

Interaction Forces between Hydrophobic and Hydrophilic Self-Assembled Monolayers

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An investigation is presented of the interaction of charged self-assembled monolayers (SAMs) with a monoprotic ionizable acid functional group (–COOH) and uncharged SAMs with a methyl terminated functional group (–CH₃). The strength of the interactions are determined using an atomic force microscope. For all electrolyte conditions investigated the interactions are not well described by a summation of van der Waals attractions and electrostatic repulsions in a manner suggesting that van der Waals attractions are screened. The repulsions are accurately described as corresponding to two surfaces of different charge interacting with surface charges that are independent of separation (i.e., the constant charge model). A small adhesion force was observed under all conditions and its magnitude increased with NaCl concentration. © 2000 Academic Press

Key Words: surface forces; self-assembled monolayers; hydrophobic surface; hydrophilic surface; dissimilar surfaces; atomic force microscope.

INTRODUCTION

Numerous studies have characterized the interactions of homogenous hydrophobic or hydrophilic surfaces. The key to these studies has been to characterize interactions between surfaces with similar properties. In the majority of industrial and technological areas, however, surfaces are heterogeneous, containing both hydrophobic and hydrophilic sites, at both the microscopic and the macroscopic level. The interaction between surfaces with radically different wetting properties are poorly understood and remain controversial (1–8). For example, large attractive forces were observed between a bare mica surface and a mica surface coated with dimethyldioctylammonium ions (1, 2). Similarly, the interaction between an air bubble or a silanated silica surface and a hydrophilic silica particle (5) was also much more attractive than predicted by classical models composed of a summation of van der Waals attractions and electrostatic repulsions referred to as the DLVO model (9, 10). In addition, force measurements between bare and silanated silica surfaces suggested that there exists a weak attraction ascribed to arising from hydrophobic interactions (8).

On the other hand, the interaction between a hydrophilic glass surface and a hydrophobic silanated glass surface (4) or between a glass sphere and a silanated silica plate (3) and the interactions of silica and polypropylene (6, 7) were found to be in agreement with the classical DLVO theory.

Here we present studies on different classes of dissimilar surfaces. We have directly measured forces with an atomic force microscope (AFM) between a 20- μm sphere covered with hexadecanethiol and a surface of close packed, carboxylic acid terminated hydrocarbon chains (16-mercaptohexadecanoic acid) in different NaCl concentrations. Force curves have been analyzed to gather information about adhesion forces and electrostatic interactions. We have chosen to work with SAMs of alkanethiols because they are robust, well characterized, easily prepared surfaces (11–15) and represent an excellent method of modifying the surface characteristics in a molecularly rationalized way. The interaction between like pairs of these surfaces has been well characterized. Methyl terminated thiol surfaces are strongly hydrophobic, and remain uncharged at all ionic strengths studied. The strength of adhesion between two surfaces consisting of methyl terminated thiols grows with the chemical potential of the solute (16) and can be manipulated further through changes in the contact angle of the surface (17). The interaction of the carboxylate terminated thiols is more complex, showing a suppressed tendency to ionize and an affinity for binding sodium ions (18). In a pH range where the surfaces are charged, standard electrostatic repulsions are observed. Here we explore the interaction of charged carboxyl terminated and methyl terminated surfaces as a function of ionic strength at neutral pH.

MATERIALS AND METHODS

Surface force measurements were performed using a Nano-scope E atomic force microscope (Digital Instruments, Santa Barbara, CA). All experiments were carried out at pH conditions 5–6, without any addition of acid or base, and at room temperature.

Standard 100 μm V-shaped silicon nitride AFM cantilevers with pyramidal tips (Digital Instruments, Santa Barbara, CA) were used for the force measurements. The colloid probe tips

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were prepared as follows. A glass sphere (SPI Supplies, West Chester, PA) of approximately $10\ \mu\text{m}$ radius (the radius was measured by optical microscopy) was attached to the cantilever with an epoxy resin, Epon Resin 1004F (Shell Chemical, Houston, TX). A heated thin copper wire ($\sim 30\ \mu\text{m}$ diameter) attached to a three-dimensional translation stage was used to position a small portion of the glue near the apex of the cantilever. Another clean wire was used to put a glass sphere onto the tip. The cantilever was heated just enough to melt the Epon and secure the particles in place.

Substrates of the desired size were cut from Si (100) wafers (WaferNet, San Jose, CA; test grade). These substrates and colloid probe tips were coated by thermal evaporation with 250–500 Å of gold (99.999%; Alfa, Ward Hill, MA). Care was taken to avoid overheating the colloid probe tips or evaporating too much gold on them since in both cases the cantilevers bend. The spring constant of the gold-coated colloid probe tips was determined using the resonant frequency method (19). An average value of 2.98 N/m was used in this study after calibrating 20 colloid probe tips from our wafer.

Hydrophobic spheres were prepared by forming SAMs of hexadecanethiol (Aldrich, Milwaukee, WI) on the gold coated probes (12, 13, 15). The 16-mercaptohexadecanoic acid was synthesized in our laboratory according to the protocol of Bain *et al.* (12).

RESULTS AND DISCUSSION

The gold and SAM surfaces were first characterized by using a silicon nitride tip and a colloid probe tip to image the substrate surface. For all systems, the substrate was smooth with a root mean square roughness of less than 1 nm (Fig. 1).

Interaction forces were measured between a hydrophobic uncharged $-\text{CH}_3$ terminated $20\text{-}\mu\text{m}$ sphere and a hydrophilic charged $-\text{COOH}$ SAM surface. Previous work between two hydrophobic $-\text{CH}_3$ SAMs in different aqueous electrolytes suggests that the surfaces are not charged and that ions do not bind specifically to the methyl terminated thiols since the interaction was purely attractive at all salt concentrations (16). Figure 2 shows typical force curves obtained in NaCl solutions of 5×10^{-3} , 0.01, 0.03, and 0.05 M between a $20\text{-}\mu\text{m}$ $-\text{CH}_3$ terminated sphere and a $-\text{COOH}$ SAM surface. On approach, the interactions of the charged and uncharged surfaces were always repulsive, with the repulsive interaction being screened as the ion concentration is increased. The forces decayed exponentially with distance. The two surfaces did not appear to jump into contact, indicating that a strong attraction was not observed, as would be expected for van der Waals attractions. For the cantilevers used here, the theoretical jump-in distance for two gold surfaces in water is 6.6 nm (using an unretarded Hamaker constant of $A = 2.5 \times 10^{-19}$ J (20)) and for hexadecane surfaces

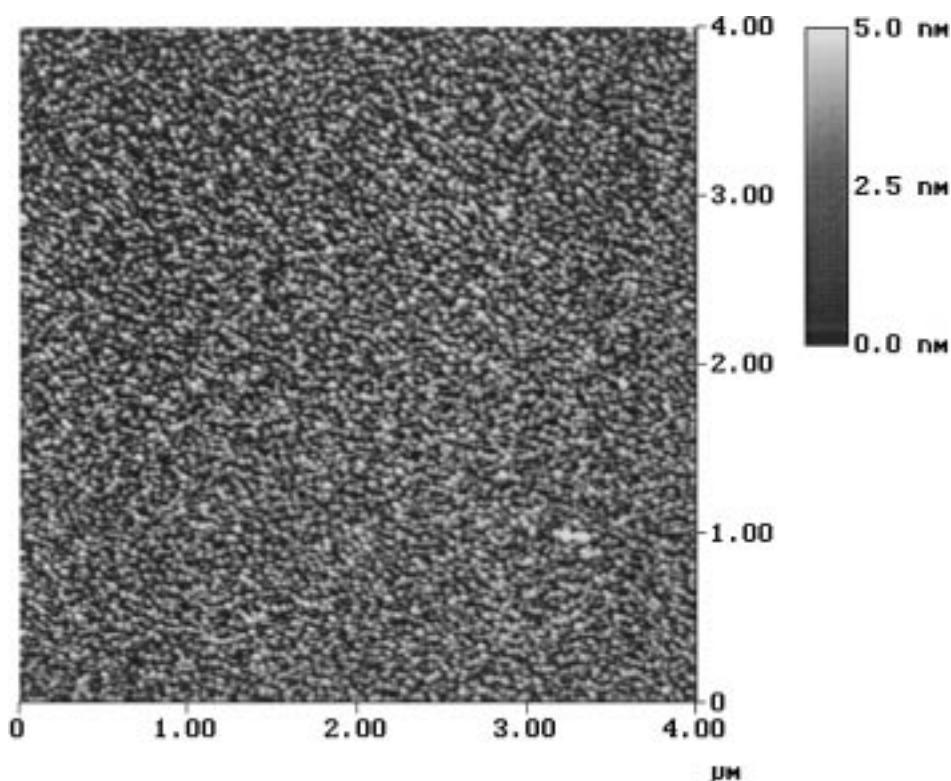


FIG. 1. An AFM image of a 16-mercaptohexadecanoic acid SAM on gold. The image was taken in water with a $10\text{-}\mu\text{m}$ -radius probe that has been functionalized with SAM of hexadecanethiol. The root mean square roughness of the surface is 0.86 nm.

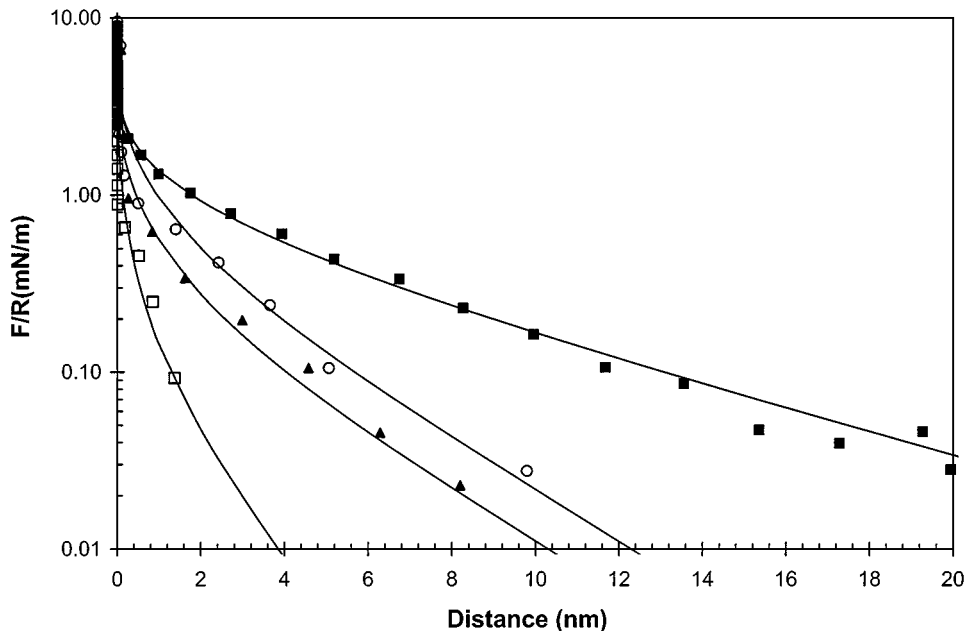


FIG. 2. Normalized forces recorded between a 20- μm hydrophobic ($-\text{CH}_3$) sphere and a hydrophilic ($-\text{COOH}$) substrate in different concentrations of NaCl. The solid line is the best fit to Eq. [3]. (■) 5×10^{-3} M NaCl $\psi_o = -22$ mV, (○) 0.01 M NaCl $\psi_o = -14$ mV, (▲) 0.03 M NaCl $\psi_o = -10$ mV, (□) 0.05 M NaCl $\psi_o = -5$ mV.

in water it is 1.8 nm. For the hexadecane surfaces an unretarded Hamaker constant of $A = 5 \times 10^{-21}$ J was used. This Hamaker constant was calculated on the basis of the Lifshitz theory for hexadecane surfaces interacting across water (21). However, upon retraction of the probe from a surface at contact, a small adhesive interaction was observed (not shown). The lack of a jump into contact and the presence of a weak adhesion suggests that van der Waals forces are screened and that attractions act over a distance of less than 1 nm. As jumps into contact, characteristic of van der Waals attractions, were not observed, the exponentially decaying repulsion was analyzed solely in terms of repulsive electrical double-layer forces.

When two surfaces approach one another it has been usual to assume, as boundary conditions for the electrostatic problem, that constant charge or potential is maintained on either or both surfaces through the interaction. However, in the case of surfaces with ionizable groups, the interaction may itself influence the degree of dissociation of surface groups so that neither the potential nor the charge is constant. This condition known as surface regulation (22) may then be more appropriate. The electrical double-layer interaction under regulation by surface ionization between two similar (22, 23) or dissimilar (24, 25) amphoteric surfaces has been considered by a number of authors. The regulated approach analysis of double-layer penetration has two important limits. For surfaces where the Nernst equation is sensibly obeyed at infinite separation the system approaches constant potential conditions, whereas if the potential is such that the potential-charge relationship is essentially insensitive to changes in potential, the approach is essentially

constant charge interaction until very small distances (23). For two dissimilar amphoteric surfaces the constant charge approximation becomes valid when the collision time is too fast for the surfaces to regulate, and the surfaces interact under constant potential when the regulation of the potential is perfect (24). In our case, where we measure the interaction between a surface that has ionizable acid groups and a methyl terminated surface with zero charge, we will show that the boundary condition of constant charge can accurately describe this interaction.

The measured force, F , is scaled by the radius of the sphere, R , in order to relate the force between a curved and a flat surface to the interaction energy, V , between plane parallel plates of unit area by (26)

$$F/R = 2\pi V. \quad [1]$$

For two planar surfaces interacting at constant unequal low ($ze\psi/k_B T < 1$) potential, the repulsion potential energy is given by (27)

$$V_R^\psi = \frac{\varepsilon\varepsilon_0\kappa}{2} [(\psi_{o1}^2 + \psi_{o2}^2)(1 - \coth \kappa D) + 2\psi_{o1}\psi_{o2} \operatorname{cosech} \kappa D], \quad [2]$$

where z is the valency of the cationic species, e is the electronic charge, k_B is the Boltzmann's constant, T is the temperature, ε is the dielectric constant of the solvent, ε_0 is the permittivity of the vacuum, κ is the Debye length, ψ_{o1} and ψ_{o2} are the potentials on the surfaces, and D is the surface to surface separation

distance. The corresponding expression for V_R when the plates interact under conditions of constant charge and low potential ($ze\psi/k_B T < 2$) is given by (28)

$$V_R^\sigma = \frac{2n_b k_B T}{\kappa} \left[2y_o \ln \left\{ \frac{B + y_o \coth(\kappa D/2)}{1 + y_o} \right\} - \ln(y_o^2 + \cosh \kappa D + B \sinh \kappa D) + \kappa D \right], \quad [3]$$

where $y_o = \frac{ze\psi_o}{k_B T}$, $\psi_o = (\psi_{o1} + \psi_{o2})/2$ and $B = [1 + y_o^2 \operatorname{cosech}^2(\kappa D/2)]^{1/2}$. Note that in Eq. [3], ψ_{o1} and ψ_{o2} are the surface potentials of surfaces 1 and 2 at infinite separation.

Theoretical fits were calculated for the surfaces interacting at both constant charge and constant potential boundary conditions. The values of ψ_o were obtained from the best fit of the model to the data. Equation [2] suggests that two surfaces with different constant potentials, i.e., the surface potentials are held constant as D decreases, feel an attraction at all separations. On the other hand, Eq. [3] predicts a repulsion at all separations even if one of the surfaces has a zero surface potential at large separations. The data are consistent with an interaction at the constant surface charge boundary condition, shown as solid lines in Fig. 2. Our data clearly demonstrate that the interaction between $-\text{CH}_3$ and $-\text{COOH}$ surfaces are repulsive and the repulsions are due to the compression of the double layer of the charged surface by the presence of the uncharged sphere.

The electrical potential profile between the two dissimilar surfaces $-\text{COOH}$ (surface 1) and $-\text{CH}_3$ (surface 2) can be described as part of the profile between two plates of equal potential, if the second plate is placed at the appropriate position (C in Fig. 3). When the $-\text{CH}_3$ plate is at distance $D/2$ from the first one and $\psi_{o2} = \psi_m$ (where ψ_m is the potential midway between two plates of potential ψ_{o1} and separation D) then $d\psi/dx = 0$ at the surface of $-\text{CH}_3$ and the surface is uncharged (29). For small degrees of double-layer overlap ($D > 1/\kappa$) the midplane potential is given

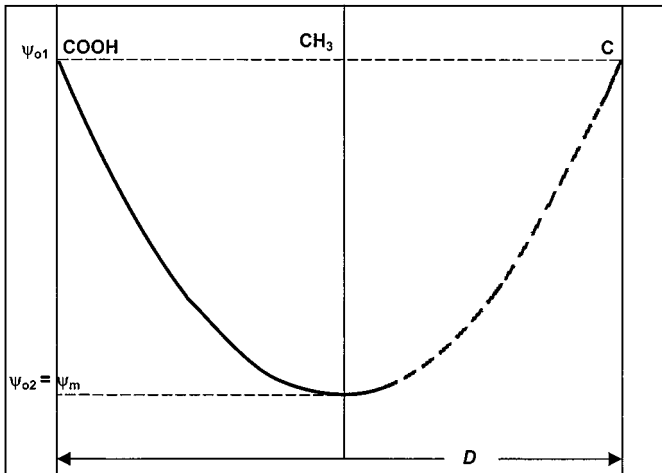


FIG. 3. The potential profile between two dissimilar plates $-\text{COOH}$ and $-\text{CH}_3$ of surface potential ψ_{o1} and ψ_{o2} .

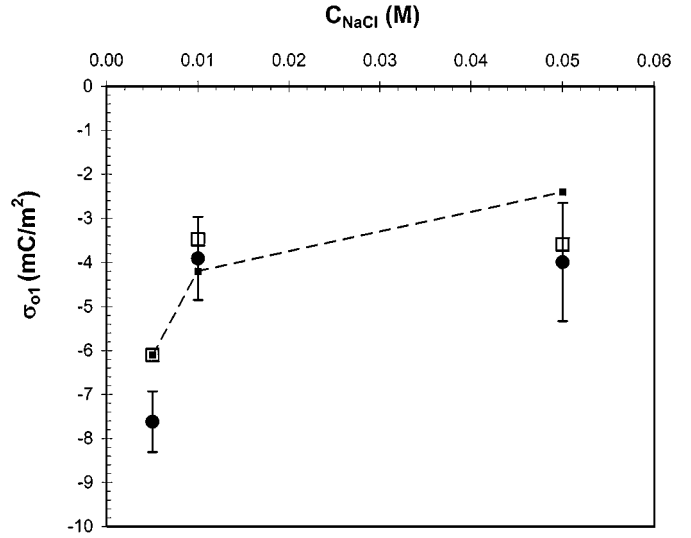


FIG. 4. Effect of NaCl on the surface charge of a $-\text{COOH}$ surface when it is interacting with a $-\text{CH}_3$ surface (●). The error bars correspond to the standard deviations that resulted from 10 to 15 force measurements all over the hydrophilic surface. For comparison we have also included the surface charge of $-\text{COOH}$ surface when it interacts with another $-\text{COOH}$ surface (□) and theoretical predictions of the surface charge from a competitive binding model by sodium ions (—■—).

by (29)

$$\psi_{o2} = \psi_m = \frac{8k_B T}{ze} \tanh\left(\frac{ze\psi_{o1}}{4k_B T}\right) \exp(-\kappa D/2). \quad [4]$$

In Eq. [4] $\psi_{o2} = 0$ mV and $\psi_{o1} = 2\psi_o$. Thus from the curve fits in Fig. 2 we can extract the surface potential on the charged surfaces and from this the surface charge density. The surface potential and surface charge density are correlated through (30)

$$\sigma_{o1} = 2(2\epsilon\epsilon_0 k_B T n_b)^{1/2} \sinh(ez\psi_{o1}/2k_B T). \quad [5]$$

Figure 4 shows the surface charge of the $-\text{COOH}$ surface as a function of the NaCl concentration when it interacts with a $-\text{CH}_3$ surface. The surface charge of a $-\text{COOH}$ surface when it interacts with another $-\text{COOH}$ surface at neutral pH conditions is also shown in Fig. 4 (18). In a previous work we demonstrated that the charge on the carboxylic acid terminated thiol surface can be understood if the acid groups have a $\text{p}K_a$ of 6.3 and sodium ions bind with a binding constant of $\text{p}K_{\text{Na}} = 3.7$ (18). This competitive site binding model demonstrates that the surface charge is around 5% of the maximum possible. For comparison we have included in Fig. 4 the predictions of this site binding model. The agreement of the charges measured between identical surfaces with those measured here demonstrates that the repulsive forces observed between uncharged and charged surfaces are well understood with conventional electrostatic models.

The adhesive forces observed at different NaCl concentrations were in the range 0.2–0.8 mN/m (Fig. 5). The adhesion increased as the electrolyte concentration was increased (Fig. 5).

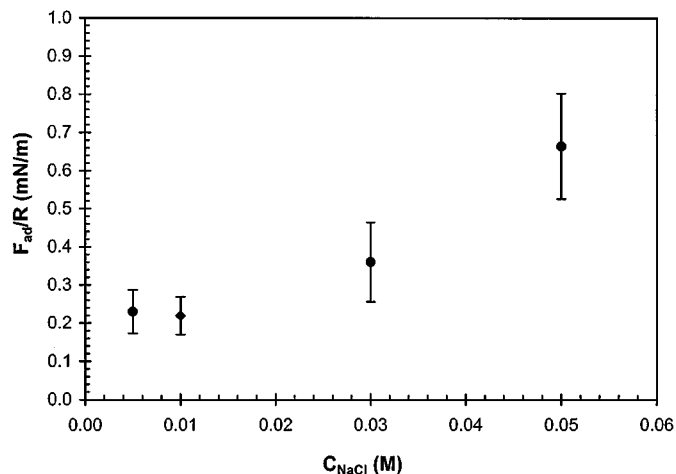


FIG. 5. Adhesion forces scaled by the radius of the sphere versus NaCl between a 20- μm hydrophobic ($-\text{CH}_3$) sphere and a hydrophilic ($-\text{COOH}$) surface. The error bars correspond to the standard deviations the resulted from 10 to 15 force measurements all over the surface.

The results demonstrate that the intervening fluid moderates the attractive interaction.

The absence of van der Waals attractions is poorly understood. In contrast, attractive forces with a range longer than could be predicted by van der Waals forces were observed for two hydrophobic $-\text{CH}_3$ thiol surfaces (16) where pull-off forces increased with ionic strength (16). Jumps into contact with a range again longer than could be predicted by van der Waals forces were also observed at pH 5–6 for interactions between hydrophilic $-\text{COOH}$ thiol surfaces (18). Thus, the absence of strong adhesion appears to be the result of hydrophobic/hydrophilic surface interactions, demonstrating that attractive interactions between surfaces are not simply additive.

CONCLUSIONS

Here we show that as a 20- μm hydrophobic uncharged sphere approaches a hydrophilic charged surface, repulsions dominate the interaction before contact. The forces are characterized by an exponentially decreasing component that can be described by an electrostatic repulsion. As the electrolyte concentration is increased, the magnitude and range of the repulsions decrease, as expected from electrostatic models developed for interactions of two identical carboxylic acid terminated surfaces. Adhesive interactions were observed and the strength of this interaction grew with ionic strength.

Studies reported in the literature between a hydrophilic and a hydrophobic surface lead to somewhat confused picture, as discussed earlier. There has been a wide diversity of experimental results and it seems likely that differences in the method of preparation of the surfaces are the main cause. However, the surfaces studied here are quite robust and there are no instabilities such as surfactant turn-around or desorption which are possible for surfactant-coated substrates.

Our studies demonstrate that the repulsive electrostatic interactions between the $-\text{CH}_3$ sphere and the $-\text{COOH}$ surface are well described by standard electrostatic interaction models. However, since the surfaces did not appear to jump into primary contact at a separation characteristic of van der Waals interactions, the standard DLVO model appears to fail to describe this system. The repulsive interactions measured here are well described by models developed for two surfaces interacting under constant charge conditions and a competitive site binding model by sodium ions, developed to describe the repulsions between two $-\text{COOH}$ surfaces at different pH and NaCl concentrations (18).

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