BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1005—1006 (1973)

Ion-exchange Equilibria on a Crystalline Zirconium Phosphate Exchanger

Hiroko Sekino and Isao Tomita
Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo

(Received August 25, 1972)

Ahrland and Albertsson have suggested that the zirconium phosphate gels contain, besides the ordinary phosphate groups, small amounts of a functional group capable of interacting more or less strongly with various cations.[1] They studied the ion selectivity by plotting the logarithm of the distribution coefficients, K_d, as a function of the pH at a constant value of the load.

Albertsson extended the study to the sorption of Na^+, Cs^+, Sr^{2+}, $UO_2{}^{2+}$ and Ce^{3+} ions on a crystalline zirconium phosphate.[2] The log K_d *vs.* pH curves for Na^+ and Cs^+ have the theoretical slopes, but the slopes for $UO_2{}^{2+}$ and Ce^{3+} curves have somewhat lower values than those expected. Strontium ion behaves peculiarly, and the sorption by no means proceeds *via* a perfect ion exchange.

The aim of the present experiment is the further investigation of the ion-exchange equilibria of divalent ions such as Zn^{2+} on a crystalline zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$ (abbreviated as α-ZP). The equilibrium of the Cs^+ ion was also reexamined. Both Cs^+ and Zn^{2+} ions have appreciably high K_d values in acidic-solution media and are suitable for the study.

Theoretical

If α-ZP behaves as a monofunctional exchanger, the mass action law can be applied to the following equilibrium:

$$n\overline{\mathrm{AH}} + \mathrm{M}^{n+} \rightleftharpoons \overline{\mathrm{A}n\mathrm{M}} + n\mathrm{H}^+$$

$$K_d = \frac{[\overline{\mathrm{A}n\mathrm{M}}]}{[\mathrm{M}^{n+}]} = K\cdot\frac{[\overline{\mathrm{AH}}]^n}{[\mathrm{H}^+]^n} \qquad (1)$$

where the bar denotes the exchanger phase; A, an anionic functional group; M^{n+}, metal ions, and K, an equilibrium constant. When the load is sufficiently small, $[\overline{\mathrm{AH}}]$ is nearly equal to the H^+ ion concentration before loading, $[\overline{\mathrm{AH}}]_0$. Thus, the plots of log K_d *vs.* pH should result in a straight line with a slope of n.

If the exchanger contains some kinds of functional groups, A_i, whose affinities for cations are different from each other, K_d is expressed as follows:

$$K_d = \frac{\sum[\overline{\mathrm{A}_{in}\mathrm{M}}]}{[\mathrm{M}^{n+}]} = \frac{\sum(K_i\cdot[\overline{\mathrm{A}_i\mathrm{H}}]^n)}{[\mathrm{H}^+]^n}$$

$$\log K_d = \log(\sum K_i\cdot[\overline{\mathrm{A}_i\mathrm{H}}]^n) + n\,\mathrm{pH} \qquad (2)$$

When one functional group is of an amount comparable to the load, but has an appreciable affinity for the cations involved, the first term of Eq. (2) is no longer constant and the log K_d *vs.* pH plot does not give a straight line with a slope of n. This is actually the case for zirconium phosphate gels.

As a simple case, let us consider an exchanger containing two kinds of functional groups, A and B, where A is a major component with an equilibrium constant of K_A, and where B is a minor component with K_B and $K_B \gg K_A$. We obtain:

$$K_d = \frac{1}{[\mathrm{H}^+]^n}\{K_B[\overline{\mathrm{BH}}]^n + K_A[\overline{\mathrm{AH}}]^n\}$$

Now that the load is kept sufficiently low in comparison with the exchange capacity, *i.e.*, $[\overline{\mathrm{AH}}] \gg [\overline{\mathrm{A}_n\mathrm{M}}]$, the above equation can be re-written as follows:

$$K_d = \frac{1}{[\mathrm{H}^+]^n}[K_B\{[\overline{\mathrm{BH}}]_0 - [\overline{\mathrm{B}_n\mathrm{M}}]\}^n + K_A[\overline{\mathrm{AH}}]_0{}^n] \qquad (3)$$

where the subscript 0 denotes the concentration before loading. Further, the following cases can be considered under these conditions:

i) If the initial amount of $\overline{\mathrm{BH}}$ is larger than the load, C_M, the latter is considered to be equal to $[\overline{\mathrm{B}_n\mathrm{M}}]$. Then

$$K_d = \frac{1}{[\mathrm{H}^+]^n}[K_B\{[\overline{\mathrm{BH}}]_0 - C_M\}^n + K_A[\overline{\mathrm{AH}}]_0{}^n] \qquad (4)$$

ii) If $C_M > [\overline{\mathrm{BH}}]_0$, then $[\overline{\mathrm{B}_n\mathrm{M}}] = [\overline{\mathrm{BH}}]_0$ and

$$K_d = \frac{1}{[\mathrm{H}^+]^n}\cdot K_A[\overline{\mathrm{AH}}]_0{}^n \qquad (5)$$

This value is constant when pH is kept constant.

From the above considerations, it is at least possible to deduce whether or not the exchanger in question is monofunctional from the general shape of the K_d *vs.* C_M curve determined experimentally.

Experimental

Exchanger. α-ZP was prepared and treated as has been reported previously.[3] The particle sizes range from 100 to 200 mesh. Identification was made by means of X-ray powder diffraction.

Distribution Coefficients. All the measurements were carried out at 25°C using 250 mg of α-ZP and 25 ml of a contact solution in the same manner as before.[3] The hydrogen-ion concentrations were adjusted with hydrochloric acid for the cesium chloride solution and with nitric acid for the zinc nitrate solution. Radioactive tracers such as ^{65}Zn and ^{137}Cs with known specific activities were used to determine the concentrations of the cations. The radioactivities were measured with a well-type NaI(Tl) scintillation counter.

Usually, three runs were carried out under the same conditions and the mean values of the K_d values thus obtained were taken.

Results and Discussion

In general, it is difficult to keep the experimental media at a constant ionic strength in this kind of ion-

---

[1] S. Ahrland and J. Albertsson, *Acta Chem. Scand.*, **18**, 1861 (1964).

[2] J. Albertsson, *ibid.*, **20**, 1689 (1966).

[3] Y. Hasegawa and I. Tomita, This Bulletin **43**, 3011 (1970).

exchange study because small amounts of functional groups might have an unusual affinity for cations other than those in question. In this experiment, the variation in the involved activity coefficients is disregarded over the pH range studied, but this does not seem to have influenced the discussion given below.

Dependence of K_d upon C_M at a Constant pH. Figure 1 shows typical examples of the plots of K_d *vs.* C_M at constant pH values for the Cs^+ and Zn^{2+} ions respectively. Similar curves have been obtained at pH values of 0.70, 1.08. 1.58, and 2.03 for Cs^+, and at 1.59, 2.08, 2.50, and 2.99 for Zn^{2+} ions. In the region of very low loading, the K_d values decrease rapidly with an increase in C_M for both metal ions. This is what is to be expected from Equation (4). However, as the value of C_M increases further, the K_d values still decrease slowly and do not attain constant values over the C_M range studied. It is not easy to judge from the results whether or not the left part of the cesium curve is rectilinear or whether or not that of the zinc curve is parabolic. There might be an oversimplification of the assumptions in deriving Eq. (3)~(5), and the possible existence of more than one kind of functional group with a high affinity can not be excluded. However, it is possible roughly to estimate the upper limit of concentration of the B group by intercepting the extrapolated parts of the left- and right-hand sides of each curve. Values of about 0.01 meq/g α-ZP for cesium and of about 0.05 meq/g α-ZP for zinc were thus obtained. The total exchange capacity of α-ZP is theoretically 6.64 meq/g, and the quantity of the high-affinity group is less than 1%. This makes the chemical identification and characterization of the group extremely difficult.

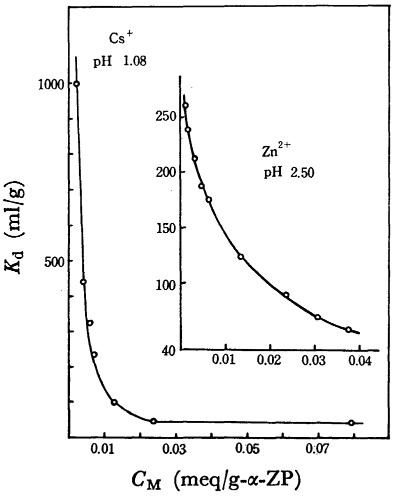

Fig. 1. The plot of K_d *vs.* C_M at constant pH values.

The purity of the exchanger used is good, and so is the crystallinity. Thus, the existence of any functional group other than the phosphate group is not likely. However, the incorporation of amorphous zirconium phosphate into the crystals is probable, because the crystals have been prepared from the gels by refluxing them in phosphoric acid. Further, from steric considerations,[4] the phosphate groups on the crystal surface should have a higher affinity for Cs^+ and Zn^{2+} ions than those inside the crystal. Even inside the crystal, there might be small amounts of sorption sites which occupy particular positions leading to a different acidity of the phosphate protons from that of a majority of the monohydrogen phosphate groups. If each of the above-mentioned phosphate groups is responsible for the sorption of cations, but to a different extent, K_d values which are independent of the C_M can not be attained within the range of the present experiment, in which the extent of the exchanged sites is only about 1% of that of the total exchangeable ones.

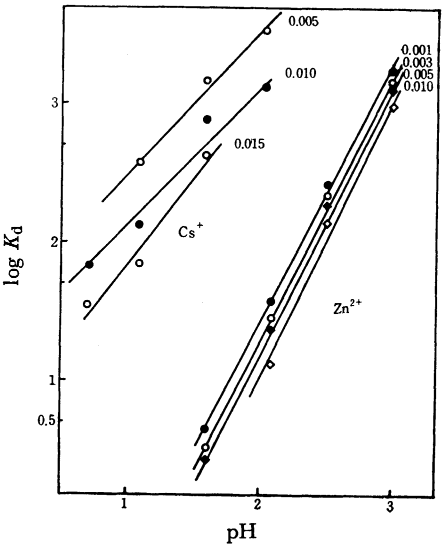

Fig. 2. The plot of log K_d *vs.* pH at constant C_M values. Numerical value beside each line denotes C_M in meq/g α-ZP.

The log K_d vs. pH Plots at Constant Loads. From the curves of K_d *vs.* C_M at different constant pH values, it is possible to find the K_d values for a constant C_M. The logarithm of the values were then plotted against the pH, as is shown in Fig. 2. The slopes of the resulting straight lines were calculated by a least-squares method. For cesium, these values are 1.01, 1.02, and 1.24 for the C_M values (meq/g α-ZP) of 0.005, 0.010, and 0.015 respectively. With regard to zinc, the slopes are 1.86, 1.91, 1.97, and 2.05 for the C_M values of 0.001, 0.003, 0.005, and 0.010 respectively. The approximate values of +1 for cesium and +2 for zinc are what can reasonably be expected from their normal valency states. Figure 2 also shows the parallel displacement of straight lines with the change in the C_M values. This is again to be expected from Eq. (4).

The authors wish to express their thanks to Professor Kozo Nagashima for his interest and encouragement. They are also indebted to Mr. Yoshitsugu Hasegawa for his valuable discussions. Finally, they are grateful to Mr. Yasuhiko Saito for his help with the experiments.

---

4) The ion-sieving property of α-ZP is known for relatively large ions, such as cesium and rubidium. A strongly hydrated polyvalent ion is considered also to be hindered to a considerable extent.