Adsorption of Benzoic Acid on Gold in Perchlorate Solutions

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(Received September 9, 1970)

The adsorption of benzoic acid from solutions of 10^{-2} to 10^{-5} M on gold electrode surface in perchlorate solutions of pH 1—4 was studied from differential capacity data obtained by a single pulse method. Strong adsorption is observed in the more acidic solutions. This points to predominant adsorption of benzoic acid molecule, rather than benzoate anions, possibly due to the π-electron interaction. At pH 1, benzoic acid replaces four water molecules. This interprets the flat adsorption of benzoic acid molecule on the gold electrode and the π-electron interaction with free electron of the metal surface. The standard free energy of adsorption $\Delta \bar{G}^\circ$ is -10.4 kcal/mol.

The adsorption of organic substances at metal-solution interface and the influence of surface coverage on kinetics of electrochemical reactions are important aspects of the study of heterogeneous processes.[1] Classically, on an electrode that is liquid and ideally polarizable, such as mercury, the surface excess of an organic substance can be measured as a function of potential and concentration with interfacial tension data using Gibbs' adsorption equation.[2] On solid electrodes, however, the interfacial tension is not accessible with the required precision and adsorption measurements have to be made by other means. Radioactive tracer techniques,[3] determination of concentration changes in solution,[4] and differential capacity measurements are being used for this purpose.[5]

In the adsorption of organic substances, the π-electron interaction between the adsorbing molecule and the metal substrate plays a dominant role.[7] However, the electrostatic attraction force between organic ions and an oppositely charged metal surface should also be important, especially for large molecules, where the solvation energy may be small. To investigate the relative importance of the π-electron interaction and electrostatic attraction, the adsorption of benzoic acid from aqueous solution was studied as a function of both pH and potential. Concentration ratio of benzoic acid to benzoate anions is controlled by pH with the dissociation constant of benzoic acid in aqueous solution. This allows the π-electron interaction with the substrate to remain relatively constant though the concentration of benzoate ions is changed by several orders of magnitude. Differential capacity measurements were made to evaluate the adsorption coverage. Gold was chosen as a substrate. There seems to be no hydrogen adsorption region[7] and gold approaches

closer to the ideal polarizable electrode than, *e.g.* in the case of platinum.

Little is known about the electrochemical behavior of benzoic acid, which can be reduced on metals with high hydrogen overvoltage, *e.g.* lead, to benzyl alcohol.[8-11] Apparently, it can not be oxidized electrochemically in aqueous solution.[12] Both the acid and the free anions are used as corrosion inhibitors,[13] *e.g.* for steel, and are electrochemically stable under corrosion conditions.

Experimental

The gold electrodes were made from polycrystalline fine gold metal (Engelhard Industries, Newark, N.J. USA) and inserted in Teflon rod (cf. Fig. 3). They were polished before each run with 600 mesh polishing powder, washed in hot cleaning solution and thoroughly rinsed with triply distilled water. The exposed apparent surface area of the gold electrode was 0.071 cm².

An all Pyrex glass cell contained, in addition to the gold working electrode, a cylindrical bright platinum wire gauze counter electrode, a platinum flag polarizing electrode and a saturated calomel electrode (SCE). The polarizing electrode and the SCE were in side compartments separated from the main cell through two glass frits (platinum flag side) and a closed stopcock (SCE side).

Solutions of pH 1, 3, and 4 were made up from triply recrystallized sodium perchlorate, 70% reagent grade perchloric acid, and water distilled once from alkaline permanganate then twice in a quartz still. Reagent grade benzoic acid was used to prepare the solutions of 10^{-2} to 10^{-5} M. All solutions were deoxygenated with helium before and during the run.

The working electrode was polarized by a potentiostat according to Harrar.[14] Currents were measured as a voltage drop across a 1 or 10 kΩ precision resistor and potentials of the working electrode were measured against SCE. A Keithley 610B electrometer was used for the voltage measurements.

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Differential capacity measurements were made with a rapid single pulse technique.[15] The differential capacities were measured from the slope of the potential-time curve of a fast rise rectangular current pulse on the working electrode at the start (t=0). The potential-time curves were displayed on the screen of a Tektronix 549 storage oscilloscope. Sometimes, the curves were bent near the start point, and the slope was measured at 25 μ sec and 50 μ sec. The curves were measured by the storage oscilloscope with a differential preamplifier. Voltage and time scales were 10 mV/cm and 5 μ sec/cm. The pulses were taken from the gate of the oscilloscope and passed between the working and the counter electrode through a 33 kΩ resistance. This gave a current of 0.76 mA. Potential range was between 0.0 V and 1.40 V vs. SCE.

The reproducibility of the differential capacity measurements was usually ±15%. This was attributed to differences of the surface condition of electrodes caused by unavoidable differences in pretreatment. In this experiment, the data were normalized to 17.9 μF/cm^2 at 1.40 V, the value was found for 10^{-2} M benzoic acid solution of pH 1. The reproducibility was then ±5%.

Results and Discussion

Study of adsorption coverage on solid electrodes using differential capacity measurements is hampered by the fact that the measurements are sensitive to impurities in solution, faradaic processes occurring at the interface, the crystal structure exposed, and the roughness of the electrode surface. The capacity-potential curves measured on gold electrode in acidic solutions by different workers are similar, although some difference is evident.[16-20] Recent work on single crystal surface of gold electrodes indicates that small discrepancies in the capacities might be due to the nature of the crystal surface exposed.[19-20] It seems that on polycrystalline electrodes the broad maximum at 0—0.2 V and the anodic maximum at 1.2 V are of about equal height (~20 μF/cm^2),[18] whereas on (100) and (110) faces at gold electrode surfaces the anodic maximum is considerably large (~30 μF/cm^2).[17,19,20] On the (100) face electrodes, the broad maximum at 0—0.2 V splits into two peaks of about equal height, the one at the (110) face electrode into one peak and a small shoulder.[17] Small differences in the capacity curves on gold electrode may therefore simply be a matter of the structure of the crystal surface exposed. Thus, differential capacity measurements should be reliable for measuring the adsorption of organic substances on gold electrodes in acidic solutions.

Differential capacity vs. potential data obtained in 0.1 M perchloric acid and from 10^{-2} to 10^{-5} M benzoic acid are shown in Fig. 1. A significant depression
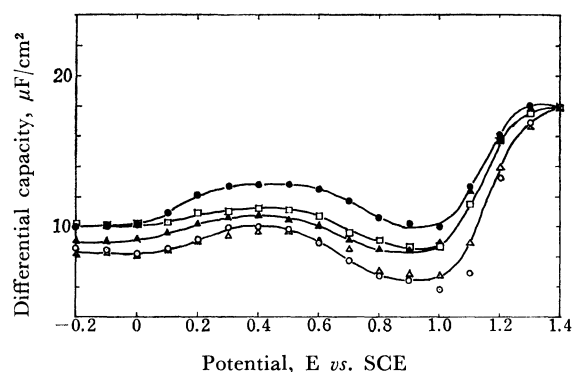

Fig. 1. Differential capacity vs. potential, Au in 0.1 M HClO$_4$ and 0, 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} M benzoic acid. Capacities normalized at 1.4 V.
●: 0, □: 10^{-5}, ▲: 10^{-4}, △: 10^{-3}, ○: 10^{-2}

in the capacity due to the adsorption of benzoic acid was evident in 10^{-5} M solutions in the range 0—1.0 V. An additional significant depression occurred for 10^{-2} and 10^{-4} M benzoic acid at 0.8—1.2 V.

Coverage-potential curves were calculated from the data shown in Fig. 1 and Frumkin's equation[21] in the differentiated form:

$$C = C_0(1-\theta) + C_1\theta + (q_1-q_0)d\theta/dE \qquad (1)$$

where C_0 and q_0 are capacity and charge of the uncovered surface, C_1 and q_1 those of the fully covered surface, and θ is the coverage with an organic substance. As seen in Fig. 1, no characteristic peaks of adsorption-desorption were present in this case. In our high speed capacity measurements these peaks are expected to be much smaller than those in data taken with alternating current at 1 kHz.[22] This may indicate that the adsorption-desorption region lies outside the potential range investigated, or alternatively, that the dependence of adsorption on potential in the range is small.

In general, the surface tension between a metal electrode surface and a solution becomes small on account of the adsorption of an organic substance on the electrode, and the correlation among differential capacity, charge, and surface tension is as follows:

$$C = (\delta q/\delta E)_\mu \qquad q = -(\delta \gamma/\delta E)_\mu$$

where C, q, E, γ, and μ is differential capacity, charge, potential, surface tension, and chemical potential, respectively. We can deduce that the differential capacity becomes small with the adsorption of an organic substance. From Fig. 1, we see that the coverage of adsorption in 10^{-3} and 10^{-2} M benzoic acid solutions showed almost fully coverage in this potential range, but not for 10^{-4} and 10^{-5} M solutions. In any case, if $d\theta/dE \approx 0$, we have

$$C = C_0(1-\theta) + C_1\theta \qquad (2)$$

The coverage-potential curves are shown in Fig. 2 for 10^{-4} and 10^{-5} M benzoic acid. Differential capacities of 10^{-3} M benzoic acid solution were taken as C_1 because both data in 10^{-3} and 10^{-2} M solutions were almost the same.

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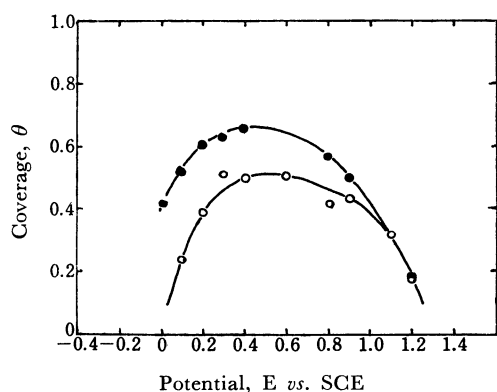
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Fig. 2. Covereage vs. potential, Au in 0.1 M HClO$_4$ and 10^{-4} M, 10^{-5} M benzoic acid.
—●—: 10^{-4} M, —○—: 10^{-5} M

The coverage in higher potential range in Fig. 2 was unknown and could not be determined by going to higher potentials because of imminent oxygen evolution and electrode surface oxidation. It is known that adsorption of "oxygen" in acidic solution starts at approximately 1.0 V vs. SCE[23] and this is substantiated by the capacity curves shown in Fig. 1. Taking into account the fact that the electrode is covered with adsorbed oxygen, it is reasonable to assume that the amount adsorbed of benzoic acid becomes zero, and that the calculated θ values represent the actual fractional coverage with benzoic acid.

The change in the adsorption coverage with pH at constant concentration of benzoic acid can be assessed from the relative change of differential capacity. Values of this relative change are shown in Table 1 for 10^{-3} M benzoic acid and pH 1 and 4. It is seen

TABLE 1. RELATIVE CHANGE IN CAPACITY, $(C_0-C)/C_0$, vs. POTENTIAL AND PH FOR 10^{-3} M BENZOIC ACID

E vs. SCE	pH = 1	pH = 4
+0.1	0.229	0.072
+0.5	0.250	0.015
+0.6	0.280	0.075
+0.7	0.274	0.139

that an increase in pH remarkably reduces the amount of benzoic acid adsorbed. This leads to the conclusion that the adsorbing species is the benzoic acid molecule, rather than the benzoate anions and that in this case electrostatic attractive force between the anions and the positively charged electrode is not important.
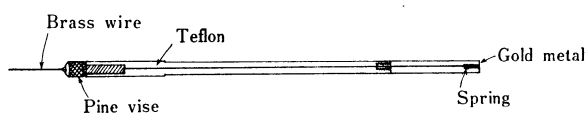

Fig. 3. Schematic diagram of a gold electrode.

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Adsorption of a solute molecule from solution onto an electrode surface must be considered as a competitive adsorption of the solute molecule and the solvent one. The competitive adsorption of two species from a liquid phase has been treated by numerous authors by means of the Langmuir isotherm.[24-26] Recently, a Temkin isotherm was applied to the adsorption of neutral molecules on electrodes.[27] The competitive adsorption of species of different sizes on electrode was treated by Dahms and Green.[28]

For competitive adsorption, equilibrium is assumed to be established between solvent, adsorbed solvent, solute species, and adsorbed solute species as Eq. (3). Thus, in aqueous solution:

$$n\,\text{Water}_{\text{ads}} + \text{Org}_{\text{sol}} \rightleftarrows n\,\text{Water}_{\text{sol}} + \text{Org}_{\text{ads}} \qquad (3)$$

where n is the number of molecules of water which occupies the same surface area as one molecule of the organic compound, $n = \Gamma_{\text{max.w}}/\Gamma_{\text{max.org}}$, with Γ_{max} (in mol/cm^2) the amount forming a monolayer of water or of organic species, respectively.

Under ideal conditions, one can write for equilibrium according to Eq. (3):

$$\bar{\mu}_{\text{org.sol}} + n\,\bar{\mu}_{\text{w.ads}} = \bar{\mu}_{\text{org.ads}} + n\,\bar{\mu}_{\text{w.sol}} \qquad (4)$$

where $\bar{\mu}_i$ is the electrochemical potential of species i. This gives the isotherm

$$\frac{X_{\text{w.sol}}}{(1-\theta)^n \times X_{\text{org.sol}}} = \exp\,(-\Delta\bar{G}^\circ/RT) \qquad (5)$$

Here X_i represents the mole fraction of species i and

$$\Delta\bar{G}^\circ = \bar{\mu}^\circ_{\text{org.ads}} - \bar{\mu}^\circ_{\text{org.sol}} - n(\bar{\mu}^\circ_{\text{w.ads}} - \bar{\mu}^\circ_{\text{w.sol}}) \qquad (6)$$

In dilute solutions of the organic species the mole fraction $X_{\text{w.sol}} \approx 1$ and the isotherm can be written as follows.

$$\frac{\theta}{(1-\theta)^n} = X_{\text{org.sol}} \times \exp(-\Delta\bar{G}^\circ/RT)$$

$$= K_{\text{ads}} \times X_{\text{org.sol}} \qquad (7)$$

The equation differs from the Langmuir equation only by the power factor n.

By means of this equation, n was calculated to be 4 for benzoic acid in 10^{-1} M perchloric acid, and K_{ads} 4.5 × 10^7 at potentials 0.1 to 0.9 V. Replacement of 4 water molecules with one benzoic acid molecule is very reasonable (Stuart-Briegleb Models) and K_{ads} yields a $\Delta\bar{G}^\circ$ of -10.4 kcal/mol which is consistent with the weak adsorption of benzoic acid on gold electrode.

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