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Thermodynamic data of ion exchange on amorphous titanium(IV) phosphate

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Abstract

The proton of amorphous titanium(IV) phosphate was exchanged with divalent cations (Zn, Ni, Co, Cu, Cd, Pb, and Hg) in aqueous solution at 298.15 ± 0.02 K. For these cations, the values for the number of moles exchanged were in the sequence: Hg > Pb > Cu > Co > Ni > Cd > Zn, which is also that of the hydration volume of the cation. A suspension of the exchanger was calorimetrically titrated with a cation solution in a heat-flow microcalorimeter. After subtracting the thermal effect of dilution, the thermodynamic data for this process were calculated. All enthalpies obtained are endothermic in nature; the values were: (Zn) 13.20 ± 0.35; (Hg) 6.93 ± 0.21; (Cd) 5.36 ± 0.21; (Ni) 3.85 ± 0.09; (Cu) 3.47 ± 0.10; (Cd) 3.41 ± 0.07 and (Pb) 1.87 ± 0.06 kJ mol^{-1}, which can be ordered as Zn > Hg > Cd > Ni > Cu > Co > Pb. With the exception of mercury, this sequence of enthalpy is the reverse of that obtained for the number of moles exchanged.

Keywords: Divalent cations; Enthalpy; Ion exchange; Thermodynamic data; Titanium phosphate

1. Introduction

Synthetic inorganic ion exchangers have been used in many analytical applications where the main property is the selectivity for certain compounds [1]. Some of them possess high selectivities for a given cation or mixture of cations, which can be utilized, for example, in chromatographic separations [2–9]. Most investigations are related to acid salts of tetravalent metals, such as titanium phosphate of various types, with relatively high exchange capacity [10].

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Titanium phosphate is initially obtained as an amorphous material at room temperature. The gel formed can, however, be crystallized by refluxing in phosphoric acid for a long time [11], giving, in many cases, several crystalline forms and intermediate stages of crystallinity [12].

Depending on the working conditions, many different products can be formed during the preparation of this gel. This fact is related to the presence of the easily hydrolysable tetravalent titanium cation, which gives a high degree of polymerization during the precipitation, and also to the possible exchange of hydroxy groups or molecules of coordinated water bound to the backbone of the polymer by the hydrogen phosphate species [13]. The gel prepared under different conditions can be used as an exchanger, after immersing in an acid solution, where the effective capacity of cation exchange depends on the pH of the solution and the nature of the ingoing ion. Considering all these features, the use of the amorphous material as an exchanger has received some unfavourable criticism, owing to the difficulties of comparing results because of the variable behaviour of the gel [14]. Some exchanger thermodynamic values involving titanium phosphate with alkali metal ions have, however, been derived by using: (i) isotherms obtained at different temperatures with the crystalline compound [15, 16] and (ii) calorimetric determinations of half and total sodium substitution in amorphous and crystalline titanium phosphate [17, 18].

Attention has been devoted to the exchanger properties of amorphous titanium phosphate with some divalent cations; high selectivity is shown for lead and mercury [19]. In an attempt to acquire more information about the thermodynamics of this exchange, a series of calorimetric titrations with this system will be presented. To the best of our knowledge the results presented in this publication are the first thermodynamic determinations, through calorimetric measurements, obtained with the exchange of divalent cations in the solid–liquid interface.

2. Experimental

2.1. *Synthesis of titanium(IV)* phosphate

The exchanger was prepared by addition of 5.0×10^{-2} mol dm^{-3} of titanium tetrachloride solution to an equivalent solution of disodium hydrogen phosphate in a 1 : 2 volume proportion. A gel started to form immediately and the pH of solution was adjusted to 2.0 with an ammonia solution. The gel was left to stand at room temperature for 24 h. The material was then filtered, washed with twice distilled water and dried at 313 K. The dried material was treated with 1.0 mol dm^{-3} nitric acid solution for 72 h, washed with twice distilled water and dried at 313 K. The material was sieved and the 48–60 mesh fraction was used [19].

2.2. *Ion exchange in solution*

All salts were analytical grade and were used without purification. The adsorption process was followed batchwise in aqueous solution at 298.2 ± 0.2 K for all divalent cations ($CoCl_2$, $CuCl_2$, $NiCl_2$, $CdCl_2$, $Zn(NO_3)_2$, $Hg(NO_3)_2$, $Pb(NO_3)_2$). Samples of the exchanger (~ 0.12 g) were suspended in metal-containing solutions (50.0 cm^3), with cation concentrations varying from 1.0×10^{-3} to 3.0×10^{-2} mol dm^{-3}. The system was mechanically stirred for 6 h. The amount of supernatant cations was determined by atomic absorption spectrometry [19].

2.3. *Calorimetry*

The heat evolved in the solid–liquid interface was followed by means of an LKB 2277 heat-flow microcalorimeter [20]. A sample of exchanger (~ 2.0×10^{-2} g) was suspended in water (2.0 cm^3) with vigorous stirring at 298.15 ± 0.02 K. A thermostatted solution of the cation in the range 0.50–0.90 mol dm^{-3} was incrementally added into the calorimetric vessel and the heat of reaction (Q_t) recorded. The heat of dilution (Q_d) was obtained by means of an identical titration of the metal solution, also in water. Then, the net heat of reaction (Q_r) is given by $Q_r = Q_t - Q_d$. A null heat was observed when water was added to the calorimetric vessel containing the exchanger. The variation of the enthalpy of the reaction (ΔH) can be calculated by use of the expression $Q = n\Delta H$, where n is the number of cations exchanged [19].

2.4. *Solid state ^{31}P nuclear magnetic resonance spectroscopy*

CP–MAS NMR measurements were performed using a Bruker AC300P spectrometer, operating at 121 MHz and at room temperature. A pulse sequence with contact time of 3 ms, with 3 s interval between pulses, and a 86 ms acquisition time were used. H_3PO_4 (85%) was used as a reference to calibrate the chemical shift scale.

3. Results and discussion

The elemental analysis of the synthetic material showed a molar proportion of 2.8:1.0 between titanium and phosphorus. From the thermogravimetry curves a loss of mass of 20.5% was detected. Combining both data gave the formula $Ti(HPO_4)_{0.35} \cdot 1.17H_2O$ [19, 21]. The ^{31}P CP–MAS NMR spectrum of this compound showed only one peak at −19.3 ppm. This peak is assigned to the presence of phosphorus in the polymeric unit $P(TiO)_3(OH)$, as observed for similar zirconium compound related to the HPO_4^- species [22]. The ion exchange capacity, obtained by a batch process, using a 0.10 mol dm^{-3} aqueous solution (NaCl + NaOH), was 1.70 mmol g^{-1}.

The exchange of the $Ti(HPO_4)_{0.35} \cdot 1.17H_2O$ proton with divalent cations (MX_2) in water has been demonstrated through well defined isotherms [19]. The proton of the acidic matrix (TH) in water was exchanged with the divalent cation (M), as expressed by the general equation:

$$2TH + M^{+2} \rightleftharpoons T_2M + 2H^+$$

At the equilibrium condition, this exchange process can be characterized by the number of moles (n_f) exchanged in the surface, which is calculated by $n_f = (n_i - n_s)/m$, where n_i and n_s are, respectively, the initial and equilibrium number of moles of cation in solution and m is the mass of the exchanger in grams. The maximum amounts of cations exchanged are listed in Table 1; the sequence is in good agreement with experimental n_f values.

The exchanger had the largest ion exchange capacity with Pb and Hg, 1.16 and 2.03 mmol g^{-1}, respectively, and the smallest with Zn, 0.24 mmol g^{-1}. The sequence of the amount of metal exchanged was found to be Hg > Pb > Cu > Co > Ni > Cd > Zn. This sequence is very similar to that observed for amorphous zirconium phosphate with phosphorus:metal in the proportion 0.9:1, when nitrate salt solutions are used in the batchwise process [23]. Although the Stokes radii [24] for nickel and mercury are missing, the values of the hydration volume listed in Table 1, are useful for explaining the ion exchange properties of these cations. Thus, a cation with a large hydration volume obstructs the exchange of the exchangeable neighbouring protons on the polymer backbone, and consequently causes a decrease in the number of cations exchanged. For example, the hydration volume for Pb is 143.4 cm^3 mol^{-1} and the number of moles adsorbed for this metal is 1.16 mmol g^{-1}. On the other hand, for Zn, with a hydration volume of 178.2 cm^3 mol^{-1}, the number of cations exchanged decreases to 0.24 mmol g^{-1}.

The isotherms for the exchange resemble those for the adsorption of cations by immobilized surfaces [26]. Then, taking into account the similarities of these interface processes, a modified Langmuir equation was applied and the results shown to conform to the expression:

$$\frac{C_s}{n_f} = \frac{C_s}{n^s} + \frac{1}{n^s b}$$

where C_s is the concentration of supernatant cation (mol dm^{-3}) in the equilibrium, n_f is defined as before (mol g^{-1}), n^s is the maximum amount of solute exchanged per gram of the exchanger (mol g^{-1}) and b is a constant. The values of n^s and b are obtained through

Table 1
Number of moles exchanged (n_f), hydration volume (V_{hyd}), maximum exchange coefficient (n^S) and correlation coefficient (r) for the interaction of metal(II) with amorphous titanium phosphate at 298.15 ± 0.02 K

Metal(II)	n_f/mmol g^{-1}	V_{hyd}/cm^3 mol^{-1} [a]	n^S/mmol g^{-1}	b	r
Zn	0.24	178.2	0.26 ± 0.01	510.65 ± 33.01	0.999
Cd	0.26	173.2	0.27 ± 0.01	817.05 ± 18.80	0.998
Ni	0.30	–	0.42 ± 0.01	82.58 ± 5.24	0.995
Co	0.46	169.6	0.58 ± 0.01	141.78 ± 6.42	0.999
Cu	0.48	147.8	0.57 ± 0.01	167.87 ± 16.62	0.998
Pb	1.16	143.4	1.28 ± 0.03	420.00 ± 48.84	0.998
Hg	2.03	–	2.74 ± 0.06	368.76 ± 41.56	0.997

[a] Ref. [25].

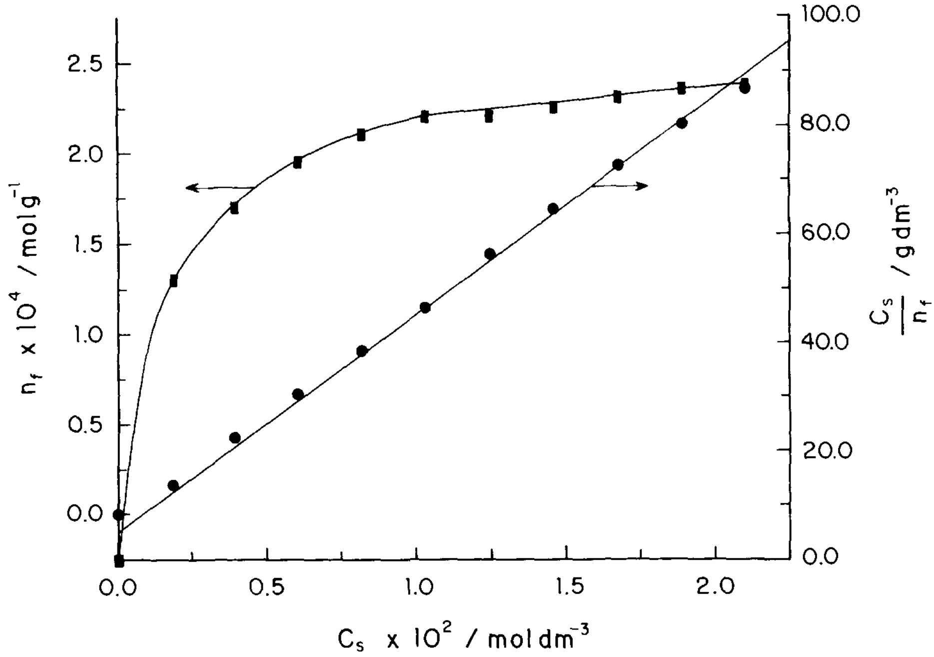

Fig. 1. Exchange isotherm for $Zn(NO_3)_2$ with amorphous titanium(IV) phosphate versus the equilibrium concentration of cation. The straight line is the linearized form of the isotherm.

the angular and linear coefficients, respectively, of the linearized form of the exchange isotherms, i.e., by considering the plot of C_s/n_f versus C_s, as illustrated in Fig. 1.

Table 1 also shows the values of n^s and b for all the cations used. The values of n_f, obtained by the batch process, are very close to these n^s values. For Cd, these values are 0.26 mmol g^{-1} and 0.27 ± 0.01 mmol g^{-1}, respectively. The sequence of exchanging values found for n^s is very similar to that of n_f, although inversion has occurred between Co and Cu.

These systems were calorimetrically titrated to obtain more information about cation–proton exchange interactions. Fig. 2 illustrates the calorimetric titration of amorphous titanium(IV) phosphate with copper chloride in aqueous solution.

As observed before, the thermal effect of a given adsorbed species on an immobilized surface and its concentration under equilibrium conditions enable the determination of the enthalpy of adsorption [26]. The same procedure was applied for the present ionic exchange process, and can be fitted to the following equation:

$$\frac{N}{Q_r} = \frac{1}{(K-1)Q_m} + \frac{N}{Q_m}$$

where N is the mole fraction of the cation in solution, Q_r is the integral enthalpy of exchange (J g^{-1}), K is a proportionality factor that includes the equilibrium constant, and Q_m is the integral heat of exchange for unity mass of exchanger. For each addition

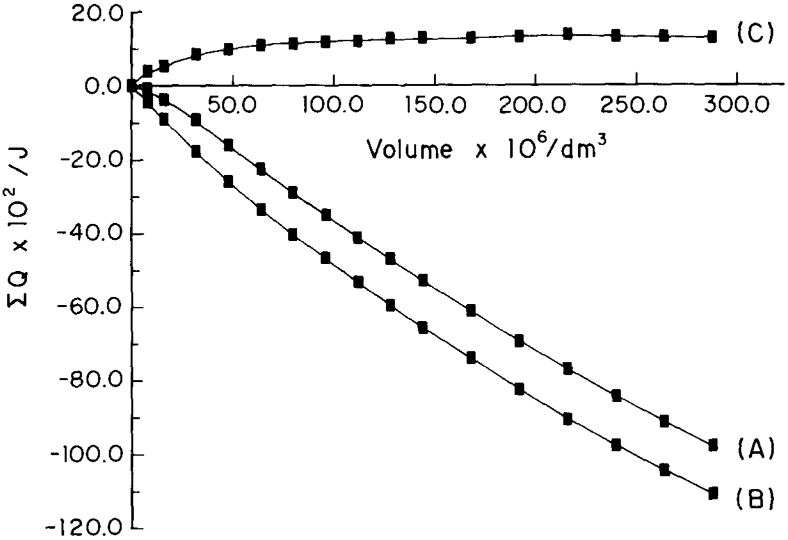

Fig. 2. Calorimetric titration of 0.06962 g of amorphous titanium(IV) phosphate suspended in 2.0 cm^3 of water with 0.7205 mol dm^{-3} aqueous solution of $CuCl_2$. The experimental points (A) and (B) represent, respectively, the sum of the dilution and the interactive effects of $CuCl_2$. The calculation points (C) represent the sum of the net heat of titration.

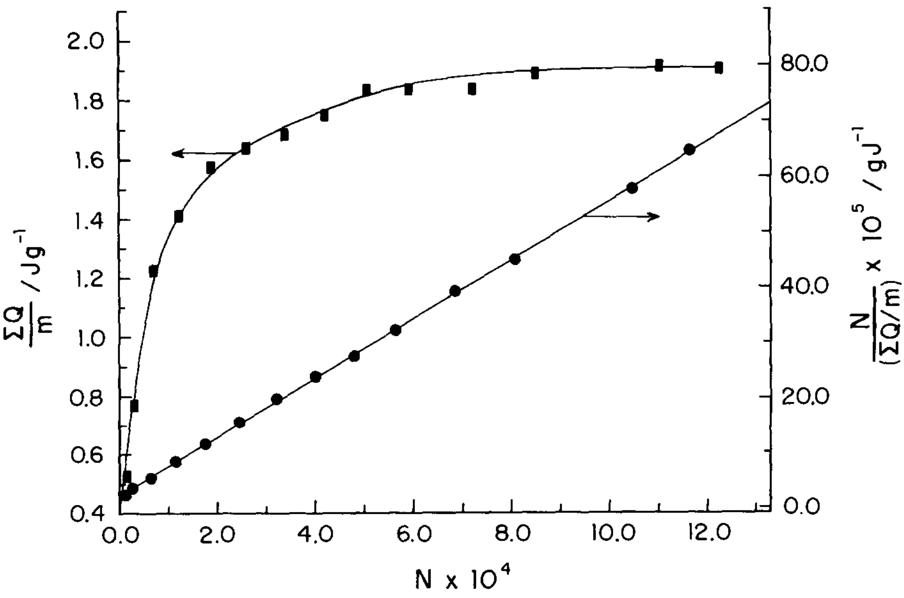

Fig. 3. Isotherm of the calorimetric titration of amorphous titanium(IV) phosphate with an aqueous solution of $CuCl_2$ at 298.15 K. The straight line is the linearized form of the isotherm.

Table 2
Thermodynamic values for the interaction of metal(II) with amorphous titanium phosphate at 298.15 ± 0.02 K

Metal(II)	Q_m/J g^{-1}	ΔH/kJ mol^{-1}	ln K	$-\Delta G$/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	r
Zn	3.42 ± 0.06	13.20 ± 0.35	7.66	18.98 ± 0.57	108 ± 3	0.999
Cd	1.46 ± 0.06	5.36 ± 0.21	8.39	20.81 ± 0.64	88 ± 3	0.995
Ni	1.61 ± 0.04	3.85 ± 0.09	8.28	20.53 ± 0.62	82 ± 2	0.998
Co	1.96 ± 0.01	3.41 ± 0.07	8.18	20.28 ± 0.61	79 ± 2	0.998
Cu	1.96 ± 0.02	3.47 ± 0.10	12.45	30.86 ± 0.93	115 ± 3	0.999
Pb	2.40 ± 0.04	1.87 ± 0.06	9.89	24.51 ± 0.74	88 ± 2	0.999
Hg	19.01 ± 0.14	6.93 ± 0.21	8.91	22.09 ± 0.66	88 ± 3	0.999

of the solute, the value of N can be calculated. A plot of N/Q_r versus N gives the values of Q_m and K, from the angular and linear coefficients, respectively, as shown in Fig. 3.

The values of Q_m, K and the coefficient correlation (r) for all systems are shown in Table 2. The value of each ΔH was calculated from the expression $\Delta H = Q_m/n^S$, by considering Q_m and the respective n^s value as listed in Table 1. The deviations quoted for the ΔH values were calculated by considering the propagating uncertainties for the experimental Q_m and n^s values.

In Fig. 4, the variation of ΔH with the sequence of the n_f values for the divalent cations is plotted. The enthalpies for these cations are endothermic in nature and

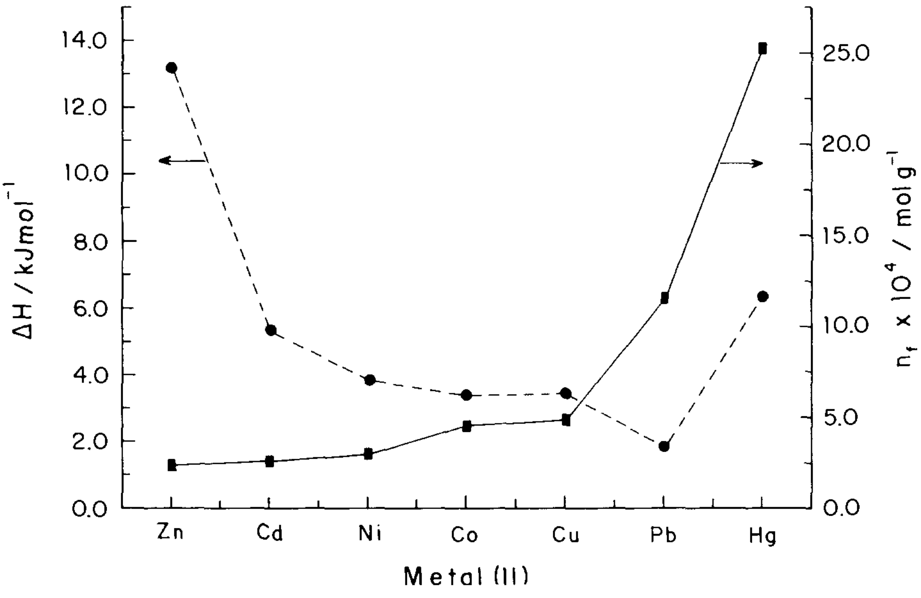

Fig. 4. The variation of ΔH (dashed line) and the maximum number of moles exchanged plotted against the sequence of cations.

decrease with an increase in the maximum number of moles exchanged. This behaviour is illustrated, for example, for Cu and Ni, which have n_f values of 0.48 and 0.30 mmol g^{-1}. The calculated ΔH are 3.47 ± 0.10 and 3.85 ± 0.09 kJ mol^{-1}, respectively, as shown in Table 2. The graphical representation of ΔH values for the sequence of cations in Fig. 4 reveals that the corresponding enthalpy for mercury, 6.93 ± 0.21 kJ mol^{-1}, is located in the upper part of the end of the descending curve. Thus, considering that mercury has the highest n_f value, a small ΔH value should be expected. To be coherent the enthalpic values must be arranged downwards from lead, with n_f 1.16 mmol g^{-1}, for which a ΔH value of 1.87 ± 0.06 kJ mol^{-1} is derived.

4. Conclusion

Ion exchange with amorphous titanium(IV) phosphate gave data with good reproducibility. The material has a high affinity for mercury and lead, which is shown by the sequence for the maximum number of moles exchanged: $Hg > Pb > Cu > Co > Ni > Cd > Zn$. The enthalpy of interaction for solute–exchanger showed the sequence $Zn > Hg > Cd > Ni > Cu > Co > Pb$. With the exception of mercury, the sequence is the reverse of that observed for n_f values.

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