Depth Sensitivity of Wetting: Monolayers of ω-Mercapto Ethers on Gold

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Wettability is a property of surfaces that is both theoretically and practically important.[2] We[3] and others[4] have shown qualitatively that the wettability of a solid is determined by the structure of its outermost few angstroms. A more quantitative knowledge of the influence on wetting of the depth of functional groups beneath the surface would be invaluable in understanding the intermolecular forces acting at interfaces.[5] Here we correlate the wettability of ordered monolayers of ω-mercapto ethers ($HS(CH_2)_{16}O(CH_2)_nCH_3$; $n = 0$–5)[6] adsorbed on gold with the depth of the polar ether functional group below the solid–liquid interface. Long-chain alkanethiols adsorb from solution onto gold surfaces and form monolayer films in which the hydrocarbon chains are densely packed, all-trans, and tilted about 30° from the normal to the surface.[7,9] Assuming a similar structure for monolayers formed from mercapto ethers (Figure 1), variation in the chain length, n, of the terminal alkyl group provides angstrom-scale control over the position of the polar ether group beneath the surface.

X-ray photoelectron spectroscopy (XPS) and external reflection infrared spectroscopy of these monolayers confirmed their composition. The C–H stretching modes in the infrared indicated crystalline packing in both the polymethylene backbones and the terminal O-alkyl chains.[8] Progressive attenuation of the O(1s)

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(6) These ethers were prepared from $CH_2{=}CH(CH_2)_{14}Br$ by displacement of bromide by RO^-, photochemical addition of thiolacetic acid (Janssen, M. J. In *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Interscience: New York, 1969; pp 720–723), and acidic hydrolysis. $CH_2{=}CH(CH_2)_{14}Br$ was prepared by coupling $CH_2{=}CH(CH_2)_9MgBr$ to excess $Br(CH_2)_5Br$ in the presence of catalytic Li_2CuCl_4 (Tamura, M.; Kochi, J. *Synthesis* **1971**, 303–305). The mercapto ethers were pure by ^1H NMR spectroscopy: mp 29.5–30.5 °C (Me), 29.5–31 °C (Et), 22–23 °C (Pr), 26–27 °C (Bu), 25–27 °C (Pent), 30.5–32 °C (Hex).

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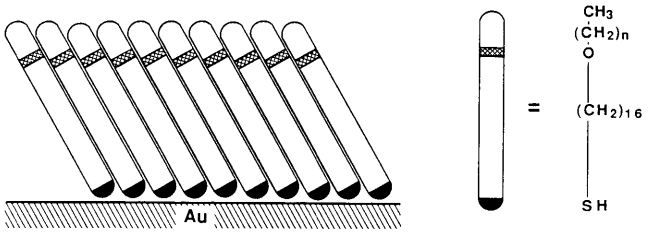

Figure 1. A schematic illustration of a monolayer of $HS(CH_2)_{16}O(CH_2)_nCH_3$ on gold.

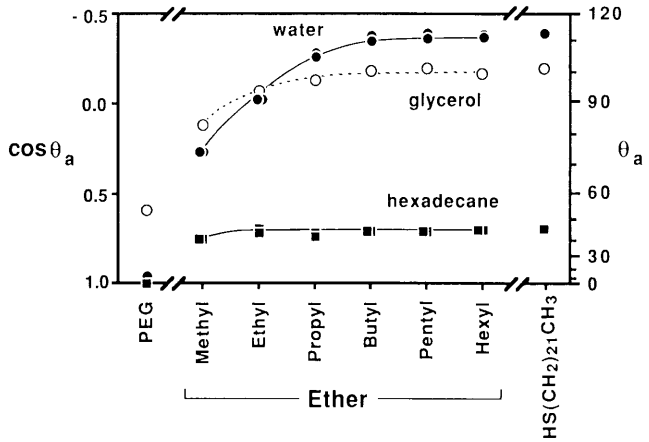

Figure 2. Advancing contact angles of water (●), glycerol (○), and hexadecane (■) on monolayers of $HS(CH_2)_{16}O(CH_2)_nCH_3$ on gold, as a function of the length of the terminal alkyl chain. PEG (poly(ethylene glycol)) is a model for a surface in which the ether linkage is exposed to the contacting liquid. A monolayer of docosanethiol ($HS(CH_2)_{21}CH_3$) on gold models the case in which the oxygen of the ether has no influence on the contact angle. Errors in measurement are within the size of the data points. The value of the contact angle of water on PEG is approximate since PEG rapidly dissolves in the water drop.

peak in XPS with increasing chain length of the alkyl group supported our proposed structural model.

We measured the advancing contact angle, θ_a, of water, glycerol, and hexadecane on the monolayers as the ether group was progressively screened from the contacting liquid by alkyl chains of increasing length.[9] Figure 2 relates cos θ_a to the length of the terminal alkyl chain. A smooth poly(ethylene glycol) (PEG) surface[10] provided a reference for a surface in which ether linkages are exposed to the contacting liquids.[11]

We note two features of Figure 2. First, for sufficiently long terminal alkyl chains, the contact angles approach those observed on monolayers of simple *n*-alkanethiols adsorbed on gold. Thus, the influence on wettability of the ether oxygen disappears entirely. Second, the length of the alkyl chain for which the ether group no longer influences the contact angle varies with the nature of the contacting liquid. Hexadecane, which interacts only by dispersion interactions, is largely screened from the influence of the ether oxygen by a single methyl group and completely screened (to within experimental precision) by an ethyl group. Water, which interacts primarily by hydrogen bonding, senses the ether group at greater depths; limiting contact angles are only reached for the butyl ether. Clearly, water cannot form hydrogen bonds through 4 Å of hydrocarbon. It is more likely that the water molecules are able to penetrate through the terminal alkyl chains, possibly by disordering the outermost part of the monolayer. Water–hydrocarbon contacts are, however, energetically unfavorable and beyond a certain depth the energy of a hydrogen bond to an ether no longer compensates for the concomitant hydrophobic interactions. Glycerol not only forms strong hydrogen bonds but also has considerable dispersive character.[12] The contact angles of glycerol reach a plateau at the propyl ether: at this point the glycerol molecules are beyond the range of significant dispersive interactions with the ether functionality but are perhaps too sterically hindered to penetrate through the terminal alkyl chain to form hydrogen bonds to the oxygen atom of the ether.[13]

In conclusion, the sensitivity of the contact angle of hexadecane to the ether group in this monolayer system extends only ~2 Å, whereas water senses the ether group down to ~5 Å beneath the surface. The greater sensing depth of water may reflect its penetration through short alkyl chains at the surface of the monolayer.

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(8) The C–H stretching modes of the methyl ether are complex; we have not yet analyzed them thoroughly. Full spectroscopic data will be published separately.

(9) For experimental details, see: Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.*, in press.

(10) PEG (MW 7500 av, Polysciences) was cooled from the melt against a polished silicon wafer that had been cooled with a monolayer of $CF_3(CF_2)_7(CH_2)_2SiCl_3$ (Petrarch) to prevent adhesion to the surface. PEG dissolves rapidly in water: the contact angle of water shown in Figure 2 is an estimate of the angle immediately after application (~1 s) of the drop to the surface.

(11) An alternative reference surface—a monolayer of $HS(CH_2)_{11}OH$ on gold—is wet by all three liquids ($\theta_a < 10°$).

(12) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56*(*12*), 40–52.

(13) Relatively long-range polar interactions could also play a role in determining the contact angle. Experiments with monolayers of thiols on silver, in which the alkyl chains are less canted and hence have less freedom to become disordered in the presence of water, should help to distinguish between these two mechanisms.