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

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Experimental results are provided that correlate the differential interfacial capacitance of electrode surfaces to the pH properties of surface-confined monolayers of molecular bases such as 4-mercaptopyridine and 4-aminothiophenol. In accord with theoretical predictions, the fractional degree of monolayer protonation is shown to be a function of the solution pH and the electrode potential.
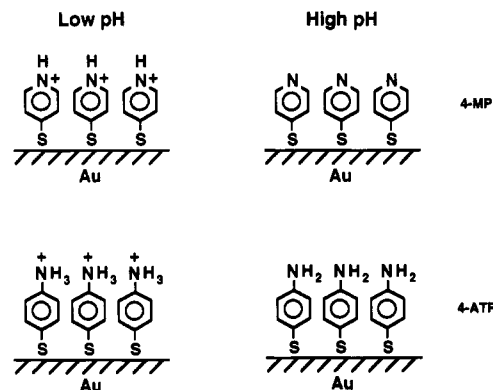
Introduction

We report experimental results which indicate that the interfacial capacitance of electrode surfaces derivatized with molecules containing pH-sensitive pendant groups is related to the fractional degree of acid or base dissociation. Here, we discuss the particular case of the surface-confined bases 4-mercaptopyridine and 4-aminothiophenol, Chart I. When interpreted within the context of the appropriate theory,[1,2] interfacial capacitance measurements reveal the surface pK_a of the organic adsorbates.[3] In this paper we present the measurement technique used to obtain interfacial capacitance-versus-solution pH data, interpret the results in terms of the appropriate theory,[1] and compare surface pK_a data with those obtained in bulk-phase liquids.

A few techniques have previously been used to estimate surface pK_a values for surface-confined monolayer systems. For example, Whitesides et al. used an approach based on contact angle titration to investigate carboxylic acid-terminated *n*-alkanethiol monolayers.[4] Several groups have studied monolayers confined to the water/air interface using surface potential measurements[5,6] and ex situ infrared spectroscopic methods.[7] There have also been reports that relate the interfacial impedance of films on Hg electrodes to their acid–base properties.[8-12] Recently, Mullen et al. used surface-enhanced Raman spectroscopy to investigate the surface acid–base characteristics of several pH indicators and 4-mercaptopyridine adsorbed on Ag surfaces,[13] and Unwin and Bard have reported using microelectrodes to measure the surface acidity of aluminosilicate surfaces.[14] To our knowledge, however, the results presented here provide the first example of a good correlation between experimental results and a theoretical analysis of a well-characterized chemical system.

Chart I

Experimental Section

Interfacial capacitances were determined by an ac impedance method. Au wire electrodes (0.5-mm diameter, 99.999%, Johnson Matthey) were cleaned in "piranha solution" (3:1 concentrated H_2SO_4:30% H_2O_2; *Caution*: piranha solution reacts violently with organic compounds, and it should not be stored in closed containers) and then derivatized in 1–10 mM organomercaptan-EtOH solutions for 1–3 h. After thorough rinsing, the monolayer-modified electrodes were analyzed in $NaClO_4$ solutions containing 10 mM carbonate buffer. The pH of the solutions was adjusted with either $HClO_4$ or NaOH and monitored by a Beckman pH meter. A Solartron Model 1255 frequency response analyzer and EG&G Princeton Applied Research Model 273 potentiostat, both under computer control, were used for data acquisition. Capacitance values were calculated[15] by extrapolating the linear portions of plots of log|Z| vs log(angular frequency) to log(angular frequency) = 0. The resulting data were modeled as a simple circuit consisting of a resistor and capacitor in series. All potentials are reported vs Ag/AgCl, KCl(satd).

The following chemicals were used as received: absolute ethanol (Midwest Grain Products); H_2O_2 (30%), H_2SO_4, and NaOH (Baker); $NaClO_4$ (Smith); $HClO_4$ (70%) and Na_2CO_3 (Fisher); and 4-thiocresol (98%, Aldrich). 4-Mercaptopyridine and 4-aminothiophenol (both 90%, Aldrich) were recrystallized before use. Water was purified with a Milli-Q (Millipore) deionization system.

Results and Discussion

Smith and White[1] recently provided a theoretical basis for relating the differential interfacial capacitance of a metal electrode coated with a monolayer film of a molecular acid or base, such as those shown in Chart I, to the fractional extent of monolayer protonation. In their model, the total interfacial capacitance (C_T) is a function of the film capacitance (C_F), the diffuse layer capacitance (C_S), and the degree of protonation ($C(f)$):

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(3) We define the surface pK_a as the solution pH at which the fractional degree of monolayer protonation is 0.5.

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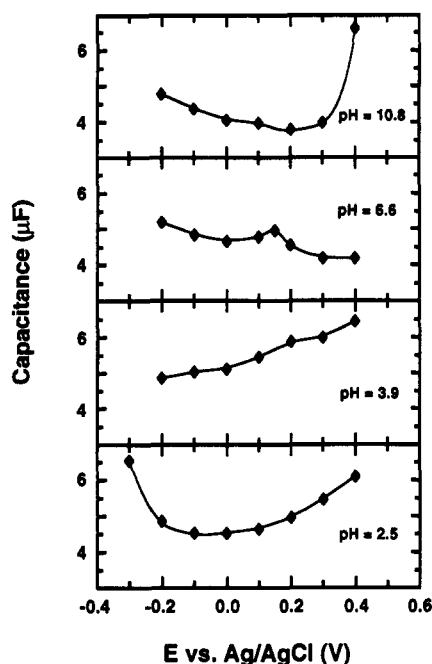
Figure 1. Differential capacitance vs potential for 4-mercaptopyridine (4-MP) confined to Au surfaces in 0.02 M NaClO$_4$ and 0.01 F Na$_2$CO$_3$ at the solution pH values indicated. Electrode area 0.2 cm^2.

$$1/C_T = 1/C_F + 1/[C_S + C(f)]$$

Here, we assume C_F remains constant, while the term $1/[C_S + C(f)]$ varies with potential and solution pH. When the film is uncharged, a plot of capacitance versus potential exhibits a minimum at the potential of zero excess charge (E_{pzc}).[1,16] Since surface-confined bases, such as 4-mercaptopyridine (4-MP), acquire positive charge upon protonation, the E_{pzc} shifts to more negative potentials when the solution pH is lowered. At pH values near the pK_a of the film, $C(f)$ reaches its maximum value which results in a local maximum in C_T.

Figure 1 is a plot of C_T versus potential for a monolayer of 4-MP confined to a Au electrode immersed in 0.02 M NaClO$_4$ at different solution pH values. At pH 10.8, the 4-MP monolayer is deprotonated and a capacitance minimum at about +0.2 V is apparent. This potential corresponds to E_{pzc} for the base form of the 4-MP modified electrode, and it is similar to previously reported values.[17] The experimentally determined capacitive minimum is broader than the theoretical model predicts, but the magnitude of the deviation is typical for Gouy–Chapman-based theories.[16] As the solution pH is lowered to 6.6 and further to 3.9, a peak, which correlates to $C(f)$ in the theoretical model, emerges near +0.2 V. At pH 2.5, a new capacitance minimum appears centered near –0.1 V, which corresponds to E_{pzc} for the fully charged monolayer. These data qualitatively confirm the essential features of the theoretical treatment.[1]

A plot of differential capacitance versus pH for a 4-MP-modified Au electrode is shown in Figure 2a. The measurement was made at +0.2 V, which is near E_{pzc} for the uncharged 4-MP film. The general shape of this curve agrees with that predicted by the theory,[1] although it predicts a less pronounced capacitance maximum. Ac-
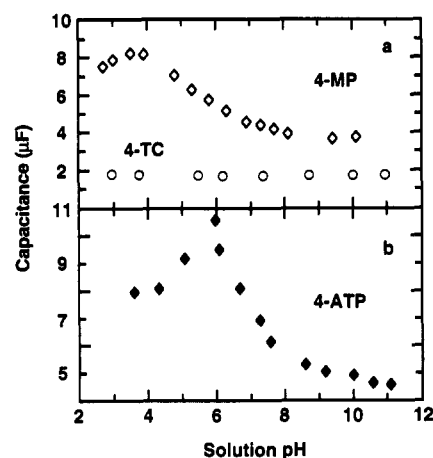

Figure 2. Differential capacitance vs solution pH for monolayer films confined to Au surfaces: (a) ◇, 4-mercaptopyridine (4-MP) in 0.02 M NaClO$_4$ and 0.01 F Na$_2$CO$_3$; ○, 4-thiocresol (4-TC) in 0.02 M NaClO$_4$ and 0.01 F Na$_2$CO$_3$; (b) ◆, 4-aminothiophenol (4-ATP) in 0.02 M NaClO$_4$ and 0.01 F Na$_2$CO$_3$. Electrode area 0.3 cm^2. Electrode potential +0.2 V.

cording to the theory, the potential separation between the E_{pzc} for the charged and uncharged films is dependent only upon C_F. Using the data shown in Figure 1, we estimate a value of 35 μF/cm^2 for C_F. This value is of the same magnitude as that calculated for a 0.5-nm-thick monolayer of pyridine (ϵ = 12.3): 22 μF/cm^2.[18] Taking C_F = 35 μF/cm^2 and C_S = 40 μF/cm^2 (at E_{pzc}),[19] we calculate a theoretical value for the surface pK_a about 1 pH unit higher than the solution pH at the capacitance maximum (pH 3.6) for the conditions used to obtain the data in Figure 2. Therefore, we estimate that the 4-MP surface pK_a is 4.6 ± 0.5 at +0.2 V. This value can be compared to the bulk-phase pK_a of 4-MP which is 1.4.[20] This surprisingly low bulk-phase pK_a value probably results from keto-enol tautomerism.[21] Theoretical calculations indicate that, in the absence of tautomerism, the bulk-phase pK_a would be at about pH 6.[22] Importantly, the surface pK_a is a strong function of the electrode potential, varying over about 6 pH units within a potential range of ±1 V versus E_{pzc},[1] so the experimental value reported here is only correct at +0.2 V. At more positive potentials the surface pK_a will shift to lower values, while at negative potentials it shifts in the opposite direction.

To ensure that the characteristic shape of the capacitance-versus-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 4-thiocresol (4-TC), which should not be affected by changes in the solution pH. These data are also shown in Figure 2a, and they clearly indicate no pH-dependent change in capacitance.

We have also used this approach to determine the surface pK_a of 4-aminothiophenol (4-ATP). A maximum in the plot of capacitance versus solution pH, Figure 2b, is observed at about pH 5.9, from which we estimate the surface pK_a to be 6.9 ± 0.5 at +0.2 V. This value is also higher than the bulk-phase value, pH 4.3, determined by titration. However, the magnitude and direction of the offset are similar to those found for 4-MP, which provides

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(17) Under a variety of conditions, the Au E_{pzc} has been reported as +0.2 ± 0.1 vs Ag/AgCl, KCl(satd). See: (a) Hamelin, A.; Stoicoviciu, L. *J. Electroanal. Chem.* 1987, 234, 93. (b) Van Huong, C. N.; Parsons, R.; Marcus, P.; Montes, S.; Oudar, J. *J. Electroanal. Chem.* 1981, 119, 137.

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additional support for our contention that maxima in capacitance-versus-pH plots correlate to surface pK_a values. Experiments not shown here indicate that the capacitance-versus-solution pH behavior for 4-MP and 4-ATP is largely independent of the identity of the supporting electrolyte.

Conclusions

To summarize, we have presented a new method for in situ electrochemical measurement of surface pK_a values as a function of the electrode potential. The results are in qualitative agreement with a recently developed theory,[1] but a number of discrepancies are apparent. These probably arise from intramonolayer interactions and double layer effects which are not presently accounted for by the theoretical treatment. We are presently trying to better correlate the theory to the experimental results by examining surface pK_a values for other monolayer-

modified metal surfaces and then correlating the results to effects arising from intramonolayer interactions, such as hydrogen bonding and ion-pair formation, and the electrode potential.[23]

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