

# Cation Exchange of Divalent Metal Ions on Zirconium (IV) Phosphosilicate Cation Exchanger

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As constantes de seletividade da troca iônica do Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) e Pb(II) com a forma protonada do fosfosilicato de zircônio (IV) foram calculadas a 298 K, fornecendo os seguintes resultados: Ni(II) =  $0.25 \times 10^{-3}$ , Cu(II) =  $1.0 \times 10^{-3}$ , Zn(II) =  $0.40 \times 10^{-3}$ , Cd(II) =  $0.79 \times 10^{-3}$ , Hg(II) = 0.10 e Pb(II) = 0.16. A ordem da seletividade deste trocador iônico foi: Pb(II) > Hg(II)  $\gg$  Cu(II) > Cd(II) > Zn(II) > Ni(II).

The ion exchange selectivity constants of Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) ions with hydrogen form of zirconium (IV) phosphosilicate have been calculated at 298 K, giving the following results: Ni(II) =  $0.25 \times 10^{-3}$ , Cu(II) =  $1.0 \times 10^{-3}$ , Zn(II) =  $0.40 \times 10^{-3}$ , Cd(II) =  $0.79 \times 10^{-3}$ , Hg(II) = 0.10 and Pb(II) = 0.16. The selectivity order of this ion exchanger for the metal ions was found to be: Pb(II) > Hg(II)  $\gg$  Cu(II) > Cd(II) > Zn(II) > Ni(II).

**Key words:** zirconium (IV) phosphosilicate separation, selectivity constants, ion exchange.

## Introduction

Inorganic ion exchangers, compared with organic resins, have a higher thermal and chemical stability, are more resistant to gamma radiation and have a smaller tendency to swell in contact with water.

The synthetic crystalline inorganic ion exchangers are currently under extensively study mainly due to their applications in chromatography and also as support for various metal ions having catalytic activity<sup>1</sup>.

Zirconium (IV) phosphosilicate has received some attention in this regard. Although the preparation of this inorganic exchanger was first described in 1961<sup>2</sup>, reports of new preparative methods, exchanger properties, and analytical applications have only recently appeared in the literature<sup>3-7</sup>.

In order to explore the potential use of this class of material, the thermodynamic study of the ion exchange process of Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) with H(I) ions on the hydrogen form of zirconium (IV) phosphosilicate cation exchanger is reported.

## Experimental

Zirconium (IV) phosphosilicate was prepared according to the procedure already described in the literature<sup>4</sup>. To a solution of sodium silicate (1 l, 0.1 M) was added a solution of zirconium oxychloride (1 l, 0.1 M) previously acidified with 50 ml of concentrated HCl. The pH of the solution was adjusted between 9-10 by adding concentrated NH<sub>4</sub>OH. The precipitate formed at this pH was left for 12 h and then filtered and the solid washed with bidistilled water. Solutions containing H<sub>3</sub>PO<sub>4</sub> (1 l, 1 M) and HNO<sub>3</sub> (1 l, 1 M) were added to the precipitate obtained above, with vigorous stirring, and the resulting suspension left for 12 h at room temperature. The solid was then filtered and washed with bidistilled water. The precipitate was dried in an oven at a temperature of 318 K and the resulting vitreous solid placed in a solution of 1M HNO<sub>3</sub>.

The exchange isotherm were determined by the batch technique at a temperature of 298 K. The material (0.2 g), hereafter designated as HZPS, was shaken during 12 h with the metal ions. This time was shown to be sufficiently long for the system to achieve equilibrium. The solutions were separated by decantation and the metal ions determined in the supernatant by conventional complexometric titrations using EDTA as titrant. The pH of each solution was determined, with a calibrated combined glass electrode, before and after the exchange process.

The amount of exchanged metal ion,  $N_f$ , was calculated by use of the equation:

$$N_f = \frac{N_a - N_s}{w}$$

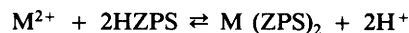
where  $N_a$  is the initial amount of the metal ion,  $N_s$  is the amount of metal ion in equilibrium with the solid phase and  $w$  is the mass of the exchanger.

The distribution coefficient,  $D$ , was calculated by use of the equation:

$$D = \frac{N_f}{C}$$

where  $C$  is the equilibrium concentration of the metal ion in contact with the solid phase.

Considering the exchange reaction:



The selectivity coefficient was calculated by using the equation:

$$K_d = \frac{H_X \cdot m_H^2 \cdot \gamma_H^2}{X_H^2 \cdot m_M \cdot \gamma_M}$$

where  $X_M$  and  $X_H$  are the equivalent fractions of the metal ion and the hydrogen ion in the exchanger phase. These values were calculated from the equation:

$$X_M = \frac{Z_M N_f}{N_0}$$

and

$$X_M + X_H = 1$$

where  $Z_M$  is the charge of the metal ions and  $\frac{N_0}{w}$  is the exchange capacity of the material.

$m_M$  and  $m_H$  are the molalities in solution,  $\gamma_M$  and  $\gamma_H$  the activity coefficients. These coefficients were calculated at each point of the isotherm through the Debye-Huckel equation:

$$\ln \gamma_i = \frac{AZ_i^2 I^{1/2}}{1 + aB I^{1/2}}$$

where A and B are constants,  $Z_i$  the charge of the ion, a the ion size parameter and I the ionic strength of the solution.

The selectivity constant can be calculated by applying the equation:

$$K = \frac{X_M \cdot m_H^2 \gamma_H^2 f_M}{X_H \cdot m_M \gamma_M f_H} = K_d \frac{f_M}{f_H^2}$$

where  $f_M$  and  $f_H$  are the activity coefficients of the metal ion and the hydrogen ion in the exchanger phase.

Evaluation of K can be made by using the approximation of Gaines-Thomas<sup>8</sup>.

$$\ln K = -(Z_M - Z_H) + \int_0^1 \ell n K_d dX_M$$

## Results and Conclusions

The exchange isotherms of the metal ions are shown in Figure 1, where  $N_f$  is plotted against the equilibrium concentration, C, of the metal ion in solution in contact with the solid phase. The graph showed that for every metal ion the isotherm achieved a constant value at higher concentration of the metal ion in solution. In this case, the exchange capacity was determined for each metal at the limit of saturation of the surface i.e.,  $N_f^{\max} = |N_f|_{C \rightarrow \infty}$ . The values obtained using this procedure were (in mmol g<sup>-1</sup>): Ni(II) = 0.53, Cu(II) = 0.92, Zn(II) = 0.63, Cd(II) = 0.68, Hg(II) = 1.70 and Pb(II) = 1.73.

Along the experimental points on the isotherm, the sorption of a metal ion is followed by liberation of an equivalent number of protons to the solution phase. The pH of solution will increase as the value of distribution coefficient increases, as in shown in Figure 2. The plot of log D vs pH showed a linear relationship with a correlation coefficient  $r \geq 0.99$  for Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and  $r = 0.93$  for Pb(II).

In this graph it is observed that there is a clear distinction between the values of the distribution coefficients of Hg(II) and Pb(II), compared with those of Ni(II), Cu(II), Zn(II) and Cd(II). At pH = 2 the H<sup>+</sup> concentration in solution is of such an order that, with the exception of Hg(II) and Pb(II), the values of distribution coefficients are very small. The values of log D were: Hg(II) = 4.1, Pb(II) = 3.8, Cd(II) = 1.8, Cu(II) = 1.1, Zn(II) = 0.99 and Ni(II) = 0.63. The affinity order at this pH is therefore: Hg(II) > Pb(II) > Cd(II) > Cu(II) > Zn(II) > Ni(II).

The affinity order is however very dependent on the pH of the solution, since the slope of the straight line in the Figure 2 is not the same for all metal ions.

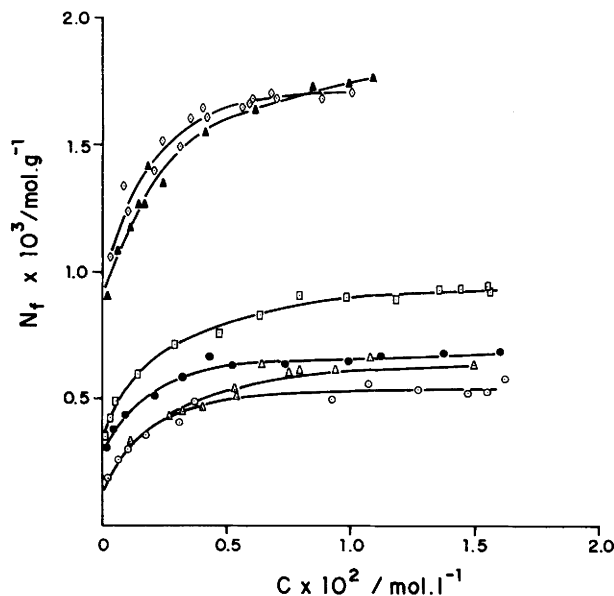


Figure 1. Exchange isotherms of metal ions on zirconium (IV) phosphosilicate at 298 K: (○) Ni(II), (□) Cu(II), (△) Zn(II), (●) Cd(II), (◇) Hg(II) and (▲) Pb(II).

Since the distribution coefficients change with the variation of the concentration of the metal ions and H<sup>+</sup> in the solution phase, the thermodynamic equilibria constants were calculated using the procedure given before. The following values of K were found: Ni(II) =  $0.25 \times 10^{-3}$ , Cu(II) =  $1.0 \times 10^{-3}$ , Zn(II) =  $0.40 \times 10^{-3}$ , Cd(II) =  $0.79 \times 10^{-3}$ , Hg(II) = 0.10 and Pb(II) = 0.16.

There is a linear correlation between the selectivity constants, K, and the effective ionic radius (EIR) of the metal ions as is shown in Figure 3. The higher affinities shown by HZPS for Hg(II) and Pb(II) are presumably due to the lower dehydration energies involved when these ions enter into the solid phase in comparison with those of the lighter elements, as pointed out by Abe in recent work<sup>10</sup>.

The high selectivity constants for Hg(II) and Pb(II) in comparison with the remaining lighter metal ions, makes the material potentially useful in chemical analysis processes. The separation factors defined as  $\alpha_{AB} = K_A/K_B$  where,  $K_A$  and  $K_B$  are the selectivity constants of metals A and B respectively, are shown in Table 1. These results indicate that some selective separation is feasible for heavier metal ions, i.e. Hg(II) and Pb(II), from lighter ones, i.e. Ni(II), Cu(II), Zn(II) and Cd(II).

Table 1. Separation factor<sup>a</sup>  $\alpha_{AB}$  on zirconium (IV) phosphosilicate ion exchanger at 298 K.

	Pb(II)	Hg(II)	Cd(II)	Zn(II)	Cu(II)
Ni(II)	640	400	3.2	1.6	4.0
Cu(II)	160	100	0.79	0.4	—
Zn(II)	400	250	2.0	—	—
Cd(II)	202	126	—	—	—
Hg(II)	1.6	—	—	—	—

<sup>a</sup> $\alpha_{AB} = K_A/K_B$  where  $K_A$  and  $K_B$  are the selectivity constants of the metal A and B respectively.

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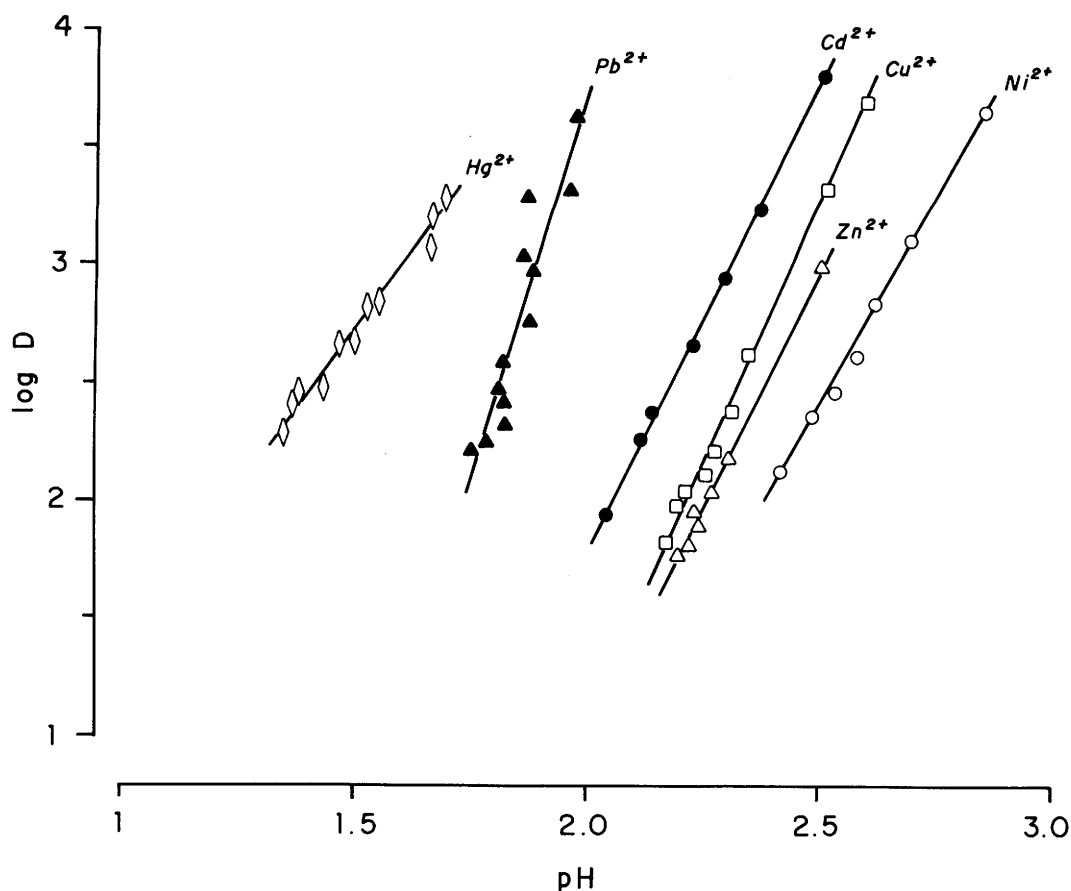


Figure 2. Log of distribution coefficients vs pH of metal ions on zirconium (IV) phosphosilicate at 298 K.

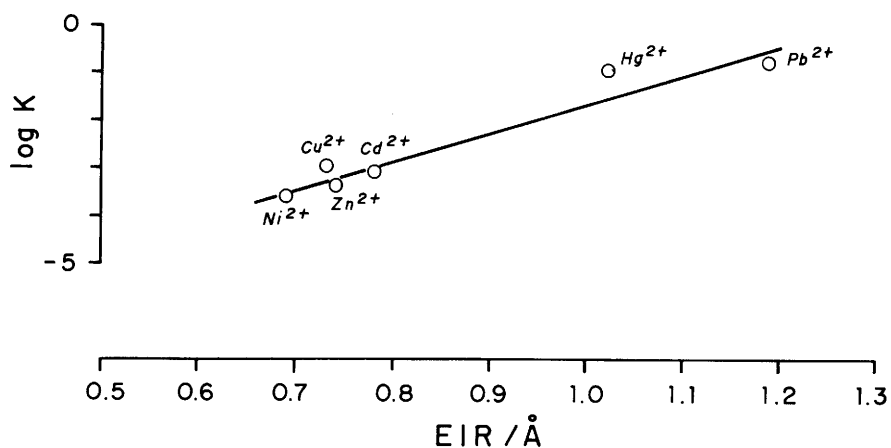


Figure 3. Log of selectivity constants vs effective ionic radii (EIR) of metal ions on zirconium (IV) phosphosilicate at 298 K. The values of EIR are those of ref. 9.

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