

in ethylene dichloride since dilution of solutions was impractical due to the instability of the Co(III) complexes in this solvent.

The ion-pair association constants (K_{ip}) from fits of kinetic data to concentration of BF_4^- are below 10 for all the reactions in acetonitrile. Such slight association is expected in species of low charge-to-size ratio. The ion pairing of $[\text{Co}(\text{nox})_3(\text{BF})_2]^+$ and $[\text{Co}(\text{dmg})_3(\text{BF})_2]^+$ calculated here can be compared with that of the same complexes in their reaction with ferrocene from an earlier study.¹⁴ The extent of association in both studies should be the same, within the precision of the measurements, since the rate variation is being attributed to the same ion-pairing process. Table V shows that similar values are obtained, but in this study the *nox* complex showed more association, while in the previous study the dimethylglyoxime complex gave a larger K_{ip} . The differences are not considered large enough to justify an interpretation. Also shown in Table V is the agreement in K_{ip} observed in the two reactions where $[\text{Co}(\text{dpg})_3(\text{BPh})]\text{BF}_4$ reacts in acetonitrile.

Data from the salt dependences in various solvents also agree with ion-pairing of the charged reactant. The fifth column in Table VI shows that, as expected, the association of $\text{Co}(\text{nox})_3(\text{BF})_2^+$ with BF_4^- increased as the dielectric constant of the solvent decreased. Again, a comparison of ion-pairing constants is possible. The K_{ip} values calculated here can be compared with those of $[\text{Co}(\text{dmg})_3(\text{BF})_2]^+$ in the same solvents⁵ as shown in the last column of the same table. The $[\text{Co}(\text{nox})_3(\text{BF})_2]^+$ studied here gives somewhat lower K_{ip} values than the previous work with $\text{Co}(\text{dmg})_3(\text{BF})_2^+$, but the trend in K_{ip} with the changing dielectric of the solvents is the same in both studies. The effect of added salt observed here corroborates previous findings^{5,14,21} that ion pairing decreases the rate constant for electron transfer between a neutral reactant and a charged reactant.

The ratio of the free-ion rate to the ion-paired rate, (k_0/k_{ip}), is typically 4 but it increases to 10 for acetone, the lowest dielectric solvent studied. This agrees generally with predictions from Marcus theory as discussed above for the second-order rate

constants. The ratio of the rate constants for the $[\text{Co}(\text{nox})_3(\text{BF})_2]\text{BF}_4$ reactions in various solvents can also be compared with previous results⁵ for the ferrocene reduction of $[\text{Co}(\text{dmg})_3(\text{BF})_2]\text{BF}_4$ as shown in Table VI. Comparable values are obtained with the possible exception of the reaction in nitrobenzene, the only solvent with an aromatic ring. A review of the k_0 and k_{ip} values for the two reactions in all solvents indicates that the k_0 value for the present study in nitrobenzene is uncharacteristically low. As discussed above, the rate constants for each path are predicted by Marcus theory to increase in the order $\text{MeCN} < (\text{CH}_3)_2\text{CO} \ll \text{C}_6\text{H}_5\text{NO}_2$ after correction for the driving force of the reaction. In the present work, the rate constant for neither path fulfills this expectation. This supports the conclusion, based on the rate constants at 0.1 M Bu_4NBF_4 shown in Table II, that precursor complex stability changes are influencing the reactivity pattern.

Conclusion

In conclusion, a series of reactions between cobalt clathrochelates has been studied as a function of the structure of the complexes, concentration, temperature, added electrolyte, and solvent. In general, the rate constants agree with Marcus theory predictions, decrease in the presence of added salt, and are consistent with previous measurements on the same complexes reacting with ferrocene. The possible exception is the oxidation of $\text{Co}(\text{nox})_3(\text{BPh})_2$ by $[\text{Co}(\text{dpg})_3(\text{BPh})_2]\text{BF}_4$, which occurs more slowly than predicted. The activation parameters and solvent dependence indicate that subtle changes in solvation or precursor complex structure or stability are occurring which do not lead to large changes in rate constants.

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Supplementary Material Available: Tables of all kinetic data, their standard deviations, and their conditions (6 pages). Ordering information is given on any current masthead page.

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Lamellar Inorganic Ion Exchangers. Alkali Metal Ion Exchange on α - and γ -Titanium Phosphate

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Alkali metal ion exchange on α - and γ -titanium phosphate is reported. In α -titanium phosphate, Li^+ and Na^+ exchange in acidic solution but K^+ and Cs^+ do not. Phases of half and full exchange are formed. In the γ -titanium phosphate, Li^+ , Na^+ , K^+ , and Cs^+ exchange in acidic solution. Phases of 25, 50, and 100% substitution are formed. The selectivity sequences are obtained from the study of binary systems, and their validity for polyionic systems is discussed. Free energy, enthalpy, and entropy of the exchange reactions are also presented. A mechanism of exchange is proposed.

Introduction

The existence of molecular sieves with a pore size between 6 and 40 Å obtained from clays by intercalation of organic compounds has been known for a long time. These compounds can only be used at low temperatures, since temperatures higher than 300 °C result in their decomposition and a drastic decrease of the interlayer spacing.¹ In recent years, special attention has been paid to the properties of a new type of synthetic inorganic material, mainly in the catalysis field. These are the clays with pillars. Under this name are known the clays that, after the intercalation of inorganic polymeric species into their interlayer spacing, present a basal spacing close to 18 Å. These intercalation compounds

show a microporous system and a thermal stability similar to those of the zeolites.^{2,3}

In the last 20 years, noticeable efforts in the synthesis and characterization of a group of lamellar phosphates of tetravalent metals have been made.⁴⁻⁶ These compounds behave as cationic exchangers. The viability of intercalating polar organic molecules

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Table I. Acid Phosphates of Zirconium or Titanium with Layered Structure

compd	formula	interlayer dist, Å	ion-exchange capacity, mequiv/g
α -ZrP	Zr(HPO ₄) ₂ ·H ₂ O	7.56	6.64
α -TiP	Ti(HPO ₄) ₂ ·H ₂ O	7.6	7.75
γ -ZrP	Zr(HPO ₄) ₂ ·2H ₂ O	12.2	6.26
γ -TiP	Ti(HPO ₄) ₂ ·2H ₂ O	11.6	7.24
β -ZrP	Zr(HPO ₄) ₂	9.4	7.06
β -TiP	Ti(HPO ₄) ₂	9.1	8.33

into their interlayer spacing is also well-known. The ionic substitution processes as well as those of the intercalation of organic molecules usually result in an increase (only sometimes a contraction) of the interlayer distance of the system. The structural characteristics and the chemical behavior make the lamellar phosphates of tetravalent metals comparable with clay materials.⁷⁻⁹ Besides, catalytic properties have been detected in the metallic phases of some lamellar phosphates originated during the ion-exchange processes.^{10,11} These types of compounds might be expected to exhibit similar behavior to that observed in many phyllosilicates relative to pillaring reactions¹² with the additional advantage that the system is now very easy and regular.

Titanium phosphate can be prepared as a gel, in several crystalline forms and in intermediate stages of crystallinity.^{13,14}

In the preparation of the amorphous titanium phosphate many different products can be obtained depending on the working conditions. This is explained by the presence of Ti(IV) in the solutions as complex species Ti(OH)_x^{4-x} (x = 2, 3) by their polymerization and by the possible exchange of OH⁻ groups or molecules of coordination water by H₂PO₄⁻ or HPO₄²⁻ groups during the precipitation.¹⁵ In these gels, the P₂O₅:TiO₂ ratio varies between 0.5 and 1.0 and it approaches unity when the acidity, the digestion time, and the ratio P₂O₅:TiO₂ in the reactants increases.^{16,17} In the main, a chemical composition of Ti₄O₂·(HPO₄)₃(H₂PO₄)_x(OH)_{6-x}·yH₂O for these materials was proposed, where x varies between 0 and 6 and the water content depends on the drying method.^{18,19}

The results obtained in the study of ion exchange in titanium phosphate gels are difficult to compare owing to the different behavior of the gel, which is dependent on the preparation conditions. In addition, the effective capacity of the exchanger varies with the pH of the solution and the nature of the ingoing ion. These factors were not properly taken into account in many studies. These materials should be prepared and characterized by standardized methods in order to obtain reliable results.²⁰

The main factors affecting the ion-exchange behavior of the phosphates of tetravalent metals are their structures and the degree of crystallinity. In order to obtain a crystalline product, the gel needs to be refluxed in concentrated H₃PO₄ for a long time. The crystallization mechanisms occur through a dissolution of the gel

and subsequent nucleation and growing of the crystals, and the H₃PO₄ concentration determines the crystallinity and type of product obtained.

When the tetravalent metal is titanium and the concentration of H₃PO₄ is 10 M, the solid obtained after 50 h of reflux is a crystalline product with the composition Ti(HPO₄)₂·H₂O (α -TiP).¹⁹ It is a lamellar compound isomorphous with the Zr(HPO₄)₂·H₂O (α -ZrP).^{5,22-26} If the concentration in H₃PO₄ is 15.5–17.0 M, the product obtained after 7–10 days and washed with deionized water has a composition Ti(HPO₄)₂·xH₂O (x = 0.8–1.1).²⁷ This quasi-stable form is in fact a mixture of two phases: Ti(HPO₄)₂·2H₂O (γ -TiP) and Ti(HPO₄)₂ (β -TiP).^{14,28,29} γ -TiP loses its two molecules of hydration water in the temperature range 40–100 °C, being transformed into β -TiP, which tends to rehydrate in air.^{27,30,31} The similar compound of zirconium is also known: Zr(HPO₄)₂·2H₂O (γ -ZrP).³² Some data about these compounds are collected in Table I. The structure of the γ -compounds is so far unknown, but their layered composition is well proved.^{33,34} The structure of the α - and γ -layers seems to be different, the latter being more compact.³⁵ An idealized model for the structure of γ -ZrP is proposed by Clayden³⁶ on the basis of solid-state ³¹P magic-angle-spinning NMR spectroscopy. According to this author, there are two chemically distinct types of phosphate groups in equal proportions, one a framework-type phosphate and the other a dihydrogen phosphate group. The fact that the interlayer distance of γ -type compounds is higher than that of the α -type (Table I) allows a better ionic diffusion to large cations to be expected.

In the systematic determination of the ion-exchange properties of a material, it is very important that the study of its behavior against that of ions with similar chemical characteristics but different size be carried out. A suitable group is the alkali-metal ions, since they are monovalent, with a noble gas electronic configuration, and thus, the size of the cation can be directly related to the structural characteristics of the exchanger solid.

Experimental Section

Reagents. All chemicals used were of reagent grade. α -TiP was obtained by the method described by Alberti et al.,²¹ using 10 M H₃PO₄ and reflux times of 50 h. γ -TiP was obtained by using 16.5 M H₃PO₄ and reflux times of 10 days, as previously described.²⁷

Analytical Procedures. The analysis of the concentration of phosphorus in the solid was carried out gravimetrically as magnesium pyrophosphate, while the titanium was determined with cupferron.³⁷ The pH measurements were made in a Crison Model 501 pH meter. The released phosphate groups were measured spectrophotometrically³⁸ by using a Perkin-Elmer Model 200 instrument. The alkali metals in solution were determined by atomic absorption spectrometry by using a Perkin-Elmer Model 372 spectrometer. Thermal analysis (tga and dta) was performed by a Chio Model TRDA-3H instrument (rate of heating 8 °C/min). The

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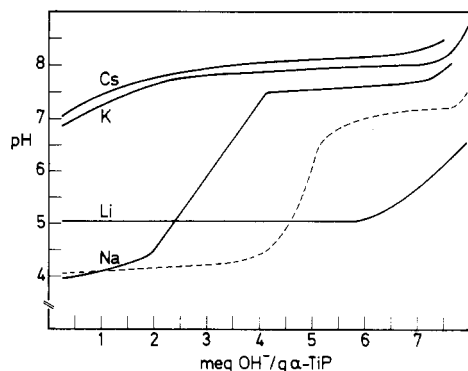


Figure 1. H^+/M^+ system in α -TiP: pH curves at 25.0 °C. The dashed line represents the pH curve of the H^+/Na^+ system at 5.0 °C.

diffractometer used was a Philips Model PV 1050/23 with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 2θ scan rate $0.125-2^\circ/\text{min}$, chart speed $2 \text{ cm}/\text{min}$). The quantitative X-ray measurements were obtained by cutting out the areas of the 002 reflections of the crystalline phases and weighing them.

Ion-Exchange Studies. The α -TiP was equilibrated with 0.1 M (Li, Na, K, Cs)Cl + (Li, Na, K, Cs)OH solutions at 25.0 + 0.1 °C, following the procedure described by Clearfield et al.³⁹ The equilibration time was 48 h. The solid was present in the solution in an approximate ratio of 500 mL:1 g.

The γ -TiP was equilibrated with (Li, Na, K, Cs)Cl + HCl or (Li, Na, K, Cs)Cl + (Li, Na, K, Cs)OH solutions at 25.0 ± 0.1 °C. The concentration of the MCl + HCl solutions was $(2-4) \times 10^{-2}$ M. The MCl + MOH solutions were prepared with constant amounts of 4×10^{-2} M HCl and increasing amounts of MOH in such a manner that the ionic strength in the equilibrium is constant if the exchange process behaves ideally. The equilibration time was 48 h. The solid was present in the solution in an approximate ratio of 250 mL:1 g.

Calorimetric Measurements. A Setaram Calvet Standard Model 1201 isothermic differential calorimeter was used. The processes occur under static conditions (without shaking). The solutions used were distilled water in the reference cell and (Li, Na, K, Cs)Cl + HCl or (Li, Na, K, Cs)Cl + (Li, Na, K, Cs)OH in the laboratory cell.

Results and Discussion

The forward and backward titration curves of alkali metal ion exchange on lamellar ion exchangers of the α - and γ -zirconium phosphate type have been found to exhibit hysteresis loops.^{5,6} This stems from the formation of different solid phases in the titrations. Thus, the ion-exchange reactions can be nonreversible and true thermodynamic values cannot be associated with the process. Nevertheless, insight into the exchange reactions can be obtained by examining pseudothermodynamic variables obtained from the forward-exchange reactions.

The gels of the zirconium phosphate type show a high retention capacity for the alkali-metal ions. Ionic diffusion in the solid phase is very favored by the irregular structure, the high specific surface, and the large number and variety of the active sites. The exchanger selectivity will mainly depend on the magnitude of the interaction between the counterion and the solid lattice. Measurements of the ionic conductivity in zirconium phosphates with different crystallinity show that the conductivity decreases as the degree of crystallinity increases.⁴⁰ Therefore, ionic diffusion must play an important role in the ion-exchange properties of crystalline phosphates of tetravalent metals.

Ion Exchange on α -TiP. In α -TiP the number of zeolitic cavities is equal to the number of the titanium atoms.²⁴ In these cavities are lodged the ions involved in the ion-exchange process. The stability of a defined crystalline phase will depend (as in the gels) on the magnitude of the interaction between the counterion and the solid lattice. However, the exchanger selectivity can be affected by other parameters. The zeolitic cavities can be inaccessible for a determined cation, since the cation must go through the con-

Table II. Phases Formed upon Alkali Metal Ion Exchange on α -TiP

ionic compn	n_{H_2O}	interlayer dist, \AA	ionic compn	n_{H_2O}	interlayer dist, \AA
\overline{HH}	1	7.6	\overline{HNa}	0	6.9
\overline{HH}	0	7.4	\overline{NaNa}	3	9.9
\overline{HLi}	1	7.6	\overline{NaNa}	1	8.4
\overline{HLi}	0	6.8	\overline{NaNa}	0	7.6
\overline{LiLi}	1	7.6	\overline{KK}	3	10.4
\overline{LiLi}	0	7.6	\overline{KK}	2	9.6
\overline{HNa}	4	10.4	\overline{KK}	1	8.9
\overline{HNa}	1	8.4	\overline{KK}	0	8.9

necting tunnels whose dimensions are smaller than the cavities.

Figure 1 shows the equilibrium pH curves for alkali metal ion-hydrogen ion exchange on α -TiP. The titration curves show clearly defined plateaus. Alberti et al. have presented a similar set of titration curves.^{21,41} Along each plateau the solution composition is approximately constant. Phase rule considerations require that for these binary systems, with no degrees of freedom at constant temperature and pressure, two solid phases of constant composition be in equilibrium with a solution of constant composition.⁴² Phases formed upon exchange have been identified and characterized by X-ray diffraction methods and chemical and thermal analysis.⁴³⁻⁴⁵ The compositions of the phases formed are listed in Table II.

Lithium and sodium exchange on α -TiP occurs in two stages, phases of half and full exchange being formed. The formation of half- and full-exchanged lithium phases takes place approximately at the same equilibrium pH. In the H^+/Li^+ ionic substitution, the interlayer distance and the hydration degree of the solid does not vary. The sodium half-exchanged phase is formed at a relatively low pH, being transformed into the fully exchanged phase at a much higher pH. Titration curves obtained by addition of NaCl + NaOH solutions to the α -TiP are a function of the temperature. The process is even more complicated at temperatures higher than 18–20 °C^{41,46} because in these conditions the half-exchanged and full-exchanged phases can present in more than one degree of hydration. Hysteresis phenomena, or very low rates of hydration (or dehydration), might explain the coexistence of differently hydrated phases of the same salt form at a given relative humidity and temperature.⁶ Quantitative measurements in X-ray diffraction⁴⁷ show the coexistence of only two crystalline phases with different ionic composition in the plateaus of the titration curves, while the pH increases in a continuous way when the number of crystalline phases coexisting is greater (Figure 2). This can be clearly seen from the experiment when it is carried out at 5.0 °C, since the plateau of the titration curve finishes when the fully exchanged phase appears and the commencement of the second plateau coincides with the almost disappearance of the $\overline{HH}\cdot H_2O$ phase. The low proportion of the $\overline{NaNa}\cdot 3H_2O$ phase, which at the beginning of the titration should be formed in the external part of the crystal, is not detected by X-ray diffraction in our experimental working conditions. At 25.0 °C the presence of the fully exchanged phase at the beginning of the substitution is observed. The marked increase of pH observed when the $\overline{HNa}\cdot nH_2O$ and $\overline{NaNa}\cdot nH_2O$ phases coexist may be due to the presence of half-exchanged phase with low hydration, $\overline{HNa}\cdot H_2O$, since, due to its interlayer distance being 8.4 against 10.4 \AA for

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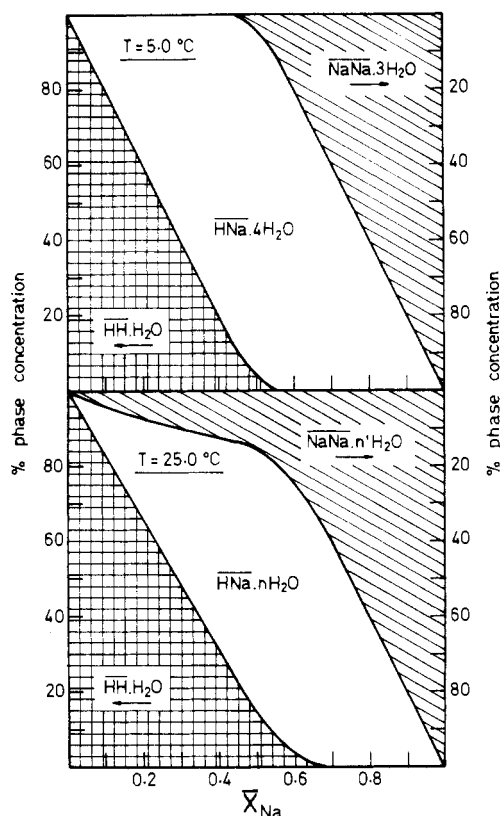


Figure 2. H^+/Na^+ system in α -TiP: distribution of solid phases as a function of the degree of loading.

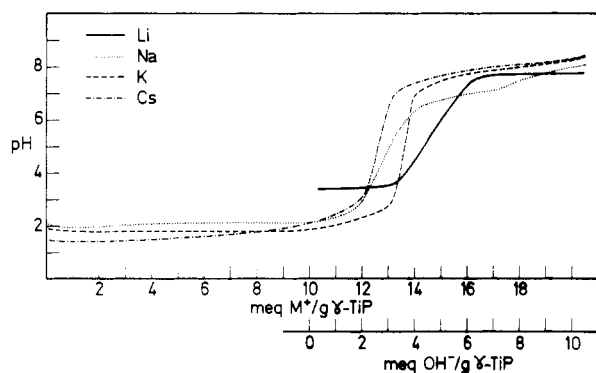


Figure 3. H^+/M^+ system in γ -TiP: pH curves at 25.0 °C.

the $\overline{HNa} \cdot 4H_2O$ phase, the former phase will need greater energy to be transformed into the $\overline{NaNa} \cdot 3H_2O$ (9.9 Å) phase. Moreover, it could be transformed into $\overline{NaNa} \cdot H_2O$ (8.4 Å), but in any case, the mechanism will be different and the entry of the second ion sodium will lead to variation in the pH. The potassium titration curve exhibits only one plateau at the concentration range studied. The phase formed in this exchange system has been identified as a 100% cation-exchanged phase. Alberti et al.⁴¹ reported the existence of a half-exchanged monohydrated phase: $\overline{HK} \cdot H_2O$ (8.3 Å). The cesium titration curve has a shape similar to that for potassium. The largest retention observed (0.2 mequiv/g), the specific surface of α -TiP (10 m²/g), and the number of formula weights contained in 1 cm² of a layer⁶ indicate that the exchange of cesium ions is only a superficial phenomena. The neutralization of the cesium added is a consequence of the α -TiP hydrolysis processes, with release of phosphate to the solution and formation of $TiO_2 \cdot nH_2O$ solid.

Ion Exchange on γ -TiP. Figure 3 shows the curves of equilibrium pH for alkali metal ion-hydrogen ion exchange on γ -TiP. Phases formed upon exchange have been identified and characterized by X-ray diffraction methods and chemical and thermal

Table III. Phases Formed upon Alkali Metal Ion Exchange on γ -TiP

ionic compn	n_{H_2O}	interlayer dist, Å	ionic compn	n_{H_2O}	interlayer dist, Å
\overline{HH}	2	11.6	\overline{HNa}	0	10.1
\overline{HH}	1	11.4	\overline{NaNa}	2	12.8
\overline{HH}	0	9.1	\overline{NaNa}	1	11.5
$\overline{H_{1.5}Li_{0.5}}$	2	11.0	\overline{NaNa}	0	10.6
\overline{HLi}	2	11.3	$\overline{H_{1.5}K_{0.5}}$	1	11.0
\overline{HLi}	0	9.6	$\overline{H_{1.5}K_{0.5}}$	0	10.8
\overline{LiLi}	1-2	11.3	\overline{HK}	0	10.8
$\overline{H_{1.5}Na_{0.5}}$	1	11.0	\overline{KK}	2-3	14.2
$\overline{H_{1.5}Na_{0.5}}$	0	10.1	\overline{KK}	0	12.2
\overline{HNa}	3	13.2	$\overline{H_{1.5}Cs_{0.5}}$	2	11.6
\overline{HNa}	2	12.6	$\overline{H_{1.5}Cs_{0.5}}$	0	9.9
\overline{HNa}	1	11.1	\overline{HCs}	2	

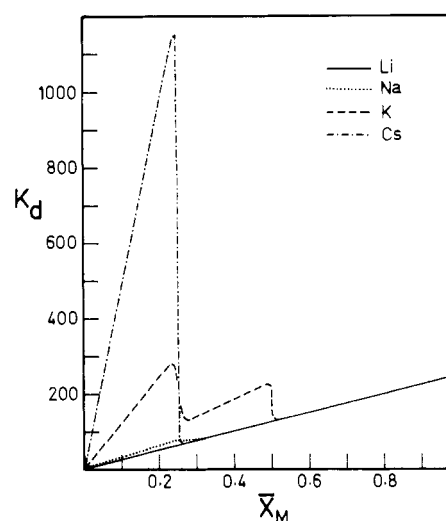


Figure 4. H^+/M^+ system in γ -TiP: distribution coefficients as a function of the degree of loading.

analysis.⁴⁸⁻⁵⁰ The compositions of the phases formed are listed in Table III.

The exchange of alkali metals in γ -TiP takes place in three steps with formation of 25, 50, and 100% substitution phases. The titration curves show defined plateaus associated with the formation of crystalline solid phases. The distribution of solid phases as a function of the degree of loading indicates that there are not more than two crystalline solid phases in the same sample simultaneously.^{50,51}

Selectivity Sequences. Equilibrium pH curves suggest that the solubility of alkali-metal ions in the α -TiP phase is a function of the conversion degree of the material. The selectivity sequence for the formation of the half-exchange phases is $Na^+ > Li^+ > K^+ > Cs^+$, while for the full-exchanged phases the sequence is $Li^+ > Na^+ > K^+ > Cs^+$.

Equilibrium pH curves of the H^+/M^+ (M = alkali metal) processes in γ -TiP overlap in some zones so they give less information. For some practical applications, it is useful to express the equilibrium situation in terms of the distribution coefficients of the counterions:

$$K_d = (\bar{X}_M / X_M)(V/W) \quad (1)$$

where \bar{X}_M is the molar fraction of the M^+ in the solid phase, X_M the molar fraction of M^+ in the solution, and V the total volume

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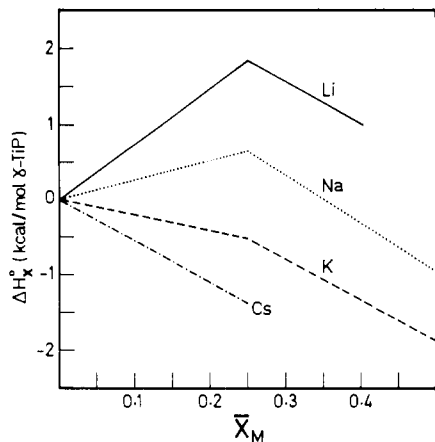


Figure 5. H^+/M^+ system in γ -TiP: standard heats of partial exchange as a function of the degree of loading.

of the solution in contact with a mass W of the exchanger. In Figure 4 K_d against \bar{X}_M is plotted. When $\bar{X}_M < 0.25$, the alkali-metal ion solubility in γ -TiP decreases as $Cs^+ > K^+ > Na^+ > Li^+$. When $0.25 < \bar{X}_M < 0.50$, the sequence is $K^+ > Na^+ > Li^+ \approx Cs^+$. For conversions higher than 50% of the γ -TiP exchange capacity, the distribution coefficients do not give useful information, since the high equilibrium pH's and the noticeable concentration of alkali-metal ion in solution lead \bar{X}_M to take values close to 1, and thus K_d is only a linear function of \bar{X}_M .

Heat Data. Direct calorimetric measurements for the H^+/M^+ ($M = Li, Na, K, Cs$) ion exchange on γ -TiP were carried out at different degrees of conversion.^{52,53} In the sodium, potassium, and cesium cases, the calorimetric curves always show the same shape: a unique and fast peak, the intensity of which quickly decreased. In the lithium case, the shape of the calorimetric curves is a function of the extent of the ion-exchange process. For $\bar{X}_{Li} < 0.24$, these curves are very similar to those obtained for the other alkali-metal cations. Most of heat released was recorded 1–2 min after the beginning of the reaction. When $\bar{X}_{Li} > 0.24$, a new maximum appears, 10–20 min after the reaction starts, with an intensity lower than in the first case.

Assuming that the ion-exchange process takes place without secondary reactions, the enthalpy variation (ΔH) can mainly be attributed to (a) the ion-exchange reaction (ΔH_x^0) and (b) the neutralization reaction when (MCl + MOH) solutions were used (ΔH_N). When the initial solution contains MOH, the exact knowledge of the molar enthalpy of neutralization from our experimental measurements makes the calculation of the enthalpy in part a possible ($\Delta H_x^0 = \Delta H - \Delta H_N$).

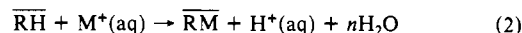
Figure 5 shows the standard heats of the alkali metal ion exchange in γ -TiP, ΔH_x^0 's, as a function of the metal ion loading. The linear parts of the heat functions show clearly that the reactions proceed in distinct and separate steps. The intersection of the two almost linear parts of the curve is very close to the theoretical value for 25% conversion. For lithium and sodium, the first step, going from 0 to 25% of exchange, is endothermic, while the second one, in which the half-exchange phase is formed, is exothermic. For potassium ion, two different slopes are also observed but, in this case, both have a negative value. Cesium data indicate that the transformation of γ -TiP into the $\bar{X}_{Cs} = 0.25$ phase is an exothermic reaction. Due to slowness of the reactions and high hydrolysis effects, these heat curves could not be extended to higher loadings. The titration data seem to indicate some solid solution formation in the exchange systems. This is apparently not reflected in the enthalpy term, since the ΔH_x^0 curves consist of unbroken straight lines over each two-phase region.

The exchange reactions in γ -TiP and similar materials are, as previously mentioned, generally not reversible so that it is not

Table IV. Thermodynamic Data for Alkali Metal Ion Exchange Reactions with γ -TiP

alkali metal	exchange reactn	ΔG° , kcal/mol of M^+	ΔH° , kcal/mol of M^+	ΔS° , eu/mol of M^+
Li	$\overline{HH} \rightarrow \overline{H_{1.5}Li_{0.5}}$	2.60	3.72	3.8
Na	$\overline{HN} \rightarrow \overline{H_{1.5}Na_{0.5}}$	0.55	1.24	2.3
K	$\overline{HK} \rightarrow \overline{H_{1.5}K_{0.5}}$	-1.54	-1.05	1.6
Cs	$\overline{HCs} \rightarrow \overline{H_{1.5}Cs_{0.5}}$	-3.39	-2.38	3.4
Li	$\overline{H_{1.5}Li_{0.5}} \rightarrow \overline{HLi}$	3.02	-4.20	-24.2
Na	$\overline{H_{1.5}Na_{0.5}} \rightarrow \overline{HNa}$	1.64	-3.33	-16.7
K	$\overline{H_{1.5}K_{0.5}} \rightarrow \overline{HK}$	0.17	-2.86	-10.2

legitimate to derive equilibrium constants. However, following a procedure previously invoked for the H^+/Na^+ exchange on α -ZrP,⁴² one can think of the ion-exchange reactions as being ideally



The thermodynamic equilibrium constant, $K_{M/H}$, for this reaction is given by

$$K_{M/H} = (\bar{a}_M/a_{M^+})(a_{H^+}/\bar{a}_H)a_w^n \quad (3)$$

where the barred quantities represent activities of the ions in the solid phase and the unbarred ones activities of the ions in the aqueous phase.

Along a plateau one solid of constant composition is converted into another of constant composition. If we choose as the standard reference state an activity of 1 for the pure solids, we arrive at

$$K_{M/H} = (a_{H^+}/a_{M^+})a_w^n \quad (4)$$

The water activity, a_w , of the solutions is close to 1. Thus, from the pH of the plateaus and the metal ion activities of the solution, values of $K_{M/H}$ were calculated. The free energies, G° , were obtained from

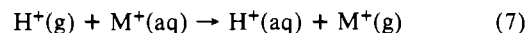
$$-\Delta G^\circ = RT \ln K_{M/H} \quad (5)$$

The enthalpy changes for the same reactions were obtained from the slopes of the ΔH_x^0 curves multiplied by a factor of 0.5. This factor arises because the ΔH_x^0 values are expressed in kilocalories per mole of exchanger, while the thermodynamic parameters of reaction 1 are given in kilocalories per mole of exchanged alkali-metal ion (M^+). Finally, the entropies of exchange are calculated from the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

ΔG° , ΔH° , and ΔS° are given in Table IV.

The enthalpic change for the exchange reaction represented by eq 2 can be thought to result from four sources,⁵⁴ namely (i) the heat consumed in bond breaking when H^+ is released from the exchanger, (ii) the heat released in the formation of bonds to the incoming cation, (iii) the heat corresponding to the increase or decrease of the interlayer distance, and (iv) the enthalpy changes accompanying hydration and dehydration. This last term is equivalent to the enthalpy change for the hypothetical reaction



for which $-\Delta H = 136.2, 164.0, 184.1,$ and 194.6 kcal/mol for $M = Li, Na, K,$ and Cs , respectively.⁵⁵ If the crystalline phases involved in the reaction have similar interlayer distances, the enthalpic variation corresponding to source iii must be small. Due to the differences in heats of hydration the most exothermic exchange heats are expected to be found for Cs^+ , while the smallest heats should be found for Li^+ . Table IV shows that the released heats in the exchange reactions vary parallel to those of reaction 7 ($Li < Na < K < Cs$).

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Sherry⁵⁶ has shown that for ion-exchange reactions such as the ones described (cf. eq 1), the observed entropies, ΔS° , can be divided into two terms as

$$\Delta S^\circ = \Delta S_{\text{ex}}^\circ + (S_{\text{H}}^\circ - S_{\text{M}}^\circ) \quad (8)$$

where $\Delta S_{\text{ex}}^\circ$ represents the entropy difference between the cation and hydrogen ion forms of the exchanger. That is, $\Delta S_{\text{ex}}^\circ$ reflects changes in hydration of the exchanger and differences in lattice distortion of the two forms of exchanger. The quantity in parentheses refers to the difference in entropies of the exchanging ions, i.e., the entropy for reaction 7. This entropy difference, $S_{\text{H}}^\circ - S_{\text{M}}^\circ$, is equal to 2.4, -5.1, -13.6, and -17.2 eu for M = Li, Na, K, and Cs, respectively.⁵⁷ Moreover, Kullberg and Clearfield⁵⁸ have described that the entropy of the exchanger decreases about 6.8 eu for each mole of water added in the ion-exchange reaction in α -ZrP of alkali metals. This agrees well with the entropy decrease accompanying "binding" of water on freezing (6.1 eu/mol water at 25 °C).⁵⁹ The hydration degree of the solids obtained "in situ" and stabilized in air can be different. This fact as well as the fact that the change in entropy is constrained by the values found for the free energies and enthalpies (the uncertainty in the value of ΔS° can be high, since it is obtained from ΔG° and ΔH°) makes difficult the interpretation of the entropy data.

Mechanism of Exchange. α -TiP has a layered structure. The packing of the layers is such as to create cavities that are connected by openings. A water molecule sits in the center of each cavity. There is one such cavity per α -TiP formula in the crystal. The ion-exchange behavior of α -TiP is conditioned by two features of its structure: the size of the openings into the cavities and the weak forces holding the layers together. In α -ZrP it has been shown that the largest entranceways into the cavities would allow a spherical cation of 2.61-Å diameter to diffuse unobstructed into the cavities.²⁶ This should allow Li⁺, Na⁺, and K⁺ to enter, if unhydrated, but excludes Cs⁺. Clearfield et al.⁵⁸ show that Li⁺, Na⁺, and K⁺ do exchange in acid solution but Cs⁺ does not. In the α -TiP, as a consequence of the substitution of zirconium by a smaller quadrivalent metal such as titanium, the tunnels connecting the cavities become narrower and the ion-exchange reaction of large cations has a greater activation energy. Figure 1 shows that Li⁺ and Na⁺ do exchange in acid solution but K⁺ and Cs⁺ do not. This suggests that unhydrated or, for small cations, partially rehydrated cations are exchanged and that no expansion of the layers occurs unless base is also added.

γ -TiP has a layered structure. It is very difficult to obtain a crystal large enough to determine the crystal structure of γ -materials by X-ray procedures. Therefore, their crystalline structure is as yet unknown. However, there are some data available about the γ -compounds. While in the α -layers each tetravalent metal atom is octahedrally coordinated to six oxygens of six different |PO₄| groups, in the γ -layers it is proposed that six-coordination is instead obtained with only four |PO₄| groups.^{35,36} Two |PO₄| groups could be bonded to the tetravalent metal via two oxygens. Whatever the case, the planar density of the fixed negative charges of the γ -macroanions is higher than that of the α -macroanions. Therefore, the distance between adjacent fixed charges in a layer of γ -TiP is expected to be shorter than that in the corresponding α -compound. Moreover, exchange on γ -TiP gives rectilinear isotherms and enthalpy curves consisting of linear parts of different slopes, which reflect the phase transitions occurring upon exchange and also the uniformity of the exchange sites within each phase. It might be expected zeolitic type cavities exist in γ -TiP. The difficulty in obtaining conversions higher than

50% may be explained by assuming that γ -TiP has two hydrogen ions in each zeolitic cavity and, thus, the counterions would be very close in the fully exchanged phases and the electrostatic repulsive forces between them should be very high. Moreover, the formation of 25% substitution phases^{28,48,49} suggests the existence of two different zeolitic cavities in γ -TiP. If we take into account the reversible transformation during the thermal treatment of the 25% substitution phases into mixtures of unexchanged phases and half-exchanged phases,^{30,48,49} we can assume that the two different types of zeolitic cavities are placed in alternate interlayer spacings. If the tunnels connecting the zeolitic cavities are not great enough, at the surface of the crystal the hydrated cation gives up most its water and diffuses into the cavity as either an unhydrated or at most partially hydrated species replacing a hydrogen ion. If the tunnels enable the access of the alkali-metal ion into the types of zeolitic cavities, the heat released in the formation of bonds between the anhydrous cation and the layers of the γ -titanium phosphate is greater when the sizes of the cavities and the alkali-metal ion become closer. In the γ -TiP, the potassium ion forms phases of 50% exchange in acidic medium. The tunnels leading to both zeolitic cavities allow the diffusion of the anhydrous potassium ions. Nevertheless, cesium ions only attain 25% conversion in acidic medium. Cesium cannot go into one of the zeolitic cavities without deforming the γ -TiP structure.

In the cases of α - and γ -TiP, the ion exchange never exceeds 50% of the material capacity in acidic medium. This can be obtained when a base is added. Under the influence of the hydroxide ions the layers presumably move apart, allowing metal ions to enter into the cavities. In basic medium both hydrogen ions of each cavity may be neutralized and a high metal ion containing phase is formed. This situation is reached in the potassium exchange in α -TiP, where the fully exchanged phase is directly obtained.⁴⁵ If the saturation of the material is not reached, a much slower subsequent process of ion diffusion into the solid can be imagined. A similar situation was observed by Bernasconi et al.,⁶⁰ who found that a fully exchanged potassium ion phase was initially formed when KCl + KOH was added to α -ZrP. In nonsaturated materials, the fully exchanged phase was subsequently slowly converted into a half-exchanged phase.

The selectivity sequences for the ions that exchange without addition of hydroxide are Na⁺ > Li⁺ in α -TiP and Cs⁺ > K⁺ > Na⁺ > Li⁺ in γ -TiP. The solubility decreases as the hydration heat of the ion increases.⁵⁵ In polyionic systems, the selectivity sequence established in the study of binary systems can be altered. The uptake of a cation by the crystalline exchanger can be largely affected by the presence of other ions. The extent of the cation going into the interior of the crystal is determined by the activity of the ion on the surface of the crystal rather than by the activity of the ion in the bulk solution. On the basis of the results obtained by Clearfield et al.^{61,62} in crystalline α -ZrP, the partial inhibition of the Li⁺ and Na⁺ retention in α -TiP might be expected due to the presence of K⁺ or Cs⁺. Nevertheless, the relative retention of a metallic ion in a mixture (from the results obtained in binary systems) is supposed to be predicted from the order in solubility of the alkali-metal ions in γ -TiP. Results verifying this hypothesis have been obtained in the study of the system H⁺/Na⁺/K⁺ in γ -TiP.⁶³

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Registry No. Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; Co, 7440-46-2; Ti(HPO₄)₂·2H₂O, 14635-14-4; Ti(HPO₄)₂·H₂O, 15844-56-1.

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