

Direct Force Measurements between Silica and Alumina[§]

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AFM force measurements were carried out between a silica colloid sphere and an alumina flat crystal over a wide pH range and in both 1×10^{-4} and 1×10^{-3} M KNO₃ aqueous solutions. Microelectrophoresis and streaming potential experiments were performed on the silica colloid sample and the alumina plate, respectively. The potentials measured by the different techniques were in very good agreement. The results clearly indicate that AFM force measurements can be used to accurately determine diffuse layer potentials of metal oxide materials under these solution conditions.

Introduction

Over the last few years there has been a rapid increase in the number of investigations in which the atomic force microscope (AFM)¹ has been used to measure DLVO² interaction forces between a single colloid particle and, usually, a flat surface in aqueous solution.³ There has been little systematic effort made, however, to compare these results from AFM force measurements to results on the same materials obtained by traditional electrokinetic techniques such as microelectrophoresis and streaming potential.^{4,5} To establish the ability of the AFM to make accurate force measurements, it is imperative to match AFM data with other techniques on identical surfaces.

In this study both surfaces used in an AFM experiment have been independently characterized using traditional electrokinetic techniques. Silica colloids and α -alumina flat single crystals were chosen because of the large quantity of information available for these materials. Also, these surfaces have different isoelectric points (iep's), so that at certain pH values the surfaces can be oppositely charged, which enabled us to study both attractive and repulsive electrostatic interactions between the surfaces. Electrophoretic mobility measurements on the colloid sample and streaming potential experiments on the flat single crystals have been performed to allow a direct comparison with the results obtained from the AFM technique.

Theory

AFM force measurements were made between a spherical colloid and a flat plate. The force (F) measured between the sphere of radius (R) and the flat plate can be related to the interaction free energy between flat parallel plates by the Derjaguin approximation.⁶ In this approximation the total force, scaled by the radius of the sphere, has the form

$$F/R = 2\pi(V_A + V_R)$$

where V_A is the van der Waals interaction free energy per unit area and V_R is the electric double-layer interaction free energy per unit area between two flat parallel plates.

Here the total interaction free energy between the charged surfaces is separated into the sum of two separate contributions: the van der Waals component and the electrical double-layer term. The van der Waals term will generally be attractive for two metal oxide surfaces separated by an aqueous solution. The method described by Hough and White,⁷ that employs the Ninham–Parsegian⁸ representation of dielectric data, was used to calculate the value of the Hamaker constant using Lifshitz theory.⁹ Dielectric data are used to construct the function $\epsilon(i\xi)$ —the dielectric constant at imaginary frequency $i\xi$. At $\xi = 0$, $\epsilon(0)$ is the static dielectric constant ϵ_{DC} . As ξ increases $\epsilon(i\xi)$ is real and decreases toward 1 as $\xi \rightarrow \infty$. We used the representation

$$\begin{aligned} \epsilon(i\xi) &= \epsilon_{DC} && \text{when } \xi = 0 \\ \epsilon(i\xi) &= 1 + \frac{C_{IR}}{1 + (\xi/\omega_{IR})^2} + \frac{C_{UV}}{1 + (\xi/\omega_{UV})^2} && \text{when } \xi > 0 \end{aligned}$$

where C_i is the oscillator strength and ω_i is the absorption frequency in the infrared, IR, and ultraviolet, UV, regions. In this approach for calculating the Hamaker constant the function $\epsilon(i\xi)$ is sampled at frequency steps of $\approx 2.4 \times 10^{14}$ rad s⁻¹. Therefore there are many more sampling points in the UV region of $\epsilon(i\xi)$, and consequently this region has a greater importance in calculating Hamaker constants than the microwave and infrared, IR, regions. The more important parameters in calculating the Hamaker constant are the oscillator strength, C_{UV} , and the relaxation frequency, ω_{UV} . Effective C_{UV} and ω_{UV} parameters can be obtained from a Cauchy plot of refractive index data in the visible region.⁷ The oscillator strength in the IR region can be worked out from

$$C_{IR} = \epsilon(0) - C_{UV} - 1$$

For simplicity we have ignored the effect of retardation¹⁰ on the van der Waals force, so we have

$$V_A = \frac{-A_H}{12\pi H^2}$$

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where A_H is the Hamaker constant¹¹ and H is the distance of closest approach between the sphere and the plate. Including retardation had negligible effect on the total interaction in the regime of separation considered in this work. A nonretarded Hamaker constant of 1.8×10^{-20} J was calculated for the silica/water/ α -alumina system.

For identically charged surfaces the double-layer term will be repulsive, but for surfaces with dissimilar charges this component can be repulsive or attractive or even change from one to the other through regulation of the surface charge during the interaction. The method of McCormack et al.¹² has been used to calculate V_R for both the constant potential and constant charge limits of the nonlinearized Poisson–Boltzmann equation.

Experimental Section

SiO₂ Colloids. The silica colloid sample used in this study was made by the Stöber method.¹³ The sample was a gift from Allied Signal. XPS analysis (performed by Thomas Gengenbach, CSIRO Division of Chemicals and Polymers) showed the composition of the sample to be pure silica. The colloids were all in the 4–5 μm diameter size range. The sample was Soxhlet washed for approximately 72 h, changing the water every 8–12 h, before use. Using the now commonplace technique, a single colloid was glued to the end of an AFM cantilever using a heat-softening wax (Shell Epikote Resin 1002).¹⁴ The radius of this colloid probe was determined by optical microscopy. Cleaning the colloid probe before use involved rinsing with ethanol and blow drying with nitrogen.

Al₂O₃ Flat Plates. The α -alumina (alumina with the sapphire structure) plates were purchased from Harrick Scientific, NY. X-ray diffraction measurements (performed by David Hay, CSIRO Division of Material Science and Technology) showed that the sapphire crystals had the expected rhombohedral structure and also indicated that the c -axis was perpendicular to the face that was used for the streaming potential and force measurements. XPS analysis (performed by Thomas Gengenbach, CSIRO Division of Chemicals and Polymers) showed their composition was that of α -alumina, with minor (0.7%) contamination due to fluoride. The plates were polished to optical smoothness, AFM contact mode images showed the root mean square roughness to be <0.5 nm over $5 \mu\text{m}^2$. To clean the plates, they were first soaked in concentrated nitric acid, washed in a 1:1 mixture of ethanol and a 1% solution of RBS Cleaning Agents (Chemical Concentrates U.K.) in an ultrasonic bath for 1.5 h, and finally, steamed for approximately 4 h. At no time were the plates in contact with a possible source of silica contamination. (The point of this will become clearer later.)

Reagents. Analytical grade KNO₃, KOH, and HNO₃ were used without further purification. High-grade nitrogen (99%) and AJAX AR-grade ethanol were used as supplied. Millipore “Milli-Q” water was used throughout, which had a conductivity of less than 10^{-6} S cm⁻¹ at 20 °C and whose air water surface tension was 72 mN m⁻¹ at 20 °C.

Electrophoresis Measurements. A Rank Bros Mk II instrument was used to measure the electrophoretic velocity of the colloidal silica, v_e , as a function of pH. The physical dimensions of the colloid sample allowed the ζ -potentials to be calculated from these velocities by employing the Helmholtz–Smoluchowski equation:¹⁵

$$\zeta = v_e \eta / E \epsilon_0 \epsilon_r$$

where η is the viscosity of the medium, E is the electric field strength, and ϵ_0 and ϵ_r are the permittivity of free space and the relative permittivity, respectively. The electrophoretic measurements were taken at 25 °C.

Streaming Potential Measurements. The flat plate streaming potential apparatus was based on the design of Van

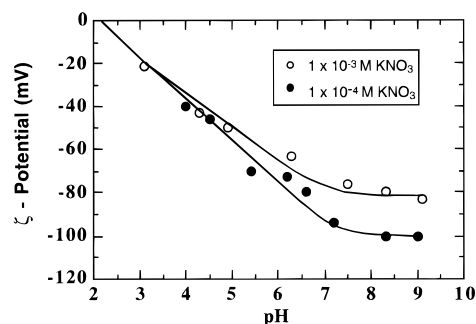


Figure 1. Electrophoretically determined ζ -potentials of the SiO₂ colloid sample as a function of pH and electrolyte concentration. Within experimental error the iep indicated by both experiments is pH 2.2.

Wagenen.¹⁶ In this design a Teflon gasket separated flat plates to form a flat capillary through which the electrolyte solution was pumped.¹⁷ A potential difference was measured across this capillary. The capillary in this study was formed by four alumina plates, each $50 \times 20 \times 2$ mm³, mounted two a side and laid end on end to create a capillary 100 mm long \times 20 mm wide. The thickness of the gasket determined the thickness of the gap, which was approximately 0.1 mm in these experiments. In the case of an applied pressure gradient, ΔP , across a charged capillary, the Smoluchowski equation relates the ζ -potential to the streaming potential ΔE :¹⁸

$$\zeta = (\eta \lambda / \epsilon_0 \epsilon_r) (\Delta E / \Delta P)$$

where λ is the conductivity of the capillary and the other symbols are as defined before. The apparatus was connected to a PC, enabling acquisition of ΔE and ΔP at five data points per second. In this study the pressure and voltage changes across the cell were recorded as the pressure was increased linearly.

Force Measurements. The force measurements were taken with a Digital Instruments, Inc. (Santa Barbara, CA) Nanoscope III atomic force microscope. The technique used to make these measurements is well documented.^{3,12} A commercially available program¹⁹ was used to convert the experimental cantilever deflection versus piezodisplacement data to force versus separation. The spring constants of the cantilevers used in these experiments were determined by the method of Cleveland et al.²⁰ and found to be 0.054 ± 0.002 N m⁻¹.

Results and Discussion

(i) Electrophoresis Measurements. In Figure 1 we show ζ -potential curves obtained from electrophoretic mobility measurements over a range of pH. Electrolyte concentrations of 1.0×10^{-4} and 1.0×10^{-3} M KNO₃ were used, as these were the concentrations used in the force measurements. When extrapolated to low pH, both curves show an isoelectric point (iep) of between 2 and 2.5, which is typical for silica.

(ii) Streaming Potential Measurements. The ζ -potential curves obtained from the streaming potential measurements on the single α -alumina crystals are shown in Figure 2; both curves show an iep of approximately pH 4.2.

Electrokinetic measurements on α -alumina powder indicate an iep of approximately pH 9.0;²¹ however,

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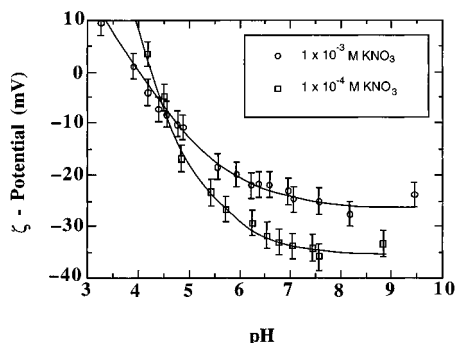


Figure 2. ζ -potentials determined by streaming potential measurements on the single flat α -alumina crystals as a function of pH and electrolyte concentration. Within experimental error the iep in both experiments is pH 4.2.

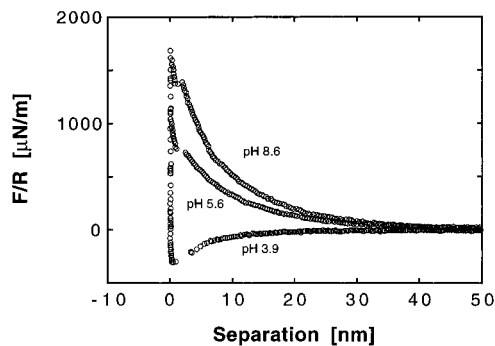


Figure 3. Force-separation curves for the silica/alumina system as a function of pH. The curves correspond to the pH values, from top to bottom, 8.6, 5.6, and 3.9. The iep of the alumina is pH 4.2; at pH values below this there is an electrostatic attraction as well as the van der Waals attraction between the surfaces. The background electrolyte concentration is 1×10^{-3} M KNO_3 .

streaming potential measurements on single α -alumina crystals indicate a much lower iep of between pH 3 and 5.²² The reason(s) for this difference is not known to us. The possibility the discrepancy is due to the effects of contamination of the alumina surface by silica can be excluded. In order to eliminate glass from the experimental setup, all the tubing and the reservoir were plastic, pH and conductivity measurements were taken in 50 mL aliquots in a separate beaker, all salt, acid, and base solutions were made and kept in polyethylene containers, and all cleaning and washing were done in plastic. XPS measurements did not reveal the presence of any silica on the surface of the plates used in the experiments. XPS cannot rule out organic contamination of the surface, but we believe the cleaning procedures used limit this as a possibility.

(iii) Force Measurements. For pH values between the iep's of the silica and the alumina, we expect an electrostatic attraction between the oppositely charged surfaces. For pH values above the iep of alumina, we expect an electrostatic repulsion between the unequally charged negative surfaces which will increase in magnitude as the pH increases. These features can be seen clearly in the force-separation curves in Figure 3 when the pH ranges from 8.6 to 3.9 with a background electrolyte concentration of 1.0×10^{-3} M KNO_3 . A similar increase

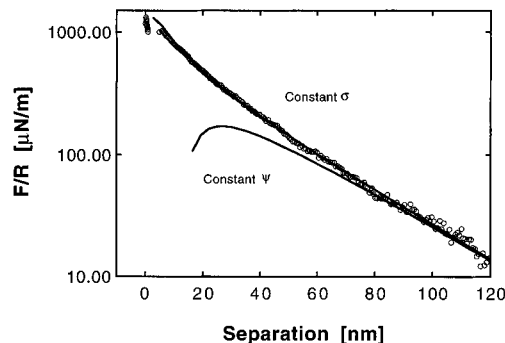


Figure 4. Force-separation curve taken at pH 8.2 and an electrolyte concentration of 1×10^{-4} M KNO_3 . The upper fitted curve is the constant charge limit (just visible in the upper left hand corner), and the lower curve is the constant potential limit. The repulsive experimental data clearly lie closer to constant charge than constant potential. The fitting parameters are as follows: silica potential, -100 mV; alumina potential, -34 mV; and Debye length, 31 nm. A Hamaker constant of 1.8×10^{-20} J was used in the calculations.

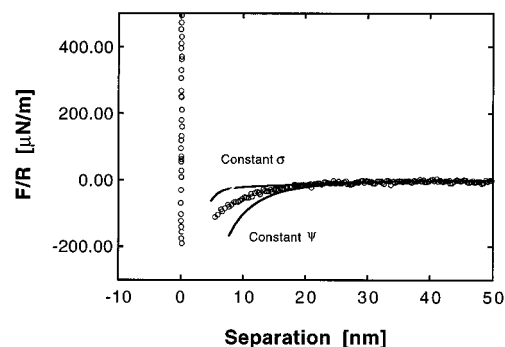


Figure 5. Force-separation curve taken at pH 3.9 and an electrolyte concentration of 1×10^{-3} M KNO_3 . The upper fitted curve is the constant charge limit, and the lower curve is the constant potential limit. The fitting parameters are as follows: silica potential, -25 mV; alumina potential, $+3$ mV; Debye length, 10 nm. A Hamaker constant of 1.8×10^{-20} J was used in the calculations.

in the strength of repulsion between the colloid and the plate was seen with an increase in pH in a 1.0×10^{-4} M KNO_3 solution (not shown). It should be noted that at no time was there any deviation from DLVO theory in the experimental force curves; there was no evidence of an "extra" short range repulsion that has been seen before between silica or glass surfaces.¹⁴

When analyzing force-separation data for unequally charged surfaces exhibiting an electrostatic repulsion, there is not one unique pair of diffuse layer potentials that will fit the experimental force curves.²³ For this reason it was necessary to use potentials from the independent measurements as a guide in fitting the experimental force curves with theory. In Figure 4 we show an experimental force curve taken at pH 8.2 with a salt concentration of 1×10^{-4} M KNO_3 ; it is fitted with diffuse layer potentials of -100 mV for silica and -34 mV for alumina with a Debye length of 31 nm (theory value 30.5 nm). The calculated Hamaker constant of 1.8×10^{-20} J was included in the fitting calculations. At this pH both the silica and alumina are negatively charged, resulting in an electrostatic repulsion between the surfaces. The data clearly lie closer to the constant charge limit than the constant potential limit. For solution pH values in between the iep's of the two metal oxides, we see an electrostatic attraction, seen in the experimental force

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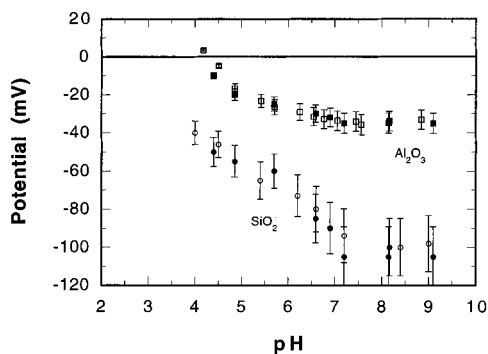


Figure 6. Comparison of the AFM-measured diffuse layer potentials and the independently measured ζ -potentials for the silica/alumina system as a function of pH with a background electrolyte concentration of 1×10^{-4} M KNO_3 . The agreement between the silica electrophoresis results (\circ) and the silica AFM results (\bullet) is very good, as is the agreement between the alumina streaming potential results (\square) and the alumina AFM results (\blacksquare).

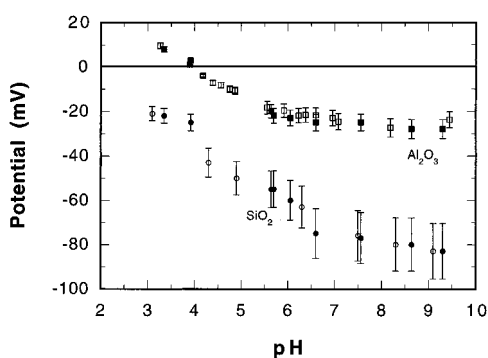


Figure 7. Comparison of the AFM-measured diffuse layer potentials and the independently measured ζ -potentials for the silica/alumina system as a function of pH with a background electrolyte concentration of 1×10^{-3} M KNO_3 . The agreement between the silica electrophoresis results (\circ) and the silica AFM results (\bullet) is very good, as is the agreement between the alumina streaming potential results (\square) and the alumina AFM results (\blacksquare).

curve shown in Figure 5, which was taken at pH 3.9. In this case the salt concentration was 1.0×10^{-3} M KNO_3 . This force curve has been fitted with potentials of -25 mV for silica and $+3$ mV for alumina with a Debye length of 10 nm (theory value 9.6 nm) and a Hamaker constant of 1.8×10^{-20} J. Experimental force curves showing an electrostatic attraction can be uniquely fitted with a positive and a negative potential, but independent information (e.g., electrokinetic measurements) is still needed to unambiguously assign which surface is positive and which is negative.

A comparison of the AFM-derived diffuse layer potentials and the independently obtained ζ -potentials is shown

in Figure 6 with a salt concentration of 1.0×10^{-4} M KNO_3 . The same comparison but in 1.0×10^{-3} M KNO_3 solution is shown in Figure 7. In both figures 15% error bars are included on all data. In the AFM measurements this error is representative of the combined errors from the determination of the cantilever's spring constant and the radius of the colloid probe from optical microscopy. Errors in the measured mobility data for the silica colloids and in the determination of the streaming potential change with pressure variation are also 15%. As can be seen, there is very good agreement between the potentials measured by the different techniques.

Conclusions

This work finalizes a series of studies aimed at validating the AFM force measurement technique as an accurate method for measuring electrokinetic properties of hard, nondeformable surfaces at low electrolyte concentrations. In earlier metal oxide work the electrokinetic properties of one, but not both, of the surfaces used in force measurements were characterized by traditional electrokinetic techniques.^{4,5,23} In this study the same surfaces used in the AFM force measurements were characterized. The potentials measured by the different techniques were in very good agreement in both 1.0×10^{-4} and 1.0×10^{-3} M KNO_3 solutions. Collectively this series of studies shows that the diffuse layer potentials derived from fitting the AFM forces-separation curves with DLVO theory are equivalent to electrokinetic ζ -potentials. The important point to emphasize is that the AFM direct force measurements between two interacting surfaces not only give a profile of the interaction with separation but also yield potentials that are equivalent to the macroscopic electrokinetic properties of the solid surfaces.

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Note added in proof: While this paper was in press another AFM study of silica/ α -alumina interaction was reported (Veeramasuneni, S.; Yalamanchili, M. R.; Miller, J. D. *J. Colloid Interface Sci.* **1996**, *184*, 594). The iep of the α -alumina crystal used in their study was 9.3. We suspect that this high iep is associated with a high degree of surface hydroxylation as a consequence of treating the crystal with 0.1 M KOH and 30 min of exposure to an oxygen plasma.

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