

Interactions between Hydrophobic Self-Assembled Monolayers. Effect of Salt and the Chemical Potential of Water on Adhesion

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The focus of this paper was to obtain an understanding of the forces acting between hydrophobic surfaces submerged in aqueous solutions. An atomic force microscope was used to measure hydrophobic forces between self-assembled monolayers of hexadecanethiol. Electrolytes do not alter the solvent/surface interactions as indicated by the lack of electrostatic repulsive forces at any concentration and the insensitivity of contact angles to salt type or concentration. The jump in distances were systematically larger than can be predicted for gold/gold and hexadecane/hexadecane surfaces interacting across water. Adhesive forces increase with electrolyte concentration and are sensitive to electrolyte type at a given concentration. However, the adhesive forces fall onto a master curve when plotted as a function of the water chemical potential. Our studies suggest that lowering the solvent chemical potential produces an increase in the pull-off force.

Introduction

Hydrophobic interactions have been used in the biochemical literature to describe a variety of biochemical processes, including conformational changes of a biopolymer, the binding of a substrate to an enzyme, and the association of subunits to form a multisubunit enzyme.¹ They are equally important in the formation of detergent micelles and act as an organizing force in the formation of lipid bilayers, protein–amphiphile complexes, and biological membranes.² These same forces are associated with low-polarity surfaces interacting across aqueous solutions and are the key to many technological and industrially significant phenomena including wetting,³ froth flotation,⁴ deinking technology,⁵ and adhesion.⁶

Forces between hydrophobic, macroscopic surfaces in water have been measured for various systems over the past decade.^{7–18} Attractive forces have been measured

up to surface separations of 90 nm¹⁰ with magnitudes that are 1–2 orders larger than those predicted by van der Waals interactions. The origin of these forces is unclear and there is a debate whether the deviation from continuum behavior should be attributed to molecular properties of the liquid or to surface interactions. One explanation is based on the influence of the surface on water structure.¹⁹ The surface is assumed to induce order into the water molecules in close proximity. This order decays into the liquid and gives rise to a long-range interaction with the same decay length as the order profile. Another proposal uses classical continuum electrostatics to illustrate how electrostatic correlations, arising from a surface-induced perturbation in the fluid next to a hydrophobic surface, could give rise to a long-range force.^{20,21} A more qualitative suggestion is that the formation of vapor cavities between the hydrophobic surfaces plays some role in generating the force.^{10,11}

None of these theories accounts for all of the experimental observations. However, there is also considerable ambiguity in the measurements. The magnitude and the range of the force seems to depend not only on the material comprising the hydrophobic surface but also on the method of surface preparation. Forces between surfaces prepared from processes such as Langmuir–Blodgett deposition^{10,11,13,14,22} and silanation^{23–25} are measurable at separations up to 250 nm. For surfaces which have been formed from equilibrium adsorption,^{7,26,27} forces are of short range (<10 nm) and for polymer surfaces^{28,29} are of moderate range (<30 nm).

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Controversy exists on the connection between the hydrophobic effect between nonpolar solute molecules and hydrophobic interactions measured between macroscopic surfaces. For example, Christenson and Claesson¹¹ state that the hydrophobic interactions may not be related to the hydrophobic effect seen between molecules. This conclusion comes as a consequence of their suggestion that the long-range forces between hydrophobic surfaces are due to the metastability of water films between these macroscopic surfaces. This hypothesis has not been confirmed. On the other hand Israelachvili³⁰ mentions that hydrophobic interactions and the hydrophobic effect are closely related. In addition it has been shown that there is a way to reconcile the magnitudes of the microscopic hydrophobic effect, as measured from the solubility of hydrocarbons in water, and the macroscopic measure of the hydrophobic free energy per unit area, as measured from liquid hydrocarbon–water surface tensions.³¹

Early results suggest that electrolytes strengthen the hydrophobic effect relative to pure water.³² Recent studies show that the addition of electrolytes has a different effect depending on the nature of the surface. For example, the addition of salt rapidly diminishes the long-range attraction^{13,16,33} and pull-off force^{13,16,22,34} between surfactant-coated mica surfaces. On the other hand, the addition of electrolytes increases slightly the characteristic length scale of the attraction and the adhesion between silanated glasses,^{24,25} but has no effect on the interaction forces between silanated mica^{35,36} and polymer surfaces.^{28,29}

Understanding these diverse observations requires more experimental studies that establish how the force depends on external parameters and surface properties. Model hydrophobic surfaces should satisfy the double criteria of electroneutrality and stability, so that the resulting interactions can be easily interpreted. In this study we have chosen to work with self-assembled monolayers (SAMs) of hexadecanethiol, which satisfy both criteria. SAMs are robust, well-characterized, and easily prepared surfaces.^{37–44} They represent an excellent method of modifying the surface characteristics in a molecularly rationalized way and have successfully been used in atomic force microscopy (AFM) measurements of adhesion forces and friction.^{45–47}

The focus of this paper is to characterize the interaction between hydrophobic surfaces by using an AFM and study how the magnitude of the adhesive force can be modified through changes in surface wettability and solvent chemical potential.

Methods and Materials

Surface force measurements were performed using commercial atomic force microscopes (AFM), a Topometrix TMX 2010 (Topometrix, Santa Clara, CA), and a Nanoscope E (Digital Instruments, Santa Barbara, CA). All experiments were carried out at room temperature. The data were converted to a force–distance curve using the method developed by Ducker et al.^{48,49}

Standard 100- μm V-shaped silicon nitride AFM cantilevers with pyramidal tips (Topometrix, Santa Clara, CA and 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 μm (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 (~ 30 μm diameter) attached to a three axis 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.⁵⁰ The stiffness of the cantilevers used in the present work was in the range 0.67–2.98 N/m. 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 separated after initial contact.

Hydrophobic surfaces were prepared by forming self-assembled monolayers (SAMs) of hexadecanethiol (Aldrich, Milwaukee, WI) on the gold-coated surfaces.^{38,39,44}

Results and Discussion

The SAM surfaces were first characterized by using the colloid probe tip to image the substrate surface. For all systems, the substrate was smooth, showing large regions (70 $\mu\text{m} \times 70 \mu\text{m}$) where the root mean square roughness was less than a nanometer. On occasion and due to the presence of a sharp asperity on the colloidal probe, atomic resolution images were produced, permitting individual terminal methyl groups to be visualized. Figure 1 shows "raw data" of AFM images of two glass spheres that clearly show the degree of surface roughness. These images were taken with an oxide-sharpened silicon nitride tip. Figure

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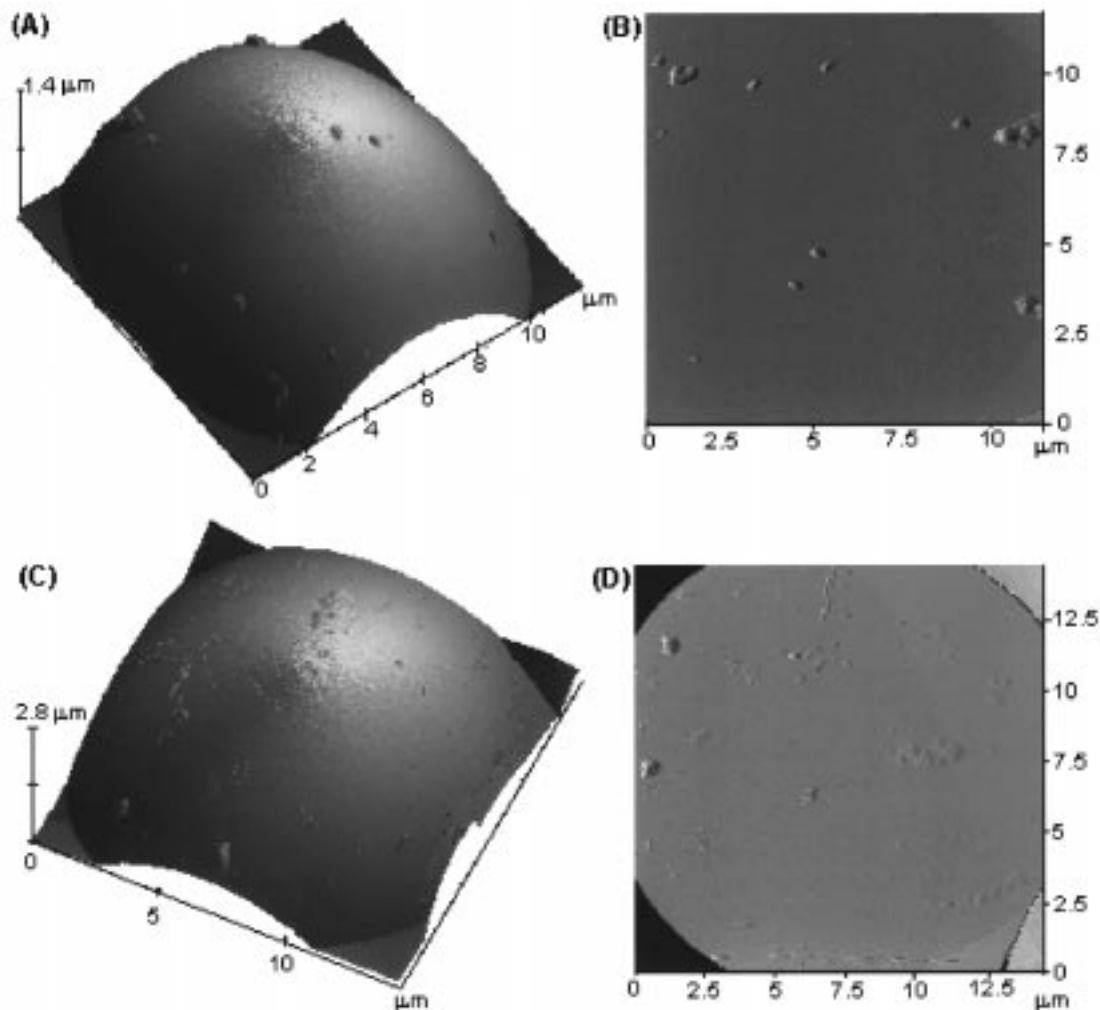


Figure 1. AFM images of 20 μm glass spheres taken in air with an oxide-sharpened silicon nitride tip. The images are shown as taken, without any further processing. (A) 3-D representation of the sample-height data of the first sphere. (B) Cantilever deflection data for the first sphere. This image was acquired simultaneously with (A). (C) 3-D representation of the sample-height data of the second sphere. (D) Cantilever deflection data for the second sphere, acquired simultaneously with (C).

1A,C gives a 3-D representation of the sample-height data of the two glass spheres. Figure 1B,D were acquired under constant height mode and show the variation in the deflection signal as the sample height remained almost constant, for these two spheres. Deflection data give accurate information about the surface topography but no information about the height of the features on the surface.

The interactions between SAM surfaces in water and 5×10^{-3} M NaCl (Figure 2) are purely attractive (there are no repulsions suggesting the surfaces are not charged), with a jump into contact as the force gradient exceeds the spring constant. Due to the sharpness of the force/distance curves near contact, this distance is weakly sensitive to the spring constant used. The extent of the attraction must be measured relative to some force scale (i.e., the separation where the attractive force goes to zero). In our case, within the sensitivity of our measurements, no attractions were measured up to the point where the probe jumped into contact. Thus, the force changes dramatically over a small change in separation. Under these circumstances the jump in distance provides a qualitative measure of the extent of attraction. In the remainder of this paper we use the jump in distance to characterize the extent of the attractive interactions. Note however that order of magnitude decreases in the spring constant will greatly increase this characteristic length. Thus, this

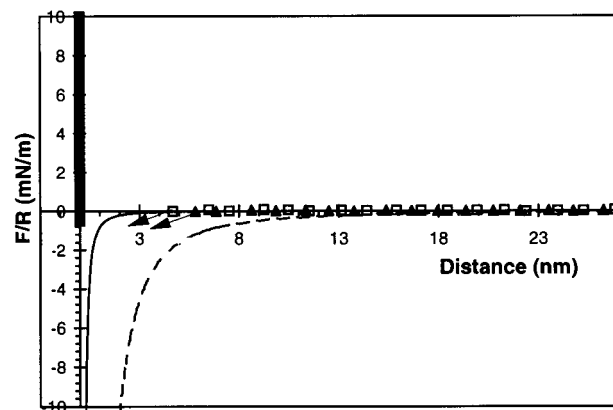


Figure 2. Normalized forces recorded between SAMs of hexadecanethiol in water (\square) and in 5×10^{-3} M NaCl (\blacktriangle). The solid and dashed lines indicate fits to van der Waals theory using a Hamaker constant for hexadecane and gold surfaces in water, respectively.

method provides a relative rather than an absolute method of probing the extent of attractive forces. In water, the thiol surfaces are pulled into an adhesive contact from a distance of 4.7 nm and upon addition of 5×10^{-3} M NaCl, jump to contact occurs at a surface separation of 5.8 nm. Figure 2 contains theoretical curves, van der Waals

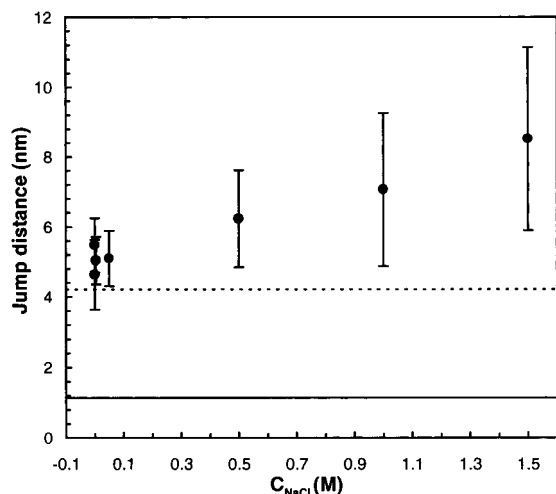


Figure 3. Jump in distances versus the NaCl concentration in water, for hexadecanethiol SAMs. The error bars correspond to the standard deviations that resulted from 10 to 15 force measurements all over the surface. The dashed and solid lines correspond to the van der Waals jump distances for gold and hexadecane surfaces in water.

attractive interactions, that were calculated using an unretarded Hamaker constant of 2.5×10^{-19} J,⁵¹ for gold surfaces in water, and a Hamaker constant of 5×10^{-21} J,³⁰ for hexadecane surfaces separated by pure water. These two systems are used as upper and lower bounds on the magnitude of van der Waals attractions. The theoretical van der Waals jump in distance for two gold surfaces in water is 4.2 nm and for two hexadecane surfaces in water is 1.1 nm. These results are characteristic of interactions measured for a wide variety of electrolyte types and concentrations.

Without producing a repulsion, the addition of an electrolyte appears to increase the range of the attraction (i.e., the jump in distance increases). No repulsions were observed even at concentrations as small as 5×10^{-4} M NaCl. While these results, with NaCl as an electrolyte and repeated studies with a variety of other electrolytes (CaCl_2 and Na_2SO_4) and concentrations (10^{-4} –1.5 M), suggest that the surfaces are uncharged during the experiment, we can only conclude that the repulsions, should they exist, are extremely small. The accuracy of the AFM force measurements is ± 0.016 nN. At an electrolyte concentration of 10^{-3} M NaCl, for a particle radius of $10 \mu\text{m}$ and at a surface separation of 5 nm, an electrostatic repulsion of 0.016 nN corresponds to a surface potential of approximately 1.7 mV. Thus, we can argue that if the SAMs are charged, the surface potential is less than this very small limit.

The jump in distances for SAMs surfaces are given in Figure 3 as a function of NaCl concentration. Each data point is the average of 10–15 force measurements and the error bars correspond to the standard deviations. As more electrolyte is added to the solution, the interaction between the SAMs becomes of a longer range. For example, after the addition of 1.5 M NaCl the surfaces jump into contact at an average distance of 8.5 nm, an 85% increase of the value in pure water (the average jump in distance in water is 4.6 nm). In Figure 3, the experimental jump in distances are compared to those predicted by the classical van der Waals theory for gold and hexadecane surfaces interacting across water.

The force profiles for hexadecanethiol surfaces, in water and electrolyte, are different from those obtained for other

type of surfaces (silanated glasses,^{18,24,25} fluorocarbon surfaces,^{11,13,16} and surfactant-coated mica^{15,17,33}) where the attractive potential energies can be fitted to a single- or double-exponential function, depending on the range of the interaction. The data obtained for our thiol surfaces, within the sensitivity of the AFM, show no discernible interaction until the gradient of the force exceeds the spring constant of the force sensor, after which the surfaces jump into a strong adhesive contact (illustrated by the arrows). As a result, we cannot provide any fitting information for the force curves. In the cases mentioned above where double exponentials have been fitted to hydrophobic interactions, a substantial variation in attractive forces could be measured as the surfaces approach. Thus, the authors were able to fit their data to double-exponential force curves. Our forces show qualitatively different behavior. The only other hydrophobic system, to our knowledge, that exhibits the same type of behavior is polymerized octadecyltriethoxysilane (OTE)^{35,36} on mica. Like the SAMs studied here, the OTE surfaces are very stable and robust and do not possess the long-range attraction observed in other studies. Both polymerized OTE hydrophobic layers and SAMs of thiols have an attractive range only slightly longer than that predicted from van der Waals forces between gold surfaces. Short-range attractions between hydrophobic surfaces have also been measured between surfaces which have been formed from equilibrium adsorption.^{7,26,27}

Addition of electrolytes also increases the strength of the hydrophobic interaction and adhesion between silanated glasses. The strength of the attractive forces and the adhesion are only about 10% stronger in 5 M NaCl than in pure water²⁵ and are thus smaller than the thiol systems studied here. Similar results are observed between silanated glasses in 10^{-3} – 10^{-2} M KBr where jump in distances increase by a factor of 2–3 compared to pure water whereas the adhesion is unaffected.²⁴

The influence of electrolyte type on the force profiles of SAMs surfaces has been investigated using CaCl_2 and Na_2SO_4 . Within the instrument sensitivity, there appears to be no obvious relationship between the jump in distance and the ionic concentration. As with NaCl, the forces were monotonically attractive and jump in distances remained systematically larger than what could be predicted from van der Waals forces using Hamaker coefficients for gold or hexadecane surfaces interacting across water.

The pull-off force or adhesion force is defined as the minimum force that must be applied to separate the two surfaces. The rate (0.5–2 Hz) at which the surfaces were separated out of contact or the time that the opposed surfaces rested in contact ($50 \mu\text{s}$ –0.5 s) before the pull-off forces were applied did not have an effect on the magnitude of the adhesive forces. Here, we present forces scaled by the radius of the sphere, R , to relate the force between a curved and a flat surface to the interaction free energy, E , between plane parallel plates of unit area by $F/R = 2\pi E$.⁵⁴

Shown in Figure 4 are scaled pull-off forces as a function of electrolyte concentration. For all three systems the trend is the same: as the concentration of the electrolyte is increased, there is an increase in the adhesive force that holds the two surfaces together. Some variability in the force measurements is expected because of variations

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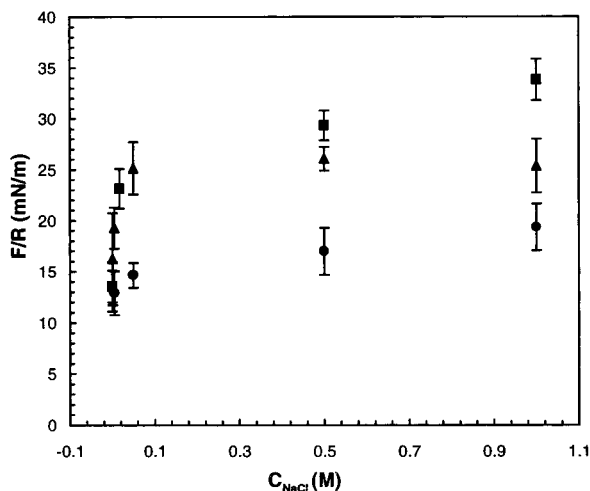


Figure 4. Pull-off force/radius of sphere versus the NaCl concentration in water, for hexadecanethiol SAMs. Data are shown for three different tips and surfaces: A (■), B (▲), and C (●). The error bars correspond to the standard deviations that resulted from 10 to 20 force measurements all over the surface. Data are normalized such that there is a fixed adhesive force in pure water.

in the spring constant used to convert the cantilever deflection to forces. Here, however, measurements have been normalized such that there is a fixed adhesive force in pure water and even after accounting for this normalization, the data do not superimpose. For example, at 1 M NaCl, the average $F/R = 33.83$ mN/m for tip A and $F/R = 19.32$ mN/m for tip C. This variation in the measurements from one tip to another can be attributed to the surface roughness. It is well-known that asperities as small as 1–2 nm can significantly lower adhesion.^{30,55,56} As shown in Figure 1, the glass probes display asperities of this size. On the basis of these results, we conclude that comparisons of interaction forces in different solutions should be done only with the same tip and surface.

The effect that CaCl_2 and Na_2SO_4 concentration has on adhesion has also been investigated. Both of the electrolytes have the same qualitative effect on hydrophobic interactions as the 1:1 electrolyte (NaCl). The case of CaCl_2 is shown in Figure 5. These results indicate that the three electrolytes investigated act in a similar manner to increase the adhesion between SAMs of hexadecanethiol.

A key question is whether a particular additive affects the interactions by its presence in the intervening medium or by changing the properties of the surface itself. To investigate the effect of electrolytes on the wetting properties of the system, the advancing and receding contact angles of different electrolyte concentrations were measured on the hexadecanethiol surfaces. Both the advancing and receding contact angles were not influenced by electrolyte type or concentration, indicating that SAMs are stable in the presence of electrolytes. Typical results are shown for the case of NaCl in Figure 6. Our measurements in pure water are in excellent agreement with previous studies.^{40,57} While the liquid/vapor surface tension of aqueous solutions is a weak function of electrolyte type and there is a small increase with increased electrolyte concentration, these changes are not

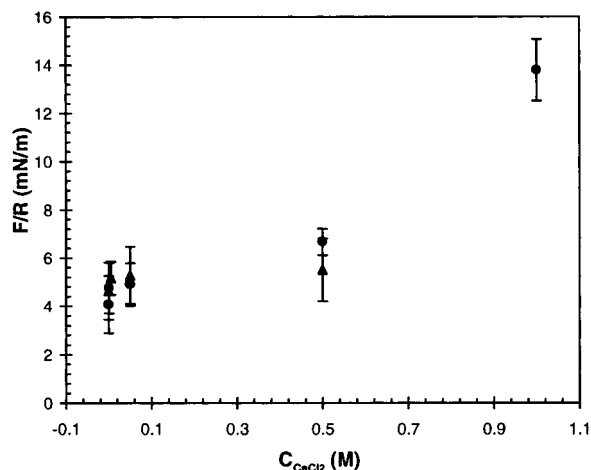


Figure 5. Pull-off force/radius of sphere versus the CaCl_2 concentration in water, for hexadecanethiol SAMs. Data are shown for two different tips and surfaces: D (●) and E (▲). The error bars correspond to the standard deviations that resulted from 10 to 20 force measurements all over the surface.

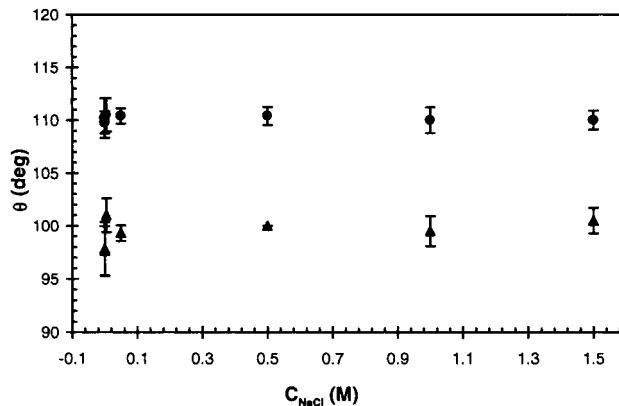


Figure 6. Effect of NaCl concentration in water on advancing (●) and receding (▲) contact angles for NaCl solution drops at the SAMs of hexadecanethiol. The error bars correspond to the standard deviations that resulted from 12 different measurements.

observable within our levels of uncertainty. If these small changes were significant, we would expect contact angles to follow changes in surface tension with electrolyte type and decrease with increased salt concentration: a result not observed.

In conjunction with the adhesive force data given above, these results demonstrate that increasing electrolyte concentration in water increases hydrophobic interactions between SAMs without changing the wetting properties of the surface. Our case is different but in no way contradictory to results described by Rabinovich and Yoon¹⁸ and Yoon et al.⁵³ where they suggest that the hydrophobic force is uniquely determined by contact angles. Their results demonstrate that the jump in distances and adhesion forces increase with contact angle, while we have shown that for a certain surface with a specific value of contact angle, adhesions can further be increased without altering the surface characteristics. We conclude that the electrolytes alter some property of the system other than the affinity of the solvent for the surface.

Density functional theory calculations recently demonstrated that changes in solvent chemical potential (expressed in terms of a reduced bulk density) induce alterations in the interactions between surfaces.⁵⁸ This work suggests that attractive forces between hydrophobic surfaces are increased through a reduction in solvent

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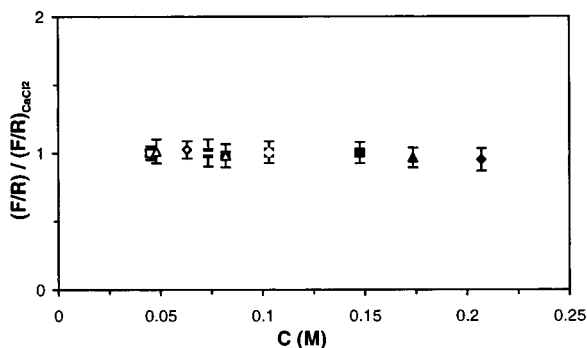


Figure 7. Pull-off force/radius of the sphere normalized to that measured for CaCl_2 versus the electrolyte concentration in water for hexadecanethiol SAMs. Measurements are shown for three different osmolalities. The open symbols correspond to $O = 0.119$ Os/kg of water, the half-filled ones to $O = 0.192$ Os/kg of water, and the black-filled symbols to $O = 0.382$ Os/kg of water. These three sets of data were measured with a different colloid probe tip and surface. The error bars correspond to the standard deviations that resulted from 10 to 20 force measurements all over the surface. Three different electrolytes were used for each value of the osmolality: CaCl_2 (squares), Na_2SO_4 (triangles), and NaCl (diamonds).

chemical potential, thus demonstrating the role played by the thermodynamic state of the solvent. In the simulations, reductions in chemical potential were accomplished through variations in the solvent bulk density. In our study, the chemical potential is reduced by adding electrolytes to the solvent, thus creating a multicomponent mixture. We hypothesize that if the electrolytes have no specific interactions with the surface and the hydrophobic forces are dominated by water/solvent interactions, the addition of electrolytes acts much like a reduction of solvent bulk density in a single-component system.

To test this, we have performed the following experiment. The chemical potential of the water was set by adding three different electrolytes (NaCl , CaCl_2 , and Na_2SO_4). This experiment was repeated for a total of three chemical potentials, each one measured with a different tip/surface. In Figure 7 we compare the adhesive forces between the thiol surfaces at three fixed osmolality values: $O = 0.119$, 0.192 , and 0.382 Os/kg of water (the osmolality is a measure of the chemical potential of the water^{59,60}). The adhesive forces were very reproducible with standard deviations varying from 5 to 25% (other AFM studies^{45–47} of adhesive forces between SAMs of *n*-alkanethiols show standard deviations that vary from 10 to 70%). As the tips were different for each osmolality, adhesive forces for the three osmolalities cannot be compared directly and we have normalized the forces to that measured for CaCl_2 to emphasize that the adhesive force is independent of salt type despite the fact that the salts are in solution at different concentrations.

As indicated in Figures 4 and 5, adhesive forces increase monotonically with salt concentration. When combined with the data in Figure 7, these results suggest that there is a single master curve characterizing the influence of these simple electrolytes on the hydrophobic adhesive force between methyl-terminated SAMs. This hypothesis was confirmed by measuring the adhesion force with the same tip for several concentrations for each electrolyte. At the same concentration, each electrolyte has a different

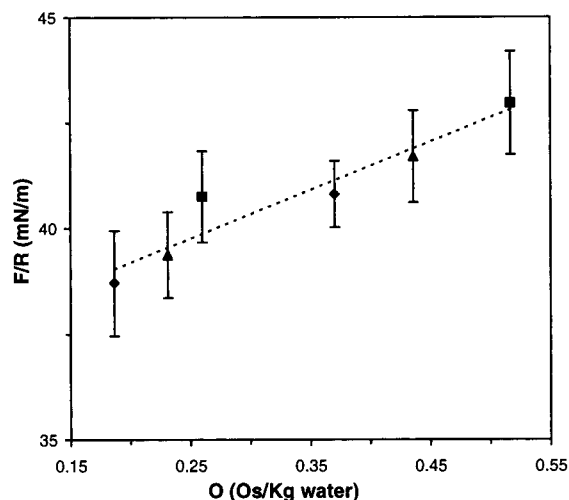


Figure 8. Pull-off force/radius of the sphere versus the osmolality for hexadecanethiol SAMs. Measurements are shown for three different electrolytes: CaCl_2 (■), Na_2SO_4 (▲), and NaCl (◆). All measurements were done with the same colloid probe tip and surface. Each symbol is the average of 10 to 15 adhesion forces measured all over the surface. The error bars correspond to their standard deviations. The dashed line represents the best fit to these data (the average values and their standard deviations as well).

osmolality. By plotting the resulting adhesive forces as a function of osmolality, all of the data fall onto a single master curve (Figure 8) where forces were measured at concentrations of 0.1 and 0.2 M for NaCl , Na_2SO_4 , and CaCl_2 . The dashed line in Figure 8 represents the best master curve for all these data. To determine whether these data could be fitted to a single master curve and find the best fit, we used the maximum likelihood estimation method.⁶¹ The advantage of this technique is that it estimates the best fit, taking into consideration the errors, in this case the standard deviations, for each data point. The best fit was found to be a single curve (linear fit), within a 95% confidence interval, with a positive slope. These data clearly show that the adhesion between the two hydrophobic SAMs increases as the osmolality of the solution is increased or the chemical potential of the water is decreased. This result is novel because it demonstrates that adhesion between a given set of hydrophobic surfaces can be increased and controlled in a systematic way.

In discussions of the role played by electrolytes on hydrophobic interactions, electrolytes and their effect on the force profiles between surfaces have been discussed elsewhere in terms of the electrolyte ionic strength, which characterizes ionic effects in terms of concentration and ionic charge, but which neglects important properties such as their chemical specificity and interactions with the aqueous phase. We have chosen to characterize them by their osmolality and consequently by the chemical potential of the water, because there are certain advantages for using the osmolality versus the ionic strength. The osmolality takes into account the degree of dissociation or association of an electrolyte and includes both long-range and short-range ion–solvent and ion–ion interactions, particularly at high concentrations. The osmolality also accounts for the reduction of the dielectric constant by increased electrolyte concentration and the ionic strength dependence of the short-range forces effect in ion–ion binary interactions.⁶⁰

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We can conclude that both computer simulations and experimental data support the hypothesis that hydrophobic interactions can be manipulated through changes in the solvent chemical potential without altering the wetting properties of the system.

Conclusions

Our results demonstrate that adhesion is sensitive to surface roughness. As a result, comparisons can only be made using the same tip and surface.

In this study we have demonstrated that the adhesive interactions of hydrophobic surfaces can be controlled in a systematic way by varying the electrolyte concentration. An important parameter in modulating the adhesion between hydrophobic surfaces is the osmolality and not the ionic strength of the solution because the latter neglects important electrolyte properties, such as chemically specific ion-ion and ion-solvent interactions. These interactions are difficult to describe in terms of a single easily calculable parameter. As a consequence, we propose here that the measured osmolality of the solution be used to link specific ion effects.

For the SAMs studied here, electrolytes do not alter the solvent/surface interactions as indicated by the lack of electrostatic repulsive forces at any concentration and the insensitivity of contact angles to salt type or concentration. The jump in distances, typically used to characterize the extent of the attractive interactions, were systematically larger than what can be predicted for gold/gold and hexadecane/hexadecane surfaces interacting across water. Combined with the large contact angles of electrolyte drops on the thiol surfaces, these results lead us to believe that the forces we measure are due to hydrophobic interactions.

Adhesive forces increase with electrolyte concentration and are sensitive to electrolyte type at a given concentration. However, the adhesive forces fall onto a master curve when plotted as a function of the water chemical potential. Electrolytes appear to affect the surface interactions by their presence in the water rather than altering the wetting properties of SAM surfaces which are robust and stable upon salt addition. This behavior is different to the one that solvents exhibit. Solvents alter the chemical potential of the water as well as altering the wetting properties of the surfaces.⁶² These changes can be measured through the solvent/thiol surface contact angle. Changes in wetting properties appear to be able to dominate over the effect of changes in solvent chemical potential. In the case of the electrolytes, we were unable to measure changes in contact angles, as described in this study, indicating that wetting properties of the surfaces are not changed. These electrolytes, when dissolved, decrease the water chemical potential. Our studies suggest that lowering the solvent chemical potential produces an increase in the pull-off force. Due to the lack of interaction of the salts with the surface, reductions in solvent chemical potential dominates how the adhesive force changes.

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