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ION EXCHANGE OF SOME DIVALENT AND TRIVALENT CATIONS ON THE SURFACE OF ZIRCONIUM ACID PHOSPHATE MICRO-CRYSTALS

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SUMMARY

Kinetic ion-exchange experiments have shown that, under appropriate conditions, it is possible to replace the exchangeable protons present on the surface of $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals with several divalent and trivalent cations, without exchanging the inner protons. This has made it possible to investigate the ion-exchange properties relative to the surface of micro-crystals of this exchanger, and the isotherms relative to the surface exchange of H^+–Mg^{2+}, H^+–Ca^{2+}, H^+–Ba^{2+}, H^+–Cu^{2+}, H^+–Zn^{2+} and H^+–La^{3+} have been determined.

The surface selectivity towards these cations is discussed on the basis of the crystalline structure of $Zr(HPO_4)_2 \cdot H_2O$. Large differences in the separation factors indicate that interesting separations of micro-amounts of cations can be achieved by thin-layer or column chromatography.

INTRODUCTION

It is known[1,2] that counter ions with a crystalline radius greater that 1.32 Å cannot diffuse, or can diffuse only very slowly, within the layered structure of $Zr(HPO_4)_2 \cdot H_2O$; therefore, they are unable to exchange the inner protons of this inorganic exchanger. However, the surface protons can be exchanged in a very short time and therefore large cations can be used to investigate the surface ion-exchange properties of micro-crystals of $Zr(HPO_4)_2 \cdot H_2O$. The Cs^+ ion, owing to its large size, is a very suitable cation for this purpose and it has been employed to determine the surface ion-exchange capacity and to obtain the H^+–Cs^+ ion-exchange isotherms relative to the surface of the micro-crystals of zirconium phosphate[3]. It has also been found that, under suitable experimental conditions, the surface ion-exchange isotherms for K^+, Na^+ and Li^+ can be obtained.

It seemed of interest to determine similar isotherms for some divalent and trivalent cations in order to obtain additional information on the surface ion-exchange properties of $Zr(HPO_4)_2 \cdot H_2O$.

The variation in the selectivity with the degree of exchange of the surface protons is discussed on the basis of the crystalline structure of $Zr(HPO_4)_2 \cdot H_2O$.

EXPERIMENTAL

Chemicals

All reagents used were Carlo Erba (Milan, Italy) R.P.E. materials, except for $ZrOCl_2 \cdot 8H_2O$, which was a Merck (Darmstadt, G.F.R.) pro analisi product.

Ion-exchange materials

Crystalline zirconium phosphate was prepared by slow decomposition of zirconium fluoro complexes in the presence of orthophosphoric acid, as described earlier[4]. The crystals were washed with distilled water to pH 4.5–4.6 and stored over P_4O_{10}.

Determination of the exchangeable protons at the surface of micro-crystals of Zr-$(HPO_4)_2 \cdot H_2O$

The total amount of surface exchangeable protons was determined by the Cs^+ procedure according to the method described previously[3]. The surface ion-exchange capacity of the micro-crystals used was 3.1 ± 0.1 μequiv. per gram of exchanger.

Kinetic experiments

A 3-g amount of $Zr(HPO_4)_2 \cdot H_2O$ was equilibrated, with stirring at $25 \pm 1°$, with 25 ml of distilled water, then 5 ml of a MCl_2 or MCl_3 solution ($6.0 \cdot 10^{-3}$ M) were added and the variation of pH with time was followed with a Beckman Research pH meter.

Ion-exchange isotherms on the surface of Zr(HPO_4)_2 · H_2O micro-crystals

A weighed amount of $Zr(HPO_4)_2 \cdot H_2O$ was equilibrated, at $25 \pm 1°$, with a suitable volume of a $5 \cdot 10^{-4}$ M MCl_2 or MCl_3 solution. After a few minutes of equilibration, the micro-crystals were separated from the solution by centrifuging. The pH values of the solutions were measured and their metal ion contents were determined with a Perkin-Elmer 305 atomic-absorption spectrophotometer. Lanthanum was determined colorimetrically[5] after complexation with alizarin red S ($\lambda =$ 550 nm). The ionic fraction of the counter ions at the surface, X_M^S, was obtained from the initial and final metal ion content, taking into account the surface ion-exchange capacity previously determined; in some samples the amounts of metal ions taken up by the solid were also determined by regeneration of the micro-crystals with a suitable volume of 1 M hydrochloric acid.

RESULTS AND DISCUSSION

Because of its large size, hydrated Mg^{2+} is unable to exchange, at room temperature, the inner protons of $Zr(HPO_4)_2 \cdot H_2O$ [6,7]. It is also known that some divalent metal ions such as Ba^{2+}, Cu^{2+} and Zn^{2+} and trivalent cations such as La^{3+} are not exchanged at room temperature[1,2,6,8] (or are very slowly exchanged) by $Zr(HPO_4)_2 \cdot H_2O$. Hence, these may be suitable cations for investigating the surface ion-exchange properties of micro-crystals of zirconium phosphate.

In order to confirm this expectation, preliminary kinetic experiments were performed, as described under Experimental. The results for Mg^{2+} are shown in Fig. 1.
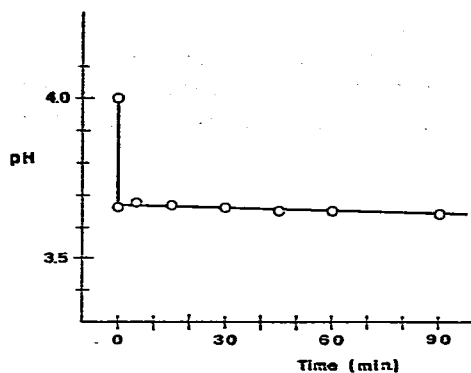
Fig. 1. Variation of the pH, as a function of time, due to H^+/Mg^{2+} exchange by $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals ($t = 25°$).

It can be seen that there is a sharp decrease in pH in a few seconds (owing to the rapid exchange of the surface protons) and then the pH remains constant for a relatively long period, indicating that inner protons are not exchanged (or are exchanged only very slowly). Similar results have been obtained with Ba^{2+}, Cu^{2+}, Zn^{2+} and La^{3+}, confirming that ion-exchange isotherms, relative to the surface of micro-crystals, can be obtained for all of these ions.

In a previous paper[3], it was shown the surface ion-exchange isotherms can also be obtained with monovalent ions such as K^+, Na^+ and Li^+ [which are known to exchange inner protons of $Zr(HPO_4)_2 \cdot H_2O$] provided that sufficiently dilute solutions are employed. Thus, it was of interest to see if surface ion-exchange isotherms could also be obtained with divalent cations, such as Ca^{2+}, which are able to exchange inner protons[6].

Kinetic experiments performed with 10^{-3} M calcium chloride solution showed that, after the rapid exchange of the surface protons, the pH remains almost constant for a long period (Fig. 2), indicating that, at the concentration used, the inner protons are not exchanged (or are exchanged only very slowly); therefore, a good discrimination between the exchange of external and inner protons can be made.
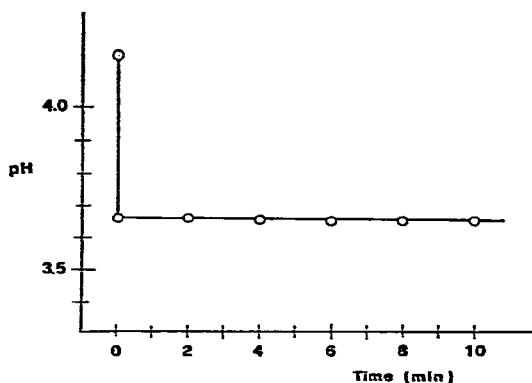

Fig. 2. Variation of the pH, as a function of time, due to H^+/Ca^{2+} exchange by $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals ($t = 25°$).

Ion-exchange isotherms of divalent and trivalent cations

In Fig. 3 are shown the H^+/M^{z+} isotherms ($M^{z+} = Mg^{2+}$, Ca^{2+}, Ba^{2+} and La^{3+}) relative to the surface of micro-crystals of $Zr(HPO_4)_2 \cdot H_2O$ together with, for comparison, the ion-exchange isotherms of alkali-metal ions obtained previously[3] (dotted curves).
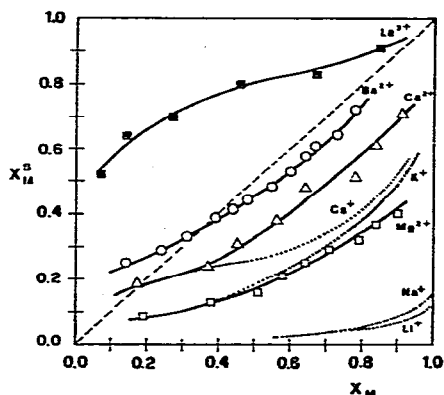

Fig. 3. H^+/M^{z+} ion-exchange isotherms for the surface of $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals ($C = 5 \cdot 10^{-4} M$; $t = 25°$). Isotherms of alkali-metal ions, obtained previously[3], are reported for comparison (dotted curves).

As expected, the selectivity increases with increasing charge of the cation; also, the selectivity for alkaline-earth metal ions, as already found for alkali-metal ions, increases with increasing crystalline radius[7]; hence it is probable that hydrated cations are involved in the ion-exchange processes at the surface of $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals. Further, it can be seen from Fig. 3 that S-shaped isotherms are also obtained for divalent and trivalent cations, as already found[3] for Cs^+. This means that the separation factor, $\alpha_{H^+/M^{z+}}$, changes considerably as divalent and trivalent counter ions progressively replace the protons at the surface.

Some $\alpha_{H^+/M^{z+}}$ values are reported in Table I and a plot of the rational selectivity coefficient, $K_{H^+/M^{z+}}$, against the ionic fraction at the surface, X_M^s, is shown in

TABLE I

SEPARATION FACTORS, $\alpha_{H^+/M^{z+}}$, AT VARIOUS IONIC FRACTIONS IN SOLUTION

$\alpha_{H^+, M^{z+}} = \dfrac{X_M^s \, X_H}{X_M \, X_H^s}$, where X_M and X_H are ionic fractions of M^{z+} and H^+ in the solution and X_M^s and X_H^s are ionic fractions at the surface.

M^{z+}	X_M			
	0.2	*0.4*	*0.6*	*0.8*
Mg^{2+}	0.35	0.22	0.19	0.13
Ca^{2+}	0.94	0.55	0.44	0.34
Ba^{2+}	1.48	0.92	0.75	0.67
Cu^{2+}	1.63	1.56	1.71	1.67
Zn^{2+}	0.65	0.67	0.67	0.64
La^{3+}	8.12	4.75	3.25	2.02

Fig. 4. It must be pointed out that the exchange of hydrated species and the decrease in $K_{H^+/M^{z+}}$ with the degree of conversion are in agreement with expectations based on the crystalline structure of Zr(HPO$_4$)$_2$·H$_2$O. This compound possesses a layer structure, each layer consisting of plane of zirconium atoms bridged through phosphate groups located alternately above and below this plane[1,9]. Three oxygen atoms of each tetrahedral phosphate group are bonded to three zirconium atoms in the plane and the fourth oxygen atom bears the fixed negative charge neutralized by protons. It is probable that the structure of the external layers remains similar to that of the inner layers, but with a certain degree of disorder. Thus, if such a disorder is not taken into consideration (at least in a first approximation), the surface structure of the oxygen atoms carrying the fixed negative charges similar to that shown schematically in Fig. 5 would result. The distance between adjacent fixed charges is 5.3 Å and a similar average distance would be expected for adjacent monovalent counter ions. Initially, the fixed charges are balanced only by the protons which are progressively replaced with other counter ions during the ion-exchange process. For low degrees of exchange, only interactions between the incoming counter ions and the protons originally present would be expected. However, as the degree of conversion increases, the incoming M^{z+} is compelled to occupy one position adjacent to another M^{z+}. Thus, especially for highly hydrated cations, interactions between their water molecules can take place and consequently the affinity decreases with increasing degree of conversion.
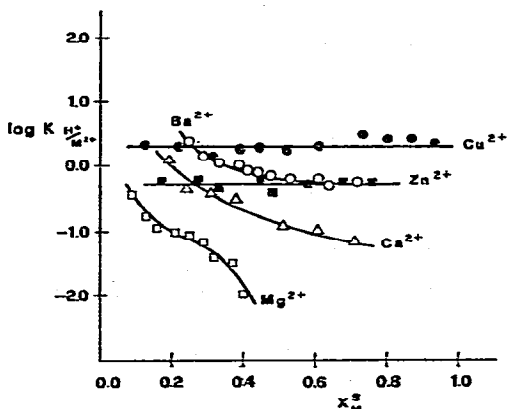

Fig. 4. Rational selectivity coefficients, $K_{H^+/M^{z+}}$, relative to the surface of Zr(HPO$_4$)$_2$ · H$_2$O microcrystals as a function of the ionic fraction of the cation on the surface (X_M^S): $K_{H^+/M^{z+}} = \dfrac{X_M^S}{X_M}\left(\dfrac{X_M}{X_H^S}\right)^z$.

From the idealized surface structure of the fixed charges (Fig. 5), it can be seen that the degree of conversion beyond which a cation M^{z+} is forced to occupy an adjacent position to another M^{z+} depends on its charge, $z+$. This value is 25% for monovalent, 50% for divalent and 75% for trivalent counter ions but, taking into account the structural disorder on the surface, direct $M^{z+}(H_2O)_n$–$M^{z+}(H_2O)_n$ interactions are expected to take place even at lower degrees of conversion.
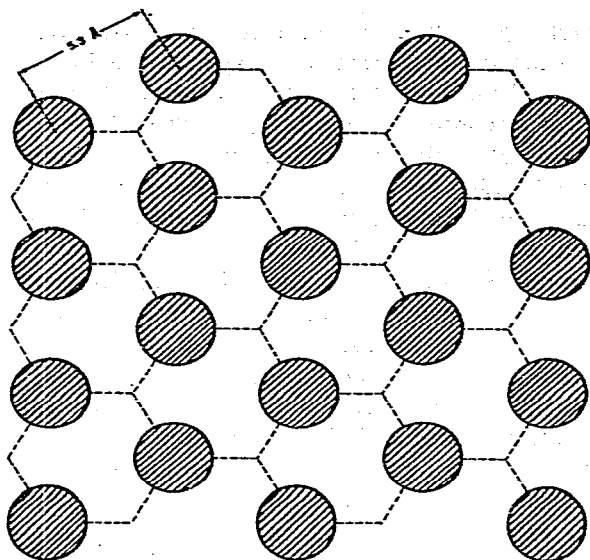
Fig. 5. Idealized position of the oxygen atoms carrying the fixed charges at the surface of $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals.

Ion-exchange isotherms of divalent copper and zinc

It is known that the selectivity can be influenced by the charge and size of the counter ions as well as by their electronic configuration. In particular, cations with an electronic configuration $nd^x(n+1)s^0$ (typical of transition metal ions) have a stronger polarizing effect than cations with the noble-gas configuration $ns^2np^6(n+1)s^0$ (e.g. alkali-metal and alkaline-earth metal ions) and ionic covalent bonds with oxygen atoms carrying fixed charges are possible. It was therefore of interest to obtain some preliminary data on the selectivity of copper(II) on the surface of $Zr(HPO_4)_2 \cdot H_2O$. The behaviour of zinc(II) was also examined on account of its pseudo-noble gas electronic configuration, $nd^{10}(n+1)s^0$, and its tendency to give four-coordinate species. The isotherms relative to the ion-exchange processes H^+/Zn^{2+} and H^+/Cu^{2+} are shown in Fig. 6. The separation factors and the rational selectivity coefficients for the various X_M^S values are reported in Table I and Fig. 4, respectively.

In contrast to alkali-metal and alkaline-earth metal ions, these cations do not exhibit S-shaped isotherms and $K_{H^+/M^{z+}}$ remains roughly constant for the various X_M^S values. This constancy seems to indicate that interactions among adjacent hydrated metal ions are weak relative to the bonds with the fixed charges.

CONCLUSION

The results clearly indicate that the surface ion-exchange properties of $Zr(HPO_4)_2 \cdot H_2O$ (and probably of other insoluble acid salts of tetravalent metals) can be investigated with a large number of inorganic cations. Preliminary results seem to indicate that large complex cations of transition elements and large organic cations are taken up on the surface of $Zr(HPO_4)_2 \cdot H_2O$ with very high affinity[10]. The large differences in the separation factors relative to various H^+/M^{z+} surface-exchange
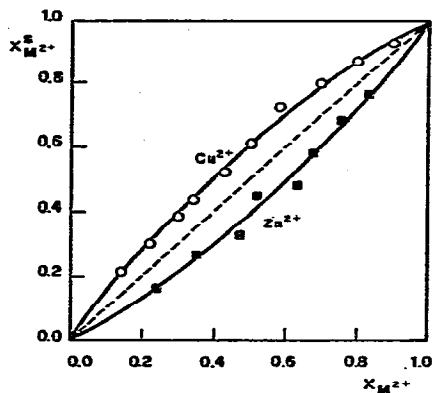
Fig. 6. H^+/Cu^{2+} and H^+/Zn^{2+} ion-exchange isotherms relative to the surface of $Zr(HPO_4)_2 \cdot H_2O$ micro-crystals ($C = 5 \cdot 10^{-4} M$; $t = 25°$).

processes indicate that interesting separations of micro-amounts of inorganic cations could be performed by thin-layer or column chromatography. Further, the knowledge of the counter-ion composition at the surface of micro-crystals of insoluble acid salts of tetravalent metals will be useful in clarifying their ionic conductance, their catalytic activity and the electrochemical properties of membranes consisting of these inorganic exchangers.

Finally, as the insoluble acid salts of tetravalent metals seem to be very good supports in gas chromatography[11,12], a better knowledge of their surface properties and composition will also be very useful for this latter application.

ACKNOWLEDGEMENT

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