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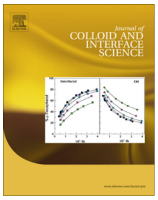

AFM forces between mica and polystyrene surfaces in aqueous electrolyte solutions with and without gas bubbles

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ABSTRACT

Force curves between a flat mica substrate and a polystyrene microsphere were measured with an atomic force microscope (AFM) in carefully degassed water and aqueous NaCl, $CaCl_2$, and $AlCl_3$ solutions. The pH of the water used does not change significantly with degassing treatment, and its value remains close to 6. Electrolyte concentration ranges from 10−4 to 10−2 M and pH from 4.7 to 5.1. We have found that the repulsive long-range electrostatic force between mica and polystyrene is attenuated by the presence of electrolytes and counterbalanced by a long-range attractive force, which we referred to as a hydrophobic force, which is longer-ranged than the ever present attractive van der Waals force. This force, which includes the adhesive bridging of residual air bubbles and newborn vapor cavities, and any other unknown forces, is reasonably well represented by a unique exponential law. Prefactor and decaying length are not very sensitive to electrolyte type, concentration, and pH, suggesting that any new force included in the law, in addition to adhesive bridges, should obey a non-classical electrostatic mechanism. However, we also know that liquid/solid contact angle and liquid/vapor surface tension increase with electrolyte concentration and valence increasing the stability of bubbles and cavities which in turn increase the bridging force. Clearly, these effects are hidden in the empirical force law.

1. Introduction

Nonsymmetrical hydrophilic–hydrophobic interactions in electrolyte solutions are central in many industrial processes, for instance, in flotation operations for which hydrophobic forces determine the fate of particle–bubble interactions. The origin and characteristics of this non-DLVO hydrophobic surface have been the subject of intense research activity in the last 30 years. Despite this enormous effort, the origin of the force is not yet resolved. Several explanations for its origin, strength, and range are available, i.e., this force originates from the structuring of water between two hydrophobic surfaces [1]; from an electrostatic mechanism including polarization of water close to hydrocarbon–water interfaces [2], from adsorbed but laterally mobile ions [3], and from electric fields associated with large ordered crystalline domains [4]; from the metastability of water films separating two hydrophobic surfaces, which produces vapor cavities that give rise to capillary bridges between the surfaces [5–12]. Sakamoto et al. instead propose that air bubbles which are introduced during the preparation of solutions are responsible and therefore proposed a method of degassing [13]. The interaction between hydrophobic surfaces shows extremely long-range interactions, in some cases reaching 300 nm [9], 600 nm [14], and 1200 nm [4], and forces of so high intensity that are not easy to explain. Most of the studies of hydrophobic interactions have been made in symmetrical hydrophobic-hydrophobic systems [1,4,5,11–37] and comparatively few in asymmetrical hydrophilic–hydrophobic systems [4,9,15–17,38–42]. This paper presents the results of direct AFM measurement of force curves between a flat mica substrate and a polystyrene microsphere in water and in aqueous NaCl, $CaCl_2$, and $AlCl_3$ solutions. Electrolyte concentration ranges from 10^{-4} to 10^{-2} M and pH from 4.7 to 5.1. Measurements were made with and without gas bubbles at ambient conditions. We have found that the repulsive long-range electrostatic force between mica and polystyrene is attenuated by the presence of electrolytes and counterbalanced by a long-range attractive force. This force, which is longer-ranged than van der Waals forces, includes the adhesive bridging of residual air bubbles and newborn vapor cavities and any other unknown forces, is reasonably well represented by a unique exponential law. Prefactor and decaying length are not very sensitive to electrolyte type, concentration, and pH, suggesting that any new force included in the law, if any, should obey a non-classical electrostatic mechanism. However, we also know that liquid/

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solid contact angle and liquid/vapor surface tension increase with electrolyte concentration and valence increasing the stability of bubbles and cavities which in turn increase the bridging force. Clearly, these effects are hidden in the empirical force law.

2. Methods

Three types of water were used as ambient fluid to measure interaction forces: bi-distilled (Jencons Scientific Ltd., England), tetra-distilled (Heraeus Schott, Germany), and milli-Q (Milli-pore, USA). Water was used "as received" and after two processes of degassing; sonication in an ultrasonic bath (Branson Ultrasonic Corporation, USA) for three hours and three cycles of boiling for 15 min, followed by rapid freezing with liquid nitrogen, evacuated by a vacuum pump, and subsequent melting at ambient conditions [13]. The pH of the water used does not change significantly with treatment, and its value remains close to 6 (5.8 in bi-distilled water, 5.6 in tetra-distilled water, and 5.5 in milli-Q water). All previous measurements have been performed at atmospheric pressure and ambient temperature of 20 °C. Interaction forces were also measured in electrolyte solutions as ambient fluid; such solutions were prepared in degassed milli-Q water in vacuum. 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, and pH ranges from 4.7 to 5.1. Under these conditions, mica surfaces in water or in aqueous solutions were negatively charged. All glassware used in the preparation of solutions previously was detergent and alkali washed with final thorough rinsing in bi-distilled water.

The AFM used in this study was a Multimode Atomic Force Microscope (Veeco, USA) equipped with a Nanoscope IIIa SPM control station, fluid cell (0.1 cm^3), silicone pad for vibration isolation and acoustic enclosure. Muscovite mica substrates typically 1×1 cm^2 were used. Freshly cleaved mica sheets were obtained at time of use from a native muscovite mica block available in our laboratory. The flat substrates were glued to AFM stubs before use. Polystyrene probes were prepared by adhering a polystyrene microsphere of approximately 20 μm in diameter (Duke Scientific Corporation, USA) to the end of a contact Si_3N_4 tipless V-shaped, 200 μm long, 0.6 μm thick cantilever (Thermo, USA) with Norland Optical Adhesive 61 (Norland Products, USA). A simple adaptation of Huntington and Nespolo protocol for attaching microspheres to AFM cantilever tips was implemented in a Dimension 3100 (Veeco) atomic force microscope [43]. The size of the microspheres was determined by SEM (ETEC, Autoscan). Probes were UV-heated enough to secure the microsphere-cantilever bonding. Spring constants of individual cantilevers were determined by the method of standards (standards provided by Park Scientific) with the Dimension 3100 AFM microscope and were typically 0.14 N/m. SEM and AFM images verified the quality of the modified cantilevers. Prior to force measurement, the mineral and polystyrene surfaces were thoroughly rinsed in high-purity water (18.6 MΩ/cm) and then with ethanol and then again with pure water. Surface roughness, assessed by AFM imaging with the Dimension 3100, was typically subnanometer in size for both substrate and microsphere.

Samples were manipulated with tweezers to avoid contamination. Once substrate and probe were appropriately mounted, the cell was flooded with ambient fluid. The system was allowed to reach equilibrium for few minutes before probe and substrate were approached one to another. Measurement of a typical force curve took less than 20 min; during this time, the AFM roughness of the substrate remained unaltered. AFM allows continuous measurement of cantilever deflection vs. position as probe and substrate approach each other, commonly named extension, or separate, commonly named retraction. Data were provided by Nanoscope IIIa DI v4.42 instrument software (Veeco). To convert these data into force vs separation curves, we used commercial software and own routines based on the procedure of Ducker et al. [44,45]. Detail of this procedure was published previously [46]. Extension and retraction driving speeds were low (0.5 Hz) in order to minimize hydrodynamic contribution to the measured force. Typically, four or five force data points per nanometer were acquired. Forces are reported normalized by the microsphere probe radius, that is, as interaction energy between mica and polystyrene flat surfaces by virtue of Derjaguin's approximation [47]. Interaction curves between the sphere and the flat substrate in water were measured at two different points, three measurements per point, whereas for the interaction in electrolyte solutions, curves were measured several times but at a single point.

3. Results and discussion

Here, we are interested in the forces that arise in the approaching of a colloidal polystyrene microsphere to a flat mica substrate in aqueous electrolyte media with and without bubbles.

3.1. Non-degassed water

Fig. 1 shows approaching force curves between a flat mica surface and a polystyrene microsphere probe in bi-distilled, tetra-distilled, and Milli-Q water, all them "as received." Dissolved air appears as bubbles. Fig. 1a shows six approaching force curves in bi-distilled water: three of them measured at one point on the substrate, the other three at a different point. Results show a strong repulsion as the surfaces approach. In the long range, this repulsion is attributable to electrostatic effects, bubbles adhered onto the surface of the polystyrene probe acquire charge in water and thus a surface potential. Mica has a surface potential of around −50 mV, and the polystyrene has a zeta potential between −30 and −60 mV [48], which is very similar to zeta potentials that have been measured on the surface of a bubble [49]. In shorter distance ranges, comparable to the size of bubbles, the repulsive effect is enhanced by compression of such air bubbles between the approaching surfaces. Repulsion reaches a peak at a distance of ~15 nm. Then, unexpectedly, the surfaces jump into contact. Extensive literature is available on this "hydrophobic" force and working mechanism; however, no generally acceptable explanation is available. For the data here, it is plausible to argue that this attractive force has its origin in two mechanisms: the electrical fields of unaligned charges on both surfaces at very short distance cooperate to produce an attractive force [50] and the breaking of large bubbles into nanobubbles that migrate away from the contact area thus eliminating the hindrance to the contact. Thecontinuous approach between the mica and polystyrene may end up with a few nanobubbles trapped between the surfaces. The approaching force curves are not significantly different at the two points studied. For distances of 5 nm and less, repulsive forces become stronger again dominating the interaction. The origin of this very short-range force is better understood and is related to hydration and water structuring [53]. Fig. 1b shows the results for the interaction between mica and polystyrene in tetra-distilled water. Approaching force curves are similar to those obtained in bi-distilled water. Repulsion values obtained are similar, and jumps occur at the same range of separation distances, i.e., 10–15 nm. There were no differences between the force curves measured at different points on the substrate. Fig. 1c shows results for the mica-polystyrene interaction in milli-Q water. It is clear that these curves differ significantly from those obtained in bi-distilled and tetra-distilled water. Approaching force curves present repulsion values significantly