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Determination of Surface pK_a Values of Surface-Confined Molecules
Derivitized with pH-Sensitive Pendant Groups

by

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Determination of Surface pK_a Values of Surface-Confined Molecules Derivatized with pH-Sensitive Pendant Groups

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ABSTRACT

Two methods for *in-situ* electrochemical measurements of surface pK_a values are reported. The methods are applied to surface-confined monolayers consisting of organomercaptan molecules derivitized with pH-sensitive pendant groups. The first technique relies upon pH-dependent electrostatic binding of redox probe molecules to the charged monolayer surface: the surface concentration of the probe molecules reflects the degree of surface protonation. The second method relates the differential capacitance of the monolayer-modified electrode surface to the surface pK_a . The two methods yield essentially identical results and are consistent with a recently developed theoretical model. The surface pK_a values of 4-mercaptopyridine and 4-aminothiophenol are 3.7 and 5.7, respectively.

We wish to report two new electrochemical methods for measuring surface pK_a ¹ values of molecules confined to metal surfaces.^{2,3} The methods are applied to surface-confined monolayers consisting of organomercaptan molecules derivitized with pH-sensitive pendant groups, Scheme I. The first technique relies upon pH-dependent electrostatic binding⁴ of redox probe molecules to the charged monolayer surface: the surface concentration of the probe molecules reflects the degree of surface protonation. The second method relates the differential capacitance of the monolayer-modified electrode surface to the surface pK_a . The purpose of this communication is to present the two methods, confirm that they yield similar results, and provide preliminary data that indicate molecules confined to surfaces have different pH sensitivities compared to their bulk-phase analogs.

The first approach for determining surface pK_a values relies on the pH-dependent ion-pairing interaction between many protonated organomercaptan derivatives, such as 4-mercaptopyridine, 4-MP, and 2,6-anthraquinonedisulfonate, 2,6-AQDS, a redox-active probe molecule that undergoes a 2-electron reduction in aqueous solution.⁴ If we assume a linear correspondence between the surface concentrations of protonated 4-MP and 2,6-AQDS, the number of coulombs required to fully reduce 2,6-AQDS reflects the pH-dependent behavior of 4-MP.^{4,5}

Figure 1 shows the titration curve for a surface-confined monolayer of 4-MP, obtained by measuring the charge required to fully reduce adsorbed 2,6-AQDS, as a function of solution pH. A detailed discussion of the method used to obtain the surface

concentration of 2,6-AQDS, $\Gamma_{2,6\text{-AQDS}}$, has been given previously.⁶ Several points are worth noting. First, the half-titration point, which we associate with the surface pK_a , occurs at a different value than for solution-phase 4-MP: $\text{pH} = 3.7 \pm 0.3$ and $\text{pH} = 1.4$,⁷ respectively. The surface pK_a of 4-MP will be affected by the electronic interaction between it and the Au surface, the electrode potential, the nature and concentration of the electrolyte, the 2,6-AQDS/4-MP ion-pairing interaction, and intramonolayer interactions such as hydrogen-bonding. At the present time we are not prepared to comment on the relative importance of these contributions, except to point out that pK_a shifts of similar magnitude have been estimated previously for surface-confined carboxylic acid-terminated *n*-alkanethiol monolayers.^{3e}

Second, the shape of the surface titration curve is different than for an uncomplicated solution-phase titration. About 80% of a solution titration occurs over a range of 2 pH units, while for the surface titration 3-4 pH units are required, again suggesting the importance of intramonolayer interactions.

Finally, the shape of the surface titration curve is largely independent of the nature of the supporting electrolyte, . . . indicating the generality of this technique.

Smith and White⁸ have recently provided a theoretical basis for relating the differential capacitance of a metal electrode coated with a monolayer film of a molecular acid or base, such as that shown in Scheme I, to the fractional extent of protonation. Their model predicts a maximum in a plot of differential

capacitance vs. solution pH close to the surface pK_a of the monolayer film when the electrode potential is held near the potential of zero charge, E_{pzc} .⁹

The differential capacitance-vs.-pH plot for a 4-MP-modified Au electrode is shown in Figure 2a.¹⁰ A capacitance maximum, which we correlate to the surface pK_a , is observed at a solution pH of about 3.6. The general shape of this curve agrees with that predicted by Smith and White's model,⁸ and the surface pK_a derived from these data is in excellent agreement with that observed using the electrostatic binding method discussed earlier (*vide supra*). To insure that the characteristic shape of the capacitance-vs.-pH plot for 4-MP is primarily a function of its pH-dependent properties, we evaluated the differential capacitance of a Au electrode coated with a monolayer of thiophenol, TP, which should not be affected by protonation reactions below pH 10. These data are also shown in Figure 2a, and they clearly indicate no pH-dependent change in capacitance.

We have also determined the surface pK_a of 4-aminothiophenol, 4-ATP. A maximum in the plot of capacitance vs. solution pH, Figure 2b, is observed at about pH 5.7, which can be compared to the solution-phase value, 4.3, determined by titration. The magnitude and direction of the offset is similar to that found for 4-MP, which provides additional support for our contention that maxima in capacitance-vs.-pH plots correlate to surface pK_a values.

We have presented two methods for *in-situ* electrochemical measurement of surface pK_a values. The two methods yield essentially identical results and are consistent with a recently

developed theoretical model.⁸ We are presently examining surface pK_a values for other monolayer-modified metal surfaces, determining the effect of electrode potential on the surface pK_a , and correlating these results to intramonolayer interactions such as hydrogen bonding and ion-pair formation.¹¹

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10. Au wire electrodes were cleaned in "piranha solution" and then immersed in 1-10 mM organomercaptan/EtOH solutions for 1-3 h. The monolayer-modified electrode was immersed in 0.1 M NaClO₄ solutions containing 1 mM carbonate buffer for impedance measurements. Capacitance values are calculated from extrapolation of the linear portions of plots of $\log |Z|$ vs. $\log$ (angular frequency) to the intercept of angular frequency = 0 at each solution pH in the frequency range 10 kHz to 1 Hz. All data were obtained at +0.20 V vs. Ag/AgCl, KCl (sat'd).

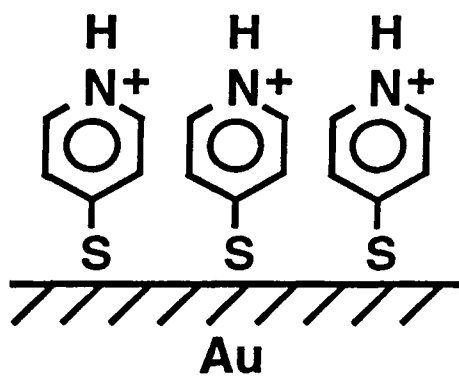
11. Bryant, M. A.; Crooks, R. M.; Smith, C. P.; White, H.S., to be published.

FIGURE CAPTIONS

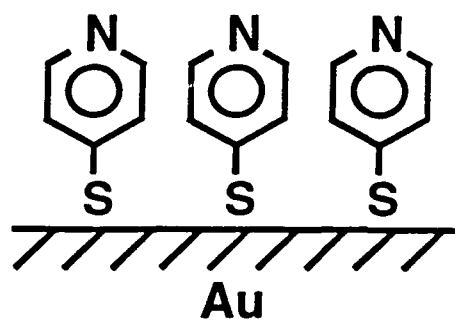
Figure 1. Surface coverage vs. solution pH for 2,6-anthraquinonedisulfonate, (2,6-AQDS), electrostatically bound to 4-mercaptopyridine, (4-MP), confined to Au surfaces in $\diamond$ 0.1 M PO_4^{3-} and $\blacklozenge$ 0.1 M NO_3^- solutions. Electrode area = 0.16 cm².

Figure 2. Differential capacitance vs. solution pH for monolayer films confined to Au surfaces: (a) $\diamond$ 4-mercaptopyridine, (4-MP), in 0.1 M NaClO_4 , decreasing pH; $\blacklozenge$ 4-MP in 0.1 M NaClO_4 , increasing pH; $\circ$ TP in 0.1 M NaClO_4 . (b) Δ 4-aminothiophenol, (4-ATP), in 0.1 M NaClO_4 . Electrode area = 0.30 cm².

Low pH



High pH



Scheme 1/Bryant et al.

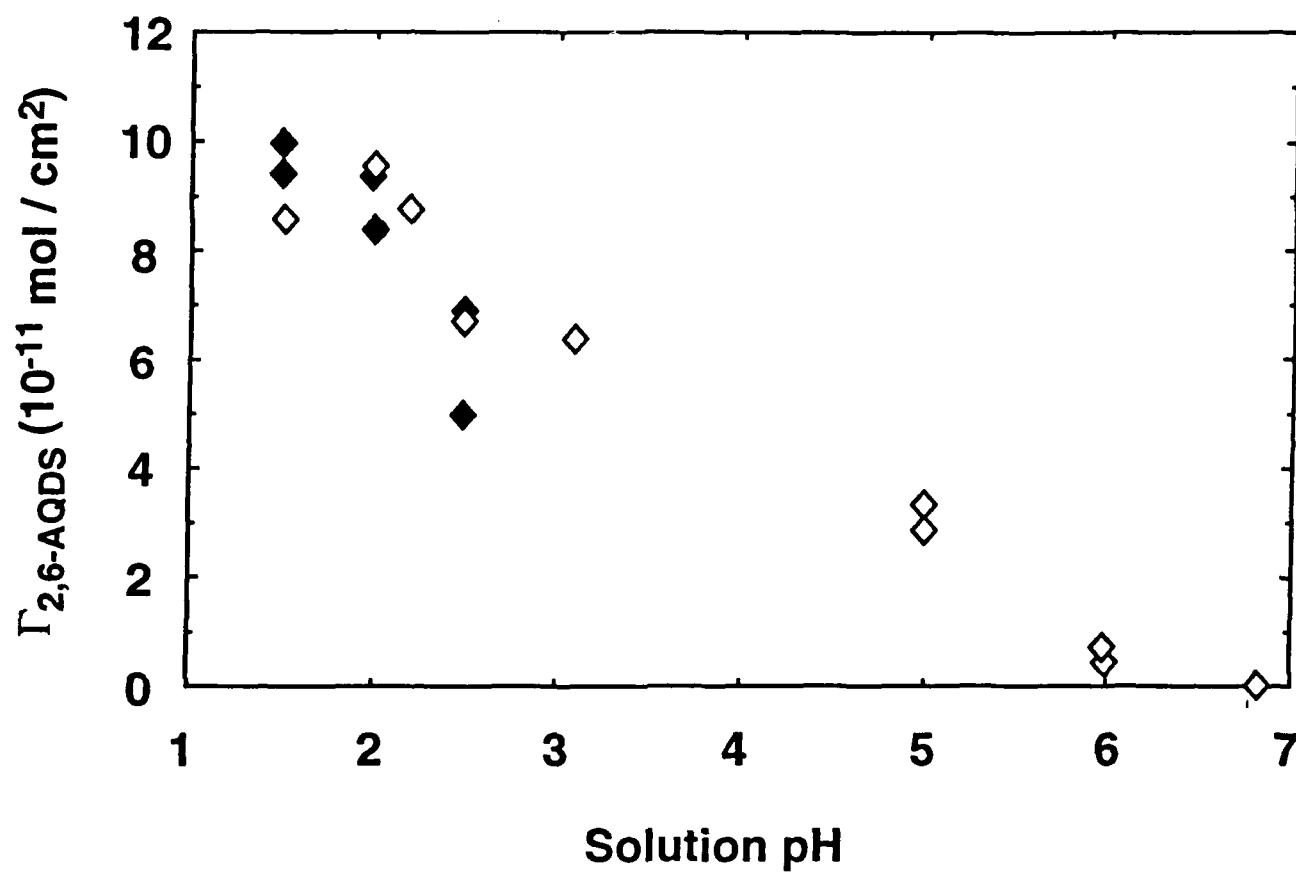


Figure 1/Bryant et al.

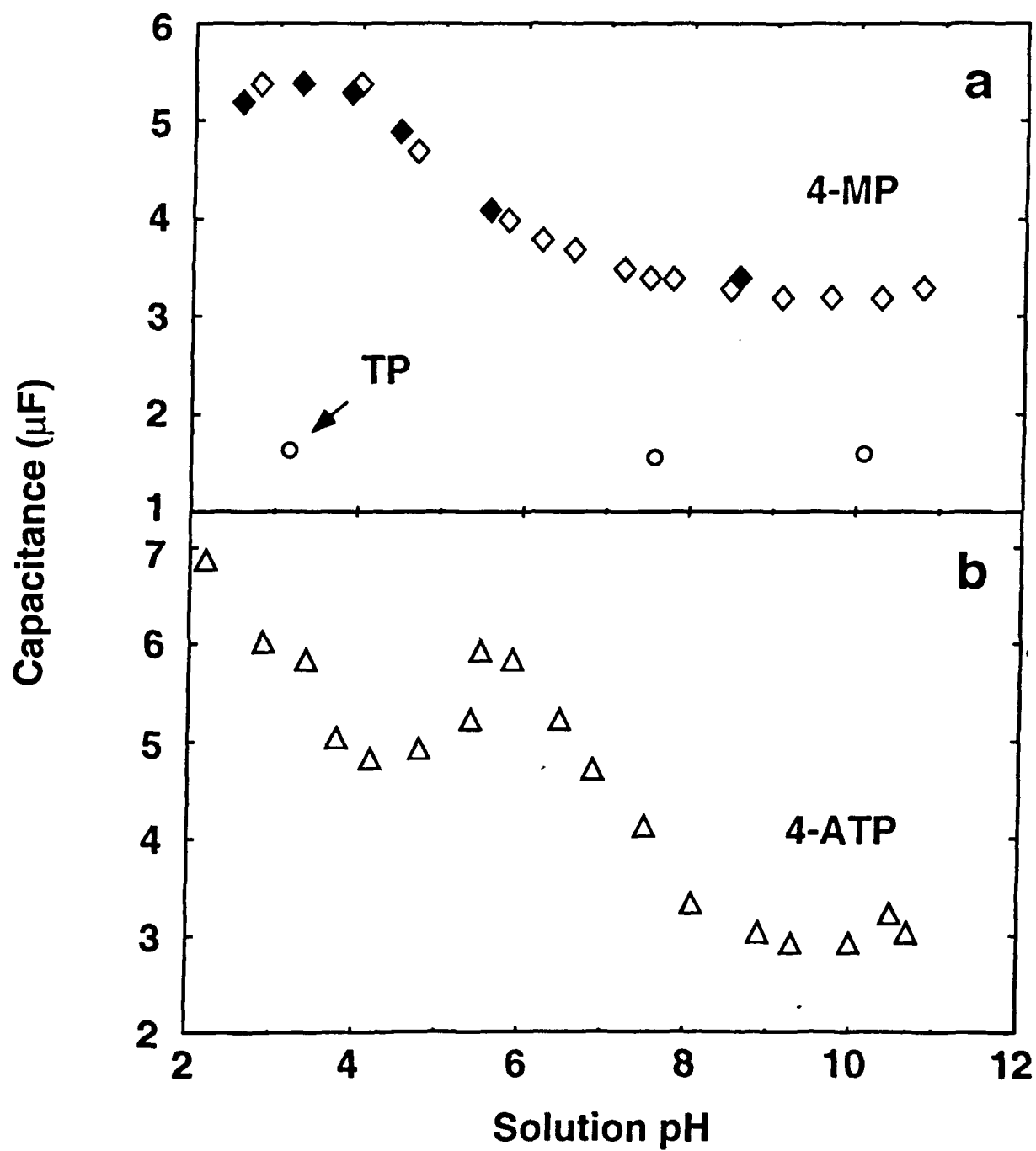


Figure 2/Bryant et al.