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ION-EXCHANGE PROCESSES OF SOME TRIVALENT ELEMENTS ON AMORPHOUS ZIRCONIUM PHOSPHATE UP TO 250°C

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SUMMARY

The effect of temperature in the range 25–250° on the distribution of trace amounts of radioactive Eu^{3+} , Ce^{3+} and Fe^{3+} on amorphous zirconium phosphate, and also the effect of nitric acid concentration, have been studied. The experiments were carried out at 25°, 50°, 110°, 150°, 200° and 250°. With increasing temperature, the distribution of the trace amounts of Eu^{3+} and Ce^{3+} increased very slightly, while the increase in the distribution of Fe^{3+} was greater. Furthermore, it was concluded that the reactions investigated are endothermic.

These distribution data were used for the calculation of the thermodynamic equilibrium constants and other thermodynamic data.

INTRODUCTION

Zirconium phosphate, which is used as a sorbent to remove the ionic impurities from the cooling water of PWR and BWR reactors*, has become of interest in connection with its ion-exchange, chemical and mechanical properties at high temperatures¹⁻⁷.

In order to continue the study of ion-exchange processes on amorphous zirconium phosphate at high pressure and high temperature, experiments with trace amounts of radioactive Ce^{3+} , Eu^{3+} and Fe^{3+} in nitric acid solutions were carried out. The effect of temperature in the range 25–250° on the ion-exchange processes was studied as a function of nitric acid concentration.

EXPERIMENTAL

Preparation of zirconium phosphate

Granulated amorphous zirconium phosphate was prepared by the method described by VESELY AND PEKAREK⁸. After drying at 110°, a grain-size 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 found to be 2.40 mequiv. per gram of air-dried zirconium phosphate.

Procedure.

A 2.5 g amount of amorphous zirconium phosphate was equilibrated in an autoclave⁹ in 250 ml of solution. The samples were removed from the autoclave

* PWR = pressure water reactor; BWR = boiling water reactor.

through a water-cooled stainless-steel tube. The equilibration time was 6 h, which was found to be a sufficient period for equilibrium to be attained.

Analytical methods

The P/Zr ratio was determined in the zirconium phosphate sample by the method described by VESELY AND PEKAREK⁸. Radiometric determinations were performed by means of a γ -scintillation detector (Nuclear Chicago M-DSS5B, with a NaI (Tl) crystal).

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

All the reagents used were of "pro analysi" grade.

RESULTS AND DISCUSSION

The results for two runs which prove the reversibility of the ion-exchange reactions of the trivalent cations studied are presented in Fig. 1. In the first run, the trace amounts of radioactive Eu^{3+} ions were present in the initial solution, while in the second run they were adsorbed at the start on amorphous zirconium phosphate. It is clear from these two runs that the ion-exchange process studied is reversible.

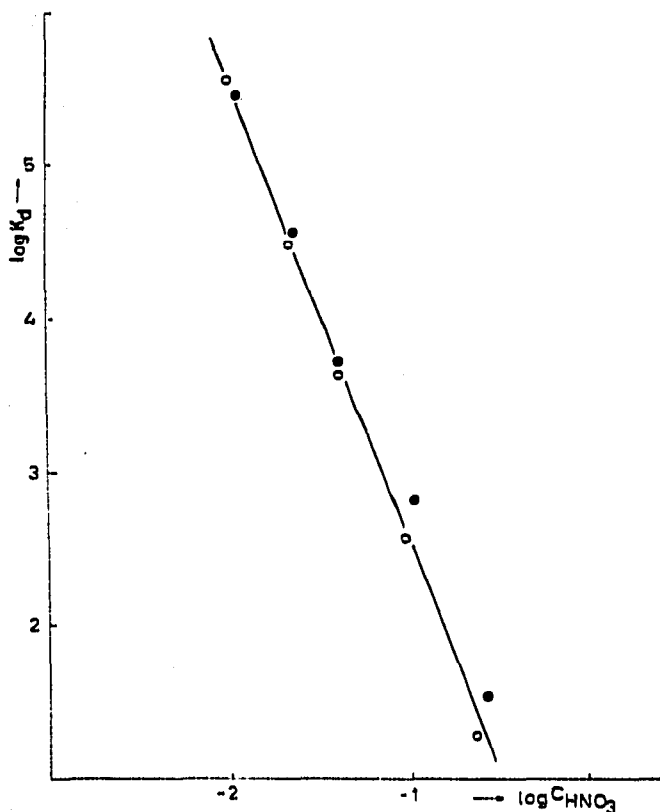


Fig. 1. Reversibility of $\text{Eu}^{3+}/\text{H}^+$ ion-exchange reaction on amorphous zirconium phosphate at 25°. O, $\text{Eu}^{3+}/\text{H}^+$ ion-exchange process; ●, $\text{H}^+/\text{Eu}^{3+}$ ion-exchange process.

In order to study the effect of temperature on the ion-exchange process as a function of the concentration of nitric acid, experiments were carried out in an autoclave. The pressure was maintained constant at 80 atm and experiments with different acidities in the aqueous phase were carried out at 25°, 50°, 110°, 150°, 200° and 250°C. The results are shown in Figs. 2-4.

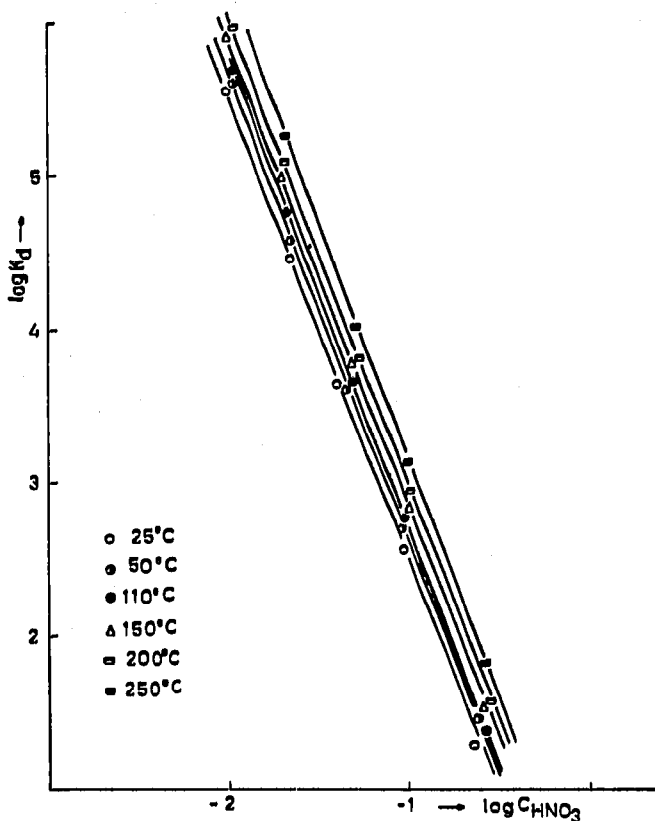


Fig. 2. The exchange of Eu^{3+} as a function of the nitric acid concentration in the aqueous phase in the temperature range 25–250°.

It is obvious from Fig. 2 that the effect of temperature on the distribution of Eu^{3+} between aqueous nitric acid and zirconium phosphate is very small. This result was also obtained by BAETSLE⁶ in the temperature range 25–75°. In our work the effect of temperature on the $\text{Eu}^{3+}/\text{H}^+$ ion-exchange process was opposite to that on the Cs^+/H^+ and $\text{Ca}^{2+}/\text{H}^+$ ion-exchange processes^{6,7}. The distribution coefficient ($K_d = n_M/m_M$, where n is the number of millimoles of an ion per gram of the air-dried exchanger and m is the aqueous molality of ion) for the $\text{Eu}^{3+}/\text{H}^+$ ion exchange slowly increases with increasing temperature.

The effect of temperature on the $\text{Ce}^{3+}/\text{H}^+$ ion-exchange process is shown in Fig. 3. In this instance the effect of temperature is greater than in the $\text{Eu}^{3+}/\text{H}^+$ ion-exchange process.

The effect of temperature on the distribution of Fe^{3+} between aqueous nitric

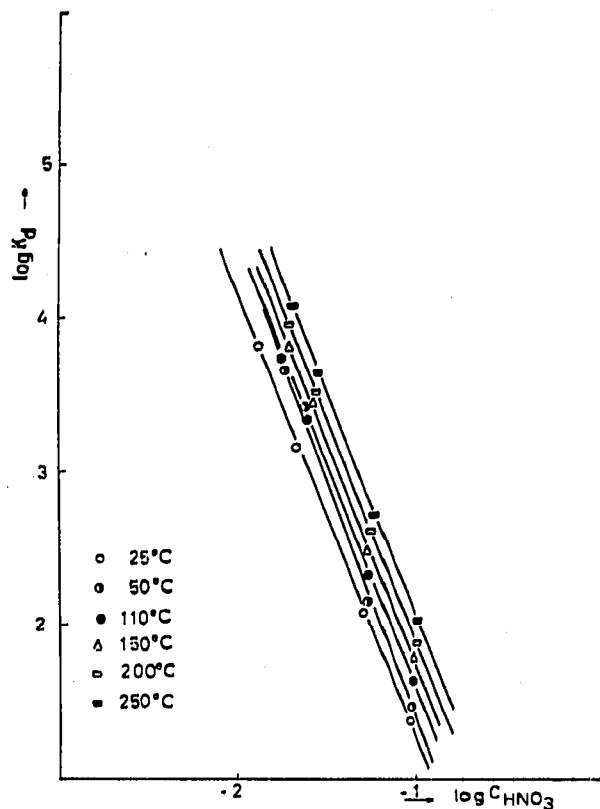


Fig. 3. The exchange of Ce^{3+} as a function of the nitric acid concentration in the aqueous phase in the temperature range 25–250°.

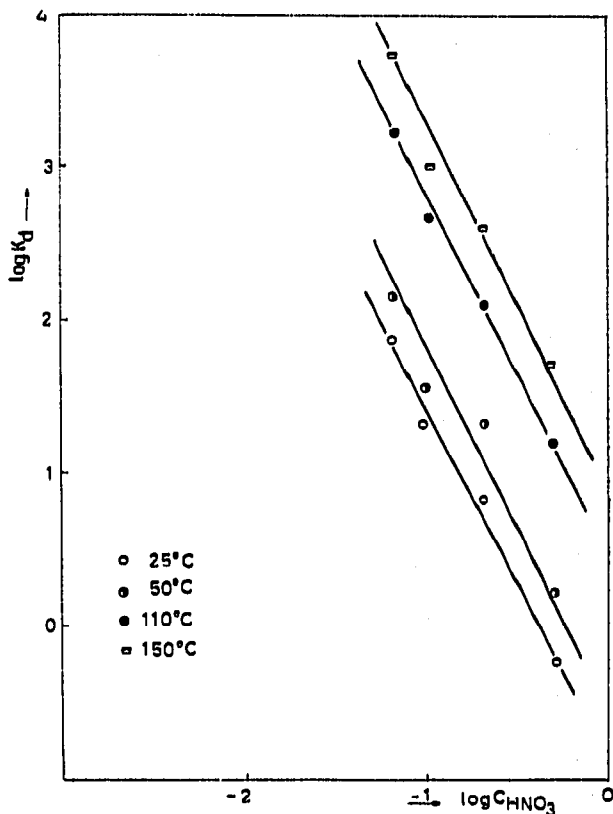


Fig. 4. The exchange of Fe^{3+} as a function of the nitric acid concentration in the aqueous phase in the temperature range 25–150°.

acid and amorphous zirconium phosphosphate (Fig. 4) is greater than in the $\text{Eu}^{3+}/\text{H}^{+}$ ion-exchange process.

In the study of the $\text{Fe}^{3+}/\text{H}^{+}$ ion-exchange process at temperatures above 150°, extensive hydrolysis of Fe^{3+} occurred.

The hydrolysis of Fe^{3+} at higher temperatures could be an advantage in water purification systems. The product of the hydrolysis is magnetite, $(\text{Fe}_3\text{O}_4)^{10}$, which is removed by means of a micropore filter.

The $\text{Fe}^{3+}/\text{H}^{+}$ ion-exchange process was not studied at temperatures above 150° owing to the extensive hydrolysis. However, the results obtained below 150° also have to be accepted with reserve because of the unknown state of the iron ions under such hydrothermal circumstances.

The exchange of an M^{z+} ion on the ion exchanger HR in the H^{+} form, can be expressed by the equation:



where the subscript (aq) denotes the aqueous phase and (s) denotes the solid phase.

According to an earlier paper¹¹, where M^{z+} is present at trace concentration, the following equation is obtained:

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

where γ_{\pm} is the mean molar activity coefficient and $C = n_H$ is the "unifunctional" capacity of the ion exchanger.

The last two terms in eqn. 2 are constant. Therefore, the graph of $\log K_d$ on the logarithm of the term in the square brackets should be a straight line with a

TABLE I

EQUILIBRIUM CONSTANTS FOR THE Eu^{3+}/H^+ ION-EXCHANGE PROCESS ON AMORPHOUS ZIRCONIUM PHOSPHATE AT 25°, 50°, 110°, 150°, 200° AND 250° CALCULATED BY EQN. 2

Temperature (°C)	z		K
	Theoretical	Calculated	
25	3	3.4	$(7.25 \pm 2.88) \cdot 10^{-2}$
50	3	3.3	$(8.75 \pm 5.41) \cdot 10^{-2}$
110	3	3.4	$(1.03 \pm 0.41) \cdot 10^{-1}$
150	3	3.3	$(2.09 \pm 1.18) \cdot 10^{-1}$
200	3	3.3	$(2.49 \pm 1.02) \cdot 10^{-1}$
250	3	3.4	$(3.57 \pm 1.35) \cdot 10^{-1}$

TABLE II

EQUILIBRIUM CONSTANTS FOR THE Ce^{3+}/H^+ ION-EXCHANGE PROCESS ON AMORPHOUS ZIRCONIUM PHOSPHATE AT 25°, 50°, 110°, 150°, 200° AND 250° CALCULATED BY EQN. 2

Temperature (°C)	z		K
	Theoretical	Calculated	
25	3	2.8	$(5.81 \pm 0.51) \cdot 10^{-11}$
50	3	3.1	$(8.09 \pm 1.25) \cdot 10^{-11}$
110	3	3.0	$(1.01 \pm 0.04) \cdot 10^{-10}$
150	3	3.0	$(1.51 \pm 0.07) \cdot 10^{-10}$
200	3	2.9	$(2.05 \pm 0.09) \cdot 10^{-10}$
250	3	3.0	$(2.78 \pm 0.11) \cdot 10^{-10}$

TABLE III

EQUILIBRIUM CONSTANTS FOR THE Fe^{3+}/H^+ ION-EXCHANGE PROCESS ON AMORPHOUS ZIRCONIUM PHOSPHATE AT 25°, 50°, 110, 150°, 200° AND 250° CALCULATED BY EQN. 2

Temperature (°C)	z		K
	Theoretical	Calculated	
25	3	2.8	$(5.81 \pm 2.62) \cdot 10^{-11}$
50	3	3.1	$(1.28 \pm 0.68) \cdot 10^{-10}$
110	3	3.2	$(8.33 \pm 2.06) \cdot 10^{-10}$
150	3	3.4	$(1.89 \pm 0.64) \cdot 10^{-10}$

slope z . By determining the value of the slope, z , the equilibrium constant of the observed ion-exchange reaction can be calculated. The values for $\gamma_{\pm} \text{HNO}_3$ were taken directly from LIETZKE's tables¹², while the values for $\gamma_{\pm} \text{M}(\text{NO}_3)_z$ were calculated assuming the validity of the Guggenheim's case of HARNED's rule¹³.

From the calculated slopes, which are approximately three, we concluded that the ion-exchange processes studied involve the exchange of three hydrogen ions from zirconium phosphate and one trivalent ion from the solution.

Equilibrium constants calculated by using $z = 3$ are shown in Tables I-III.

TABLE IV

CALCULATED THERMODYNAMIC VALUES FOR THE $\text{Eu}^{3+}/\text{H}^+$ ION-EXCHANGE PROCESS ON AMORPHOUS ZIRCONIUM PHOSPHATE

Temperature in K (°C)	ΔH° (kcal/mole)	ΔG° (kcal/mole)	ΔS° (cal/mole·degree)
25	—	0.65 ^a	1.14 ^a
25	-2.62	2.20	1.54
50	-2.43	2.20	1.56
110	-2.27	2.20	1.72
150	-1.56	2.20	1.31
200	-1.39	2.20	1.30
250	-1.01	2.20	1.15

^a Values obtained by BAETSLE⁹.

TABLE V

CALCULATED THERMODYNAMIC VALUES FOR THE $\text{Ce}^{3+}/\text{H}^+$ ION-EXCHANGE PROCESS ON AMORPHOUS ZIRCONIUM PHOSPHATE

Temperature in K (°C)	ΔH° (kcal/mole)	ΔG° (kcal/mole)	ΔS° (cal/mole·degree)
25	-5.15	2.00	3.04
50	-4.82	2.00	3.10
110	-4.58	2.00	3.48
150	-4.18	2.00	3.50
200	-3.89	2.00	3.64
250	-3.59	2.00	3.79

TABLE VI

CALCULATED THERMODYNAMIC VALUES FOR THE $\text{Fe}^{3+}/\text{H}^+$ ION-EXCHANGE PROCESS ON AMORPHOUS ZIRCONIUM PHOSPHATE

Temperature in K (°C)	ΔH° (kcal/mole)	ΔG° (kcal/mole)	ΔS° (cal/mole·degree)
25	-5.22	5.60	3.11
50	-4.32	5.60	2.78
110	-2.49	5.60	1.89
150	-1.67	5.60	1.40

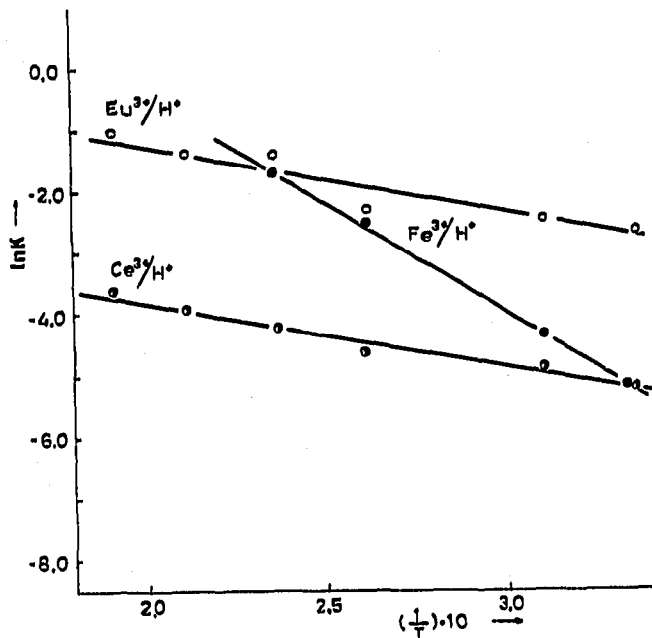


Fig. 5. Temperature dependence of the thermodynamic equilibrium constants for $\text{Eu}^{3+}/\text{H}^+$ (○) $\text{Ce}^{3+}/\text{H}^+$ (●) and $\text{Fe}^{3+}/\text{H}^+$ (●) ion-exchange processes.

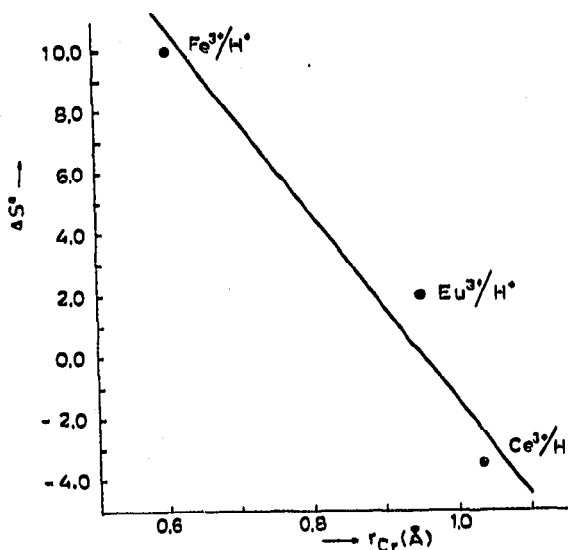


Fig. 6. The entropy changes of the ion-exchange processes as a function of the crystalline ionic radii.

The change of enthalpy, ΔH° , of free energy, ΔG° , of entropy, ΔS° , and the temperature dependence on $\ln K$ (Fig. 5), have been calculated and the results are given in Tables IV-VI. Furthermore, Fig. 5 shows that the $\ln K = f(1/T)$ plot is

linear over a wide range of temperature (25–250°). The exchange reactions are therefore endothermic.

The results obtained in the present study of the $\text{Eu}^{3+}/\text{H}^{+}$ ion-exchange process can be compared with those obtained by BAETSLE⁹. The values of the enthalpy change, ΔH° , show a notable difference, owing to the method of evaluation of the thermodynamic equilibrium constants.

The dependence of the entropy changes determined for the ion-exchange processes on the crystalline radii of the ions is presented in Fig. 6, and can be seen to be linear. The linear dependence of the entropy change could be explained if it is assumed that the material used in our experiments has a semicrystalline structure. This change of crystalline structure in the amorphous samples treated at higher temperature was observed in our earlier work¹⁴.

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