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Ion-Selective Monolayer Membranes Based upon Self-Assembling Tetradentate Ligand Monolayers on Gold Electrodes. 2. Effect of Applied Potential on Ion Binding

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Abstract: The role of the externally applied potential in the functioning of self-assembled organized monolayers on electrodes is investigated for the first time. It is shown that the selective ion binding to monolayer membranes comprising thiobis(ethyl acetoacetate) (TBEA) is crucially dependent upon the applied potential. Thus, while at a certain applied potential (0.15 V vs SCE) no ion binding can be detected electrochemically in acid or neutral solutions, the amount of bound ions increases markedly at either positive or negative excursions from this potential. These findings are supported by independent optical and wettability measurements. The potential of minimal ionic binding is experimentally identified with the potential of zero charge (the PZC), and a mechanism is suggested which accounts for the influence of the applied potential on the ionic binding to TBEA monolayers. The mechanism involves field-driven enolization and complexation at positive rational potentials and the formation of weaker, positively charged complexes at negative rational potentials.

Introduction

We have previously shown that molecular self-assembly on gold electrodes of mixed monolayers comprising a "receptor molecule" (2,2′-thiobis(ethylacetoacetate) (TBEA) or 3,3′-thiobis(propyl acetoacetate) (TBPA) and a surface-sealing long-chain amphiphile (*n*-octadecylmercaptan (OM) or *n*-octadecyltrichlorosilane (OTS)) can produce ion-recognizing monolayer membranes.[1,2] Thus, selective response for certain divalent ions, such as Cu^{2+} or Pb^{2+}, has been observed, in the presence of otherwise interfering ions, such as Fe^{2+} or Fe^{3+} (see Figure 1a). This ionic recognition is based upon selective binding of ions of appropriate coordination and geometric requirements to the ligand molecules in the monolayer membranes,[2] thereby allowing electron transfer with the gold electrode to occur, while nonbinding ions are denied access to the electrode by the same monolayer membrane. We have shown that the electrochemical behavior provides an effective means for probing the selective nature of such systems.

The formation of metal ion complexes with β-diketonate ligands usually requires transformation of the ligand to the enol from (see e.g. Figure 1 in ref 2), as is indeed indicated in our earlier experiments with TBEA monolayer membranes.[1] The complexation process involves the release of protons and is therefore pH dependent, occurring primarily in basic solutions; in acid solutions the equilibrium is shifted in the other direction, strongly inhibiting complex formation. The fact that the above-mentioned experiments with TBEA-based monolayer membranes, indicating the binding of certain ions (e.g. Cu^{2+}),[1,2] have been mostly conducted in acid media, where the formation of a complex between the metal ion and TBEA in the monolayer is highly unfavorable, is therefore rather intriguing.

It appears quite clear that other factors influence ion binding to TBEA monolayer membranes under our experimental conditions. The most prominent element likely to have a substantial influence is the externally applied potential. A thin insulating film on an electrode may experience enormous electric fields under quite mild conditions, as already pointed out by e.g. Middleton and Pethica.[3] Thus, as an example, a 10-Å insulating monolayer on an electrode immersed in an electrolyte solution and subjected to an applied voltage of, say, 1 V would experience an electric field of the order of 10^7 V/cm. Such an electric field may be expected to affect considerably the structure or functioning of monolayer systems on electrodes. This notion prompted us to conduct a detailed study of the importance of the applied potential in such cases.

In the present paper the influence of the applied potential on the ionic binding of TBEA monolayer membranes is explored. It is shown that the external voltage promotes the complexation; moreover, the amount of bound ions depends strongly on the applied potential, with little or no binding at the potential of zero charge (the PZC). These findings are strongly supported by independent, nonelectrochemical techniques, i.e. ellipsometry and wettability measurements. A mechanism for the ionic binding to TBEA monolayer membranes under the influence of an electric field is presented.

Experimental Section

Details on chemicals used, synthetic procedures, and contact angle measurements are given elsewhere.[2] Monolayer-coated gold electrodes, i.e. Au/TBEA, Au/(TBEA+OTS) (sequential adsorption of TBEA and OTS), and Au/(TBEA+OM+OTS) (simultaneous adsorption of TBEA and OM followed by OTS adsorption), have been prepared as previously described.[2] Ethyl acetoacetate (EAA) (BDH, 99%) and EDTA, disodium salt (Baker, AR) were used as received.

Ellipsometry. Ellipsometric measurements were carried out with a Rudolph AutoEL-IV null ellipsometer, at two discrete wavelengths of 546.1 and 632.8 nm and an angle of incidence of 70°. Film thicknesses were calculated with use of a film refractive index of $n_f = 1.54$, $k_f = 0$. $\delta\Psi$ and $\delta\Delta$ were calculated by subtraction of Ψ and Δ of the same gold slide prior to monolayer adsorption. The standard deviation in the results (typically for 10 experimental points on a 1-cm^2 area) for transparent films (see below) was usually <±1 Å. Slides were thoroughly rinsed (with chloroform after adsorption, and with water after treatment in aqueous solution) and dried under a flow of argon before measurements.

UV-Vis spectroscopy. UV-vis spectra were measured with a Hewlett-Packard Model 8450A diode array spectrophotometer.

Electrochemical Measurements. DC measurements were performed in a conventional three-electrode cell, as described elsewhere.[2] All potentials are given with respect to a KCl-saturated calomel electrode (SCE). First scan voltammograms are always shown in the figures.

AC-impedance measurements were carried out with a Solartron Model 1286 potentiostat coupled with a Solartron Model 1250 frequency response analyzer. The impedance was measured at seven discrete frequencies per decade, in the range 0.1 Hz to 65 kHz, at an amplitude of 5 mV (rms). The results were treated by using the complex capacitance presentation.[4]

Gold Electrodes. The gold electrodes were prepared by sputter deposition of ≈1000 Å gold on glass microscope slides, as described elsewhere.[2] The deposition was followed by annealing for 2.8 h at 250 °C

[†] Department of Materials Research.

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(1) Rubinstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988**, *332*, 426; **1989**, *337*, 514.

(2) Steinberg, S.; Tor, Y.; Shanzer, A.; Rubinstein, I. Submitted for publication.

(3) Middleton, S. R.; Pethica, B. A. *Faraday Symp. Chem. Soc.* **1981**, *16*, 109.

(4) Rubinstein, I.; Sabatani, E.; Rishpon, J. *J. Electrochem. Soc.* **1987**, *134*, 3078.

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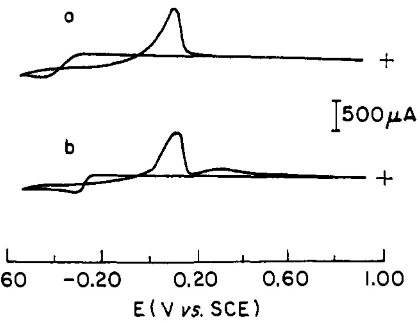

Figure 1. Cyclic voltammograms in 0.10 M H_2SO_4 containing 1.0 mM Cu^{2+} and 3.0 mM Fe^{3+} (electrode area 0.63 cm^2; scan rate 0.10 V/s) for (a) Au/(TBEA+OTS) and (b) Au/TBEA.

(Chidsey et al.[5] reported that long annealing at 225 °C of evaporated gold films gave rise to larger crystallites with flatter tops). This thermal procedure produces polycrystalline gold, the voltammogram of which in sulfuric acid is qualitatively similar to that of gold substrates treated according to our previous procedure[1,2] (i.e. annealing for 10 min at 400 °C, see Figure 2a in ref 2). However, the new annealing procedure results in a surface area lower by ≈50% with respect to the previous treatment, indicating a higher degree of surface smoothness.

A significant result concerning the effect of the gold surface smoothness is shown in Figure 1b, where the electrochemical response for Cu^{2+} and Fe^{3+} is examined with a "smoother" gold electrode (annealed 2.8 h at 250 °C) coated with a monolayer of TBEA alone (Au/TBEA), i.e. without any additional blocking component. The resultant electrode is effectively blocking toward Fe^{3+}, displaying a behavior qualitatively similar to that shown in Figure 1a for a Au/(TBEA+OTS) electrode (except for the existence of a small Cu UPD oxidation peak in the positive scan). This observation is a marked improvement with respect to the results obtained with the previous gold thermal treatment (10 min/400 °C), where no blocking of Fe^{3+} ions can be achieved in the absence of a monolayer blocking component (see e.g. Figure 2b in ref 1). Note, however, that Au/(TBEA+OTS) or Au/(TBEA+OM+OTS) electrodes are used below in those cases where blocking is essential, due to the superior electrochemical behavior compared with Au/TBEA (see Figure 1).

The result in Figure 1b demonstrates the influence of the gold substrate smoothness on the monolayer packing and space-filling properties, and hence on the functioning of the monolayer system. While a self-assembled TBEA monolayer on our previous (10 min/400 °C) sputter deposited gold covers up to ≈80% of the gold surface[1] and thus does not block it, the same monolayer adsorbed under similar conditions onto the "smoother" gold (2.8 h/250 °C) packs densely enough and with essentially no defects, so as to provide in itself the necessary surface blocking and selectivity.

Results and Discussion

Ionic Stripping Experiments. Stripping experiments were designed to quantitatively assess the effect of the applied potential on the binding of various ions to TBEA-based monolayer membranes on gold electrodes. The monolayer-coated electrode was dipped in a solution containing the ion of interest (e.g. Cu^{2+} or Pb^{2+}) and then electrochemically pretreated either by cycling the potential in the usual manner (i.e. as in Figure 1a) or by polarizing the electrode at a certain fixed potential for a certain length of time. The electrode was then thoroughly rinsed with water and transferred to a background solution (0.1 M H_2SO_4), where a voltammogram was recorded and the amount of bound ions determined by integration of the charge under the reduction or the re-oxidation peaks for the bound ions. (Upon repetitive cycling in background solution the monolayer-bound ions are gradually lost to the solution, hence the term "stripping".)

Figure 2 presents the results of two stripping experiments, emphasizing the intringuing questions that prompted this study. It is clear from Figure 2 that some Cu^{2+} binding to a TBEA monolayer is obtained at open circuit when the electrode is dipped for a prolonged period of time in a slightly basic solution containing Cu^{2+}, where complex formation is favored (Figure 2b; compare with Figure 3 in ref 1). On the other hand, no Cu^{2+} stripping peaks are observed with the same electrode after cycling (either one cycle or repetitive cycling) in acid solution containing Cu^{2+} (Figure 2a).

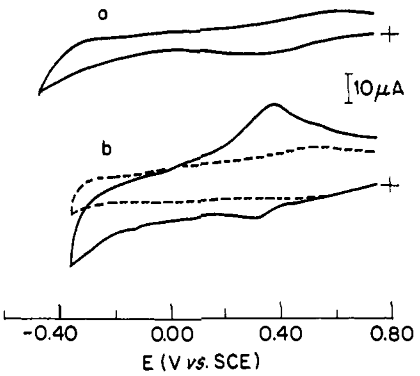

Figure 2. Cyclic voltammograms in pure 0.10 M H_2SO_4 for an Au/TBEA electrode (electrode area 0.63 cm^2; scan rate 0.10 V/s): (a) after one cycle in 0.10 M H_2SO_4 + 1.0 mM Cu^{2+}; (b) after 60 min in saturated Cu(II) acetate + acetic acid (pH 7.5) at 50 °C. Dashed line, after 2 min of continuous cycling.

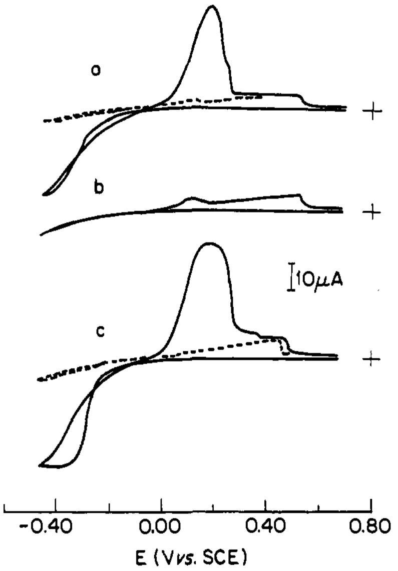

Figure 3. Cyclic voltammograms in pure 0.10 M H_2SO_4 for an Au/(TBEA+OM+OTS) electrode (electrode area 0.63 cm^2; scan rate 0.10 V/s) after pretreatment in 0.10 M $HClO_4$ + 1.0 mM Cu^{2+} as follows (dashed lines, after 5 min of continuous cycling): (a) 4 min at 0.55 V; (b) 4 min at 0.15 V; (c) 4 min at −0.05 V.

These results raise two contradicting questions: (i) If the enolate form is required for ion binding to a TBEA monolayer, then how can we obtain results such as in Figure 1a, where Cu^{2+} appears to bind to the monolayer[1] in a strongly acidic solution? (ii) If binding does occur in acid solutions (under the influence of an applied potential, as discussed below), then why is there no sign of Cu^{2+} stripping in Figure 2a? The first of these questions will be addressed in this section; the second will be discussed in the next section.

The effect of the applied potential on the binding of Cu^{2+} ions to a (TBEA+OM+OTS) monolayer membrane on a gold electrode[2] is demonstrated in Figure 3. Here are presented stripping curves, following the binding of Cu^{2+} in 0.1 M $HClO_4$ with the electrode held at several applied potentials. As seen in Figure 3, the applied voltage induces the binding of Cu^{2+} ions to the monolayer membrane under conditions where otherwise no stripping is observed. Note that the amount of bound ions increases with the polarization time, i.e. the binding reaches a plateau after 4 min, and therefore all the stripping results are reported for 4 min of applied potential.

The results in Figure 3 are quite striking in demonstrating the decisive role of the applied potential in promoting the binding of

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[5] Chidsey, C. E. D.; Loiacono, D. N.; Sleator, T.; Nakahura, S. *Surf. Sci.* **1988**, *200*, 45.

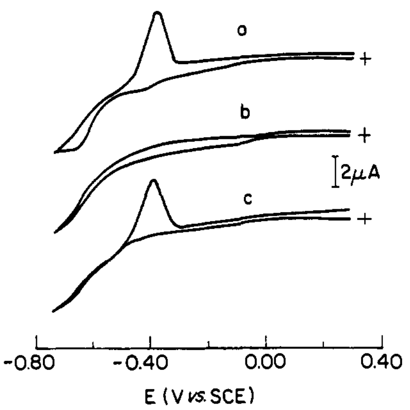

Figure 4. Cyclic voltammograms in pure 0.10 M H_2SO_4 for an Au/(TBEA+OM+OTS) electrode (electrode area 0.63 cm^2; scan rate 0.10 V/s) after pretreatment in 0.10 M $HClO_4$ + 1.0 mM Pb^{2+} as follows: (a) 4 min at 0.25 V; (b) 4 min at 0.15 V; (c) 4 min at -0.20 V.

Cu^{2+} ions to TBEA monolayer membranes. Hence, Figure 3b indicates that at a certain applied potential, i.e. around 0.15 V, no ion binding can be detected by stripping experiments, and the degree of binding increases markedly both positive and negative of this potential.

Two additional significant results should be mentioned: (i) No Cu^{2+} binding to Au/(TBEA+OM+OTS) occurs in the presence of 8.0 mM Zn^{2+} in the solution, under conditions where otherwise (no Zn^{2+}) sizable Cu^{2+} stripping peaks are obtained (i.e., at positive or negative potentials). This agrees well with our previous ionic competition results,[2] showing that the electrochemical response for Cu^{2+} at TBEA monolayer membranes is strongly suppressed in the presence of Zn^{2+} ions in solution, due to the effective competition of Zn^{2+} for ionic binding sites in the monolayer. (ii) No stripping peaks are observed after immersion of Au/(TBEA+OTS+OM) in 3.0 mM Fe^{3+} solution, under conditions where substantial Cu^{2+} binding is observed in similar stripping experiments. This demonstrates again the selective nature of the system.

To examine the general nature of the effect of the applied potential, similar binding/stripping experiments were performed with Pb^{2+} ions in $HClO_4$, shown previously to generate an electrochemical response at TBEA monolayer membranes on gold.[2] Typical results are shown in Figure 4. The following conclusions can be drawn from a comparison of Figures 3 and 4: (i) With respect to the trend in the influence of the applied potential on the amount of bound ions, the results are essentially identical for Pb^{2+} and Cu^{2+}. They are also qualitatively similar to results of Cu^{2+} binding experiments carried out in 0.1 M H_2SO_4, suggesting that the identity of the anion has little effect in this case. (ii) The absolute amount of Cu^{2+} which binds at a certain potential is about five times larger than the corresponding amount of Pb^{2+} (note the scales in Figures 3 and 4). This appears to be the result of the larger ionic radius of Pb^{2+}, limiting the amount of ions capable of coordinating to a closely packed monolayer, as discussed in detail elsewhere.[2]

Figure 5b–e presents results of Cu^{2+} binding experiments performed in neutral solution (0.1 M Na_2SO_4).[6] Here, too, the ionic binding is governed by the applied potential (Figure 5b–d) in the same manner as in the previous cases, with a potential of minimal binding at 0.15 V. A difference in the behavior is, however, observed, upon comparing Figures 5e and 2a. After one cycle in Cu^{2+}/Na_2SO_4 (as in Figure 5a) one clearly observes Cu^{2+} stripping peaks (Figure 5e), whereas no stripping is observed after a similar pretreatment in Cu^{2+}/H_2SO_4 (Figure 2a). This is most likely due to the effect of the higher pH, which promotes the enolization and binding.

The effect of the applied electric field on the ion binding to an Au/(TBEA+OM+OTS) electrode is summarized in Figure 6, for two ions (Cu^{2+} and Pb^{2+}) in different solutions. Note that the experimental points on each curve in Figure 6, corresponding to different applied potentials, were measured at a random order. Figure 6 emphasizes the major observation of the stripping experiments: In all the examined cases, there is a pronounced, well-defined potential of minimal ion binding around 0.15 V. At this applied potential there is practically no ionic binding to the TBEA monolayer membrane, and it may thus be termed the "potential of minimal binding" (PMB); the amount of bound ions increases sharply on either side of this potential.

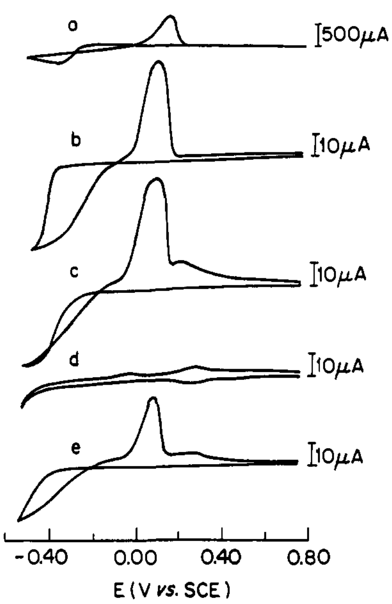

Figure 5. Cyclic voltammograms for an Au/(TBEA+OTS) electrode (electrode area 0.63 cm^2; scan rate 0.10 V/s) (a) in 0.10 M Na_2SO_4 + 1.0 mM Cu^{2+} and (b–d) in pure H_2SO_4, after pretreatment in 0.10 M Na_2SO_4 + 1.0 mM Cu^{2+} as follows: (b) 4 min at 0.75 V; (c) 4 min at 0.10 V; (d) 4 min at 0.15 V; (e) in pure H_2SO_4, after one cycle in 0.10 M Na_2SO_4 + 1.0 mM Cu^{2+}.

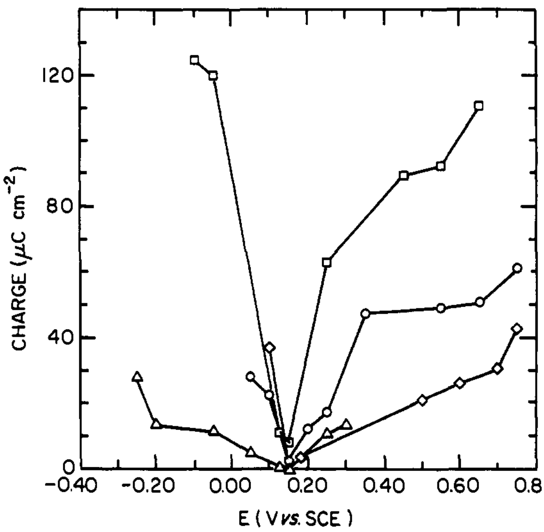

Figure 6. The dependence of the integrated stripping charge (in pure 0.10 M H_2SO_4) on the applied potential for an Au/(TBEA+OM+OTS) electrode (electrode area 0.63 cm^2), held 4 min at the indicated potentials in (□) 0.10 M $HClO_4$ + 1.0 mM Cu^{2+}, (○) 0.10 M H_2SO_4 + 1.0 mM Cu^{2+}, (△) 0.10 M $HClO_4$ + 1.0 mM Pb^{2+}, and (◇) 0.10 M Na_2SO_4 + 1.0 mM Cu^{2+}.

Two other points may be noted with respect to Figure 6. First, one can use the measured charges in Figure 6 to get a rough estimate of the fraction of TBEA molecules in (TBEA+OM+OTS) monolayer membranes. Using the following numbers and assumptions—the highest value measured for Cu^{2+} stripping in $HClO_4$, i.e. 125 μC/cm^2; a roughness factor of 2 (determined electrochemically by gold oxide removal[2]); and an approximate

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[6] Figure 5a shows the response of an Au/(TBEA + blocking component) electrode to Cu^{2+} in a solution of neutral pH. The behavior is qualitatively similar to that in acid solution (compare Figures 5a and 1a).

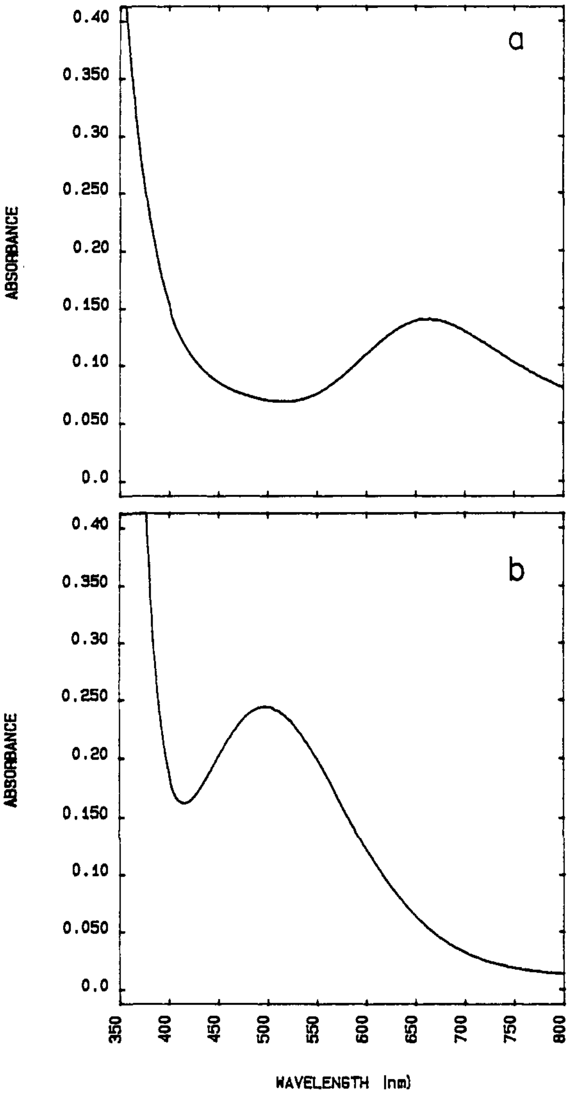

Figure 7. UV–vis spectra of (a) 3.0 mM Cu^{2+}–EAA complex in water (containing 3% v/v methanol to increase the complex solubility), adjusted to pH 7.5 with sodium acetate, and (b) 3.0 mM Fe^{3+}–EAA complex in water, adjusted to pH 7.5 with sodium acetate.

value of 30 Å²/TBEA molecule—and assuming that one Cu^{2+} ion is bound to each TBEA molecule, we obtain a surface coverage of about 50% by TBEA (the rest comprises OM and OTS). Although this is a rough calculation, it supports our previous conclusion that simultaneous adsorption of TBEA and OM produces monolayer membranes with a TBEA fraction of about one–half.[1,2]

Second, since a higher pH promotes the complexation, one would intuitively expect a larger amount of Cu^{2+} ions to bind in Na_2SO_4 compared to H_2SO_4, while Figure 6 generally indicates otherwise. This may be explained by the competition of Na^+ ions for TBEA binding sites. The binding constants of Cu^{2+} and Na^+ to β-diketones (in solution) are both quite large (typical values for log K are 6.7[2] and 4.18[7], respectively), while the concentration of Na^+ is 200 times that of Cu^{2+}, which would introduce a competition to Cu^{2+} binding. This explanation was verified by performing a similar Cu^{2+} stripping experiment in pure 1.0 mM copper acetate (pH ~7), with no added electrolyte. For adsorption at 0.75 V, the stripping charge was 84 μC cm^{-2}, i.e. markedly higher than in H_2SO_4.

Optical Properties. To confirm the electrochemical results and gain a better understanding of the mechanism, two independent, nonelectrochemical techniques have been employed, namely ellipsometry and contact-angle measurements. The results are described in this section (ellipsometry) and in the next section (contact angles).

Table I. Ellipsometric Results for TBEA Monolayer Membranes on Gold

electrode treatment	wavelength, nm	$-\delta\Delta$	$-\delta\psi$	calcd thickness, Å
Au/TBEA	632.8	1.10	0.39	9.3 ± 0.5
	546.1	0.98	0.42	9.1 ± 0.6
after cycling in 1.0 mM Cu^{2+} (H_2SO_4)	632.8	1.87	0.42	(15.9 ± 1.6)
	546.1	1.64	0.48	(14.3 ± 1.4)
2 min in H_2O	632.8	1.11	0.40	9.3 ± 0.8
	546.1	0.99	0.44	9.1 ± 0.8
4 min at 0.75 V in 1.0 mM Cu^{2+} (H_2SO_4)	632.8	3.87	0.33	(34.1 ± 2.3)
	546.1	2.01	0.39	(18.2 ± 0.9)
5 min in H_2O	632.8	3.71	0.33	(32.6 ± 1.7)
	546.1	1.93	0.43	(17.5 ± 1.2)
after Cu stripping in 0.1 M H_2SO_4	632.8	1.23	0.44	10.3 ± 0.8
	546.1	1.06	0.43	10.2 ± 1.0
4 min at 0.75 V in 3.0 mM Fe^{3+} (H_2SO_4)	632.8	1.09	0.08	9.4 ± 0.9
	546.1	1.29	0.02	9.7 ± 1.2
4 min at 0.75 V in 1.0 mM Cu^{2+} (H_2SO_4) + 8.0 mM Zn^{2+}	632.8	1.20	0.35	10.5 ± 0.8
Au/(TBEA+OTS)	632.8	1.09	0.32	9.5 ± 0.9
after cycling in 1.0 mM Cu^{2+} (H_2SO_4)	632.8	2.13	0.43	(18.8 ± 1.6)
5 min in H_2O	632.8	1.10	0.33	9.6 ± 0.7
4 min at 0.15 V in 1.0 mM Cu^{2+} (H_2SO_4)	632.8	1.18	0.34	10.2 ± 1.0

Ellipsometry is based upon the measurement of changes in the state of polarization of a light beam reflected from a surface.[8] The measured ellipsometric parameters are the amplitude parameter, Ψ, and the phase parameter, Δ. When dealing with the properties of a film (i.e. film thickness and refractive index) on a solid substrate, one usually measures the difference in the ellipsometric parameters, δΨ and δΔ, introduced upon formation of the film. In ellipsometric measurements aimed at the determination of the thickness of self-assembled organic monolayers, which are transparent in the visible optical range, it is common to use for the calculation the values n_f = 1.45–1.55, k_f = 0, respectively, for the real and imaginary components of the film refractive index.[9] In the results discussed below, we have used the values $n_f = 1.54$, $k_f = 0$ for TBEA monolayers.

The ellipsometric measurements had two objectives: (i) to measure the thickness of TBEA monolayers, and thus to provide an indication of the orientation of the molecules on the surface; and (ii) to follow the formation of ionic complexes in the monolayer. As shown in Figure 7, the complexes of Cu^{2+} and Fe^{3+} with ethyl acetoacetate (EAA) absorb light in the visible region, with absorption maxima around 660 nm (Cu^{2+}–EAA, Figure 7a) and 500 nm (Fe^{3+}–EAA, Figure 7b). Accordingly, the binding of either of these ions to a TBEA monolayer would result in substantial changes in the refractive index of the film. One can thus anticipate significant changes in the ellipsometric ψ and Δ upon complexation of these ions to the monolayer membrane, with the largest deviations expected in the vicinity of the wavelength of the absorption maxima.

Ellipsometric results for TBEA monolayer membranes on gold substrates, subjected to various experimental protocols, are summarized in Table I. Two points should be noted concerning the numbers reported in Table I: (i) The major changes in the film optical properties following complexation are in the value of δΔ,

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(7) Fernelius, W. C.; Van Uitert, L. G. *Acta Chem. Scand.* **1954**, *8*, 1726.

(8) Gottesfeld, S. In *Electroanalytical Chemistry*; Bard, A. J., Ed., Dekker: New York, 1989, Vol. 15.

(9) (a) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559. (b) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5852.

with relatively smaller changes in $\delta\Psi$; (ii) in the last column in Table I ("calcd thickness") are given film thickness values. These values are calculated assuming a transparent film with $n_f = 1.54$, $k_f = 0$, using a standard program supplied with the ellipsometer. This assumption is valid for the nonabsorbing TBEA films, for which the calculated thicknesses may be safely assumed to represent "real" thicknesses. For absorbing films with $k_f \neq 0$ and n_f which may also vary, this program would calculate unreasonable thicknesses, which do not reflect actual changes in film thickness, but serve to qualitatively indicate the variation in the film refractive index upon complexation; these values are therefore given in parentheses.

The ellipsometric thickness of a TBEA monolayer on a gold substrate, measured at 632.8 nm, is 9.3 Å, highly reproducible and with a very small standard deviation. This value is in excellent agreement with the thickness calculated from a model of perpendicularly oriented TBEA molecules (9.5 Å). The ellipsometric thickness of a (TBEA+OTS) monolayer on gold is 9.5 Å (Table I), essentially equal to that of a TBEA monolayer, although the length of OTS is more than twice that of a TBEA molecule. This indicates that the OTS in Au/(TBEA+OTS) (adsorbed sequentially, not simultaneously as in Au/(TBEA+OM)[2]) comprises a minute fraction of the monolayer, while serving efficiently to improve the blocking properties of the system (compare Figure 1b to Figure 5b in ref 2).

The ellipsometric results reveal the answer to the intriguing question presented above, namely, whether or not a complex is formed when an Au electrode coated with a TBEA monolayer is cycled in acidic Cu^{2+} solution. On the one hand, the voltammogram shows Cu^{2+} response, reflecting Cu^{2+} binding (Figure 1a); on the other hand, no stripping peaks are observed in background solution following this treatment (Figure 2a). As shown in Table I, ellipsometric measurement after one cycle reveals a significant change in the refractive index of the film (as changes in $\delta\Delta$ and calculated thickness), clearly indicating the formation of a Cu^{2+} complex. However, the optical parameters return to the original values (for Au/TBEA) after short immersion of the electrode in water. This indicates that cycling the electrode in acidic Cu^{2+} solution involves the formation of a weak Cu^{2+}/TBEA complex, which readily dissociates upon transfer to background solution, hence the absence of stripping peaks. Similar results are obtained with the Au(TBEA+OTS) electrode (Table I).

A different situation is encountered when the same Au/TBEA electrode is pretreated in acidic Cu^{2+} solution under conditions where prominent Cu^{2+} binding is evidenced by stripping (4 min at 0.75 V). This results in much greater changes in $\delta\Delta$ (and calculated thickness), pointing to the formation of a different, more stable complex (di-enolic, see below) under these conditions. As expected, the deviation of the ellipsometric parameters is greater at 632.8 nm, i.e. in the vicinity of the absorption maximum (see Figure 7a), than at 546.1 nm. Moreover, in this case the electrode is not affected by immersion in water, and the metal ions can be removed only by electrochemical stripping in background solution, upon which the ellipsometric parameters return to the same values (within experimental error) of the original free ligand (see Table I).

In full agreement with the ionic stripping results, essentially no change in the optical properties of the monolayer is observed when a Au/(TBEA+OTS) electrode is immersed in acidic Cu^{2+} solution and polarized for 4 min at 0.15 V, i.e. at the potential of zero ionic binding (Table I, bottom; see Figure 6).

The ellipsometric results provide independent evidence for the selectivity of TBEA monolayers toward different ions. On the basis of the absorption curve in Figure 8b, the formation of a Fe^{3+}/TBEA complex on the surface should result in a modification of the film refractive index, particularly at 546.1 nm. However, quite different results are observed experimentally. No change in $\delta\Delta$ or the calculated thickness is evident after 4 min at 0.75 V in Fe^{3+} solution, indicating that Fe^{3+} does not bind to TBEA arranged in a compact monolayer.[2] This result clearly supports our model for the ionic recognition in TBEA monolayer membranes, where the selective electrochemical response to certain ions is assumed to reflect selective coordination of these ions to TBEA molecules in the monolayers.[1,2]

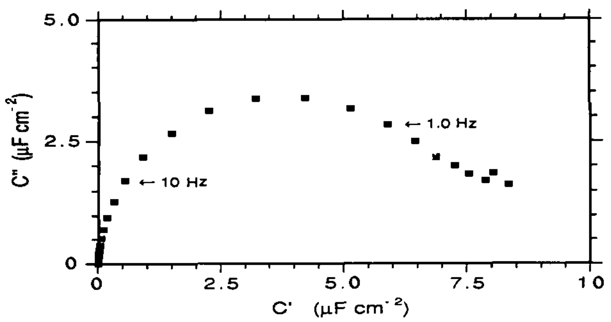

Figure 8. Complex capacitance plot in 1 × 10^{-3} M $NaClO_4$ for an Au/TBEA electrode (electrode area 0.50 cm^2) polarized at 0.30 V.

The Zn^{2+}–EAA complex does not absorb light in the visible region, and therefore the binding of Zn^{2+} to TBEA monolayers cannot be detected directly by ellipsometry. As shown in Table I, the binding of Zn^{2+} can be detected indirectly, using ionic competition experiments, as described previously.[2] Hence, the binding of Zn^{2+} ions to a TBEA monolayer from a mixed solution with Cu^{2+} is evidenced by the invariance of the film optical parameters, indicating that Zn^{2+} binding prevents the formation of the absorbing Cu^{2+}/TBEA complex at 0.75 V.

The binding of Cu^{2+} to a TBEA monolayer in a neutral (Na_2SO_4) solution can also be followed by ellipsometry, and the results are quite similar to those presented in Table I for acidic solution. A difference is observed, however, upon cycling a Au/TBEA electrode in a neutral solution containing Cu^{2+}, where significantly larger $\delta\Delta$ is measured compared with the same experiment performed in acid solution. This is in agreement with the stripping results described above, indicating the pronounced tautomerism (enol formation) at the higher pH.

It should be pointed out that blank stripping and ellipsometric measurements for various applied potentials were carried out with *bare* Au electrodes. In none of these experiments did any change in the electrochemical or optical state of the electrode occur.

To complete the ellipsometric picture, some problems should be noted. The first is the changes in Ψ for e.g. Au/TBEA. For the gold substrate in Table I ($n_s = 0.233$, $k_s = 3.459$), covered with a 9.5-Å transparent film ($n_f = 1.54$, $k_f = 0$), the expected ellipsometric $\delta\Delta$ and $\delta\Psi$[10] are −1.09 and 0.02, respectively. Hence, the experimental $\delta\Psi$ is substantially different than expected. This deviation of Ψ is most likely due to the chemical bond between the monolayer sulfur end and the gold, which modifies the optical properties of the interface between the monolayer and the gold substrate. The change in Ψ is not recognized by the standard transparent film program, which calculates thicknesses (as given in Table I) from $\delta\Delta$ alone. To check the effect of $\delta\Psi$ on the calculated thickness, we recalculated the thickness using an ellipsometric parameter-fitting program which uses both $\delta\Delta$ and $\delta\Psi$ while allowing the film parameters to vary.[10] A good fit to the experimental results is thus generated, with $n_f \approx 1.2$, $k_f \approx 0.6$, and a thickness of ≈9.5 Å. The value of the calculated refractive index, and particularly of k_f, is quite unexpected; it should be realized, however, that we have used a simplistic model, which assignes all the changes (resulting from the chemical attachment) to the monolayer refractive index. A more elaborate model is clearly needed but is beyond the scope of the present work. On the otherhand, a calculated monolayer thickness of ≈9.5 Å is practically the same as that given in Table I. It therefore seems that the ellipsometric thickness of Au/TBEA is quite reliable, but the monolayer chemical attachment to the gold introduces a substantial modification of the optical properties of the interface.

The second problem concerns the magnitude of $\delta\Delta$ observed upon ion binding, e.g. after 4 min at 0.75 V in Cu^{2+} solution.

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(10) Ellipsometric calculations and parameter fitting were carried out with programs received from A. Redondo, Los Alamos National Laboratory. See: Gottesfeld, S.; Paffett, M. T.; Redondo, A. *J. Electroanal. Chem.* **1986**, *205*, 163.

Table II. Advancing (a) and Receding (r) Contact Angles for TBEA Monolayer Membranes on Gold, Measured with H_2O, Bicyclohexyl (BCH), and Hexadecane (HD)

	contact angles		
electrode treatment	H_2O	BCH	HD
Au/TBEA	(a) 107	52	46
	(r) 102	50	40
after cycling in	98	46	30
1.0 mM Cu^{2+} (H_2SO_4)	85	34	
2 min in H_2O	107	50	44
	102	48	38
4 min at 0.75 V in	83	36	22
1.0 mM Cu^{2+} (H_2SO_4)	69	24	
after Cu stripping	106	50	44
in 0.1 M H_2SO_4	102	47	39
Au/TBEA	108	54	46
	103	52	44
4 min at 0.75 V in	108	54	46
3.0 mM Fe^{3+} (H_2SO_4)	103	52	43
Au/(TBEA+OTS)	111	57	47
	109	56	46
after cycling in	108	54	45
1.0 mM Cu^{2+} (H_2SO_4)	105	52	42
after cycling in	103	50	40
1.0 mM Cu^{2+} (H_2SO_4) +8.0 mM Zn^{2+}	100	48	37
40 min in	111	56	46
0.01 M EDTA	109	55	44

Calculation shows[10] that changes of such magnitude in Δ require not only an increased k_f but also a n_f of 3.5–4, which is totally unreasonable. It is therefore clear that the transformation to an absorbing film cannot be the sole source of the dramatic changes in the apparent film refractive index upon Cu^{2+} binding. These intringuing questions, though not affecting the major conclusions of the present ellipsometric study, will be further investigated in the future.

Wettability Properties. At each step of the ellipsometric measurements described above, the monolayers on gold were also characterized by contact-angle measurements, in order to detect possible changes in their wetting properties upon ionic complexation. Both advancing (a) and receding (r) contact angles were measured, for three liquids: water, bicyclohexyl (BCH), and hexadecane (HD).

Typical results for several electrodes, subjected to different experimental protocols, are summarized in Table II. The major conclusion from the data in Table II is that the contact angle values are most significant, closely following the trends in the ellipsometric results. Thus, ionic binding to a TBEA monolayer clearly changes the wetting properties of the film, evident as a substantial lowering of the contact angles to water and organic solvents. This change is almost completely reversible upon removal of the ions.

In full agreement with the electrochemical and ellipsometric results, the changes in the contact angles confirm the formation of a weak Cu^{2+}–TBEA complex after cycling the electrode in acidic Cu^{2+} solution, which easily dissociates in water, and the formation of a more stable complex after 4 min at 0.75 V. The inability of Fe^{3+} to form a complex with an organized monolayer of TBEA is again evidenced by the complete invariance of the contact angles upon exposure of the electrode to Fe^{3+} solution under conditions where complexation is favored (Table II).

As shown in Table II, the contact angles of Au/(TBEA+OTS) are consistently higher than those measured for Au/TBEA. Moreover, the changes in the contact angles upon Cu^{2+} binding are considerably smaller for the mixed monolayer (Table II). These observations show that the added OTS, although comprising a small fraction of the mixed monolayer (see above), improves substantially the monolayer uniformity and structural integrity.

Unlike the ellipsometric measurements, the contact angles provide a direct indication of Zn^{2+} binding to a TBEA monolayer. As seen in Table II, a marked decrease in the contact angles is observed after treatment in a mixed solution of Cu^{2+} and Zn^{2+}, shown previously[2] to result in complete Zn^{2+} binding; as noted above, pretreatment in a mixed Cu^{2+}–Zn^{2+} solution results in no change in the measured ellipsometric parameters, as the Zn^{2+}–TBEA complex is transparent in the visible. Note that the original contact angles are practically fully recovered after removal of the strongly bound Zn^{2+} ions[2] by EDTA (Table II).

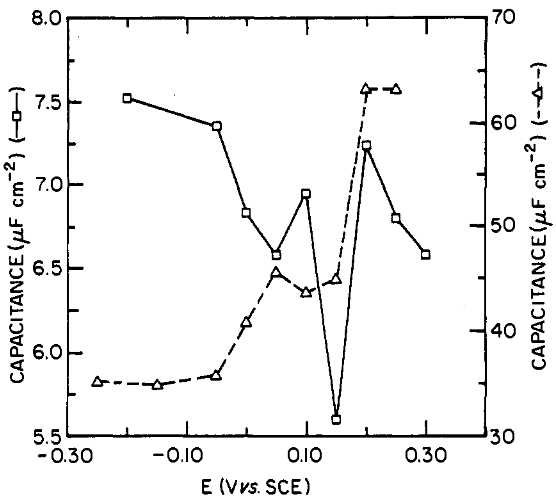

Figure 9. Differential capacitance vs electrode potential for (△) bare Au and (□) Au/TBEA (electrode area 0.50 cm^2) in 1×10^{-3} M $NaClO_4$.

Mechanism of the Ionic Binding. As shown in Figure 6 (and supported by the optical and wettability measurements), the applied potential plays a decisive role in the binding of ions to TBEA monolayers. Thus, at a certain applied potential (termed the PMB, see above) there is little or no ionic binding; deviations from the PMB, either positive or negative, induce substantial ionic binding, with a qualitative correlation between the shift from the PMB and the amount of bound ions.

Having convinced ourselves that the applied potential provides the driving force for ionic binding, a logical conclusion would be that minimal binding should occur under conditions where no electric field is imposed at the interface, i.e. at the potential of zero charge (the PZC).[11] It is therefore reasonable to assume that the PMB represents the PZC, noting also that the measured PMB (≈0.15 V) falls within 0.1–0.2 V to published values of the PZC of gold[11a] (which is practically constant in the pH range 0–8[12]).

In order to test this hypothesis, we set out to measure the PZC experimentally. This was done by measuring the differential capacitance of Au and Au/TBEA electrodes in dilute electrolyte solution (10^{-3} M $NaClO_4$) at varying DC potentials. Under these conditions, the differential capacitance should largely reflect the diffuse double-layer capacitance and show a local minimum at the PZC.[13] The capacitance was measured by the AC-impedance method[14] in a wide frequency range and presented as complex capacitance plots[4] (the complex capacitance $\tilde{C}$ is defined as $\tilde{C} = 1/j\omega\tilde{Z}$, $\tilde{Z}$ being the impedance). For a series RC circuit, which is the electrical analogue of an ideally polarizable electrode, one should obtain a semicircle in the complex capacitance plot,[4] and the capacitance can then be obtained from the extrapolated intercept with the real axis, at $\omega \to 0$.

A typical complex capacitance plot for Au/TBEA (at 0.30 V) is shown in Figure 8, from which the double-layer capacitance can be determined by extrapolation of the semicircle. A summary of such results is presented in Figure 9 as differential capacitance vs electrode potential plots. For Au/TBEA, a pronounced min-

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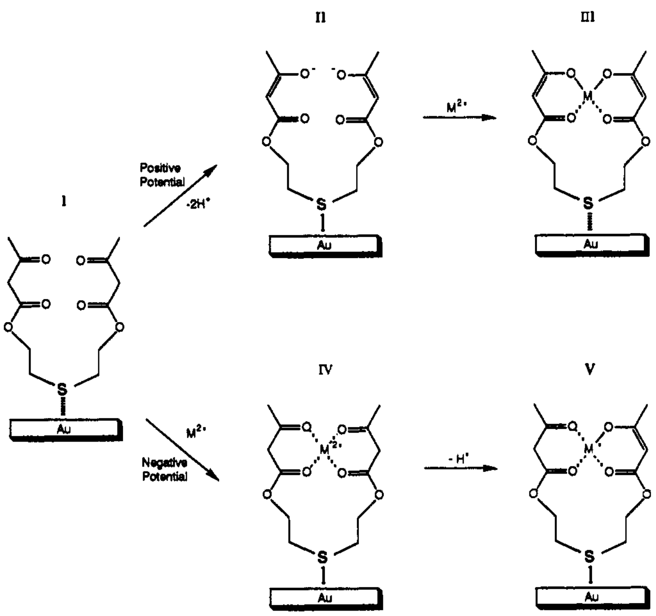
[11] (a) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum: New York, 1970; Vol. 2, pp 703–708. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 495–498.

[12] Seo, M.; Jiang, X. C.; Sato, N. *J. Electrochem. Soc.* **1987**, *134*, 3094.

[13] Reference 11b, pp 501–511.

[14] *Impedance Spectroscopy*; Macdonald, J. R., Ed.; Wiley: New York, 1987.

Scheme I



imum is observed at 0.15 V (quite close to the local minimum in the capacitance vs potential curve for the bare Au (Figure 9)[15]). Hence, a direct determination of the PZC confirms our intuitive suggestion that the minimal ionic binding to TBEA monolayers on gold electrodes occurs at the zero charge potential.

The identification of the potential of minimal ionic binding with the PZC requires careful consideration of a possible mechanism. The electric charge of the gold electrode has an opposite sign on either side of the PZC, implying that a different (field-driven) binding mechanism must operate at positive vs negative excursions from the PZC.

Scheme I presents a possible mechanism for the field-driven ionic binding to TBEA moieties arranged in a compact monolayer on a gold electrode, at positive or negative rational potentials, $\bar{E}$.[16] At positive $\bar{E}$, a reasonable mechanism would include a field-assisted enolization step, i.e. the ligand, existing as the diketo I in acid solutions, may lose two protons and transform to the dienolate II under the influence of the electric field. This would be followed by the binding of the metal ion to form the stable dienolic complex III, provided that the loss of electrical energy in this step is compensated for by the gain in free energy of complexation, which is a reasonable assumption.

At negative $\bar{E}$, the first step may include penetration of the ion into the monolayer to form the weak diketo complex IV, stabilized by the negative charge on the electrode. This may be followed by loss of one proton, to form the monoenol complex V, which is much more stable chemically than IV[17] while still enjoying an electrical energy gain by being positively charged. (A subsequent loss of another proton to form the neutral complex III cannot be ruled out.)

The mechanism presented in Scheme I, though not established by direct experimental evidence, provides a reasonable explanation for the effect of the applied potential at positive or negative rational potentials. Moreover, it predicts the existence of several TBEA–metal ion complexes, some weaker than others, which agrees well with the ionic stripping and ellipsometric results discussed above. Thus, for example, the formation of a weak Cu^{2+}–TBEA complex (which could be e.g. complex IV in Scheme I) was suggested to occur upon cycling of Au/TBEA in Cu^{2+}-containing acid solution, as discussed above.

Conclusions

Organized organic monolayers on electrodes, studied or operated under normal electrochemical conditions, are necessarily subjected to very large electric fields, which should be considered when dealing with the structure and function of such systems. In the case of ion-selective TBEA monolayer membranes, we have shown that the applied potential provides the driving force for ionic binding to TBEA moieties in the monolayer, notably in acid solutions. Essentially no ion binding can be detected under these conditions at the potential of zero charge (the PZC), while deviations from the PZC, either negative or positive, promote substantial ionic binding.

The use of nonelectrochemical techniques, i.e. ellipsometry and contact-angle measurements, proved essential and rewarding in several respects: (i) it provided independent evidence for the selective binding of certain ions to TBEA monolayers; (ii) it established the influence of the applied potential upon the binding; and (iii) it added vital information for the elucidation of fine details of the suggested mechanism.

The use of the above or similar solid-supported monolayer systems as efficient molecular sensing elements requires the possibility of measuring a change in a certain physical property upon binding of a certain ion (or molecule) to a monolayer constituent. The use of the gold substrate as an electrode enabled us to apply electrochemical procedures to generate and detect a measurable signal, i.e. an electrical current. The ellipsometric results (Table I), though not completely understood at this point, suggest a viable alternative, i.e. detection of changes in the optical properties of the system upon binding. This may prove particularly beneficial for the sensing of species which cannot produce direct electrochemical response.

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(15) The relatively small deviation of the PZC for Au/TBEA from that of bare Au may be explained by the opposing effects of the adsorbed sulfide, i.e. the chemisorption of a sulfur-bearing compound (increases the positive charge of the metal) and the replacement of adsorbed anions (decreases the positive charge).

(16) The rational potential is defined as the potential with respect to the PZC; see e.g.: (a) Gileadi, E.; Kirowa-Eisner, E.; Penciner, J. *Interfacial Electrochemistry*; Addison-Wesley: Reading, 1975; p 103. (b) Koryta, J.; Dvorak, J. *Principles of Electrochemistry*; Wiley: New York, 1987; p 226.

(17) Williams, R. J. P. *Private* communication.