

Surface characterization of hydroxyapatite: Potentiometric titrations coupled with solubility measurements

Kyriaki Skartsila, Nikos Spanos *

School of Science and Technology, Hellenic Open University, 262 23 Patras, Greece

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Abstract

The acid–base properties of synthetically prepared and well-characterized hydroxyapatite (HAP) in contact with KNO_3 solutions were investigated at 25°C , through potentiometric titrations, ζ -potential measurements, and surface complex modeling. Aliquots of suspension were withdrawn every 0.5 pH unit during the titration procedure and analyzed for calcium and phosphate. It was found that, even for rapid titration experiments, a remarkable amount of H^+ ions ($\text{H}_{\text{dissol}}^+$) is consumed in the bulk solution in reacting with species coming from the dissolution of HAP. These H^+ ions must be taken into account in the H^+ mass balance, in order for true value for the point of zero charge ($\text{pzc} = 6.5 \pm 0.2$) and consequently true value for the surface charge (σ^0) to be obtained. Besides the conventional potentiometric titration technique, it was found that pzc may be determined much more easily as the intersection point of the suspension titration curve and the blank one modified to include the amount of $\text{H}_{\text{dissol}}^+$ obtained at one ionic strength. Finally, a surface complexation model was proposed for the development of surface charge. Experimental data were satisfactorily fitted by using the value of 4.2 F m^{-2} for the capacitance.

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1. Introduction

Knowledge of the surface properties of apatites in contact with an electrolyte solution is very important in science and several industrial processes. Apatites may be used for the remediation of metal-contaminated soils and waters [1–4] or the confinement of industrial or nuclear wastes [5–7], due to their capacity to retain durably a large variety of trace elements. Specifically, their crystalline structure allows isomorphous substitutions, diffusion phenomena, and complexation reactions with surface functional groups. Furthermore, apatites are important raw materials for the manufacture of fertilizers, animal-feed additives, detergent components, and many chemicals, which find a large number of industrial applications [7]. On the other hand, the selective separation of apatites from other minerals is usually achieved by flotation using modifying inorganic and organic agents and collectors of high surface activity [8]. The

optimum separation is related to the understanding of the adsorption mechanism of these reagents on mineral surfaces. The elucidation of this mechanism requires the determination of the acid–base properties of these minerals in contact with an electrolyte solution.

Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP), which is the thermodynamically most stable crystalline phase of calcium phosphate, is known to be a highly biocompatible material [9,10]. Hard tissues of higher mammals including bone, dentin, and dental enamel are natural composites that contain hydroxyapatite (or a similar mineral) bound with proteins, other organic materials, and water. The interaction of biomolecules with the surface of HAP is of great importance in systems where biological fluids are in contact with hard tissues. The characteristics of the electrical double layer (EDL) developed at the interface between HAP and electrolyte solution play a crucial role in these interactions.

A number of studies has been reported in the literature aiming at the investigation of the acid–base properties of apatites in contact with an electrolyte solution. Potentiometric titrations

* Corresponding author. Fax: +30 2610 367520.
E-mail address: nspanos@eap.gr (N. Spanos).

were extensively used in these studies [11–14]. However, although apatites are sparingly soluble materials exhibiting a limited solubility, the interference of the species coming from the dissolution of apatites during the titration process was not taken into account in the analysis of the experimental results.

In the present study, which is part of a larger project devoted to the surface characterization of sparingly soluble materials in aqueous solution, potentiometric titrations of HAP suspension were, for the first time, carried out in conjunction with the determination of the composition of the bulk solution during the titration process. It was therefore possible to include in the calculations done for the determination of the point of zero charge (pzc) and surface charge (σ^0) the effect of the ions coming from the dissolution of HAP. The experimental data, obtained in the present study, were evaluated on the basis of a surface complexation model for the charging mechanism of the surface of HAP, using the constant capacitance model (CCM) for the structure of EDL.

2. Materials and methods

2.1. Materials

Reagent-grade chemicals were used throughout. The preparation of HAP has been reported in detail in our recent work [15]. The specific surface area (SSA) of the prepared solid, determined by N_2 gas adsorption (Gemini, Micromeritics) using a multiple-point B.E.T. method, was $23 \text{ m}^2/\text{g}$. The mean particle size measured by laser diffraction (Mastersizer S, Malvern) was $8.3 \text{ }\mu\text{m}$, while examination of the morphology of the crystalline material with scanning electron microscopy (SEM, JEOL ISM 5200 and LEO SUPRA 35VP) showed agglomerates of prismatic crystallites (50–150 nm). Fourier transform infrared spectroscopy (FTIR, Spectrum BX II, Perkin–Elmer), in addition to the characteristic bands for HAP, showed the presence of a weak peak at 875 cm^{-1} and a weak shoulder at 866 cm^{-1} , implying the presence of small amounts of hydrogen phosphate and carbonate [16–20]. Powder X-ray diffraction spectra (XRD, Philips 1830/40) exhibited reflections corresponding to stoichiometric HAP exclusively ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). Finally, the molar Ca/P ratio in the obtained solid was determined by chemical analysis for calcium (atomic absorption, Aanalyst 700, Perkin–Elmer) and phosphate (UV–vis spectroscopy, Lambda 35, Perkin–Elmer) following dissolution of the solid in hydrochloric acid. The value was found equal to 1.71 ± 0.05 .

2.2. Potentiometric titrations

Titrations were performed at $25 \text{ }^\circ\text{C}$ in the ionic strength range 0.0001–1.0 M, adjusted with KNO_3 . A quantity of 0.6 or 1.2 g of HAP was suspended in 200 ml of a solution of a given ionic strength, thermostated in a double-walled, water-jacketed vessel, and the suspension was equilibrated for 20 h. Following equilibration, a small quantity of 0.1 M KOH solution was added to the suspension to shift pH to values higher than 10 (pH_{in}). The suspension was then titrated with 0.0454 M

HNO_3 solution and the pH was recorded after each addition of titrant as a function of its volume. pH was measured using a digital pH meter (Metrohm) standardized by NBS buffers. Due to the dissolution of HAP, especially at relatively low pH values, the rate at which the titrant is added to the suspension is an important parameter for acid–base titration experiments. Consequently, in order to minimize the effect of HAP dissolution, the delay separating two consecutive additions of titrant was 2 min. Equilibration and titration procedure were carried out under an inert atmosphere, which was achieved by bubbling with gaseous nitrogen saturated with water vapor. During titration, small amounts of suspension were withdrawn every 0.5 pH unit, filtered through membrane filters (Millipore, $0.22 \text{ }\mu\text{m}$), and analyzed for calcium and phosphates. The titration of the suspension was repeated without sampling. It was demonstrated that sampling does not affect the titration curves obtained. Finally, blank titrations were carried out on the appropriate electrolyte.

2.3. Mass titrations

Different amounts of hydroxyapatite were suspended in 0.01 M KNO_3 solutions and equilibrated for 24 h under N_2 atmosphere at $25 \text{ }^\circ\text{C}$. The pH of each suspension was then measured. The plateau obtained by plotting the pH as a function of the added amount of HAP yields pzc [21].

2.4. Microelectrophoresis

Measurements of ζ -potential, that is, the potential at the shear plane of the EDL, of the HAP particles were performed at a constant ionic strength of 0.01 M KNO_3 at $25 \text{ }^\circ\text{C}$ and at different pH values. The electrophoretic mobility of HAP particles was measured with a laser Doppler velocimetric device (Zetasizer 5000, Malvern Instruments Ltd., Worcestershire, UK) with applied field strength ca. 80 V cm^{-1} . Velocity measurements were performed at the center of the capillary. To avoid polarization of the electrode and to eliminate electroosmosis, the polarity of the electrodes was reversed at a frequency of 50 Hz. The concentration of the suspensions was adjusted within the operational limits of the instrument and the suspension pH was adjusted by the addition of 0.1 M HNO_3 and KOH solutions. The suspension pH value was measured before and after the ζ -potential measurement. The reported ζ -potential values are the average of at least five measurements (spread of values $\pm 10\%$ of the reported mean values).

3. Results and discussion

3.1. Determination of the point of zero charge (pzc)

The pzc corresponds to the pH of the common intersection point (cip) of curves obtained at various ionic strengths, which represent the variation of the number of H^+ ions taken up by the surface of the solid, $\text{H}^+_{\text{uptake}}$, as a function of the pH [22]. In the case of insoluble solids, e.g., some mineral (hydr)oxides, $\text{H}^+_{\text{uptake}}$ is determined by subtracting the number of H^+ ions

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