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Mixed Self-Assembled Monolayers of Alkanethiolates on Ultrasooth Gold Do Not Exhibit Contact-Angle Hysteresis

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Self-assembled monolayers (SAMs) of organic thiolates,^{1,2} with their well-ordered structures, have been shown to be particularly useful for studies of many surface interaction phenomena, such as wetting,³ adhesion,⁴ nucleation and growth,⁵ surface-initiated polymerization,⁶ and most recently, for protein adsorption⁷ and cell attachment.⁸ In addition, proper functioning of many modern nanostructured devices, such as MEMS,⁹ nanoscale switches,¹⁰ and biosensors¹¹ whose design could rely on surface interactions, strongly depends on the interfacial properties of the SAMs.

In principle, direct regulation of the chemical composition of SAMs can be achieved by the preparation of mixed SAMs. One route is to expose a substrate to a solution of two adsorbates in a defined concentration ratio.^{3,12} However, controlling surface concentration requires no preferential adsorption of one of the components and no surface phase separation. Often, higher affinity among adsorbates of the same type could result in the formation of the mixed SAM with the two adsorbates not being randomly distributed.¹³ In this case, mixed SAMs cannot be regarded as mixed at a molecular level. However, because wetting and external reflection Fourier transform infrared (ER-FTIR) spectroscopy measurements are carried out on relatively large surface areas, observed macroscopic surface properties for such mixed SAMs might still resemble those observed for mixed SAMs composed of the molecules distributed randomly.¹⁴ Wetting is uniquely valuable in characterizing surfaces for its combination of high surface sensitivity and applicability to disordered surfaces.¹⁵ Contact angle measurement of a liquid on a solid surface typically yields a single number. The area of a solid in contact with a liquid is large ($\sim 1 \text{ mm}^2$), and the contact angle averages contributions to solid–liquid and solid–vapor free energies from smaller regions ($10\text{--}100 \text{ \AA}^2$) relevant to molecular-scale characterization of surfaces. The form of Young's equation [$\gamma_{LV} \cos \theta = (\gamma_{SV} - \gamma_{SL})$, where γ_{LV} , γ_{SV} , and γ_{SL} are the liquid vapor, solid vapor, and solid liquid tensions, respectively]¹⁶ is such that contact angles can be interpreted only in terms of differences and ratios of surface-free energies, rather than as a direct measure of solid/liquid interfacial free energy or solid/vapor interfacial free energy. Many features of the theoretical underpinnings of wetting remain unsatisfying, and the technique retains a strongly empirical character. For these reasons, the technique of contact angle measurement has been considered to be information-poor, at least relative to some of the modern surface spectroscopy

techniques. As in most instrumental techniques, measurement of contact angles relies heavily on comparisons of measurements in similar systems rather than on interpretation of absolute values obtained from only one system.

It should be emphasized that in using this approach, limitations and approximations of the method should be considered and that for many systems in organic surface chemistry the hysteresis in contact angle ($\Delta\theta$), i.e. the difference between the advancing (θ_a) and receding (θ_r) contact angle (angle, $\Delta\theta = \theta_a - \theta_r$) is far from zero. A large value in hysteresis is commonly taken to indicate a system not at equilibrium. Thus, we use contact angles because they are convenient, very sensitive to details of interfacial structure at the angstrom scale, and applicable to the characterization of solid–liquid interfaces. We believe these measurements at least correlate with thermodynamically significant measures of surface and interfacial free energies. In previous studies, this hysteresis¹⁷ has been greatest for polar contacting liquids and surfaces that are polar, heterogeneous, or rough, and has been least for nonpolar liquids and for surfaces that are smooth, uniform, or nonpolar. Hysteresis appears to be greater on contaminated surfaces, and on monolayers in which a polar group is “buried” beneath the surface.

A second factor that complicates comparisons is the effect of the roughness of the surface on the measured contact angle and the relationship of the measured value to the true contact angle for the surface. Simple thermodynamic arguments¹⁸ predict that on a chemically homogeneous surface with a roughness factor¹⁹ r the observed angle θ is related to the true angle θ_{true} on a smooth surface according to

$$\cos \theta = r \cos \theta_{\text{true}} \quad (1)$$

Consequently, in the absence of metastable states, roughness should increase angles that are greater than 90° and decrease those that are less than 90° . Other investigators^{20,21} have observed that upon roughening a smooth nonpolar surface the advancing contact angle increased, the receding angle decreased, and as a consequence, the hysteresis increased. As the surfaces were made progressively smoother, both the advancing angle and the hysteresis decreased.

The wettability of mixed monolayers is nonideal.²² If the two components of a monolayer were to act independently, then the contact angles would follow Cassie's law,²³

$$\cos \theta_{\text{obs}} = q_1 \cos \theta_1 + q_2 \cos \theta_2 \quad (2)$$

where q_1 and q_2 are the mole fractions of the two components in the monolayer ($q_1 + q_2 = 1$) and θ_1 and θ_2 are the contact angles of the monolayers prepared from each individual component. The wettability of mixed monolayers is not linear in the composition of the surface. In a surface composed of a polar and a nonpolar

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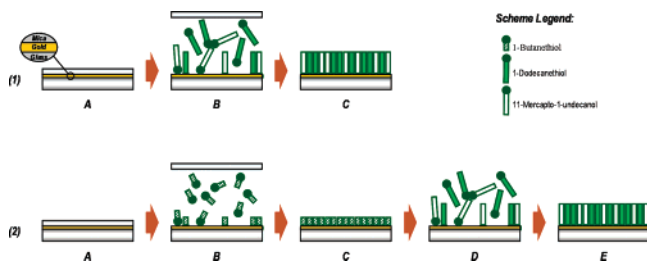
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Scheme 1. Cartoons Showing the in Situ (1) and ex Situ (2) Preparations of Mixed SAMs on Ultrasmooth Gold Surfaces



component, the polar component is more hydrophilic when its concentration in the monolayer is composed largely of the polar component.²²

Recently, we have demonstrated that self-assembled monolayers of both aliphatic and aromatic thiols can be produced with no apparent contact-angle hysteresis.²⁴ This was accomplished by using the thiol solution as a splitting reagent for the removal of the mica from the gold surface in the template-stripping technique. The apparent elimination of surface roughness allows, for the first time, addressing the effect of surface chemical heterogeneity on contact-angle hysteresis. Here we present a study of mixed alkanethiolate SAMs on ultrasmooth gold surfaces, showing that surface chemical heterogeneity does not contribute to contact-angle hysteresis. Determining the critical surface feature size above which contact-angle hysteresis persists is now under investigation in our group.

Mixed SAMs of 11-hydroxyundecane-1-thiol ($\text{HO}-(\text{CH}_2)_{11}-\text{SH}$) (**1**) and dodecanethiol ($\text{CH}_3-(\text{CH}_2)_{11}-\text{SH}$) (**2**) were prepared on gold (111) surfaces by two different methods as shown in Scheme 1. In case of an in situ preparation, the mica layer was stripped by submerging a series of the mica/gold/glass assemblies (prepared according to our published procedure²⁴) in solutions of **1** (1 mM), **2** (1 mM), and mixtures of **1** and **2** in a range of mole fractions, but with the same total concentration of thiolate moieties (50/50, 25/75, and 75/25), respectively, in ethanol for ~ 1 h; the mica was removed easily with tweezers.²⁴ The resulting surfaces were left in the respective thiol solution overnight, were then washed repeatedly with ethanol (3×30 mL), dried with a soft stream of nitrogen, and stored under nitrogen.

Since the two thiols penetrated from solution into the gold mica interface, there was a concern that the interaction of the terminal OH group in **1** with the mica surface might skew the results. Therefore an ex situ preparation was developed. The mica was first stripped by submerging the mica/gold/glass sandwich in a 100 μM solution of butanethiol (**3**) in ethanol; the resulting SAMs were then immersed into solutions of **1**, **2**, and mixtures thereof, using the same procedure. The new SAMs were thus produced by exchanging the short $\text{CH}_3(\text{CH}_2)_3\text{S}^-$ with the longer $\text{CH}_3(\text{CH}_2)_{11}\text{S}^-$ and $\text{HO}(\text{CH}_2)_{11}\text{S}^-$ adsorbates. The composition of the mixed SAMs was precisely determined by ER-FTIR spectra recorded on Thermo Nicolet 760 spectrometer equipped with an MCT-A detector with 2 cm^{-1} resolution (2048 scans) using a 80° fixed grazing-angle attachment (SpectraTech), and showed direct correlation with their wetting properties.^{3,12}

The thickness of these mixed SAMs was estimated by ellipsometry. At least three individual points were measured on each sample, with an assumed refractive index of 1.462 for the organic film. The results (Table 1) are in a good agreement with the theoretical predictions and earlier results for perfect SAMs.²

Static contact angles were determined at room temperature by the sessile-drop method. Maximum advancing and minimum receding contact angles for water were found at a tilt angle of $\sim 40^\circ$. From the results (Table 1), it becomes obvious that contact-angle

Table 1. Contact Angle Measurements and Ellipsometric Film Thickness for SAMs of Organic Thiols Produced by Thiol Splitting (in situ) and by Thiol Exchange (ex situ)

	θ_a ($\pm 0.5^\circ$)	θ_r ($\pm 0.5^\circ$)	$\Delta\theta$ ($\pm 1^\circ$)	thickness (± 1 Å)
Gold Substrate				
Au (111)	71°	71°	0°	—
In Situ Preparation				
1	32°	32°	0°	11
2	112°	112°	0°	14
1:2 (50:50)	71°	70°	1°	13
1:2 (25:75)	45°	45°	0°	11
1:2 (75:25)	111°	110°	1°	11
Ex Situ Preparation				
1	33°	33°	0°	11
2	112°	112°	0°	13
1:2 (50:50)	72°	71°	1°	11
1:2 (25:75)	45°	45°	0°	11
1:2 (75:25)	111°	110°	1°	11

hysteresis ($\Delta\theta$) is significantly lower than the previously reported values²⁵ and in most cases completely disappears.

In conclusion, we presented the first study of mixed alkanethiolate SAMs on ultrasmooth gold surfaces. By eliminating surface roughness it became possible to investigate wetting properties as a function of surface chemical composition. It was found that contact-angle hysteresis apparently vanished in three different surface compositions. This suggests that surface chemical heterogeneity does not contribute to contact-angle hysteresis in mixed SAMs on ultrasmooth gold surfaces.

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