

Inorganic Ion Exchangers

III. Equilibrium Studies on Zirconium Phosphate Gels

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The sorption on zirconium phosphate gels has been investigated for a number of ions which are of importance for the processing of irradiated nuclear fuels, *viz.* U(IV), UO_2^{2+} , Ce^{3+} , Y^{3+} , Sr^{2+} , Cs^+ , Rb^+ , and Na^+ . For gels of a high ratio phosphate to zirconium, ≥ 1.5 , the sorption takes place as an ideal cation exchange, except in the case of U(IV) which reacts irreversibly with the phosphate groups of the gels. For gels of a low phosphate to zirconium ratio, on the other hand, more metal ions are sorbed than hydrogen ions released. Such gels thus retain part of the amphoteric character of zirconium hydrous oxide. Besides the ordinary monohydrogen phosphate groups, which make up the vast majority of the sorption sites, the gels also contain small amounts of another functional group of high affinity to certain cations, especially Cs^+ . This leads, among other things, to a very selective sorption of Cs^+ and Rb^+ at low loads. The selectivity of the gels decreases with increasing phosphate content, but is still fairly satisfactory even at a ratio phosphate to zirconium ≈ 2 which is the highest value that can be reached.

The hydrolysis of the gels (which becomes extensive as pH exceeds a value of ≈ 8) depends appreciably upon the cations present in the solution. For a certain value of pH, it decreases along the sequence $\text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$. From the neutralization curves obtained in Cs^+ and Rb^+ media, it seems moreover as if the "ordinary" monohydrogen phosphate groups would exist in two states of different acidity.

Since 1956 several papers concerning the sorption properties of zirconium phosphate gels (denoted ZrP) have been published.¹⁻¹² The first paper in the present series¹ deals with the selection of ZrP among other basic salts examined for further investigation. Composition, acidity and hydrolysis of various preparations of ZrP are studied. By certain precautions, gels of a fairly reproducible ratio phosphate to zirconium, $(\text{P}/\text{Zr})_s$, can be prepared.

The second paper² is devoted to the sorption rates of some characteristic ions. It is found that this quantity depends both on the composition of the gel and on the nature of the ions sorbed. Dehydration affects the sorption rate

and causes, at last, a destruction of the sorption properties of ZrP. The amount of Sr^{2+} sorbed per functional group at equilibrium is, however, found to be unaffected by dehydration as long as more than 1.5 mole H_2O per mole Zr remains in the gel. Thermogravimetical experiments² show that the phosphate is most probably present as monohydrogen groups. This view has been confirmed by Clearfield and Stynes,³ primarily from investigations of crystalline ZrP. For the crystals, Clearfield⁴ has later on proposed a layer structure. The gels are supposed to be made up by fragments of this structure, of an average size very much depending upon the mode of preparation.

The present investigation deals with the nature of the sorption on various preparations of ZrP and, as the main subject, their selectivity. The metal ions used in these studies are those predominant in dissolutions of nuclear fuels which have been allowed a reasonable cooling time. U(IV) is selected as a model for Pu(IV) and beside this ion Y^{3+} , Ce^{3+} , UO_2^{2+} , Sr^{2+} , Cs^+ , Rb^+ , and Na^+ are investigated.

A convenient way to study the selectivity is to plot the logarithm of the distribution coefficient, φ , as a function of pH at a constant value of the load, C_{MG} . By comparing such curves for different metal ions one gets a good picture of the sorption. Among the results obtained, the high sorption of Cs^+ even in comparison with Ce^{3+} and UO_2^{2+} and the selective sorption of Cs^+ and Rb^+ are perhaps the most striking ones.

If C_{MG} is kept sufficiently low in comparison with the exchange capacity, a variation of C_{MG} should neither alter the activity conditions, nor the concentrations of hydrogen ions and monohydrogen groups within the gel. In such a case φ should be independent of C_{MG} , provided ZrP acts as a monofunctional cation exchanger, as will be further discussed in the theoretical treatment below. For most ions, however, φ still increases with decreasing C_{MG} even at loads so low that the conditions pointed out above are fulfilled. This applies most strikingly to Cs^+ . Following Fronæus,¹³ these findings lead us to postulate that the gel contains, beside the ordinary phosphate groups, HA, *small* amounts of a group, HB, capable of interacting more or less strongly with the various cations employed. It will be shown below that in this way the variations of φ with C_{MG} can be perfectly explained and the good selective sorption of Cs^+ and Rb^+ at least partly understood.

THEORETICAL TREATMENT

The following notation is used:

A bar denotes a species within the gel phase.

C_{M} , C_{H} = total concentrations of metal ion, M, and hydronium ion in the solution before addition of ZrP;

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

C_{AG} , C_{BG} = total concentrations of the functional groups A and B, respectively, in the gel phase;

C_{MG} = total concentration of M in the gel phase at equilibrium;

$[\overline{\text{M}^{n+}}]$, $[\overline{\text{MA}_j^{n-i}}]$, $[\overline{\text{MB}^{n-1}}]$ = equilibrium concentrations of the species $\overline{\text{M}^{n+}}$, $\overline{\text{MA}_j^{n-i}}$ and $\overline{\text{MB}^{n-1}}$;

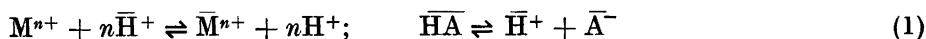
h, \bar{h} = equilibrium concentrations of hydronium ions in the solution and the gel, respectively;

v = volume of the solution before addition of the gel;

m = weight of the added gel;

$\varphi = \frac{C_{MG}}{C_{MS}} =$ distribution coefficient.

Assuming an ideal cation exchange between the gel and the solution, we apply the mass action law to the following equilibria:



and get

$$\frac{[\bar{M}^{n+}]}{C_{MS}} = k_1 \left(\frac{\bar{h}}{h} \right)^n; \quad \frac{\bar{h}[\bar{A}^-]}{[\bar{H}\bar{A}]} = k_{CA} \quad (3)$$

$$\frac{[\bar{M}\bar{A}_j^{n-j}]}{[\bar{M}^{n+}][\bar{A}^-]^j} = \beta_j \quad (4)$$

If ZrP is a monofunctional ion exchanger, *i.e.* the equilibria of eqns. (1) and (2) are the only ones present, we get from eqns. (3) and (4):

$$\varphi = k_1(\bar{h}/h)^n \left(1 + \sum_{j=1}^N \beta_j [\bar{A}^-]^j \right) \quad (5)$$

where N is the maximum coordination number of M^{n+} . Eqn. (5) gives

$$\log \varphi = n \text{p}[H^+] + D \quad (6)$$

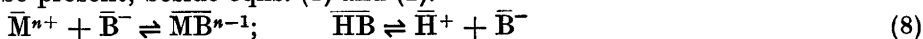
where $D = \log k_1 \left(1 + \sum_{j=1}^N \beta_j [\bar{A}^-]^j \right) + n \log \bar{h}$ is a function of C_{MG} *solely*, apart from variations in the involved activity coefficients. If $C_{MG} \ll C_{AG}$, $C_{AG} = [\bar{H}\bar{A}] + [\bar{A}^-]$ and

$$[\bar{A}^-] = \frac{C_{AG}}{1 + \bar{h}(C_{MG})k_{CA}^{-1}} \quad (7)$$

Once the load is sufficiently small, $\bar{h}(C_{MG}) = \bar{h}(0)$ and then eqn. (7) shows that $[\bar{A}^-]$ is a constant too. D will thus be independent of C_{MG} , provided this quantity is sufficiently small.

By plotting $C_{MG} = \frac{v}{m}(C_M - C_{MS})$ versus C_{MS} at different constant values of h we may obtain $\log \varphi$ as a function of $\text{p}[H^+]$ at either constant C_{MG} or constant C_{MS} . If we use the representation with constant C_{MG} , eqn. (6) shows that the curve will be a straight line with slope n , if k_1 (and the β_j 's) are independent of variations in the ionic medium of the solution along a curve, or if these variations can be corrected for. For sufficiently low values of C_{MG} , the straight lines must coincide.

Next we presuppose that ZrP contains *small* amounts of an acid group $\overline{\text{HB}}$ and that $\overline{\text{B}}^-$ can interact with $\overline{\text{M}}^{n+}$. Thus we assume the following equilibria to be present, beside eqns. (1) and (2):



and get

$$\frac{[\overline{\text{MB}}^{n-1}]}{[\overline{\text{M}}^{n+}][\overline{\text{B}}^-]} = \gamma; \quad \frac{\overline{h}[\overline{\text{B}}^-]}{[\overline{\text{HB}}]} = k_{\text{CB}} \quad (9)$$

We will now study the influence of the group $[\overline{\text{B}}^-]$ upon the sorption. To do this we assume $C_{\text{MG}} \ll C_{\text{AG}}$, $C_{\text{BG}} \ll C_{\text{AG}}$ and $\overline{h}(C_{\text{MG}}) = \overline{h}(0)$ at the low values of C_{MG} used. The last assumption is confirmed for ZrP by the experiments with Na^+ (*vide infra* p. 1871). For the sake of simplicity we also neglect MA_j^{n-i} when $j \geq 2$. With the aid of these assumptions we get

$$\begin{aligned} C_{\text{MG}} &= [\overline{\text{M}}^{n+}] + [\overline{\text{MA}}^{n-1}] + [\overline{\text{MB}}^{n-1}] = [\overline{\text{M}}^{n+}](1 + \beta_1[\overline{\text{A}}^-] + \gamma[\overline{\text{B}}^-]) = \\ &= [\overline{\text{M}}^{n+}] \left(1 + \beta_1 \frac{C_{\text{AG}}}{1 + \overline{h}(0)k_{\text{CA}}^{-1}} + \gamma[\overline{\text{B}}^-] \right) = [\overline{\text{M}}^{n+}](a + \gamma[\overline{\text{B}}^-]) \end{aligned} \quad (10)$$

$$\begin{aligned} C_{\text{BG}} &= [\overline{\text{B}}^-] + [\overline{\text{HB}}] + [\overline{\text{MB}}^{n-1}] = [\overline{\text{B}}^-](1 + \overline{h}(0)k_{\text{CB}}^{-1} + \gamma[\overline{\text{M}}^{n+}]) = \\ &= [\overline{\text{B}}^-](b + \gamma[\overline{\text{M}}^{n+}]) \end{aligned} \quad (11)$$

where a and b are constants at the low loads used. Defining k_0 by

$$\varphi = k_0(\overline{h}/h)^n \quad (12)$$

and using eqns. (3) and (10) we arrive at

$$k_0 = k_1(a + \gamma[\overline{\text{B}}^-]) \quad (13)$$

Fronæus¹³ has studied k_0 as a function of C_{MG} . As to ZrP, of medium acidity, \overline{h} cannot easily be found, and the value of k_0 is thus unknown. For low values of C_{MG} , however, \overline{h} may be presumed to be approximately constant = $\overline{h}(0)$ and if further h is kept constant, the measured quantity φ will be proportional to k_0 (*cf.* eqn. (12)). A study of $\varphi(C_{\text{MG}})$ under these conditions will thus be almost equivalent to Fronæus' study of $k_0(C_{\text{MG}})$. The following cases may be considered:

(i) $C_{\text{MG}} < C_{\text{BG}}$ and γ has a great value. In this case $C_{\text{MG}} = [\overline{\text{MB}}^{n-1}]$ and then eqns. (10) and (11) gives $[\overline{\text{B}}^-] = (1/b)(C_{\text{BG}} - C_{\text{MG}})$, which, with eqns. (12) and (13) yields:

$$\varphi = k_1 \left(\frac{\overline{h}(0)}{h} \right)^n \left(a + \frac{\gamma}{b}(C_{\text{BG}} - C_{\text{MG}}) \right) \quad (14)$$

If the load on ZrP is very low and the constant value of h so high that the solution has a constant ionic medium, the quotients of activity coefficients which are involved in k_1 and γ can be presumed to be nearly constant. C_{BG} is fixed for a given gel and thus φ is a rectilinear, (rapidly) decreasing function of C_{MG} only.

(ii) C_{MG} is of about the same order of magnitudes as C_{BG} or γ has not a great value. From eqns. (10) and (11) we get

$$\frac{C_{\text{BG}} - b[\overline{\text{B}}^-]}{C_{\text{MG}}} = \frac{\gamma[\overline{\text{B}}^-]}{a + \gamma[\overline{\text{B}}^-]} \quad (15)$$

It is seen from eqn. (15) that $[\bar{B}^-]$ and consequently φ decrease with increasing value of C_{MG} .

(iii) $C_{MG} > C_{BG}$ and γ has a great value. In this case $C_{BG} = [\overline{MB}^{n-1}]$. Eqns. (10) and (11) give $\gamma[B] = a C_{BG}/(C_{MG} - C_{BG})$ and then we have

$$\varphi = k_1 a \left(\frac{\bar{h}(0)}{\bar{h}} \right)^n \left(1 + \frac{C_{BG}}{C_{MG} - C_{BG}} \right) \quad (16)$$

i.e. $\varphi(C_{MG})$ is a decreasing function.

For a fairly wide range of C_{MG} (irrespective of the value of γ), $\varphi(C_{MG})$ will thus be a decreasing function. At sufficiently high values of C_{MG} , however, eqn. (16) will take the form $\varphi = k_1 a (\bar{h}(C_{MG})/\bar{h})^n$. In this region it will depend on the relative magnitude of the constants k_{CA} and β_j ; whether $\bar{h}(C_{MG})$, and hence φ , will decrease or increase with increasing C_{MG} .

Because of the many quantities which are involved in eqns. (14)–(16), it is impossible to determine values of k_1 and γ from a plot of $\varphi(C_{MG})$ at constant \bar{h} . But if such a plot has a decreasing rectilinear left part, eqn. (14) shows that by extrapolating this part to the C_{MG} -axes we can get an upper limit of C_{BG} , as the value of C_{MG} at the crossing point is $C_{BG} + (ab/\gamma)$. From the shape of the $\varphi(C_{MG})$ -curves we can further conclude whether γ has a great value or not. It should be recalled that a perceptible dependence of φ upon C_{MG} at so low values of C_{MG} that eqn. (7) is valid cannot be due to the formation of species \overline{MA}_j^{n-i} .

Also if a group B is present, eqn. (6) is valid but now, as is found from eqn. (12), with $D = n \log \bar{h}(C_{MG}) + \log k_0(C_{MG})$. If the quotients of activity coefficients which are involved in k_1 and γ can be presumed to have constant values, a plot of $\log \varphi$ versus $p[H^+]$ at a constant value of C_{MG} will give a straight line with slope n . Thus if ZrP contains a small amount of \bar{B} -groups, *i.e.* $C_{BG} \ll C_{AG}$, as postulated above, and if the value of γ for the ion sorbed is high, eqn. (14) shows that the straight lines $\log \varphi(p[H^+])$ corresponding to different values of C_{MG} ought to be discernibly separated, even if C_{MG} is negligible in comparison with the total capacity of the gel ($= C_{AG} + C_{BG}$). As regards plots of $\log \varphi$ versus $p[H^+]$ at constant C_{MS} , they cannot be interpreted as easily as plots at constant C_{MG} if there is a group \overline{HB} in ZrP. We have (from eqn. (12)) $\log \varphi = n p[H^+] + n \log \bar{h}(C_{MG}) + \log k_0(C_{MG})$. If γ is zero or has a small value and C_{MS} (and thus C_{MG}) is so small that k_0 and \bar{h} can be presumed to be constants, $\log \varphi(p[H^+])$ at constant C_{MS} must be represented by a straight line with slope n . Curves corresponding to different small C_{MS} coincide. If either γ , C_{MS} or both have great values, however, the variation in C_{MG} along the $\log \varphi(p[H^+])$ -curve at constant C_{MS} will cause it to deviate from a straight line with slope n . If the deviation is due to a great value of γ , the curves corresponding to different small values of C_{MS} will be discernibly separated also in this representation.

EXPERIMENTAL

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

Three different preparations of *zirconium phosphate gel* were used for the sorption experiments. They were prepared and analysed according to Ref.¹ and had $(P/Zr)_s = 1.1, 1.75, \text{ and } 1.95$. Their ignition losses were 50, 44, and 45 %, respectively, and the grain size used was 60–100 mesh.

Stock solutions of the following chemicals were prepared to be used in the sorption experiments: *sodium chloride, rubidium nitrate, cesium nitrate, strontium nitrate, yttrium nitrate, cerium(III) nitrate, uranyl nitrate, and uranium(IV) perchlorate*. Their metal ion concentrations were determined with standard methods.

Procedure. The metal ion sorption on ZrP at $20.0 \pm 0.2^\circ\text{C}$ was established as described in Ref.² A shaking time of at least 15 h was used.² Values of $\text{pH} < 2$ were brought about by addition of nitric or perchloric acid, values of $\text{pH} > 2$ by acetate buffers (for the sorption of Ce^{3+} and Sr^{2+} on ZrP of $(P/Zr)_s = 1.1$). The acetate concentration was kept so low that complex formation with the metal ions was of no account.¹⁴

For solutions of UO_2^{2+} , U(IV) , Ce^{3+} , Sr^{2+} , and Cs^+ , C_{MS} was determined as described in Ref.² In the present study, C_{MS} had further to be determined for solutions of Na^+ , Rb^+ , and Y^{3+} . This was done radiometrically. As tracers we used ^{22}Na ($t_{1/2} = 2.6 \text{ y}$), ^{86}Rb ($t_{1/2} = 18.7 \text{ d}$) and ^{91}Y ($t_{1/2} = 58 \text{ d}$). For ^{22}Na , the γ -activity (mainly annihilation radiation) was measured, for ^{86}Rb and ^{91}Y the β -activity, in the manner described in Ref.²

For all solutions h was determined, as a rule by alkalimetric titration. In the case of the easily hydrolysed UO_2^{2+} , however, h was determined potentiometrically, with the aid of a quinhydrone electrode. The measurements were performed at a constant ionic strength = 1 M, brought about by addition of sodium chloride. The potentiometer was calibrated with solutions of known h at the same ionic strength. In this way h was also determined when Cs^+ , Se^{2+} , and Ce^{3+} were sorbed on the gel of $(P/Zr)_s = 1.1$. In the strongly acid solutions of U(IV) we put $h = C_H$.

The neutralization and hydrolysis curves were determined as described in Ref.¹ with $v/m = 100 \text{ ml}\cdot\text{g}^{-1}$ and at a temperature of 20.0°C . A gel of $(P/Zr)_s = 1.95$ was used, of a grain size 100–150 mesh. Carbonate free solutions of *rubidium hydroxide* and *cesium hydroxide* were prepared by precipitating a hot barium hydroxide solution with a slight excess of rubidium and cesium sulphate solutions, respectively, in a closed system filled with nitrogen. When the precipitate had settled, the supernatant liquid was transferred to a storage vessel *via* a filter stick. The solutions were analysed for metal, hydroxide and carbonate ions. No carbonate was detected in spite of the extremely strong tendency of these solutions, readily to absorb carbon dioxide. Also the actual titrations were performed under careful exclusion of carbon dioxide.

RESULTS

Swelling and hydrolysis. From Fig. 1, showing C_{MG} as a function of C_{MS} for Na^+ at different values of v/m and C_H , it is evident that such curves are independent of v/m . This result was checked with other metalions, *viz.* Rb^+ and Cs^+ . The gels were also shaken with 1 M nitric acid. No significant change in C_H occurred in these experiment. From Fig. 1 we can furthermore conclude that the amount of phosphate released by hydrolysis² in the course of an experiment does not influence the sorption properties of the gel.

Data ($\text{p}[\text{H}^+]$, $\log \varphi$) at constant C_{MG} . The description of the sorption properties of ZrP given here is based upon isotherms obtained at 20.0°C for the metal ions examined, *i.e.* C_{MG} has been determined as a function of C_{MS} for different values of C_H . The sorption isotherms have been intersected at either constant C_{MG} or constant C_{MS} . Plots of $\log \varphi$ versus $\text{p}[\text{H}^+]$ at constant C_{MG} for the gels with $(P/Zr)_s = 1.75$ and 1.95 are shown in Figs. 2–4. $\text{p}[\text{H}^+]$ has been determined by interpolation between the values of $\text{p}[\text{H}^+]$ actually measured for the experimental points along the isotherm. We use the symbols put together in Table 1. In Table 2 slopes of the $\log \varphi(\text{p}[\text{H}^+])$ -curves, n_{exp} , are

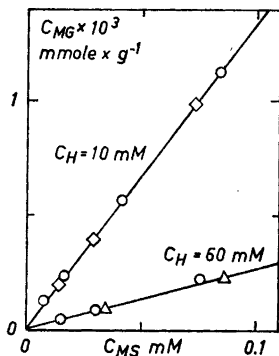


Fig. 1. The dependence upon v/m of the sorption of Na^+ on ZrP of $(\text{P}/\text{Zr})_s = 1.95$. The signs refer to: $v/m = 0.01 \text{ l}\cdot\text{g}^{-1}$, \circ ; 0.02 , \triangle ; 0.04 , \diamond .

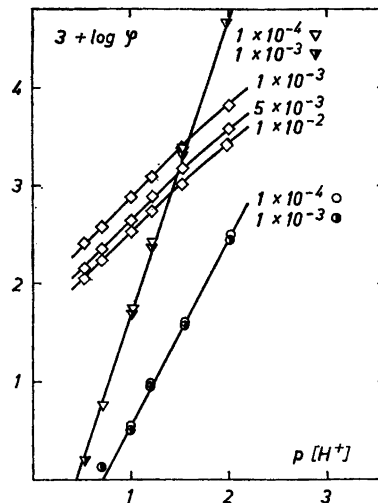


Fig. 2. Sorption at constant C_{MG} ($\text{mmole}\cdot\text{g}^{-1}$) of Ce^{3+} , Sr^{2+} , and Cs^+ on ZrP of $(\text{P}/\text{Zr})_s = 1.75$, ignition loss 44 %. Symbols in Table 1.

collected. They are in almost perfect agreement with the ionic charges, n_{theor} , of the respective ions, *i.e.* eqn. (6) is valid, with a constant value of D along each curve of constant C_{MG} . It follows that the sorption for all the investigated ions takes place as an ideal cation exchange and, moreover, that the equilibrium constant k_1 must be independent of the variation of the ionic medium along a curve of constant C_{MG} (*cf.* pp. 1863 *et seq.*). The latter condition implies that the expression containing the activity coefficients involved in k_1 , *viz.* $(f_{\bar{\text{H}}})^n/f_{\bar{\text{M}}}(f_{\text{H}})^n$, must have a constant value along each curve. This is possible on account of that ion invasion into the gel which most certainly has to take place in order to satisfy the Donnan equilibrium, because under these circumstances $(f_{\bar{\text{H}}})^n/f_{\bar{\text{M}}}$ may vary with the ionic medium of the outer solution in much the same way as $(f_{\text{H}})^n/f_{\text{M}}$. Consequently, k_1 will depend very little upon the activity variations of the solution. If, on the other hand, no ion invasion would occur, $(f_{\bar{\text{H}}})^n/f_{\bar{\text{M}}}$ should be a constant for constant C_{MG} which implies that $(f_{\text{H}})^n/f_{\text{M}}$ must be a constant too. This is not very probable, considering the

Table 1. Symbols used in Figs. 2–4 and 9–11.

Species	Na^+	Rb^+	Cs^+	Sr^{2+}	Y^{3+}	Ce^{3+}	UO_2^{2+}	U(IV)
Symbol	●	□	◇	○ ●	△ ▲	▽ ▼	■	■

Table 2. The values of the slopes of the $\log \varphi(p[H^+])$ curves, n , at a constant value of $C_{MC} = 10^{-2}$ mmole·g⁻¹

Gel, (P/Zr) _s	Metal ion	n_{theor}	n_{exp}
1.75	Cs ⁺	1	1.00
1.75	Sr ²⁺	2	1.96
1.75	Ce ³⁺	3	3.00
1.95	Na ⁺	1	1.00
1.95	Rb ⁺	1	1.00
1.95	Cs ⁺	1	1.00
1.95	Sr ²⁺	2	1.97
1.95	Y ³⁺	3	2.98
1.95	Ce ³⁺	3	3.00

great variation of pH ($0.5 < \text{pH} < 2$) along a curve $\log \varphi([H^+])$. Especially if M^{n+} is a polyvalent ion, this possibility seems completely ruled out.

The equivalence between the metal ions sorbed and the hydrogen ions set free. The result that preparations of ZrP act as ideal cation exchangers can be further corroborated by an investigation of the equivalence between the metal ions sorbed and the hydrogen ions set free by measurements of both quantities. We define

$$Q = \frac{h - h_p - C_H}{n(C_M - C_{MS})} \quad (17)$$

where h_p is the concentration of the hydrogen ions from the protolysis of the phosphoric acid, set free by hydrolysis of the gel; n is the charge of the sorbed metal ion. If h is determined potentiometrically, we calculate the value of h_p from Fig. 3 of Ref.¹, using $\text{p}K_1 = 1.7$ for the first step of the protolysis of the phosphoric acid. In the case of a volumetric determination, $h - h_p$ can be computed directly, *cf.* Ref.¹ If necessary, a correction is also introduced for the strong acid possibly washed out from the gel during the experiment. This correction was determined separately by shaking the gels with water.

To make reliable calculations of Q according to eqn. (17) possible, we chose the following conditions: $1 < \text{pH} < 2$, $C_M - C_{MS} > 3$ mM. Q was determined for UO_2^{2+} , Ce^{3+} , Sr^{2+} , and Cs^+ . Several preparations of ZrP were used and, in the case of UO_2^{2+} , gels with different ignition losses.

The results are collected in Table 3 A, B. As to the gels with $(\text{P/Zr})_s > 1.5$, the value of Q is close to 1, confirming that an ideal cation exchange occurs. When $(\text{P/Zr})_s < 1.2$, Q is significantly less than 1. Thus these gels do not behave as ideal cation exchangers; they sorb metal ions without releasing an equivalent amount of H^+ . This is in agreement with the amphoteric behaviour of ZrP's with low contents of phosphate reported earlier.¹

Affinity series. Fig. 3 shows that the affinity to ZrP of alkali metal ions decreases in the order $\text{Cs}^+ > \text{Rb}^+ > \text{Na}^+$, *i.e.* in the order of increasing radii of the hydrated ions.¹⁵ In this behaviour ZrP reminds of many organic ion

Table 3. The equivalence between metal ions sorbed and hydrogen ions set free on ZrP's with different values of $(P/Zr)_s$ and different ignition losses.

Table 3 A. The sorption of UO_2^{2+} .

Gel $(P/Zr)_s$	Ignition loss, %	C_M mM	C_{MS} mM	h mM	Q
1.12	50	10	1.27	24.6	0.75
1.12	50	30	13.0	35.7	0.71
1.12	50	60	35.9	46.8	0.74
1.12	50	100	70.1	54.3	0.72
1.12	50	100	76.1	124	0.5
1.58	50	10	0.35	28.8	0.97
1.58	40	10	0.27	29.4	0.99
1.58	30	10	2.36	25.9	1.04
1.73	50	10	0.20	30.6	0.98
1.89	50	10	0.15	31.1	1.01
1.89	50	30	4.3	64.2	1.04
1.89	50	60	23.7	89.1	1.08
1.89	50	100	51.8	103	0.96
1.89	50	60	32.0	161	1.09
1.89	30	10	0.17	32.0	0.96
1.95	50	10	0.11	31.0	0.98
1.98	50	10	0.16	31.2	1.01

Table 3 B. The sorption of Ce^{3+} , Sr^{2+} and Cs^+ . The ignition loss of the gels used is 50 %.

Gel $(P/Zr)_s$	C_M mM	C_{MS} mM	h mM	Q
Ce^{3+}				
1.05	10.13	6.44	21.3	0.5
1.05	30.4	23.5	23.4	0.4
1.95	30.0	11.9	64.9	1.00
1.95	10.0	4.0	27.6	0.96
Sr^{2+}				
1.73	10.2	3.5	13.9	0.93
1.89	10.0	2.0	16.7	0.97
1.89	30.0	18.0	24.9	1.00
1.95	10.2	2.05	16.9	0.93
1.98	10.2	2.00	16.6	0.92
Cs^+				
1.15	31.6	17.9	17.5	0.5
1.15	10.35	2.48	7.0	0.7
1.89	9.97	0.26	10.8	0.97
1.89	29.91	4.33	24.0	0.94
1.89	9.97	1.54	109.1	1.00
1.89	29.91	9.88	118.6	0.90

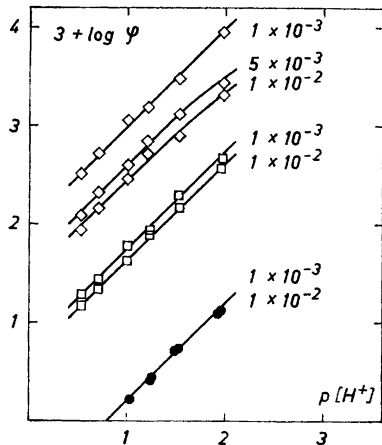


Fig. 3. Sorption at constant C_{MG} (mmole·g⁻¹) of Cs⁺, Rb⁺, and Na⁺ on ZrP of $(P/Zr)_s = 1.95$, ignition loss 45%. Symbols in Table 1.

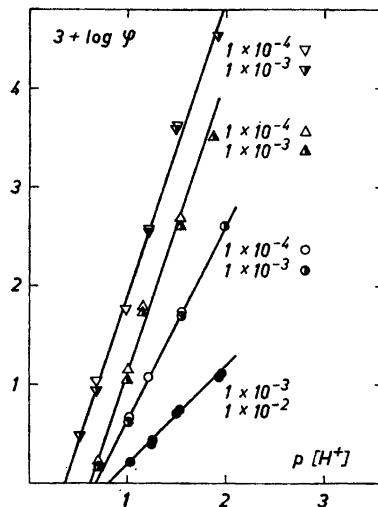


Fig. 4. Sorption at constant C_{MG} (mmole·g⁻¹) of Na⁺, Sr²⁺, Y³⁺, and Ce³⁺ on ZrP of $(P/Zr)_s = 1.95$, ignition loss 45%. Symbols in Table 1.

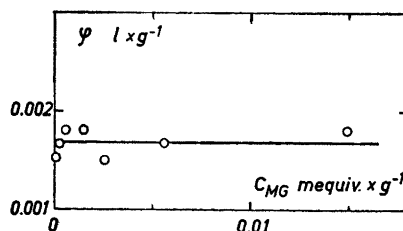
exchangers, not too crosslinked.¹⁶ There is, however, a difference; Cs⁺ and Rb⁺ appear to be very selectively sorbed on ZrP.

Fig. 4 shows another affinity series, *viz.* Na⁺ < Sr²⁺ < Y³⁺ < Ce³⁺. In this series, the sorption increases with the ionic charge from Na⁺ to Y³⁺, in spite of the simultaneous increase of the radius of the hydrated ion.¹⁵ As to Ce³⁺, its hydrated radius is certainly smaller than that of Y³⁺, of the same charge. Consequently, Ce³⁺ should be more strongly sorbed,¹⁷ as is in fact observed. Another effect which ought to bring about the same order as the increase of charge is certainly also the increasing affinity of the metal ions to the phosphate groups.¹⁸ As each such group is, however, coordinated ⁴ to three Zr(IV), the donor properties of the remaining phosphate oxygen must decrease. Consequently Zr(IV) enhances the acid strength of the monohydrogen groups enormously as compared with the third step of phosphoric acid in water solution.

Comparing Fig. 2 ($(P/Zr)_s = 1.75$) and Figs. 3–4 ($(P/Zr)_s = 1.95$), it is seen that the sorption of Ce³⁺, as well as of Sr²⁺, is of equal magnitude on both gels and no large differences in selectivity occur. For Cs⁺ (and Rb⁺) there are anomalies to be discussed in the following paragraphs.

The existence of different sorption sites. The log ϕ (p[H⁺])–curves for Cs⁺ and Rb⁺ which are shown in Figs. 2–3 are very dependent on C_{MG} , especially those for Cs⁺. As discussed above (p. 1864) this is most certainly due to the existence of *small* amounts of a functional group capable to interact with the sorbed cations. In order to confirm this assumption, experimental values of ϕ ,

Fig. 5. φ as a function of C_{MG} for Na^+ at $C_H = 100$ mM. $(P/Zr)_s = 1.95$, ignition loss 45 %.



found for the gel of $(P/Zr)_s = 1.95$, were plotted *versus* C_{MG} at constant values of $C_H > 60$ mM. C_{MG} was kept very low. At the conditions used $h = C_H$ and the *rational* activity coefficients should have approximately constant values. The results are collected in Figs. 5–8.

For Na^+ , Fig. 5, φ has a constant value in the range of C_{MG} examined. We conclude that $\gamma = 0$ for Na^+ (eqn. (14)) and that \bar{h} is independent of C_{MG} at least for $C_{MG} < 0.02$ mequiv. g^{-1} .

As regards Cs^+ , the plots are made for four values of C_H , viz. 60, 100, 200, and 300 mM, Fig. 6. The curves obtained have the shape which is expected if γ has a great value (eqns. (14)–(16)). Extrapolation of the left rectilinear parts to the C_{MG} -axes gives $C_{BG} + (ab/\gamma) < 0.003$ mequiv. g^{-1} (cf. p. 1865). The left rectilinear parts of the curves are parallel, even if eqn. (14) shows that, when extrapolated to the C_{MG} -axes, they should cross at the same point. Thus the slope $k_1(\bar{h}(0)/h)^n \times \gamma/b$ does not decrease with increasing h , but has

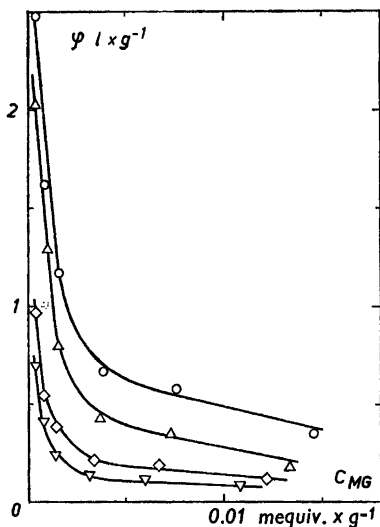


Fig. 6. φ as a function of C_{MG} for Cs^+ at different values of C_H . The signs refer to: $C_H = 60$ mM, \circ ; 100, \triangle ; 200, \diamond ; 300, ∇ . $(P/Zr)_s = 1.95$, ignition loss 45 %.

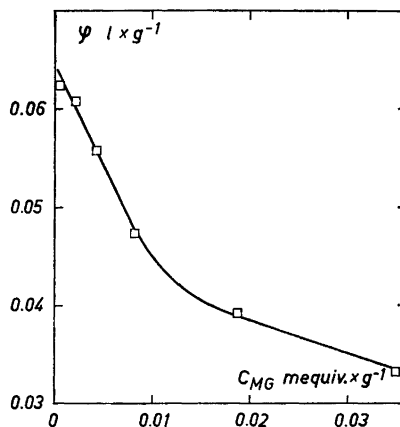


Fig. 7. φ as a function of C_{MG} for Rb^+ at $C_H = 100$ mM. $(P/Zr)_s = 1.95$, ignition loss 45 %.

a constant value. This is most probably due to an ion invasion into the gel (cf. p. 1867).

The $\varphi(C_{MG})$ -curve for Rb^+ obtained at $C_H = 100$ mM, Fig. 7, shows also a rectilinear left part. Extrapolation of this part to the C_{MG} -axis gives $C_{BG} + (ab/\gamma) < 0.03$ mequiv. g^{-1} ; hence we conclude that $\gamma_{Rb} < \gamma_{Cs}$. The affinity to \bar{B}^- seems to be dependent upon the sizes of the hydrated ions; the value of γ decreases in the order $\gamma_{Cs} > \gamma_{Rb} > \gamma_{Na} = 0$. As a much more stable species \bar{MB} is formed with Cs^+ than with Rb^+ , the hydration number, which is about the same for both ions,¹⁵ cannot be the only factor determining the equilibria. The somewhat unexpectedly good selective sorption of Rb^+ and Cs^+ at low values of C_{MG} must at least partly be due to formation of species with different stability in the ZrP phase.

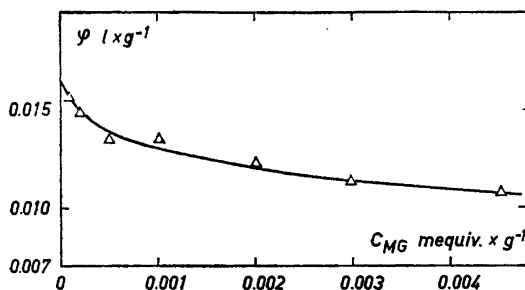


Fig. 8. φ as a function of C_{MG} for Y^{3+} at $C_H = 100$ mM. $(P/Zr)_s = 1.95$, ignition loss 45 %.

Sr^{2+} , Y^{3+} and Ce^{3+} have decreasing φ 's for small increasing values of C_{MG} , although their hydrated radii are much larger than that of Na^+ . The curves obtained for these three ions have almost the same shape and the curve for Y^{3+} at $C_H = 100$ mM is shown in Fig. 8. Donor properties of \bar{B}^- , the high charge of these ions and, possibly, a reduction of their hydration shells may account for the increased affinity between \bar{B}^- and these ions.

From the Cs^+ -curves in Fig. 2 we can see that the dependence of φ on C_{MG} remains but it is less pronounced for a gel of $(P/Zr)_s = 1.75$. At $C_{MG} = 10^{-3}$ mmole. g^{-1} the gel of $(P/Zr)_s = 1.95$ sorbs more effectively than that of $(P/Zr)_s = 1.75$, but at $C_{MG} = 5 \times 10^{-3}$ and 10^{-2} mmole. g^{-1} the order is reversed. Obviously $\varphi(C_{MG})$ does not decrease as rapidly when $(P/Zr)_s = 1.75$ as when $(P/Zr)_s = 1.95$. Nevertheless a plot of φ versus C_{MG} at $C_H = 100$ mM shows that the left part of the $\varphi(C_{MG})$ -curves are rectilinear when $(P/Zr)_s = 1.75$ too. We have found $C_{BG}(1.75) < 0.004$ mequiv. g^{-1} and $\gamma_{Cs}(1.75) < \gamma_{Cs}(1.95)$.

It is very probable that, when $(P/Zr)_s < 2$, \bar{OH} has replaced \bar{HPO}_4 in such a manner that a six-coordinated structure for Zr(IV) remains. Thus C_{OHG} is much greater than C_{BG} for the gel with $(P/Zr)_s = 1.75$. We conclude that the \bar{OH} -groups are not identical with the \bar{HB} -groups. This is also very improbable judging from the known properties of zirconium hydroxide gels.¹⁹ So far we

have not been able to identify the groups $\overline{\text{HB}}$ with certainty. Presumably they are monohydrogen phosphate groups occupying very particular positions within the gel.

Gels prepared according to Baetslé. To check if the mode of preparation is essential for the existence of the group $\overline{\text{HB}}$, gels were also prepared according to Baetslé and Pelsmaekers.⁶ The main difference between their method of preparation and ours is the medium used. They precipitate a zirconyl chloride solution containing 6 M hydrochloric acid, whereas we use a nitrate solution, containing 1 M nitric acid. Following their direction, we got, when mixing phosphate and zirconium salt in the ratios 1.4, 2.0, and 3.0, gels with $(\text{P}/\text{Zr})_s = 1.40, 1.83$ and 1.89 , determined according to Ref.¹ Sorption experiments with Cs^+ were carried out on the gel of $(\text{P}/\text{Zr})_s = 1.83$. The $\log \varphi(p[\text{H}^+])$ -curves at constant C_{MG} thus obtained resemble those of Fig. 3 and the $\varphi(C_{\text{MG}})$ -curves those of Fig. 6. We conclude that the existence of the group B is not exclusively connected with the conditions used by us in preparing ZrP.

Data ($p[\text{H}^+]$, $\log \varphi$) at constant C_{MS} . Selectivity as a function of $(\text{P}/\text{Zr})_s$. In the theoretical treatment we have found that curves $\log \varphi(p[\text{H}^+])$ for constant values of C_{MS} are not of as great a theoretical interest as curves for constant C_{MG} . But the affinity of ZrP to the sorbed ions is, of course, independent of the representation used. From a practical point of view, it is easier to design column separations from data $(p[\text{H}^+], \log \varphi)$ for constant values of C_{MS} than from corresponding data for constant values of C_{MG} . Figs. 9–11 show the curves obtained at constant C_{MS} on ZrP of $(\text{P}/\text{Zr})_s = 1.95$ (Figs. 9–10) and 1.1 (Fig. 11). The symbols in Table 1 are used. This time curves for UO_2^{2+} and U(IV) are included.

In Fig. 9 the curves for UO_2^{2+} , Ce^{3+} , Sr^{2+} and Na^+ behave as can be expected, if the values of γ for these sorptions are small. The greater the

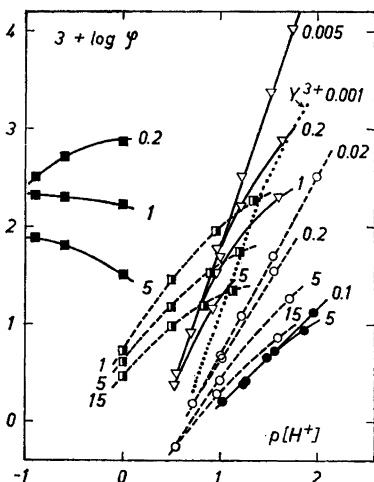


Fig. 9. Sorption at constant C_{MS} (mM) of U(IV), UO_2^{2+} , Ce^{3+} , Y^{3+} , Sr^{2+} , and Na^+ on ZrP of $(\text{P}/\text{Zr})_s = 1.95$, ignition loss 45%. Symbols in Table 1.

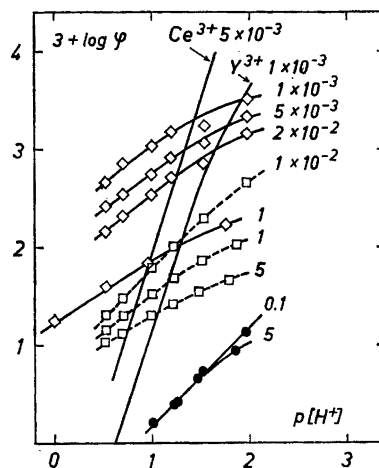


Fig. 10. Sorption at constant C_{MS} (mM) of Na^+ , Rb^+ , and Cs^+ (Y^{3+} and Ce^{3+} indicated) on ZrP of $(\text{P}/\text{Zr})_s = 1.95$, ignition loss 45%. Symbols in Table 1.

Table 4. The values of the slopes of the $\log \varphi(p[H^+])$ -curves, n , at constant values of C_{MS} on the gel with $(P/Zr)_s = 1.95$.

Metal ion	C_{MS} mM	n_{theor}	n_{exp}
Ce ³⁺	5×10^{-3}	3	3.00
Y ³⁺	1×10^{-3}	3	3.00
Sr ²⁺	2×10^{-2}	2	1.84
Na ⁺	1×10^{-1}	1	1.00
Rb ⁺	1×10^{-2}	1	0.96
Cs ⁺	1×10^{-3}	1	0.77

values of C_{MS} are, the more the members of each family deviate from a rectilinear curve with a slope = the charge of the metal ion, but at sufficiently low values of C_{MS} they apparently reach such a limiting straight line. The slopes, n_{exp} , of the curves with the lowest values of C_{MS} are collected in Table 4. As to Y³⁺, only the "limiting curve" is drawn in Figs. 9–10.

The value of γ for Cs⁺ is known to be high from Fig. 6. In agreement with this, the parallel curves for Cs⁺ in Fig. 10 have slopes, the values of which are all far from +1, even if the curves have almost rectilinear parts, Table 4. The marked dependence on C_{MS} is also required by the theory, if γ has a great value. Rb⁺ shows a behaviour intermediate to those of Cs⁺ and Na⁺, the latter being unaffected by B⁻.

The gel of $(P/Zr)_s = 1.1$ shows the same affinity sequence as the other gels. Nevertheless it is considerably more selective, the curves for different metal ions being more separated. The sorption capacity is lower, however, than on the gel of $(P/Zr)_s = 1.95$. The sorption of Sr²⁺ on the gel with $(P/Zr)_s = 1.1$ is somewhat affected by Na⁺ from the acetate buffer present at $p[H^+] > 2$ (cf. p. 1866).

For both gels, the affinity decreases in the order U(IV) > UO₂²⁺ > Ce³⁺. This is the order to be expected from considerations of both the charge and the phosphate affinity of these species. It should then be remembered that the high positive charge located on the central uranium atom in UO₂²⁺ produces, around the middle of this linear ion, an electrostatic field which is much stronger than that surrounding a spherical ion of the charge +2. As a rule, therefore, UO₂²⁺ will rather react in the manner of more highvalent ions.²⁰ Contrary to this rule, however, the affinity of UO₂²⁺ for cation exchangers is fairly low in such cases where only electrostatic forces are at work. This is evident from the low sorption of UO₂²⁺, even when compared with that of other two-valent ions,¹⁶ on ion exchange resins containing sulphonate as functional groups, where no complex formation is likely to occur. The high affinity of UO₂²⁺ for ZrP, which is even higher than that of most three-valent ions, must therefore mainly be due to its ability to form extraordinarily strong complexes with the phosphate groups. The preference of UO₂²⁺ for ZrP relative to organic resins may also in part be due to steric factors; the importance of these are however difficult to assess. The curves found for U(IV) are very peculiar, especially as regards the gel of $(P/Zr)_s = 1.95$. This is certainly due to the very

high affinity of U(IV) to phosphate.¹⁸ In strongly acid solutions soluble phosphate complexes are formed, and for $p[H^+] > 0$ the formation of insoluble basic phosphates of U(IV) is readily observed. Thus the decreasing parts of curves indicate a destruction of the gels.

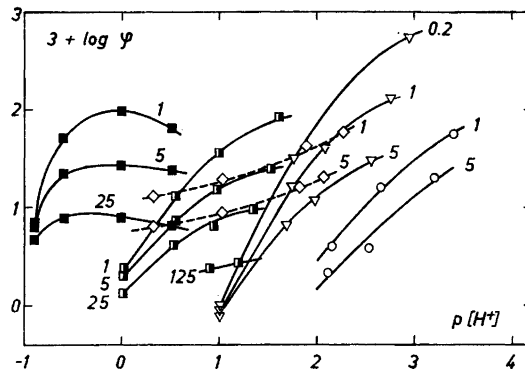


Fig. 11. Sorption at constant C_{MS} (mM) of U(IV), UO_2^{2+} , Ce^{3+} , Sr^{2+} , and Cs^+ on ZrP of $(P/Zr)_s = 1.1$, ignition loss 50%. Symbols in Table 1.

From Figs. 9–11 it is easily seen that many useful separations on ZrP can be designed. A discussion of this aspect will, however, be postponed to a following paper of this series.

Neutralization and hydrolysis curves of a phosphate rich gel in various media. In Ref.¹ neutralization and hydrolysis curves for different gels have been reported, both in media of varying and approximately constant ionic strength. Apart from H^+ , these media contained, however, Na^+ as the only cation. To investigate the effect of ions of various affinity to the gels, experiments have now been performed where Cs^+ and Rb^+ have been used instead of Na^+ to create a constant ionic strength, $I = 0.1$ M. All experiments were performed with the gel of $(P/Zr)_s = 1.95$. The results are shown in Figs. 12–13 together with the $NaOH(HCl) + NaCl$ -curves at $I = 0.1$ M reported in Ref.¹ The filled squares in the inset of Fig. 12 belong to a series with Cs^+ at $I = 0.5$ M. For

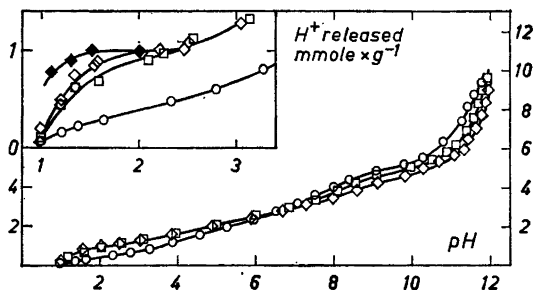


Fig. 12. Neutralization curves for various ionic media at an approximately constant ionic strength, I . The signs refer to: $I = 0.1$ M, Na^+ , \circ ; Rb^+ , \square ; Cs^+ , \diamond . $I = 0.5$ M, Cs^+ , \blacklozenge (inset). $(P/Zr)_s = 1.95$, ignition loss 41%.

pH < 6.5 (and especially for pH < 2.5), the amount of H⁺ released for a certain value of pH increases in the order Na⁺ < Rb⁺ ≤ Cs⁺, Fig. 12. This is exactly what to expect from the increasing affinity to the gel, displayed by these ions in the same order. The steep fall of the curves for pH < 1.5 depends mainly upon the decreasing concentration of metal ion in the solution. In order to reach low values of pH at constant ionic strength, it is necessary to replace more and more of the metal chloride by hydrochloric acid. For I = 0.1 M, all curves will evidently converge towards that point on the pH-axis where pH = 1, Fig. 12.

For pH > 6.5, the order between the curves of Fig. 12 is reversed so that the amount of H⁺ released now increases according to the sequence Cs⁺ < Rb⁺ < Na⁺. This depends upon that the hydrolysis of the gel, and hence the consumption of H⁺, increases as the positive ion of the medium is changed according to the sequence just given, Fig. 13.

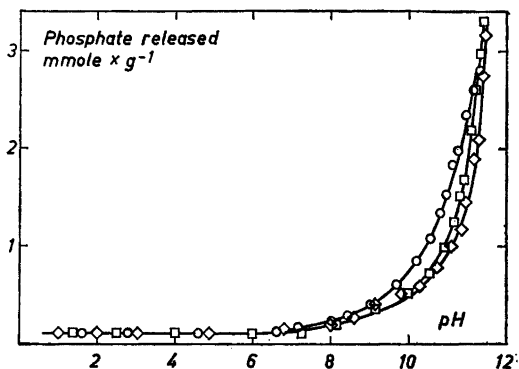


Fig. 13. Phosphate released to the solution as a function of pH for various ionic media at an approximately constant ionic strength = 0.1 M. The signs refer to: Na⁺, O; Rb⁺, □; Cs⁺, ◇. (P/Zr)_s = 1.95, ignition loss 41 %.

The neutralization curves of Fig. 12 are thus increasingly affected by the final hydrolysis of the gel in the order Cs⁺ < Rb⁺ < Na⁺. This means that the neutralization of the monohydrogen phosphate groups of the gel will be less complete before the hydrolysis interferes, as we proceed along this sequence. The inflexion point just below pH = 10 which would have indicated the complete protolysis of the monohydrogen groups exactly, had no hydrolysis existed in this range of pH, should therefore do so with better and better approximation as we proceed along the series Na⁺ → Rb⁺ → Cs⁺. This is in fact the case, as is shown by a comparison of the actual phosphate content of the gel, found by gravimetric analysis, with the values yielded by the inflexion points. For a gel containing 50 % water, the analytical value is 3.72 mmole P/g gel, while the readings from Fig. 12, corrected to the same water content, give 4.3, 4.1 and 3.9 mmole·g⁻¹ for Na⁺, Rb⁺, and Cs⁺, respectively.

For Rb^+ and Cs^+ media, another inflexion point is noticeable around $\text{pH} = 2.5$, which indicates that the functional groups are of various acidity, presumably depending upon how they are situated within the gel structure. From 12, the concentration of the more acid groups can be estimated to ≈ 1 mequiv·g⁻¹. It should be pointed out that the group $\overline{\text{HB}}$, postulated from the results of the sorption experiments, is present in a concentration $C_{\text{BG}} < 0.003$ mequiv·g⁻¹ and thus cannot possibly be detected in the neutralization curves.

COMPARISON WITH PREVIOUS WORK

A comparison with earlier investigations of sorption equilibria on ZrP must be a qualitative one for the following reasons:

1. The values of $(\text{P}/\text{Zr})_s$ of the gels used by various investigators are as a rule not the same. Very often it has not even been stated.

2. We have used gels with defined ignition losses rather than gels dried to constant weight at some specific temperature. The reason for this is that both the sorption rates and the sorption equilibria may depend very much upon the actual water content of the gels, as has been shown previously.²

3. The existence of the groups $\overline{\text{B}}^-$ has not been observed by the previous authors. Equilibrium constants have been computed with the assumption that ZrP is a strictly monofunctional ion exchanger in the pH-range examined.⁶⁻⁹ As discussed above, this assumption is not true. For certain ions, the mass action constant, k_0 , depends very much upon C_{MG} if this quantity is low.

From the present work it is, however, possible to conclude that equilibrium constants computed for the exchange of H^+ with Li^+ and Na^+ on ZrP^{6,7} will not depend on the B group. We have found $\gamma_{\text{Na}} = 0$ and, as the hydration number of Li^+ is greater than that of Na^+ ,¹⁵ γ_{Li} is most certainly = 0.

Amphlett *et al.*¹⁰ have reported the following affinity series for alkali metals and alkaline earths: $\text{Li}^+ < \text{Na}^+ < \text{K}^+, \text{NH}_4^+ < \text{Rb}^+ < \text{Cs}^+$ and $\text{Mg}^{2+} > \text{Ca}^{2+}, \text{Sr}^{2+} > \text{Ba}^{2+}$. Rb^+ and Cs^+ were found to be selectively sorbed.^{8,10} Our results for $\text{Na}^+, \text{Rb}^+,$ and Cs^+ are in agreement with this as well as the results of other authors.^{6,7,11} As discussed above, the good selective sorption of Rb^+ and Cs^+ at low values of C_{MG} can be described as a formation of $\overline{\text{CsB}}$ and $\overline{\text{RbB}}$, $\overline{\text{CsB}}$ being more stable than $\overline{\text{RbB}}$.

Vesely and Pekárek¹¹ have found that the affinity of Sr^{2+} to ZrP is less than that of Na^+ at $C_{\text{H}} = 100$ mM, $C_{\text{M}} = 1$ mequiv·l⁻¹. At almost identical conditions we have found $\text{Na}^+ < \text{Sr}^{2+}$ in agreement with other authors.^{6,10}

The affinity series $\text{UO}_2^{2+} > \text{Ce}^{3+} > \text{Sr}^{2+}$ of the present investigation is in agreement with previous work.^{6,11,12}

The deviations from the theoretical rectilinear behaviour of the $\log \varphi(\text{pH})$ -curves which were reported by Baetslé and Huys⁶ and by Gal and Ruvarac¹² must at least partly be due to lacking constancy of the load on ZrP.

Clearfield and Stynes³ have titrated crystalline ZrP in various media of constant as well as varying ionic strength. When the cation is $\text{Li}^+, \text{Na}^+,$ or K^+ , two neutralization steps are found, equal amounts of the phosphate groups being neutralized in each step. As to the gels used by us, the amount neutralized

in the first step is certainly smaller than that neutralized in the second one, Fig. 12. A very close similarity between the gels and the crystalline compound is, however, hardly to expect, on account of the structural differences. Their importance for the sorption properties is further demonstrated in a striking way by the behaviour of Cs^+ which is completely excluded³ from the crystalline ZrP, though strongly sorbed by the gels.

These investigations have been performed under a contract with *AB Atomenergi (The Swedish Atomic Energy Company)*, Stockholm, whose generous support is most gratefully acknowledged. Our most sincere thanks are further due to Professor Sture Fronæus, for enlightening discussions, and to Mr. Lars Johansson, Fil.mag., Mr. Lennart Nilsson, Fil.kand. and Mr. Bengt Nihlgård, for valuable help with part of the experimental work.

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