Isoelectric Point of Fluorite by Direct Force Measurements Using Atomic Force Microscopy

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Interaction forces between a fluorite (CaF_2) surface and colloidal silica were measured by atomic force microscopy (AFM) in 1×10^{-3} M $NaNO_3$ at different pH values. Forces between the silica colloid and fluorite flat were measured at a range of pH values above the isoelectric point (IEP) of silica so that the forces were mainly controlled by the fluorite surface charge. In this way, the IEP of the fluorite surface was deduced from AFM force curves at pH ∼9.2. Experimental force versus separation distance curves were in good agreement with theoretical predictions based on long-range electrostatic interactions, allowing the potential of the fluorite surface to be estimated from the experimental force curves. AFM-deduced surface potentials were generally lower than the published zeta potentials obtained from electrokinetic methods for powdered samples. Differences in methodology, orientation of the fluorite, surface carbonation, and equilibration time all could have contributed to this difference.

Introduction

The surface charge of ionic solids in water is determined by differential hydration of their lattice ions at the surface, which depends on the crystal structure and the cleavage plane of the crystal. Miller and Clara[1,2] demonstrated that the hydration energy of the surface ions can be calculated for fluorite by considering the lattice energy and surface Madelung constants.

Microelectrophoresis of powdered fluorite samples and streaming potential measurements of fluorite crystals have yielded different results. Several studies have shown that in the absence of surface carbonation a high positive zeta potential for fluorite is obtained.[3−6] Surface carbonation results in the change of the character of the surface from fluorite (CaF_2) to calcite ($CaCO_3$), with a low, positive surface potential and thus a lower IEP.[7] A few studies report a lower IEP (∼pH 6.6) or a completely negative surface.[8,9]

The advent of atomic force microscopy (AFM)[10] has made it possible to measure the interaction forces between a broad range of surfaces and thus allow for the estimation of their surface charge in different electrolyte solutions.[11] Interaction forces between two particles can be measured by AFM using the colloidal probe technique, where a sphere of the particle of choice can be glued to the AFM tip. Attachment of a sphere to the tip removes uncertainties in the interaction radius and allows a quantitative analysis of the force data by fitting the data to existing models.[11−14] AFM has been widely used to determine the isoelectric point of oxide surfaces such as silica and α-alumina.[11−13,15] In this letter,

we report the application of the colloidal probe technique to estimate the surface potential and isoelectric point of CaF_2 in a dilute electrolyte (1×10^{-3} M $NaNO_3$). This method can be particularly useful for estimating the IEP of small mineralogical samples at their different crystallographic planes.

Materials and Methods

Materials. Fluorite (CaF_2) optical windows (13 mm × 2 mm) were purchased from Harrick Scientific Corp. (Ossining, NY). The fluorite window was cleaned using UV/ozone for 15 min prior to AFM measurements. Characterization of the surface by X-ray diffraction (X'Pert Texture, Phillips Analytical, MA), revealed a (110) plane of orientation.

Silica particles with a nominal diameter of 4.70 μm (Bangs Laboratories, Inc., IN) were cleaned by soaking in SC1 solution (5:1:1 $H_2O/NH_4OH/H_2O_2$) and holding the suspension at about 80 °C for 15 min. The suspension was filtered through a 0.45 μm disposable filter and left to dry inside the filter. The filter was then cut, and the silica particles were spread on a precleaned glass slide using a clean tungsten wire.

The AFM fluid cell, O-ring, and tubings were cleaned prior to the experiment by rinsing with acetone/methanol/acetone and several portions of deionized water, followed by blow drying with high-purity nitrogen.

Deionized water was obtained from a Milli-Q system. The resistivity of the water was above 18 MΩ cm in all experiments. All of the glassware and plasticware were cleaned by overnight soaking in 10% HNO_3 and copious rinses with deionized water. Solutions were prepared using analytical-grade reagents.

Atomic Force Microscopy Measurements. AFM force measurements were made using a Nanoscope IIIa (Veeco, Santa Barbara, CA) scanning probe microscope in a fluid cell (Veeco). V-shaped, gold-coated tipless silicon nitride cantilevers were obtained from Veeco. The spring constant of the cantilevers was reported to be 0.12 N m^{-1} by the manufacturer. The spring constant of the cantilevers was determined to be 0.10 ± 0.003 N m^{-1} using the Cleveland method,[16] which relies on monitoring the shifts in the resonance

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(1) Miller, J. D.; Clara, J. V. In *Froth Flotation*; Fuerstenau, M. C., Ed.; AIME: New York, 1976.
(2) Clara, J. V.; Miller J. D. *J. Chem. Phys.* **1976,** *65,* 843.
(3) Hu, J. S., Ph.D. Thesis, University of Utah, Salt Lake City, UT, 1985.
(4) Haas, S. R.; Nascimento, F. R.; Schneider I. A. H.; Gaylarde, C. *Rev. Microbiol.* **1999,** *30,* 225.
(5) Yuehua, H.; Chi, R.; Xu, Z. *Ind. Eng. Chem. Res.* **2003,** *42,* 1641.
(6) Miller, J. D.; Fa., K.; Clara, J. V.; Paruchuri, V. K. *Colloids Surf., A* **2004,** *238,* 91.
(7) Miller, J. D.; Hiskey, J. B. *J. Colloid Interface Sci.* **1972,** *41,* 567.
(8) Oberndorfer, J.; Dobias, B. *Colloids Surf.* **1989,** *41,* 69.
(9) Fa, K.; Jiang, T.; Nalaskowski, J.; Miller, J. D. *Langmuir* **2003,** *19,* 10523.
(10) Binnings, G.; Quate C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986,** 56, 930.
(11) Ducker, W. A.; Senden T. J.; Pashley R. M. *Nature* **1991,** *353,* 239.
(12) Hartley, P. G.; Larson, I.; Scales, P. J. *Langmuir* **1997,** *13,* 2207.
(13) Larson, I.; Drummond, C. J.; Chan D. Y. C.; Greiser F. *Langmuir* **1997,** *13,* 2109.
(14) Yalamanchili, M. R.; Veeramasuneni, S.; Azevedo, M. A. D.; Miller, J. D., *Colloids Surf., A* **1998,** *133,* 77.
(15) Veeramasuneni; S.; Yalamanchili, M. R.; Miller, J. D. *J. Colloid Interface Sci.* **1996,** *184,* 594.
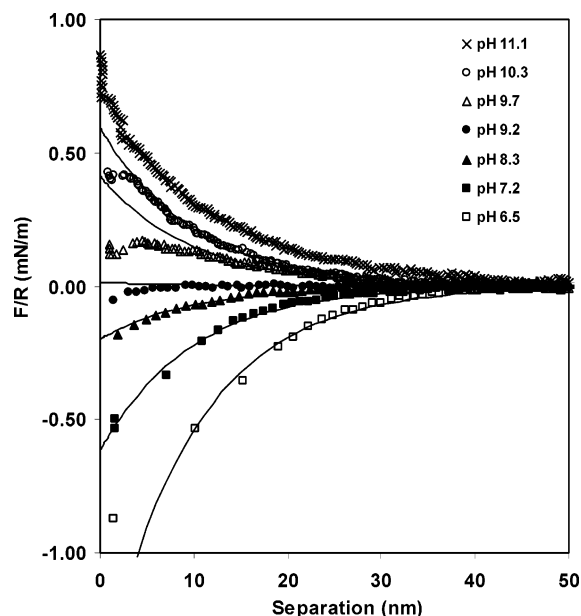(16) Cleveland, J. P.; Manne, S.; Bocek, D. *Rev. Sci. Instrum.* **1993,** *64,* 403.

Figure 1. Force versus separation for interactions between a 4.7 μm silica colloid probe and a fluorite optical window in 1×10^{-3} M NaNO₃ as a function of pH. The symbols show the AFM results, and the line shows the theoretical curve, obtained from eq 4, using a surface potential of −50 to −80 mV for silica[12] and a Debye length of 9.71 nm for all pH values (10.8 nm for pH 11.1).

frequency of the cantilever as a function of known masses attached to the cantilever (in our case, a tungsten sphere).

A glue mix was made using Loctite 325 adhesive and Loctite 7075 activator (Loctite Corp., NM). Using a micromanipulator with a tungsten wire attached to the end, monitored by an optical microscope attached to a CCD camera and monitor, a very small piece of glue was placed at the apex of the cantilever tips. A single silica sphere was then placed on each cantilever using a clean tungsten wire.

Interaction forces between the silica sphere glued to the cantilever tip and a fluorite wafer were measured in solutions with different pH values (6.5–11.1) and 1×10^{-3} M NaNO₃ as the background electrolyte. The solution pH was adjusted using NaOH or HNO₃ using a benchtop pH meter (Accumet Basic, Fisher Scientific, Pittsburgh, PA) and was measured again immediately before injection into the fluid cell. All of the force curves presented in this letter are collected in the same experiment.

Starting from pH 5.7, forces were measured at three different points on the fluorite surface, and 30 force curves were collected at each solution pH. The raw AFM data (voltage versus piezo extension) were converted to force/radius versus separation distance by using the AFM Analysis software[17] using the spring constant and the radius of the silica sphere. Zero force was chosen where the deflection was constant (complete separation), and zero separation was chosen where the cantilever deflection was linear with respect to sample displacement (constant compliance region).

Results and Discussion

Figure 1 presents the forces measured between a silica colloidal probe and the fluorite surface in solutions of varying pH. Silica particles are known to have an isoelectric point of about pH 2.[12] Therefore, it is expected that the silica probes carried a negative charge at all the pH values examined and that the interaction forces between the two surfaces would be mainly controlled by the surface charge of the fluorite.

At pH values greater than 9.2, a repulsive force dominated the interactions up to about 4 nm separation (except for pH 11.1).

A distinct "jump to contact" was observed at pH values of 9.7 and 10.3, where the gradient of the van der Waals attractive forces overcame the spring constant of the cantilever.

At pH 9.2, the repulsive double layer forces were completely eliminated. At pH 8.3 and below, attractive forces, increasing with decreasing pH, were observed, indicating that the charge of the fluorite surface reversed from negative to positive. Thus, the isoelectric point of the fluorite surface used in this study can be deduced to be about pH 9.2.

The potential of the fluorite surface can be estimated by fitting the AFM approach curves to equations for electrostatic interactions. The electrostatic double layer interaction energy between a sphere and a flat surface was calculated using an equation developed by Gregory,[18] based on the linear superposition approximation (LSA), that gives intermediate values between those for constant potential and constant charge cases

$$\Delta G^{\text{EL}} = 64\pi\epsilon R \left(\frac{kT}{z_j e}\right)^2 \gamma_1 \gamma_2 \exp(-\kappa h) \tag{1}$$

and

$$\gamma_i = \tanh\left(\frac{z_j e \psi_{0,i}}{4kT}\right) \tag{2}$$

where h is the separation distance, ϵ is the permittivity of the medium, K is the Boltzmann constant, T is the temperature, κ is the inverse Debye length, z_j is the valance of the ion, e is the charge of an electron, and $\psi_{0,i}$ is the surface potential.

The derivative of energy with respect to distance gives the force

$$F = -\frac{\Delta G}{dh} \tag{3}$$

Thus, from eq 1 the electrostatic force between a sphere and a plate can be obtained as

$$\frac{F_{\text{EL}}}{R} = \kappa 64\pi\epsilon \left(\frac{kT}{z_j e}\right)^2 \gamma_1 \gamma_2 \exp(-\kappa h) \tag{4}$$

The AFM approach curves were fitted to eq 4 using a Debye length of 9.71 nm (theoretical value for a 1 mM 1:1 electrolyte) for the pH range of 6.5–10.3 (Figure 1, solid lines). Fitting the AFM approach curve at pH 11.1 to eq 4 required a Debye length of 10.8 nm, which is higher than the theoretical value of 9.71 nm. The first 2 to 3 nm of the AFM approach curve for pH 11.1 (Figure 1) shows additional repulsive forces instead of the attractive van der Waals force expected from DLVO theory. It can be speculated that condensation of ions on one or both surfaces could have resulted in ion depletion in the bulk solution and thus a larger double layer thickness between the surfaces. This issue warrants more investigation, which is beyond the scope of this letter.

The surface potential for colloidal silica at 1×10^{-3} M NaNO₃ has been reported to be −50 to −55 mV (corresponding to pH 6.5 and pH 7.2–10.3, respectively) from AFM fits and −60 to −65 mV from electrokinetic measurements.[12] Slightly higher potentials have been reported by Larson et al. for colloidal silica in 1×10^{-3} M KNO₃ (−70 to −80 mV for pH 6.5 to 9).[13]

Using the above-mentioned surface potential values for silica, the diffuse layer potential of the fluorite surface at different pH values was generated from fitting the AFM approach curves to eq 4. The estimated surface potential for fluorite surfaces is

(17) Chan, D. Y. *AFM Analysis*; Department of Mathematics, University of Melbourne: Melbourne, Australia, 1994.

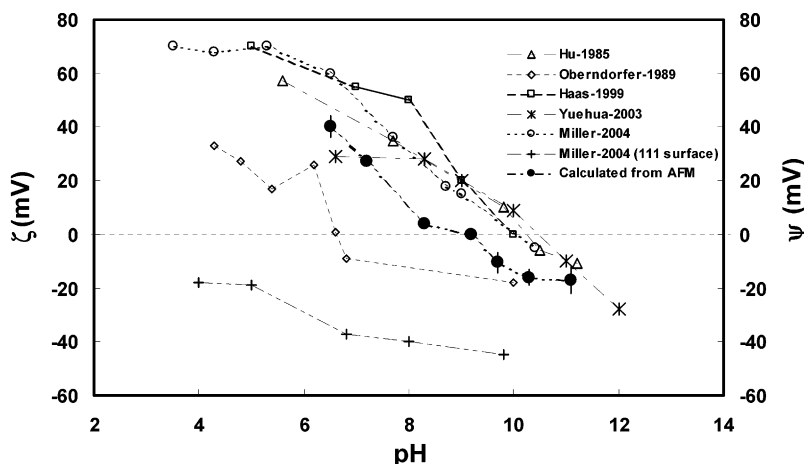(18) Gregory, J. *J. Colloid Interface Sci.* **1975**, *51*, 44.

Figure 2. Comparison of the surface potential of the fluorite surface, derived from AFM force curves, with the zeta potentials reported for powdered and crystalline fluorite samples using electrokinetic measurements. Values reported by Miller et al.[6] are averages for 16 different fluorite samples. The value reported for the (111) surface was obtained by streaming potential measurements. Error bars on AFM measurements correspond to one standard deviation for seven measurements.

compared to zeta potential values reported for powdered and crystalline fluorite from the literature (Figure 2).

Electrokinetic measurements on fluorite powder from the literature suggest an IEP of about pH 10 for fluorite, which agrees well with pH 9.2 deduced from AFM measurements. The fluorite surface potentials calculated from AFM data seem to be between 5 and 20 mV lower than published zeta potentials of the powdered sample obtained by from electrokinetic measurements. In AFM surface force measurements, errors can arise from the determination of the spring constant of the cantilever, from the determination of the size of the colloidal probe, and from piezo calibration. Because our solutions have been exposed to air, we should also consider the possibility of surface carbonation.

AFM measurements can provide an opportunity to study the IEP of fluorite at different planes of cleavage. Although the surface charge of the powdered fluorite samples has almost always been reported as positive below pH 9−10 in the literature, a negative zeta potential at all pH values was reported for a (111) fluorite plane.[8] It was explained that for a (111) plane, in which the topmost layer consists only of fluoride ions, perhaps a much greater equilibration time (compared to that of powdered samples) is required so that the fluoride ions with a more negative free energy of hydration would be removed from the surface and would leave an excess of calcium ions behind, resulting in a positive zeta potential. The (110) fluorite used in our experiments exhibited a positive surface charge similar to that of the powdered

samples, possibly because in a (110) plane both calcium and fluoride ions are on the topmost layer.

It can be hypothesized that the equilibration time for each plane of cleavage is different because of the number of fluoride ions to be hydrated. Further research may include an examination of surface charge using AFM and streaming potential measurements, along with the calculation of surface Madelung constants and the prediction of hydrated surface charge for different crystallographic planes of fluorite.

Conclusions

Forces between a silica colloidal probe and a (110) fluorite plane were measured in 1×10^{-3} M NaNO$_3$ solutions for pH values ranging from 6.5 to 11.1. AFM results showed an isoelectric point of pH ~9.2 for this fluorite surface. This value agrees well with the IEP of pH ~10 reported for powdered fluorite based on electrokinetic measurements, although the surface potentials deduced from AFM are slightly lower than zeta potentials found from electrokinetic measurements, perhaps because of the differences in surface orientation, surface carbonation, or calibration of AFM components. This letter suggests that direct surface force measurements by AFM can provide an opportunity to study the surface charges of the complex ionic solids at different planes of cleavage and at different electrolyte concentrations.