Lamellar Inorganic Ion Exchangers. H^+/Cs^+ Ion Exchange in γ-Titanium Phosphate

Eliana González, Ricardo Llavona, José R. García, and Julio Rodríguez *
Area de Química Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain

The H^+/Cs^+ ion-exchange process in γ-titanium phosphate (γ-TiP) was studied. Exchange isotherms and titration and hydrolysis curves were obtained at 25.0, 40.0, and 55.0 (±0.1) °C by using CsCl + HCl and CsCl + CsOH solutions. The ion-exchange process and the thermal behaviour of the exchanged solids were followed by *X*-ray diffraction. In acidic media the easy retention of the Cs^+ by γ-TiP led to the formation of the crystalline phase $\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$ (11.6 Å) without hydrolysis of the exchanger. The elution of Cs^+ and the regeneration of the γ-TiP were achieved by treatment with solutions of HCl. Equilibrium constants, and the free energy, enthalpy, and entropy of the exchange reaction were determined. Conversions higher than 25% with partial decomposition of γ-TiP and precipitation of $TiO_2\cdot nH_2O$ were obtained by using CsCl + CsOH solutions. The hydrolysis increased with temperature. The results are compared to those obtained in the study of other alkali-metal cations. A structural model for γ-TiP is proposed on the basis of its ion-exchange properties.

The phosphates of polyvalent metals are very interesting due to their ion-exchange properties. Moreover, in the recent past, exciting new developments in the areas of surface chemistry, catalysis, electrochemistry, and fast ion conduction have taken place. Several excellent reviews have appeared.[1–6] According to Alberti and Costantino,[4] the acid salts of quadrivalent metals can be subdivided according to their crystalline structure as: (*a*) acid salts with layered structures of the α type, (*b*) acid salts with layered structures of the γ type, (*c*) acid salts with fibrous structures, (*d*) acid salts with three-dimensional structures, and (*e*) acid salts having an as yet unknown structure.

γ-Titanium phosphate (γ-TiP), $Ti(HPO_4)_2\cdot 2H_2O$, has monoclinic symmetry and a basal spacing of 11.6 Å.[7,8] This material shows good exchange properties with NH_4^+, Cu^{2+}, or Ca^{2+} ions.[9–12] The behaviour of an ion exchanger in simple binary systems (H^+/M^+, M = alkali metal) gives useful information that could be used to explain more complicated systems. The behaviour of γ-TiP with respect to the retention of Li^+,[13] Na^+,[7,14] and K^+ [15,16] has been studied. Corresponding data for Cs^+ have not been reported.

Caesium is the fortieth most prevalent element in the earth's crust and is found in minerals such as pollucite, an hydrated silicate of aluminium and caesium. There are deposits of pollucite containing as much as 30% of caesium. Caesium compounds can be derived from pollucite by treating the finely powdered mineral with hydrochloric acid, dehydrating the silica, and filtering off the insoluble residue. Caesium is separated from the filtrate by precipitation of a double chloride of lead or antimony by lead nitrate or antimony trichloride, respectively. Caesium chloride can be recovered from the compounds by hydrolysis, which leaves caesium chloride in solution. Several other complex chlorides can also be used to effect the separation of caesium chloride quite free of other alkali metals, one of the best being the caesium chlorostannate intermediate.[17] Moreover, there is caesium in low concentrations in deposits used for the extraction of other metals. This is the case of some lepidolites containing less than 1% of caesium, used for the extraction of lithium. The obtaining of caesium from lepidolites will increase the value of these deposits containing 3—5% of Li_2O against other ores with higher concentrations of Li_2O such as spomudene (approximately 8% Li_2O). The separation by precipitation is of low effectivity for small caesium concentrations. Ion exchange should be an adequate procedure for this purpose.

Inorganic ion exchangers are usually stable against ionizing radiation. If a material of this type shows high affinity toward caesium, even in acidic solution, it must be suitable for the recovery of caesium from the waste solutions resulting from the processing of irradiated nuclear fuels.[18]

In this paper, the exchange H^+ and Cs^+ in γ-TiP is reported. For the sake of brevity the various ionic forms are simply indicated by their counter ions (under a bar) and water content while their interlayer distances are reported in parentheses.

Experimental

Reagents.—All chemicals used were of reagent grade. The γ-TiP was obtained by using 16.5 mol dm^{-3} H_3PO_4 and a reflux time of 10 d as previously described.[19]

Analytical Procedures.—Analysis of phosphorus and titanium in the solids was carried out gravimetrically.[20] The pH measurements were made with an Orion model SA-720 pH meter. The released phosphate groups were measured spectrophotometrically as molybdovanadophosphoric acid[21] using a Perkin-Elmer model 200 instrument. The caesium ion in solution was determined by atomic absorption spectrometry, using a Perkin-Elmer model 372 spectrometer. Thermal analysis (t.g. and d.t.a.) was performed by a Chio model TRDA-3H instrument. The diffractometer used was a Philips model PV 1050/23 (λ = 1.7902 Å, Co-K_α radiation); 2θ scan rate 0.125—2° min^{-1}, chart speed 2 cm min^{-1}.

Ion-exchange Studies.—In the forward reaction the exchanger was equilibrated with 0.04 mol dm^{-3} (CsCl + HCl) or 0.04 mol dm^{-3} CsCl + *c* mol dm^{-3} CsOH ($0.003 \leqslant c \leqslant 0.04$) solutions at 25.0, 40.0, and 55.0 (±0.1) °C by following the procedure described by Clearfield *et al.*[22] The equilibration time was 48 h. The solid was present in the solution in the ratio of *ca.* 1 g:250 cm^3.

In the backward reaction, the γ-TiP was treated with a solution 0.04 mol dm^{-3} CsCl; the product obtained, after

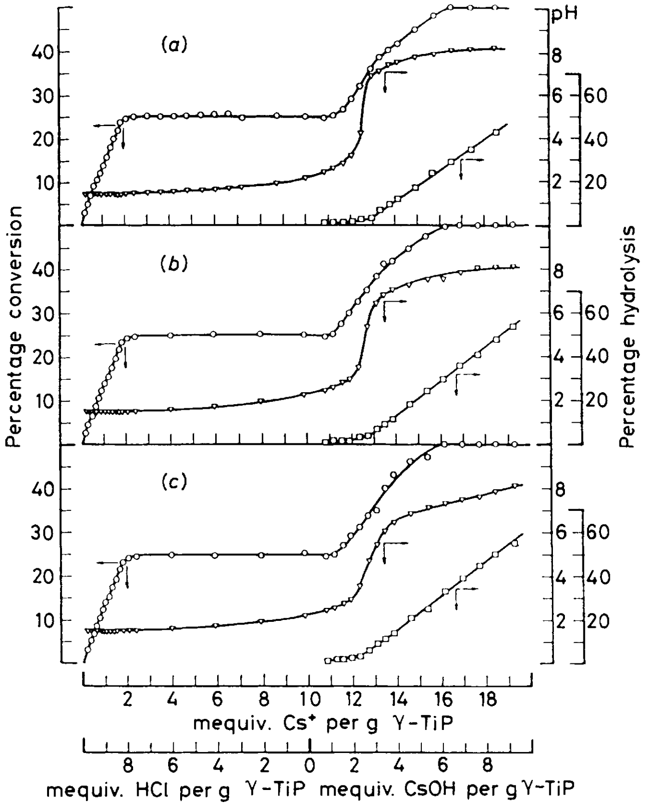

Figure 1. Equilibrium pH (▽) and hydrolysis (□) curves and exchange isotherms (○), at 25.0 (*a*), 40.0 (*b*), and 55.0 °C (*c*)

equilibration at 25.0 °C, was separated from the mother-liquor, washed with water, and dried in air at room temperature. This solid was equilibrated with solutions of 0.1—0.9 mol dm^{-3} HCl at 25.0 °C. The equilibrium time and solid/solution ratios were the same as in the forward reaction.

Results and Discussion

Figure 1 shows plots of the exchange isotherms and pH and hydrolysis curves against the initial concentration of caesium added. It can be observed that the equilibrium pH remains constant for additions of 0.2—2.0 mequiv. CsCl per g γ-TiP at the three working temperatures. In this zone the three exchange isotherms indicate that the retention increases in a continuous way until 25% exchange of the solid. The process takes place without hydrolysis of the γ-TiP. For additions of CsCl from 2.5 to 10.0 mequiv. per g γ-TiP the retention of Cs^+ is constant and thus the equilibrium pH increases. Conversions higher than 25% of the γ-TiP exchange capacity are reached only when CsCl + CsOH solutions are added. By addition of 6.0—6.5 mequiv. CsOH per g γ-TiP a 50% conversion is reached and the equilibrium pH increases in a continuous way. Partial decomposition of the exchanger is observed due to the presence of the hydroxyl groups in solution.[23] The hydrolysis increases with temperature and with the concentration of CsOH in the initial solutions. Additions of CsOH higher than 6.5 mequiv. per g γ-TiP do not increase the γ-TiP conversion but they produce degradation of the material.

The solid, after its separation from the equilibrium solution, was dried in air at room temperature. The *X*-ray diffraction behaviour is shown in Figure 2(*a*). In the range of $0.00 \leqslant \bar{X}_{Cs} \leqslant 0.25$ (where $\bar{X}_{Cs}$ is the molar fraction of exchange defined as the fraction of hydrogens substituted in the γ-TiP) the interlayer distance of the material does not vary. Nevertheless, the appearance of new diffraction lines and the disappearance by degrees of the reflections corresponding to γ-TiP is observed as the conversion increases. These latter reflections are not observed when $\bar{X}_{Cs} = 0.25$.

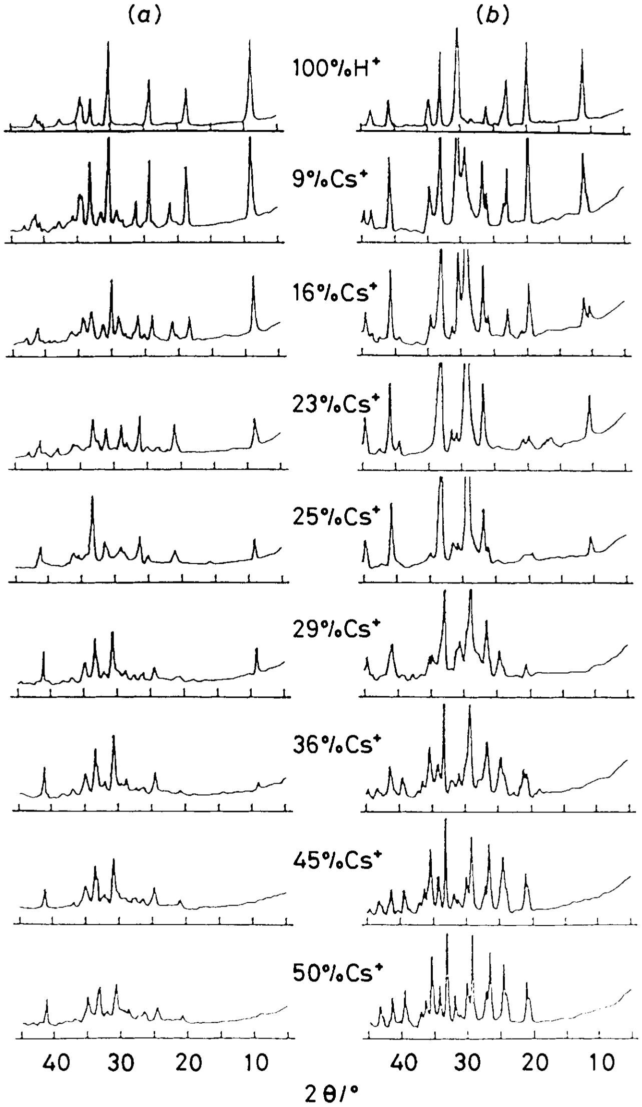

Figure 2. *X*-Ray patterns of some exchanged solids in the forward reaction: stabilized in air at room temperature (*a*) and heated at 200 °C (*b*)

The thermal analysis of the 25% substitution sample stabilized in air (Figure 3) shows the existence of two different zones of mass loss. The first occurs at temperatures under 200 °C, its value corresponding to 2 mol H_2O per mol Ti. In this kind of compound this zone of temperature is associated with the loss of crystallization water.[24,25] Moreover, the d.t.a. curve shows two minima at 95 and 175 °C indicating two steps in the dehydration as in γ-TiP.[16] At higher temperatures (300—550 °C) the material again loses mass as a consequence of the condensation of the hydrogenphosphate groups into pyrophosphate ones. The minimum values in the d.t.a. curve at 385 and 455 °C suggest that this dehydration also takes place in two steps. A similar behaviour of γ-TiP was explained by La Ginestra and Massucci[25] as the formation of an intermediate phosphate/pyrophosphate phase with an interlayer distance of

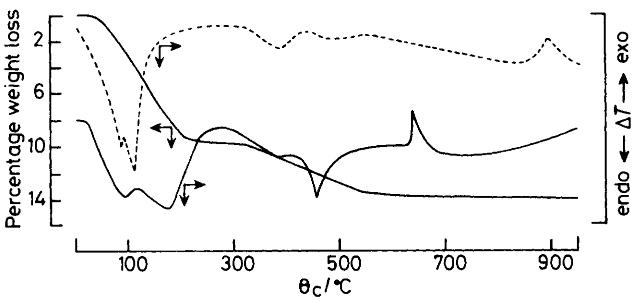

Figure 3. D.t.a. and t.g. curves of the $\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$ phase. The dashed line represents the d.t.a. curve of the $\overline{HH}\cdot 2H_2O$ phase (ref. 19)

Table. *X*-Ray diffraction data for exchanged phases

$\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$		$\overline{H_{1.5}Cs_{0.5}}$		$\overline{HCs}$	
d/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0
11.6	30	9.9	15	5.01	10
4.90	25	3.99	5	4.92	25
4.14	15	3.89	20	4.33	10
3.94	40	3.59	100	4.25	45
3.62	10	3.16	70	3.93	50
3.56	15	3.13	20	3.83	15
3.53	5	2.58	30	3.57	70
3.33	10	2.36	15	3.47	25
3.31	25			3.28	20
3.12	100			3.16	100
2.88	10			3.06	25
2.55	30			2.95	55
				2.88	15
				2.82	10
				2.66	30
				2.54	20
				2.44	15

8.3 Å. A sharp maxima appears in the d.t.a. curve at higher temperatures (638 °C) whilst the material weight hardly varies over 600 °C. An exothermic peak was also detected for γ-TiP at 880 °C corresponding to the transformation of α-TiP_2O_7 into the high-temperature phase. The presence of Cs^+ in the interlayer spacing of γ-TiP gives rise to a strong decrease in the temperature corresponding to this phase change.

The heat treatment of the solids with $0.00 \leqslant \bar{X}_{Cs} \leqslant 0.25$ at 200 °C during 72 h produces anhydrous materials. *X*-Ray patterns of the solids heated at 200 °C [Figure 2(*b*)] show an evolution by degrees from $\bar{X}_{Cs} = 0.00$ to $\bar{X}_{Cs} = 0.25$. The presence of two reflections in the region of the interlayer distance is observed, one of them (corresponding to the 002 plane of β-TiP) at 9.1 Å and the other at 9.9 Å. The relative intensity of this latter reflection increases with increasing caesium content. The reflections characteristic of the γ-TiP are not observed when $\bar{X}_{Cs} = 0.25$. *X*-Ray patterns of intermediate samples may be reproduced by combination of the patterns corresponding to the limiting samples, showing the coexistence of two crystalline phases in this composition range.

In the Table are collected *X*-ray diffraction data for the crystalline phases $\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$ (11.6 Å) and $\overline{H_{1.5}Cs_{0.5}}$ (9.9 Å).

Figure 2(*a*) shows *X*-ray patterns of solids with $0.25 \leqslant \bar{X}_{Cs} \leqslant 0.50$ stabilized in air at room temperature. The relative intensity of the reflection characteristic of the basal spacing of the material increases as the caesium concentration in the solid decreases and it is not observed when $\bar{X}_{Cs} \geqslant 0.40$. This fact can be imputed to a high deformation of γ-TiP layers. A similar situation is observed in the anhydrous single-layer silicates in which the $|SiO_4|$ layers are deformed to a variable extent due to the presence of univalent cations of various sizes between the layers.[26] The rest of the pattern varies noticeably as does the $\bar{X}_{Cs}$. The fact that the equilibrium pH changes in a continuous way between $\bar{X}_{Cs} = 0.25$ and 0.50 suggests that this exchange step occurs via a solid solution. The attainment of the half-exchanged phase is a difficult process which takes place with a high hydrolysis degree with values of 30—40% of the former material. This makes it impossible for us to effect an exact characterization of the half-exchanged phase. The heat treatment of the exchange solids at 200 °C for 72 h must produce anhydrous materials. *X*-Ray patterns obtained under these conditions [Figure 2(*b*)] do not show any reflection in the zone of the interlayer distance. There are new reflections in addition to those characteristic of $\overline{H_{1.5}Cs_{0.5}}$ (9.9 Å). The anhydrous half-exchanged phase has many different interplanar distances and this fact suggests that its structure has a low symmetry (Table).

The structure of γ-TiP is so far unknown. In a previous paper[14] a structural model was proposed on the basis of the ion-exchange properties of this material by assuming the existence of zeolitic cavities (in number equal to that of the titanium atoms) each one containing two hydrogens. The existence of two different types of zeolitic cavities was also suggested as well as a distribution of the layers such that in an interlayer spacing all the zeolitic cavities are similar between them and different from those of the adjacent interlayer spacings. It might be expected that the tunnels connecting the zeolitic cavities in both interlayer spacings would be different. The use of KCl + HCl solutions results in the formation of the $\overline{H_{1.5}K_{0.5}}\cdot H_2O$ (11.0 Å) phase which transforms into $\overline{HK}$ (10.8 Å)[15] at higher concentrations of KCl. In the half-exchanged phase all the zeolitic cavities contain a potassium ion, therefore the tunnels connecting both types of zeolitic cavities enable the free diffusion of anhydrous potassium ions. When CsCl + HCl solutions are used the $\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$ (11.6 Å) phase is formed. An increase in the CsCl concentration does not increase the conversion of the material. This can be obtained with solutions of CsCl + CsOH which give rise to a high hydrolysis degree and to a big deformation of the titanium phosphate layers. Therefore, only one type of tunnel allows access of the anhydrous caesium ions into a type of γ-TiP cavities. The other type of tunnel might have a size intermediate between the diameter of the anhydrous K^+ and Cs^+ ions (2.66—3.38 Å).

Comparison between the forward and reverse exchange isotherms gives information about the reversibility of the ion-exchange reaction.[6] When the hysteresis loops are small it might be assumed (as in zeolites[27]) that the organization of the new crystalline phase is delayed by the extent of the potential activation energy. Large hysteresis loops are associated with the formation of different crystalline phases in the two exchange processes. Figure 4 shows the forward and reverse isotherms for the H^+/Cs^+ ion exchange in γ-TiP up to 25% exchange. On the basis of these data the process must be considered reversible. Nevertheless, the *X*-ray patterns are very similar and the γ-TiP reflections are not observed when $\bar{X}_{Cs}$ decreases (Figure 5). The new organization of the $\overline{HH}\cdot 2H_2O$ (11.6 Å) phase must have a high potential energy. From the point of view of the practical applications of these materials, it is interesting to determine how the original phase (γ-TiP) is regenerated. In this way, the $\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$ (11.6 Å) phase was equilibrated during 3 h with 2 mol dm^{-3} HCl in the same ratio as used in the ion-exchange studies. The solid was separated by centrifugation. This process was repeated four times. One sample from each treatment step was washed with deionized water until pH 3.0—3.5. The *X*-ray patterns are compiled in Figure 6. The sample treated only once had a pattern similar to the one corresponding to the solids obtained in the reverse isotherm when

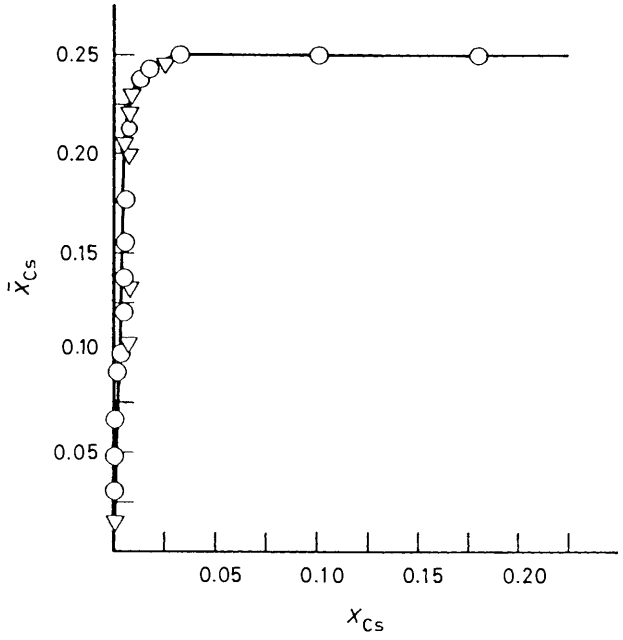

Figure 4. H^+/Cs^+ Ion-exchange isotherms in the composition range $0.00 \leqslant \bar{X}_{Cs} \leqslant 0.25$: forward reaction (○) and backward reaction (▽)

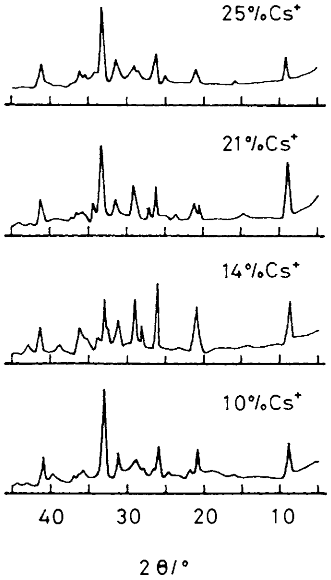

Figure 5. *X*-Ray patterns of some exchanged solids in the backward reaction stabilized in air at room temperature

$\bar{X}_{Cs} < 0.25$. Nevertheless, after the second treatment, the reflections corresponding to the γ-TiP begin to appear and they are the only ones which persist when the washing was carried out four times. This solid was stabilized in air at room temperature. Chemical analysis, thermal analysis (d.t.a. and t.g.), i.r. spectroscopy, and *X*-ray diffraction indicates that it is γ-TiP. The high concentration of hydrogen ions in the solution facilitates the reorganization of the $\overline{HH}\cdot 2H_2O$ (11.6 Å) phase. The results presented in Figure 5 are a consequence of the slowness with which the solid phase returns to the γ-TiP structure on back titration.

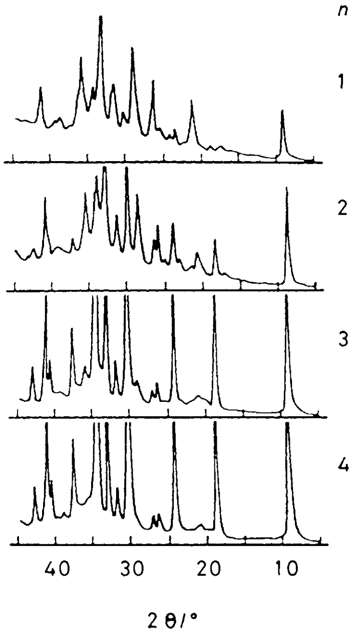

Figure 6. *X*-Ray patterns of the $\overline{H_{1.5}Cs_{0.5}}\cdot 2H_2O$ phase treated *n* times with 2 mol dm^{-3} HCl

When CsCl + HCl solutions are used the exchange process takes place without secondary reactions. The exchange reaction is reversible so that it is legitimate to derive an equilibrium constant. From equation (1) the equilibrium quotient can be

$$\mathrm{Ti(HPO_4)_2\cdot 2H_2O\ (c)} + \tfrac{1}{2}\mathrm{Cs^+\ (aq)} \rightleftharpoons \mathrm{TiH_{1.5}Cs_{0.5}(PO_4)_2\cdot 2H_2O} + \tfrac{1}{2}\mathrm{H^+\ (aq)} \qquad (1)$$

defined as in (2). The quantities with bars represent the species

$$K' = (\bar{X}_{\overline{H_{1.5}Cs_{0.5}}}\, m_{H}^{\frac{1}{2}} / \bar{X}_{\overline{HH}} m_{Cs}^{\frac{1}{2}})(f_M/f_{Cs})^{\frac{1}{2}} \qquad (2)$$

in the solid phase and those without bars represent the species in solution. The concentrations of the species in the solid phase are expressed in terms of the corresponding molar fraction of phase ($\bar{X}_j$). The concentration of the species in solution are expressed in terms of molalities (m) corrected by the activity coefficients in a binary solution (f).[28]

In solution, the usual standard state where the activities of the ions are equal to the corresponding molalities in solution at infinite dilution is taken. The reference state of the solvent is also as usual in that $a_w = 1$ for the pure solvent. For the solid phase we choose the reference state in which the solid is in equilibrium with an infinitely dilute solution of the counter ion.

The equilibrium quotient expressed by equation (2) is evaluable over the entire composition range. The equilibrium constants are obtained from equation (3).[10,29] The integral is calculated by plotting $-\log K'$ against $\bar{X}_{\overline{H_{1.5}Cs_{0.5}}}$.

$$\log K = \int_0^1 \log K' \mathrm{d}\bar{X}_{\overline{H_{1.5}Cs_{0.5}}} \qquad (3)$$

By plotting the equilibrium constant against $1/T$ (Figure 7), the value of $\Delta H^{\ominus} = -4.97$ kJ mol^{-1} is obtained; $\Delta G^{\ominus} = -7.06$ kJ mol^{-1} is obtained from K and $\Delta S^{\circ} = 7$ J K^{-1} mol^{-1} from the values of $\Delta H^{\ominus}$ and ΔG°.

As it was discussed in a previous paper,[13] when the interlayer distance of the solid is hardly modified in the ion-exchange reaction the enthalpic variation must be mainly associated with the following sources: (*i*) the heat released in the formation of

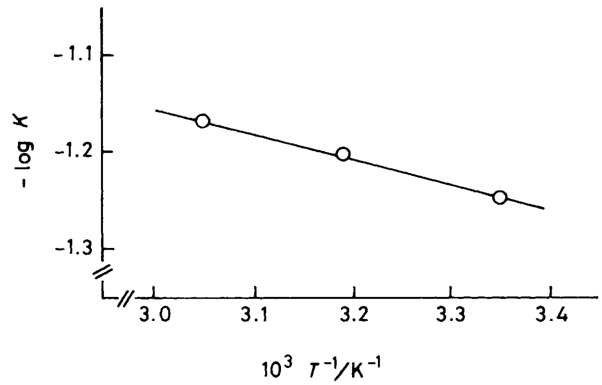

Figure 7. Influence of temperature on the equilibrium constant for $\overline{HH} \rightleftharpoons \overline{H_{1.5}Cs_{0.5}}$

bonds to the incoming cation and (*ii*) the enthalpy changes accompanying hydration and dehydration in solution. This last term is equivalent to the enthalpy change for the hypothetical reaction (4) for which $-\Delta H$ = 569.3, 685.5, 769.5, and 813.4 kJ

$$H^+(g) + M^+(aq) \longrightarrow H^+(aq) + M^+(g) \quad (4)$$

$$Ti(HPO_4)_2{\cdot}2H_2O(c) + \tfrac{1}{2}M^+(aq) + (n-2)H_2O \longrightarrow TiH_{1.5}M_{0.5}(PO_4)_2{\cdot}nH_2O(c) + \tfrac{1}{2}H^+(aq) \quad (5)$$

mol^{-1} for M = Li, Na, K, and Cs respectively.[30] The heats released in the exchange reactions (5) vary in parallel to those of reaction (4) ($-\Delta H^\circ$ = −7.77, −2.59, 2.19, and 4.97 kJ mol^{-1} for M = Li, Na, K, and Cs respectively.[13,14,16]

Sherry[31] has shown that, for ion-exchange reactions such as (4), the observed entropies can be divided into two terms: (*i*) the entropy change for reaction (4) and (*ii*) the entropy difference between the cation and hydrogen-ion forms of the exchanger. This last term reflects changes in hydration of the exchanger and differences in lattice distortion of the two forms of the exchanger. The hydration degree of the solids obtained '*in situ*' is unknown. This fact as well, as the fact that the entropy change is constrained by the values found for the free energies and enthalpies, make difficult interpretation of the entropy data.

γ-TiP has a great affinity towards Cs$^+$ ($pK_{Cs} = -1.25$) but its affinity towards lithium is much lower ($pK_{Li} = 0.96$).[13] From the results obtained in the study of H$^+$/M$^+$ (M = Li or Cs) binary systems it might be expected that no marked retention of the lithium is possible if the γ-TiP solution has a pH between 1.5 and 3.0, whilst caesium-ion exchange will be almost quantitative. This fact and the possibility of elution of the Cs$^+$ [by treatment of the substituted phase with HCl solutions, producing the crystalline phase $\overline{HH{\cdot}2H_2O}$ (11.6 Å)] makes γ-TiP a material suitable for the extraction of Cs$^+$ from aqueous solutions containing high concentrations of lithium. This fact should be confirmed by a study of the ternary system H$^+$/Li$^+$/Cs$^+$, since one cannot generalize to ternary systems from the binary cases. This is because new phases may form in the ternary which are more stable than any binary phases.[32]

Acknowledgements

This work was supported by the Comision Asesora de Investigacion Cientifica y Tecnica (Project no. 84-0878) for which grateful acknowledgement is made.

References

1 C. B. Amphlett, 'Inorganic Ion Exchangers,' Elsevier, Amsterdam, 1964.
2 V. Vesely and V. Pekarek, *Talanta*, 1972, **19**, 219.
3 A. Clearfield, G. H. Nancollas, and R. H. Blessing, in 'Ion Exchange and Solvent Extraction,' vol. 5, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973.
4 G. Alberti and U. Costantino, *J. Chromatogr.*, 1974, **102**, 5.
5 G. Alberti, *Acc. Chem. Res.*, 1978, **11**, 163.
6 'Inorganic Ion Exchange Materials,' ed. A. Clearfield, CRC Press, Boca Raton, Florida, 1982.
7 S. Allulli, C. Ferragina, A. La Ginestra, M. A. Massucci, and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1043.
8 E. Kobayashi and S. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1632.
9 G. Alberti, M. G. Bernasconi, M. Casciola, and U. Costantino, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1637.
10 C. Alvarez, R. Llavona, J. R. García, M. Suárez, and J. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1987, 2045.
11 G. Alberti, U. Costantino, and M. L. Luciani, *J. Chromatogr.*, 1980, **201**, 175.
12 C. Alvarez, R. Llavona, J. R. García, M. Suárez, and J. Rodríguez, *Inorg. Chem.*, 1987, **26**, 1045.
13 E. González, R. Llavona, J. R. García, and J. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1989, 829.
14 R. Llavona, J. R. García, C. Alvarez, M. Suárez, and J. Rodríguez, *Solvent Extr. Ion Exch.*, 1986, **4**, 567, 585.
15 R. Llavona, C. Alvarez, J. R. García, M. Suárez, and J. Rodríguez, *Solvent Extr. Ion Exch.*, 1985, **3**, 931.
16 R. Llavona, J. R. García, M. Suárez, and J. Rodríguez, *Thermochim. Acta*, 1986, **101**, 101.
17 C. A. Hampel, in 'Rare Metals Handbook,' ed. C. A. Hampel, Reinhold, London, 1961.
18 S. Komerneni and R. Roy, *Nature (London)*, 1982, **299**, 707.
19 R. Llavona, J. R. García, M. Suárez, and J. Rodríguez, *Thermochim. Acta*, 1985, **86**, 281.
20 M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, 'Quantitative Chemical Analysis,' Nigar, Buenos Aires, 1972.
21 O. B. Michelsen, *Anal. Chem.*, 1957, **29**, 60.
22 A. Clearfield, A. Oskarsson, and C. Oskarsson, *Ion Exch. Membr.*, 1972, **1**, 91.
23 M. Suárez, J. R. García, and J. Rodríguez, *J. Phys. Chem.*, 1984, **88**, 159.
24 D. Dollimore, N. J. Manning, and D. V. Nowell, *Thermochim. Acta*, 1977, **19**, 37.
25 A. La Ginestra and M. A. Massucci, *Thermochim. Acta*, 1979, **32**, 241.
26 F. Liebau, 'Structural Chemistry of Silicates,' Springer, Berlin, 1985.
27 R. M. Barrer and L. Hinds, *J. Chem. Soc.*, 1953, 1879.
28 R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959.
29 G. L. Gaines and H. C. Thomas, *J. Chem. Phys.*, 1953, **21**, 714.
30 D. F. C. Morris, *Struct. Bonding (Berlin)*, 1968, **4**, 63.
31 H. S. Sherry, in 'Ion Exchange,' vol. 2, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1969.
32 L. Kullberg and A. Clearfield, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2543.

Received 6*th October* 1988; *Paper* 8/03983F