Crystalline α-titanium(IV) hydrogenphosphate and its sodium- and *n*-butylammonium-intercalated forms: ion exchange and thermochemistry

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Crystalline α-titanium(IV) hydrogenphosphate and its sodium- and *n*-butylammonium-intercalated forms were used as exchangers with MX_2 (M = Zn or Cu; X = Cl, NO_3 or $MeCO_2$) in aqueous medium at 298.2 ± 0.2 K. An enhancement of the exchange capacity was observed for α-$Ti(HPO_4)_2$ and its sodium form when acetate was used as the counter ion for both zinc and copper cation solutions. Thermodynamic determinations for all ion-exchange processes were performed by titrating calorimetrically a suspension of a given exchanger in water (2.0 cm^3) with an aqueous cation solution in a heat-flow microcalorimeter at 298.15 ± 0.01 K. In all cases the net thermal effects were calculated after subtracting the corresponding dilution thermal effects. With the exception of exothermic ion-exchange processes involving $CuCl_2$ with the α-$Ti(HPO_4)_2$ and sodium forms, and $Zn(NO_3)_2$ with α-$Ti(HPO_4)_2$, which gave −2.40 ± 0.12, −1.01 ± 0.01 and −12.26 ± 0.15 kJ mol^{-1}, respectively, all other exchange processes were endothermic in nature with low enthalpy values, varying from 0.010 ± 0.001 to 8.59 ± 0.14 kJ mol^{-1} for the $Zn(NO_3)_2$ and $Zn(O_2CMe)_2$ systems, with the sodium form. The number of moles exchanged did not correlate with the corresponding enthalpies. However, the thermodynamic data are in agreement with the occurrence of a spontaneous and entropically favourable ion-exchange process for all systems considered.

The interest in ion-exchange materials grew after World War II when compounds having greater stability at high temperatures were needed, mainly for use in high radiation fields in nuclear technology.[1] The selectivity of these compounds towards cations has led to many applications in chromatographic separations.[2–10]

The initial studies of ion exchangers were focused on hydrated oxides such as $ZrO_2 \cdot xH_2O$ and $SiO_2 \cdot xH_2O$. These compounds are normally prepared in amorphous or poorly crystalline forms and show amphoteric properties in sorbing or coprecipitating many ions from aqueous solutions. These hydrated oxides exhibit small ion-exchange capacities in the range from 1.0 to 2.0 mmol g^{-1} and are easily hydrolysed in alkaline media or in hot water.[1] However, these properties can be drastically changed when the oxides are chemically combined with other anions such as phosphates, arsenates, molybdates, *etc.* The resulting compounds present exchange capacities up to 8.0 mmol g^{-1}, as is observed for example with zirconium and titanium phosphates.[1]

Zirconium phosphate played an important part in this field, being widely used as an ion exchanger. It was initially isolated by precipitation at room temperature as an amorphous compound.[11] However, this preparation method is not clearly reproducible because of the presence of the easily hydrolysable tetravalent titanium cations in the medium. This exchanger shows a high capacity, however hot water and variation in pH of the medium drastically changed its effective capacity. For these reasons the use of this kind of material has been criticized.[12]

The amorphous zirconium phosphate compound undergoes a complete change in properties when transformed into a crystalline form by refluxing with concentrated phosphoric acid. The new compound, often designated as the α form,[13] behaves as a new exchanger. The crystalline arrangement is basically a layered structure with the metal atoms in a plane, bridged by phosphate groups which are located above and below the metal atom plane. Three oxygens of each tetrahedral phosphate are linked to three distinct metal atoms and each metal is octahedrally co-ordinated by six oxygens of six different phosphate groups. The fourth oxygen atom of each phosphate group is bonded to a proton in the interlayer space.[14,15] This phosphate group distribution creates zeolitic semicavities on both layer faces, containing water molecules hydrogen bonded to three of the acid phosphate groups on the same layer. This arrangement permits the diffusion of spherical particles with a theoretical size of 261 pm.[16,17] This kind of structure was found for a series of isomorphic phosphates of other tetravalent metals and can be represented by the general formula α-$M(HPO_4)_2 \cdot H_2O$ (M = Zr, Ti, Sn, *etc.*).[1]

The lamella are only weakly held together by dispersion forces, which produce an extensible two-dimensional space.[18] Each phosphate group presents an area available for exchange of 24.0×10^4 pm^2, and the OH groups are hydrogen bonded to water molecules present in the zeolitic cavities, but not with other phosphate groups located in the opposite layer.[19] This regular phosphate group distribution along the inorganic layers favours a large ion-exchange capacity which can reach 8.0 mmol g^{-1}. Consequently, this class of crystalline phosphates is useful in ion exchange,[1,20–24] intercalation of polar organic molecules[25–32] and catalysis.[33–35]

The interlamellar space of 756 pm would theoretically permit the diffusion of molecules up to 261 pm through the gallery, such as the K^+ cation without its water of solution. However, since the lamella are weakly bonded together, the entry of species causes separations, diffusion into the free space of the galleries and also exchange with larger cations. Ion exchange is also favourable in basic solutions and at high temperatures.[1] The zeolitic nature of the crystals and the weak forces between the layers are the basis for the selective behaviour and the expansion of the interlamellar space during the exchange process.[36]

The proposed mechanism for ion exchange initially involves diffusion of non-hydrated or partially hydrated cations into the cavities. Proximity of the cation to the exchange centre of the phosphate groups can occur without any disturbance of the interlamellar distance, until over half of the protons available are exchanged. The subsequent diffusion of water into the crystal lattice rehydrates the cations and also facilitates exchange of the remaining protons of the phosphates. This process is accompanied by an increase in the interlamellar distance. Ion exchange involves diffusion of the hydrated cations into the cavities of the adsorbate, inducing an exchange, which can be performed in distinct steps.[37–40]

The large number of studies of ion exchange reported deal mainly with structural features and thermodynamic data for these reactions are very scarce. Some thermodynamic values have been obtained for titanium phosphate as exchanger for alkali and some divalent metals by determination of isotherms at different temperatures with the crystalline compound[14,17,41,42] and by calorimetric determinations with amorphous and crystalline zirconium or titanium phosphates.[43–45]

The main objective of this publication is to report some calorimeric determinations involving the interaction of α-titanium(IV) hydrogen phosphate, α-$Ti(HPO_4)_2$, and its sodium and *n*-butylammonium intercalated forms with MX_2 (M = Zn or Cu; X = Cl, NO_3 or $MeCO_2$), in order to contribute to the understanding of the energetics of the exchange process.

Experimental

Materials

All chemicals used were reagent grade. Demineralized water was used throughout the experiments. Titanium tetrachloride (Riedel), disodium hydrogenphosphate (Anidrol), *n*-butylamine (Aldrich), and phosphoric acid (Carlo Erba) were used for preparations. All salts, copper and zinc chloride, nitrate and acetate, sodium chloride and sodium hydroxide, were analytical grade and used without purification.

Preparations

Amorphous titanium phosphate was prepared by slowly adding 5.0×10^{-2} mol dm^{-3} disodium hydrogenphosphate solution to an equivalent hydrochloric acid solution of titanium tetrachloride in 2 : 1 (v/v) proportion. The gel formed was allowed to stand in the mother-liquor for 24 h at room temperature. Then the solid was filtered off, washed with twice distilled water and dried at 313 K. α-Titanium hydrogenphosphate was prepared by refluxing the amorphous material (1.0 g) with a solution (40.0 cm^3) of 12.0 mol dm^{-3} H_3PO_4 for 160 h at 433 K. The crystalline solid was washed until pH 4.0, dried to constant weight over P_2O_5 and analysed as before.[46]

The α-titanium phosphate sodium and *n*-butylammonium intercalated compounds were obtained by leaving α-$Ti(HPO_4)_2$ in contact with mixtures of 0.10 mol dm^{-3} sodium chloride and sodium hydroxide solutions[47] or with *n*-butylammonium chloride and *n*-butylamine solutions,[48] respectively. The modified phosphates obtained were dried overnight at 313 K and analysed as before.[46–48]

Ionic exchange in solution

The adsorption process was followed batchwise in aqueous solution at 298.2 ± 0.2 K for the divalent cations as their salts MX_2 (M = Zn or Cu; X = Cl, NO_3 or $MeCO_2$). The ionic exchange in aqueous solution was performed by using a batch process at 298.2 ± 0.2 K. First, the time required to obtain maximum exchange was established. A sample of the exchanger (≈0.12 g) was suspended in 50.0 cm^3 of 1.0 mol dm^{-3} MX_2 with controlled mechanical stirring. Aliquots of the supernatant were pipetted and the cation determined by complexiometric titration with ethylenedinitrilotetraacetate (edta). The amount of cation exchanged (n_f) was expressed as $(n_i - n_s)/m$, where n_i is the initial number of moles of cation in solution, n_s the number of moles of cation in solution in equilibrium with the solid phase and m the mass of the lamellar compound. A plot of n_f as a function of time showed that 4 h was sufficient to obtain maximum adsorption. To obtain the complete ion-exchange isotherm for each salt considered the same procedure was used with concentrations varying from 4.0×10^{-3} to 1.0 mol dm^{-3}. At the end the solid was separated by centrifuging the suspension and dried at 373 K, and aliquots of the supernatant were analysed as before. The reproducibility of the experimental determinations was checked by using at least one duplicate run.

Analytical procedures

The three titanium phosphate forms and the exchanged solids were characterized by the following techniques. Determinations of the mass losses were performed on a DuPont model 1090B thermogravimetric instrument coupled with a 951 thermobalance. Samples varying in weight from 15.0 to 30.0 mg were heating at a rate of 8.2×10^{-2} K s^{-1} in a flux of dry nitrogen. X-Ray powder patterns were obtained with nickel-filtered Cu-K radiation on a Shimadzu model XD3A diffractometer and the interlayer spacing of the compounds was calculated from the 002 plane. Infrared spectra were obtained on a Perkin-Elmer FTIR 1600 spectrometer, using pulverized samples. Phosphorus-31 NMR spectra were obtained for α-$Ti(HPO_4)_2$ and its sodium form on an AC 300/P Bruker spectrometer at 121 MHz with magic angle spinning at room temperature with 85% H_3PO_4 used as external reference to calibrate the chemical shift scale. The amount of sodium intercalated was determined by flame photometry and the amount of butylammonium intercalated by a Perkin-Elmer PE-2400 elemental analyser.

Calorimetry

The thermal effect at the solid–liquid interface during the exchange process was followed by means of an LKB 2277 heat-flow microcalorimeter.[49] A sample of an exchanger (≈0.2 g) was suspended in deionized water (2.0 cm^3) with vigorous stirring at 298.15 ± 0.01 K. A thermostatted aqueous cation solution with concentration in the range 0.50 to 0.90 mol dm^{-3} was incrementally added to the calorimetric vessel. For each increment, the thermal effect was recorded and the process was continued until maximum thermal effect was achieved. From this procedure the sum of the thermal effects of all titration steps ($\Sigma\Delta_{tit}h$) was obtained. Identically, to the same volume of water a sequence of increments of the cation was added and the sum of the thermal effect of dilution ($\Sigma\Delta_{dil}h$) was obtained. A null thermal effect was observed when only twice distilled water was added to the calorimetric vessel containing a suspension of the exchanger, which showed that there was no thermal effect due to the hydration of the exchanger. Therefore, the net thermal effect of reaction ($\Sigma\Delta_r h$) is given by: $\Sigma\Delta_r h = \Sigma\Delta_{tit}h - \Sigma\Delta_{dil}h$. The ion exchange can be described by the general equation (1) where TPY_2 and TPM are the original and

$$TPY_2(hyd) + M^{2+}(aq) \xrightleftharpoons{\Delta_{exch}H} TPM(hyd) + 2Y^+(aq) \quad (1)$$

exchanged phases, respectively, M^{2+} and Y^+ are the cations to be exchanged and the exchanged cations, respectively. From the data obtained for $\Sigma\Delta_r H$ the enthalpy of the reaction ($\Delta_{exch}H$) was determined by adjusting the collected values to a modified Langmuir equation.

Results and Discussion

The elemental analysis of the synthetic layered α-titanium hydrogenphosphate showed a 1.0 : 2.0 molar proportion between titanium and phosphorus.[46] The interlamellar distance of 756 pm obtained by means of X-ray measurements is in complete agreement with the reported value.[50] The ion-exchange capacity of 7.70 mmol g^{-1} was assayed from the exchange with *n*-alkylamine aqueous solution.[46] The thermogravimetric curve indicated mass losses in two distinct steps. In the first stage 9.1% is lost in the range 313 to 550 K due to elimination of the hydrated water. This step is followed by a 4.2% loss in the range 670 to 790 K which is attributed to the loss of water of condensation, resulting from the interaction of the free hydroxyl groups of the phosphate distributed on the backbone of the inorganic sheet into pyrophosphate.[46] This total mass loss corresponds to the presence of two molecules of water per mole of exchanger in the lattice.[15,46] The infrared spectrum showed the presence of the main characteristic bands expected. Two bands at 3555 and 3010 cm^{-1} are attributed to asymmetric and symmetric O–H stretching vibrations, respectively, consistent with the presence of water molecules in the lamellar space. The P–OH stretching vibration appeared at 3478 cm^{-1}, the corresponding bending vibration at 1617 cm^{-1} and the in- and out-of-plane bending modes at 1250 and 614 cm^{-1}, respectively. Other intense stretching bands attributed to the PO_4 group occurred at 1033, 1010, 1116 and 970 cm^{-1} and the stretching P–O–P mode at 722 cm^{-1}. These data corroborated the successful synthesis of this lamellar compound.[46,51,52] The ^{31}P cross polarization magic angle spinning (CP MAS) NMR spectrum showed only a narrow and intense peak at δ −18.4 which was attributed to the protonated phosphate group.[53,54]

The α-titanium phosphate sodium form was successfully prepared by completely exchanging the available protons by sodium cations in a mixture of chloride and hydroxide solutions. X-Ray diffractometry indicated the coexistence of three different phases with interlamellar distances of 837 (30), 997 (39) and 1057 pm (31%). As the ^{31}P CP MAS NMR spectrum showed only a narrow and intense peak at δ −15.1, attributed to the deprotonated phosphate,[55] the presence of distinct phases can be attributed to different numbers of water molecules.[14,37,47,56] The infrared spectrum showed a peak at 1653 cm^{-1}, also attributed to the deprotonated phosphate, in agreement with the NMR spectrum. The thermogravimetric curve showed a total mass loss of 14.3%, which can be attributed to the loss of the water molecules presented in the interlayer space. Therefore, these results indicate the coexistence of the following phases in this material: $Ti(NaPO_4)_2\cdot H_2O$ (30), $Ti(NaPO_4)_2\cdot 3H_2O$ (39) and $Ti(NaPO_4)_2\cdot 4H_2O$ (31%).

The amount of *n*-butylammonium intercalated into the crystalline compound was determined from the exchange isotherms as 1.02 mol per mol, which corresponds to half of the expected acid centres available. This value was confirmed by the thermogravimetric curve, which shows a total mass loss of 37.1%. However, it is possible to distinguish an amount of 14.0 %, which is coherent with the loss of two molecules of water. The remaining 23.1% was attributed to loss of the amine, which corresponds to 1.02 mol *n*-butylammonium cations per mol of α-$Ti(HPO_4)_2$. The distribution of the amine molecules into the lamella drastically changes the interlamellar distance to 1839 pm, which is more than twice that of the unintercalated compound. The infrared spectrum showed characteristic bending vibrations peaks of the NH_3^+ group at 1515 and 1465 cm^{-1}, and a broad band between 3000 and 3400 cm^{-1} due to the stretching vibrations.[57] Based on the results obtained from different techniques, the minimum formula is $Ti(HPO_4)_2\cdot 1.02[H_2N(CH_2)_3CH_3]\cdot H_2O$.

Table 1 Amount of cations intercalated (n_f) for the interaction of MX_2 (M = Zn or Cu; X = Cl, NO_3 or $MeCO_2$) with crystalline α-titanium hydrogenphosphate acid and its sodium- and *n*-butylammonium-intercalated forms at 298.2 ± 0.2 K

	n_f/mmol g^{-1}		
Compound	α-$Ti(HPO_4)_2$	Sodium form	$NBu^nH_3^+$ form
$Cu(O_2CMe)_2$	0.133	1.91	3.13
$CuCl_2$	0.033	1.98	1.50
$Cu(NO_3)_2$	0.207	1.52	1.52
$Zn(O_2CMe)_2$	0.131	1.25	1.97
$ZnCl_2$	0.057	1.40	0.85
$Zn(NO_3)_2$	0.028	1.36	1.40

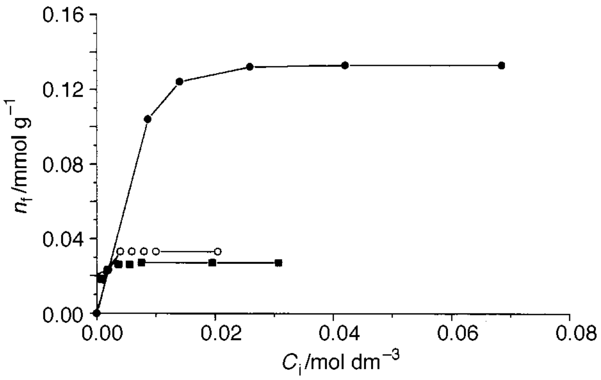

Fig. 1 Isotherms for ion exchange of crystalline α-titanium hydrogenphosphate with $Cu(O_2CMe)_2$ (●), $CuCl_2$ (○) and $Cu(NO_3)_2$ (■)

The general ion-exchange processes on the surface involve the replacement of the protons, sodium or *n*-butylammonium cations disposed between the lamella by the divalent cations zinc and copper, in chloride, nitrate and acetate forms, as represented by equations (2)–(4). The ion-exchange isotherms shown in Fig. 1 for α-$Ti(HPO_4)_2$ with the copper salts illustrate clearly the influence of the counter anion. From the shape of the three isotherms the exchange in the presence of acetate represents a much more favourable system than those observed for nitrate and chloride. This behaviour can be explained by the fact that the acetate anion reacts with the proton released from the acidic exchanger to cause an increase in the number of moles exchanged. The specific values for these exchange processes are listed in Table 1. These data suggested that the influence of the anion also occurred for the *n*-butylammonium- but not in the sodium-intercalated exchanger. This behaviour can be explained by the presence of protonated and deprotonated phosphate groups in the former and the released proton will react with the acetate anion causing an increase in n_f for both exchangers. The same behaviour was observed with zirconium phosphate giving values which are comparable to those obtained here.[58,59]

$$2{\equiv}P{-}OH(hyd) + M^{2+}(aq) \rightleftharpoons ({\equiv}P{-}O)_2M(hyd) + 2\,H^+(aq) \qquad (2)$$

$$2{\equiv}P{-}O^-\ Na^+(hyd) + M^{2+}(aq) \rightleftharpoons ({\equiv}P{-}O)_2M(hyd) + 2\,Na^+(aq) \qquad (3)$$

$$2{\equiv}P{-}O^-\ {}^+H_3N(CH_2)_3CH_3(hyd) + M^{2+}(aq) \rightleftharpoons ({\equiv}P{-}O)_2M(hyd) + 2\,CH_3(CH_2)_3NH_3^+(aq) \qquad (4)$$

The values in Table 1 show that ion exchange occurs to a much greater extent with the sodium and *n*-butylammonium compounds. In the acidic phosphate exchanger hydrogen is strongly bonded to the oxygen atom which hinders the exchange process. The observed n_f values correspond to only 0.7 to 3.5% of the total exchange capacity of the original compound. For the modified compounds, where direct exchange between the ionic species occurs, the exchange capacity increases to 23% for the *n*-butylammonium compound–$ZnCl_2$ system and a maximum of 83% for the exchange of copper acetate with the same exchanger.

The small n_f values for α-$Ti(HPO_4)_2$ can be explained by considering also the size of the hydrated cations. Both cations in this medium have a complete hydration sphere which results in the formation of charged species with volumes of hydration of 178.2 and 147.8 cm^3 mol^{-1} for copper and zinc, respectively.[45] Assuming these geometries, their diameters are 340 and 320 pm, respectively. These values are larger than the free hole diameter of 261 pm of the lamella, and consequently diffusion of both cations into the interlamellar gallery is hindered. This behaviour was previously described for the exchange process of α-zirconium phosphate and an improvement in the ion exchange was obtained only by using high temperatures, together with an increase in contact time, or by using a mixture of the chloride and hydroxide of the desired metal.[15,60,61] An alternative method to increase the number of moles exchanged is to increase the interlamellar distance by modifying the exchanger with sodium or by introducing an organic spacer into the lamellar gallery.[48,58] The efficiency of the latter procedure was confirmed by the present results as can be seen in Table 1. For both the sodium and *n*-butylammonium intercalated forms, a significant increase in the number of moles fixed for copper and zinc was observed. These results are consistent with an increase in the interlamellar distance which facilitates diffusion of the cations and favours enhancement of the exchange process. For example, for zinc chloride the exchange with the acid form α-Ti(HPO$_4$)$_2$ was 0.057 mmol g^{-1}, whilst with the sodium form, the ionic exchange increased nearly 25-fold to 1.40 mmol g^{-1}. On the other hand, the ion exchange with the sodium or butylammonium materials gave similar values, although the organic cation results in a larger interlamellar distance. Therefore, these values suggest that the sodium lamellar separation is sufficient for a normal diffusion of zinc and copper cations in the ion exchange process.

X-Ray diffractometry was used to obtain additional information about the interlamellar distance of the exchangers. For the α-Ti(HPO$_4$)$_2$–MX$_2$ system, the original interlamellar distance of 756 pm was maintained. On the other hand, the sodium exchanger displayed two distinct distances of 975 and 756 pm, which can be attributed to the sodium and the phase where the exchange occurred, respectively. In the case of the *n*-butylammonium exchanger, the resulting compounds after ion exchange showed only one peak at 756 pm, which is consistent with the removal of the *n*-butylammonium cation previously intercalated.

The Fourier-transform spectra obtained for the exchanged phosphates derived from nitrate salts showed a peak at 1385 cm^{-1}, which can be attributed to the presence of the mentioned anions in the interlamellar space.[57] However, the other compounds obtained from the acetate salts did not show any peak that could be attributed to the presence of acetate in the gallery space.

In the present ion-exchange process, the proton, sodium and *n*-butylammonium groups are available for exchange. These groups are covalently or ionically bonded to phosphates of the inorganic sheets, which can be considered as a phosphate surface. This arrangement resembles various inorganic organofunctionalized supports with available pendant groups to adsorb or exchange species dissolved in solutions. For these processes, a well established modified Langmuir equation has been successfully applied to describe the phenomenon in different surfaces, for example modified silica gel,[62,63] soil[64] and amorphous titanium phosphate.[45] Therefore, the interactive process that takes place at the solid–liquid interface can be represented by the general equation (5) where C_s is the concentration

$$\frac{C_s}{n_f} = \frac{C_s}{n^s} + \frac{1}{n^s b} \qquad (5)$$

(mol dm^{-3}) of the supernatant cation, n_f (mol g^{-1}) is defined as before, n^s is the maximum amount of solute exchanged per gram of exchanger (mol g^{-1}) and b is a constant related to the thermodynamic constant by the expression ($K_x M$)/ρ, where M and ρ are the molar mass and density of the solvent, respectively.[64] From its value, the free energy of the system can be calculated which is denoted here as $\Delta_b G$ to distinguish it from that obtained by calorimetry. The n^s and b values are derived from the linearized form of the exchange isotherms, through the angular and linear coefficients, where C_s/n_f values are plotted against C_s values, as illustrated by Fig. 2. The values obtained for all exchangers are listed in Table 2.

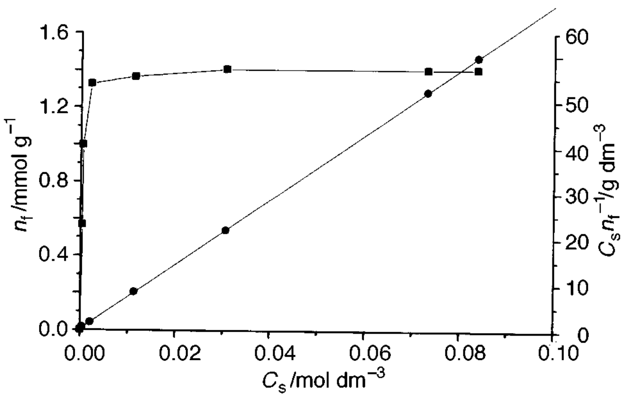

Fig. 2 Isotherms for ion exchange of Zn(NO$_3$)$_2$ with the crystalline *n*-butylammonium intercalated form. The straight line is the linearized form of the isotherm

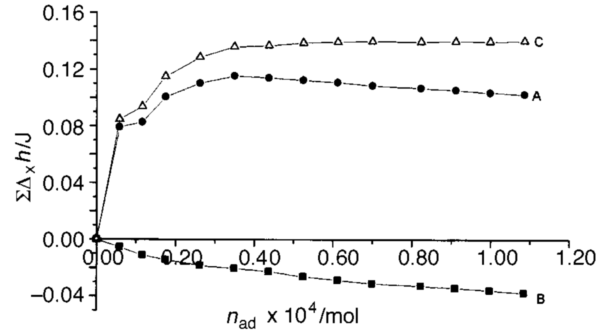

Fig. 3 Calorimetric titration of an initial volume of 2.0 cm^3 of a suspension of mass 0.020 96 g of the crystalline sodium form in water with Zn(NO$_3$)$_2$ of concentration 0.1350 mol dm^{-3} in the same solvent at 298.15 ± 0.01 K. The experimental points in curves A, B and C represent the sum of the thermal effects the cation titration ($\Sigma\Delta_{tit}H$), cation dilution ($\Sigma\Delta_{dil}H$), and the net thermal effect of exchange ($\Sigma\Delta_r H$), respectively

The number of moles exchanged in any operation n_f listed in Table 1 can be compared with the maximum amount of the solute exchanged n^s, shown in Table 2, a close agreement for any pair of values considered being observed. For example, in the ion exchange involving copper nitrate with α-Ti(HPO$_4$)$_2$ values of 0.027 and 0.028 mmol g^{-1} for n_f and n^s respectively were obtained. However, in an attempt to obtain information about the energetics of the interaction between the hydrated cation and the expected regularly disposed phosphate groups centred on the polymeric sheets of the support, a series of calorimetric titrations was considered for all systems studied using the general ion-exchange equation (1). An illustration of the calorimetric titration is shown in Fig. 3, where n_{ad} is the sum of the number of moles added during the calorimetric titration.

As previously described, the adsorption or exchange enthalpies can be determined from the thermal effect for a given adsorption or exchange process on an immobilized surface or by considering an exchanger and the concentration under equilibrium conditions.[45,62,64] The same procedure was applied for the present ion-exchange process, and can be fitted by the general equation (6) where ΣX is the sum at each point of the molar

$$\frac{\Sigma X}{\Sigma \Delta_R h} = \frac{1}{(K-1)\Delta_{mono} h} + \frac{\Sigma X}{\Delta_{mono} h} \qquad (6)$$

fraction of the cation in solution after exchange, $\Sigma\Delta_R h$ the integral enthalpy of exchange (J g^{-1}) obtained through division

Table 2 Maximum amount of cation exchanged per gram of exchanger (n^s), constant *b*, correlation coefficient *r* and free energy for the exchange process ($\Delta_b G$) for MX_2 (M = Zn or Cu; X = Cl, NO_3 or $MeCO_2$)

Compound	Exchanger	n^s/mmol g^{-1}	*b*	*r*	$-\Delta_b G$/kJ mol^{-1}
$Cu(O_2CMe)_2$	α-$Ti(HPO_4)_2$	0.14 ± 0.01	766.96 ± 39.40	0.999	26.42 ± 0.01
	Na^+	1.92 ± 0.01	3775.38 ± 318.79	0.999	30.37 ± 0.01
	$NBu^nH_3^+$	3.14 ± 0.01	2496.23 ± 203.84	0.999	29.34 ± 0.01
$CuCl_2$	α-$Ti(HPO_4)_2$	0.035 ± 0.001	2253.51 ± 139.69	0.996	29.10 ± 0.01
	Na^+	2.00 ± 0.02	2265.20 ± 142.25	0.999	29.10 ± 0.01
	$NBu^nH_3^+$	1.50 ± 0.01	1009.86 ± 25.13	0.999	27.10 ± 0.01
$Cu(NO_3)_2$	α-$Ti(HPO_4)_2$	0.028 ± 0.001	3797.76 ± 203.43	0.998	30.38 ± 0.01
	Na^+	1.53 ± 0.01	1618.74 ± 108.49	0.999	28.27 ± 0.01
	$NBu^nH_3^+$	1.52 ± 0.01	3351.17 ± 298.52	1.000	30.07 ± 0.01
$Zn(O_2CMe)_2$	α-$Ti(HPO_4)_2$	0.13 ± 0.01	693.70 ± 23.90	0.999	26.17 ± 0.01
	Na^+	1.30 ± 0.02	3055.13 ± 97.19	0.999	29.84 ± 0.01
	$NBu^nH_3^+$	1.97 ± 0.02	703.26 ± 27.34	0.999	26.20 ± 0.01
$ZnCl_2$	α-$Ti(HPO_4)_2$	0.059 ± 0.002	1247.13 ± 61.10	0.998	27.62 ± 0.01
	Na^+	1.43 ± 0.02	3531.07 ± 159.50	0.999	30.20 ± 0.01
	$NBu^nH_3^+$	0.85 ± 0.01	1706.53 ± 104.60	0.999	28.40 ± 0.01
$Zn(NO_3)_2$	α-$Ti(HPO_4)_2$	0.032 ± 0.002	622.91 ± 46.31	0.995	25.90 ± 0.01
	Na^+	1.35 ± 0.002	766.96 ± 39.40	0.999	26.42 ± 0.01
	$NBu^nH_3^+$	1.54 ± 0.03	604.01 ± 29.30	0.999	25.82 ± 0.01

Table 3 Thermodynamics values for the interaction of MX_2 (M = Zn or Cu; X = Cl, NO_3 or $MeCO_2$) with the crystalline ion exchangers at 298.15 ± 0.01 K

Compound	Exchanger	$\Delta_{mono}h$/J g^{-1}	$\Delta_{exch}H$/kJ mol^{-1}	ln *K*	$-\Delta G$/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	*r*
$Cu(O_2CMe)_2$	α-$Ti(HPO_4)_2$	0.54 ± 0.02	4.02 ± 0.14	13.42	33.26 ± 0.01	125 ± 1	0.993
	Na^+	14.58 ± 0.34	7.61 ± 0.20	11.48	28.45 ± 0.01	121 ± 1	0.996
	$NBu^nH_3^+$	18.40 ± 0.24	5.86 ± 0.09	13.13	32.54 ± 0.01	129 ± 1	0.999
$CuCl_2$	α-$Ti(HPO_4)_2$	−0.083 ± 0.002	−2.40 ± 0.12	9.01	22.35 ± 0.01	67 ± 1	0.997
	Na^+	1.87 ± 0.06	0.94 ± 0.03	8.69	21.54 ± 0.01	75 ± 1	0.994
	$NBu^nH_3^+$	−1.52 ± 0.02	−1.01 ± 0.01	9.02	22.35 ± 0.01	70 ± 1	0.999
$Cu(NO_3)_2$	α-$Ti(HPO_4)_2$	0.21 ± 0.01	7.52 ± 0.28	9.56	23.69 ± 0.01	105 ± 1	0.997
	Na^+	6.68 ± 0.04	4.36 ± 0.05	11.40	28.26 ± 0.01	117 ± 1	0.999
	$NBu^nH_3^+$	4.24 ± 0.06	2.79 ± 0.04	10.80	26.78 ± 0.01	99 ± 1	0.999
$Zn(O_2CMe)_2$	α-$Ti(HPO_4)_2$	0.74 ± 0.02	5.52 ± 0.16	9.87	22.46 ± 0.01	94 ± 1	0.997
	Na^+	11.12 ± 0.04	8.59 ± 0.14	14.06	34.86 ± 0.01	154 ± 1	0.999
	$NBu^nH_3^+$	0.93 ± 0.02	0.47 ± 0.01	12.55	31.12 ± 0.01	106 ± 1	0.996
$ZnCl_2$	α-$Ti(HPO_4)_2$	0.51 ± 0.03	8.58 ± 0.54	7.82	19.39 ± 0.01	94 ± 1	0.990
	Na^+	0.14 ± 0.01	0.011 ± 0.001	10.68	26.47 ± 0.01	89 ± 1	0.999
	$NBu^nH_3^+$	2.66 ± 0.03	3.13 ± 0.03	11.84	29.35 ± 0.01	109 ± 1	0.999
$Zn(NO_3)_2$	α-$Ti(HPO_4)_2$	−0.40 ± 0.03	−12.26 ± 0.14	9.22	22.85 ± 0.01	36 ± 1	0.980
	Na^+	0.14 ± 0.01	0.010 ± 0.001	12.79	31.69 ± 0.01	106 ± 1	0.999
	$NBu^nH_3^+$	4.22 ± 0.02	3.00 ± 0.01	12.21	30.26 ± 0.01	91 ± 1	0.999

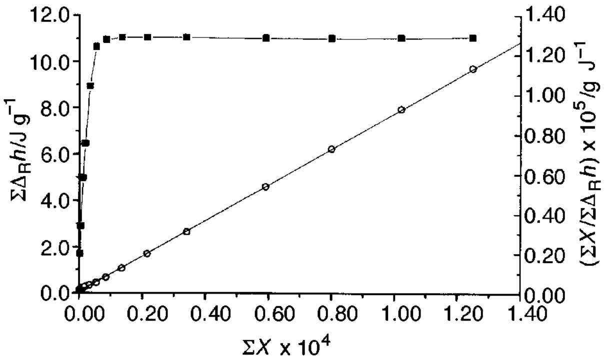

Fig. 4 Isotherm for the integral enthalpy exchange ($\Sigma\Delta_R h$) *versus* molar fraction (ΣX) obtained from a calorimetric titration of a suspension of 0.019 70 g of the crystalline sodium form in water (2.0 cm^3), with $Zn(O_2CMe)_2$ of concentration of 0.1350 mol dm^{-3} in the same solvent at 298.15 ± 0.01 K. The straight line is the linearized form of the isotherm

of the enthalpy of reaction $\Sigma\Delta_r h$ by the mass of exchanger, *K* is a constant, of proportionality, which includes the equilibrium constant, and $\Delta_{mono}h$ the integral enthalpy of the ion exchange for formation of a monolayer per unit mass of exchanger (J g^{-1}). For each amount of solute added, a corresponding *X* value can be calculated. Thus, a plot of $\Sigma X/\Sigma\Delta_R h$ *versus* ΣX gives $\Delta_{mono}h$ and *K* values from the angular and linear coefficients, respectively, of the linearized form of the equation as shown in Fig. 4.

For these systems, $\Delta_{mono}h$, *K* and the correlation coefficient (*r*) values for all ion-exchange systems are shown in Table 3. The calculation of $\Delta_{exch}H$ was based on the expression $\Delta_{exch}H = \Delta_{mono}h/n^s$, where $\Delta_{mono}h$ is the thermal effect of forming a monolayer per gram of exchanger and n^s is the respective maximum amount of solute exchanged per gram of the exchanger listed in Table 2. The deviations quoted for $\Delta_{exch}H$ values were calculated by considering the propagation of the uncertainties for the experimental $\Delta_{mono}h$ and n^s values, which were obtained from the linear regression.

It is worth mentioning that investigations involving calorimetric techniques for detection of the thermal effects associated with ion-exchange processes on exchangers are rare[14,17,41–45] and this work reports the first results obtained for the interaction of lamellar surfaces with divalent cations dispersed in an aqueous medium. The majority of the enthalpic results are endothermic in nature and are small in magnitude, as shown in Table 3. The set of values varies from the extreme exothermicity −12.26 ± 0.14 kJ mol^{-1} to the endothermicity of 8.59 ± 0.14 kJ mol^{-1}, for the ion exchanges involving zinc nitrate with α-$Ti(HPO_4)_2$ and zinc acetate with the sodium form.

The ion exchange of sodium by divalent cations exhibited endothermic enthalpies for all anions. In the presence of acetate the enthalpy values found were 7.61 ± 0.20 and 8.59 ± 0.14 kJ mol^{-1} for copper and zinc, respectively, which are larger than those obtained for the other anions. With the exception of copper chloride with a small exothemic ion-exchange enthalpy of -1.01 ± 0.01 kJ mol^{-1}, all other enthalpic values with the *n*-butylammonium compound are endothermic. On the other hand, α-$Ti(HPO_4)_2$ showed the most pronounced fluctuation in the enthalpic values in relation to the endo- or exo-thermic behaviour of the processes. Therefore, only copper chloride and zinc nitrate have exothermic enthalpic values with this exchanger, with the latter compound inhibiting the larger value of -12.26 ± 0.14 kJ mol^{-1}.

On examining the set of enthalpy values listed in Table 3 for the three exchangers, one notes the low magnitudes for the ion-exchange processes. Among the scarce values found in the literature, the interaction of monovalent cations are with zirconium phosphate have exothermic values of -10.5, -14.2 and -9.2 kJ mol^{-1} for potassium, cerium and rubidium, respectively.[65–67] Nevertheless, for the exchange with divalent cations, the available data are limited to titanium phosphate in γ form. The enthalpies 9.31 and 30.0 kJ mol^{-1} were obtained with strontium and barium cations, respectively.[68,69] Other endothermic values involved cobalt and copper, 42.7 and 35.5 kJ mol^{-1}, respectively.[2,42] A direct comparison of these available data is difficult. For example, the differences between the above values for copper with ours can be attributed to the amount of metal intercalated, since in the case of γ phosphate only half of the ion-exchange capacity was reached, and also to the different crystalline characteristics of the α and γ forms. Another point to consider is the interlamellar distance, which remains unchanged in the α form. The apparent discrepancy in the results may be partly due to the difference in methodology used to obtain the final results, beyond the lack of the same crystalline forms and also the same series of cations, but having a common counter anion. In the previous study the enthalpy values were calculated from a series of isotherms at various temperatures, which differ considerably from our calorimetric methodology. In the technique used here the thermal effects involved in all interaction steps in the ion exchange were obtained, under thermostatted conditions.

The small enthalpies obtained from the calorimetric titration of the ion exchange with divalent cations also reflect the changes in the interlamellar distance during the process. Under normal conditions the exchange results in the formation of a more stable final compound with a low value for this kind of enthalpy. On the other hand, when the interlamellar distance increased during the intercalation, as is the case for *n*-alkylamines or *n*-alkyldiamines, the resulting enthalpies were larger and exothermic for all compounds.[46,70]

The free energy calculated from the calorimetric data showed values in the sequence acetate > nitrate > chloride for all exchangers. For example, the ionic exchange involving the sodium form and copper gave values of -28.45 ± 0.01, -28.28 ± 0.01 and -21.54 ± 0.01 kJ mol^{-1} for acetate, nitrate and chloride, respectively, as listed in Table 3. These values are very close to those calculated from the isotherms. Both methods led to exothermic values for all systems, indicating that favourable reactions occurred. The entropy values listed in Table 3 are also consistent with the favourable reactions. This effect can be explained by the fact that during the exchange processes cations lose molecules of water of hydration to the environment. This occurs because the cation must decrease its size to diffuse into the interlamellar space to reach the bonded proton, sodium or *n*-butylammonium cations, where the exchange occurs. This transfer of water molecules from the hydration sphere to the bulk will consequently promote a disturbance in the medium with an increase in entropy.[71–73]

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