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The Ion-exchange Behavior of Some Cations on Crystalline Zirconium Phosphate

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The distribution coefficients of Ag^+, Tl^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+}, Y^{3+}, and Ce^{3+} have been determined on a crystalline zirconium phosphate ion-exchanger in chloride solution media, and the affinity sequences are presented. pH titration curves and X-ray powder diffraction data were obtained for calcium and barium ions. The ion-exchange capacity of the exchanger for barium ions was found to be 4.4 meq/g, but the X-ray powder patterns were rather unusual as compared to those of other ions studied previously.

Extensive investigations have been made of the crystalline zirconium phosphate ion-exchanger, $Zr(HPO_4)_2 \cdot H_2O$ (c-ZrP). Studies of the exchanger at lower loadings have mainly been concerned with the distribution coefficients (K_d) of alkali metal ions and their pH dependence.[1,2] In the first half of the present study, the measurement of K_d values was extended to monovalent cations, such as Ag^+, K^+, Tl^+, and NH_4^+, alkaline earth cations, and some polyvalent cations such as Co^{2+}, Zn^{2+}, Y^{3+}, and Ce^{3+}.

On the other hand, studies of the ion-exchange at higher loadings include pH titrations on the exchanger for alkali or alkaline earth metal ions and X-ray studies of cation-replaced exchangers as well as of the original hydrogen-form.[3–7] With regard to the uptake of alkaline earth metal ions onto c-ZrP, Clearfield and Smith have shown that strontium ions can be sorbed, but barium ions are not taken up from acidic media.[4] Harvie and Nancollas have given the pH titration curve for calcium-hydrogen exchange.[5] Dyer *et al.* have reported that the barium form of c-ZrP was prepared.[6] Further, Alberti *et al.* have shown that hydrolysis starts at a 10% conversion of barium ions.[7]

In the second half of this paper, the results of detailed examination of the pH titration curves for barium ions as well as of the X-ray diffraction patterns of the metal ion-replaced solid are given.

Experimental

The crystalline zirconium phosphate (c-ZrP) was prepared by refluxing a gelatinous precipitate in 6.7M phosphoric acid for 120 hr, as has been reported previously.[2] The resulting crystalline solid was an extremely fine powder, and after drying it was made into tablets under a pressure of about 4200 Kg/cm^2 and then sieved to a grain size of 100—200 mesh.

Distribution Coefficients. The batch distribution coefficients were measured at 25 °C by equilibrating a weighed amount of c-ZrP with known volumes of suitable solutions, followed by analysis of the supernatant liquid. The ratio of volume to the solid weight was usually 100 ml/g.

For all the metal concentrations studied, the exchange reaction attained to equilibrium within 6 hr. The determination of the batch distribution coefficients was made after the reaction mixtures had been shaken for at least 24 hr.

Chemical analyses included the use of such radioisotopes as ^{110m}Ag, ^{133}Ba, ^{89}Sr, ^{60}Co, ^{65}Zn, ^{90}Y, and ^{144}Ce as isotopic tracers. The yttrium-90 tracer was prepared from its parent, ^{90}Sr, using the c-ZrP column as an example of the practical application of the exchanger. For the determinations of potassium, magnesium, and calcium, atomic-absorption photometry was employed. The thallium and ammonium were determined colorimetrically by the use of rhodamine B[8] and the Nessler reagent[9] respectively.

For some cations, the values of the distribution coefficients were determined as a function of the acidity.

pH Titration. A 250 mg portion of c-ZrP was placed in contact at 25 °C with 50 ml of a solution $CaCl_2+Ca(OH)_2$. The ratio of chloride to hydroxide was varied for each run, keeping the total calcium concentration at 0.1 N. After equilibration, the pH of the supernatant was measured with a glass electrode. Since the solubility of calcium hydroxide is rather low, the amount of hydroxide used was limited up to about 6 meq/g of c-ZrP. The experiment with the barium solution was performed in a similar way. In this case, the barium-ion content in the supernatant was determined by EDTA titration. The solid phase obtained at the neutralization point was analyzed for Zr, P, and Ba.

X-Ray Powder Diffraction. The X-ray powder patterns of the exchangers taken during the titration were obtained with Ni filtered copper X-rays using a Geigerflex (Rigaku Denki Co., Ltd.).

Results and Discussion

Affinity series. Table 1 gives the values of the distribution coefficients, K_d, for several ions on the hydrogen-form of c-ZrP. For Zn^{2+} ions, the initial pH of the solution was set at 4.12 in order to suppress hydrolysis. The sorption of monovalent cations increases in the following order:

$$Ag^+ < NH_4^+ < K^+ \simeq Tl^+$$

As compared with the affinity of these ions on a gelatinous zirconium phosphate,[10] less sorption of silver ion is found. The affinity increases with an increase in the crystal radii except for the ammonium ion.

For alkaline earth cations, the sequence is as follows:

$$Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$$

The series of these ions on a gel has been reported by Amphlett *et al.*[10]:

$$Mg^{2+} < Ca^{2+},\ Sr^{2+} < Ba^{2+}$$

Separation factors calculated from the $\alpha_{M_1}^{M_2} = K_d(M_2)/K_d(M_1)$ relation are rather constant and give a value of about 1.46 for a pair of adjacent alkaline earth cations in the sequence.

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TABLE 1. DISTRIBUTION COEFFICIENTS (K_d values) FOR CATIONS WITH INITIAL CONCENTRATION OF 1×10^{-3} N

ion	pH of solution		K_d
	initial	final	
Ag^+	5.10	3.68	30
NH_4^+	5.30	3.11	63
K^+	5.85	3.07	94
Tl^+	5.20	3.51	110
Mg^{2+}	5.50	3.01	90
Ca^{2+}	5.55	3.00	190
Sr^{2+}	5.88	3.00	130
Ba^{2+}	5.85	2.97	280
Co^{2+}	5.60	2.93	230
Zn^{2+}	4.12	2.94	340
Y^{3+}	5.35	2.96	$\sim5.7\times10^3$
Ce^{3+}	5.30	3.39	$\sim3.6\times10^4$

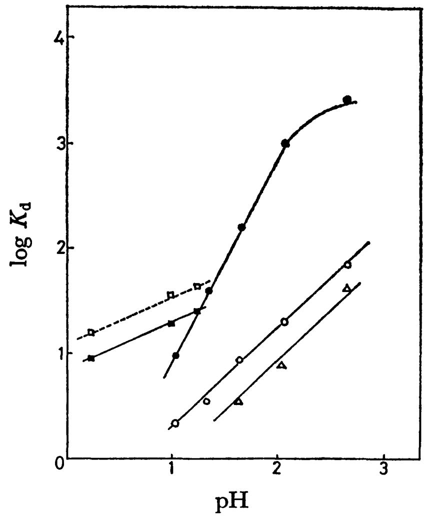

Fig. 1. Distribution coefficients for some cations on c-ZrP at different acidities
○: Ba^{2+}, △: Co^{2+}, ●: Ce^{3+}, ■: Rb^+, □: Cs^+
(total metal ion concentration is 1.0×10^{-3} N)

For other polyvalent cations, the K_d values increase in the order shown in Table 1:

$$Co^{2+} < Zn^{2+} < Y^{3+} < Ce^{3+}$$

This sequence is identical with that reported by Ahrland *et al.* for a gelatinous zirconium phosphate.[11)]

When the values of K_d are plotted as a function of pH, straight lines are obtained (see below). Hence, the affinity sequences obtained may hold in the acidic media.

One of the possible factors which determine the distribution coefficients on the crystalline zirconium phosphate ion-exchanger might be the formation of a stable, less soluble phosphate of polyvalent cations.

In Figs. 1 and 2, the logarithmic values of the distribution coefficients are plotted against the pH. In the cases of Ba^{2+} and Co^{2+} ions whose concentrations are 1×10^{-3} N in the initial solutions, straight lines with a slope of nearly unity were obtained. For Ce^{3+}, the slope was about 2 up to the pH value of 2, beyond this point a serious deviation from the straight line resulted. For the metal-ion concentrations of 1.0×10^{-5} N, the log K_d *vs.* pH plots again exhibit straight lines for these ions, with slopes of somewhat higher values for each case. The slopes are certainly correlated with the charge of the sorbed cations, but no quantitative explanation can be made on the basis of the data given here, because they were not based upon the constant loading of exchanging ions along the curves.[12,13)]

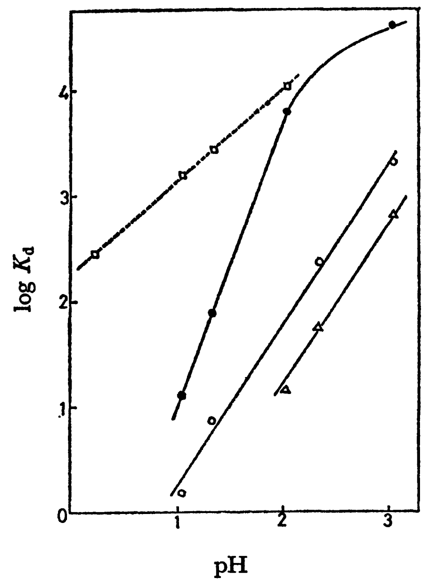

Fig. 2. Distribution coefficients for some cations on c-ZrP at different acidities
○: Ba^{2+}, △: Co^{2+}, ●: Ce^{3+}, □: Cs^+
(total metal ion concentration is 1.0×10^{-5} N)

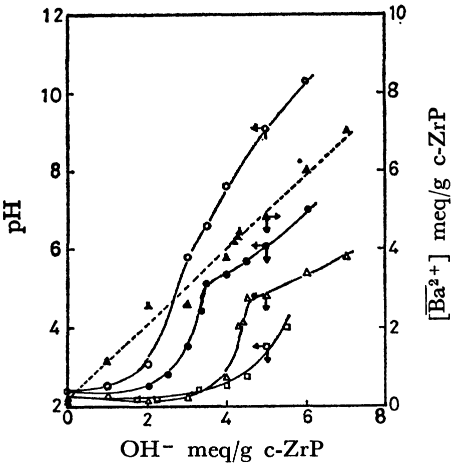

Fig. 3. pH titration curves
□: titrant $CaCl_2+Ca(OH)_2$. (the ratio of solution volume to exchanger weight is 200 (ml/g))
Others: titrant $BaCl_2+Ba(OH)_2$. (the ratio of solution volume to exchanger weight is 100 (ml/g)) reaction time, ○: 6 hr, ●: 24 hr, △: 6 days.
▲: Ba^{2+} content in the exchanger [$\overline{Ba^{2+}}$] calculated for 6 days samples.

pH Titrations. The results of the pH titrations for Ca^{2+} and Ba^{2+} are given in Fig. 3. The titration curve for Ca^{2+} agreed with those given by Harvie and Nancollas and by Alberti *et al.*[5,7)]

In the barium titration, the dependence of the pH of a supernatant on the time was determined at three different compositions (see Fig. 4). It is inferred that the neutralization reaction proceeds in two steps: that is, at an earlier stage the reaction takes place on a surface of the exchanger, and then the diffusion of the cations into the exchanger proceeds gradually. Under those experimental conditions, it took about four days to reach equilibrium. In Fig. 3 the titration curves at different reaction times and the barium-ion contents in the exchanger calculated from those in the supernatants of 6-day sample are shown. The titration curves show that the ion-exchange capacity of c-ZrP for barium ions is equal to 4.4 meq/g (corresponding to 66% of the total exchange capacity) and that the reaction time between 50 and 66% of exchange is quite long.

Beyond 66% of exchange, the exchanger itself is hydrolyzed and the phosphates of barium and zirconium hydroxide are precipitated.

The exchanger at 66% of exchange was stored on a saturated sodium chloride solution, then placed in contact with *ca.* 1 N hydrochloric acid and warmed on a water bath for two days. After cooling, the suspension was centrifuged. The barium ions in the supernatant were analyzed by EDTA titration, and the zirconium and phosphate were analyzed as has been described previously.[14)] Found: Zr 22.2%, PO_4^{3-} 42.3%, Ba^{2+} 20.4 and H_2O 10.3% (weight loss at 120 °C). These data correspond to the $ZrBa_{0.67}H_{0.67}(PO_4)_2 \cdot 2.39H_2O$ formula. The barium content is lower than that calculated from the supernatant in the pH titration. This suggests that the barium ion is held strongly in the exchanger. The phosphate ion was not detected in the supernatant.

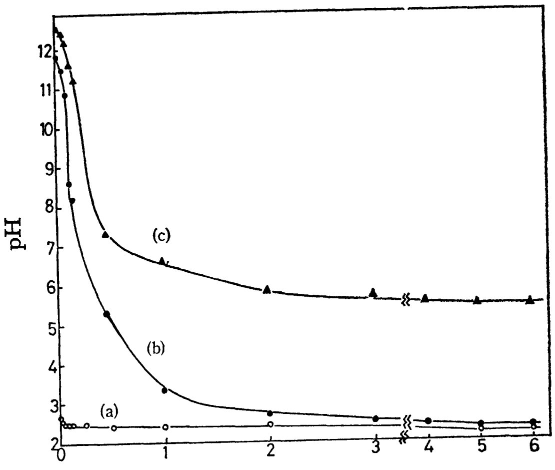

Fig. 4. The dependence of pH of supernatants on time a 0, b 3, c 6 meq/g OH^- addition

X-Ray Studies. X-Ray powder patterns of the exchanger at different titration stages are shown in Fig. 5. The first reflection of c-ZrP was detectable in the diffractograms up to a 5 meq/g addition of OH^-. In the diffraction patterns of the ignited exchanger, the peaks of zirconium pyrophosphate resulting from c-ZrP were found up to 5 meq/g. Moreover, exchanger at 10 meq/g showed the peaks to be those of zirconium oxide.

In conclusion, in 0~66% of exchange, the mixture of c-ZrP and its barium form, and at 66% of exchange the $ZrBa_{0.67}H_{0.67}(PO_4)_2 \cdot nH_2O$ phase was present, while beyond 67% of exchange the complex mixtures including the hydrolysis product were present.

The crystalline zirconium phosphate is known to have a layered structure and to contain a zeolitic cavity between the layers, and the expansion of the interlayer distance is caused by an uptake of cations.[15,16)] According to Clearfield *et al.* the opening to the cavity permits only the cations with a 2.6Å diameter to diffuse into the crystal lattice unless c-ZrP swells considerably. Hence, the ionic radius of sorbed cations has a significant effect on the ion-exchange capacity of c-ZrP. However, as has been shown above, the ion-exchange capacity for barium ions is equal to 4.4 meq/g, which is equal to that for lithium and ammonium ions.[14,17)]

In Table 2, the interplanar spacing (*d* values) of the Ca^{2+} and Ba^{2+} ion-replaced exchangers are shown. For the Ca^{2+} ion-replaced exchanger, an increase in the interlayer distance (7.6→10.05Å) was observed, as had been expected from the previous works. On the

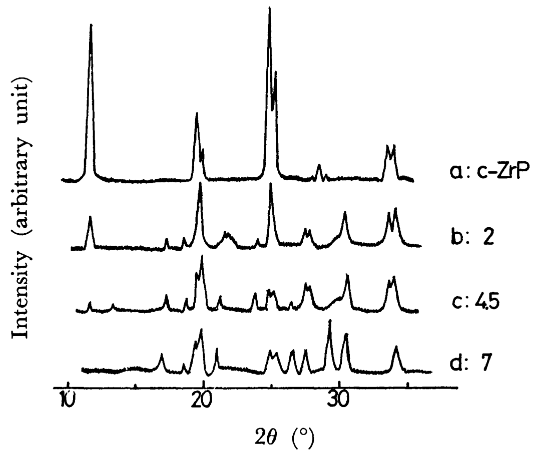

Fig. 5. Schematic diagrams of X-ray diffraction patterns. Numerals correspond to those of abscissa in Fig. 3.

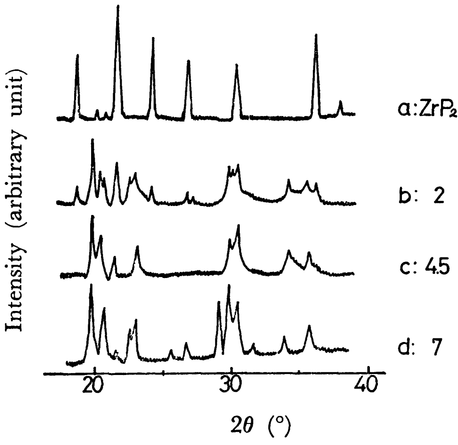

Fig. 6. Schematic diagrams of X-ray diffraction patterns for ignited samples. Numerals correspond to those of abscissa in Fig. 3.

TABLE 2. *d*-VALUES OF CALCIUM AND BARIUM FORMS OF c-ZrP (A)

Ca-ZrP	Ba-ZrP
10.05 s	7.69 vw
5.01 m	5.13 vw
4.58 s	4.51 m
4.48 s	3.72 vw
4.11 s	3.56 m
3.93 s	3.23 w
3.75 s	3.01 vw
3.19 s	2.94 m
3.13 m	2.65 m
3.06 w	2.63 m
2.76 w	1.90 vw
2.65 s	1.73 vw
2.61 m	1.71 vw
2.06 vw	
1.96 vw	
1.87 vw	

other hand, for the Ba^{2+} ion-replaced exchanger, no change in the interlayer distance was observed.

The above results should be further considered in terms of the behavior of hydrated water molecule during exchange; an investigation along this line is needed. It should be worthwhile, also, to mention how much the press treatment influences the exchange behavior.

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