the TD analysis of our experimental results.

Appendix. Second-Order Effects on the ENDOR Spectrum of Equivalent Nuclei

We compute here the second-order splittings due to couplings between electronically equivalent nitrogen nuclei. Such second-order effects have been seen by ENDOR of d^9 model CuTPP and AgTPP complexes that nearly possess the D_{4h} symmetry. We have assumed as a worst possible case that diagonally opposite heme nitrogens are equivalent. We estimate the magnitude of the splittings from the values of A_{11}, A_{22}, and A_{33} that we have found for [^{15}N]heme. For two equivalent ^{15}N nuclei interacting with an unpaired electron spin there are eight combined electron–nuclear spin states (shown in Figure 9); four of these have electron spin up and four of these have the electron spin down. Instead of having two transitions as predicted by eq 5a, there are four allowed transitions as shown in Figure 9. (These transitions are caused by the ENDOR RF field that is perpendicular to the externally applied field.) The splitting induced by second-order effects is given by $(9^{15}A_{22}{}^2 + {}^{15}A_{33}{}^2)/(4\nu_e) \approx 0.03$ MHz for the two nitrogens having the magnetic field along their axis 1 and $(9^{15}A_{11}{}^2 + {}^{15}A_{33}{}^2)/(4\nu_e) \approx 0.05$ MHz for the other two heme nitrogens having the magnetic field along their 2 axis.[27] (Second-order effects of the out-of-plane parameter A_{13} and of $g_x - g_y$ anisotropy along axis 1 or 2 are much less than these splittings.) The calculated splittings are an order of magnitude *less* than the observed extra, non-Zeeman splittings for [^{15}N]heme nitrogens. The [^{15}N]heme peaks of axis 1 near 21 MHz $\approx \frac{1}{4}g_{eff}{}^{15}A_{11}$ in Figure 3a have non-Zeeman splittings of about 0.85 MHz while those of axis 2 near 15 MHz $\approx \frac{1}{4}g_{eff}{}^{15}A_{22}$ have a non-Zeeman splitting of about 0.61 MHz.

For ^{14}N, because of the quadrupole splitting, there are 18 instead of eight combined electron–nuclear spin states for each pair of equivalent ^{14}N nuclei. We expect each pair of equivalent [^{14}N]heme nuclei to give four pairs (i.e., eight lines total) of ENDOR transitions with each pair centered at a frequency predicted by an equation like eq 5b. We have computed the splittings within an individual pair and have found them to be $(9^{14}A_{22}{}^2 + {}^{14}A_{33}{}^2)/(2\nu_e) \approx 0.03$ MHz for the two nitrogens that have the magnetic field along axis 1 and $(9^{14}A_{11}{}^2 + {}^{14}A_{33}{}^2)/(2\nu_e) \approx 0.05$ MHz for the two nitrogens that have the magnetic field along axis 2. Again, these splittings are an order of magnitude less than the observed splittings for the [^{14}N]heme nitrogens. The [^{14}N]heme peaks of axis 1 centered near $\frac{1}{4}g_{eff}{}^{14}A_{11} \approx 15$ MHz in Figure 2b have a non-Zeeman $\frac{1}{4}g_{eff}{}^{14}A_{11}$ of about 0.68 MHz while the [^{14}N]heme peaks of axis 2 centered near $\frac{1}{4}g_{eff}{}^{14}A_{22} \approx 10.5$ MHz have a non-Zeeman splitting of about 0.41 MHz. We note that the overall ratio of the observed non-Zeeman inequivalences for ^{15}N and ^{14}N is approximately the ratio of the magnitudes of ^{15}N to ^{14}N nuclear g values (i.e., 1.40). Thus, as stated in the text, we attribute the observed splittings to an electronic inequivalence of heme nitrogens.[46]

(46) In the case where all four heme nitrogens are equivalent and the magnetic field is along the heme normal, the problem becomes considerably more difficult than the problem of two magnetically equivalent nitrogens. There would be 32 ^{15}N or 162 ^{14}N combined electron–nuclear states. Having unambiguously found that a first-order inequivalence of hyperfine couplings readily accounts for the simpler case with two nitrogens, we did not proceed with the four nitrogen exercise. However, if nitrogens were equivalent only in pairs when the magnetic field was along the heme normal, then the theory which we have worked out for equivalent pairs would predict second-order splittings ~0.07 MHz for both [^{15}N]heme and [^{14}N]heme.

Determination of the Orientation of Adsorbed Molecules at Solid–Liquid Interfaces by Thin-Layer Electrochemistry: Aromatic Compounds at Platinum Electrodes

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Abstract: Accurate measurements of the limiting coverages of adsorbed molecules on smooth platinum electrodes are reported. Comparison of measurements with values calculated for various possible molecular orientations indicates the predominant orientations of the adsorbed molecules. Experimental data were obtained by linear potential scan voltammetry and potential-step chronocoulometry using thin-layer electrodes. Calculations were based upon covalent and van der Waals radii as tabulated by Pauling and were tested against the results of classical adsorption experiments. Forty compounds were studied, representing a wide range of structures and chemical properties: simple diphenols and quinones; alkyl-substituted diphenols and quinones; dihydroxybenzaldehydes; halogenated diphenols and quinones; polyhydroxybenzenes and quinones; hexaoxocyclohexane; N-heteroaromatics; diphenols having surface-active side chains; polycyclic diphenols and quinones. The most probable orientation was determined for each adsorbed compound.

Introduction

Methods to determine the orientation of an adsorbed molecule have been sought for a long time. Some progress toward this objective, at least at solid surfaces in ultra-high vacuum, has been reported by using methods based upon electron and neutron diffraction and electron spectroscopy.[1,2] Also, there is an excellent

literature of studies involving monolayers of insoluble substances such as stearic acid on liquid surfaces.[3] However, the method presented in this article, applicable to smooth solid surfaces in solution, is the first of its kind. This method employs thin-layer electrochemical techniques to obtain precise measurements of adsorbed amounts that define the orientations of adsorbed molecules by revealing the electrode surface area required for formation of the adsorbed state.

The orientation of an adsorbed molecule is potentially a function of each variable of the interfacial system such as surfactant molecular structure, electrolyte, solute concentration, solvent, potential, temperature, pH, electrode material, surface structure, and perhaps others. The present introductory article describes adsorbed molecule orientation as a function of the first of these factors, the chemical nature of the adsorbing species, under conditions where the other factors play a small or nearly constant role. Future articles will explore those other factors in greater detail.

Described here are studies of an assortment of 40 quinones and phenols (listed in Table I). These compounds are advantageous for a first study because they adsorb strongly on Pt electrodes,[4] display uncomplicated electrochemical reactivity, and represent a range of structures and chemical properties. Each compound possesses one or more distinct features whose influence is to be explored, such as: bulky, chemically inert substituents; multiple surface-active functional groups; substituents that are acidic or basic; heterocyclic aromaticity; lengthy, flexible aliphatic side chains; substituents having large or systematically varying electronegativity; or various spatial arrangement of substituents.

Little is known regarding the quantitative details of competitive adsorption between water and aromatic compounds at Pt electrodes, although all available evidence indicates that aromatic compounds are adsorbed on Pt strongly enough to displace water. Aromatic compounds achieve space-limited densities on clean Pt (111) surfaces even at pressures in the ultra-high-vacuum range (about 10^{-9} torr);[2] in comparison, water is not adsorbed on room-temperature Pt (111) at pressures as high as 10^{-3} torr.[1,6] Strength of aromatic adsorption is similar to dimethyl sulfoxide,[1] which has been shown to displace water *totally* and *irreversibly* from the Pt surface[7] and to prevent electrolysis of aqueous Pt(II) and Pt(IV) complexes.[8] Conversely, water does not displace chemisorbed layers already in place such as pyridine on Pt (111) single-crystal planes[5] as well as other aromatic compounds ad-
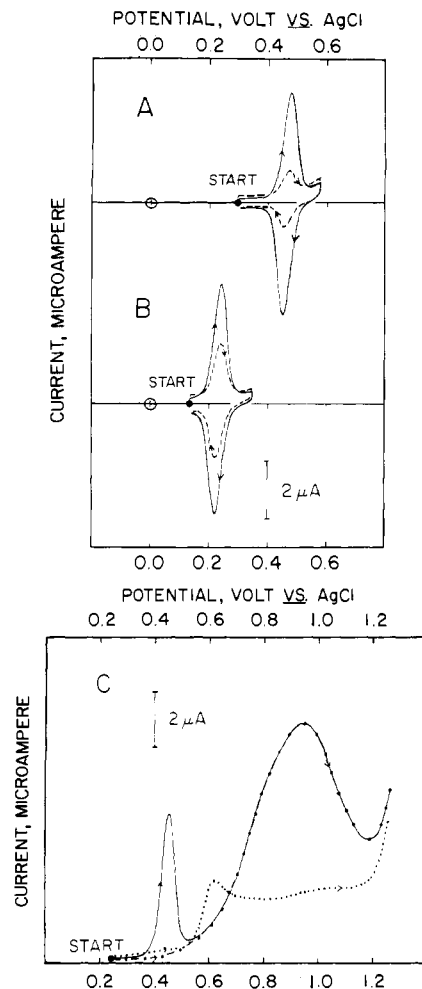

Figure 1. Thin-layer current–potential curves for (A) hydroquinone, (B) durohydroquinone, and (C) hydroquinone at a polycrystalline platinum electrode: (- - -) first filling; (—) presaturated surface; (-·-·-) presaturated surface rinsed to remove dissolved reactant; (···) clean surface. The solutions contained initially 0.15 mM reactant and 1 M HClO$_4$ (thin-layer volume, V, 4.08 μL; platinum electrode area, A, 1.18 cm^2; rate of potential sweep, r, 2.00 mV s^{-1}; solution temperature, T, 296 ± 1 K).

sorbed on smooth polycrystalline Pt electrodes.[4]

Perchlorate and dilute phosphate supporting electrolyte was chosen for this study because these species adsorb only weakly and reversibly at Pt surfaces, based upon voltammetric curves that show that reversible electrodeposition of H atoms at the Pt surface proceeds readily and completely in perchlorate and phosphate media, in contrast to strongly adsorbing species such as iodide, for which H deposition is prevented.[9]

All of the data presented in this article were obtained with 10^{-4} M solutions of the adsorbing aromatic compound. *At this concentration* the coverage was relatively insensitive to concentration (adsorbed amounts changed less than 3% for a 7-fold variation in concentration) indicating that saturation had taken place for the given orientation (see below).

Adsorption is of course a potential-dependent phenomenon.[10] In the present study adsorption was carried out at open circuit, resulting in rest potentials in the range 0.1–0.5 V (vs. AgCl reference), for which the Pt electrode is relatively free of surface oxide or hydrogen. Preliminary experiments in which the potential was controlled during adsorption indicated that density and orientation did not vary substantially over this range of potentials.

The dependence of adsorbed molecule orientation on electrode structure was not investigated in this study. Electrodes were

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employed that consisted of nearly equal proportions of atomically smooth Pt (111) and Pt (100) planes.[9]

Measurement of Adsorbed Amounts

Electrochemistry using thin-layer cells has been reviewed,[11,12] and the thin-layer electrodes employed for this study have been described.[13] In cells of this design a thin layer of electrolyte is contained between a cylindrical Pt electrode and surrounding precision glass tubing. Spent solution is removed by application of pressurized inert gas. Filling occurs due to capillary action when the pressure is released (solution layer thickness, 40 μm; electrode area, A, 1.18 cm^2; volume, V, 4.08 μL). If the clean thin-layer electrode is filled only once, a single aliquot of electrolyte containing a precise molar amount of solute enters the thin-layer cavity. When this solute is surface active and its initial concentration is moderately low ($C° \leq 10^{-4}$ M), a major portion of the solute is adsorbed, producing a significant change in solute concentration, C:

$$VC = VC° - A\Gamma \qquad (1)$$

where Γ (mol/cm^2) is the interfacial concentration of adsorbed solute molecules. The adsorbed states of 1–30, 31–34 (at pH <7), and 35–40 are much less reactive electrochemically than the dissolved form, as illustrated by the thin-layer linear scan voltammetric data presented in Figure 1C. Each of these compounds was so characterized, Figure 1 being typical of the results for each compound. Electrolysis of the dissolved material occurs at less extreme potentials than the adsorbed material. Accordingly, when electrolysis is carried out at a potential about 0.1 V beyond the formal standard potential (Table I; equal to the reversible peak potential as in Figure 1), conversion of the dissolved material proceeds to completion prior to the onset of appreciable reaction of the adsorbed material. The electrolytic charge, Q, required for electrolysis of unadsorbed solute in the thin-layer cavity is related to the interfacial concentration of adsorbed solute, Γ, by the Faraday law, eq 2, where Q_1 denotes electrolytic charge ob-

$$Q_1 - Q_b = nFVC = nFVC° - nFA\Gamma \qquad (2)$$

served for a single filling of the thin-layer cavity, Q_b is the background electrolytic charge consumed in an otherwise identical experiment in which the dissolved reactant has been rinsed from the cell, and n is the number of faradays of charge F consumed per mole. On the other hand, if the thin-layer cavity is rinsed with an excess of the reactant solution, then the reactant concentration equals that in the bulk solution, $C°$, so that the electrolytic charge, Q, is given by eq 3. Combining eq 2 and 3 yields

$$Q - Q_b = nFVC° \qquad (3)$$

an expression for interfacial concentration, Γ, in terms of measured charges:

$$\Gamma = (Q - Q_1)/nFA \qquad (4)$$

If, on the other hand, an adsorbed form *is* electroactive, the interfacial concentration of this adsorbed material is again readily determinable. The charge obtained on the first filling is equal to the simple Faraday law value, so that eq 2 becomes

$$Q_1 - Q_b = nFVC° \qquad (2')$$

And, after the thin-layer cavity has been rinsed with an excess of the reactant solution, the reactant concentration in solution equals the bulk concentration, and there is an interfacial excess of electroactive material:

$$Q - Q_b = nFVC° + nFA\Gamma \qquad (3')$$

Combining 2' and 3' gives an expression for Γ of the *electroactive* form which is the same as eq 4. Indeed, adsorption takes both forms, electroactive and inactive, in some systems such as I_2 solutions at Pt electrodes;[15] in such cases, the total Γ is obtained

by means of eq 4.[11,12,15] Compounds 31–34 at pH $\geq$7 are in this category. Electrodes rinsed with 31–34 followed by pure electrolyte display linear-scan voltammetric peaks for reversibly electroactive adsorbed material and for irreversibly electroactive material, determined as described above.

Experimental Section

The Pt electrode surfaces were smoothed with successive grades of wet emery paper and polished with 7- and 0.25-μm diamond compund (Buehler Ltd., Evanston, IL 60204). After polishing, the electrodes were treated with hot concentrated nitric acid and heated to redness in a gas–oxygen flame. In between experimental trials the electrode was cleaned by electrochemical oxidation in 1 M HClO$_4$ at 1.2 V (vs. the AgCl/Ag reference electrode) and reduction at −0.2 V; repolishing was never required. Electrodes thus pretreated consisted of 55% Pt (111) planes and 45% Pt (100), based upon comparison of their linear potential scan voltammetric hydrogen atom electrodeposition curves with those for well-defined Pt single-crystal surfaces.[1,9,16] Electrolytic solutions were prepared from pyrolytically distilled water[17] and analytical reagent grade perchloric acid (Mallinckrodt Chemical Works, Paris, KY 40361) or sodium perchlorate (G. Frederick Smith Chemical Co., Columbus, OH 43223). Buffer solutions (pH 7.0) were prepared from analytical reagent grade sodium dihydrogen phosphate and sodium hydroxide (Mallinckrodt). Solutions were deaerated with pure nitrogen. Potentials are reported with reference to the AgCl/Ag half-cell prepared with 1 M NaCl.

The compounds were obtained as follows: 1, Allied Chemical Corp. (Morristown, NJ 07960); 2, Chemical Procurement Labs., Inc. (College Point, NY 11356); 3, Sigma Chemical Co. (St. Louis, MO 63178); 4–7, 9, 12, 13, 17–19, 21, 23–26, 35–39, Aldrich Chemical Co., Inc. (Milwaukee, WI 53233); 8, J. T. Baker Chemical Co. (Phillipsburg, NJ 08865); 11, 30, Pfaltz and Bauer, Inc. (Stamford, CT 06902); 14, 16, ICN Pharmaceuticals, Inc. (Plainview, NY 11803); 15, PCR Research Chemicals, Inc. (Gainesville, FL 32602); 27, 28, Burdick and Jackson Labs., Inc. (Muskegon, MI 49442). Compounds 2 and 38 were repurified by sublimation; the remaining commercial substances were used as received. Compounds 31–34 were prepared by Alice C. L. Cheng.[18] Compounds 10 and 40 were prepared by Stanley E. Anderson.[19] We prepared the following compounds according to published procedures: 20, 22, 35, and 37;[20] 29.[14]

Results

Conversion of *o*- and *p*-diphenols and quinones from the electrochemically reactive dissolved form to a virtually unreactive adsorbed state is illustrated by the data in Figure 1, obtained by using thin-layer linear potential scan cyclic voltammetry. The dashed curve in Figure 1A was obtained when the initially clean thin-layer cavity was supplied with a single aliquot of hydroquinone. Peak potentials are equal to the formal standard potential as expected for reversible interconversion of the quinone and diphenol, eq 5, in a thin-layer cell. Averaging the peak potentials

$$\text{(OH-phenol)} \rightleftharpoons \text{(O-quinone)} + 2H^+ + 2e^- \qquad (5)$$
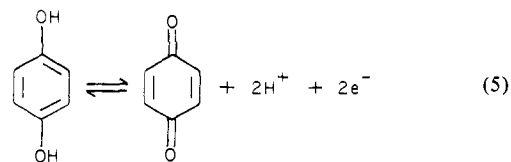
of positive and negative scan directions cancels out slight ohmic and kinetic components. These average values are included in Table I. The areas under the peaks are as expected if a fraction of the entering hydroquinone has been converted to an unreactive form (eq 2). In contrast, the solid curve in Figure 1A shows that when the electrode surface is presaturated with adsorbed hydroquinone (or other surfactants) and filled with hydroquinone solution, the area under the current–potential curve has the much

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Table I. List of Compounds, Formal Standard Potentials ($E^{\circ\prime}$), and Adsorption Data

compound	$E^{\circ\prime\,a}$	σ (found, A^2 molecule^{-1})^b	σ (calcd, A^2 molecule^{-1})^c		
			flat	edgewise	endwise
1, hydroquinone	0.46	51.6 ± 1.4	53.8	28.6 (2, 3) 25.2 (1, 2)	24.8 (2) 21.8 (1)
2, benzoquinone	0.46	52.7 ± 1.4 53.0 ± 1.4 (pH 7)	52.5	27.9 (2, 3) 25.2 (1, 2)	24.1 (2) 21.8 (1)
3, pyrocatechol	0.56	56.1 ± 1.4	54.0	26.9 (2, 3; 3, 4) 25.2 (1, 2; 4, 5)	23.3
4, methylhydroquinone	0.41	66.7 ± 2.8	62.6	34.4 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	31.5 (3; 6) 30.4 (1; 4) 29.6 (2; 5)
5, 4-methylpyrocatechol	0.52	64.1 ± 2.8	62.3	36.4 (2, 3; 5, 6) 31.6 (1, 6; 3, 4) 29.6 (1, 2; 4, 5)	31.6 (2; 3; 5; 6) 27.4 (1; 4)
6, *tert*-butylhydroquinone	0.39	76.9 ± 2.1	73.5	70.7 (1, 6; 3, 4) 58.8 (2, 3; 5, 6) 51.8 (1, 2; 4, 5)	64.3 (3; 6) 61.6 (1; 4) 50.9 (2; 5)
7, 4-*tert*-butylpyrocatechol	0.52	73.5 ± 2.1	72.1	74.2 (2, 3; 5, 6) 55.3 (1, 6; 3, 4) 51.8 (1, 2; 4, 5)	64.3 (2; 3; 5; 6) 47.9 (1; 4)
8, 3,4-dihydroxybenzaldehyde	0.71^d	59.9 ± 1.4	61.9	30.9 (2, 3; 5, 6) 26.7 (1, 2; 4, 5) 25.2 (1, 6; 3, 4)	26.8 (2; 3; 5; 6) 23.3 (1; 4)
9, 2,5-dihydroxybenzaldehyde	0.69^d	59.9 ± 1.4	62.6	29.2 (2, 3; 5, 6) 28.6 (1, 6; 3, 4) 25.2 (1, 2; 4, 5)	25.3 (2; 5) 24.8 (1; 6; 3; 4)
10, 2,3-dimethylhydroquinone	0.36	51.9 ± 1.4	67.8	34.4 (1, 2; 4, 5) 33.6 (2, 3; 5, 6)	31.6 (2; 5) 29.8 (1)
11, 2,5-dimethylhydroquinone	0.36	74.4 ± 2.8	71.3	39.2 (3, 4) 33.6 (2, 3) 29.6 (1, 2)	33.9 (1; 3) 29.1 (2)
12, 1,4-dimethoxybenzene	1.05^d	75.1 ± 2.1	70.4	44.0 (2, 3) 29.6 (1, 2)	38.1 (2; 3) 25.6 (1)
13, trimethylhydroquinone	0.30	83.0 ± 2.1	77.2	39.2 (1, 2; 4, 5) 34.4 (1, 6; 3, 4) 33.6 (2, 3; 5, 6)	33.9 (1; 2; 4; 5) 31.6 (3; 6)
14, durohydroquinone	0.24	80.2 ± 2.1	83.3	39.2 (1, 2) 33.6 (2, 3)	33.9
15, tetrafluorohydroquinone	0.49	112.2 ± 3.5	61.1	28.6	24.7
16, tetrachlorohydroquinone	0.47	110.4 ± 3.5	87.0	36.0 (1, 2) 30.2 (2, 3)	31.3
17, tetrafluorobenzoquinone	0.49	395.3 ± 6.5	59.6	28.6 (1, 2) 27.9 (2, 3)	24.8
18, 1,2,3-benzenetriol	0.51^d	60.7 ± 1.4	57.7	26.9	24.8 (2; 5) 23.1 (1; 3; 4; 6)
19, 1,2,4-benzenetriol	0.36	61.9 ± 1.4	57.5	28.6 (2, 3; 5, 6) 26.9 (1, 6; 3, 4) 25.2 (1, 2; 4, 5)	24.8 (2; 3; 5; 6) 23.1 (1; 4)
20, 1,2,4,5-tetrahydroxybenzene	0.22	64.2 ± 1.4	61.1	28.6 (2, 3) 25.2 (1, 2)	24.7
21, 2,5-dihydroxybenzoquinone	0.22	63.6 ± 1.4	59.6	27.9 (2, 3) 28.6 (3, 4) 25.2 (1, 2)	24.7
22, hexahydroxybenzene	0.13	70.7 ± 1.4	70.6	28.6	24.7
23, tetrahydroxybenzoquinone	0.13	68.6 ± 1.4	70.6	29.0 (1, 2) 27.9 (2, 3)	24.7
24, hexaoxocyclohexane	0.90^d	128.7 ± 7.1	58.2	27.9	24.1
25, 2,3-dihydroxypyridine	0.73^d	39.1 ± 1.4 31.4 ± 0.7 (pH 7)	54.4	26.9 (1, 2; 1, 6; 3, 4; 4, 5) 22.4 (2, 3; 5, 6)	23.3
26, 3,6-dihydroxypyridazine	1.02^d	26.0 ± 0.7 24.7 ± 0.7 (pH 7)	48.0	28.6 (1, 2; 4, 5) 22.4 (2, 3; 3, 4)	24.7 (1; 4) 19.4 (3)
27, allylhydroquinone	0.42	52.4 ± 1.4	62.6	34.4 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	31.5 (3; 6) 30.4 (1; 4) 29.6 (2; 5)
28, 4-allylpyrocatechol	0.52	52.7 ± 1.4	62.3	36.4 (2, 3; 5, 6) 31.6 (1, 6; 3, 4) 29.6 (1, 2; 4, 5)	31.8 (2; 3; 5; 6) 27.4 (1; 4)
29, 2-(1-hydroxy-5-hexenyl)hydroquinone	0.40	70.7 ± 2.8	74.8	38.8 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	35.3 (3; 6) 33.6 (1; 4) 29.1 (2; 5)
30, phenylhydroquinone	0.44	87.4 ± 3.5	85.1	39.8 (1, 6; 3, 4) 28.6 (2, 3; 5, 6) 25.2 (1, 2; 4, 5)	35.9 (3; 6) 34.4 (1; 4) 24.7 (2; 5)
31, 2-(2-aminoethyl)hydroquinone	0.45	64.9 ± 1.4 53.0 ± 1.4 (pH 7)	62.3	34.4 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	31.5 (3; 6) 30.4 (1; 4) 29.6 (2; 5)

Table I *(Continued)*

compound	$E^{\circ\prime\,a}$	σ (found, Å^2 molecule^{-1})^b	σ (calcd, Å^2 molecule^{-1})^c		
			flat	edgewise	endwise
32, 2-(2-aminoethyl)-5-methylhydroquinone	0.40	76.9 ± 1.4 63.6 ± 1.4 (pH 7)	71.3	39.2 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	33.9 (1; 3; 4; 6) 29.1 (2; 5)
33, 2-(2-aminoethyl)-5-bromohydroquinone	0.47	80.2 ± 2.8 66.7 ± 2.1 (pH 7)	76.8	42.0 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	36.4 (1; 3; 4; 6) 29.1 (2; 5)
34, 2-(2-aminoethyl)-5-nitrohydroquinone	0.61^d	78.3 ± 1.4 65.4 ± 2.1 (pH 7)	76.2	39.6 (1, 6; 3, 4) 33.6 (2, 3; 5, 6) 29.6 (1, 2; 4, 5)	34.4 (1; 3; 4; 6) 29.1 (2; 5)
35, 1,4-dihydroxynaphthalene	0.23	66.7 ± 1.41	69.5	28.6 (2, 3; 6, 7) 32.3 (1, 2; 5, 6)	29.9 (1; 4) 27.2 (2; 6)
36, 1,4-naphthoquinone	0.23	70.0 ± 2.1	68.6	27.9 (2, 3; 6, 7) 32.3 (1, 2; 5, 6)	29.9 (1; 4) 27.0 (2; 6)
37, 1,2-dihydroxynaphthalene	0.34	68.0 ± 1.4	70.5	34.0 (3, 4; 7, 8) 32.3 (1, 2; 5, 6) 26.9 (2, 3; 6, 7)	31.3 (1; 4; 5; 8) 27.2 (3; 7) 25.8 (2; 6)
38, anthraquinone-1,5-disulfonic acid, disodium salt	0.01	140.7 ± 1.4	138.0	75.5 (2, 3) 74.2 (1, 2; 3, 4)	74.2 (1; 5; 9) 73.0 (3) 56.3 (2)
39, anthraquinone-2,6-disulfonic acid, disodium salt	0.01	130.7 ± 7.1	126.3	102.4 (3, 4) 74.2 (1, 2) 52.5 (2, 3)	98.6 (1; 5; 9) 73.0 (3) 56.3 (2)
40, 2,3-dimethylbenzoquinone	0.36	50.5 ± 0.7	67.1	34.4 (1, 2; 4, 5) 32.8 (2, 3; 5, 6)	31.2 (2; 5) 29.6 (1)

^{a} Experimental conditions as in Figure 1. Unless otherwise indicated, the value reported was obtained by averaging the thin-layer voltammetric peak potentials of positive and negative scans. Ag/AgCl in 1 M NaCl reference electrode was employed. ^{b} Experimental conditions: The polycrystalline Pt thin-layer electrode was rinsed once at open circuit with a 10^{-4} M solution of the subject compound in 1 M HClO$_4$ (unless otherwise indicated) for 3 min. The electrolytic charge for the oxidation (or reduction) of the dissolved solute was determined coulometrically, and the interfacial concentration of the adsorbed material was obtained by using eq 4. A pH of 7.0 was maintained by means of a phosphate buffer (6.3×10^{-3} M NaH$_2$PO$_4$ + 3.7×10^{-3} M NaOH) in 1 M NaClO$_4$. All other conditions as in Figure 1. ^{c} Numbers appearing in parentheses in this column designate the ring positions nearest the electrode surface for those compounds having more than one unique endwise or edgewise orientation. ^{d} Peak potential of the positive scan only.

larger value, characteristic of unadsorbed reactants (eq 3). Figure 1B shows similar results obtained for tetramethylhydroquinone ("durohydroquinone"), in which the smaller limiting interfacial concentration of this compound compared to hydroquinone gives rise to a smaller difference in area between the solid and dashed (one aliquot) curves. The comparative unreactivity of adsorbed material is illustrated by experiments in which the potential scan was continued in the positive direction beyond the first peak; a broad maximum was observed in the vicinity of 1 V vs. AgCl (Figure 1C). This is characteristic of the oxidation of adsorbed hydrocarbon materials[4] and corresponds to irreversible oxidation of the adsorbed form[14] of hydroquinone to products that have not been identified. This same irreversible oxidation behavior was also observed when the thin-layer cell was pretreated by rinsing with any one of the subject compounds followed by thorough rinsing with the pure supporting electrolyte to remove dissolved material prior to recording the scan (Figure 1C). Voltammetric curves for oxidation of the adsorbed form are unchanged by thorough rinsing with aqueous perchlorate; therefore, (i) the adsorption of aromatic on Pt is irreversible, and (ii) water and supporting electrolyte do not displace the adsorbed aromatic. Figure 1 is typical of results obtained for all 40 subject compounds.

The results are summarized in Table I. Adsorption data are given in terms of σ, the average area (Å^2) occupied by a molecule in the adsorbed layer:

$$\sigma = 10^{16}/6.023 \times 10^{23}\Gamma \qquad (6)$$

The data of Table I were obtained by using 10^{-4} M solute. Coverage was essentially independent of concentration in this range, typified by hydroquinone for which σ decreases slightly (from 53.0 to 57.2 to 52.4 to 51.6 Å^2) as the concentration was increased 7-fold (from 0.020 to 0.0374 to 0.086 to 0.140 mM). Adsorption time was 180 s although no change in σ was noted when the exposure time was varied from 60 to 300 s. Experiments performed with compound 31 in which the total phosphate concentration at pH 7 was varied from 0 to 0.1 M demonstrated that the coverage, $\sigma = 53.0 \pm 1.4$ Å^2, was not affected by phosphate

concentration. As expected, the same values of σ were obtained with different thin-layer cells.

Hydroquinone derivatives having bulky, inert substituents yield comparatively high σ values. Examples and their σ values (Å^2) are methylhydroquinone (66.4), *tert*-butylhydroquinone (77.0), 2,5–dimethylhydroquinone (74.2), durohydroquinone (80.5), and anthraquinone-1,5-disulfonic acid (141). The influence of molecular size on the amount that can adsorb can be seen directly in the voltammetric data of Figure 1 by comparing the curves for hydroquinone (part A) with those for the much larger molecule, durohydroquinone (part B). The difference between the solid and dashed curves in Figure 1A is much greater than in Figure 1B, due to the greater uptake of the smaller hydroquinone molecule by the Pt surface.

These results indicate that the adsorption process is energetically favorable, being limited primarily by the space available at the surface. It therefore should proceed until the surface is fully covered. In order to go from coverage data to conclusions about molecular orientation, it is necessary to calculate the surface area requirement for each possible orientation. Comparison of calculated areas with those found then provides the needed quantitative insight.

Applicable calculation methods have been described and tested by numerous workers.[3,21–24] The method most often reported is based upon liquid density measurements and the assumption of spherical molecules, which is not appropriate in the present instance. For this study, molecular models were used, based primarily upon tabulated covalent and van der Waals radii. The area occupied by an adsorbed molecule was represented as the cross-sectional area of the rectangular solid unit cell in a plane parallel to the electrode surface, as illustrated in Figure 2. Dimensions of the unit cells were calculated as follows: Intera-

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(22) Livingston, H. K. *J. Colloid Sci.* 1949, 4, 447.
(23) Hill, T. L. *J. Chem. Phys.* 1948, 16, 181.
(24) Vold, M. J. *J. Colloid Sci.* 1952, 7, 196. Kipling, J. J.; Norris, A. D. *Ibid.* 1953, 8, 547.
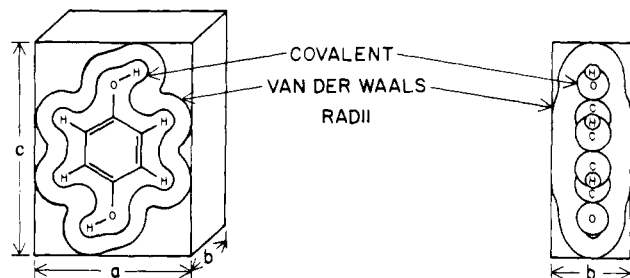
Figure 2. Molecular unit cell assumed in theoretical estimates of σ.

tomic distances within the molecule were determined by combining the appropriate covalent radii tabulated by Pauling.[25] Aromatic rings were taken to be perfectly hexagonal. Substitution of exact crystallographic bond-length data (where available) did not affect the results significantly. Each molecule was considered to be surrounded by an envelope, representing probable distances of closest approach between molecules determined from van der Waals radii, again as tabulated by Pauling.[25] Possible orientations of cyclic molecules are of three general types: the "flat" orientation in which the ring is more or less parallel to the electrode surface plane, various "endwise" orientations in which a C–H bond (or other substituent) of the ring is perpendicular to the surface, and "edgewise" orientations in which one edge is parallel and the ring is perpendicular to the surface. Depending on the substitution of the ring, one or more unique endwise and edgewise orientations are possible. On the basis of nomenclature proposed by Cotton,[26] the flat orientation for benzene, for example, will be termed η^6, the edgewise orientation η^2, and the endwise orientation, η^1.

In selection of the rectangular solid for an adsorbed molecule, the longest axis passing through the center of the plane of the ring was taken to be the length, while the projection of the remaining substituents on the axis normal to the length determined the width. The thickness of the molecule at its thickest point was employed as the thickness of the rectangular solid cell. The calculated σ values are in Table I.

When our method is applied to calculation of the cross-sectional areas of saturated carboxylic acid and long-chain alkylphenol molecules oriented vertically on a water surface, the calculated values agree with those obtained experimentally by Langumuir,[27] Adam,[3] and others, as shown in Table II. Furthermore, although the compounds described in this article had not been studied previously in this regard, data were available for several other aromatic compounds with which to compare our calculated values. These results are included in Table II. Our method produces calculated molecular areas in good agreement with the *averages* of experimental values reported by other workers in spite of scatter on the order of 20% among the findings of various workers.

Discussion

Inspection of area/molecule (σ) data in Table I shows that most of the compounds examined can be categorized as adsorbing close packed in the flat orientation from 10^{-4} M solutions, as shown in I. Compounds **1–9, 11–14, 18–23,** and **30–39** belong to this

I
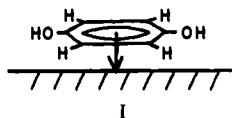
category. Linear least-squares analysis of measured and calculated σ for compounds in this category expresses consistent agreement: the least-squares line has a slope of 0.98, compared with unity; an intercept of σ (calcd) = 2.8 at σ (measd) = 0.0; and, a correlation coefficient of 0.99. More important than the observed absolute agreement is the observation that the calculated values

Table II. Calculated and Experimental Molecular Cross-Sectional Areas

compound	σ (exptl, A^2 molecule^{-1})	σ (calcd, this study, A^2 molecule^{-1})
stearic acid (on water)	20.5; 25.1[b]	22.5
4-octadecylphenol (on water)	24.0[b]	26.8
4-octadecylresorcinol (on water)	28[b]	28.6
4-octadecyl-1,3,5-trihydroxybenzene (on water)	32[b]	30.4
benzene (on solid substrate)	46 ± 10 (av of 25 values)[c]	47.4
toluene (on solid substrate)	55.2 (1 value)[c]	55.1
1,3,5-trimethylbenzene (on solid substrate)	70 ± 12 (2 values)[c]	72.9
pyridine (on solid substrate)	39 ± 1 (2 values)[c]	42.0

[a] Method of calculation described in text. [b] From force-area measurements; molecule assumed to have perpendicular orientation.[3] [c] From BET measurements on various solid surfaces; molecule assumed to have η^6 orientation.[21]

parallel the experimental values for a large variety of compounds and over a full 3-fold variation in molecular size. In contrast, coverages calculated assuming η^1 or η^2 orientations are much larger than measured for these compounds. Incidentally, this consistent agreement between experimental and theoretical σ also eliminates the possibility that these compounds are adsorbed in multiple or random orientations and rules out drastic changes in structure upon adsorption.

Allylhydroquinone (**27**), 4-allylpyrocatechol (**28**), 2-(1-hydroxy-5-hexene)hydroquinone (**29**), phenylhydroquinone (**30**), and a series of 2-(2-aminoethyl)hydroquinones (**31–34**), belong to a second category in which a surface-active side chain is present in addition to the aromatic ring system. Compounds **27–29** achieve greater surface densities than their counterparts because a fraction of the adsorbed material is attached through the comparatively small CH=CH$_2$ moiety; see II. This observation is corroborated

II
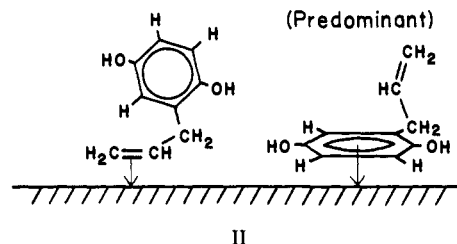
by earlier studies[14,28] in which simple alkenes were found to have σ values as low as 14.1 A^2. Values of σ for compounds **27** and **28**, 52.3 and 53.0, respectively, are smaller than calculated for η^6-phenyl attachment, 62.9, or dual attachment (η^6-phenyl and η^2-allyl), 78.4, but larger than for attachment solely through the side chain. A mixture of adsorbed states is thus indicated. Calculations of σ for compound **30** assumed coplanarity of the two phenyl rings. The experimental results indicate that the rings are parallel to the surface.

Compounds **31–34** each contain a primary amine side chain, which, by analogy with simple amines,[4] is expected to chemisorb appreciably from neutral but not from acidic media. As the data of Table II indicate, this occurs: adsorption from acidic solution (1 M HClO$_4$) yields coverages appropriate to adsorption exclusively through the phenyl ring in the η^6 orientation. Adsorption of compounds **31–34** from neutral solutions, however, gives a

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(26) Cotton, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 6230.
(27) Langmuir, I. *Proc. R. Soc. London, Ser. A* **1939**, *A170*, 1.

(28) Lane, R. F.; Hubbard, A. T. *J. Phys. Chem.* **1973**, *77*, 1411.

substantial increase in coverage, although the increase was considerably less than would be expected for attachment solely through the amine side chain. Control experiments performed with compounds lacking this amine or similar function such as benzoquinone confirmed that coverage was not pH dependent or phosphate dependent. These findings strongly suggest that the adsorbed layer is a mixture of adsorbed states in which some molecules are attached exclusively through the phenyl ring, others solely through the amine group, and possibly some attached through both at the same time. Our data provide one further clue as to the nature of this mixture of adsorbed states: approximately 20% of the material adsorbed from neutral solution is reversibly electroactive, at potentials similar to those for the dissolved compounds, and since compounds adsorbed through the phenyl group did not display this type of electroactivity, it appears likely that this electroactive adsorbed material is attached to the surrface solely through the amine-containing side chain; see III.
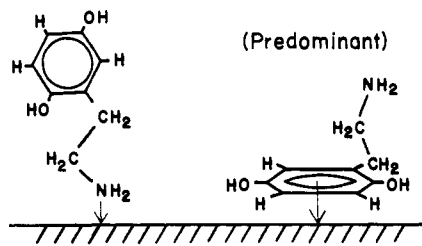

III

A further noteworthy characteristic of compounds 31–34 is flexibility of the side chain. Calculated σ for η^6 orientation depends markedly on the assumed conformation of the chain; for example, calculated σ for compound 31 is about 22% larger when the chain is assumed to rest on the surface than when it is extended away from the surface. This pertains of course only to acidic solutions in which the amine function is not chemisorbed. The observed σ values for each of these compounds correspond to the latter conformation in which the amine side chain is folded away from the surface, as in IV.
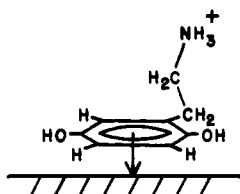
IV

The presence of heteroatoms in the aromatic ring introduces the possibility that specific interactions between the heteroatom and the surface will influence orientation. 2,3-Dihydroxypyridine (25) and 3,6-dihydroxypyridazine (26) belong in this category. The affinity of Pt for nitrogenous ligands, demonstrated by numerous complexes of Pt(II) and Pt(IV),[29] extends also to complexes containing zero-valent Pt[30] and is not unexpected for metallic Pt. Indeed, these two compounds achieve much larger coverages than their homocyclic analogues, suggesting occurrence of a mode of attachment other than η^6 bonding. Furthermore, the limiting coverage displays the pH dependence expected for binding through the aromatic nitrogens, which of course are somewhat basic. Most notably, 2,3-dihydroxypyridine has a σ value of 39.1 Å^2 in molar acid but 28.1 Å^2 in neutral solution. The σ values (Å^2) observed in neutral or basic solution correspond rather closely in each case to the calculated value for one particular

orientation: calcd for 1,6-η^2-(2,3-dihydroxypyridine), 26.8 (found, 26.9); calcd for 1-η^1-(3,6-dihydroxypyridazine), 24.7 (found, 24.7). However, it is also possible that a mixture of orientations is present, such that the sizable (but not maximal) observed magnitude of σ results from a mixture of η^1 or η^2 states with a minority of the more space-filling η^6 form. Evidently, the nitrogen heteroatoms have sufficiently strong surface affinity and suitably rigid steric requirements to coax the aromatic ring into a perpendicular orientation, such as in V.
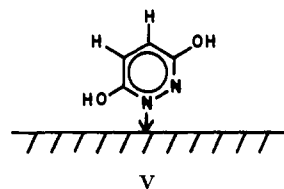
V

Fluorobenzenes and chlorobenzenes are less strongly adsorbed than their nonhalogenated counterparts, the highly halogenated examples such as hexafluorobenzene being almost totally inactive toward Pt.[4] This appears to result from the inductive effect, related to the considerable electronegativity of fluorine and chlorine, in which withdrawal of electron density from the aromatic ring diminishes its activity for the Pt surface. Thus, it is not surprising that the heavily fluorinated (or chlorinated) diphenols and quinones (15–17) are less extensively adsorbed than their nonfluorinated counterparts. Accordingly, the adsorbed amounts are less than the size-limited magnitude and thus have not reached saturation at 10^{-4} M concentration [at 0.7 mM there is further uptake of 15 (σ = 83.1 Å^2), although still less than the size-limited value; the concentration dependence of orientation and coverage of adsorbed aromatic is the subject of a future study]. It appears that the OH groups (and not the tetrafluorinated aromatic ring) are responsible for adsorption of these compounds: for example, thin-layer voltammetry revealed that 1,4-cyclohexanediol is more active toward Pt than 1,4-cyclohexanedione or cyclohexane. Likewise, hexaoxocyclohexane (24) exhibits little affinity for the Pt surface while the corresponding aromatic compound hexahydroxybenzene (22) is strongly surface active.

Two exceptions to the η^6 orientation of compounds in the "simple aromatic" category have emerged: 2,3-dimethylhydroquinone (10) and 2,3-dimethylbenzoquinone (40) display σ values of 52.3 and 50.2 Å^2, respectively, at 10^{-4} M concentration compared with calculated values of 67.8 for η^6, 34.4 and 33.6 for η^2, and 31.6 and 29.8 Å^2 for η^1 orientations. These compounds have one side shrouded with methyl groups and in view of the observed coverages evidently prefer a tilted η^2 orientation or mixed η^6 and η^2 configurations. This hypothesis would also explain the observation in a previous study[4] that 1,2,3,4-tetrafluorobenzene reached an abnormally high coverage relative to its expected place in the series of mono-, di-, tri-, tetra-, penta- and hexafluorobenzenes. That is, the presence of bulky or electronegative substituents along one side of the molecule perhaps induces adsorption of a portion of the material in other than the η^6 orientation.

Comparison of molecular orientation phenomena at solid–liquid interfaces with previous data obtained from gas–solid experiments is worthwhile, in spite (or because) of the possibility that considerable differences might prove to exist. For instance, vibrational and electronic spectral data pertaining to the orientation of benzene chemisorbed on Ni, Pd, Pt, and Ir surfaces in ultra-high vacuum have been obtained by high-resolution electron-energy-loss spectroscopy,[2a,c,g,h,k] ultraviolet photoemission spectroscopy,[2b,e,i] neutron inelastic scattering,[2j] and work-function measurements.[2d] These data have been successfully interpreted by assuming that benzene was chemisorbed in the η^6 orientation. Pyridine has been studied likewise,[2d,k,n,o] and the results suggest that pyridine adopts the N-η^1 orientation. Work-function studies comparing the behavior of 2,6-dimethylpyridine, in which access to the nitrogen atom is sterically hindered by methyl groups, with that of 3,5-dimethylpyridine support the view that steric hindrance forces the former compound into the η^6 orientation while the latter compound adopts the N-η^1 configuration.[2d] Ellipsometric evidence is con-

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(30) Watt, G. W.; McCarley, R. E.; Dawes, J. W. *J. Am. Chem. Soc.* 1957, 79, 5163. Watt, G. W.; Helvenston, E. P.; Sharif, L. E. *J. Inorg. Nucl. Chem.* 1962, 24, 1067.

sistent with the N-η^1 orientation of pyrazine adsorbed on Ni.[2m] In addition to the spectroscopic data obtained in ultra-high vacuum, in situ laser Raman spectroscopy of pyridine adsorbed on roughened Cu, Ag, and Au electrodes in aqueous solution has been interpreted by some workers in terms of N-η^1 oriented pyridine molecules located at or near the electrode surface;[31] benzene does not adsorb on Cu or Ag to an appreciable extent.[2n] The above findings are not in disagreement with those of the present study. In fact, the degree to which these findings correlate is striking in view of the widely differing conditions employed.

Conclusions

The results of this study enable the formulation of certain rules regarding the orientation of adsorbed aromatic molecules. Perhaps these rules will serve as a summary of our findings and a target for future investigations.

Under the conditions of the present experiments: (i) Homocyclic aromatic ring systems are parallel to the surface, except as noted below. (ii) Chemisorbable functional groups tend to interfere with interaction of the homoaromatic framework with the surface. (iii) Bulky or electronegative substituents situated in four adjacent positions on the homoaromatic framework decrease the stability of the parallel orientation relative to other orientations. (iv) Inert electronegative substituents decrease the

tendency of the homoaromatic framework to adsorb. (v) Inert flexible substituent chains of moderate length are situated as far from the metal surface as permitted by the chemisorbed functional groups. (vi) Nitrogen heteroaromatic rings (such as pyridine) are N-bonded perpendicularly to the surface, unless the N atom has been protonated or otherwise modified. (vii) Quinones adsorb in a way identical with their dihydroxyaromatic counterparts.

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Determination of the Orientation of Aromatic Molecules Adsorbed on Platinum Electrodes:[1] The Influence of Iodide, a Surface-Active Anion

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Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. Received August 3, 1981

Abstract: Accurate measurements of the limiting coverages of species adsorbed on smooth platinum electrodes from solutions of aromatic compounds and iodide are reported. Comparison of the measurements with calculations describing various possible orientations of the adsorbed aromatic molecules defines the changes in orientation that occur as a result of coadsorption of iodide. Experimental data were obtained by electrochemical methods based upon the use of thin-layer electrodes, and calculations were based upon covalent and van der Waals radii tabulated by Pauling as described in the preceding article. A total of 28 compounds representing a variety of structures and chemical properties were included in this study: simple diphenols; alkyldiphenols; polyhydroxybenzenes and -quinones; halogenated diphenols; N-heteroaromatics; diphenols having surface-active side chains; polycyclic phenols and quinones; and a dihydroxythiophenol. The orientations prior to and following exposure to iodide solution were determined for each adsorbed compound.

Introduction

A method to determine the orientation of a molecule adsorbed on a smooth solid surface in solution has been described and employed to determine the orientations of 40 aromatic compounds adsorbed at smooth polycrystalline platinum electrodes in aqueous solution.[1] Experiments leading to selection of aqueous perchlorate as the supporting electrolyte for studies in the preceding article[1] revealed that orientation depends upon the identity of the electrolyte anion, a discovery that prompted the present study, an investigation of the interaction of oriented adsorbed aromatic molecules with iodide, a surface-active anion.

Interaction of iodide with clean platinum has been studied at polycrystalline and well-defined single-crystal surfaces in solution and in ultra-high vacuum.[2–4] Briefly, adsorption of aqueous or

gaseous hydrogen iodide is dissociative, forming hydrogen gas and adsorbed iodine atoms:

$$\text{HI} \xrightarrow{\text{Pt surface}} \text{I (adsorbed)} + {}^1/_2\text{H}_2 \qquad (1)$$
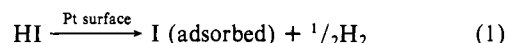
Adsorption from vacuum produces a highly ordered layer (superlattice) of I atoms.[4] Maximum coverage from solution is the

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