

CHROM. 5460

## Ca<sup>2+</sup>/H<sup>+</sup> EXCHANGE ON ZIRCONIUM PHOSPHATE AT TEMPERATURES UP TO 250°

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### SUMMARY

The ion exchange of trace amounts of <sup>45</sup>Ca<sup>2+</sup> on amorphous zirconium phosphate as a function of temperature and concentration of nitric acid was studied.

The effect of temperature, at constant pressure (80 atm.), was investigated as a function of nitric acid concentrations in aqueous solution. The experiments were made at 25, 50, 110, 150, 200 and 250°. Ion exchange of <sup>45</sup>Ca<sup>2+</sup> decreases with increasing temperature in the investigated temperature range. From these results, equilibrium constants for the Ca<sup>2+</sup>/H<sup>+</sup> ion exchange on amorphous zirconium phosphate and thermodynamic quantities for these reactions were calculated.

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### INTRODUCTION

The use of zirconium phosphate as a sorbent to remove ionic impurities from the cooling water from the PWR and BWR reactors has raised interest in the study of the ion-exchange, chemical and mechanical properties of zirconium phosphate at higher temperature<sup>1-6</sup>.

The purpose of this work was to study the dependence of the ion exchange of tracer amounts of <sup>45</sup>Ca<sup>2+</sup> on amorphous zirconium phosphate on temperature and aqueous phase composition. For this reason we have carried out experiments to determine the effect of temperature over the range 25 - 250° on the dependence of the ion exchange of calcium on the concentration of nitric acid.

### EXPERIMENTAL

#### *Preparation of zirconium phosphate*

Granulated amorphous zirconium phosphate was prepared by the method of VESELY AND PEKAREK<sup>7</sup>. After drying at 110°, a grain-sized fraction of  $r = 0.04$  mm was separated. The P/Zr ratio in the exchanger was 2.02. The capacity of the ion exchanger was determined as 2.40 mequiv./g of air-dried zirconium phosphate.

#### *Experimental procedure*

2.5 g of amorphous zirconium phosphate were equilibrated in an autoclave<sup>5</sup> with 250 ml solution. The samples were removed from the autoclave through a water-

cooled stainless steel tube. The equilibration time was 6 h, which was found to be sufficient to reach equilibrium.

#### Analytical methods

The zirconium phosphate sample was analyzed by the method developed by VESELY AND PEKAREK<sup>7</sup>. Radiometric determination of  $^{45}\text{Ca}$  was performed by means of a Nuclear Chicago 186A  $2\pi$  - detector.

The concentration of nitric acid was determined by titration against standard sodium hydroxide solution.

All reagents used were of "pro analysi" purity.

#### RESULTS AND DISCUSSION

In order to prove the reversibility of the  $\text{Ca}^{2+}/\text{H}^{+}$  exchange reaction, experiments with amorphous zirconium phosphate in the  $\text{Ca}^{2+}$  form were carried out. The zirconium phosphate contained  $5 \mu\text{Ci}$  of carrier-free  $^{45}\text{Ca}^{2+}$  per g of the exchanger. Results from desorption experiments (*i.e.*  $\text{H}^{+}/\text{Ca}^{2+}$  exchange), together with distribution coefficients of the  $\text{Ca}^{2+}/\text{H}^{+}$  exchange, are presented in Fig 1. It is clear that the ion-exchange process studied is reversible.

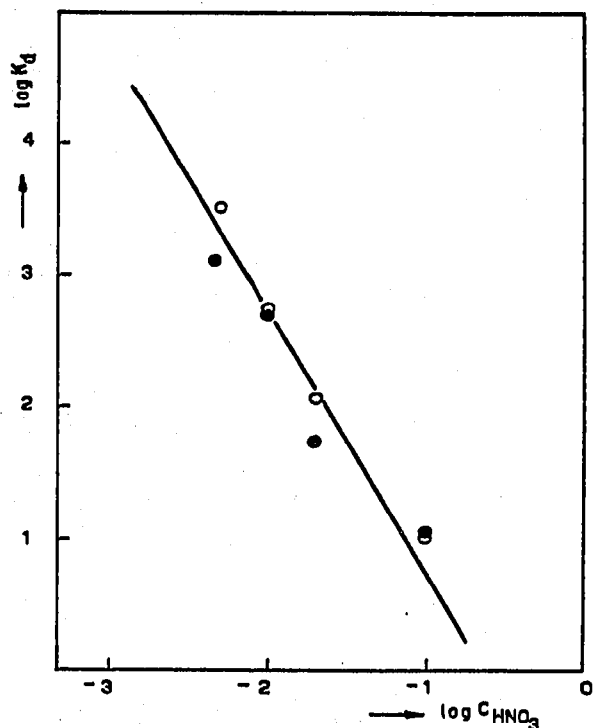


Fig. 1. Reversibility of  $\text{Ca}^{2+}/\text{H}^{+}$  exchange reaction at  $25^\circ$ . ○,  $\text{Ca}^{2+}/\text{H}^{+}$  exchange on amorphous zirconium phosphate; ●,  $\text{H}^{+}/\text{Ca}^{2+}$  exchange on amorphous zirconium phosphate.

The experiments were carried out in the autoclave mentioned above. The pressure was maintained constant (80 atm.) and experiments were carried out at  $25$ ,  $50$ ,  $110$ ,  $150$ ,  $200$  and  $250^\circ$ , with different acidities of the aqueous phase. The results are shown in Fig. 2.

From the results in Fig. 2, the Ca<sup>2+</sup>/H<sup>+</sup> exchange on amorphous zirconium phosphate can be considered according to the method of GAL AND RUVARAC<sup>8</sup>.

The exchange of M<sup>z+</sup> on an ion exchanger, HR, in the H<sup>+</sup> form, can be expressed by the equation

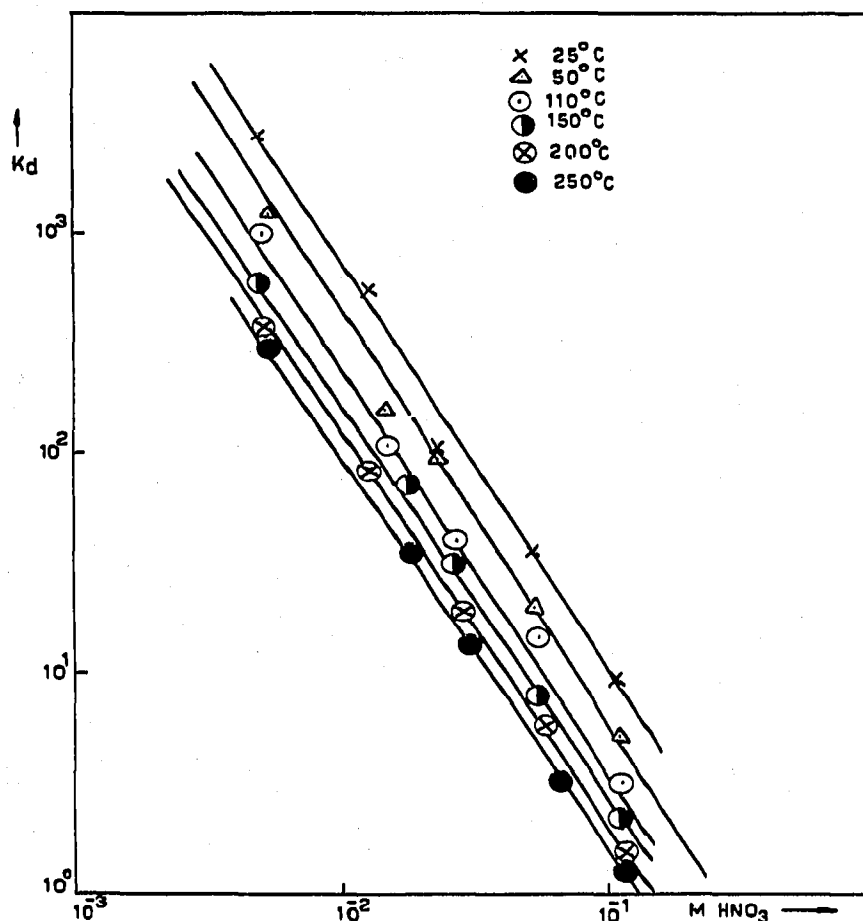


Fig. 2. The exchange of Ca<sup>2+</sup> as a function of nitric acid concentration in the aqueous phase over the temperature range 25 - 250°.

In eqn. 1 the subscript (aq) denotes the aqueous phase and (s) denotes the solid phase. The thermodynamic equilibrium constant for reaction (1) is expressed by

$$K = \frac{a_{MR_{z(s)}} \cdot (a_{H^+_{(aq)}})^z}{(a_{HR_{(s)}})^z \cdot (a_{M_{(aq)}})^z} \quad (2)$$

According to the earlier paper<sup>8</sup>, when M<sup>z+</sup> is present in trace concentration, one obtains the equation

$$\log K_d = -z \log \left[ m_H (\gamma_{\pm HNO_3})^2 \cdot (\gamma_{\pm M(NO_3)_z})^{-\frac{z+1}{z}} \right] + \log C + \log K \quad (3)$$

where  $K_d = n_M/m_M$ ,  $n$  is the number of millimoles of ion per g of the exchanger,  $m$  is the aqueous molality of ion,  $\gamma$  is the mean molal activity coefficient, and  $C$  the 'unifunctional' capacity of the exchanger. The last two terms in eqn. 3 are constant. The plot of eqn. 3 should therefore be a straight line with slope  $-z$ . Determining the value of the coefficient  $z$ , we can calculate the equilibrium constant of the ion exchange reaction. The values for  $\gamma_{\pm\text{HNO}_3}$  were taken directly from LIETZKE's tables<sup>9</sup>, while the values for  $\gamma_{\pm\text{Ca}(\text{NO}_3)_2}$  were calculated assuming the validity of Guggenheim's case of HARNED'S rule<sup>10</sup>.

From the calculated slopes, which are approximately equal to two, it is concluded that  $\text{Ca}^{2+}$  adsorption on amorphous zirconium phosphate occurs as the exchange of two hydrogen ions from zirconium phosphate and one calcium ion from solution.

Using the value  $z = 2$ , equilibrium constants were calculated by eqn. 3. The mean values of equilibrium constants, with standard deviation, are given in Table I.

From the dependence of  $\ln K$  on  $1/T$  (Fig. 3), the change of enthalpy ( $\Delta H$ ), free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) have been calculated (Table II). Furthermore, the plot shows that the dependence of  $\ln K$  on  $1/T$  is linear over a wide range of temperatures (25–250°). The exchange reaction is thus exothermic, which is in accordance with the results obtained by BAETSLÉ<sup>11</sup>.

TABLE I

EQUILIBRIUM CONSTANTS FOR  $\text{Ca}^{2+}/\text{H}^+$  ION EXCHANGE ON AMORPHOUS ZIRCONIUM PHOSPHATE AT 25, 50, 110, 150, 200 AND 250°.

Temperature $t(^{\circ}\text{C})$	$z$	$K$	
		Theoretical	Calculated
25	2	2.02	$(2.73 \pm 0.17) \cdot 10^{-2}$
50	2	1.78	$(1.82 \pm 0.47) \cdot 10^{-2}$
110	2	1.84	$(1.28 \pm 0.21) \cdot 10^{-2}$
150	2	1.86	$(0.968 \pm 0.12) \cdot 10^{-2}$
200	2	1.84	$(0.598 \pm 0.12) \cdot 10^{-2}$
250	2	1.96	$(0.406 \pm 0.057) \cdot 10^{-2}$

TABLE II

CALCULATED THERMODYNAMIC VALUES FOR  $\text{Ca}^{2+}/\text{H}^+$  EXCHANGE ON AMORPHOUS ZIRCONIUM PHOSPHATE.

Temperature $t(^{\circ}\text{C})$	$\ln K$	$\Delta H$ (kcal/mole)	$\Delta G$ (kcal/mole)	$\Delta S$ (cal/mole/degree)
20		-0.86 <sup>11</sup>	1.93 <sup>11</sup>	-9.3 <sup>11</sup>
25	-3.610	-2.30	2.12	-14.8
50	-4.260	-2.30	2.57	-15.1
110	-4.360	-2.30	3.32	-14.7
150	-4.630	-2.30	3.88	-14.6
200	-5.120	-2.30	4.80	-15.0
250	-5.500	-2.30	5.71	-15.3

If we compare our values for enthalpy change,  $\Delta H$ , entropy change,  $\Delta S$ , and free energy change,  $\Delta G$ , with the values obtained by BAETSLÉ<sup>11</sup> for Ca<sup>2+</sup>/H<sup>+</sup> exchange on zirconium phosphate, small differences are noticeable. These are due to the different crystalline forms of zirconium phosphate, and to different methods of calculation of thermodynamic values.

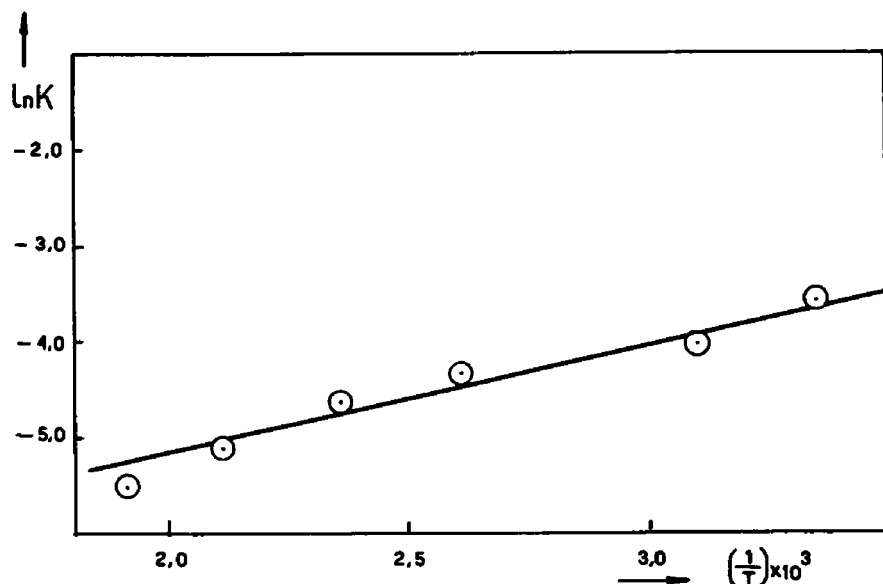


Fig. 3. Temperature dependence of the thermodynamic equilibrium constants.

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