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Calorimetric Determination of H^+/M^+ ($M = Li, Cs$) Ion Exchange in γ-Titanium Hydrogen Phosphate

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Abstract. H^+/M^+ ($M = Li, Cs$) ion exchange in γ-titanium phosphate (γ-TiP) at 25°C and under static conditions has been studied. Titration and hydrolysis curves and the exchange isotherms were determined. The substitution was followed by X-ray diffraction. Direct calorimetric measurements were carried out at different degrees of conversion and the variation of the exchange enthalpy was obtained. The shape of the calorimetric curves is discussed. The results are compared to the values of ΔH^0 obtained from titration data.

Key words. Ion exchange, lamellar phosphates, intercalation.

1. Introduction

Cesium is the fortieth most prevalent element in the earth's crust and is found in minerals such as pollucite, a hydrated silicate of aluminium and cesium. Lithium is widely distributed in the earth's crust, calculated to be approximately 0.004 per cent. Some of the lepidolites used in lithium extraction contain low amounts of cesium. The extensive processing of these lithium ores in recent years has resulted in an increasing availability of cesium by-product concentrates that are being used as sources of cesium compounds. Ion exchange can be an adequate procedure for this purpose.

The insoluble acid salts of tetravalent metals have been known for a long time, interest in them having increased in the fifties as a consequence of their practical applications as ion exchangers, given that they possess good exchange properties and high resistance to temperature and radiation [1–4]. $Ti(HPO_4)_2{\cdot}2\,H_2O$ (γ-TiP) is a lamellar compound with a basal spacing of 11.6 Å [5, 6]. Its structure is so far unknown, but it has monoclinic symmetry [7]. The dimensions of the unit cell are $a = 5.29$, $b = 6.44$, $c = 23.94$ Å, and $\beta = 103.9°$.

Earlier investigations [8, 9] have shown that γ-TiP has a high affinity toward cesium ions in an aqueous medium, even at low pH (< 2), while lithium ion retention only happens noticeably when base is added. Moreover, treatment of the cesium or lithium exchanged phases with HCl elutes alkali ions and the γ-TiP is regenerated. This exchanger shows potential practical application in the retention of Cs^+ ions from solutions containing low concentrations of Cs^+ and high concentrations of Li^+. For this reason, obtaining the thermodynamic data for the exchange processes H^+/M^+ ($M = Li, Cs$) in γ-TiP is very important.

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In a previous paper [10] we have pointed out that thermodynamic data are usually obtained by determining the exchange isotherm at different temperatures, and that usually, in compounds of the γ-TiP type, the variation of the enthalpy in the ion exchange reaction is small, and this can bring about high relative errors in its determination. The solution proposed is the direct determination of the ion exchange enthalpies in order to confirm the results obtained by the determination of ΔH from the variation with temperature of the equilibrium constants of the ion exchange reaction.

The evaluation of the enthalpic variation of the H^+/Cs^+ ion exchange process in γ-TiP is difficult from titration data. The high solubility of cesium in γ-TiP leads to low equilibrium pHs and this makes the exact determination of the hydrogen ion concentration difficult. Besides, the exchange isotherms are very similar in the studied temperature range.

In this paper, the enthalpy variations of ion exchange in the H^+/M^+ ($M = Li, Cs$) process in γ-TiP have been determined by direct calorimetric measurements. In the following discussion, for the sake of brevity, the various ionic forms are simply indicated by their counterions (under a bar) and water content, while their interlayer distances are given in parentheses.

2. Experimental

2.1. REAGENTS

All chemicals used were of reagent grade. γ-TiP was obtained by using 16.5 M H_3PO_4 and reflux times of 10 days, as described previously [6].

2.2. ANALYTICAL PROCEDURES

The pH measurements were made with a Orion Model SA-720 pH-meter. The released phosphate groups were measured spectrophotometrically [11] using a Perkin-Elmer Model 200 spectrophotometer. The lithium and cesium ions in solution were determined by atomic absorption spectroscopy, using a Perkin-Elmer Model 372. The diffractometer used was a Philips Model PV 1050/23 ($\lambda = 1.7902$ Å).

2.3. CALORIMETRIC MEASUREMENTS

A Setaram Calvet Standard, Model 1201 isothermic differential calorimeter, was used. The processes occur at 25°C and under static conditions (without shaking). Equal amounts of γ-TiP were introduced in the laboratory and reference cells. The solutions used were distilled water in the reference cell and (0.04 M LiCl + cM LiOH) ($8 \times 10^{-4} \leqslant c \leqslant 1.5 \times 10^{-2}$) or 0.04 M (CsCl + HCl) in the laboratory cell.

2.4. ION EXCHANGE STUDIES

After each calorimetric measurement, the solid and solution phases were separated by filtration. The pH of the solution was measured and the concentrations of P and M ($M = Li, Cs$) were determined. The reaction times varied between 1 and 3 h. The solid was present in the solution in a ratio of 250 mL : 1 g.

3. Results and Discussion

3.1. LITHIUM ION EXCHANGE

The pH at the end point, the degree of decomposition of the solid (percentage of phosphorus released from the solid phase to the liquid phase) and the amount of Li^+ retained by the solid (percentage of hydrogen ions substituted by Li^+ ions in the hydrogen phosphate groups remaining in the solid phase) of each calorimetric measurement were determined. These values are plotted against the amount of LiOH added in Figure 1. The pH initially increases with the amount of LiOH added until a value of 7.5 is reached corresponding to the addition of 1.2 meq LiOH/g γ-TiP (15–25% conversion). In this zone, the γ-TiP hydrolysis is low. For addition of 1.2–2.4 meq LiOH/g γ-TiP the pH remains almost constant, the conversion degree (15–25%) and the hydrolysis degree (1–4%) being increased. For higher additions of LiOH, the pH, the conversion and the hydrolysis keep increasing. When this system is studied under dynamic conditions (shaking) with reaction times of 48 h, the result is different [8]. The plotting of the end pH against the fraction of exchange allows the behavior of γ-TiP in both working conditions to be compared (Figure 2). Under dynamic conditions, an equilibrium pH constant is reached. Along each plateau the solution composition is approximately constant. Under equilibrium conditions, 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 are in equilibrium with a solution of constant composition [12]. The slope of the titration curve observed at $\bar{X}_{Li} = 0.00$–0.03 and $\bar{X}_{Li} = 0.42$–0.50 indicates solid solution formation. As a consequence of our working conditions, the results reported in this paper were obtained without shaking and with short reaction times. Thus, the end point reached is not a situation of thermodynamic equilibrium.

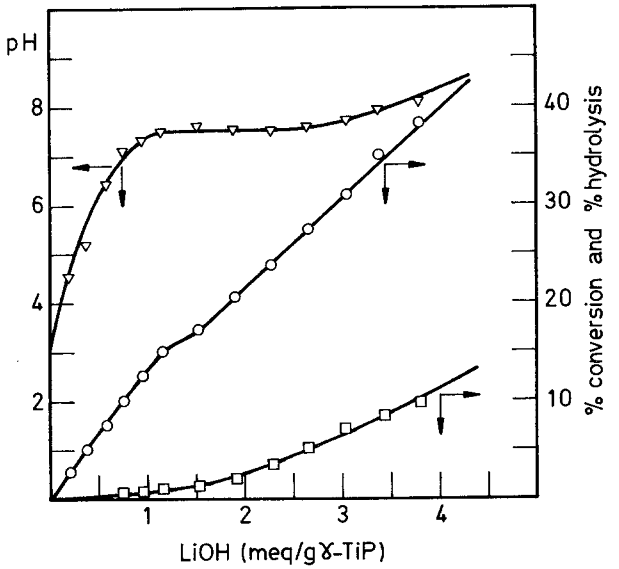

Fig. 1. H^+/Li^+ system: titration (▽) and hydrolysis (□) curves and exchange isotherm corrected by the hydrolysis effect (○).

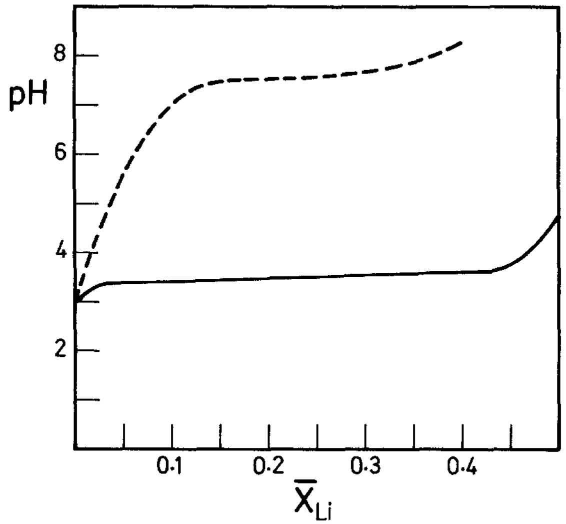

Fig. 2. H^+/Li^+ system: titration curve under dynamic conditions [8]. The dashed line represents the titration curve reproduced from Figure 1.

By X-ray diffraction of the samples that are stable in air, the following crystalline phases were detected: $\overline{HH}\cdot 2\,H_2O$ (11.6 Å), $\overline{H_{1.5}Li_{0.5}}\cdot 2\,H_2O$ (11.0 Å) and $\overline{HLi}\cdot 2\,H_2O$ (11.3 Å). The best drying conditions to determine the relative concentration of each phase with different ionic content as a function of the degree of the solid conversion, were found to be: 80°C in samples $0.00 \leqslant \bar{X}_{Li} \leqslant 0.25$, the $\overline{HH}$ (9.1 Å) and $H_{1.5}Li_{0.5}2\cdot H_2O$ (11.0 Å) phase being detected and 220°C for samples $0.00 \leqslant \bar{X}_{Li} \leqslant 0.50$ with the presence of the $\overline{HH}$ (9.1 Å) and $\overline{HLi}$ (9.6 Å) phases. The treatment at 220°C transforms the $H_{1.5}Li_{0.5}\cdot 2\,H_2O$ (11.0 Å) phase into a mixture of the two phases $\overline{HH}$ (9.1 Å) and $\overline{HLi}$ (9.6 Å). A similar behaviour has been detected in the 25% substitution phases of Na and K in γ-TiP [13–15]. In Figure 3, X-ray patterns of some exchanged solid treated under the stated conditions, can be seen. In the exchanged solids, only two crystalline phases with different ionic content coexisted. It should be noted that the ratio of the crystalline phases for a defined fraction of exchange concurred with the ratio found in dynamic systems. From the data reported, the existence of the following steps during the ion exchange process is inferred:

$$\overline{HH}\cdot 2\,H_2O + \tfrac{1}{2}\,Li^+ \rightleftharpoons \overline{H_{1.5}Li_{0.5}}\cdot n_1\,H_2O + \tfrac{1}{2}\,H^+ + (2-n_1)\,H_2O, \qquad (1)$$

$$\overline{H_{1.5}Li_{0.5}}\cdot n_1\,H_2O + \tfrac{1}{2}\,Li^+ \rightleftharpoons \overline{HLi}\cdot n_2\,H_2O + \tfrac{1}{2}\,H^+ + (n_1-n_2)\,H_2O. \qquad (2)$$

3.2. CESIUM ION EXCHANGE

The amount of Cs^+ retained by the solid and the pH at the end point of each calorimetric measurement were determined. These values are plotted against the amount of CsCl added in Figure 4. The pH remains almost constant (1.5) until 25% of the γ-TiP exchange capacity is reached. For additions of CsCl higher than

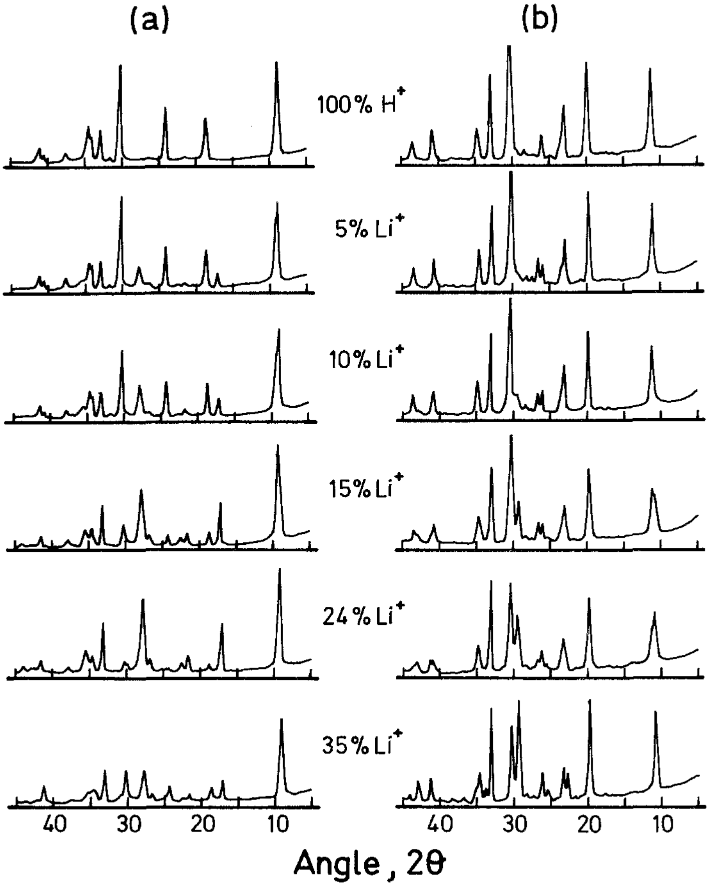

Fig. 3. H^+/Li^+ system: X-ray patterns of exchanged solids: (a) stable in air at room temperature and (b) heated at 200°C.

6.0 meq/g γ-TiP the retention remains constant so that the pH increases slightly. The experiments made under dynamic conditions [9] show a similar behaviour, but the 25% conversion is reached with the addition of only 2.1 meq CsCl/g γ-TiP. As in the lithium case, the end point reached under static conditions is not a situation of thermodynamic equilibrium.

By X-ray diffraction of the samples stabilized in air, the $\overline{HH}\cdot 2\,H_2O$ (11.6 Å) and $\overline{H_{1.5}Cs_{0.5}}\cdot 2\,H_2O$ (11.6 Å) crystalline phases were detected. The interlayer distance of both crystalline phases is the same and thus the study of low angular zones does not give information (unlike the lithium case). Nevertheless, their X-ray patterns are quite different (Fig. 5). 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. The reaction is:

$$\overline{HH}\cdot 2\,H_2O + \tfrac{1}{2}\,Cs^+ \rightleftharpoons \overline{H_{1.5}Cs_{0.5}}\cdot n_3\,H_2O + \tfrac{1}{2}\,H^+ + (2 - n_3)\,H_2O \qquad (3)$$

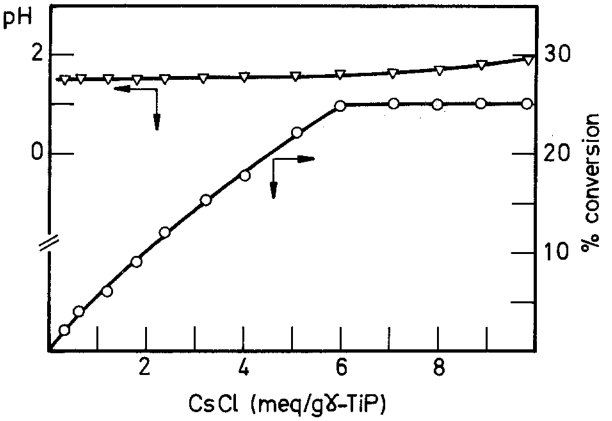

Fig. 4. H^+/Cs^+ system: pH curve (▽) and exchange isotherm (○).

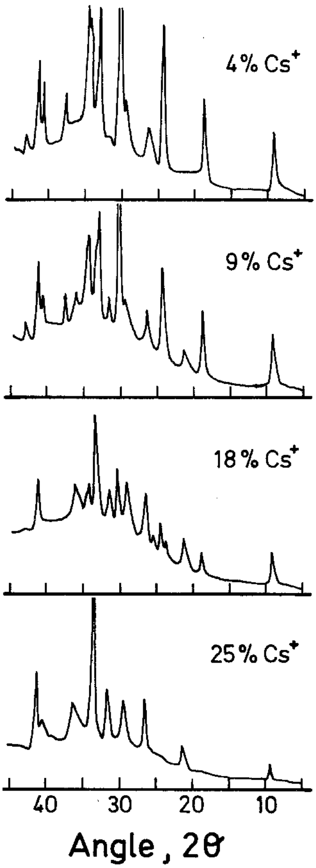

Fig. 5. H^+/Cs^+ system: X-ray patterns of exchanged solids stabilized in air at room temperature.

3.3. HEAT DATA

In the cesium case, the calorimetric curves always show the same shape: an 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 $\bar{X}_{\mathrm{Li}} < 0.24$, these curves are very similar to those obtained for cesium. Most of the heat released was recorded 1–2 minutes after the beginning of the reaction. The rate of return to the base line is a function of the amount of LiOH added. When $\bar{X}_{\mathrm{Li}} > 0.24$ a new maximum appears, 10–20 minutes after the reaction starts, with an intensity lower than in the first case (Figure 6). Both maxima are a consequence of the processes represented by Equations (1) and (2) respectively. Although the γ-TiP structure is unknown it might be expected to contain zeolitic cavities owing to its ion exchange behaviour. The difficulty in obtaining conversions higher than 50% [8, 9, 14,15] suggests that each zeolitic cavity contains two hydrogen ions, and, thus, the counterions should 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 suggests the existence of two different zeolitic cavities. If we take into account the transformation during the thermal treatment of the 25% substitution phases into mixtures of unexchanged phases and half exchanged phases, we can assume that the two different types of zeolitic cavities are placed in alternate interlayer spacings. A connection between different zeolitic cavities is not possible. By assuming an ideal γ-TiP crystal, the activity of a lithium ion at the surface will be different depending on the interlayer spacing that the ion reaches. 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 [16]. Therefore, the zeolitic cavities in the interlayer spacing with the biggest surface activity, will be first filled. Only when this process is achieved, will occupation of the other type of zeolitic cavities (placed in the interlayer spacing adjacent to the firstly occupied) occur. This would explain the existence of the two maxima in the calorimetric curves. If both types of zeolitic cavities were in the same interlayer spacing, with a connection between them, the lithium ion activity would be the same over all the γ-TiP surface and thus, under the influence of the hydroxide ions, both zeolitic cavities could be occupied simultaneously. Parallel to this process a second and presumably much slower exchange process also takes place: lithium ions diffuse into the cavities of the γ-TiP phase and exchange with hydrogen ions. The system approaches slowly to thermodynamic stability [17]. According to this model, the calorimetric curves would only have one maximum.

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 ($\Delta H_{\mathrm{x}}^{0}$) and (b) the neutralization reaction when (LiCl + LiOH) solutions were used (ΔH_{N}). When the initial solution contains LiOH, the exact knowledge of the molar enthalpy of neutralization from our experimental measurements (55.89 kJ mol^{-1}) makes the calculation of (a) possible ($\Delta H_{\mathrm{x}}^{0} = \Delta H - \Delta H_{\mathrm{N}}$). Figure 7 shows the variation of $\Delta H_{\mathrm{x}}^{0}$ as a function of the extent of the exchange in both studied systems. The dashed lines show the results obtained from titration data [8, 9]. The agreement is good for the cesium system. In the lithium system, the

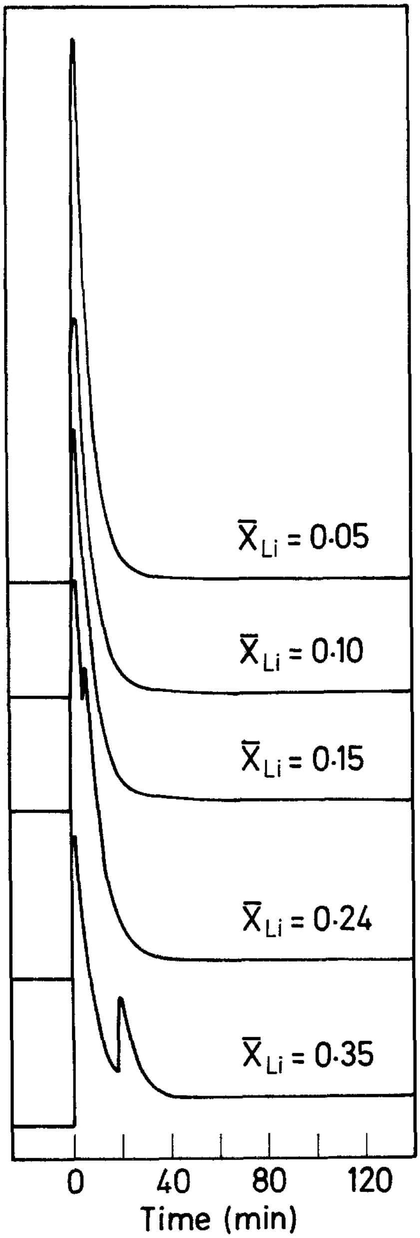

Fig. 6. H^+/Li^+ system: calorimetric curves of samples with $0.00 \leqslant \bar{X}_{Li} < 0.50$ conversion.

results obtained by both methods only concur for low conversions when the γ-TiP hydrolysis is negligible. For conversions higher than 10% there were discrepancies which increased with the degree of conversion. Hydrolysis also increases with the conversion (Figure 1). The break-up of the crystalline lattice of the γ-TiP:

$$Ti(HPO_4)_2{\cdot}2\,H_2O\,(cr) + 4\,OH^- + (n-4)\,H_2O \rightarrow TiO_2{\cdot}n\,H_2O\ (s) + 2\,HPO_4^{2-} \qquad (4)$$

$$Ti(HPO_4)_2{\cdot}2\,H_2O\,(cr) + 2\,OH^- + (n-2)\,H_2O \rightarrow TiO_2{\cdot}n\,H_2O\,(s) + 2\,H_2PO_4^- \quad (5)$$

is an endothermic process, whose heat of reaction is 500.4 ± 10 kJ mol^{-1} [10], including the enthalpic variation (3.3 kJ mol^{-1}) of the process [18]:

$$H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+. \quad (6)$$

When the enthalpy variations of the neutralization and hydrolysis processes are inferred from experimental values, a good agreement between the values of ΔH_x^0 derived from both methods was found (Figure 8). The existence of solid solutions in the process is not reflected in the enthalpy term since the ΔH_x^0 curves consist of unbroken straight lines over each two-phase region. The uncertainty in the ΔH_x^0 values obtained by calorimetric measurements increased with the degree of hydrolysis undergone by the material. This fact makes it impossible to obtain accurate calorimetric determinations for $\bar{X}_M > 0.25$ (M = Li, Cs).

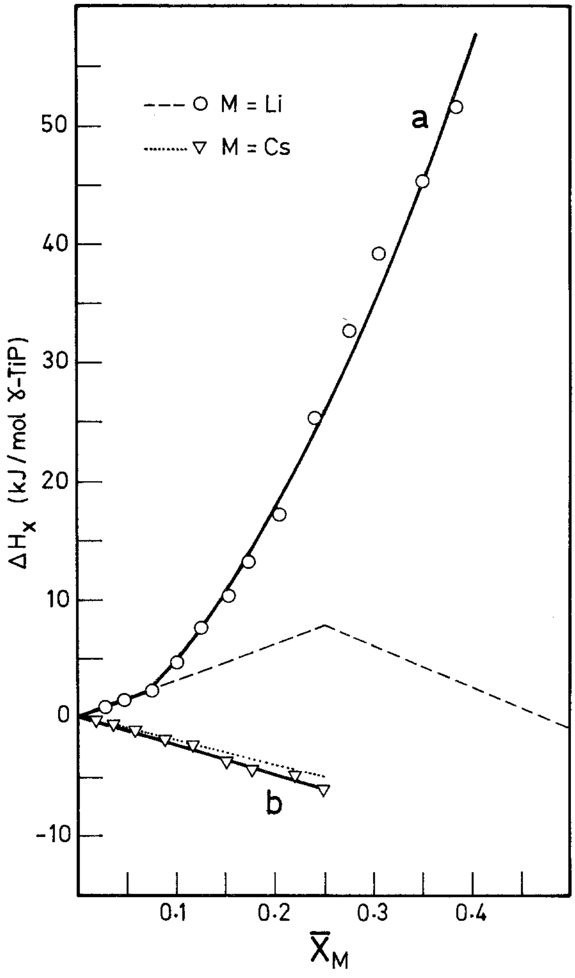

Fig. 7. Variation of the reaction heat against the substitution extent: (a) (M = Li, (b) M = Cs. The dashed lines show the results obtained from titration data [8, 9].

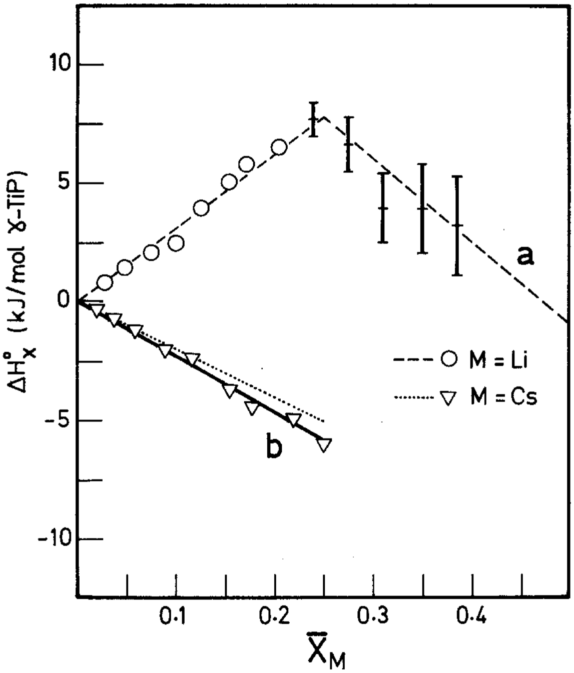

Fig. 8. Variation of the heat in the H^+/M^+ exchange in γ-TiP against the substitution extent: (a) M = Li, (b) M = Cs. The dashed lines show the results obtained from titration data [8, 9].

4. Conclusion

The results obtained in this paper verify the thermodynamic data obtained from titration data for the ion exchange processes described by Equations (1) and (3). The difference between the values of the equilibrium constants of both processes ($pK_{Li} = 0.96$, $pK_{Cs} = -1.25$) [8, 9] makes γ-TiP a possible material for the extraction of cesium from aqueous solutions containing high lithium concentrations. This fact must be proved by means of the study of the ternary system $H^+/Li^+/Cs^+$.

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