Nanoscale adhesive forces between silica surfaces in aqueous solutions

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ABSTRACT

Nanoscale adhesive forces between a colloidal silica probe and a flat silica substrate were measured with an atomic force microscope (AFM) in a range of aqueous NaCl, $CaCl_2$, and $AlCl_3$ solutions, with concentrations ranging from 10^{-6} to 10^{-2} M at pH $\sim$5.1. Notably, the measured force curves reveal large pull-off forces in water which increase in electrolyte solutions, with jump-off-contact occurring as a gradual detachment of the probe from the flat substrate rather than as a sharp discontinuous jump. The measured force curves also show that the number and size of the steps increase with concentration and notably with electrolyte valence. For the higher concentration and valence the steps become jumps. We propose that these nanoscale adhesive forces between mineral surfaces in aqueous solutions may arise from newly born cavities or persistent subnanometer bubbles. Formation of cavities or nanobubbles cannot be observed directly in our experiments; however, we cannot disregard them as responsible for the discontinuities in the measured force data. A simple model based on several cavities bridging the two surfaces we show that is able to capture all the features in the measured force curves. The silica surfaces used are clean but not intentionally hydroxylated, as contact angle measurements show, and as such may be responsible for the cavities.

1. Introduction

It is well known that silica suspensions exhibit remarkable stability at their isoelectric point [1] against coagulation and sedimentation [2,3] and low viscosity [1,4]. The short-range repulsion not predicted by DLVO theory [5,6] but usually observed in direct force measurements between silica surfaces arises from a surface-induced water effect, from the creation of a hydrogen-bonding network at the surface level [4,7–24]. This short-range repulsion as well as the small attractive van der Waals forces for silica in water and in aqueous electrolyte solutions are likely responsible for the unusual stability of silica suspensions particularly at their isoelectric point. In the past this issue has been of interest to a wide range of processes involving transport and processing of silica slurries and pulps. Interest today is even greater considering that industry is moving fast toward higher solids loadings, and thus an appropriate control of rheological behavior and physicochemical stability of the suspensions is crucial to obtain fluidity and stability as desired. A great variety of experimental techniques have been used to characterize silica–silica interactions, however for assessing interaction forces between silica surfaces mediated by aqueous solutions the surface force apparatus (SFA) and the atomic force microscope (AFM) are the favorites. Here we are interested in the forces that arise in the separation of two silica surfaces after reaching direct contact. Given the repulsive character of the interaction in the approaching of the surfaces, one might expect a separation virtually free of hysteresis. This is true for the interaction in water [20,22,25,26] but not in aqueous electrolyte solutions [18,27–31]. Although the silica–silica system has been reinvestigated several times, interest has focused on approach force curves rather than on separation force curves, therefore adhesive forces have not always been observed [14,19,25–27,32–34]. It has been reported that adhesion between silica surfaces in water occurs only when the surfaces remain in contact for a long time [19] although according to Yaminsky et al. [25,26], after several days in water the strength of the adhesion decreases. Similar behavior is reported by Chapel [18]; silica adhesion in 0.1 M NaCl at pH 5.5 disappears after few minutes. Less common in the literature is to find trends followed by silica–silica adhesion with electrolyte concentration in the measurement of forces. Yaminsky et al. [26] and Meagher [28]

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observed that adhesion between silica surfaces increases with salt concentration, Freitas and Sharma [35] found no relationship between the concentration of electrolyte and the adhesion values between two silica surfaces, but Vakarelski et al. [36,37] and Fielden [38] did find such a dependency, adhesion values decrease with increasing electrolyte concentration. These are three groups of manuscripts arriving to three different results. The experimental evidence indicates that silica particle dispersion, aggregation and gelation depend on this elusive attractive force. The origin of such a force is of great and broad scientific interest, particularly because there is as yet no single explanation of its cause. This force is in excess to continuum van der Waals and electrical double-layer DLVO forces [5,6]. Here we use AFM to directly measure the adhesive force between silica surfaces in aqueous NaCl, CaCl$_2$, and AlCl$_3$ solutions, with concentrations ranging from 10^{-6} to 10^{-2} M at pH ∼5.1. Adhesive force measured between a colloidal silica probe and a silica substrate has unusual intensity and long range. In recent articles, Atkins et al. [29] and Guleryuz et al. [31] have reported long-range adhesive forces similar to ours explaining them as originated in the compressive contact and elastic deformation of the silica surfaces, contact forces however are too short range so as to be invoked to explain their measured forces. Our force curves reveal large pull-off forces in water and in electrolyte solutions, the jump-off-contact occurs as a gradual detachment of the probe from the flat substrate rather than as a sharp discontinuous jump. Ladder type force curves have been measured several times between hydrophobic surfaces (see for instance [38]) but not between silica surfaces. Formation of cavities cannot be observed directly in our experiments; however, we cannot discard them as responsible for the discontinuities in the measured force data. We propose a simple model based on several cavities bridging the two surfaces to explain the measured force data.

2. Experimental

Glass microslides (B&C) typically 1×1 cm^2 were used. The flat silica substrates were glued to AFM stubs before use. Glass colloidal probes were prepared [39] by gluing a 20 μm in diameter sphere (Duke Scientific Corporation) to the end of a tipless V-shaped, 100 μm long, 0.6 μm thick, Si$_3$N$_4$ cantilever (Veeco) with Norland Optical Adhesive 61 (Norland Products, USA). Spring constants of individual cantilevers were determined by the method of standards (standards provided by Park Scientific, USA) with the Dimension 3100 AFM microscope and were typically 0.14 N/m. SEM and AFM images verified the quality of the modified cantilevers. Interaction forces were measured in bi-distilled water, pH was ∼5.1, and also in electrolyte solutions. NaCl, CaCl$_2$, and AlCl$_3$ (analytical chemical grade, Merck, Germany) were used in concentrations ranging from 10^{-4} to 10^{-2} M. Experiments were carried out without any buffering, pH was ∼5.1. All glassware used in the preparation of solutions was detergent and alkali washed with final thorough rinsing in bi-distilled water. Prior to force measurement the mineral surfaces, substrate and sphere, were thoroughly rinsed in high purity water (18.6 MΩ/cm), then with ethanol, and then again with bidistilled water. No efforts were made to improve hydroxylation of the glass surface groups into silanol groups, thus perfect wetting should not be expected. Contact angles were measured through the liquid phase for the various electrolyte solutions used here with the Ramé-Hart contact angle goniometer. Surface roughness, assessed by AFM imaging with the Dimension 3100 and measured as the root-mean-square roughness, was small for both substrate, ∼2 nm, and microsphere, ∼1 nm. Force measurements between AFM probes and substrates as function of separation were conducted using an SPM-3 (Thermo, USA) multimode atomic force microscope equipped with a Nanoscope IIIa SPM control station, fluid cell (0.1 cm^3), silicone pad for

vibration isolation, and acoustic enclosure. AFM allows continuous measurement of cantilever deflection vs. position as probe and substrate approach, commonly named extension, or separate, commonly named retraction. Approaching force curves can be found in Acuña and Toledo [23], here we report on retraction force curves. Measurement of a typical force curve took less than 20 min; during this time the AFM roughness of the substrate remained unaltered. The force measurement protocol is well established [14,16] and the sample manipulation procedure is available [23]. Extension and retraction driving speeds were low, 280 nm/s, in order to minimize hydrodynamic contribution to the measured force. Force curves were first verified to be independent of position on the substrate; measurements were always highly reproducible. Forces are reported normalized by the microsphere probe radius, that is, as interaction energy between silica flat surfaces by virtue of Derjaguiń's approximation, $F(D) = 2\pi RE(D)$, where F is force, D distance, R probe radius, and E energy per unit area.

3. Results and discussion

Here we are interested in the forces that arise in the separation of two perfectly clean silica surfaces but not hydroxylated after reaching direct contact. Fig. 1 shows glass contact angles measured through the liquid phase for the various electrolyte solutions of interest here. Contact angle in pure water is 27° and in electrolyte solutions increases with concentration, very rapidly in the range <0.5 M, reaching 34° in NaCl, 36° in CaCl$_2$, and 43° in AlCl$_3$. Clearly our surfaces are not perfectly wet by the liquid solutions and their hydrophilic character decreases as electrolyte concentration and valence increase.

Given the repulsive character of the silica–silica interaction in the approaching of the surfaces, one might expect a separation virtually free of hysteresis. However, this is not so because the separation forces that we have measured for the silica–silica system show significant adhesive force with unusual intensity and long range. It is important to mention that contact time between the surfaces during the measurement is very short.

Fig. 2 shows approach-separation force curves measured between a colloidal silica microsphere probe and a flat silica substrate in water and pH 5.1. Fig. 3 shows separation force curves for the same silica system immersed in aqueous NaCl, CaCl$_2$ and AlCl$_3$ solutions, with concentrations from 10^{-4} to 10^{-2} M and pH between 4.6 and 5.2. The curves clearly show the presence of an adhesive force. Force curves in Figs. 2 and 3 are representative of at least six independent AFM measurements at two different points on the substrate for each intervening liquid. Measurements were
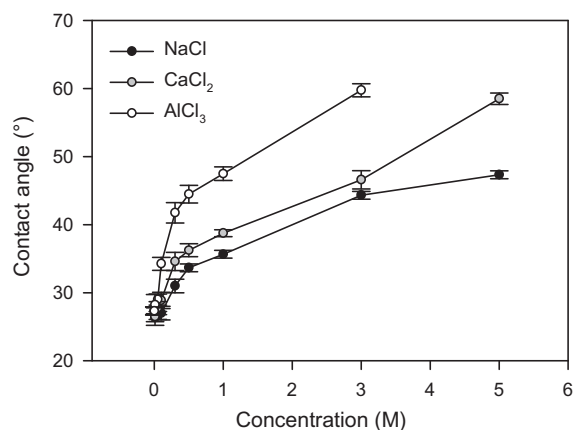

Fig. 1. Glass contact angles measured through the liquid phase for various electrolyte solutions and concentrations.