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Solution enthalpies of calcium fluorapatite in nitric acid and in pure water

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Abstract: In this study, the enthalpies of dissolution of the calcium fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ were measured in nitric acid solutions at various pH at 298.15 K with the aim of attaining the dissolution enthalpy in pure water which cannot be directly measured. Mechanisms of the reactions of dissolution involving $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , H_3PO_4 , and HF entities were proposed at different pH ranges. The solution enthalpies of the products reactions were measured in the same solvent and temperature but at various pH values. When supported by the dissolution model of the calcium fluorapatite at various pH, the extrapolation of the solution enthalpies at pH=7 leads to the solution enthalpy of this apatite in pure water $-275.1 \text{ kJ mol}^{-1}$.

Keywords: calcium fluorapatite, microcalorimetry, solution enthalpy

1. Introduction

The calcium hydroxy-apatite (CaHap) and fluor-apatite (CaFap) are important chemical compounds in various sectors of activities as biology, pharmacology, geology, fertiliser industry, and environmental science. Their interaction with water is of prime importance in spite of their weak solubility. The dissolution mechanisms of natural or synthetic calcium apatites in aqueous medium have already been deeply studied. Dorozhkin gave reviews of the literature for the dissolution of calcium apatite in acidic media (Dorozhkin, 2002; Dorozhkin, 2012). The dissolution is incongruent, at least in the first stages of the reaction (Dorozhkin, 1997a; Guidry et al., 2003). The studies were performed on both CaFap and CaHap in a wide range of acid environments (Atlas, 1977; Gramain, 1989). Many details were given about the description of the mechanisms at the interface (Christoffersen, 1996). For some authors, the kinetics are controlled by the diffusion of HPO_4^{2-} and H_2PO_4^- entities through a calcium layer formed at the surface of the apatite (Thomann, 1993; Dorozhkin, 2002). In all cases, the final phosphate products in the solution are H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} depending on the pH (Dorozhkin, 1997b; Dorozhkin, 1997c). The dissolution of apatites in pure water is much more difficult (Zhu et al., 2009). A direct determination of the enthalpy of dissolution is not possible.

Some results of the dissolution of calcium phosphates in concentrated acid solutions were already published (Brudevold et al., 1963; Elasri et al., 1995) but the dissolutions of calcium phosphates in dilute aqueous media have not been extensively investigated, probably because of their poor solubility in such solvents (Christoffersen, 1989; Valsami-Jones, 1998; Köhler, 2005). Some thermodynamic properties of phosphate compounds were measured by calorimetry in acid solutions (Craig 1974), but the dissolution enthalpy in pure water cannot be directly measured. It was shown in some previous works that this value could be extrapolated from dissolution measurements in aqueous acid solutions at various pH, for example, the study of CaHap dissolution in nitric acid (Bencherifa, 2001), and in hydrochloric and perchloric acids (Ardhaoui, 2005).

The aim of this work was to reach the enthalpy of dissolution of CaFap in pure water. This study focuses on the determination of solution enthalpies of that apatite in nitric acid solutions at various pH

values. The solution enthalpy in pure water was deduced using a dissolution model which was validated by experimental results in the concentration range where the measurements remain possible.

2. Materials and methods

2.1. Synthesis

The CaFap was prepared by solid state reaction at high temperature as described in a previous work, from stoichiometric mixtures of CaF₂ (Merck-98%), CaCO₃ (Merck-99%), Ca₂P₂O₇ (Aldrich-99.9%) as seen in Eq. 1 (Ardhaoui, 2006a):



The homogenized mixture was heated in steps during 13 hours up to 1173 K in order to slowly decompose the carbonate. After the cooling, the products were ground in an agate mortar and then sintered at 1473 K. About five grinding-sintering cycles were required to obtain a well-crystallized apatite. The purity and the crystallinity of the products were checked by classical InfraRed spectroscopy and X-Ray diffraction.

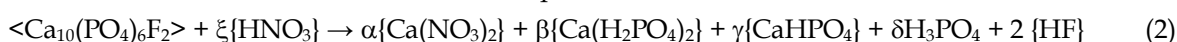
2.2. Calorimetric technique

Solution enthalpies were measured at 298.15 K using the differential solution calorimeter calsol described in (Ganteaume, 1991). The stirring of this differential heat flux calorimeter was achieved by a rocking movement of the entire apparatus around one of its axis. The sensitive element consisted in two thermopiles of 660 chromel-constantan thermocouples mounted in opposition, to measure shifts of temperatures due to the release or the absorption of energy during reactions in the calorimeter. It allowed then, to measure enthalpies of reaction developed through either rapid or slow kinetics. The calorimeter was stable within $\pm 0.1 \mu\text{V}$ during several days. Due to the PolyTetra FluorEthylene measurement cell whose usable volume is 80 cm³, the calsol calorimeter provided a wide spectrum of experiments by using all basic and acidic solvents, even with some very concentrated HF solutions (Gailhanou, 2012). In addition, the molar ratio solute/solvent could vary in a very wide range. The calorimeter was calibrated with the dissolution of TriHydroxymethyl-AminoMethanein a 0.12 mol/dm³ hydrochloric solution at 298.15 K. This reaction was used as a standard in solution calorimetry at ambient temperature. The value $(-30.19 \pm 0.05) \text{ kJ mol}^{-1}$ was issued from the literature data (Ganteaume, 1991).

2.3. Model of dissolution

The dissolution model takes into account the equilibrium between the phosphate entities in aqueous acid solution (Gramain, 1989; Dorozhkin, 1997b; Dorozhkin, 1997c). In all experiments, the concentration of initial CaFap was very low, typically less than $4 \cdot 10^{-4} \text{ mol/dm}^3$. Therefore, no complex interactions can be supposed in the solution.

The dissolution reaction of the calcium fluorapatite can be written:



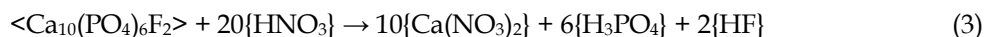
where the stoichiometric coefficients of this dissolution reaction are related as: $10 = \alpha + \beta + \gamma$ and $6 = \delta + \gamma + \beta/2$.

According to the pK_a values of the phosphoric acid (pK_{a1}=2.16, pK_{a2}=7.21, pK_{a3}=12.32 (Perrin, 1982)), three domains can be distinguished corresponding to the predominance of the H₃PO₄, the H₂PO₄⁻ and the HPO₄²⁻ entities. As the pH was always less than 7, in this study, the PO₄³⁻ anion was not present in a significant amount. Taking into account the predominance domain of the phosphate entities as a function of pH, the first domain corresponded to concentrated acid solutions, typically for negative pH (Eq. 3) where only H₃PO₄ existed, the second one, typically $0 \leq \text{pH} \leq 4.65$ (Eq. 4) where H₃PO₄ and (H₂PO₄)₂²⁻ coexisted, and the third one for pH between 4.65 and 7 (Eq. 5) where (H₂PO₄)⁻ and HPO₄²⁻ were present. Hence, as the pH gradually increases the higher the number of Ca²⁺ cations related to phosphate entities will be.

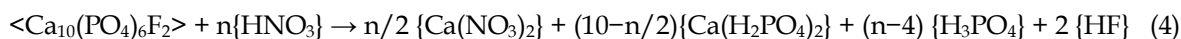
The corresponding reactions for one mole of CaFap with the nitric acid in aqueous solution can then be written for the considered pH domains with the following Eq. 3 to Eq. 5 schemes, with n, which is

the required molar number of acid to dissolve one mole of apatite. The symbols used are respectively <crystalline solid> and {in solution at a given pH}_{pH}. The dissociation states of the species depend respectively on the pK_a and on the pH. As an example, {HF} means {H⁺+F⁻} for pH > pK_a (HF) = 3.18, and {HF} for pH < 3.18.

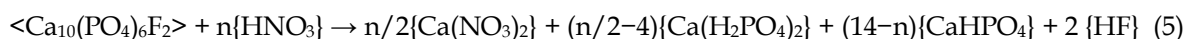
- for n = 20



- for 14 < n < 20



- for 8 < n < 14



The dissolution enthalpy of CaFap varies all along the pH domain due to (i) the number of mol of HNO₃ involved in the reaction (Eq. 4 and Eq. 5) and in all cases to (ii) the variations with the pH of the standard enthalpies of formation in solution.

Some experimental dissolutions of CaFap were performed in HNO₃ at various pH up to pH=2; where the kinetics were fast enough for calorimetric measurements. In order to validate the model, the results of the direct dissolution measurements were then compared to the enthalpy of the reactions represented by Eq. 4 or Eq. 5 calculated from the standard enthalpies of formation in solution of the various entities. For the aqueous species the concept of standard enthalpies of formation in solution was used (Bencherifa, 2001).

3. Results and discussion

3.1. Dissolution results of CaFap in HNO₃

Dissolutions of various amounts of CaFap were performed at 298.15 K in 50 cm³ nitric acid solutions of molarities [HNO₃]= 0.010; 0.025; 0.039; 0.050; 0.100, and 0.301 mol/dm³ corresponding respectively to pH= 2.00; 1.60; 1.41; 1.30; 1.00, and 0.52. The concentrations of CaFap dissolved in each experiment were less than 0.4g/dm³, therefore it can be reasonably assumed that the pH of the solution did not change significantly during the dissolution and the release of phosphate entities by the apatite. Solution enthalpies Δ_{sol}H° were determined while varying the concentration of the solute (Table 1, column 4). In accordance with the literature no solid precipitation was noticed after the apatite dissolution (Pan 2007). Confirmed by a Factsage calculation, the solubility product of CaF₂ (3.5 10⁻¹¹ (McCann, 1968)) was not reached in the solutions.

The results are presented in Table 1 confirming the previous measurements, it can be seen that these enthalpies do not change significantly with the amount of apatite dissolved in the solvent. The average value is reported in Table 2. Due to the increasing difficulty of the dissolution with the pH, the scattering of the measurements is the greatest for pH=2. At that concentration, the higher values are probably overestimated because the real end of the transformation is difficult to consider suitably.

The present measurements of the molar solution enthalpies of CaFap in HNO₃ are reported in Table 2. The enthalpy does not simply vary with the pH and a maximum is observed around pH=1.

3.2. Validation of the model and solution enthalpy of CaFap in pure water

The evolution of solution enthalpy is plotted in Fig. 1. It strongly depends on the nature of the predominant species in solution as proposed in the model and on the variation of the enthalpies of formation of that species with the pH. The pH of the solution is imposed by initial concentration of HNO₃. The over species are considered to be in dilute state, and then do not vary the pH during dissolution reactions. Such a behaviour has already been observed in previous works for the dissolution of CaHap in nitric acid (Bencherifa, 2001b), hydrochloric, and perchloric acids (Ardhaoui, 2005).

In order to check the validity of the proposed mechanisms, the solution enthalpy of CaFap in HNO₃ was calculated at pH= -0.67; -0.18; 1.30; 1.60, and 2.00 (Table 2) using the enthalpies of formation in solution of Ca(NO₃)₂, Ca(H₂PO₄)₂, H₃PO₄, HNO₃, and HF. In this work, the formation enthalpy in solution of Ca(NO₃)₂ (Δ_fH°{Ca(NO₃)₂}_{pH}) and HF (Δ_fH°{Ca(HF)}_{pH}) were obtained from the measurement of their solution enthalpies in the studied nitric acid solutions shown in Tables 3 and 4.

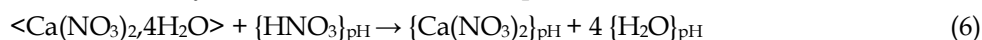
Table 1. Solution enthalpies of CaFap in HNO₃ at various pH, m and x are respectively the masses dissolved in 50 cm³ of solvent and the concentrations at 298.15 K

[HNO ₃] (mol/dm ³)	pH	m (mg)	x (g/dm ³)	Δ _{sol} H (J)	Δ _{sol} H° (kJ mol ⁻¹)
0.010	2.00	9.40	0.186	-1.62	-173.8
		15.24	0.302	-2.84	-187.8
		5.06	0.100	-0.97	-193.6
0.025	1.60	13.74	0.272	-2.37	-173.8
		7.51	0.149	-1.26	-168.8
		15.09	0.299	-2.68	-179.3
		6.52	0.129	-1.14	-175.8
		7.86	0.156	-1.31	-168.0
0.039	1.41	11.35	0.225	-1.98	-176.3
		5.60	0.111	-0.87	-156.8
		12.70	0.252	-1.95	-155.1
0.050	1.30	7.38	0.146	-1.20	-163.9
		6.08	0.121	-0.93	-153.5
		19.26	0.382	-3.04	-159.5
0.100	1.00	5.69	0.113	-0.86	-151.9
		15.32	0.304	-2.28	-150.1
		10.76	0.213	-1.73	-162.3
		9.38	0.186	-1.55	-166.7
		15.32	0.304	-2.27	-149.8
0.301	0.52	11.55	0.229	-1.77	-155.0
		5.76	0.114	-0.86	-151.6
		4.50	0.089	-0.68	-151.4
0.301	0.52	11.12	0.221	-1.86	-168.7
		6.5	0.129	-1.08	-167.8
		8.69	0.172	-1.44	-167.4

Table 2. Molar solution enthalpies Δ_{sol}H° of CaFap in HNO₃ at 298.15K and at various pH

pH	Measured (kJ mol ⁻¹)	Calculated (kJ mol ⁻¹)
-1.05	-287.9 ± 2.7 (Bencherifa 1988)	-
-0.67	-227.5 ± 2.3 (Bencherifa 1988)	-228.9
-0.18	-194.4 ± 2.2 (Bencherifa 1988)	-195.3
-0.17	-193.6 ± 3.3 (Bencherifa 2002)	-
0.28	-173.4 ± 1.2 (Bencherifa 1988)	-
0.52	-168.0 ± 0.7	-
1.00	-152.0 ± 2.2	-
1.30	-157.3 ± 6.5	-157.7
1.41	-158.6 ± 4.7	-
1.60	-173.7 ± 4.4	-171.8
2.00	-185.1 ± 10.2	-175.9

The formation enthalpy of calcium nitrate in the considered acid solutions of HNO₃; Δ_fH°{Ca(NO₃)₂}_{pH} can be obtained by the dissolution reaction Eq. 6:



$$\Delta_f H^\circ \{\text{Ca}(\text{NO}_3)_2\}_{\text{pH}} = \Delta_{\text{sol}} H^\circ \langle \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \rangle + \Delta_f H^\circ \langle \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \rangle - 4 \Delta_f H^\circ \{\text{H}_2\text{O}\}_{\text{pH}} \quad (7)$$

where Δ_fH° is the standard enthalpy of formation and Δ_fH°_{at pH} is the standard enthalpy of formation in aqueous medium at the considered pH. Then, the measured solution enthalpies of calcium nitrate

terahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$); $\Delta_{\text{sol}}H^\circ < \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} >$ are displayed in Table 3. $\Delta_f H^\circ < \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} >$ and $\Delta_f H^\circ \{\text{H}_2\text{O}\}_{\text{pH}} = \Delta_f H^\circ (\text{H}_2\text{O})_{\text{liq}}$ were taken from NBS tables at 298.15K (Wagman, 1982).

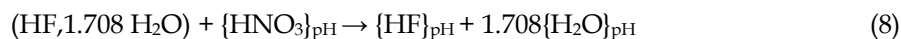
Table 3. Solution enthalpy of $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ in HNO_3 at various pH

$[\text{HNO}_3]$ (mol/dm ³)	pH	m (mg)	x (mmol/dm ³)	$\Delta_{\text{sol}}H$ (J)	$\Delta_{\text{sol}}H^\circ$ (kJ mol ⁻¹)
0.010	2.00	7.04	0.596	1.13	37.90
		7.94	0.673	1.27	37.75
		7.75	0.657	1.23	37.57
0.025	1.60	40.89	0.346	6.12	35.33
		77.44	0.656	11.91	36.30
		8.19	0.693	1.32	37.95
0.050	1.30	40.52	0.343	6.39	37.25
		47.73	0.404	7.36	36.40
		24.34	0.206	3.76	36.44
0.301	0.52	10.60	0.898	1.60	35.54
		3.20	0.271	0.48	35.08

Table 4. Solution enthalpy of $[\text{HF}, 1.708\text{H}_2\text{O}]$ in HNO_3 at various pH

$[\text{HNO}_3]$ (mol/dm ³)	pH	m (mg)	x (mmol/dm ³)	$\Delta_{\text{sol}}H$ (J)	$\Delta_{\text{sol}}H^\circ$ (kJ mol ⁻¹)
0.010	2.00	125.75	49.53	-22.88	-1.16
		116.49	45.88	-29.22	-1.48
		116.02	45.70	-28.23	-1.43
		129.46	50.99	-29.58	-1.50
0.025	1.60	100.85	39.72	-28.43	-1.44
		131.26	51.70	-29.15	-1.48
		110.97	43.71	-30.00	-1.52
0.050	1.30	128.05	50.44	-29.87	-1.52
		162.45	63.99	-28.35	-1.44
		132.50	52.19	-30.23	-1.54
		134.10	52.82	-24.51	-1.24
0.301	0.52	127.97	50.41	-29.46	-1.50
		138.15	54.42	-30.24	-1.54

Similarly, the formation enthalpy of the HF in the considered acid solutions of HNO_3 , $\Delta_f H^\circ \{\text{HF}\}_{\text{pH}}$ is calculated through the reaction Eq. 8:



$$\Delta_f H^\circ \{\text{HF}\}_{\text{pH}} = \Delta_{\text{sol}}H^\circ < \text{HF}, 1.708 \text{H}_2\text{O} > + \Delta_f H^\circ < \text{HF}, 1.708 \text{H}_2\text{O} > - 1.708\Delta_f H^\circ \{\text{H}_2\text{O}\}_{\text{pH}} \quad (9)$$

where $\Delta_f H^\circ (\text{HF}, 1.708 \text{H}_2\text{O})$ is taken from literature (Wagman, 1982).

Table 4 shows the solution enthalpies of the fluorhydric acid ($\text{HF}, 1.708 \text{H}_2\text{O}$) in the considered HNO_3 solutions. The deduced formation enthalpies of $\text{Ca}(\text{NO}_3)_2$ and HF in various HNO_3 concentrations are shown in Table 5.

Those of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, H_3PO_4 , and HNO_3 were extracted from literature and displayed in Table 5. The enthalpy of formation of the dicalcium phosphate in acid solution $\{\text{CaHPO}_4\}_{\text{pH}}$ is constant in the $-0.67 < \text{pH} < 2$ domain, at the value -1834.7 kJ/mol (Ardhaoui, 2005; Bencherifa, 2001b).

For $\text{pH} > 4.65$ complementary experiences revealed that the formation enthalpies in acid solutions for: calcium nitrate, calcium hydrogen phosphate, monocalcium phosphate, and fluorhydric acid are equal to those at $\text{pH} = 4.65$ (Bencherifa, 2001b; Ardhaoui, 2005) and also not far from the values at infinite dilution ($\text{pH} = 7$) given by NBS (Wagman, 1982).

Taking into account these results, the solution enthalpies of CaFap were calculated in dilute acid solutions ($2.9 \leq \text{pH} \leq 6.9$) as the solution enthalpies of CaFap cannot be measured. Because the solubility

Table 5. Enthalpies of formation in HNO₃ and at various pH, of the products of the dissolution reaction

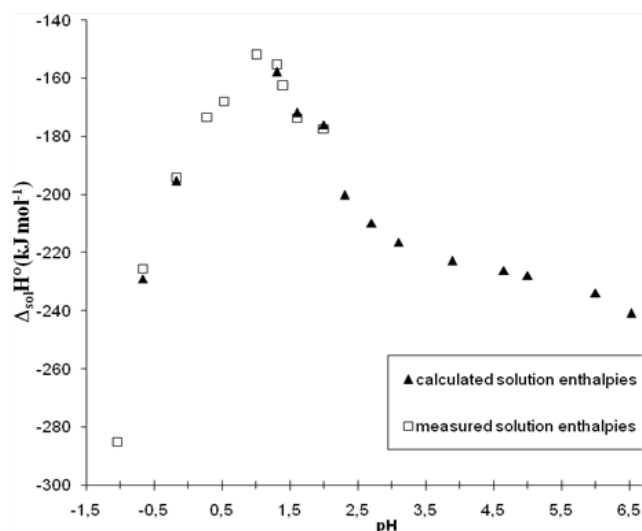
pH	$\Delta_f H^\circ / \text{kJ mol}^{-1}$					
	{Ca(NO ₃) ₂ } pH	{Ca(H ₂ PO ₄) ₂ } _{pH}	{H ₃ PO ₄ } _{pH}	{HF} _{pH}	{HNO ₃ } _{pH} (Wagman, 1982)	{CaHPO ₄ } _{pH} (Wagman, 1982)
-0.67	-959.6*	-	-1277.0 (Bencherifa 2001b)	-317.5*	-205.9	-1834.7
-0.18	-955.8*	-	-1279.6 (Bencherifa 2001b)	-319.2*	-206.8	-1834.7
1.30	-952.7*	-3123.3 (Bencherifa, 2001b)	-1280.6 (Bencherifa 2001b)	-315.2*	-207.2	-1834.7
1.60	-953.3*	-3116.5 (Bencherifa, 2001b)	-1281.1 (Bencherifa 2001b)	-315.2*	-207.0	-1834.7
2.00	-953.1*	-3115.4 (Bencherifa, 2001a)	-1281.2 (Bencherifa 2001a)	-315.2*	-207.1	-1834.7
7.00	-957.6 (Wagman, 1982)	-3115.4 (Wagman, 1982)	-1311.5 (Wagman, 1982)	-332.1 (Wagman, 1982)	-207.4	-1834.7

* present work

Table 6. Enthalpies of formation of the raw products used in dissolution reactions (Wagman, 1982)

	<Ca(NO ₃) ₂ ·4H ₂ O>	H ₃ PO ₄ ·0.756H ₂ O _{liq}	H ₂ O _{liq}	HF·1.708H ₂ O _{liq}
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-2132.3	-1271.8	-285.8	-316.8

of the fluorapatite in such solvents is small, and the dissolution has low kinetic (Dorozhkin, 2012). The variation of the solution enthalpy of CaFap in nitric acid solutions *versus* pH is shown in Fig. 1. There is a good agreement between calculated and experimental values as shown in Fig. 2. Their representation is linear and close to the identity function.

Fig. 1. Enthalpy of solution of CaFap in HNO₃ vs. pH

The variation of the solution enthalpy *versus* pH, results from the modification of the various species involved and from the formation enthalpy variation of the dissolution products. The extrapolation of the curve till pH=7 leads to the solution enthalpies of CaFap in pure water. The value found is $\Delta_{\text{sol}}H^\circ(298\text{K}) = -275.1 \text{ kJ mol}^{-1}$ and proves that the dissolution of the studied apatite in water is regressive with temperature considering the isobaric Van't Hoff's law.

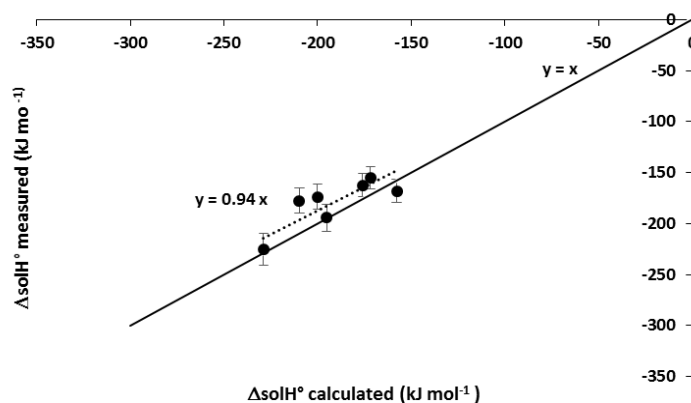


Fig. 2. Measured solution enthalpy of CaFap as a function of calculated solution enthalpy

$$\frac{d \ln(K^{\circ}s)}{dT} = \Delta \text{solH}^{\circ} / RT^2 \quad (10)$$

where $K^{\circ}s$ is the equilibrium constant of the dissolution reaction in water and R is the gas constant. As the apatites are potential materials for nuclear waste storage in deep geological disposals, their dissolution in water in such conditions, will be very limited as temperature is high.

4. Conclusion

In order to reach the solution enthalpy of fluorapatite CaFap in pure water, a value that cannot be easily measured as this phosphate presents a very low solubility in aqueous medium. CaFap was synthesized by solid state reaction, a pure and well crystallized powder was obtained. The enthalpies of solution of CaFap in nitric acid solutions at various molarities and at 298.15 K were measured.

Mechanisms for the reactions of solution of CaFap are presented in different pH ranges. A confirmed modelling of the reactions of solution allowed the extrapolation of the solution enthalpies to pH=7, and lead to the solution enthalpy of CaFap in pure water $-275.1 \text{ kJ mol}^{-1}$. This method will be exploited to deduce the solution enthalpy in pure water of any apatite without performing the dissolution itself.

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