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Some features of crystalline α-titanium hydrogenphosphate, modified sodium and *n*-butylammonium forms and thermodynamics of ionic exchange with K^+ and Ca^{2+}

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Abstract

Crystalline α-titanium phosphate (TPH) was modified to sodium (TPNa) and *n*-butylammonium-intercalated (TPBA) forms. These materials were characterized and then used as exchangers with potassium and calcium in aqueous medium by the batch method at 298.2 ± 0.2 K. Thermodynamic determinations for all ion-exchange processes were performed by calorimetrically titrating suspensions of each exchanger in water (2.0 cm^3) with an aqueous cation solution in a heat-flow microcalorimeter at 298.15 ± 0.02 K. The enthalpy of the ion exchange with the general exchanger TPY can be represented as: $n\mathrm{TPY}_{\mathrm{aq}} + \mathrm{M}^{n+}_{\mathrm{aq}} = (\mathrm{TP})_n\mathrm{M}_{\mathrm{aq}} + n\mathrm{Y}^{+}_{\mathrm{aq}}$; $\Delta_r h$, where Y = H, Na, BA and M = K^+, Ca^{2+}. In all cases, the net thermal effects were calculated after subtracting the respective thermal effect of dilution. The enthalpy of the exchange process for potassium gave the following exothermic values for all matrices: −0.54 ± 0.01, −2.67 ± 0.05 and −4.97 ± 0.04 kJ mol^{-1} for TPH, TPNa, TPBA, respectively. These values contrast with those obtained for calcium, which are endothermic for the same sequence of ionic exchangers: 5.82 ± 0.24, 3.74 ± 0.05 and 0.74 ± 0.02 kJ mol^{-1}, respectively. The Gibbs free energy values indicated that the processes are spontaneous. During the ionic exchange process, the water hydration sphere of the cation promoted deorganization by increasing the molecules of solvent in the media, entropically favoring the system. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetry; Ion exchange; α-Titanium phosphate; Thermodynamics

1. Introduction

Inorganic ionic exchangers continue to develop a wide use in many analytical applications, in which the selectivity and specificity are the main properties explored for a given cation. For this purpose, the utility can be extended to chromatographic separations, in which a relative exchange capacity is expected [1,2]. They also find application in studies relating to catalysts [5], ionic conductors [6], renal dialysis [7] and water softening [7]. In these cases, their usefulness is concerned with some modifications in their optic and electronic properties [3,4].

Crystalline titanium phosphate in the alpha form, namely α-$Ti(HPO_4)\cdot H_2O$ (TPH), has an interlayer distance (*d*) of 760 pm. This compound belongs to the family of lamellar materials and presents an interesting behaviour as ionic exchanger. It is also considered an excellent matrix for the known intercalation process [8]. Several studies on these ionic exchangers refer mainly to structural characteristics.

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On the other hand, thermodynamic data for the ion-exchange reactions are rare. Some thermodynamic values were obtained for γ-titanium and α-zirconium phosphates in studies which made use of alkali metals in ion-exchange isotherms at different temperatures [7,9–11]. The same exchange process was followed by calorimetric determinations with crystalline α-titanium phosphate and crystalline or amorphous zirconium phosphate [12–16]. In addition, the ion-exchange behaviour of those materials has been studied with the complete series of alkali and alkali-earth metals – Li^+, Na^+, K^+, Rb^+ and Cs^+ – with the matrices α-TPH, α-ZrPH and γ-TPH [7,9,10,17,18]. However, no reference is found with modified matrices, such as those containing sodium and *n*-butylammonium.

The aim of this work is to study the behaviour of the ion exchange of potassium and calcium chlorides with titanium hydrogenphosphate in α-(TPH), sodic-(TPNa) and intercalated with the butylammonium-(TPBA) forms. From the calorimetric titration of a suspension of the exchanger in water with the chosen cations, the thermochemical data of these series of ion-exchange reactions are presented.

2. Experimental

2.1. Preparation of the exchangers

All chemicals used are of reagent grade. TPH was obtained by reacting 0.126 mol of 15% titanium trichloride with 0.50 mol of 85% phosphoric acid during four days in polyethylene beaker at 333 K with periodical stirring [19]. The solid material was separated by centrifugation, washed with bidistilled water until the washed part reached the 3.5–4.0 pH range and the final product was then dried at 313 K. TPNa and TPBA were obtained with the batch method. In both the cases, the crystalline lamellar solid TPH was left directly in contact with the desired agent. The first exchanger was obtained by mixing TPH with 0.10 mol dm^{-3} sodium chloride/sodium hydroxide solution during 120 h. TPBA was prepared by using 0.10 mol dm^{-3} of butylamine solution for 24 h at 298 K. The modified phosphates were dried for 24 h at 313 K and then analyzed.

2.2. Ion-exchange reactions

The exchange of isotherms were obtained by varying the concentration and the final exchange was considered after 4 h by using the batch process at 298 ± 0.2 K. The ionic exchanger (0.15 g) was suspended in 20.0 cm^3 of aqueous solution containing a desired metallic chloride, with concentration varying between 1.0×10^{-3} and 0.2 mol dm^{-3}. The concentration of the exchangeable cations in solution was determined by flame photometry [20]. The amount of exchanged cations (n_f) was determined through the relationship $(n_i - n_s)/m$, where n_i is the initial number of moles of cation in the solution, n_s is the number of moles of cations in equilibrium with the solid phase after the exchange process and m the mass of the exchanger used.

2.3. Analytic procedure

The three forms of titanium phosphate and the exchanged solids, were characterized by the following techniques: thermogravimetry (TG) with a DuPont model 1090B instrument, X-ray diffractrometry using CuK_α radiation in Shimadzu model XD3A diffractometry apparatus, infrared spectra using a BOMEM, model MB-series instrument, and ^{31}PRMN spectra of solid samples were obtained in AC300/P Bruker instrument at 121 MHz with CPMAS at room temperature. The pulse sequence, with a contact time of 100 μs, with 10 s interval between pulses, and 45 ms acquisition time were used. Accumulation of >124 and 320 FIDs for TPH and TPNa, respectively, was necessary in order to obtain the static broad-line spectra for the determination of the anisotropy of the chemical shift tensors. H_3PO_4 (85%) was used as a reference to calibrate the chemical shift scale. The amount of inserted *n*-butylammonium was determined by elemental Perkin–Elmer PE-2400 analyzer apparatus.

2.4. Calorimetry

The calorimetric titration was performed in a differential isothermic microcalorimetric system LKB 2277. In a stainless steel ampoule, ca. 20.0 mg of the exchanger were suspended in 2.0 cm^3 of bidistilled water. The system was shaken with a gold helix and thermostated at 298.15 ± 0.02 K. After stabilization of the base line, the apparatus was standardized and a microsyringe was coupled to the system. The microsyringe was connected to a stainless-steel needle and thus used to add increments of the metallic ion solution. The thermal effect caused by the reaction was recorded after each addition. The same procedure was used to follow the thermal effect of the exchanger and the titrant solution in water. If we consider a general exchange TPY (where $\mathrm{Y} = \mathrm{H}^+$, Na^+ or BA^+), the cations exchanged in solution can be represented by the following equation:

$$n\mathrm{TPY}_{\mathrm{aq}} + M^{n+}_{\mathrm{aq}} = (\mathrm{TP})_n M_{\mathrm{aq}} + n\mathrm{Y}^{+}_{\mathrm{aq}}; \quad \Delta_{\mathrm{r}} h \qquad (1)$$

The thermal effect of hydration of the matrix was nil. Therefore, the resultant thermal effect of the reaction ($\sum\Delta_{\mathrm{r}}h$) was related to the thermal effects of titration and dilution by the expression: $\sum\Delta_{\mathrm{r}}h = \sum\Delta_{\mathrm{tit}}h - \sum\Delta_{\mathrm{dil}}h$. Considering the data from the enthalpy of reaction ($\sum\Delta_{\mathrm{r}}h$), it is possible to obtain the exchange enthalpy ($\sum\Delta_{\mathrm{exch}}H$) by using the previous data adjusted to the modified Langmuir equation [21].

3. Results and discussion

The X-ray diffractograms for the TPH, TPNa and TPBA matrices show distinct lamellar distances for each compound. In Fig. 1(a) the lamellar distance is 756 pm, which is characteristic of the crystalline α-hydrogenphosphate TPH [8,22]. On the other hand, a dramatic increase in interlayer distance to 1839 pm is observed in Fig. 1(b). This increase was caused by the insertion of the amine molecule, and its value evidenced the intercalation of the *n*-butylamine into the gallery space of the crystalline TPH support [12]. A different situation is shown in Fig. 1(c), which shows the coexistence of two distinct phases of TPNa [23]. This is indicated by the respective percentages of intensity of the corresponding bands. Thus, a characteristic lamellar distance of 1040 pm is referred to $\mathrm{TiHNa(PO_4)_2{\cdot}4H_2O}$ (67%), while the other, namely 840 pm, can be attributed to the $\mathrm{Ti(NaPO_4)_2{\cdot}H_2O}$ (33%) phases.

^{31}PNMR (CPMAS) spectrum in the solid state of the TPH matrix showed only one intense peak at $\delta = 18.4$ ppm, which is characteristic of the protonated phosphate group [24–26]. The spectrum of the exchanger TPNa, obtained under the same conditions, showed the presence of two peaks, one at $\delta = 18.4$ and the other at $\delta = 15.1$ ppm. These peaks are due to the presence of the protonated and unprotonated phosphate groups in this material, respectively. These data corroborated with the different phases obtained by the diffractogram of this material [26].

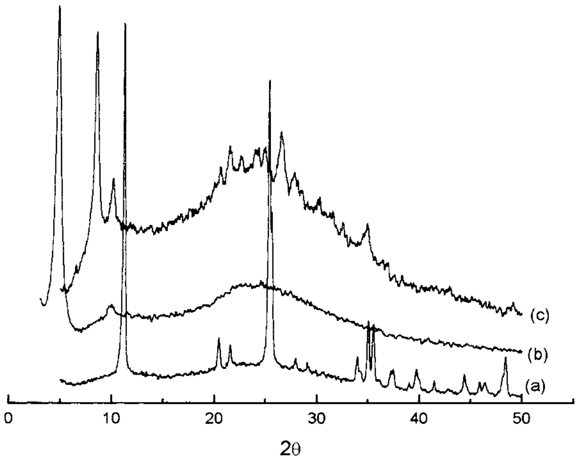

Fig. 1. X-ray diffraction for (a) TPH, (b) TPBA and (c) TPNa matrices.

The thermogravimetric curve presented in Fig. 2(a), indicated that, in the TPH matrix, the mass loss occurred in two different stages. In the first step, the water of hydration was eliminated and in the second step, which is also related to water elimination with the difference that in this latter case the water comes from the condensation of hydrogenphosphate groups to form the stable pyrophosphate group [21,27]. When the modified TPBA exchanger was heated, the recorded thermogravimetric curve showed three distinct stages. The first showed a mass loss of 8% between 323 and 373 K, which corresponded to the elimination of water of hydration. The calculation indicated the presence of 1.5 mol of water per mole of phosphate. In the second step, it was verified that there occurs a 23% mass loss between 373 and 810 K, which was fitted to the intercalated amine, and the calculation corresponded to 1.05 mol of *n*-butylamine per mole of TPH. This result is in accord with the value obtained through elemental analysis. The third stage of decomposition occurred with a mass loss of

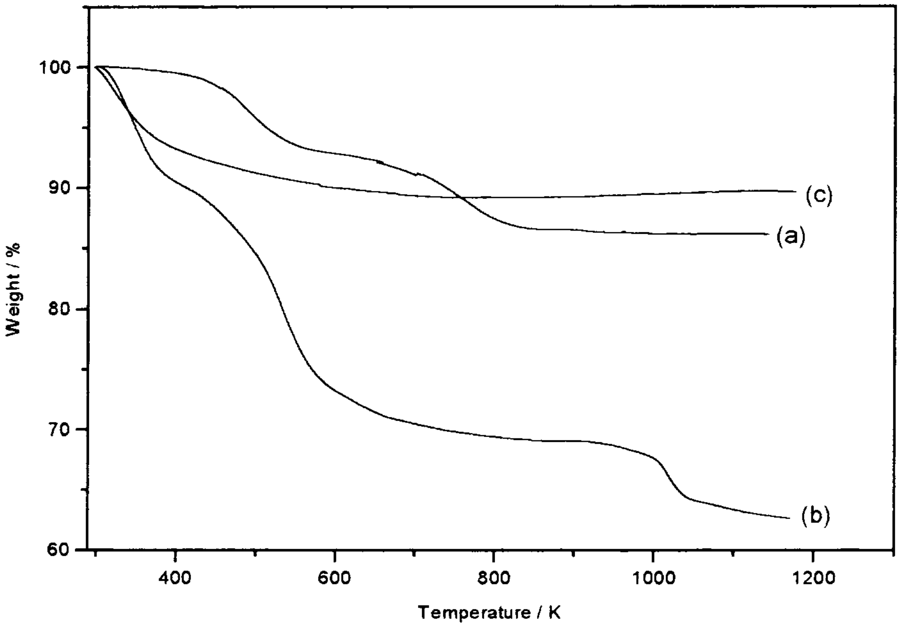

Fig. 2. Thermogravimetric curves of (a) TPH, (b) TPBA and (c) TPNa matrices.

5.9% between 937 and 1170 K, and it corresponded to the elimination of water derived from condensation of hydrogenphosphate to form pyrophosphate. Based on the results obtained with different techniques, the minimum formula is given as $Ti(HPO_4)_2 \cdot 1.05[H_2N(CH_2)_3CH_3] \cdot 1.5H_2O$. In the case of TPNa exchanger, only one stage of mass loss of 11.7% was observed between 303 and 811 K. However, the differential thermogravimetric curve showed two indications of decomposition. The first was at 333 K and the second at 573 K, in agreement with the two stages of decomposition. These values suggested that during the process there occurred an overlap in the decomposition stages. The formation of the pyrophosphate group in the final heating stage is also supported by the ^{31}PNMR spectrum. The observed peaks were assigned to protonated and deprotonated phosphate groups. Based on this fact, the decomposition of 11.7% is attributed to the loss of water, which included the hydration as well as that proceeding from condensation of the hydrogenphosphate groups to form pyrophosphate. These results are in agreement with the phases observed in X-ray diffractometry, which indicated the presence of $TiHNa(PO_4) \cdot 4H_2O$ (67%) and $Ti(NaPO_4)H_2O$ (33%).

The infrared spectrum of TPH showed the presence of the characteristic bands [28] of the PO_4 group at 1010 and 1033 cm^{-1} and the symmetrical stretching frequency of P–OH appeared at 3478 cm^{-1}. For the TPBA matrix, the spectrum showed coherent characteristic bands with the presence of NH^{3+} group at 1465 and 1515 cm^{-1}, which are attributed to the angular deformation, the large band at 3000 and 3400 cm^{-1} is due to the N–H stretching frequency. In the TPNa exchanger, the spectrum did not present significant differences in the 720 and 1100 cm^{-1} regions, where characteristic bands of PO_4 appeared. The band observed at 1653 cm^{-1} can be attributed to the deprotonated phosphate group, in agreement with the ^{31}PNMR spectrum.

In considering the general process of ionic exchange in this kind of inorganic compounds, the precursor cation bonded in the surface is exchanged with the suspended cation in solution. In the present experiments, the bonded cation (proton, sodium and *n*-butylammonium) is exchanged with potassium or calcium.

The exchange of isotherms presented in Fig. 3 show that the exchange is more effective in the modified matrices. This clearly indicates that the increase of the

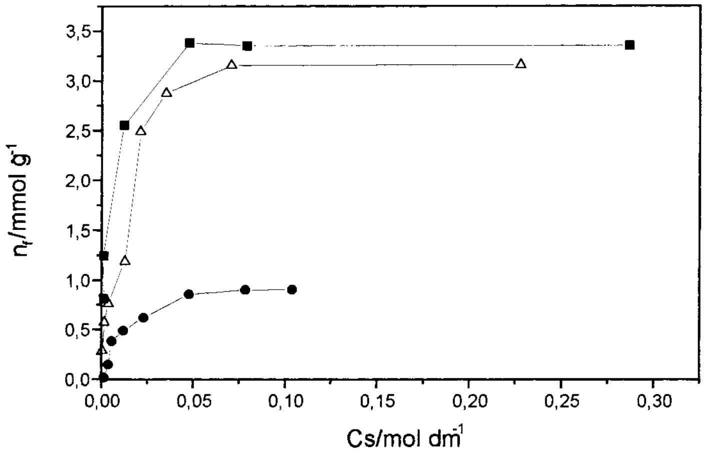

Fig. 3. Isotherms of the ion exchange of potassium with TPH (●) TPNa (△) and TPBA (■).

lamella favours the exchange, because the diffusion of the cations through the lamella becomes easy, and consequently there is an increase in the number of moles fixed [11–13]. For comparison, the maximum value of exchange for TPH with calcium is 0.729 mmol g^{-1}, which contrasted with 2.116 and 2.290 mmol g^{-1} for TPNa and TPBA exchangers, respectively. However, the ionic exchange with sodium and *n*-butylammonium presented similar values. Although the matrix with the latter cation presented a larger interlayer distance, the values showed that above a certain interlayer distance there is no additional influence on the exchange. The complexity of ionic exchange in the acid form was previously demonstrated for zirconium phosphate. In that case, the most effective exchange was obtained by modifying the exchange conditions [29,30].

Another observation on the exchange process is related to the number of fixed moles (n_f) by potassium exchange. This number is larger for potassium than for calcium in all matrices. This behaviour can be attributed to the following three factors: the exchange is dependent on the cation size, the interlayer distance and the low hydration of the potassium in aqueous solution. This last factor favours its mobility into the lamellar space and, consequently, facilitates interaction within the lamella [11,31,32]. Different quantities related to exchange processes are presented in the Table 1.

X-ray diffraction was used to obtain additional information on the interlamellar distance of the exchangers. After the exchange, the original distance of 756 pm in the TPH matrix was maintained. However, with TNPa occurred a contraction of the original lamellar distance from 1040 pm to 960 and 1000 pm for potassium and calcium, respectively. This same behaviour was observed for TPBA, where the original distance of 1839 pm changed to 980 and 1070 pm for

Table 1
Number of moles of intercalated cations (n_f), maximum of exchangeable cations per mole of exchangers (n_s), constant (b) correlation coefficient (r) and free energy for the exchange processes ($\Delta_b G$)

Exchanger	Cation	N_f/(mmol g^{-1})	N^s/(mmolg^{-1})	b	r	$-\Delta_b G$/(kJ mol^{-1})
TPH	K^+	0.91	1.02 ± 0.03	87.61 ± 2.53	0.9983	21.05 ± 0.07
	Ca^{2+}	0.73	0.79 ± 0.02	33.64 ± 0.99	0.9969	18.67 ± 0.07
TPNa	K^+	3.16	3.27 ± 0.02	146.18 ± 2.56	0.9992	22.31 ± 0.04
	Ca^{2+}	2.09	2.14 ± 0.03	48.24 ± 0.65	0.9996	19.56 ± 0.03
TPBA	K^+	3.35	3.39 ± 0.02	432.13 ± 3.18	0.9998	25.00 ± 0.02
	Ca^{2+}	2.29	2.38 ± 0.04	26.93 ± 0.41	0.9994	18.12 ± 0.04

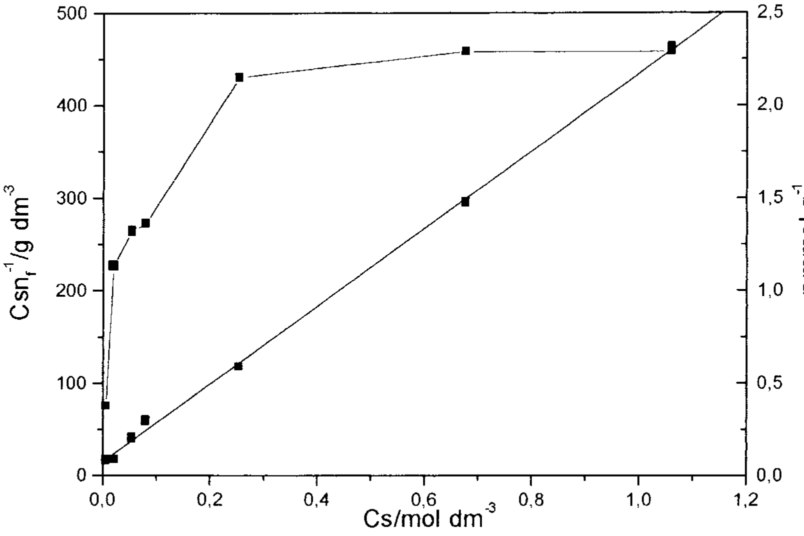

Fig. 4. Isotherms of the ion exchange of calcium with TPBA. The straight line is the linearized form of the isotherm.

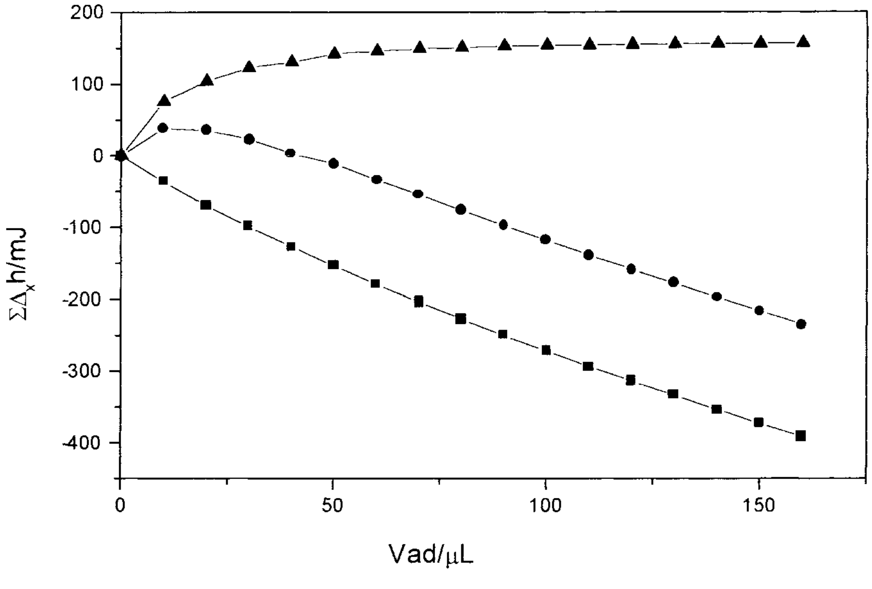

Fig. 5. Calorimetric titration of the exchanger TPNa in aqueous solution with calcium chloride. The points on the experimental curve are the sum of the thermal effects $\sum\Delta_{tit}h$ (●) , $\sum\Delta_{dil}h$ (■) and $\sum\Delta_r h$ (▲).

potassium and calcium, respectively. These values are consistent with the partial removal of the butylammonium cation from the interlamellar space.

The exchange process was also adjusted to the modified Langmuir equation, which was previously shown to be a good model for systems involving ion exchange [1,12,13], and can be represented by:

$$\frac{C_s}{n_f} = \frac{1}{n^s b} + \frac{C_s}{n^s} \qquad (2)$$

where C_s (mol dm^{-3}) is the concentration of the supernatant cation, n_f (mol g^{-1}) as previously defined,

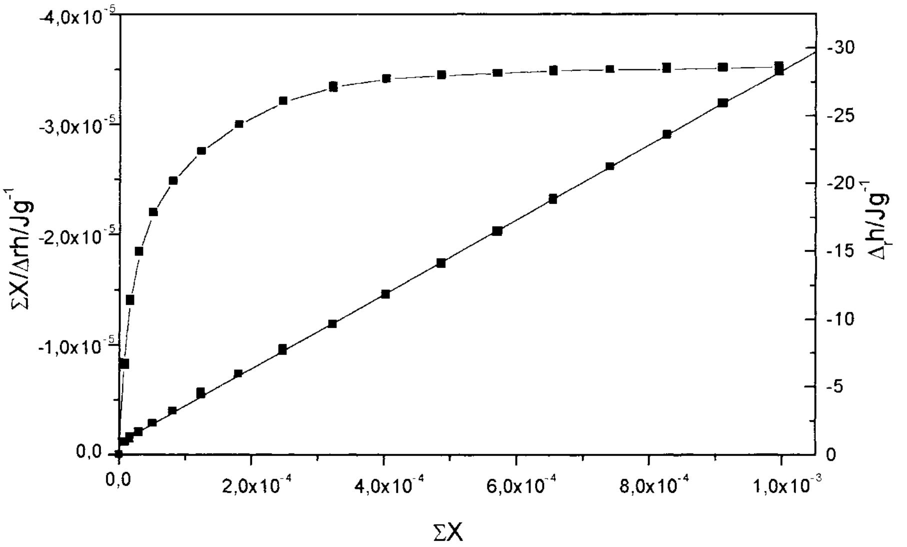

Fig. 6. Isotherm of the integral enthalpy of exchange ($\Delta_R h$) of the exchanger TPBA with potassium.

n^s the maximum amount of solute exchanged per gram of exchanger (mol g^{-1}) and b a parameter related to the thermodynamic constant by the expression (K × MM)/ρ, where MM and ρ are the mass and density of the solvent, respectively [33]. Considering these values, the free energy of the system can be calculated ($\Delta_b G$), where the b index is used to distinguish from the same value as obtained from calorimetry. The n^s and b values are obtained from the angular and linear coefficients after linearizing the exchange isotherms shown in Fig. 4. Comparing n^s and n_f (see Table 1), we notice sequences of very close values. However, in order to obtain better information about the energetics of the exchange processes, a series of calorimetric titrations was accomplished for all the studied systems, as indicated by Eq. (1). The illustration of a calorimetric titration is showed in Fig. 5, V_{ad} is the volume added in each point of the titration. The thermal effect of the hydration of the exchangers was nil. Once the sequence of values was obtained from the calorimetric titration, Eq. (3) was used to determine the enthalpy of exchange to form the monolayer per unit of mass of the exchanger, $\Delta_{mono}h$. The equation is:

$$\frac{\sum X}{\sum \Delta_R h} = \frac{1}{(K-1)\Delta_{mono}h} + \frac{\sum X}{\Delta_{mono}h} \qquad (3)$$

In Eq. (3), $\sum X$ is the sum of the molar fractions of the cations in solution after exchange (X is obtained at each point of the addition), $\Delta_R h$ the integral enthalpy of exchange (J g^{-1}), obtained by dividing the enthalpy of reaction $\sum \Delta_r h$ by the mass of the matrix, and K a proportionality constant that includes the equilibrium constant. Using the angular and linear values from the $\sum X/\Delta_R h$ vs $\sum X$ plot, it was possible to obtain the $\Delta_{mono}h$ value, shown in Fig. 6. Thus, the enthalpy of exchange $\Delta_{exch}H$, could be calculated by means of the expression $\Delta_{exch}H = \Delta_{mono}h/n_s$. Calorimetry is a useful technique to determine the energetics of ion-exchange process.

The enthalpies of the ionic exchanges of proton, sodium and n-butylammonium attached to the exchangers TPH, TPNa and TPBA with potassium are exothermic. Their respective values are -0.54 ± 0.01, -2.67 ± 0.05 and -4.97 ± 0.04 kJ mol^{-1}. In contrast, endothermic values were obtained for the same sequence of exchanges with calcium as 5.82 ± 0.24, 3.74 ± 0.05, 0.74 ± 0.02 kJ mol^{-1}, respectively. The enthalpic values for calcium decreased with the increase of the lamellar distance (see Table 2). This can be related to the mobility of the cation in entering the lamellar gallery as the space between the inorganic layers gets larger. In both the cases, there was a great variation in enthalpic values for the TPBA exchanger.

Table 2
Thermodynamic values of the ion exchange of metallic chloride with TPH, TPNa and TPBA matrices at 298.15 ± 0.02 K

Exchanger	Cation	$\Delta_{mono}h/(J\ g^{-1})$	$\Delta_{exch}H/(kJ\ g^{-1})$	ln K	$\Delta G/(kJ\ g^{-1})$	$\Delta S/(J\ K^{-1}\ mol^{-1})$	r
TPH	K^+	−0.552 ± 0.003	−0.541 ± 0.02	12.64	31.32 ± 0.01	103	0.9998
	Ca^{2+}	4.59 ± 0.14	5.82 ± 0.24	5.98	14.86 ± 0.08	69	0.9937
TPNa	K^+	−8.72 ± 0.09	−2.67 ± 0.05	9.19	22.79 ± 0.03	67	0.9988
	Ca^{2+}	8.00 ± 0.03	3.74 ± 0.04	9.67	23.97 ± 0.01	93	0.9998
TPBA	K^+	−16.85 ± 0.06	−4.97 ± 0.04	10.32	25.57 ± 0.01	69	0.9998
	Ca^{2+}	1.75 ± 0.04	0.74 ± 0.02	11.94	29.60 ± 0.06	102	0.9980

As mentioned before, data on ion exchange and its relationship with the exchange enthalpy of mono- and divalent cations are scarce. Some of the published data involve the exchanger γ-titanium phosphate and as cations, barium, strontium and potassium [7,9,10]. The respective exchange enthalpy values are 30.01, 9.31 and −4.39 kJ mol^{-1}. Another example involves zirconium phosphate as the exchange and, as cations, rubidium, potassium and lithium. The exchange enthalpy values thus are −13.46, −10.46 and −9.62 kJ mol^{-1}, respectively [11,15]. Comparison of our results with those data, however, is difficult, they involve different exchangers and techniques. In particular, while we used calorimetric titration, those data were obtained from classical thermodynamic equations.

The Gibbs free energy was calculated from the calorimetric data and is quite close to the values obtained from batch isotherms. Both these methods yielded exothermic values for all systems, indicating that the reactions are spontaneous. The exothermic entropic values listed in the Table 2 are also consistent with the argument that the reactions are entropically favoured. This can be accounted for by the fact that during the exchange process the metallic cation loses molecules of water of hydration to the medium of the reaction. This transference of water molecules from the hydration sphere promotes the deorganization of the system and, consequently, leads to an increase in the entropy of the system [1,12,14,34].

Acknowledgements

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