

# Surface Forces between Hydrophilic Self-Assembled Monolayers in Aqueous Electrolytes

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In this paper we present an atomic force microscopy (AFM) study on electrostatic and acid–base interactions between hydrophilic self-assembled monolayers (SAMs) with monoprotic ionizable acid functional groups ( $-\text{COOH}$ ). As expected for surfaces composed of weak acid groups the surface potential and strength of interaction are sensitive to pH and ionic strength. Repulsive forces grow with the degree of ionization. At low fractional ionization, the surfaces experience attractions with a range larger than that expected for van der Waals interactions and the strength of adhesion is large. The strength of adhesion and extent of attractions diminish with increasing pH. As the surface groups ionize, at intermediate pH values, jump-in distances and adhesion grow with ionic strength and at high pH they saturate with increasing electrolyte concentration at values close to those expected for van der Waals interactions. However, the maximum charge is around 5% of the total expected for the surfaces. Thus, allowing sodium ions to bind, with a binding constant of  $pK_{\text{Na}} = 3.7$  and  $pK_{\text{a}} = 6.3$ , ionic strength and pH dependencies of the surface charge can be described.

## Introduction

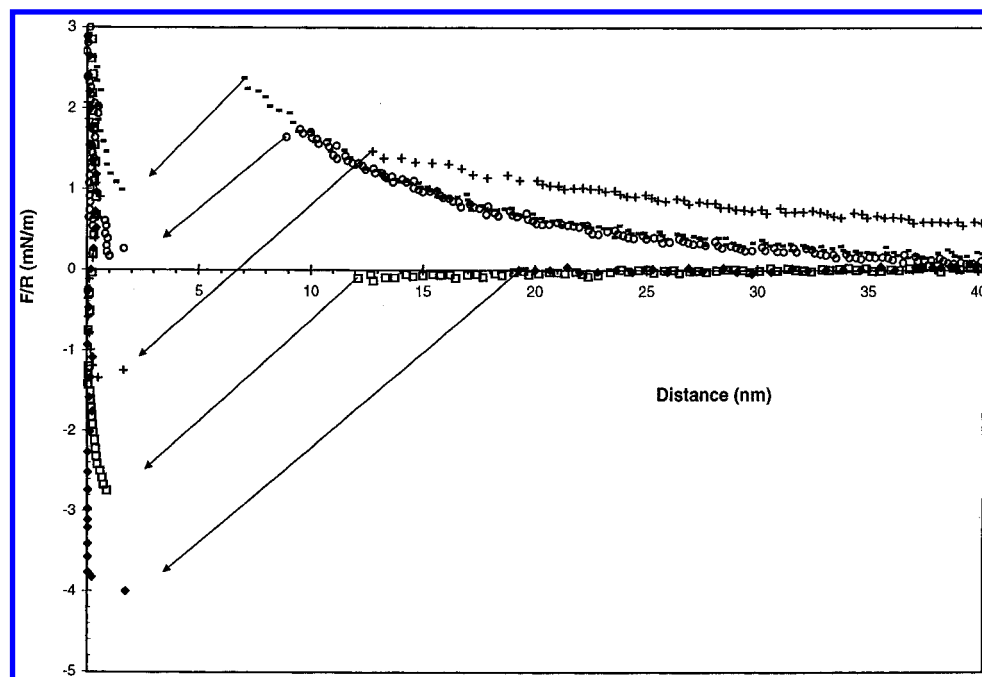
The forces acting between colloidal particles in water are of fundamental importance in many areas; for example in the printing, mineral processing, and paint industries. Knowledge about the attractive van der Waals and repulsive electrostatic forces (the DLVO theory<sup>1</sup>) and interfacial acid–base interactions are key for understanding phenomena such as polymer adhesion,<sup>2</sup> polishing,<sup>3</sup> protein folding<sup>4</sup> and adsorption,<sup>5</sup> enzymatic catalysis,<sup>6</sup> and the stability of colloids<sup>7</sup> and cells.<sup>5</sup>

In water colloidal particles acquire a charge through several mechanisms: dissociation of surface groups, charge imbalances in the crystal lattice or by selective adsorption of ions from solution onto the surface. The electrostatic repulsions generated by particle surface charge represent one of the most important mechanisms of stabilizing colloidal suspensions. As a consequence repulsion between similarly charged surfaces has seen extensive study.<sup>8–22</sup>

While the physical chemistry of the double layer overlap is well understood, the specific chemistries giving rise to charge are not as well studied or understood. In addition, the influence of the degree of ionization of weak acid or base groups on adhesion is poorly understood. Recent studies have characterized acid–base properties of different surfaces and demonstrate that adhesive forces between surfaces strongly depend on both the pH and electrolyte concentration.<sup>23–32</sup> The focus of this paper is to investigate the effect of both pH and NaCl concentration on interactions between hydrophilic SAMs with a monoprotic ionizable acid functional group. We have chosen to work with SAMs of alkanethiols because they are robust, well characterized, easily prepared surfaces<sup>33–40</sup> and

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**Figure 1.** Normalized forces as a function of distance recorded between a  $20\text{ }\mu\text{m}$  hydrophilic sphere and a hydrophilic substrate in  $3 \times 10^{-4}$ – $7 \times 10^{-4}$  M NaCl as a function of pH: ( $\blacklozenge$ ) 2.0, ( $\square$ ) 3.8, (+) 4.7, ( $\circ$ ) 8.2, (–) 9.7.

represent an excellent method of modifying the surface characteristics in a molecularly rationalized way. In what follows we characterize the interaction forces between surfaces consisting of close packed carboxylic acid terminated thiols as a function of pH and ionic strength. Only under conditions of high pH are the forces well described by the conventional DLVO model.

### Methods and Materials

Oxide-sharpened  $100\text{ }\mu\text{m}$  V-shaped silicon nitride AFM cantilevers with pyramidal tips (Digital Instruments, Santa Barbara, CA) were used for the force measurements. The colloid probe tips were prepared as follows. A glass sphere (SPI Supplies, West Chester, PA) of radius approximately  $10\text{ }\mu\text{m}$  (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 ( $\sim 30\text{ }\mu\text{m}$  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  $250\text{--}500\text{ }\text{\AA}$  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.<sup>41</sup> An average value of  $2.98\text{ N/m}$  was used in this study after calibrating twenty colloid probe tips from our wafer. An increase in cantilever stiffness results in a decrease in sensitivity of the force measurement, but it enables the measurement by allowing the two surfaces to be separated after initial contact.

The 16-mercaptohexadecanoic acid was synthesized in our laboratory according to the protocol of Bain et al.<sup>42</sup> Hydrophilic

spheres and surfaces were prepared by forming SAMs of 16-mercaptohexadecanoic acid on the gold coated surfaces.<sup>42–44</sup>

Surface force measurements were performed using a commercial AFM, Nanoscope E (Digital Instruments, Santa Barbara, CA). Solutions with different pH values were made from  $3 \times 10^{-4}$ – $7 \times 10^{-4}$  M NaCl aqueous electrolyte solutions by adjusting the pH with  $0.1\text{ M}$  HCl in the acidic region and  $0.1\text{ M}$  NaOH in the basic region. Water was Milli-Q grade, with conductivity of  $18.2\text{ M}\Omega\text{ cm}$ . The pH of the water was 5–6; therefore solutions at this pH range were used without any further addition of HCl or NaOH. All experiments were carried out at room temperature. Force data were converted to force–distance curves using the method developed by Ducker et al.<sup>17,18</sup>

### Results and Discussion

Figure 1 shows force versus separation profiles between two acid surfaces as a function of pH in  $3 \times 10^{-4}$ – $7 \times 10^{-4}$  M NaCl solutions. HCl or NaOH were used to adjust the pH of the solution. For pH values less than 4 at separations larger than  $10\text{ nm}$ , the interaction between the two surfaces is purely attractive (there are no repulsions suggesting that the surfaces are not charged), with a jump into an adhesive contact. At a pH of 4.7, a long range exponentially decaying repulsion is measured (suggesting that under these conditions the surfaces are charged) and at a distance of  $12.2\text{ nm}$  the two hydrophilic surfaces jump into contact. For pH values of 8.2 and 9.7, the magnitude and distance dependence of the repulsive portion of the interaction forces is independent of pH, while the jump-in distance continues to decrease with pH. At separations of approximately  $1\text{--}2\text{ nm}$ , a short-range soft repulsion is observed at all pH values.

The approach force can be modeled with a summation of electrostatic and van der Waals attractions.<sup>1</sup> For the attractive van der Waals interaction an unretarded Hamaker constant of  $A = 5 \times 10^{-21}\text{ J}$  was used. This

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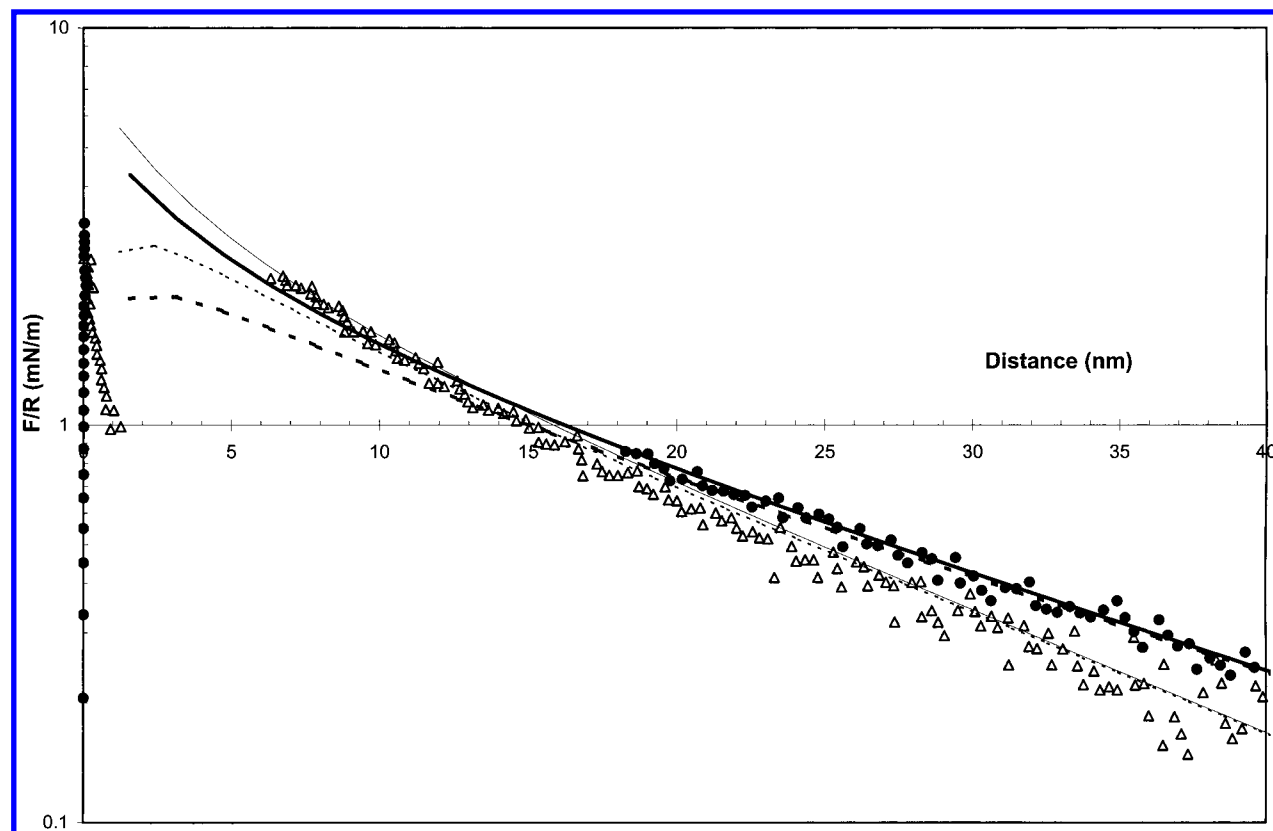
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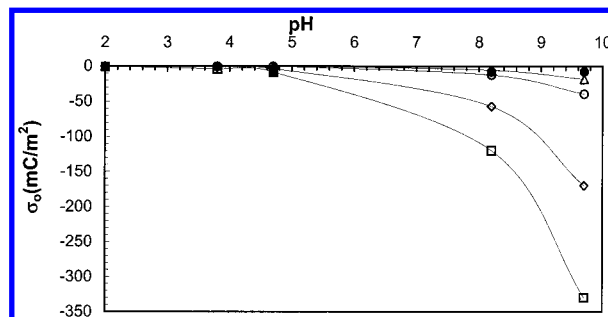
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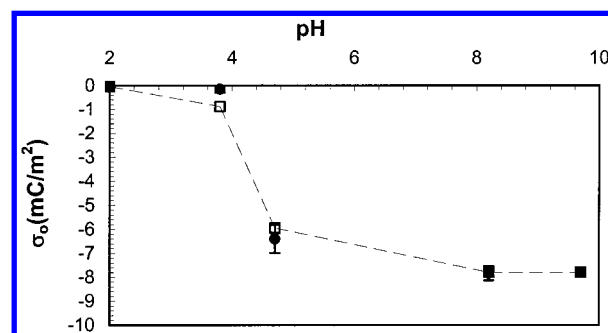
**Figure 2.** Force between a  $20\ \mu\text{m}$  hydrophilic sphere and a hydrophilic surface scaled by the radius of the sphere at  $3 \times 10^{-4}$ – $7 \times 10^{-4}$  M NaCl. The solid line is the best fit to DLVO theory at constant surface charge and the dashed line is the best fit at constant potential. The following parameters were used: (●) pH 4.7,  $A = 5 \times 10^{-21}$  J,  $\psi_0 = -90$  mV, and  $\kappa^{-1} = 17.6$  nm, the DLVO fits are shown with bold lines, (△) pH 9.7,  $A = 5 \times 10^{-21}$  J,  $\psi_0 = -92$  mV and  $\kappa^{-1} = 13.6$  nm.

Hamaker constant was calculated on the basis of the Lifshitz theory for hexadecane surfaces interacting across water.<sup>45</sup> Repulsive double-layer interactions were calculated with constant charge boundary conditions (upper solid lines) and constant potential boundary conditions (lower dashed lines), based on the full nonlinear Poisson–Boltzmann equation. The fitted theoretical curves were calculated for surface potentials of  $-83 \pm 11$  mV for pH = 4.7,  $-93 \pm 6$  mV for pH = 8.2, and  $-93 \pm 3$  mV for pH = 9.7. These values represent average values and standard deviations from 20 force measurements at each condition. The following average Debye lengths characterized the exponential decay: 15.6 nm for pH = 4.7, 11.6 nm for pH = 8.2, and 12.1 nm for pH = 9.7. Figure 2 shows two force curves and the DLVO fits for pH 4.7 and 9.7. The DLVO theory fails to capture the jump-in distances at smaller separations, where the attractive forces are much longer range than can be explained by van der Waals interactions. For the cantilevers used here, the theoretical jump-in distance for two hexadecane surfaces in water is 1.8 nm and for two gold surfaces in water is 6.6 nm (using an unretarded Hamaker constant of  $A = 2.5 \times 10^{-19}$  J<sup>46</sup>), while jump-in distances of 5–20 nm are measured.

The surfaces studied here are composed of close packed weak acid groups. As they are brought together, the pH in the gap between the surfaces will change. Thus we expect the interaction force to vary somewhere between a constant charge and constant potential type of interaction. However, as indicated in Figure 2, with the uncertainty of our measurements, we are unable to distinguish constant charge and constant potential interaction. The



**Figure 3.** Effect of pH on the surface charge. Equations 1 and 4 were used to calculate charges as a function of pH. Experimental results (●) and theoretical predictions are shown for (□)  $pK_a = 5$ , (◇)  $pK_a = 6$ , (○)  $pK_a = 8$ , and (△)  $pK_a = 9$ .

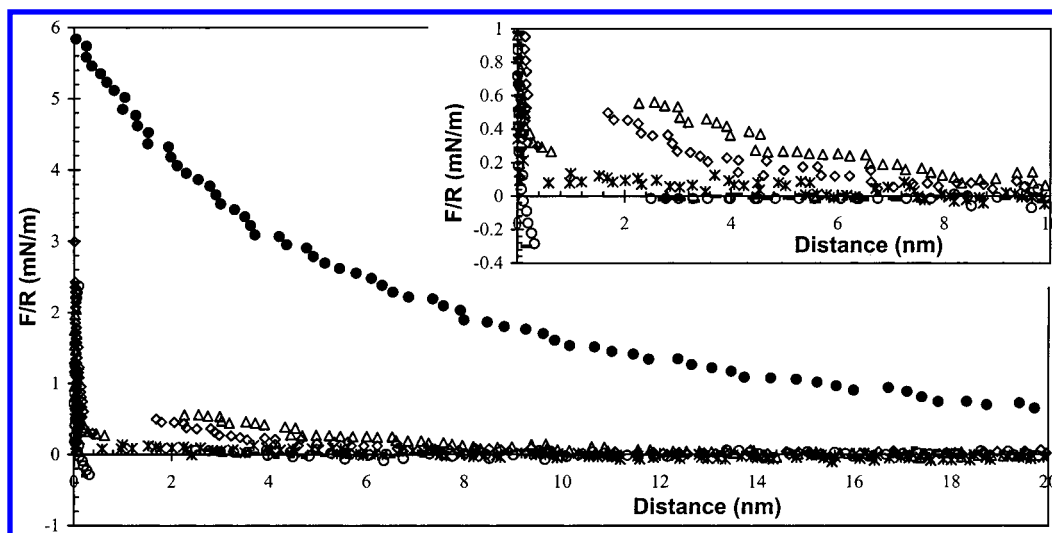


**Figure 4.** Surface charge as a function of pH: (●) experimental data, (□) fitted values according to eqs 1 and 10, using  $pK_a = 6.3$  and  $K_{Na} = 2 \times 10^{-4}$  M.

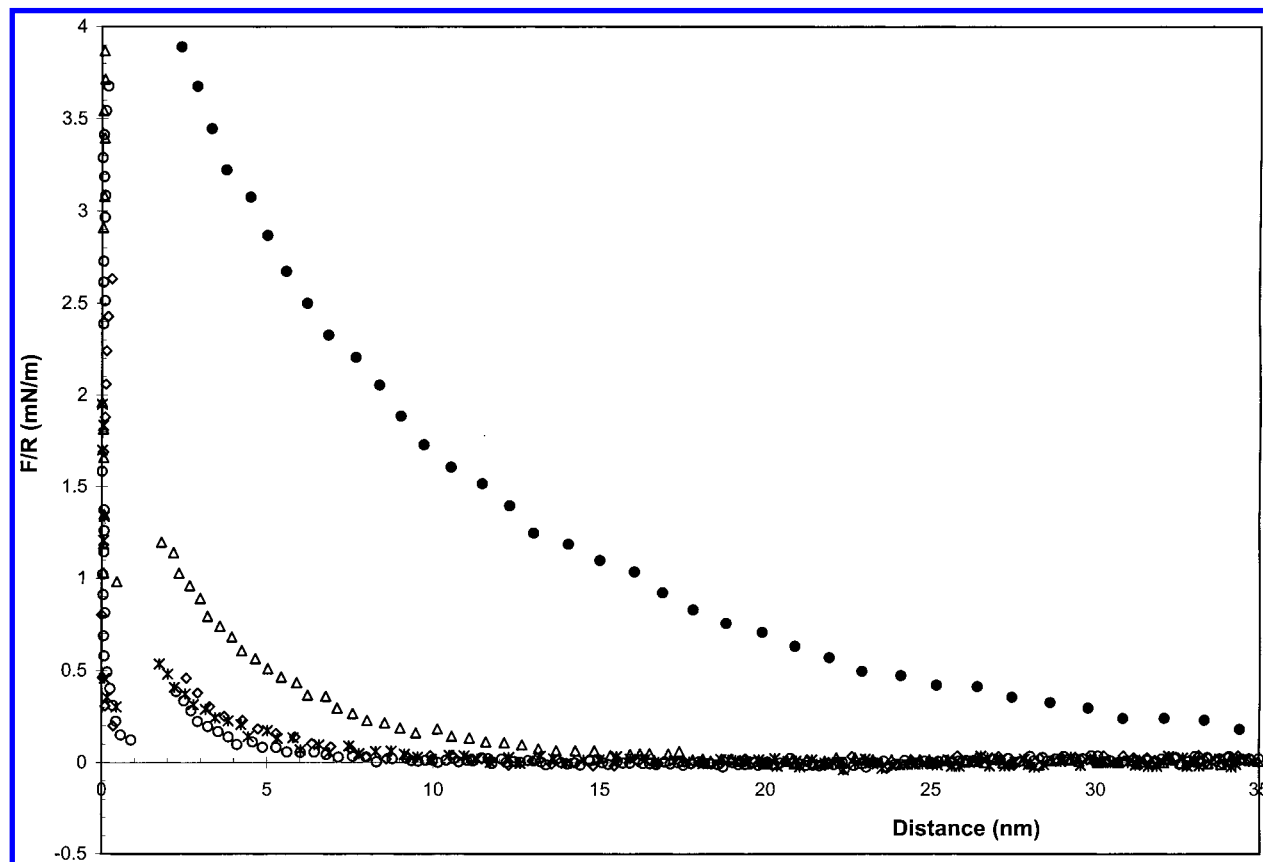
largest differences are expected at separations smaller than we were able to probe due to the sudden onset of attraction.

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**Figure 5.** Normalized force curves as a function of NaCl for a 20  $\mu\text{m}$  hydrophilic sphere and a hydrophilic surface at pH = 5.5: (●) water, ( $\Delta$ )  $5 \times 10^{-3}$  M NaCl, ( $\diamond$ )  $7 \times 10^{-3}$  M NaCl, (\*) 0.01 M NaCl, ( $\circ$ ) 0.05 M NaCl, and (—) 0.1 M NaCl. Inset: Force curves at smaller separations for  $5 \times 10^{-3}$ –0.1 M NaCl.



**Figure 6.** Normalized force curves for a 20  $\mu\text{m}$  hydrophilic sphere and a hydrophilic surface at pH 10, in water and different salt concentrations: (●) water, ( $\Delta$ )  $5 \times 10^{-3}$  M NaCl, ( $\diamond$ )  $7 \times 10^{-3}$  M NaCl, (\*) 0.01 M NaCl, and ( $\circ$ ) 0.05 M NaCl.

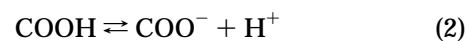
The surface potential and surface charge density are connected through:<sup>47</sup>

$$\sigma_o = 2(2\epsilon\epsilon_o k_B T n_b)^{1/2} \sinh(ez\psi_o/2k_B T) \quad (1)$$

where  $\epsilon$  is the solvent dielectric constant,  $\epsilon_o$  is the permittivity of free space,  $k_B$  is Boltzmann's constant,  $T$  is the temperature,  $n_b$  is the ion concentration in the bulk,

$e$  is the electronic charge,  $z$  is the valency of the cationic species and  $\psi_o$  is the surface potential.

The surfaces have a single type of charge group with a dissociation reaction represented:

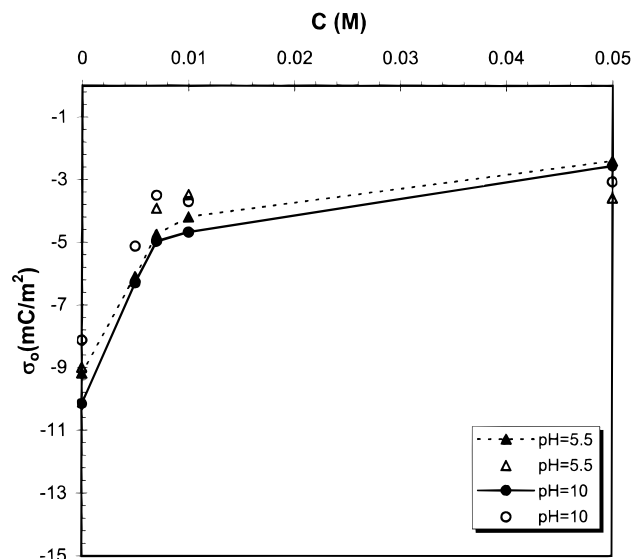


with a dissociation constant,  $K_a$ :

$$K_a = \frac{[\text{COO}^-][\text{H}^+]}{[\text{COOH}]} \quad (3)$$

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**Figure 7.** Effect of NaCl concentration on the surface charge at pH 5.5 (triangles) and pH 10 (circles). Experimental data (open symbols) are shown as well as theoretical fits (filled symbols) using eqs 1 and 10 at  $pK_a = 6.3$  and  $K_{Na} = 2 \times 10^{-4}$  M.

From the law of mass-action, the surface charge,  $\sigma_o$ , is represented by the total number of dissociated groups:<sup>48</sup>

$$\sigma_o = \frac{-eN_s}{1 + ([H^+]_b/K_a) \exp(-e\psi_o/k_B T)} \quad (4)$$

where  $N_s$  is the total number of surface sites per unit area,  $[H^+]_b$  is the concentration of protons in the bulk phase,  $\psi_o$  is the surface potential,  $e$  is the electronic charge,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature. Figure 3 shows both experimental measurements and theoretical predictions, using eqs 1 and 4, as a function of pH and for different values of  $pK_a$ . Parameters in eq 4 were calculated as follows:

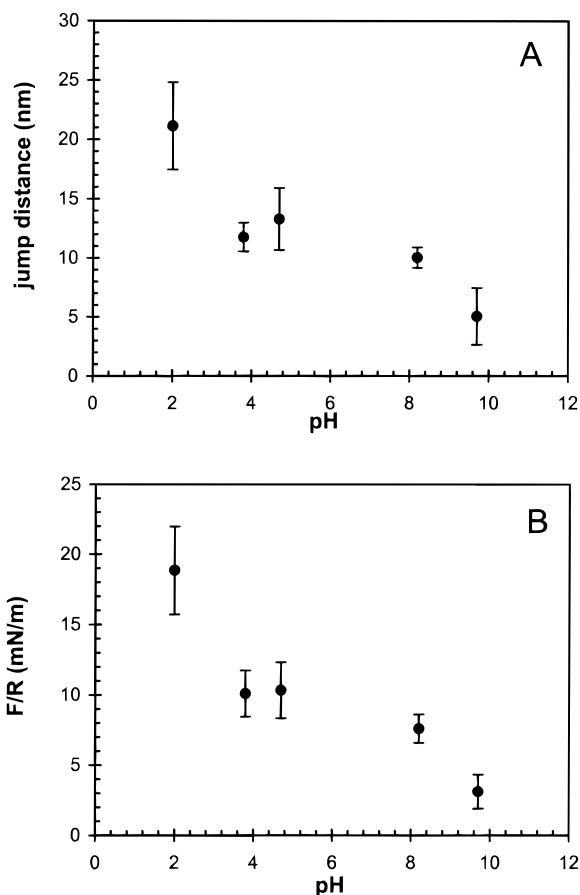
$$[H^+]_b = 10^{-pH} \quad (5)$$

$$K_a = 10^{-pK_a} \quad (6)$$

$$N_s = 1/E \quad (7)$$

where  $E$  is the area per alkyl molecule, and is equal to  $21.4 \text{ \AA}^2$ .<sup>49</sup> The surface  $pK_a$  value is the pH at which the functional groups at the interface are half-ionized. Adhesion force titration curves (adhesion forces versus pH) have recently been used to estimate the  $pK_a$  value of the carboxylate surface as  $5.5 \pm 0.5$ <sup>29–31</sup> while quartz crystal microbalance experiments suggested that the  $pK_a$  of the monolayer exceeded 8.<sup>50</sup>

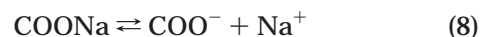
The surface charge, determined from the best fit to the force curves at large separations using the full nonlinear Poisson–Boltzmann equation (Figure 3), suggests that the surfaces achieve the maximum charge at pH 8.2 of  $-7.8 \text{ mC/m}^2$ . However, if we use a  $pK_a$  of 6, for example, the law of mass-action predicts that the maximum surface charge of  $-170.2 \text{ mC/m}^2$  will be reached by a pH of 9.7 indicating that experimentally we find that only 4.6% of



**Figure 8.** (A) Jump-in distance and (B) adhesion force normalized by the radius of the sphere, for different pH values in  $5 \times 10^{-4}$  M NaCl.

the surface groups are ionized. This could be possible if other cations bind or if the surface does not consist of close packed acid groups. Extensive evidence indicates that the surfaces consist of carboxylic acid terminated thiols.<sup>33–40</sup> Thus we turn our attention to cation binding.

Kane and Mulvaney recently demonstrated that for two 11-mercaptoundecanoic acid surfaces in  $\text{NaNO}_3$  solutions the degree of ionization of the surface carboxyl groups is very low, approximately 1–2%.<sup>32</sup> A simple model based on competitive site binding by sodium ions was proposed to explain this low degree of ionization. To model the counterion binding, a mass-action approach for both ions and protons was used. Therefore, in addition to eq 2–7, the following equations have to be included for the cation binding:<sup>32</sup>



with a dissociation constant,  $K_{Na}$ :

$$K_{Na} = \frac{[\text{COO}^-][\text{Na}^+]}{[\text{COONa}]} \quad (9)$$

The surface charge,  $\sigma_o$ , is then represented by the total number of dissociated groups:

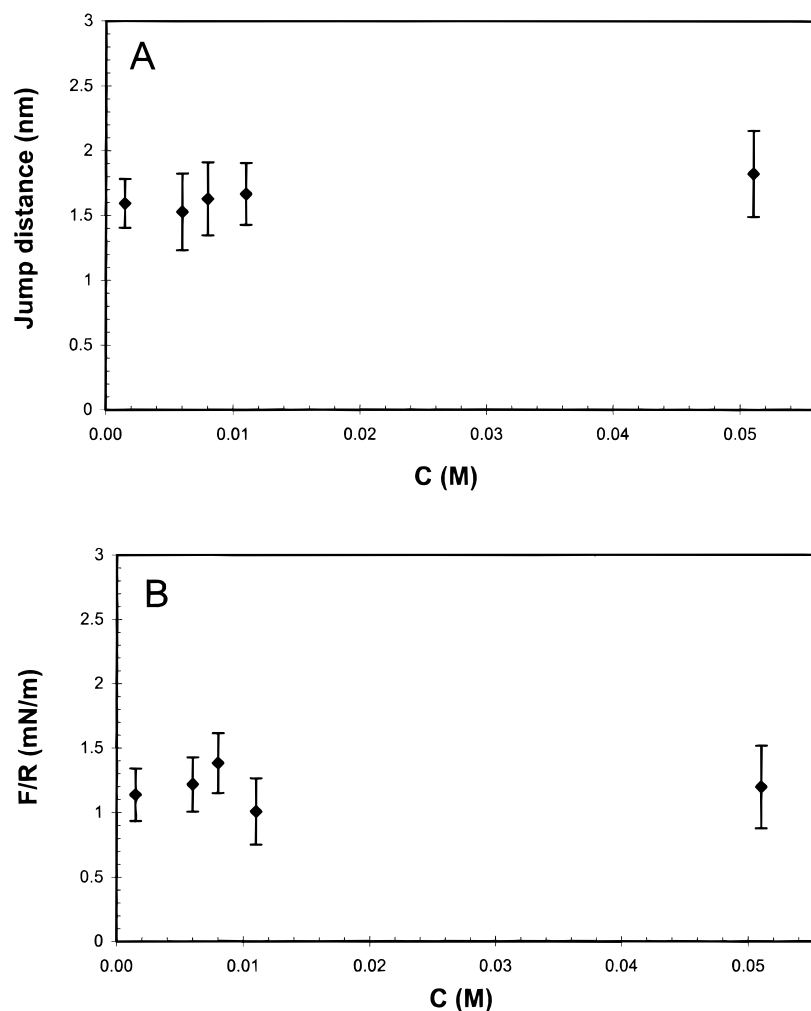
$$\sigma_o = \frac{-eN_s}{1 + ([H^+]_b/K_a + [\text{Na}^+]_b/K_{Na}) \exp(-e\psi_o/k_B T)} \quad (10)$$

where  $[\text{Na}^+]_b$  is the sodium concentration in the bulk and  $K_{Na}$  is a fitting parameter.

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**Figure 9.** (A) Jump-in distances versus the NaCl concentration at pH 10. (B) Pull-off force scaled by the radius of the sphere, versus the NaCl concentration at pH 10. In both figures the error bars correspond to the standard deviations that resulted from 10 to 20 force measurements all over the surface.

Equation 10 is solved with eq 1 to yield self-consistent values of  $\psi_0$  and  $\sigma_0$ . Figure 4 shows the effect of pH on the surface charge, using eqs 1 and 10, where a good comparison is achieved between the experimental values and the predictions with  $pK_a = 6.3$  and  $K_{Na} = 2 \times 10^{-4}$  M ( $pK_{Na} = 3.7$ ). We note substantial differences from the data presented by Kane and Mulvaney who reported  $K_{Na} = 4 \times 10^{-6}$  M ( $pK_{Na} = 5.4$ ) and  $pK_a = 6$ . The value of the surface binding constant,  $pK_{Na}$ , required to account for the experimental data using this model is high for sodium ions that are normally treated as "indifferent". In the past,  $pK_{Na}$ 's of 3–10 have been used for surface binding constants that correspond to a strong adsorption free energy that cannot be explained for nonspecifically adsorbed ions and this is a major point of criticism of the site-binding model.<sup>48</sup>

Data in Figures 1–4 qualitatively follow the expected behavior of the carboxylic acid surfaces. At low pH levels (pH 1–3.8) the acid groups are protonated and are able to form stable hydrogen bonding pairs, as suggested in previous studies.<sup>29,31,51</sup> As the pH is increased, the acid groups dissociate and become negatively charged.

Figures 5 and 6 show representative force curves for this system at both pH 5.5 and pH 10, respectively. Note that in the absence of electrolyte at pH 5.5 the ionic

strength is set by deionized water in equilibrium with the atmosphere while at pH 10 the ionic strength is set by adding base. In both cases the forces are characterized by an exponentially decreasing component at large separations and as the electrolyte concentration is increased the repulsive component of the interaction decreases in magnitude. The effect of NaCl on the surface charge at pH 5.5 and 10 is shown in Figure 7, along with fits using eqs 1 and 10. Results show that as the NaCl concentration is increased the surface charge decreases. This result is in agreement with predictions of the site binding model.

One of the curious observations in our results lies in the variation in the extent of the attraction as estimated from the jump-in distances. As mentioned above, for the cantilevers used here, the theoretical jump-in distance predicted for two hexadecane surfaces in water is 1.8 nm. In Figure 8A, these predictions are only observed at high pH. Both jump-in distances and adhesion forces decrease with increasing value of the pH (Figure 8) whereas the surface charge increases from zero to a negative value (Figure 4) as pH is increased.

Wang et al.<sup>50</sup> showed that for 16-mercaptohexadecanoic acid SAMs, an increase in the pH induced a decrease in the viscoelasticity and therefore the structure of the hydrodynamic layer that contains the monolayer and the aqueous solution associated with the monolayer. At low pH, both adhesion and jump into contact data have very

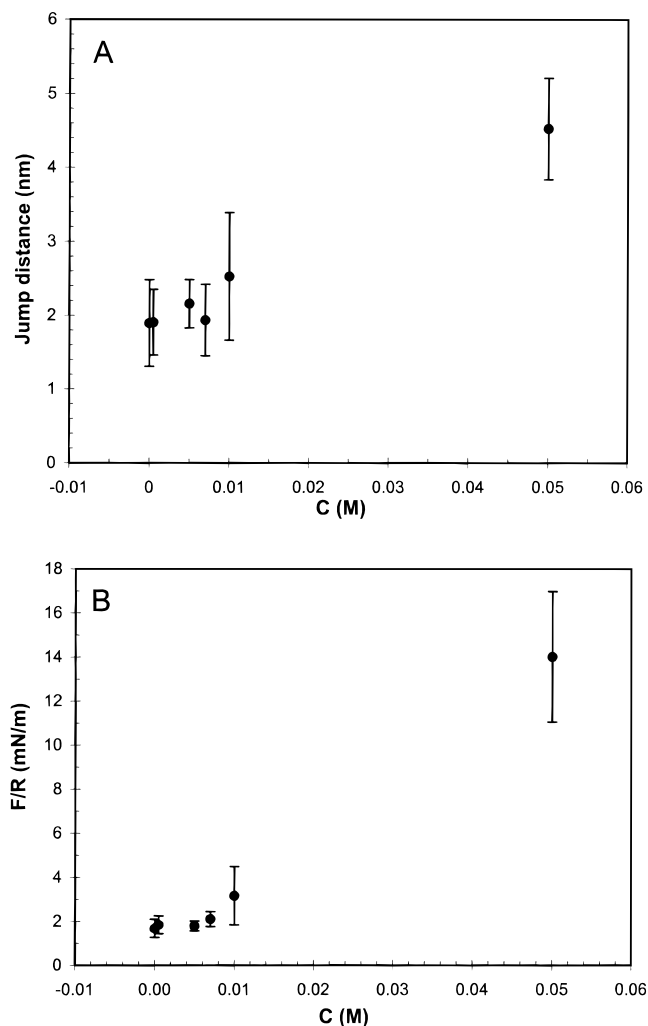
(51) Lee, T. R.; Carey, R. I.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 741.

large values. Previous studies, based on contact angle measurements<sup>51</sup> and adhesion measurements<sup>29,31</sup> suggest that at low pH values the acid groups are fully protonated and form stable hydrogen bonding pairs. As mentioned above, the theoretical van der Waals jump into contact distance for two hexadecane surfaces in water is 1.8 nm and for two gold surfaces in water is 6.6 nm. The experimental jump-in distance at pH 2, for example, is around 20 nm, and at pH 4.7 is 13 nm. These values are even larger than the ones measured for two pure hydrophobic SAMs. For example, in  $5 \times 10^{-4}$  M NaCl and neutral pH, jump-in distances for hydrophobic (methyl terminated) SAMs of hexadecanethiol are around 5.5 nm and the pull-off force is 16 mN/m.<sup>52</sup> On the other hand hydrogen bonds are of very short range. An extensive hydrogen bonding network would be required to explain the range and strength of the interaction measured under these conditions. We emphasize that the large jump-in distances and decreasing jump-in distances and adhesive forces as pH is increased are reproducible and extreme care was taken to ensure that the surfaces are not contaminated. No evidence was found that these observations arise from organic contamination. We conclude that our results demonstrate that at low pH conditions the attraction of  $-\text{COOH}$  surfaces is longer range than can be predicted from van der Waals theory and the range also exceeds that observed for hydrophobic surfaces under nearly identical conditions.

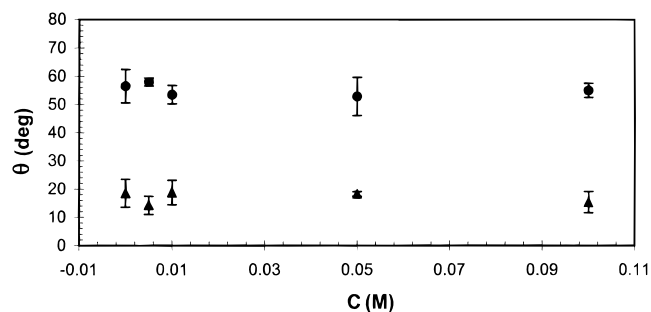
As the pH is increased, the acid groups are deprotonated and become negatively charged. Our results (Figure 8B) are in qualitative agreement with previous studies.<sup>29–31</sup> Direct comparisons with these studies are not possible as they used sharp AFM tips, functionalized with  $-\text{COOH}$  groups, and we used a  $20\text{ }\mu\text{m}$  sphere, with  $-\text{COOH}$  end groups. Our spheres though are not smooth, exhibiting asperities in the range of  $0.5\text{--}1.5\text{ }\mu\text{m}$ .<sup>52</sup>

The effect of the salt concentration on the jump-in distances and adhesion between the carboxylate terminated surfaces has also been examined for the pH values of 2.3, 5.5, and 10. Results are shown in Figure 9 for pH 10, where data points are average values from 10 to 20 force measurements taken all over the surface, and the error bars correspond to the standard deviation of these measurements. Both jump-in distances and adhesion forces are small. At this pH the surfaces are fully deprotonated and addition of salt decreases the surface charge (Figure 7) but has no effect on the jump-in distances or strength of adhesion (Figure 9).

At pH 5.5 though less than half of the functional groups are deprotonated ( $\text{p}K_{\text{a}} = 6.3$ ), the surface charge decreases as the sodium concentration is increased (Figure 7) and both jump-in distances and the strength of adhesion increase with increasing concentration of electrolyte (Figure 10). The contrast of this observation with those at pH 10 and pH 2.3 (as discussed below) suggested that at pH of 5.5 the surfaces have been altered in some manner and prompted a study of the contact angle. Lee et al.<sup>51</sup> showed that titration profiles of  $-\text{COOH}$  surfaces exhibit a "hump" around pH 5, and suggested that the hump probably arises from conformational changes of the carboxylate groups upon ionization. We studied the contact angle of water drops at pH 5.5 on the  $-\text{COOH}$  SAM as a function of the NaCl concentration. For all electrolyte concentrations, at this pH value, the advancing contact angle was in agreement with previous studies,<sup>51</sup> and was around  $55^\circ$  as shown in Figure 11, suggesting that the surface is hydrophilic under these conditions. Advancing



**Figure 10.** (A) Jump-in distances versus the NaCl concentration at pH 5.5. (B) Pull-off force scaled by the radius of the sphere, versus the NaCl concentration at pH 5.5. In both figures the error bars correspond to the standard deviations that resulted from 10 to 20 force measurements all over the surface.

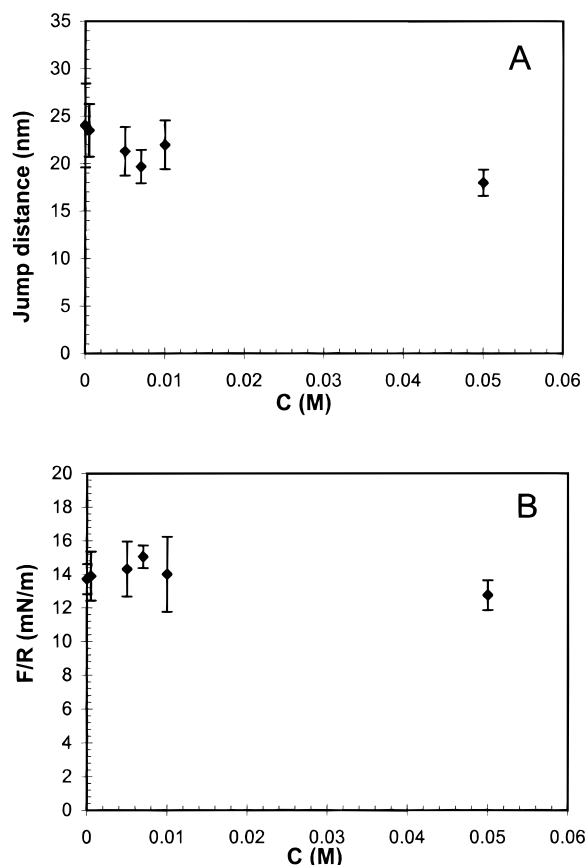


**Figure 11.** Effect of NaCl concentration in water at pH 5.5 on advancing (●) and receding (▲) contact angles for NaCl solution drops at the  $-\text{COOH}$  SAM. The error bars correspond to the standard deviations that resulted from 12 different measurements.

and receding contact angles were not influenced by the electrolyte concentration, indicating that the SAM is stable in the presence of the electrolyte.

At pH 2.3 (Figure 12) where the carboxylic acid groups are fully protonated, addition of NaCl again has little or no effect on the jump-in distances or the strength of adhesion. Notice however, that both the magnitude of the jump-in distances and adhesion are much larger compared to the other two pH conditions. Thus the strength of

(52) Kokkoli, E.; Zukoski, C. F. *Langmuir* **1998**, *14*, 1189.



**Figure 12.** (A) Jump-in distances versus the NaCl concentration at pH 2.3. (B) Pull-off force scaled by the radius of the sphere, versus the NaCl concentration at pH 2.3. In both figures the error bars correspond to the standard deviations that resulted from 10 to 20 force measurements all over the surface.

adhesion and range of attraction appear to be independent of ionic strength at high and low pH, while at intermediate pH, large changes are observed. At low pH the surfaces are fully protonated and at high pH are fully deprotonated but the charge is low due to the sodium binding. Thus, the qualitatively different influence of electrolyte on attractive interactions seen near pH 5.5 appears to be associated with the partial surface deprotonation.

### Conclusions

The carboxylate terminated thiol surfaces studied here provide robust systems with which to test models of surface ionization and the influence of ionization on surface forces. The carboxylic acids have free solution dissociation constant of  $pK_a \approx 4$  while our results suggest that the  $pK_a$  on the surface is 6.3.

As expected, at low pH no repulsive forces are observed indicating no ionization and no specific ion binding. However, for pH values  $\geq 4.7$  the surfaces experience exponentially decaying repulsions with decay lengths close to that expected from the known ionic content of the electrolyte. These observations suggest that at pH  $\geq 4.7$  the surfaces are charged. At pH 8.2 surfaces reach a maximum charge in the absence of electrolyte that is around 5% of the charge density predicted on the known close packing of the carboxylic acid terminated thiol surfaces by the site binding model. The charge density required to fit the repulsive force curves decreases with increasing NaCl concentration. A simple model based on competitive binding by sodium ions can account for this effect and gave a good agreement between experimental results and theoretical predictions using a fitting value of  $pK_{Na} = 3.7$ . The range of the attractions observed at small separations is not well predicted by van der Waals theory, except perhaps at high pH. The strength of adhesion follows the same trend as jump-in distances being largest and showing no ionic strength dependence at low or high pH, but increasing with ionic strength under neutral conditions. The electrolyte dependence of the attractive forces at pH 5.5 appears associated with the partial surface deprotonation.

The long range nature of the attractions, indicated by cantilever jump-in distances of up to 20 nm seen at low pH is perplexing. These surfaces are fully protonated and do not adsorb ions. Thus, the long range attractions cannot be due to hydrogen bonding between partially ionized surfaces. While the surfaces are hydrophilic by standard contact angle measurements, the interaction forces at low pH are very reminiscent of hydrophobic interactions measured between methyl terminated surfaces.<sup>52</sup> Thus, our results suggest that colloidal force attributes of "hydrophobic" surfaces need not be associated only with large contact angles. On the other hand, charged surfaces appear to be well described by DLVO. A natural question is to look at patchy surfaces with hydrophobic and hydrophilic charged areas, when nonadditive effects are expected.<sup>53</sup>

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