Inorg. Chem. **2004**, *43*, 7141–7145

Inorganic Chemistry

Article

Cation Mobility and Kinetics of Ion Exchange in Zirconium Hydrogen Monothiophosphate Hydrate, $Zr(HPO_3S)_2\cdot1.5H_2O$

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Received November 8, 2003

The ion conductivity of zirconium hydrogen monothiophosphate ($Zr(HPO_3S)_2\cdot1.5H_2O$) has been measured by impedance spectroscopy. The measured value of proton conductivity is 3×10^{-5} S/cm at 298 K. Conductivity was shown to decrease with increasing temperature due to a dehydration process. Above 450 K, the conductivity is likely governed by proton transport in the anhydrous phase $Zr(HPO_3S)_2$. The activation energies of proton conductivity were measured to be 18 ± 2 kJ/mol for $Zr(HPO_3S)_2\cdot1.5H_2O$ and 60 ± 3 kJ/mol for the anhydrous compound. The kinetics of ion exchange was studied with the use of potentiometric titration for several ion pairs, H^+/Na^+, H^+/Zn^{2+}, and Na^+/Zn^{2+} in $Zr(HPO_3S)_2\cdot1.5H_2O$. The diffusion coefficient values for H^+/Na^+ ion exchange in $Zr(HPO_3S)_2\cdot1.5H_2O$ are lower than those reported in α-zirconium phosphate. At the same time, the mobility of zinc ions in $Zr(HPO_3S)_2\cdot1.5H_2O$ is higher than sodium ion mobility. The ion exchange H^+/Zn^{2+} is accompanied by the slow hydrolysis of the initial compound. In all cases, the powdered solids were evaluated by powder X-ray diffraction, and particle sizes were controlled by grinding and sieving the powders.

Introduction

Inorganic ion-exchange materials such as the layered phosphates of tetravalent elements have been shown to have interesting conducting, catalytic, and ion-exchange properties.[1] Much attention was paid to the examination of ionic transport in these compounds.[2–6] In recent years, a search for similar ion-exchange materials with improved properties was performed. The greatest success was reached for some intercalation products and layered phosphates with oxygen atoms substituted for different organic groups, for example, sulfophenyl phosphonates. Thus, a series of materials with specific sorption and conductive properties were obtained.[7,8] The removal of heavy metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}, which are dangerous water impurities, is one of the most important problems in water purification. It is known that these cations have a high affinity to sulfur. Therefore, to improve the selectivity of ion-exchange materials, sulfur atoms can be introduced in their composition. Recently, we have reported the synthesis and characterization of metal(IV) thiophosphate-based compounds, $M(HPO_3S)_2$ (M = Zr, Hf).[9] These compounds were shown to demonstrate effective ion exchange and have high capacity and preference for transition metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+}). It was also shown that zinc ion exchange is reversible.[9]

In view of modern technological applications, both selectivity and the high rate of ion exchange are important. There are numerous reports on the ion-exchange kinetics studies of metal hydrogen phosphates.[6,10,11] However, the kinetics of ion exchange in zirconium monothiophosphate has not

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10.1021/ic035293m CCC: $27.50

yet been characterized. The present paper investigates the conductivity and kinetics of ion exchange of zirconium hydrogen monothiophosphate and its ion-exchange products.

Experimental Section

Synthesis of zirconium hydrogen thiophosphate was performed according to the process described earlier.[9] A 2.4-g amount of $ZrCl_4$ and 5.56 g of Na_3PO_3S were dissolved in separate 1 M HCl solutions. The two solutions were mixed, resulting in the immediate formation of a white gelatinous precipitate. The white gel mixture was stirred at room temperature for 24 h, after which it was centrifuged, and the clear aqueous portion decanted. The gel was washed several times with deionized water. Finally, the gel was isolated and dried under vacuum at room temperature for 24 h. The dried powders were ground to affect uniform particle sizes for sample evaluation.

The atomic ratio of Zr to P was confirmed for all samples by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin-Elmer P400 ICP atomic emission spectrometer equipped with a high-salt nebulizer. Thermogravimetric analysis (TGA) was performed on a TGD-700 (ULVAC SINCU-RIKO) apparatus with a heating rate of 10 K/min. According to ICP-AES and TGA data, the as-prepared compound should be formulated as $Zr(HPO_3S)_2 \cdot 1.5H_2O$.

Powder X-ray diffraction (XRD) measurements were recorded with a Guinier camera FR-552 using Cu Kα radiation and digitized using a densitometer. A scanning Scintag X2 diffractometer was also used in a study of crystallite sizes. Microphotographs were obtained on a scanning electron microscope, JSM-U3. Impedance measurements were performed using an impedance meter, IPU-62, operating from 10 Hz to 2 MHz on an orthorhombic pellet ($60 \times 70 \times 40$ mm) over the temperature range 300−590 K. Graphite electrodes were used for the measurements because of the high affinity of $Zr(HPO_3S)_2$ to transition metals, including silver. Conductivity values were obtained by the extrapolation of the semicircle to the resistance axis, Figure 1.

The ion-exchange process was investigated by means of pH value measurements. For the potentiometric titration, a Mettler-Delta 340 pH millivoltmeter was used. The details describing this method of the experiment may be found in ref 11. A 90-mg sample of $Zr(HPO_3S)_2 \cdot 1.5H_2O$ was equilibrated with 0.1 N NaCl solution at 300 ± 1 K. Portions of 0.096 M NaOH solution were added incrementally, and the pH was measured every 2 s. After equilibrium was achieved, the next portion of alkali solution was added. Rapid mixing of the solutions was carried out during the experiment. The process of mixing may have resulted in breaking apart larger particles in the suspension of solid, but the processes for all experiments were repeated several times and were consistent. Crystallite size analysis of the XRD patterns of samples before and after the exchange reactions did not indicate a dramatic change in the overall crystallite sizes of the solids. Nevertheless, XRD analysis will not effectively measure any amorphous phosphate materials that may have been present during the exchange reactions. Ion exchange for Zn^{2+} ions was studied for both the hydrogen and sodium forms of the host solids by means of 0.02 N $ZnCl_2$ solution addition.

Results and Discussion

According to the electron microscopy data, our material forms as poorly crystalline aggregates of small crystallites as seen in the micrograph, Figure 2. The average size of the particles was calculated from numerous micrographs and was observed to be about 10 μm with a fairly broad distribution (up to 40 μm for larger particles). It should be noted that the particle sizes were not necessarily equivalent to the crystallite sizes which are measured more accurately by XRD. The X-ray diffraction pattern of our $Zr(HPO_3S)_2 \cdot 1.5H_2O$ compound corresponds to that reported in ref 9, though most reflections were shifted to slightly higher 2Θ, likely a result of the drying process used in these studies.

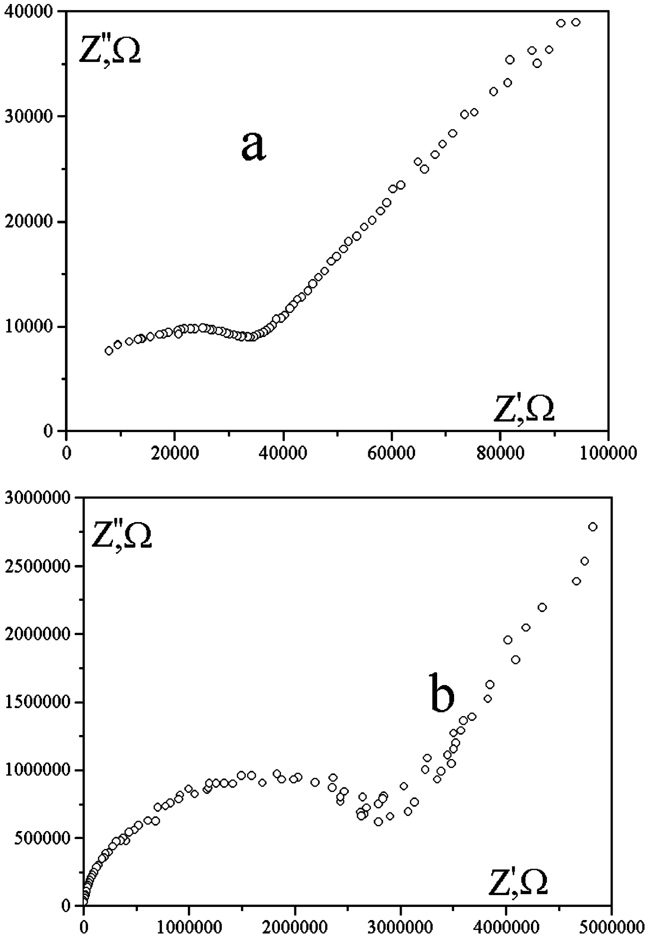

Figure 1. Impedance plots for $Zr(HPO_3S)_2 \cdot 1.5H_2O$ at (a) 299 K and (b) 500 K . Z' and Z'' are the real and imaginary impedance, respectively.

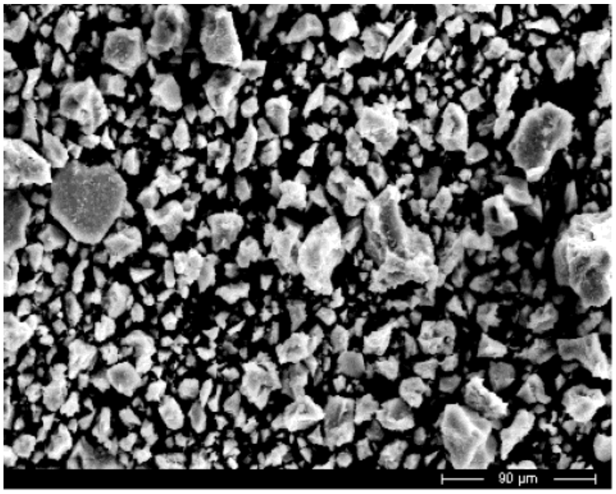

Figure 2. Scanning electron micrograph of $Zr(HPO_3S)_2$ with a 90 μm scale bar.

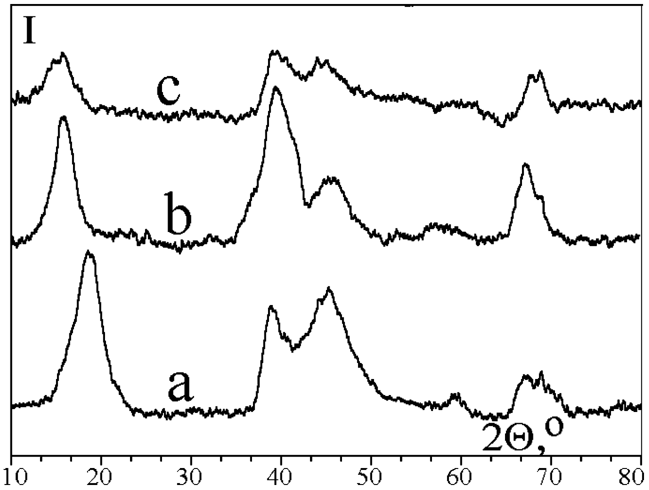

Figure 3. Selected regions (2Θ) of the X-ray powder diffraction patterns of (a) $Zr(HPO_3S)_2{\cdot}1.5H_2O$, (b) $Na_2Zr(HPO_3S)_2{\cdot}nH_2O$, and (c) $Zn_xZr(H_{1-x}PO_3S)_2{\cdot}nH_2O$.

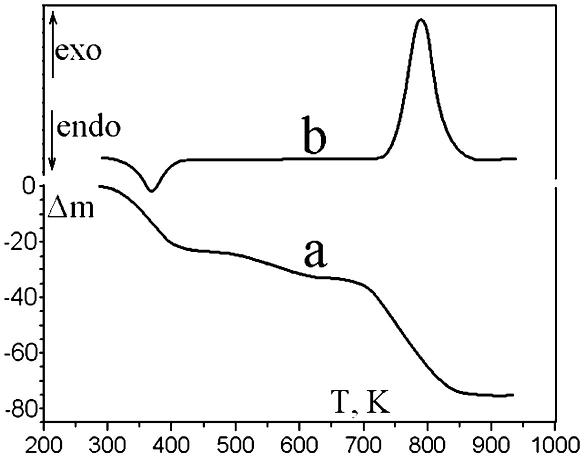

Figure 4. (a) Thermogravimetric analysis and (b) differential scanning calorimetry plots of $Zr(HPO_3S)_2{\cdot}1.5H_2O$. Δm is shown as the absolute change in atomic mass units where the initial value is 342.20 amu.

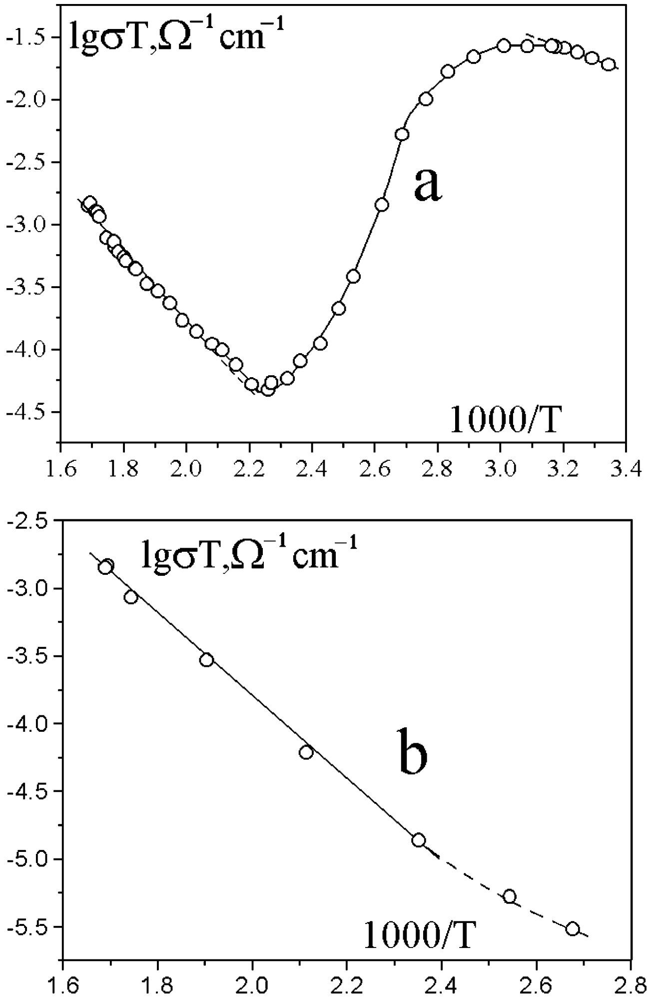

Figure 5. Temperature dependence of conductivity for $Zr(HPO_3S)_2{\cdot}nH_2O$ during (a) heating and (b) cooling.

An interlayer distance of 8.9 Å is a little bit less than that observed in ref 9, and the peak width is noticeably greater, Figure 3a. The sizes of individual crystallites (coherent scattering lengths) as indicated by the broadening of the XRD peaks at 19.9° (the (002) reflection) and the (110) reflection are between 150 and 100 Å, using the well-known Scherrer relationship.

On the basis of thermal analysis of the material, the heating of zirconium thiophosphate to greater than 315 K resulted in dehydration of the sample accompanied by an endothermic heat transfer as seen in Figure 4; the absolute mass loss in atomic mass units is plotted on the ordinate axis. The maximal rate of hydration water loss was reached at about 350 K. Anhydrous zirconium thiophosphate ($Zr(HPO_3S)_2$) was obtained at 430 K. Continued heating to about 650 K results in the loss of another half a water molecule per unit formula as a consequence of partial anion condensation (a maximum rate of weight loss occurred at about 560 K). Continual heating with further dehydration and oxidation of the thiophosphate resulted in the formation of ZrP_2O_7 at temperatures higher than 670 K. This process was accompanied by a strong exothermic event at 780 K. Thus, thermal decomposition of zirconium thiophosphate can be expressed by the following scheme according to the weight loss observed

$$Zr(HPO_3S)_2{\cdot}1.5H_2O \xrightarrow{350\ K} Zr(HPO_3S)_2 \xrightarrow{450\ K} Zr_2H_2P_4O_{11}S_4 \xrightarrow{780\ K} ZrP_2O_7 \quad (1)$$

where sulfur is probably lost as H_2S or S_2.

Because $Zr(HPO_3S)_2{\cdot}1.5H_2O$ has a structure and a nature similar to those of α-zirconium phosphate, it was likely that it would possess proton conductivity too. Conductivity of zirconium thiophosphate was measured to be 6.3×10^{-5} S/cm at room temperature and increased slightly up to 325 K, as seen in Figure 5, according to the Frenkel equation

$$\sigma T = A \exp(-E_\sigma/RT) \qquad (2)$$

where σ is the proton conductivity and E_σ is its activation energy. The calculated value of E_σ was 16 ± 2 kJ/mol. This low activation energy is similar to that for particle hydrates.[1,12] In these compounds, proton transport occurs mainly in a thin film of water sorbed on a particle surface.[12,13] It is

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Table 1. Conductivity and Activation Energies for α-$Zr(HPO_4)_2\cdot H_2O$ and $Zr(HPO_3S)_2\cdot 1.5H_2O$

compound	σ (298 K) Ω^{-1} cm^{-1}	σ (473 K) Ω^{-1} cm^{-1}	σ (573 K) Ω^{-1} cm^{-1}	E_σ, kJ/mol	ref
$Zr(HPO_3S)_2\cdot 1.5H_2O$	6.3×10^{-5}			16 ± 2	*b*
$Zr(HPO_3S)_2$		1.4×10^{-7}	1.5×10^{-6}	59 ± 3	*b*
$Zr(HPO_4)_2\cdot H_2O$[a]	1.65×10^{-6}				17
$Zr(HPO_4)_2$		1.9×10^{-7}	2.8×10^{-7}	65 ± 3	15

[a] Conductivity of crystalline α-$Zr(HPO_4)_2\cdot H_2O$ perpendicular to (001) direction. [b] This work.

necessary to note that the conductivity of layered phosphates depends strongly on their crystallinity at least for the protonic form. Microcrystalline compounds typically displayed higher conductivity values.[14] In our samples, the relative conductivities and ion-exchange rates are comparable to those for α-zirconium phosphate.

Increasing the temperature above room temperature resulted in a considerable decrease in conductivity due to sample dehydration. The minimum σ value (8×10^{-8} S/cm) was reached at 445 K. At this temperature, the loss of water molecules weakly held by hydrogen bonding in the $Zr(HPO_3S)_2\cdot 1.5H_2O$ structure or on its surface was complete. Above 450 K, conductivity was determined by proton transport in anhydrous zirconium thiophosphate and increases according to eq 2. The measured conductivity data agree very well with those for anhydrous α-$Zr(HPO_4)_2$ presented earlier in refs 15 and 16. The similarity of conductivity values confirmed that the $Zr(HPO_3S)_2$ structure is similar to that of α-$Zr(HPO_4)_2$. It is necessary to note that dehydration processes proceed much more slowly in pressed pellets. The observed linearity of temperature dependence of conductivity in coordinates ln σT vs 1000/T showed that there were not any phase transitions or chemical transformations in this temperature range. Moreover, conductivity values were readily reproduced through both heating and cooling cycles (470−580 K). Zirconium monothiophosphate displayed measurable ion-exchange properties. Addition of 0.1 N NaCl solution to $Zr(HPO_3S)_2\cdot 1.5H_2O$ led to the gradual decrease in the pH value to 2.43. Further alkali addition resulted in a sharp increase in pH followed by a subsequent decrease to an equilibrium pH value. Equilibrium pH values increased continuously with alkali addition as illustrated in Figure 6. Thus, the ion-exchange process for this compound can be considered a single-stage process that proceeds via a solid−solution formation. X-ray diffraction data confirmed that the ion-exchange products formed for each ion-exchange step were single phase products. From this behavior, zirconium thiophosphate differs from the fully crystalline α-$Zr(HPO_4)_2\cdot H_2O$ in which the uptake of cations into the structure resulted in the formation of a new phase.[17] Two phases coexist at each step of the H^+/Na^+ exchange in crystalline α-$Zr(HPO_4)_2\cdot H_2O$. The titration curve consists of two perfect plateaus. This difference could be attributed to the low degree of crystallinity of $Zr(HPO_3S)_2\cdot 1.5H_2O$. Clearfield has shown that the decrease in $Zr(HPO_4)_2\cdot H_2O$ crystallinity resulted in the transformation of titration curves from two plateaus to a continuous increasing pH.[18]

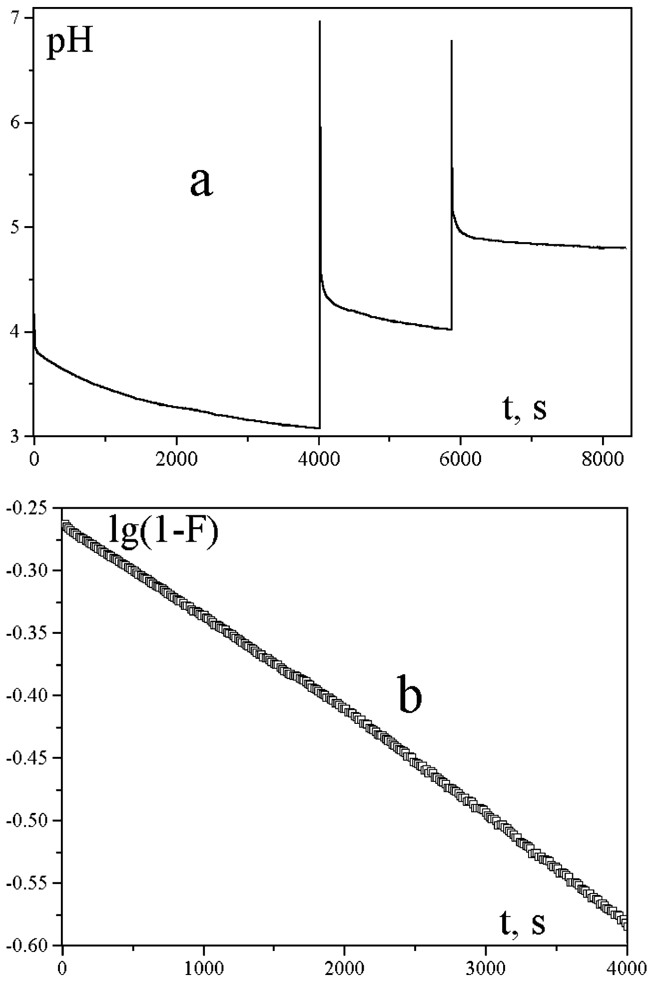

Figure 6. (a) Time dependence of the pH values after addition of the first portions of alkali solutions to $Zr(HPO_3S)_2\cdot 1.5H_2O$ in 1 M NaCl solution. (b) The same dependence plotted in log(1 − F) vs t coordinates as described in ref 19.

The Boyd equation can be used for the analysis of kinetics of ion exchange proceeding via a solid−solution formation[19]

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}(1/n^2)\exp(-Dt\pi^2 n^2/R^2) \qquad (3)$$

where R is the radius of exchanger particle and D is the effective diffusion coefficient of alkaline metal and hydrogen ions within the exchange solid. The extent of reaction, F, is expressed as a ratio of the amount of exchange at time t to the amount of exchange at infinite time.

The kinetic data behaved in a linear fashion when plotted as log(1 − F) vs t, as seen in Figure 6b. The average value of the diffusion coefficient gradually decreased from

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(4.3 ± 0.3) × 10^{-11} for zirconium thiophosphate to (1.7 ± 0.2) × 10^{-11} cm^2/s for $Na_2Zr(PO_3S)_2{\cdot}nH_2O$. This behavior suggests that hydrogen ions in $Zr(HPO_3S)_2{\cdot}1.5H_2O$ are more mobile than their sodium ion counterparts in the sodium derivative compound. The calculated diffusion coefficients for the H^+/Na^+ exchange in $Zr(HPO_3S)_2{\cdot}1.5H_2O$ were lower than those reported for $Zr(HPO_4)_2{\cdot}H_2O$, which may not be unexpected given the weaker hydrogen bonding in the sulfur derivative.[6] Nevertheless, the exact conditions in our earlier work[6] may not have been duplicated in the case of this new sulfide derivative given the sensitivity of the ion-exchange process to particle size.

Addition of zinc chloride solution to $Zr(HPO_3S)_2{\cdot}1.5H_2O$ led to a greater pH change than that observed for sodium exchange. Even after adding of 1 mL of 0.02 N $ZnCl_2$ solution, the pH value decreased to 2.0. It correlates with the data presented earlier where it was found that zirconium thiophosphate had a high selectivity for sorption of zinc ions.[9] In this case, the pH value also changed faster than that for sodium cations. On the basis of our observations, the calculated diffusion coefficients for the H^+/Zn^{2+} exchange are (8 ± 1) × 10^{-10} cm^2/s. However, contrary to the H^+/Na^+ exchange, the data are linear only as $\log(1 - F)$ vs t for the first stages of ion exchange. Even after aging this system more than 1 day, the equilibrium was not achieved completely and the pH value still decreased slightly. This can be due to slow hydrolysis of the solid according to the equations

$$(Zn_xH_{2-2x})Zr(PO_3S)_2 + H_2O \rightarrow (Zn_xH_{2-2x})Zr(PO_4)_2 + H_2S \quad (4)$$

or

$$(Zn_xH_{2-2x})Zr(PO_3S)_2 + xH_2O \rightarrow Zr(HPO_4)_2 + xZnS \quad (5)$$

It is most probable that hydrolysis proceeds via an attack on the PO_3S^{3-}-group by hydrogen ions. To minimize this process, about 50% of the protons in $Zr(HPO_3S)_2{\cdot}1.5H_2O$ were substituted for sodium ions. Thus, the pH value of a solution contacted with this sodium compound ($NaHZr(PO_3S)_2{\cdot}nH_2O$) increased up to 4.77. However, Zn^{2+} substitution in $NaHZr(PO_3S)_2{\cdot}nH_2O$ was also accompanied by a slow hydrolysis. The calculated diffusion coefficient for this exchange in the linear region, (3.8 ± 0.8) × 10^{-10} cm^2/s, is lower than that observed for the H^+/Zn^{2+} exchange due to a lower mobility of sodium ions as compared with protons in a matrix of ion-exchange solid. However, the added complexity of the hydrolysis reaction and the dependence of the kinetics on particle size can affect these values.

Conclusions

Zirconium hydrogen monothiophosphate has ion-exchange and ion-conducting properties similar to those reported for α-$Zr(HPO_4)_2{\cdot}H_2O$. The mobility of sodium ions in α-$Zr(HPO_4)_2{\cdot}H_2O$ was higher than that of ion-exchange products of $Zr(HPO_3S)_2{\cdot}1.5H_2O$. At the same time, $Zr(HPO_3S)_2{\cdot}1.5H_2O$ differed from α-$Zr(HPO_4)_2{\cdot}H_2O$ by the higher H^+/Zn^{2+} ion-exchange rate and the greater selectivity for zinc ions. However, ion-exchange products were gradually hydrolyzed accompanied by zinc sulfide formation making the assignment of a precise ion-exchange mechanism difficult.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (Grant No. 03-03-32439) and the complex program of the Russian Academy of Science, “New Principles and Methods of Development and Direct Synthesis of Materials with Given Properties” (Grant No. CB-2.13) as well as by National Science Foundation (DMR-0076180). We also wish to thank the reviewers for their insights and helpful comments.

IC035293M