Inorganic Ion Exchangers

IV. The Sorption on Crystalline Zirconium Phosphate and Its Dependence upon the Crystallinity

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Crystalline zirconium phosphate, of composition $Zr(HPO_4)_2 \cdot H_2O$, has been prepared. The X-ray powder photographs can be indexed on the basis of a hexagonal unit cell of dimensions $a = 10.5$ Å and $c = 45.6$ Å. The neutralization curve, obtained in a Na^+ medium, indicates that the monohydrogen phosphate groups exist in two states of acidity. When a Cs^+ medium is used, only the more acid portion of the groups can be loaded. The hydrolysis of crystalline zirconium phosphate depends upon the size of the cation present and is extensive when Cs^+ is sorbed. The sorption of Cs^+ on preparations of various crystallinity is investigated and a simplified picture of the sorption is developed, more especially for the gels. Besides the ordinary monohydrogen phosphate groups, all the preparations appears to contain small amounts of another functional group with a high affinity to certain cations, especially Cs^+. The sorption on crystalline zirconium phosphate of Na^+, Cs^+, UO_2^{2+}, and Ce^{3+} is probably a perfect cation exchange. The behaviour of Sr^{2+} is irregular and it appears to be irreversibly sorbed. The following affinity series is found: $Sr^{2+} \geq UO_2^{2+} \geq Ce^{3+} > Na^+ > Cs^+$.

During the last ten years, a number of investigations have dealt with the ion exchange properties of zirconium phosphate gels. The results reported before 1964 are summarized in Ref. 1. The earlier papers of the present series [2-4] have been mainly devoted to this subject also. In common with most inorganic ion exchanger materials, the sorption of metal ions on zirconium phosphate is dependent upon a variety of factors which may vary with the preparation, *e.g.* composition, crystallinity, acidity, and water content. A satisfactory description of the sorption mechanism can be obtained only if the influence of all these factors is known. It must then also be taken into account that some of these factors cannot be varied independently, *e.g.* the acidity is closely related to the crystallinity.

In the present work the sorption has been studied as a function of the crystallinity. To this end zirconium phosphates of various average crystallite size

have been investigated, as well as the truly crystalline compound, of the formula $Zr(HPO_4)_2 \cdot H_2O$. The method of preparation given by Clearfield and Stynes [1,5,6] has been used.

Some workers [1,7] have proposed molecular structures for zirconium phosphate which are not based on proper structure determinations, but rather inferred from the sorption properties of the gels. A crystal structure investigation, not yet completed, using X-ray diffraction methods has been undertaken by Clearfield.[6] The tentative structure proposed will be referred to below.

SUMMARY OF THE THEORY OF THE SORPTION EXPERIMENTS

Notation:

A bar denotes a species within the ion exchanger phase;

C_M, C_H = total concentration of metal ion, M^{n+}, and of hydronium ion in the solution before addition of ion exchanger;

C_{MS} = total concentration of metal ion in the solution at equilibrium;

v = volume of solution before addition of ion exchanger;

m = weight of the added ion exchanger;

$C_{MG} = \dfrac{v}{m} (C_M - C_{MS})$ = total concentration of $\overline{M}^{n+}$ in the ion exchanger phase at equilibrium;

$\varphi = C_{MG}/C_{MS}$ = distribution coefficient;

C_{AG}, C_{BG} = total concentrations of the functional groups $\overline{A}$, and $\overline{B}$ in the ion exchanger phase;

h, $\overline{h}$ = equilibrium concentrations of hydronium ions in the solution and in the ion exchanger phase;

$$k_1 = \frac{[\overline{M}^{n+}] \, h^n}{[M^{n+}] \, \overline{h}^n}$$

$$\beta_j = \frac{[\overline{MA_j}^{n-j}]}{[\overline{M}^{n+}][\overline{A}^-]^j}$$

$$\gamma = \frac{[\overline{MB}^{n-1}]}{[\overline{M}^{n+}][\overline{B}^-]}$$

For a perfect cation exchange [4]

$$\log \varphi = n \, pH + D \tag{1}$$

where $pH = -\log h$ and n is the ionic charge on the sorbed metal ion. If the ion exchanger is monofunctional,

$$D = \log k_1 \left(1 + \sum_{j=1}^{N} \beta_j \, [\overline{A}^-]^j\right) + n \, \log \overline{h}$$

If D is a function of C_{MG} alone, a $\log \varphi$ (pH) plot at constant C_{MG} is a straight line with slope n. When C_{MG} is sufficiently small, $\overline{h}$, $[\overline{A}^-]$, and thus D are

independent of C_{MG}. This causes the log φ (pH) plots to coincide for small values of C_{MG}. The curves are constructed in the following way: C_{MG} is plotted *versus* C_{MS} using different values of C_H. By intersecting these isotherms at constant C_{MG}, log φ may be obtained as a function of pH. This pH is determined by interpolation of the measured pH values for the experimental points.

The log φ(pH) curves for the sorption of certain metal ions on zirconium phosphate are very dependent upon C_{MG} even at values so low that $\bar{h}$ and $[\bar{A}^-]$ must be independent of them. In order to describe this effect the behaviour of φ (C_{MG}) curves have also been investigated[4] using the assumption that the ion exchanger contains, in addition to the main group $\overline{HA}$, *small* amounts of an acid group $\overline{HB}$ and that $\bar{B}^-$ interacts with $\overline{M}^{n+}$. It is found that φ increases with decreasing C_{MG} even at values of $C_{MG} \ll C_{AG}$ and so small that $\bar{h}(C_{MG}) = \bar{h}(0)$. If the interaction between $\bar{B}^-$ and $\overline{M}^{n+}$ is strong, *i.e.* γ has a large value, it can be shown that, provided $C_{MG} < C_{BG}$,

$$\varphi = k_1 \left(\frac{\bar{h}(0)}{h} \right)^n \left(a + \frac{\gamma}{b} (C_{BG} - C_{MG}) \right) \tag{2}$$

where a and b are constants. If the load on the ion exchanger is very low and the constant value of C_H ($= h$) is so high that the solution can be considered to have a constant ionic medium, it is found that φ is a rectilinear (rapidly) decreasing function of C_{MG} alone. For strong interactions, and if $C_{MG} > C_{BG}$, it can be shown that

$$\varphi = k_1 \left(\frac{\bar{h}(0)}{h} \right)^n a \left(1 + \frac{C_{BG}}{C_{MG} - C_{BG}} \right) \tag{3}$$

Eqn. (1) is still valid, even if $\overline{HB}$ groups are present, but the expression for D has altered to

$$D = n \log \bar{h} + \log k_1 (a + \gamma[\bar{B}^-]).$$

It is evident that a perceptible dependence of φ upon C_{MG}, under the conditions pointed out above, cannot be due to the formation of species $\overline{MA}_j^{n-j}$, since $[\bar{A}^-]$ has a constant value.

EXPERIMENTAL

Chemicals used. When not otherwise stated, all chemicals were of analytical grade and were used without further purification.

The neutralization and hydrolysis experiments were performed as described previously[2] having $v/m = 100$ ml/g and a temperature of 20.0°C. Carbonate free solutions of *cesium hydroxide* were prepared and analysed as described before.[4] The values of the pH and C_{MS} were determined, the latter radiometrically using ^{22}Na and ^{134}Cs. When pH did not change with further shaking it was assumed that equilibrium had been established.

The sorption experiments were performed at a temperature of 20.0°C as described in Refs. 3, 4. For the equilibrium studies the shaking time was at least 4 h. Stock solutions of *cesium nitrate, strontium nitrate, cerium (III) nitrate* and *uranyl nitrate* were used. Values of pH < 3 were adjusted using nitric acid. The sorption of Cs$^+$ and Na$^+$ was measured for values of pH > 3. *Cesium acetate-acetic acid* buffers were employed for the

Cs$^+$ experiments and *sodium hydroxide-sodium chloride* buffers for Na$^+$. In all cases C_{MS} was determined as described before.[3,4] For all solutions h was determined as a rule with the aid of a glass electrode at $I = 0.1$ M. The potentiometer was calibrated for every actual pH interval by solutions of known h.

PREPARATION, COMPOSITION AND UNIT CELL DIMENSIONS OF CRYSTAL-LINE ZIRCONIUM PHOSPHATE

Crystalline zirconium phosphate was prepared according to the method of Clearfield and Stynes.[5] A solution of $ZrO(NO_3)_2 \cdot 2 H_2O$ (3 l 0.33 M and 1 M in HCl) was added with stirring to a solution of H_3PO_4 (4 l 0.75 M and 1 M in HCl). The resulting gelatinous precipitate stood in contact with the solution for three days.[2] It was then separated from the solution and washed with phosphoric acid (2 %) until the washings were free from chloride ions. The gel was refluxed with 12 M H_3PO_4 for 24 h. After washing with water until pH $\approx$ 6, the product was dried over $CaCl_2$ to constant weight. An X-ray powder pattern showed the product to be crystalline (Fig. 1).

The zirconium content (after ignition) was determined by X-ray fluorescence, using MoO_3 as an internal standard. The phosphorus content was determined by melting and powdering a sample (0.1 g) with a glass forming tetraborate buffer (3 g) and using optical emission spectrography. (Both the analyses were carried out by *Analytica AB*, Sollentuna, Sweden). The water content was determined as the weight loss during ignition. The prepared compound contained: 30.5 % P, 20.6 % P, and 12.0 % H_2O; calculated for $ZrO_2 \cdot P_2O_5 \cdot 2 H_2O$: 30.28 % Zr, 20.58 % P, and 11.96 % H_2O.

Fig. 2 shows the dehydration curve of crystalline zirconium phosphate. The weight loss at various temperatures was measured by heating samples to constant weight. The results of Clearfield and Stynes [5] are included in Fig. 2 for comparision. Exactly at 100°C approximately one mole of water per zirconium is evolved. Another mole of water splits out at about 440°C. Below 100°C, and in the range between 100 and 440°C only a small quantity of water is released. The analysis and the dehydration curve show the compound to have the formula $Zr(HPO_4)_2 \cdot H_2O$. This is further discussed in Ref. 5. This crystalline compound is subsequently denoted as ZrP.

X-Ray powder photographs of ZrP were taken in a Guinier focusing camera using CuKα radiation and $Pb(NO_3)_2$ as a standard. Errors caused by film shrinkage were avoided
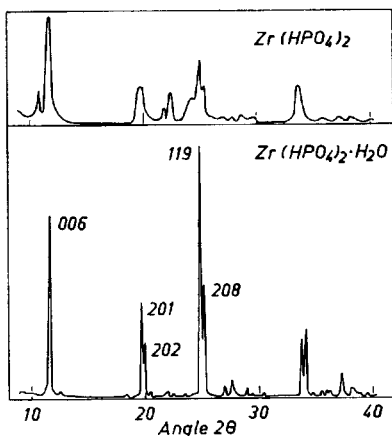

Fig. 1. X-ray diffraction patterns of $Zr(HPO_4)_2 \cdot H_2O$ and $Zr(HPO_4)_2$.
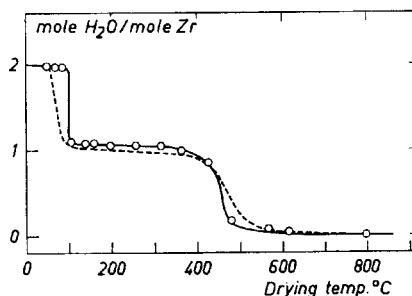
Fig. 2. The water still held by crystalline zirconium phosphate as a function of the drying temperature. The dashed line refers to Clearfield and Stynes.[5]

Table 1. Observed lines in the powder photograph of $Zr(HPO_4)_2 \cdot H_2O$. (Guinier focusing camera, intensities from a Philips commercial diffractometer).

$\sin^2\theta_{obs}$ $\times 10^4$	$\sin^2\theta_{calc}$ $\times 10^4$	h k l (This investigation)	h k l (Clearfield)	d_{obs} Å	I_{obs}
102	106	006	006	7.63	73
292	287	200			
	289	115			
	290	201	202	4.51	38
	293	0,0,10			
298	299	202	—	4.46	21
323	321	116	116	4.29	2
359	359	117	1,0,10	4.07	3
	361	205			
422	422	0,0,12	206	3.75	2
460	453	119	208	3.60	100
471	475	208	—	3.55	50
541	550	214	214	3.31	5
570	570	1,1,11	2,0,10	3.23	7
621	608	216	1,0,14	3.09	4
	637	1,1,12	1,1,12		
643	642	2,0,11	300	3.04	2
677	673	303	—	2.96	2
744	741	219	—	2.83	1
784	783	2,0,13	—	2.75	1
842	847	0,0,17	2,0,14	2.66	24
856	858	2,1,11			
	862	2,0,14	220	2.64	26
	862	220			
930	925	2,1,12	0,0,18	2.53	3
	934	310			
948	950	0,0,18	—	2.50	3
956	961	313	—	2.49	4
967	968	226	226	2.48	4
1010	1006	227	—	2.42	7
	1008	315			
1016	1022	1,0,18	2,0,16	2.41	10
1062	1063	1,1,17	3,0,12	2.37	4
1074	1078	2,1,14	—	2.35	3
	1078	317			
1082	1078	2,1,14	—	2.34	3
	1078	317			
1098	1100	229	229	2.33	2
1140	1142	3,0,13	1,1,18	2.28	2
1177	1176	403	402	2.25	2
1200	1197	404	404	2.23	2
1225	1221	3,0,14	2,1,16	2.20	4
	1223	405	2,0,18		
	1227	3,1,10	406		
1253	1253	2,1,16	—	2.18	5
1257	1256	406	—	2.17	5
1283	1285	2,2,12	2,2,12	2.15	4

by exposing a scale on the films before development. Clearfield [6] reports that oscillation and Weissenberg photographs show that the unit cell is hexagonal having $a = 10.5$ Å and $c = 45.6$ Å. Using these values, the powder lines were indexed in the conventional way by a comparison of the measured $\sin^2\theta$-values with calculated.

Calculated and observed $\sin^2\theta$-values are given in Table 1. The intensities were measured by a commercial Philips diffractometer (Fig. 1). Two sets of indices are given, one of which is reported by Clearfield.[6] However, he leaves the two strong reflexions of $\sin^2\theta_{obs} = 0.0298$ and 0.0171 unindexed. Because of the long c-axis, some of the reflexions may be given several h k l-values, more especially that having $\sin^2\theta_{obs} = 0.0292$. Since Weissenberg photographs show that the intensity of the 201-reflexion is much stroger than for the other possibilities,[6] 201 is chosen as the main component of $\sin^2\theta_{obs} = 0.0292$.

Clearfield [6] also reports that the zirconium atoms occupy the positions 000, 1/3 2/3 2/3, and 2/3 1/3 1/3 in a rhombohedral centered pseudocell having dimensions $1/2\,a$ and $1/2\,c$. The structure should then be layered with an interplanar spacing of 7.6 Å. This is the d-value of the first strong reflexion, 006.

Besides the X-ray diffraction pattern of ZrP, Fig. 1 also shows the pattern of dehydrated ZrP, *i.e.* $Zr(HPO_4)_2$. No radical change has occurred but the lines are broadened. It may be concluded that the main structural features remain but the crystallites are broken up into smaller units during the dehydration. The water that is lost can be regarded as zeolitic; the structure of ZrP should be an open one with suitable cavities.

ACIDITY AND HYDROLYSIS

In Ref. 2, 4 neutralization and hydrolysis curves for different zirconium phosphate gels and in different media were reported. It was found that gels have wide ranges of acidities but two inflexion points were found at pH's ≈ 2 and 9. The hydrolysis was small below pH ≈ 8 but above this value it increased rapidly. In this study, neutralization and hydrolysis of crystalline ZrP were investigated, by using NaOH + NaCl and CsOH + CsCl solutions with $C_M = 0.1$ M. The results are given in Figs. 3 and 4. For the neutralization experiments both C_{MG} and the OH$^-$ consumed were determined. When the Na$^+$ medium is used, the C_{MG} data show that the neutralization occurs through two stages, equal amounts of the phosphate groups being neutralized for each step. When the slight hydrolysis of ZrP is taken into account (Fig. 4), OH$^-$ and C_{MG} data coincide, showing equivalence between the metal ions sorbed and the hydrogen ions released, *i.e.* the sorption of Na$^+$ is a cation exchange. From Fig. 3 the capacity for Na$^+$ is found to be 6.50 mmole/g ZrP which may be compared with the analysis result 6.65 mmole P/g ZrP (= mmole H$^+$/g ZrP) reported
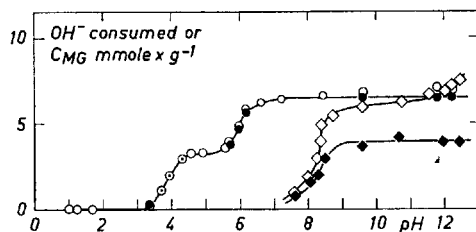

Fig. 3. Neutralization curves for Na$^+$ and Cs$^+$ media ($C_M = 0.1$ M). The symbols refer to: OH$^-$ consumed, Na$^+$, O; Cs$^+$, ◇; metal ions sorbed, Na$^+$, ●; Cs$^+$, ◆.

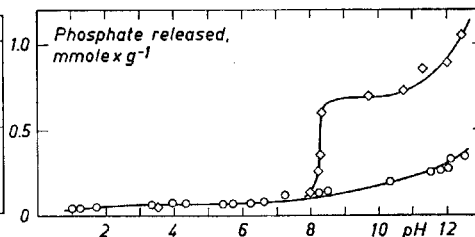*Fig. 4.* Phosphate released to the solution as a function of pH for Na$^+$, O and Cs$^+$, ◇, media ($C_M = 0.1$ M).

above (p. 1692). The neutralization curve for Na^+ resembles those reported by Clearfield and Stynes [5] and Nancollas and Pekàrek.[7]

When the Cs^+ medium is used, only one neutralization step was found. The C_{MG} data show that a little more than half of the phosphate groups can be loaded with Cs^+ ions (Fig. 3). However, many more OH^- ions were consumed that Cs^+ ions sorbed. The amount of phosphate released (Fig. 4) shows that when Cs^+ is sorbed, ZrP is destroyed by hydrolysis. One third of the difference between the amount of OH^- consumed and Cs^+ sorbed (for a certain pH) roughly equals the amount of phosphate released in accordance with the equation [2]

$$Zr(HPO_4)_2 \cdot H_2O + 6OH^- \longrightarrow ZrO(OH)_2 + 2\ PO_4^{3-} + 4\ H_2O$$
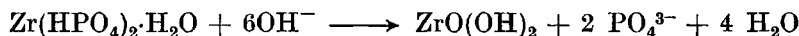
The Na^+ curve in Fig. 3 shows that the monohydrogen phosphate groups in ZrP may be divided into two categories according to the different acidities. In Fig. 5, some X-ray diffraction patterns of loaded ZrP's are collected. When the exchange with Na^+ is completed, the 006-reflexion is displaced to a lower angle, i.e. to a higher value of the corresponding d_{006} (the curve ZrP—2 Na^+). This displacement of 006 is not observed when only the first step of the sorption is completed but the reflexion is split into a doublet (the curve ZrP—Na^+). This behaviour of the X-ray diffraction patterns is also reported by Clearfield and Stynes.[5] Assuming that the structure consists of zirconium layers with an
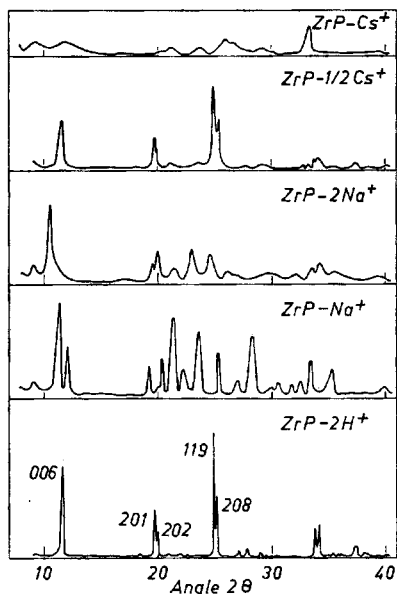

Fig. 5. X-Ray diffraction patterns of crystalline ZrP's half and fully loaded with Na^+ (the curves ZrP-Na^+, ZrP-2Na^+) and Cs^+ (the curves ZrP-$\frac{1}{2}Cs^+$, ZrP-Cs^+).
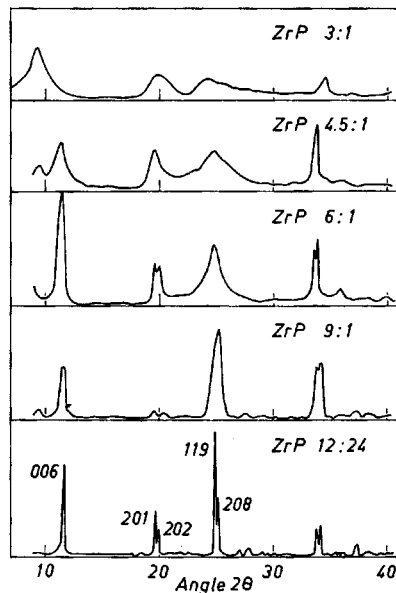
Fig. 6. X-Ray diffraction patterns of ZrP's having various crystallinities. In ZrP $i:j$, $i:j$ refers to M phosphoric acid: refluxing time in hours.

interplanar spacing corresponding to d_{006},[5,6] the phosphate groups of lower acidity appear to be involved in interplanar bonds, whilst the groups of higher acidity are involved in intraplanar bonds. However, the detailed structure of ZrP must be known before any reliable conclusions can be reached.

For sorption at values of pH$\leq$6.5, the gels have the following affinity series $Cs^+ > Rb > Na^+$. For values of pH > 6.5 the order is reversed.[4] It is thus the hydrated ions that are sorbed on the most acidic groups of the gels. Fig. 3 indicates that for crystalline ZrP it appears to be the unhydrated ions that are sorbed for all pH values, *i.e.* on all the functional groups. Clearfield [6] has collected analytical evidence for this. Fig. 5 contains two X-ray diffraction patterns of ZrP's that are half and fully loaded with Cs^+ (the curves $ZrP - 1/2\ Cs^+$ and $ZrP - Cs^+$, respectively). When Cs^+ is sorbed the 006 reflexion does not move but the line broadening indicates that the observed destruction of ZrP preferently takes place along the c-axis. The results of Figs. 3—5 can be described thus: Cs^+ is sorbed by the more acidic half of the monohydrogen phosphate groups, which are involved in the intraplanar bonds of the presumed zirconium layers. However, the large Cs^+ ion causes a destruction of the interplanar bonds. When the zirconium layers separate, some of the "interplanar" phosphate groups assume a position where they are able to sorb Cs^+. Hence, more than half of the phosphate groups may be loaded with Cs^+.

For zirconium phosphate gels, it was found that all phosphate groups sorbed Cs^+ and that the Cs^+ medium diminished the hydrolysis of the gels.[4] As discussed below (p. 1697), the X-ray diffraction pattern of ZrP 3:1 (Fig. 6) shows that there is a higher spacing of zirconium layers in the gels than in the crystalline ZrP. Then the Cs^+ ions can be sorbed on the phosphate groups participating in interplanar bonds even if the affinity changes to $Na^+ \geq Cs^+$. Since the primary reason for the destruction of ZrP by hydrolysis appears to be that the Cs^+ ion is too large to be fitted between the zirconium layers, it is reasonable that this effect cannot be found for the gels.[4]

CRYSTAL GROWTH AND THE SORPTION OF CESIUM IONS ON ZIRCONIUM PHOSPHATES OF VARIOUS CRYSTALLINITY

A gel, prepared as described previously (p. 1692), was divided into four portions. Each portion was refluxed with a different concentration of H_3PO_4 (3, 4.5, 6, and 9 M, respectively) for one hour. The products were washed with water until the pH ≥ 3.5 [2] and then they were dried to constant weights at 60°C. The preparations are denoted ZrP 3:1, ZrP 4.5:1, ZrP 6:1, and ZrP 9:1, *i.e.* M H_3PO_4: refluxing time. Using the same scheme completely crystallized ZrP is denoted ZrP 12:24. All the preparations should have the formula $Zr(HPO_4)_2 \cdot nH_2O$ (*cf.* p. 1692 and Ref. 2,3). Two grain size fractions were used, *viz.* 60—100 mesh and > 150 mesh. The last fraction was thoroughly ground using an agate pestle and mortar. Table 2 contains the ignition losses of the preparations. Both grain size fractions from each preparation had the same ignition loss.

Fig. 6 shows the X-ray diffraction patterns for the five preparations. The pattern of ZrP 3:1 resembles that of an ordinary gel (*e.g.* 3.0—VII of Ref. 8)

but the line broadenings of the remainder are lower. The first reflexion, 006, of ZrP 3:1 is at a lower angle than that found for the other preparations.[5,8] Thus, when crystallites grow, the spacing of the zirconium layers becomes shorter. A rough estimate of the mean dimensions along different directions of the crystallites, D_{hkl}, was obtained by the use of the Scherrer equation [9]

$$D_{hkl} = \frac{0.9\,\lambda}{\beta_{hkl}\cos\theta}$$

where β_{hkl} is the line breadth at half the maximum intensity of the hkl reflexion. Table 2 shows D_{006}, D_{201}, and D_{119} for ZrP 3:1, ZrP 4.5:1, and ZrP 6:1.

Table 2. Water content and crystallite dimensions of the various preparations of ZrP after drying at 60°C; n refers to $Zr(HPO_4)_2 \cdot nH_2O$.

Preparation	Ignition loss %	n	D_{006} Å	D_{201} Å	D_{119} Å
ZrP 3:1	18.6	2.37	36	—	—
ZrP 4.5:1	14.5	1.50	67	81	33
ZrP 6:1	13.4	1.28	160	107	45
ZrP 9:1	12.5	1.10	—	—	—
ZrP 12:24	12.0	1.00	—	—	—

The values of D_{201} and D_{119} are definitely too low, the actual reflexions being doublets. D_{006} gives the mean dimension along the c-axis, and D_{201} indicates the lower limit of the mean dimension along a direction almost perpendicular to the c-axis. The crystallite size increases in the order ZrP 3:1 < Zr 4.5:1 < ZrP 6:1 < ZrP 9:1 < ZrP 12:24 as is expected, but is still small for ZrP 6:1. Since the overall surface increases with decreasing crystallite size, the amount of water sorbed also increases (Table 2). The high value of d_{006} for ZrP 3:1 may permit water to be sorbed between the zirconium layers, causing the difference in ignition loss to be larger than expected for ZrP 3:1 and ZrP 4.5:1.

The neutralization experiments described previously showed that the affinity of crystalline ZrP for Cs^+ was much smaller than the affinity for Na^+. Conversely, zirconium phosphate gels have the opposite order of affinity for the most acidic functional groups. The sorption on the gels was dependent upon the radii of the hydrated ions, but crystalline ZrP sorbs unhydrated ions. In the light of these observations one can develop a simple picture of the sorption and its dependence upon the crystallinity of the used ZrP. A gel (*e.g.* ZrP 3:1) has a large surface area and a high value of d_{006}. Thus, many monohydrogen phosphate groups will have positions next to the solution or are in a position where they can be easily attained, *i.e.* they are able to sorb hydrated ions. This causes the affinity for, *e.g.*, Cs^+ to be larger than the affinity for Na^+. In terms of acidity these "surface groups" are the most acidic groups of gelatinous ZrP, and are neutralized at values of pH $\leq$ 2.[4] The monohydrogen phosphate groups situated within the crystallites, *i.e.* not adjacent to the solution, are consequently less acidic and have a range of acidities because the

structure of a gel is unordered. According to this model of the ion exchange, the affinity of ZrP for a metal ion should decrease as the crystallite size increases. The number of "surface groups" are decreased and even at small values of C_{MG} groups within the crystallites must be loaded.

Sorption experiments using small amounts of Cs^+ were performed on all the different preparations of ZrP at $C_H = 98.5$ mM. The results are collected in Fig. 7 which gives φ as a function of C_{MG}. C_{MG} and φ are measured in respectively mmole and l/g ignited ZrP to obtain the value of φ independently of the varying amount of water sorbed on the crystallites. Both grain size fractions were used, the open symbols of Fig. 7 are referring to > 150 mesh, while the filled ones refer to $60-100$ mesh. It is observed that the affinity for Cs^+ increases when going from ZrP 3:1 to ZrP 4.5:1 but then it decreases in the order ZrP 4.5:1 $>$ ZrP 6:1 $>$ ZrP 9:1 $>$ Zr 12:24, $i.e.$ in the order of increasing crystallite size. There appears to be an optimal mean dimension of the crystallites for which the sorption of small amounts of Cs^+ is most effective. Hence, the simple model of the sorption that was developed before cannot be completely true. It is, however, very probable that the ordering of the structure takes place to a great extent between ZrP 3:1 and ZrP 4.5:1. This ordering may cause the affinity to Cs^+ to increase; the overall surface does not appear to have decreased much. When a grain size
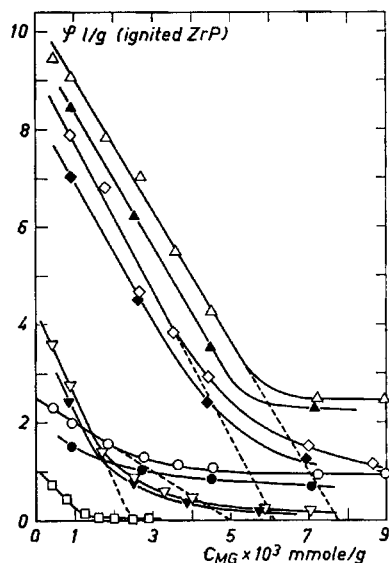

Fig. 7. φ as a function of C_{MG} ($C_H = 98.5$ mM) for Cs^+ on ZrP's of various crystallinity. The symbols refer to: ZrP 3:1, ○, ●; ZrP 4.5:1, △, ▲; ZrP 6:1, ◇, ◆; ZrP 9:1, ▽, ▼; ZrP 12:24, □. Open symbols refer to the grain size fraction > 150 mesh, filled to $60-100$ mesh.
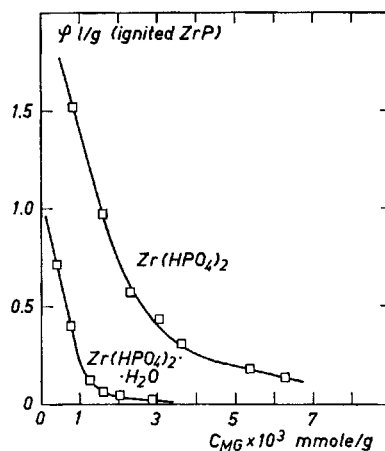
Fig. 8. φ as a function of C_{MG} at $C_H = 98.5$ mM for Cs^+ on $Zr(HPO_4)_2 \cdot H_2O$ and $Zr(HPO_4)_2$.

of 60—100 mesh was used, the sorption was smaller than for sizes > 150 mesh (Fig. 7). The clogging together of the crystallites to larger units appear to decrease the surface area attainable by the metal ions.

All the $\varphi(C_{MG})$-curves of Fig. 7 have the expected shape if the ion exchanger contains small amounts of a second functional group that is capable to interact strongly with the sorbed cation, i.e. as well as $\overline{HA}$, there are small amounts of $\overline{HB}$ having a large value of γ (vide supra p. 1691). This is even the case for ZrP 12:24. That $\bar{h}(C_{MG}) = \bar{h}(0)$ for the low values of C_{MG} used is confirmed for the gels by the experiments with Na^+ described in Ref. 4. Later (Fig. 10) it will be shown that also for ZrP 12:24, $\varphi(C_{NaG})$ has a constant value for small values of C_{NaG}. Then γ_{Na} (12:24) = 0 and $\bar{h}(C_{MG}) = \bar{h}(0)$ for crystalline preparations. The values of γ_{Cs} are of the same order for all the preparations except that of ZrP 3:1 which appears to have a lower value; the left rectilinear portion of this curve does not decrease so rapidly as for the other ones. Extrapolation of the rectilinear portions to the C_{MG}-axes gives $C_{BG} + ab/\gamma$ (measured in mmole/(g ignited ZrP)) for the different preparations (cf. eqn. (2) of p. 1691), i.e. an upper limit of the value of C_{BG}. C_{BG} diminishes in the order ZrP 4.5:1 > ZrP 6:1 > ZrP 3:1 ≥ ZrP 9:1 > ZrP 12:24 and C_{BG} (4.5:1) ≤ 7.5 × 10⁻³ mequiv./g, while C_{BG} (12:24) ≤ 1.2 × 10⁻³ mequiv./g.

In a following paper [8] it will be shown that when the zeolitic water is removed from ZrP, its affinity to certain metal ions, more especially Cs^+, increases tremendously. It is also shown that this dehydration is reversible but that the resorption of water takes a long time. The question now arises, whether the $\overline{HB}$ groups are actually monohydrogen phosphate groups in cavities where the zeolitic water is lacking. The sorption of Cs^+ on dehydrated ZrP, i.e. $Zr(HPO_4)_2$, was determined at $C_H = 98.5$ mM. If the presumption is true, $\varphi (C_{MG})$ ought to have a constant value for the low values of C_{MG} used since all $\overline{HA}$ groups then should be converted to $\overline{HB}$. Fig. 8 shows the results together with the curve for crystalline $Zr(HPO_4)_2 \cdot H_2O$, ZrP 12:24. The affinity of $Zr(HPO_4)_2$ for Cs^+ is larger than that of $Zr(HPO_4)_2 \cdot H_2O$ but the shapes of the curves are the same. Hence, the $\overline{HB}$ groups are not due to the lack of zeolitic water in the structure. Nevertheless, it is most probable that the effect, formally ascribed to the existence of a group $\overline{HB}$, is due, in fact, to structural inhomogeneities that place ca. 0.1 % of the monohydrogen phosphate groups in exclusive positions (cf. Ref. 4).

THE SORPTION OF Na^+, Cs^+, Sr^{2+}, UO_2^{2+} AND CE^{3+} ON CRYSTALLINE ZIRCONIUM PHOSPHATE

Sorption rate. A factor of great importance for the employment of a compound as an ion exchanger is its sorption rate; the optimal flow rate of a column depends mainly upon it. In order to carry out equilibrium experiments, one must also know the necessary shaking times. The sorption rate at 20.0°C on ZrP was determined for Na^+, Cs^+, Sr^{2+}, UO_2^{2+}, and Ce^{3+} with $C_M = 10$ mequiv./l and $v/m = 20$ ml/g. Sodium and cesium acetate solutions were used, the equilibrium values of pH being, respectively, 4.73 and 5.16. Nitrate

Table 3. The crystallographic ionic radii of the sorbed metal ions and the symbols used in Figs. 9 and 10.

Species	Na$^+$	Cs$^+$	Sr^{2+}	UO$_2^{2+}$	Ce^{3+}
Radius (Å)	0.95	1.69	1.13	—	1.03
Symbol	●	◇	○	◧	▽

solutions with $C_H = 10$ mM were used for Sr^{2+}, UO$_2^{2+}$, and Ce^{3+}, the equilibrium values of pH being, respectively, 1.96, 1.92, and 1.94. The results are shown in Fig. 9, the symbols used being given in Table 3. For all investigated metal ions, the sorption is almost complete after one hour, Na$^+$, Sr^{2+}, and Ce^{3+} having reached equilibrium. For UO$_2^{2+}$ and Cs$^+$, there is still a slow rest sorption but equilibrium seems to be reached within 24 h. The crystallographic ionic radii [10] of the metal ions used are shown in Table 3. The linear uranyl ion is a large one and the slow rest sorption of UO$_2^{2+}$ and Cs$^+$ may reflect the difficulties of these larger ions to diffuse into the crystallites.

Sorption at equilibrium. A convenient way of studying the selectivity of an ion exchanger and the nature of its sorption is by plotting log φ as a function of pH for different constant values of the load, C_{MG}.[4] Such curves were obtained for ZrP as described before (p. 1691). As before [4] it was controlled that the used isotherms were independent of v/m, but for each metal ion the same value (between 10 and 40 ml/g) was used. The log φ(pH) curves are shown in Fig. 10. The symbols are from Table 3. The dotted lines are the curves at $C_{MG} = 10^{-3}$ mmole/g obtained on a gel of P/Zr = 1.95 as reported in Ref. 4.
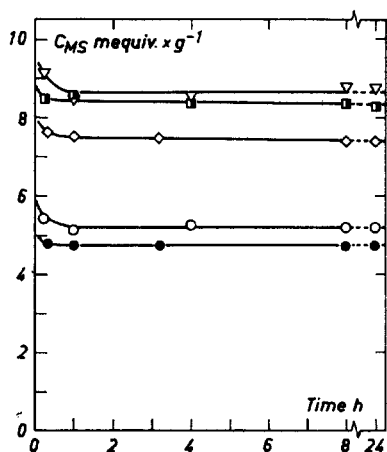

Fig. 9. Sorption rates of Na$^+$, Cs$^+$, Sr^{2+}, UO$_2^{2+}$, and Ce^{3+} on crystalline zirconium phosphate at 20°C. Symbols in Table 3.
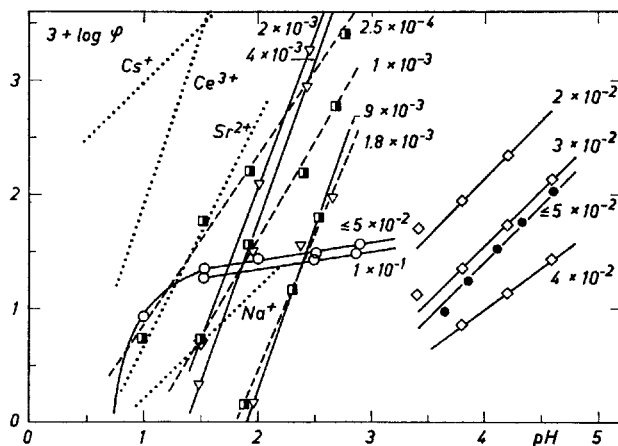
Fig. 10. The sorption at constant C_{MG} (mmole $\cdot$ g^{-1}) of Na$^+$, Cs$^+$, Sr^{2+}, UO$_2^{2+}$, and Ce^{3+} on crystalline zirconium phosphate at 20°C. Symbols in Table 3. The dotted lines refer to a gel with P/Zr = 1.94.[4]

For Na$^+$, Cs$^+$, Ce^{3+}, and UO$_2^{2+}$, the curves are approximately rectilinear. For low values of the load, the Na$^+$- and Cs$^+$-curves have the theoretical slopes, equal to the charge of the sorbed cation (*cf.* eqn. (1)). This is not found for UO$_2^{2+}$ and Ce^{3+}, the slopes having somewhat lower values. Unexpectedly, these values are decreasing slightly with decreasing load. The low values of the slopes may indicate that D of eqn. (1) varies with the ionic medium of the solution. The log φ (pH)-curves for Cs$^+$, UO$_2^{2+}$, and Ce^{3+} are very dependent upon C_{MG}, the value of φ increasing with decreasing C_{MG}. As before, this may be ascribed to the existence of small amounts of a functional group $\overline{HB}$, capable of interactions with the sorbed cations.

The shapes of the Sr^{2+} log φ (pH)-curves are peculiar. At C_H = 200 mM there is no sorption and then the curve rises steeply until above pH $\approx$ 1.5 it changes to only a small increase of log φ with increasing pH. Obviously, eqn. (1) is not valid and consequently the sorption of Sr^{2+} on crystalline ZrP can hardly be described as a perfect cation exchange.

For crystalline ZrP, the affinity decreases in the order UO$_2^{2+}$ $\geq$ Ce^{3+} > > Na$^+$ which is the same order as for the gels [4] but the sorption occurs at higher values of pH and the selectivity is lower (Fig. 10). Ignoring the small quantity of $\overline{HB}$ groups, the affinity of crystalline ZrP for Cs$^+$ is smaller than for Na$^+$ and the affinity for Sr^{2+} even larger than for UO$_2^{2+}$. The behaviour of Cs$^+$ is discussed above (p. 1699). However, the sorption of Sr^{2+} ought to be studied more closely, before a reliable description of it may be postulated. The dehydration studies [8] show that the zeolitic water of ZrP is essential for the sorption of UO$_2^{2+}$. When this is removed there is a radical decrease in φ. The UO$_2^{2+}$ ion, being larger than the others, may well be sorbed *via* the zeolitic water, possibly as a chelate complex. Thus, steric hindrance becomes

less important and the affinity appears higher than would otherwise be the case.[4]

From a practical point of view, crystalline ZrP is a poor cation exchanger, especially compared with the gelatinous preparations. In Ref. 2, seven conditions are summarized, most of which must be fulfilled by practical ion exchangers. For the use intended for the inorganic ones, *i.e.* the treatment of nuclear fuels dissolved in nitric acid, the demand for high selectivity is most important. Crystalline ZrP has a low selectivity. For most ions its sorption is low and it cannot be operated in solutions with $C_H \leq 0.1$ M. Thus zirconium phosphate gels are more suitable practically. A complete description of the ion exchange mechanism for these materials will, however, not be available until the detailed structure of crystalline zirconium phosphate and its relation to sorbed metal ions is known.

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