

Concentration-Driven Surface Transition in the Wetting of Mixed Alkanethiol Monolayers on Gold

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Abstract: The construction of mixed monolayers containing hydrophobic and hydrophilic components for which the contact angles for three different liquids vary as a highly nonlinear function of the monolayer composition is reported. It is suggested that a prewetting, crystalline-like layer of water, possibly formed from bulk vapor, is present near the hydrophilic surface, because of an enhanced surface chemical potential ("surface field"). As the concentration of the hydrophilic component is lowered, increasing "quenched randomness" in the distribution of surface fields destroys the surface condensed water phase, thus triggering the observed nonlinearity in the contact angles. The microscopic structure of the water molecules adsorbed on an OH surface is revealed by continuum Monte Carlo simulations, with realistic force fields, and the scenario is supported by mean-field calculations on a simplified lattice-gas model. The observed wetting behavior at 30% relative humidity was altered for a relative humidity $\leq 2\%$, as well as when the surface of the monolayer was molecularly roughened by the addition of two CH_2 groups to the hydrophobic (CH_3 -terminated) component of the mixed monolayers. It is suggested that this transitional phenomenon is due to a possible (true or rounded) surface phase transition, due to the formation of a prewetting water layer. This formation is triggered by variations in the quenched distribution of random surface fields.

Introduction

Wetting behavior of ordered and random surfaces has generated considerable interest recently,¹ in particular, the understanding of its relationship to the surface structure at the molecular level. Therefore, polymeric² and monolayer surfaces, especially those of thiols on gold,³ have been intensively investigated as model systems. Modern theories of wetting are based on phase diagrams representing competing ordering between bulk and surface phases.^{4,5} Recent theoretical studies model the effect of quenched randomness within a substrate, on the wetting behavior, by representing it as random surface fields, or couplings, in simple two-state models.^{6–8} In a series of experiments on borosilicate glass substrates with different relative concentrations of methyl and hydroxyl groups, Franck and collaborators investigated the effect of altered surface chemistry on the wetting of binary liquid mixtures using the capillary rise technique.^{9–11} While in these experiments the temperature was controlled to a high degree (thus allowing accurate study of temperature dependence of contact angles), only qualitative control of the relative concentration of methyl and hydroxyl groups at the surface was achieved.

In this paper we report an experimental realization of chemically tuning random distributions of surface fields (local chemical potentials) by molecular surface engineering, using self-assembled alkanethiol mixed monolayers on gold surfaces. Smooth organic surfaces, with finely controlled relative concentrations of polar (OH) and nonpolar (CH_3) groups, were carefully engineered, and their wetting properties were studied. Contact angles of several different liquids (sessile drops) on such surfaces in an ambient atmosphere (approximately 30% relative humidity) exhibit a highly nonlinear dependence on the concentration of the hydrophilic component and are sensitive to atmospheric humidity; i.e., contact angles decrease with increasing relative humidity.

It is suggested that a dense, microscopically thin prewetting

layer of water is present on the hydrophilic surfaces, because of an enhanced surface field (effective chemical potential), and that this layer is in equilibrium with bulk water vapor. Then, as the concentration of the hydrophilic component is lowered, the new quenched random distribution of surface fields can no longer support the surface condensed water phase, thus triggering an abrupt change in the surface free energy.

Results and Discussion

Monolayer Assembly and Wetting Studies. Thiol derivatives (R-SH) adsorb spontaneously onto clean, hydrophilic gold surfaces (Au/Si , surface roughness for substrates employed in this study: $p - v$ 11.00 Å and RMS 2.40 Å, for 130 μm length scale),^{12,13} to form ordered, hexagonally close-packed (hcp) monolayers, occupying a triangular lattice,¹⁴ presumably through a mercaptide gold bond.^{13,15} In these monolayers the S...S distance is 4.97 Å,¹⁴ and the alkyl chains are tilted $\sim 35^\circ$ relative to the surface normal.¹⁶

Mixed monolayers were prepared by spontaneous adsorption of the thiol mixture (in THF) onto gold surfaces.¹² All monolayers showed thicknesses of 14 ± 1 Å as estimated by ellipsometry. The surface concentration of the OH groups was determined by ESCA¹⁷ and found to be in good agreement with the relative concentrations in the adsorbing solution. The question of whether the adsorbed concentrations are controlled by thermodynamics or kinetics has been examined by Bain et al. for systems similar to these.¹³ They concluded that the adsorption of alkanethiols on gold surfaces is kinetically controlled. We, therefore, assume that in the present case we have a random distribution of the OH and CH_3 groups at the surface, although we lack conclusive experimental evidence. We note, however, that using this assumption within a framework of a simplified lattice-gas model, as presented below, reproduces qualitatively the reported behavior.

The wetting by *n*-hexadecane (HD, $\text{C}_{16}\text{H}_{34}$) of freshly prepared monolayers composed of mixtures of HUT and DDT (i.e., im-

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- (17) Measurements were carried out on a Surface Science SSX-100 instrument, with a take-off angle of 35° , using $\text{Al K}\alpha$ radiation. Values are normalized to 100 atomic % for the elements detected and were rounded to the nearest atomic percent. XPS concentration values should be used only for comparison between the two samples and are not to be taken as absolute.

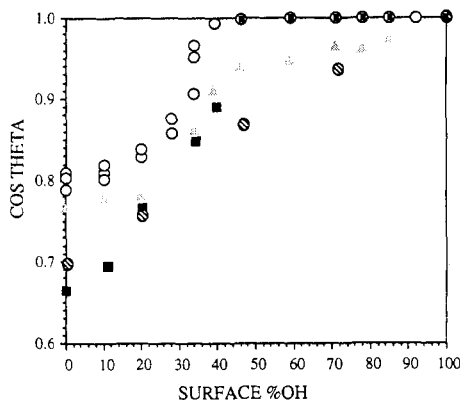


Figure 1. $\cos \theta$ of HD (open circle), BCH (triangle), and ME (solid box) for HUT-DDT and of HD (slashed circle) for HUT-TDT mixed alkanethiol monolayers on gold, as a function of the surface OH concentration.

mediately after removal from the solution) showed a highly nonlinear behavior about a concentration threshold. The cosines of the HD contact angles (θ) plotted as a function of surface OH concentration are presented in Figure 1. The sharp variation of the contact angle at ~ 30 –45% surface OH groups reflects an abrupt change in the solid-vapor (γ_{sv}), and solid-liquid (γ_{sl}) interfacial free energies. To establish that the HD contact angles for samples with surface OH concentrations higher than 40% were still nonzero, the profile of the HD drop edge on these samples was studied under dispersive red light.^{18–21} From the fringes, and the average wavelength of the red light, the average contact angles of $\sim 3.0^\circ$, 2.2° , and 1.5° for 45, 58, and 70% surface OH concentrations were calculated, respectively. These data suggest that $\cos \theta$ for HD approaches 1 in an asymptotic fashion.

If this transition reflects a surface physical phenomenon (rather than a *specific* chemical interaction between the HD molecules and the surface), it should be observed with other liquids as well and at similar surface OH concentrations. The cosines of the contact angles for bicyclohexyl (BCH, $C_6H_{11}-C_6H_{11}$) and for methoxyethanol (ME, $CH_3OCH_2H_2OH$) are also presented in Figure 1. It is thus clear that these three liquids, though characterized by different values of γ_{lv} , the liquid-vapor interfacial free energy, all sense the transition in the surface free energies γ_{sv} and γ_{sl} , between ~ 30 and 45% of surface OH concentrations.

Monte Carlo Simulations. In an attempt to understand how water molecules interact with the hydroxylated surface of HUT/Au, we carried out molecular mechanics simulations. We modeled the upper portions of the monolayer as an 8×8 hexagonal close-packed array of normal propanols. The reasoning is that short-chain alcohols, when packed in the same manner that provides maximum efficiency for the full monolayers, would display the appropriate surface characteristics. For HUT/Au, the lattice spacing is 4.97 \AA ;¹⁴ consequently, the molecules were tilted 38° from the surface normal and twisted about the chain axis to achieve optimal packing efficiency.²² In this molecular orientation, there is near perfect interlocking of the bumps of one chain with the depressions of its neighbors and there is no free methylene rotation.²²

Thirteen water molecules were then placed at random positions above, but near to, the hydroxylated surface. The low-energy conformations were then sought by a series of Monte Carlo moves, each of which was followed by energy minimization of the generated structure. The Monte Carlo steps varied combinations of water positions, water orientations, and the CH_2-OH torsional angles. In each step, four water molecules were moved, and from one to three torsional angles were changed. The effect of periodic

boundary conditions for the underlying monolayer structure was mimicked by keeping both the outer ring of molecules and the lower alkyl chain fixed during the substructure energy minimizations. We assumed that 13 water molecules would be sufficient to show whether the waters preferred clumping with each other to occupying isolated sites on the monolayer surface.

These calculations were done with the BATCHMIN version of the MACROMODEL program,²³ using the classical MM2 force field.²⁴ The program was modified slightly to restrict the Monte Carlo moves of the water positions from taking excessive excursions away from the hydroxylated surface or "falling off" the edges of the assembly. Two thousand Monte Carlo moves were generated. The substructure minimizations were done in stages. After 250 steps of minimization, those structures higher in energy by more than 50 kcal/mol than the previously achieved "lowest energy" were culled and duplicates were removed; the remaining structures were subsequently minimized to an RMS gradient of 0.01 kJ/\AA in Cartesian space. Two search methods were tried: (a) a global search in which each Monte Carlo step started with the partially optimized structure of the previous step (providing that structure is within 100 kJ of the present global minimum); (b) a local search in which each move started from the same original structure. The global search strategy was somewhat more efficient in finding low-energy structures.

The HUT/Au model surface has trigonal depressions, or holes, which seem ideally suited to hold a water molecule. Every water molecule occupying such a hole can participate in three hydrogen bonds with the hydroxyl groups that define the hole and is thereby stabilized by approximately 12 kcal/mol relative to a free water molecule (Figure 2). The latter number is crudely approximated as the molecular mechanics energy of the cluster, minus the energy of the same system with one molecule moved to a point far (10000 \AA) from the aggregate. The water molecules are almost, but not completely, buried in these holes (i.e., the water oxygens protrude about 0.6 \AA above the plane containing the hydroxyl oxygen atoms and 0.25 \AA above the mean plane of the hydroxyl hydrogen atoms). The three hydrogen bonds to any given water are not equivalent. The $RO-H\cdots OH_2$ bonds are 1.77 – 1.79 \AA and the $O-H\cdots O$ angles deviate from linearity by less than 10° . Those involving the water protons are both longer and more bent and involve two types (one at 1.92 \AA , which is 15° bent, and the other at about 2.2 \AA , with bends approaching 30°).²⁵

Two binding structures, which one might expect to be competitive with those seen in Figure 2, are found only infrequently in the low-energy configurations (within 3 kcal/mol of the lowest minimum). Situations where the three H-bonds involve both lone pairs and only one proton from the water molecule are only found in configurations at least 1 kcal/mol above the lowest minimum, and then only rarely. Such binding requires a rotation of roughly 120° for one OH group and would lower the number of water molecules that could be accommodated. Also, one must go up $\sim 2 \text{ kcal/mol}$ to find situations where any of the three surface OH groups binding a water molecule are not involved in another H-bond as well.

As seen in Figure 2, only half the holes that could potentially contain a water molecule are occupied when the H-bonding capacity of the OH groups is exhausted. The resulting H-bonding network looks strangely like a graphite lattice and leaves every other hole vacant. This, of course, permits the formation of growth islands and fault lines, where they would not mesh smoothly together. The individual 6-membered rings actually look more like somewhat flattened chair cyclohexanes rather than hexagons.²⁶ We observe no tendency to start filling a second layer until the

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(25) One should not read too much into the details of these H-bonds. After all, the MM2 force field includes no penalty for nonlinear H-bonds and will find the wrong conformation of the water dimer. However, the general nature of the holes, the three H-bonds, and the geometric arrangement should also hold for more elaborate treatments of H-bonding.

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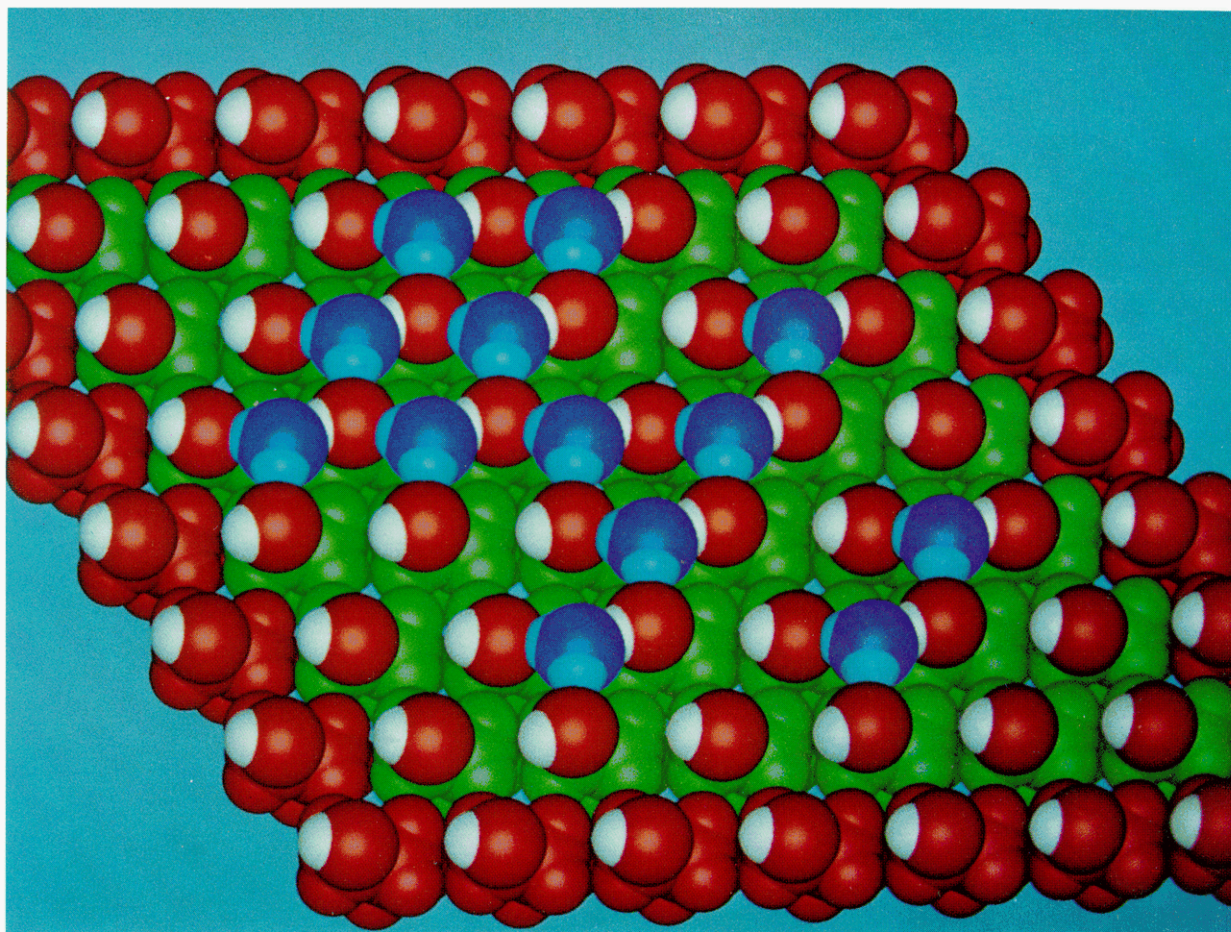


Figure 2. Monte Carlo energy minimization (0 K) of 13 water molecules on an 8×8 planar assembly of *n*-propanol (4.97-Å spacing and 38° tilt).²²

first layer is complete. It is interesting to note that the two-dimensional adsorbed water layer (Figure 2) is reminiscent of the *ab* layer of hexagonal ice.^{26,27}

The Model. To gain further understanding of the nature of the transition, it is necessary to consider surface composition at the molecular level. The starting point in this discussion is a molecularly homogeneous, low-energy, methyl (CH_3) surface of a DDT monolayer. As the fraction of HUT is increased, one may envision that methyl groups are *randomly* replaced by polar OH groups and that the surface OH/ CH_3 ratio gradually increases. Equilibrium contact angles on heterogeneous surfaces have been previously interpreted on the basis of either the phenomenological Cassie (1)^{28–32} or the Israelachvili and Gee (2)³³ equations

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (1)$$

$$(1 + \cos \theta)^2 = f_1(1 + \cos \theta_1)^2 + f_2(1 + \cos \theta_2)^2 \quad (2)$$

where θ is the observed contact angle for the mixed monolayer, f_1 and f_2 are the fractional surface coverages of chemical groups of type 1 and 2, respectively (such that $f_1 + f_2 = 1$), and θ_1 and θ_2 are the contact angles on the pure homogeneous surfaces of 1 and 2, respectively. Note that both equations above define *smooth* interpolation curves between $\cos \theta_1$ and $\cos \theta_2$, a linear one for eq 1 and a quadratic one in the case of eq 2. This is not in agreement with the wetting behavior reported here, where, as surface OH concentration increases, $\cos \theta$ gradually approaches

a threshold where it abruptly changes.

Geometrical site percolation of the surface OH groups is ruled out as a possible explanation, since its threshold on a triangular lattice is 0.5.³⁴ We suggest that water molecules adsorbed on these high free energy surfaces play a crucial role in the observed phenomenon and, therefore, have to be considered in any realistic model. These water molecules can be either residual from the monolayer preparation or, in the case of “dry” preparations, adsorbed from the ambient atmosphere.^{35–37} Consequently, a treatment based on firmer theoretical grounds is needed.

The Monte Carlo simulations described above indicate that when water molecules adsorb to such hydroxylated surfaces, they have a definite preference for sites where they can form multiple H-bonds, bridging between nearest-neighbor surface OH groups (Figure 2). This creates a situation analogous to that of a wax-coated glass microscope slide with a scratch through the wax coating. A drop of water placed on this slide will spread along the scratch where the hydrophilic surface is exposed. For mixed monolayers with partially hydroxylated surfaces, the surface OH groups, and the water “bridges” between them, form an analogous hydrophilic scratch (at the molecular level) on the hydrophobic CH_3 surface.

However, this is, again, a geometrical site percolation phenomenon with a threshold of 0.5.³⁴ Therefore, no infinitely connected cluster of water molecules exists in the *first* adsorbed water layer at the observed threshold of 0.35, if the surface OH and CH_3 groups are assigned randomly to the lattice sites. Thus, geometrical nearest-neighbor percolation, either in the OH layer

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or in the *first* adsorbed water layer, does not offer adequate explanation for the observed abrupt change in the wetting behavior.

An explanation for the observed phenomenon on the macroscopic level is possible within the framework of the modern theories of wetting.^{4,5} These typically represent two-fluid systems by two-state lattice-gas, or pseudospin models, with appropriate short- and/or long-range intermolecular interactions. The presence of a solid surface is represented by an alteration of the chemical potential differences and/or of the intermolecular interactions for molecules located on the surface. Wetting and prewetting phenomena can then be understood in terms of ordering of the various bulk and surface phases. This results in a phase diagram controlled by the magnitude of the bulk and surface couplings and the temperature.

The discussion above implies that the abrupt change in the surface free energy comes about because of competitive ordering of both polar (water) and hydrophobic (i.e., HD) molecules into various surface and bulk, liquid, or vapor phases, in the vicinity of the solid surface. Hence, a comprehensive theoretical treatment of our experimental system should be based on a three-state, rather than a two-state, pseudospin model, the three states representing the two molecular species and vacancies. Surface ordering in the three-state Blume-Emery-Griffiths model³⁸ has been previously suggested by Leibler and Peliti³⁹ as a way to achieve surface ordering before bulk ordering in a binary mixture with impurities. However, if we assume that the apparent transition in the contact angles is triggered by the presence or absence of an adsorbed *condensed* layer of water on the organic monolayer, then we can concentrate on the *water vapor-water liquid-substrate* system, which can be represented by a two-state Ising, or lattice-gas model with a surface field. For a *homogeneous* substrate (homogeneous surface field), a prewetting condense surface phase is known to coexist with bulk vapor, when the surface ordering field (chemical potential) is *dominant* over the effective pair interaction, coupling the surface to the bulk.^{40,41} Therefore, a surface condensed water phase should coexist with water vapor near a fully hydroxylated hydrophilic surface, because there the surface field is strong, whereas it is unlikely that a surface condensed water phase exists near a pure methyl hydrophobic surface because there the surface field is weak. At concentrations of the hydrophilic component lower than 100%, a quenched random distribution of strong and weak surface fields is introduced, with the potential for the destruction of the surface condensed water layer. This will happen at a particular OH concentration, which is determined by the surface field distribution, the cohesive energy of hydrogen bond formation within the surface water layer, the temperature, and the bulk water chemical potential. The latter is related to the partial pressure of water vapor and, consequently, to the relative humidity of the ambient atmosphere. Indeed, this may be why we, and others,⁴² have found that contact angles on high-energy surfaces are highly sensitive to relative humidity. If the suggested scenario is correct, then what are measured by contact angles on these, and similar surfaces, are not the free energies of the *bare* surfaces, but rather those of surfaces with adsorbed water layers.

Let us now consider, at the molecular level, the effect of increasing surface OH concentration on the possible formation of adsorbed water layers. At low concentrations, the OH groups are spaced far from each other, and there may be correlated H-bonded water clusters around them. However, when the OH concentration on the surface is large enough, correlated clusters of H-bonds can unite to form a dense prewetting water layer, thus changing the macroscopic surface free energy. The correlated H-bond mechanism involves at least two water layers, and water molecules acting as branching junctions, i.e., connected with three or four H-bonds (Figure 2). Thus, these water molecules can bridge over clusters of methyl groups. We *estimate* that correlated

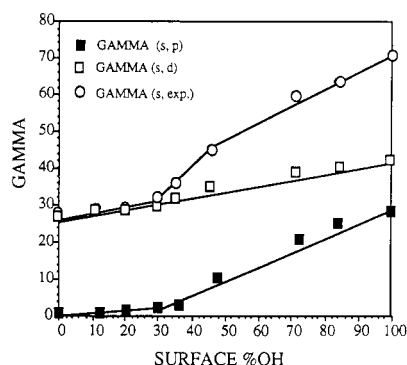


Figure 3. Experimental critical surface tension (γ_s^{exp}) and its dispersive (γ_s^{d}) and polar (γ_s^{p}) components as a function of the surface OH concentration for HUT-DDT mixed alkanethiol monolayers on gold.

H-bonds can bridge over ca. two CH_3 groups since the transition occurs at $\sim 1:2$ OH: CH_3 ratio. In other words, the strong cohesion among H-bonded water molecules in the first and *second* adsorbed water layers can overcome the barrier which CH_3 clusters impose on the adsorption of water molecules at the surface. The arguments brought so far can be further supported by the results of two-liquid wetting experiments.⁴³

If the change in surface free energy is due to the formation of a *condensed second* water layer formed by a process of hydrogen bonding, then the polar component of the surface free energy is expected to be more sensitive to it than the dispersive one. The total surface free energy (γ_s^{exp}) and its dispersive (γ_s^{d}) and polar (γ_s^{p}) components were calculated from the experimental data by using the angles of free-standing droplets of CH_2I_2 and water.⁴⁴ We note that although splitting of the surface energy into polar and dispersive components is questionable from a thermodynamics perspective, as suggested by Neumann,^{45,46} it may still prove fruitful to follow this approach. Even if γ_s^{p} does not represent the "true" polar component of the surface free energy, it may be indicative, and hence useful, for the *qualitative* interpretation of the results. From Figure 3 it is clear that an abrupt change in the polar surface free energy component, and the transition in the wetting behavior, occur approximately at about the same surface OH concentration (30–45%); this is probably due to the formation of large-scale correlated H-bonded clusters. We note that the acidity of the protons in the adsorbed water layers will be affected by the formation of the cooperative H-bonds.⁴⁷

Mean-Field Calculations. The coverage of the surface water layer, which coexists with bulk vapor on top of the self-assembled monolayer, can be derived, within a mean-field approximation, for a simplified lattice-gas model for the substrate-water-vacancy system. An example of such a calculation is given here. It provides a *qualitative demonstration* that the variation of the coverage of the surface water layer with the concentration of OH groups in the organic monolayer may indeed account for the observed abrupt transition in the contact angles and interfacial free energies, as summarized in Figures 1 and 3.

We approximate the continuous configurational space by a semi-infinite cubic lattice, which simplifies the calculations enormously. The configurational energy of the system depends on the lattice-gas occupancy variables t_i , where $t_i = 1$ if lattice site i is occupied by water and $t_i = 0$ if it is vacant. This energy is given by the Hamiltonian

$$H = -\epsilon \sum_{\langle ij \rangle} t_i t_j - \sum_i \mu_i t_i \quad (3)$$

where $\langle ij \rangle$ denotes summation over all pairs of nearest-neighbor

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sites, ϵ is the effective short-range pair interaction (for simplicity assumed to be identical within the surface layer, the bulk, and the interpolating layers), and μ_i is the effective local chemical potential at site i . The latter is assumed to be μ_b , the bulk chemical potential, if i is a bulk site not belonging to the surface layer. The bulk chemical potential enters into the Hamiltonian as a one-body interaction for the lattice-gas occupancy variables. Its physical origin is as a Lagrange multiplier conjugate to the total number of molecules, in the mapping from the canonical to the grand canonical configurational partition function. This, in turn, is mapped on the lattice-gas model. μ_b can be calculated within the ideal gas approximation for the bulk water vapor. It depends on the partial pressure of water in the ambient atmosphere and thus on its humidity at a given temperature.

The interaction of the water molecules with the substrate, at the surface layer of the semi-infinite lattice, is represented by the enhancement of the effective one-body interactions at the surface. In our case, the substrate is not homogeneous. Thus, the water molecules at the surface may interact either with an OH-rich patch of the substrate, in which case strong H-bonding interactions will be dominant, or with a CH₃-rich patch of the substrate, where only weaker, dispersive, van der Waals attractions contribute to the enhancement of the effective local chemical potential.

To proceed with the calculations, we need to know the probability distribution of OH groups on the surface of the organic substrate, given their mean concentration at the surface. Since the chemisorption of thiols on the Au/Si substrate is controlled kinetically, rather than thermodynamically,¹³ it is reasonable to assume that the probability distribution of the OH groups at the surface is quenched, rather than annealed. This means that, for a *freshly prepared monolayer*, the distribution of OH groups at the surface can be considered fixed (for the time scale of the wetting experiments), albeit out of thermal equilibrium with the rest of the system (and thus not determined by a thermal equilibrium requirement for the entire system). In the absence of a conclusive experimental determination of this quenched probability distribution, we will proceed with a simple assumption and study its consequences within the framework of the lattice gas model (eq 3). The sites i at the surface of the semi-infinite cubic lattice will have *site-independent, bimodal* probabilities $p \approx c$ (where c is the relative concentration of surface OH groups) and $q = 1 - p$ to be in either an OH or a CH₃ environment, leading to effective local chemical potentials $\mu_i = \mu_b + \mu_p$ and $\mu_i = \mu_b + \mu_q$, respectively.

In the cases $p = 1$ or $q = 1$, which correspond to a homogeneous substrate, this semi-infinite lattice-gas model and its Ising spin equivalent have been extensively studied before. Mean-field calculations^{38,39} have demonstrated a possibility of a condensed surface layer coexisting with a bulk vapor phase, at low enough temperatures and for a certain region in the parameter space. As the temperature increases, the first-order transition at the coexistence line becomes weaker, terminating at a critical point, beyond which only the bulk vapor phase remains. The effect of a quenched, bimodal, independent site probability distribution of surface fields on the *critical wetting* transition in semi-infinite Ising model has been previously addressed in the literature.⁶⁻⁸ However, the effect of such quenched randomness on the coexistence of the condensed surface layer with bulk vapor has not been previously considered, to the best of our knowledge. This effect is incorporated explicitly within the mean-field approximation scheme provided below.

The mean-field approximation method that we use here corresponds to the lowest level in the hierarchy of mean-field approximations successfully applied by Benyoussef and Boccaro⁴⁸ to bulk Ising-type models with various types of quenched disorder. The mean-field assumption approximates the total probability distribution for the lattice configurations by a product of single-site probabilities

$$P(\{t_i\}) \approx \prod_i \rho_i(t_i) \quad (4)$$

where

$$\rho_i(1) = n_i \quad (5)$$

$$\rho_i(0) = 1 - n_i \quad (6)$$

By definition, we have

$$n_i = \overline{\langle t_i \rangle} = \sum_{\{t\}} t_i P(\{t\}) \quad (7)$$

Here $\overline{\langle t_i \rangle}$ denotes a thermal average, followed by a quenched average of t_i . Let us denote by $\langle t_0 \rangle_{\text{cnf}}$ the mean value of t_0 for a given configuration of t_i on all other sites. Then the following relation should be satisfied:⁴⁸

$$\overline{\langle t_0 \rangle}_{\text{cnf}} = \left(\frac{\text{tr}_{t_0} t_0 \exp -\beta H}{\text{tr}_{t_0} \exp -\beta H} \right)_{\text{cnf}} \quad (8)$$

Averaging over all possible configurations at sites $i \neq 0$ results in self-consistency relations expressing the coverage at a central site in terms of a sum of single-site, thermal, and quenched averages, at fixed boundary configurations, cnf, multiplied by the probabilities P_{cnf} of these configurations:

$$n_0 = \sum_{\text{cnf}} \overline{\langle t_0 \rangle}_{\text{cnf}} P_{\text{cnf}} \quad (9)$$

Explicit expressions for $\overline{\langle t_0 \rangle}_{\text{cnf}}$ are given by the mean-field assumptions (eqs 4-6) and depend only upon the coverages at the adjacent sites.

For the infinite bulk lattice, the system should be invariant under lattice translations. Therefore, different sites should have identical mean site coverages, resulting in the self-consistent equation for the site coverage in the bulk

$$n_b = \sum_{i=0}^6 C_i^6 \{1 + \exp[-(6-i)\beta\epsilon - \beta\mu_b]\}^{-1} n_b^{6-i} (1-n_b)^i \quad (10)$$

where

$$C_i^k = k! / i!(k-i)! \quad (11)$$

are binomial coefficients.

This sixth-order polynomial equation has multiple roots for n_b . The physical solution corresponds to the real solution with the lowest Helmholtz bulk free energy per site $(\langle H \rangle - TS)/N$. Within the mean-field approximation (eqs 4-6), the latter is given by

$$f_b = -3\epsilon n_b^2 - \mu_b n_b + k_B T [n_b \log n_b + (1-n_b) \log (1-n_b)] \quad (12)$$

In the case of a semi-infinite lattice, one may still assume translational invariance within layers parallel to the boundary plane, but not in the direction perpendicular to it. Let us index the layers sequentially by index i . Then the following self-consistent condition should be satisfied by site coverages n_i in any three successive layers $i = 1, 2, 3$:

$$n_2 = \sum_{i=0}^1 \sum_{j=0}^4 \sum_{k=0}^1 C_i^1 C_j^4 C_k^1 \{1 + \exp[-\beta(6-i-j-k)\epsilon - \beta\mu_b]\}^{-1} n_1^{1-i} n_2^{4-j} n_3^{1-k} (1-n_1)^i (1-n_2)^j (1-n_3)^k \quad (13)$$

At the surface layer, where this succession of layers terminates, the following self-consistent condition should be satisfied

$$n_s = \sum_{i=0}^4 \sum_{j=0}^1 C_i^4 C_j^1 \{p[1 + \exp[-(5-i-j)\beta\epsilon - \beta\mu_p]]^{-1} + q[1 + \exp[-(5-i-j)\beta\epsilon - \beta\mu_q]]^{-1}\} n_s^{4-i} n_a^{1-j} (1-n_s)^i (1-n_a)^j \quad (14)$$

where n_s and n_a are the site coverages in the surface and adjacent layers, respectively.

Assuming a given number of layers interpolating between the surface layer and the bulk, we end up with a closed system of algebraic nonlinear equations in the variables $\{n_i\}$, for a known set of parameters $\{T, \mu_b, \mu_p, \mu_q, \epsilon\}$. Multiple roots of this system of equations can be found by numerical methods. The validity of the assumption on the number of interpolating layers needed for a desired accuracy can be verified a posteriori by examination

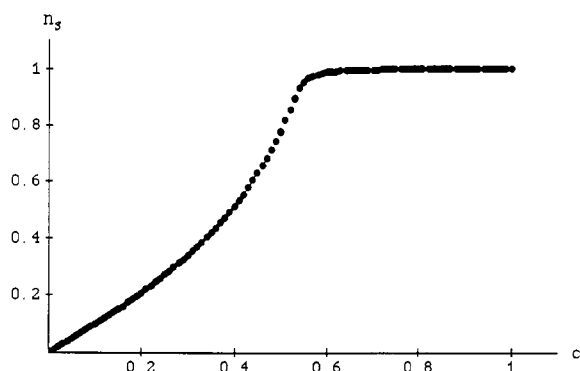


Figure 4. Calculated mean surface coverage n_s of the surface water layer, as a function of the mean concentration c of OH groups in the alkanethiol substrate. The semi-infinite lattice-gas model on the simple cubic lattice, as defined in the text, was used, with the following choice of parameters: $T = 300$ K, $\mu_b = -12$ kcal/mol, $\mu_p = 14$ kcal/mol, $\mu_q = 2$ kcal/mol, $\epsilon = 3.3$ kcal/mol.

of the convergence of the layer coverages far from the surface to the bulk coverage, which is calculated separately from eqs 10–12. For our purposes here, we have found that the choice of five layers in the interpolating layer, $\{n_0 = n_b, n_1, n_2, n_3, n_4, n_5 = n_s\}$, results in a reasonable approximation. The physical solution is selected from among the set of multiple solutions for $\{n_i\}$ by requiring it to have the lowest Helmholtz free energy per site in the interpolating region. For our choice of the interpolating layer, the latter has the following form within the mean-field approximation:

$$f_{sb} = -\frac{1}{2}\epsilon \sum_{i=1}^5 n_i(4n_i + n_{i-1}) - \frac{1}{5}[\mu_b \sum_{i=1}^5 n_i + (p\mu_p + q\mu_q)n_s] + k_B T \sum_{i=1}^5 [n_i \log n_i + (1 - n_i) \log (1 - n_i)] \quad (15)$$

The simple cubic lattice-gas model in this paper is relatively crude, and we do not expect a quantitative fit to experimental data. This requires the use of more realistic lattice-gas models, similar to those for models of ice and bulk water phases. In addition, a more realistic quenched probability distribution of local chemical potentials will be needed, rather than the simple uncorrelated bimodal one used here. Work is in progress in our group to develop and study lattice-gas models incorporating realistic features as discussed above. However, even the simple model presented here demonstrates the essential *qualitative* behavior expected in such a system and indicates how the experimental results, summarized in Figures 1 and 3, can be understood. The numerical computations show that within a certain region in the parameter space $\{T, \mu_b, \mu_p, \mu_q, \epsilon\}$ a phase transition from low to high surface coverage n_s occurs as a function of p and, thus, of c , since, according to our assumptions, $c \approx p$. At the same time, the other layers in the interpolating region remain at low coverage.

Depending on variations in the values of the above parameter set, we have observed either a true first-order phase transition, characterized by a finite jump in the surface coverage $n_s(c)$, a second-order transition, characterized by a cusp in $n_s(c)$, or a rounded transition, characterized by an analytic $n_s(c)$, which is, however, highly nonlinear near a threshold in c , whose location also depends on the particular value of the chosen parameters. Figure 4 displays an $n_s(c)$ curve of the latter type for one particular point in the parameter set. We note, however, that our model uses a mean-field approximation. It could be that the first- and second-order phase transitions between two distinct phases, resulting from the mean-field calculation, are an artifact of this approximation. In that case, the transition will become rounded, and only a single phase will be found. However, this should not affect our *qualitative* conclusions regarding the role of the surface layering in the observed highly nonlinear wetting behavior as a function of surface OH concentration. A rounded transition, though analytic, may show up as a highly nonlinear phenomenon, such as the apparent transition in contact angles versus surface

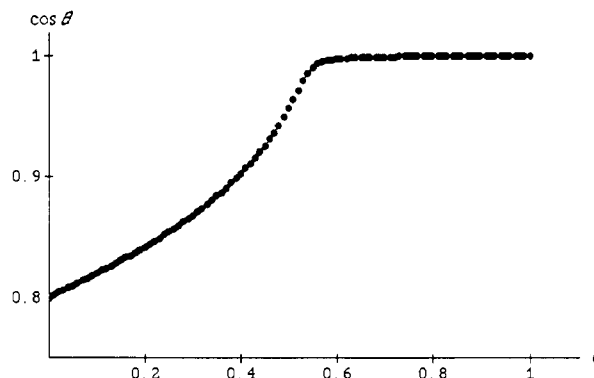


Figure 5. Calculated variation of the contact angle $\cos \theta(c)$ corresponding to wetting of the system (substrate/a single condensed water layer/bulk water vapor), for the same set of parameters as in Figure 4, assuming $\cos \theta(c = 0) = 0.8$ and $\cos \theta(c = 1) = 1$ in eq 16. Compare with the experimental curve of Figure 1.

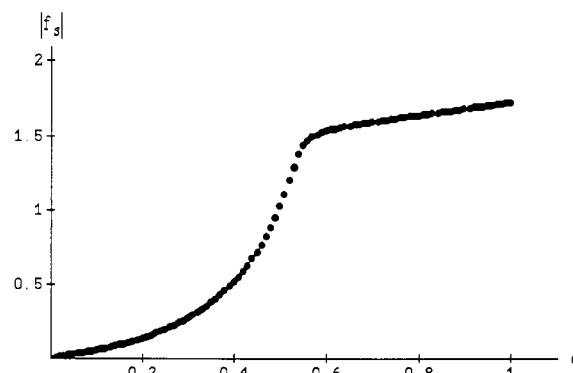


Figure 6. Calculated model variation of f_s , the magnitude of the excess surface free energy, associated with condensed water layer formation (eq 17), versus the mean surface concentration c of OH groups, for the same choice of parameters as in Figure 4. Compare with the experimental curve of Figure 3.

OH concentration, reported here.

The variation of the experimentally measured properties (Figure 1 and 3) with c , the concentration of the OH groups at the surface of the alkanethiol monolayer, is intimately connected with $n_s(c)$ in the lattice-gas model. Since the mixed alkanethiol monolayer surface is potentially covered by a condensed layer of water, the relevant substrate can be thought of as a heterogeneous surface consisting of patches of bare methylated monolayer surface and patches of condensed water on top of predominantly hydroxylated regions. Hence, as a *first approximation*, one can use either eq 1 or eq 2 to obtain the connection between the contact angles on these heterogeneous surfaces and the concentration of the OH groups. Using eq 1, for example, we obtain

$$\cos \theta(c) = n_s(c) \cos \theta(c = 1) + [1 - n_s(c)] \cos \theta(c = 0) \quad (16)$$

Thus, the observed apparent transition in the measured contact angles can be traced to a transition, or a rounded transition, within the simplified lattice-gas model, as shown in Figure 5 for the same choice of parameters as in Figure 4, estimating values for $\theta(c = 0)$ and $\theta(c = 1)$ from the experimental plots in Figure 1. The resemblance between Figure 5 and Figure 1 is striking.

The excess surface free energy f_s , associated with a condensed water layer formation between the organic substrate and bulk vapor, is approximated by the following expression:

$$f_s = f_{sb} + \frac{1}{5}q\mu_q n_s \quad (17)$$

Figure 6 shows variation of f_s with the surface OH concentration, for the same choice of parameters as in Figure 4. Again, this curve is in good qualitative agreement with experimental γ_s^{exp} curve shown in Figure 3.

Final Experiments. The question at this point was how to test experimentally the hypothesis that a formation of a *condensed*

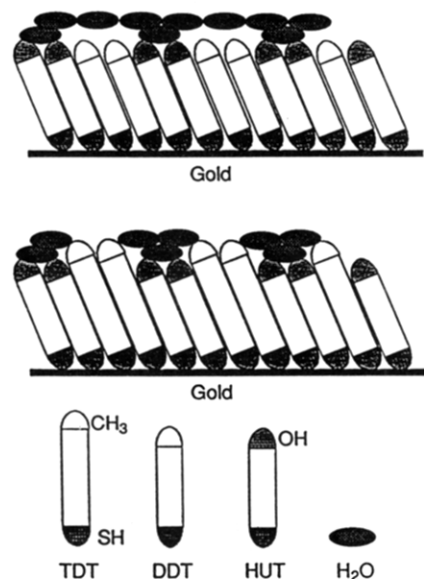


Figure 7. Schematic illustration of mixed monolayers of HUT-DDT (top) and HUT-TDT (bottom) on gold. Note the disruption of a second water layer by the longer methyl-terminated alkyl chains.

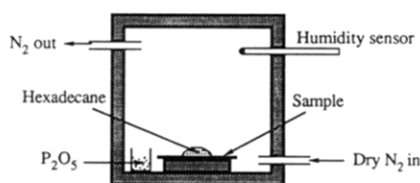


Figure 8. Experimental setup for the measurement of contact angles in controlled relative humidity.

second layer of water molecules is the physical event triggering the transition in the wetting properties. A possible test is to disrupt the formation of this adsorbed water layer, which should result in the complete elimination of the transition. This can be achieved if instead of two molecules having the same length, the C_{12} methyl-terminated component is made longer by two methylene (CH_2) units ($C_{14}H_{29}SH$, TDT). With these C_{14} molecules, the TDT-HUT mixed monolayers will have ethyl groups (C_2H_5) emerging from the surface into the second water layer, thus disrupting its formation (Figure 7). We carried out these experiments and studied the hexadecane contact angles on the TDT-HUT mixed monolayers (Figure 1). Indeed, no abrupt transition was found in the wetting properties of these monolayers. In fact, the cosines of the HD contact angles exhibit a reasonably smooth relationship with the surface OH concentration. It is important to emphasize that in other mixed monolayer systems in which the two components do not have the same length (both for OH and COOH polar groups) the wetting properties are quite smooth with the surface concentration of the polar component.^{49,50} While this result is supportive, it does not provide *direct* evidence for the suggested mechanism. For that, one should eliminate water vapor (decrease the bulk chemical potential) and study HD contact angles conditions as dry as possible. We have therefore modified the experimental setup (Figure 8) so that relative humidity can be measured accurately and quickly (the response time of the Vaisala HMP36 probe was ~ 1 s). The sample was placed in the modified Rame-Hart cell, in which a few small vials containing fresh P_2O_5 were placed. The cell was quickly purged with dry nitrogen, the flow of nitrogen stopped, the HD droplet formed, and its contact angle measured. The relative humidity was measured during the whole process, which took ≤ 5 min, following removal from the thiol solution. Figure 9 presents the hexadecane contact angles at $\leq 2\%$ and at 30% relative humidities. These results show that the wetting behavior observed at 30% relative

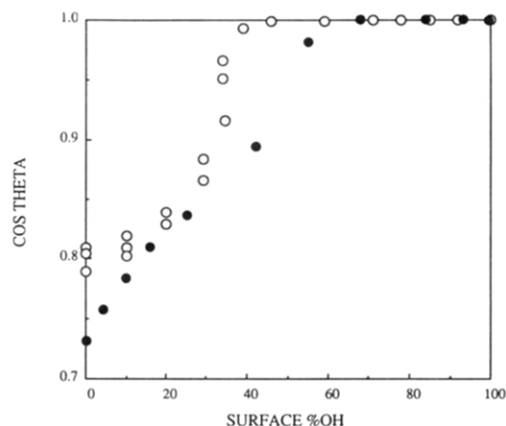


Figure 9. $\cos \theta$ of HD at 30% (open circle) and at $\leq 2\%$ (solid circle) relative humidity for HUT-DDT mixed alkanethiol monolayers on gold, as a function of the surface OH concentration.

humidity has been considerably altered at $\leq 2\%$ relative humidity. This change in behavior supports our idea that adsorbed water vapor is crucial in the wetting behavior of these hydroxylated surfaces.

Arguments and Conclusions

In concluding this paper, we feel that there are some open questions that still have to be addressed. For example, immiscibility of water and hydrocarbons may misleadingly result in a naive conclusion that HD cannot wet an OH surface. According to Zisman's theory,⁵¹ however, HD, BCH, and ME should spread completely on the relatively high energy condensed water layer, because their surface tensions are lower than γ_c for this surface (we measured for HUT/Au $\gamma_c \approx 72$ dyn/cm⁴²). In our model, we picture the 100% OH surface (100% HUT) as covered by a condensed (crystalline- or ice-like) layer of water molecules. Our data show that only HD and ME spread completely ($\theta < 10^\circ$), and we cannot explain why BCH wets the surface with $\theta \sim 13^\circ$. However, we note that while HD and ME are linear molecules, BCH is a cyclic, bulky one. The relationship between the *molecular shape* of a wetting liquid and its contact angle on a given surface has not as yet been addressed. In any case, all these liquids sense a change in wetting conditions, as demonstrated by a steep change in the contact angles when $c \sim 0.35$. This region corresponds, in our model, to the formation of a continuous condensed water layer.

At first sight, the spreading of HD on the condensed water surface seems to be at odds with the observation that HD does not spread on the surface of bulk liquid water. However, results of Monte Carlo simulations discussed above indicate that the water molecules are adsorbed at "lattice sites" on the HUT/Au monolayer, thus forming a crystalline-like, two-dimensional structure. Experimental support for such an epitaxial adsorption of water on hydroxylated surfaces is provided by a very interesting, recent work of Lahav, Leiserowitz, and co-workers.⁵² Their study monitored the inducement of ice nucleation by alcohols arranged in monolayers at the surface of water drops, indicating onset of ice-like order within water layers in the vicinity of a hydroxylated surface of the organic Langmuir monolayer. Therefore, we should not be comparing the wetting of crystalline-like water layers with that of bulk liquid water. This can be further supported by other experimental facts; for example, HD spreads completely ($\theta < 10^\circ$) on clean silica, and silica is known to have a layer of adsorbed/bound "ice-like" water.⁵³

It could be argued that wetting of hydrocarbons, C_nH_{2n+2} , on ice should serve as a test for the wetting scenario discussed in this

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paper. However, note that hexadecane, for example, freezes above 0 °C and therefore cannot serve as a test case for wetting on ice. Furthermore, even those hydrocarbons that freeze below 0 °C ($5 < n < 14$) cannot serve as test cases, since it is known that a relatively *thick* layer of liquid water (~ 100 Å) exists at the surface of ice.^{54,55} The lower limit of $n > 5$ is imposed because pentane (C_5H_{12}) spreads on liquid water.⁵⁶ We argue, however, that the crystalline-like layer of water on the OH surfaces in the present study is akin to the very thin (~ 14 Å) film of water, *in contact with water vapor only*, as observed by Garoff and co-workers in a recent study.³⁷ This is in contrast with the thicker (~ 100 Å) precursor wetting film *in the vicinity of the bulk wetting meniscus*, observed in the same study. Thus, we conclude that the adsorbed water layer, which triggers the wetting transition reported here, must be different in properties from bulk liquid water.

A question can be raised regarding the stability of the mixed monolayers with respect to phase separation and whether the latter can serve as an alternative scenario for the observed phenomenon. Phase separation in such systems should be characterized by cluster formation of one phase within the other and their growth with time. Such cluster formation can be detected, in principle, by monitoring contact angle hysteresis with time. However, we have recently reported that high surface free energy monolayers are not stable and tend to reorganize in time scales of minutes to hours.⁵⁷ Furthermore, the monolayers under study are made of chemisorbed long-chain molecules, which should impede their lateral motion within the monolayer. This makes the phase separation scenario less likely, in our opinion.

In our opinion, the current treatment of wettability of heterogeneous surfaces lacks a firm theoretical foundation. In the Cassie equation, a simple concentration-weighted averaging is performed on the contact angles of the two homogeneous surfaces. On the other hand, in the Israelachvili and Gee approach, such averaging is performed on the polarizabilities or dipole moments of the surface functionalities. Thus, both cases represent concentration-weighted interpolation between two extremes. Once those two extremes are fixed, environmental parameters, such as temperature and relative humidity, play no role in the interpolation. The definition of the contact angle is given by the Young equation:^{58,59}

$$\cos \theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \quad (18)$$

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For *homogeneous* surfaces, evaluation of the interfacial free energies γ_{sv} and γ_{sl} involves only *thermal* averaging over the appropriate equilibrium ensemble. For *heterogeneous* surfaces, on the other hand, a proper statistical treatment should involve a thermal average of the related partition functions at *each* fixed configuration of surface functionalities and not only at the two extreme cases corresponding to homogeneous surfaces. Subsequently, a quenched average of the resulting interfacial free energies, relative to a frozen probability distribution of those surface functionalities, should be performed. This can be demonstrated by simple lattice models, similar to the one discussed here. Such a theoretical investigation is currently under way in our group.

To summarize, we are reporting the first observation of an apparent concentration-driven transition in the cosine of the contact angles of liquids on mixed monolayers. Our substrates contain a quenched mixture of hydrophilic/hydrophobic groups at the surface of closely packed, smooth monolayers, with carefully controlled relative concentrations. These observations are supported by the results of a Monte Carlo simulation and by mean-field calculations on a simplified lattice-gas model. The observed wetting behavior at 30% relative humidity was altered at $\leq 2\%$ relative humidity, as well as when the surfaces of the monolayers were molecularly roughened by the addition of two CH_2 groups to the hydrophobic (CH_3 -terminated) component of the mixed monolayers. It is suggested that this phenomenon is due to a possible (true or rounded) surface phase transition, resulting in the formation of a prewetting water layer. This formation is triggered by variations in the quenched distribution of random surface fields.

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