Self-Assembly of Sulfinate Monolayers on Gold: New Membrane Mimetics

Janice E. Chadwick, David C. Myles,* and Robin L. Garrell*

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024-1569

In this communication, we report the formation and stability of self-assembled monolayers (SAMs) of arenesulfinates on gold. SAMs comprised of alkyl or aromatic thiols and disulfides have been studied extensively.[1,2] The interest in SAMs as membrane analogs is attributable to their ease of preparation and apparent stability. Adsorption of thiols onto gold results in SAMs composed of gold thiolate.[3] Despite the covalent character of the Au–S bond, the oxidative stability of alkanethiol SAMs has recently come into question. Laser-desorption and secondary ion mass spectrometric studies show that alkanethiolate monolayers on gold oxidize in air, forming varying amounts of sulfonates.[4,5] In addition to thiol, thiolate, sulfonate, and fragment ion peaks, the mass spectra contain features that went unmentioned by either Tarlov and Newman or Li et al.[4,5] These peaks are assignable to alkanesulfinates. The presence of both sulfinate and sulfonate oxidation products in the mass spectra raises important questions about SAMs. What factors determine the rate of oxidation? Is it possible to self-assemble sulfinate and sulfonate monolayers directly? Here we begin to answer these questions and demonstrate for the first time that aromatic sulfinates form self-assembled monolayers on gold.

We have used surface-enhanced Raman (SER) spectroscopy to characterize the adlayers that form from benzenethiol, benzenesulfinate, and benzenesulfonate solutions. SAMs are prepared by immersing a roughened gold electrode in a solution of the adsorbate for minutes to hours.[6] We have shown previously that the benzenethiol SAM is stable over the full range of accessible applied potentials, from about −1000mV, where water is reduced, to about +500 mV, where the gold surface is oxidized.[2c,e] A typical SER spectrum of benzenethiol on gold is shown in Figure 1a.[7] Key features are the ν C–S vibration at 694 cm^{-1}, shifted from 698 cm^{-1} in the Raman spectrum, and the absence of the ν S-H vibration found at 2568 cm^{-1} in the spectrum of benzenethiol. Storing the benzenethiol monolayer in air for 10 days caused no change in the SER spectrum. This indicates that the benzenethiol monolayer does not oxidize in air to the sulfinate or sulfonate, unlike the alkanethiolate monolayers.[4,5]

(1) (a) Ulman, A. An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly; Academic Press: New York, 1991.
(2) (a) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. J. Am. Chem. Soc. 1991, 113, 7152. (c) Garrell, R. L.; Szafranski, C. A.; Tanner, W. In Raman and Luminescence Spectroscopies in Technology II; Katzir, A., Ed. Proc. SPIE-Int. Soc. Opt. Eng. 1990, 1336, 264. (d) Bryant, M. A.; Joa, S. L.; Pemberton, J. E. Langmuir 1992, 8, 753. (e) Szafranski, C. A. Ph.D. thesis, University of California, Los Angeles, 1993.
(3) Joo, T. H.; Kim, K.; Kim, M. S. J. Phys. Chem. 1986, 90, 6071.
(4) Li, Y.; Huang, J.; McIver, R., Jr., Hemminger, J. J. Am. Chem. Soc. 1992, 114, 2428.
(5) Tarlov, M. J.; Newman, J. G. Langmuir 1992, 8, 1398.
(6) Surface and monolayer preparation: The polished electrode was roughened in an electrochemical cell with N₂-purged 0.1 M KCl, a Pt auxiliary electrode, and an SCE reference electrode. The roughening procedure consisted of 20 oxidation–reduction cycles between −0.600 and +1.200 V at a rate of 0.5 V/s, pausing at −0.600 V for 8 s and at 1.2 V for 1.2 s, and finally holding the potential at −0.600 V for 5 min. The electrode was then rinsed with distilled deionized water. SAMs were prepared as described in the text.
(7) Raman spectra were obtained with a Jobin-Yvon HR 640 single monochromator with a 1200 groove/mm holographic grating, SPEX liquid N₂-cooled CCD detector, and Kaiser supernotch holographic prefilter. A Lexel 3500 Ar⁺ laser pumped a Lexel 479 cw Ti:sapphire laser to provide 750-nm radiation (focused to a diameter of ca. 400 μm) for the Raman and SER experiments. Incident power was 100 mW, slit widths 200/300/300/200 μm, 1.5 s signal integration coadded three times.
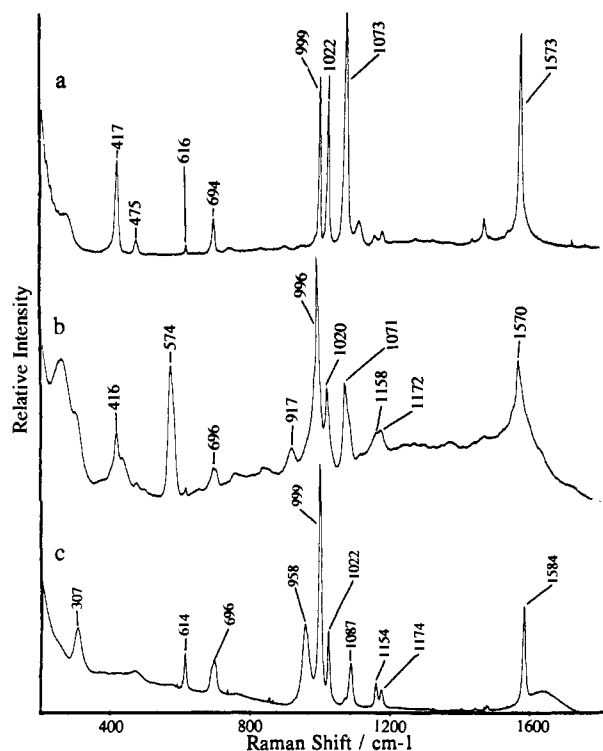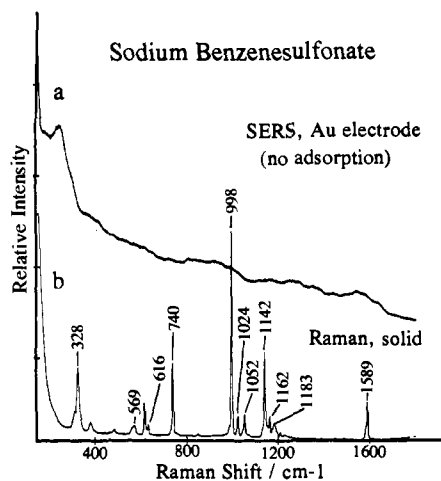

Figure 1. and SER spectra of sodium benzenesulfinate and benzenethiol. (a) SER spectrum of benzenethiol adsorbed on Au. (b) SER spectrum of sodium benzenesulfinate on Au. (c) Raman spectrum of sodium benzenesulfinate (0.01 M in H₂O), 30-s signal integration.

Two sets of conditions were used to form SAMs of benzenesulfinate. First, a roughened gold electrode was immersed for 3 h in a 1 mM solution of sodium benzenesulfinate in benzene and then rinsed gently with benzene and air dried. No benzenesulfinate SER signal could be detected, even after 24 h of immersion. In the second method, the electrode was immersed for 1 h in a 1 mM aqueous solution of sodium benzenesulfinate, air dried, and rinsed gently with water to remove sulfinate not bonded to the surface. The SER spectrum of the resulting benzenesulfinate SAM is shown in Figure 1b.[7] (For comparison, the Raman spectrum of an aqueous solution of the sodium salt is shown in Figure 1c.) To our knowledge, this is the first demonstration that sulfinate SAMs can be prepared by direct adsorption.

To assess qualitatively the packing density and prevalence of defects in the benzenesulfinate SAM, we determined the advancing contact angle for aqueous phosphate buffer.[8] The angle was 111°, comparable to that for benzenethiol monolayers (92°) and terminally functionalized alkyl chains adsorbed from ethanol onto gold (69–112°).[1] This demonstrates the nonpolarity of the outer surface of the monolayer and the lack of penetration of water into the film, evidence that the adsorbed molecules are closely packed. The degree of lateral order has not been determined.

The key feature that distinguishes the monolayer SER spectrum of benzenesulfinate from the Raman spectrum of the aqueous salt and from the SER spectrum of benzenethiol is the symmetric-SO₂⁻ bending vibration at 574 cm^{-1}.[9] This mode is intense in the SER spectrum, but is scarcely apparent in the Raman spectrum. The combined ring and SO₂⁻ stretching vibration at 958 cm^{-1} in the solution spectrum (Figure 1c) shifts

(8) Droplets (1–2 μL) of pH 7.0 phosphate buffer were deposited by micropipet onto the monolayer. The droplet was illuminated by room light and imaged by an f/1.5 lens attached to a Sony HVN-332 CCD camera and viewed on a video monitor; the advancing contact angles given in the text are an average of three successive measurements.

Communications to the Editor

J. Am. Chem. Soc., Vol. 115, No. 22, 1993 10365

Figure 2. and SER spectra of sodium benzenesulfonate. (a) SER spectrum of sodium benzenesulfonate on Au. (b) Raman spectrum of sodium benzenesulfonate (solid).

to 917 cm^{-1} in the SER spectrum (Figure 1b). The C–C ring stretch coupled to the SO$_2^-$ stretch is found at 1087 cm^{-1} in the solution spectrum and 1071 cm^{-1} in the SER spectrum. These shifts indicate that the anion adsorbs on gold through the sulfinate group. The significantly greater enhancement of the in-plane ring modes compared with the out-of-plane modes suggests that, on average, the phenyl ring is perpendicular or tilted, rather than parallel to the surface.

The SER spectrum of benzenesulfinate on gold (Figure 1b) demonstrates that it is possible to form sulfinate monolayers by self-assembly. Because thiols can oxidize in air, it is perhaps surprising that sulfinates have not been observed as routine contaminants in thiolate SAMs. Tarlov and Newman proposed an explanation for this based on the relative adsorptivities of thiols and sulfinates. They found that immersing a mixed octadecanethiol/sulfinate/sulfonate monolayer in 1 mM octa-decanethiol in ethanol results in almost complete displacement of the sulfinate and sulfonate species. Similarly, we find that immersing the benzenesulfinate SAM in fresh 2 mM benzenethiol in ethanol results in complete displacement of the sulfinate by the thiol. Subsequent reimmersion of the thiol-modified gold in a sulfinate solution does not cause thiol displacement. Thus, while oxidation products may be present in alkyl or aromatic thiol solutions used to prepare SAMs, the relative adsorptivities of sulfinates compared with thiols are small, and essentially pure thiol SAMs are expected to form from solutions containing thiol as well as sulfinic acid.

Attempts to form benzenesulfonate monolayers by self-assembly were unsuccessful. Figure 2 shows the Raman spectrum of sodium benzenesulfonate, along with the SER spectrum obtained after overnight immersion of the gold electrode in a 1 mM aqueous solution of the salt, emersion, and drying. The nearly featureless spectrum shows that self-assembly is not a viable route to sulfonate monolayer fabrication. Furthermore, benzenesulfinate SAMs, when stored in air for 10 days, do not oxidize, as assessed by SER spectroscopy. Nevertheless, we have found that it *is* possible to prepare sulfonate-containing monolayers by controlled *in situ* electrochemical oxidation of sulfinate SAMs.[10]

The fact that sulfinate monolayers form in water but not in benzene can be explained by considering solvation and ion pairing. Monolayer formation can be visualized as a two-step process, in which first the salt dissociates to form the solvated sulfinate and counterion, and then the sulfinate adsorbs, displacing solvent from the surface. In water, sodium benzenesulfinate is strongly

solvated and only weakly ion paired. Electrostatic interactions between the anion and the slightly positively charged gold surface promote adsorption. By contrast, the low polarity of benzene, disfavors dissociation of the salt. Also, the double layer formed of benzene-solvated sodium ions would be thermodynamically disfavored.

The different surface affinities of benzenethiol, benzenesulfinate, and benzenesulfonate can be understood by considering the various factors that contribute to the adsorption free energy: electrostatic, charge transfer, exchange, and polarization inter-actions.[11,12] The *relative* electrostatic, exchange, and polarization contributions to sulfinate and sulfonate adsorption can be evaluated computationally. We have calculated the electrostatic potential surface, the HOMO energy, and the HOMO–LUMO gap, which provides a measure of the polarizability, for ben-zenethiolate, benzenesulfinate, and benzenesulfonate *ab initio*.[13]

The gold surface has a slight positive charge when in contact with water with no applied potential. If the relative surface affinities of different species were determined principally by electrostatic interactions, we would predict that both the sulfinate and the sulfonate anions would adsorb more readily than the thiolate. We might expect the sulfonate to adsorb more readily, because the total electrostatic charge on the oxygen atoms [–0.70 + (2 × –0.72)] is greater than that for the sulfinate (2 × –0.79).[13] This runs counter to our observations.[14] Instead, the trend in anion adsorptivities can be explained by examining the relative HOMO energies. The nonelectrostatic (Coulombic) interactions of an adsorbate with a metal surface will be dominated by the overlap between the HOMO of the adsorbate (electron donor) and the LUMO of the metal (electron acceptor): the higher the HOMO energy of the adsorbate, the stronger its interactions with the metal surface.[12,15,16] The magnitude of this stabilizing interaction scales with the reciprocal of the HOMO–LUMO energy difference. To compare adsorbing anions having the same charge, interacting with the same surface, we can focus simply on their HOMO energies. The highest value is found for the thiolate (–1.94 eV), followed by the sulfinate (–3.03 eV) and sulfonate (–5.54 eV); thus, the thiolate interacts most strongly with the metal surface. The HOMO of the sulfinate is substantially lower in energy; hence, stabilizing interactions with the LUMO of the metal are much smaller and lead to a much less stable adsorbate–metal complex.[17]

In summary, we have shown that it is possible to prepare sulfinate monolayers directly by self-assembly on gold. Mono-layers prepared from aromatic thiols and sulfinates are stable in air, but monolayers of benzenesulfinate are easily displaced by benzenethiol. We are currently characterizing these systems by electrochemical and computational studies and are extending this work to the preparation of new types of membrane mimetic systems.

(9) For IR spectra of substituted aromatic sulfinic acids, see Lindberg, B. J. *Acta Chem. Scand.* **1967**, *21*, 2215. IR and Raman frequencies of solid sodium benzenesulfonate have also been assigned, see: Uno, T.; Kuwae, A.; Saito, Y.; Machida, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*(8), 2231.

(10) Chadwick, J. E.; Myles, D. C.; Garrell, R. L., unpublished results.

(11) (a) Morokuma, K.; Kitaura, K. Energy Decomposition Analysis of Molecular Interactions. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; Chapter 10, pp 215–242.

(12) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York 1976.

(13) *Ab initio* RHF calculations were performed with the Spartan program package on a Silicon Graphics Indigo workstation. Basis set: 3–21G* with five spherical d orbitals. Electrostatic charges were calculated by Mulliken population analysis.

(14) Alternatively, it could be argued that the surface affinity is primarily determined by the sulfur–gold electrostatic interactions. Given that the charges on sulfur in benzenethiolate, benzenesulfinate, and benzenesulfonate are –0.54, +1.1, and +1.6, respectively, we would predict the highest surface affinity for the thiol and much weaker interactions for the sulfinate and sulfonate. While this is consistent with the observed relative adsorptivities and displacement results, a more compelling argument is given in the text that follows.

(15) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(16) Pearson, R. G. *Proc. Nat. Acad. Sci. U.S.A.* **1986**, *83*, 8440.

(17) Pearson has associated higher polarizability with higher adsorptivity on soft metals such as gold.[15,16] The HOMO–LUMO gap can be used as a measure of polarizability (smaller gap corresponds to higher polarizabili-ty).[12,15,16] The gaps for the thiolate, sulfinate, and sulfonate are 10.34, 10.63, and 12.67 eV, respectively. The smaller values for the thiolate and sulfinate are consistent with their higher adsorptivities.