and also taking into account the equilibrium pH and the titration curve of phosphoric acid with a 0.1 N NaOH solution, the uptake curves can be calculated.

The titration profiles in Fig. 3 show two distinct plateaus like those reported by Alberti et al. (3, 8) for layered exchangers such as zirconium phosphate (where there were definite plateaus indicating phase transitions). These exchangeable hydrogen ions display a wide range of acidities, more like amorphous or semicrystalline inorganic ion exchangers, and hence some exchange may occur at lower pH values.

Zamin et al. (22) found that the rate of ion exchange was fast initially and then slowed down (i.e., two distinct plateaus) for zirconium phosphate.

In order to obtain more quantitative information on the selectivity of the cerium phosphate exchangers, K_d values of various inorganic ions were determined. This was carried out by equilibrating 0.2 g of CeP(Na) with 20 mL of a 1.2×10^{-4} M solution at 25°C for a week. The distribution coefficients (K_d) were measured. K_d is defined by

$$K_d = \frac{I_c - F_c}{F_c}\frac{V}{M} \qquad (\text{mL/g})$$

where I_c = initial count (i.e., standard)
F_c = final count
V = volume of solution used (mL)
M = weight of exchanger in contact with V mL solution/g

A very high selectivity of CeP(Na) for certain cations such as Ba^{II}, Pb^{II}, Zr^{IV}, and Ti^{IV}, and to a lesser extent for Te^{IV}, Mo^{VI}, and Th^{IV}, can be seen in Table 4.

The wide variation in K_d values may be due to various factors including swelling, formation of complexes, nature of the chemical bond, solvent distribution, and nature of the ion exchange (23). Ugajin and Ajuria (24) used these variations in the K_d values of inorganic ion exchangers in order to separate Sr, Cs, and Ru from the nuclear fuel cycle and radioactive liquid wastes. Barium, lead, zirconium, and titanium show total adsorption, and therefore this ion exchanger, CeP(Na), may be used for their selective removal from different systems.

CONCLUSION

By introducing different salts into the reaction mixture used to prepare cerium phosphate, robust cation-exchange materials of reproducible composition with a good cation capacity, suitable for column use, were produced. Although further investigations are needed in order to understand the ion-exchange mechanism fully, the results obtained here give a fairly good idea of its ion-exchange behavior toward several inorganic cations.

The very high selectivity toward certain cations such as Pb^{II}, Ba^{II}, Zr^{IV}, Ti^{VI}, Te^{IV}, Mo^{VI}, and Th^{IV} increases the possible practical applications of this inorganic exchanger. Research to be presented in the future will consider the disodium, dilithium, dipotassium, and distrontium forms of cerium phosphate.

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