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Adsorption of an organic film at the platinum-seawater interface

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ABSTRACT

Optical polarization analysis with an ellipsometer and microelectrophoretic and contact angle measurements all indicate that large changes in the properties of the platinum metal surface occurred on contact with Chesapeake Bay water from which particles and microorganisms had been removed. These changes were not observed with the same water from which organics had been removed by a photo-oxidation procedure. Platinum particles, electropositive in organic-free water, became electronegative in natural water. The wettability of a smooth platinum surface remained high after exposure to organic-free water but was reduced after exposure to natural water to the same magnitude as a polyamide surface. The data were consistent with adsorption of an organic film from the natural water samples onto the metal surfaces. The thickness of the film increased over a period of hours according to ellipsometric measurements and it was not removed by washing in organic-free water. The film on platinum was electrophoretically similar to that previously found on a number of nonconductors.

1. Introduction

The interface between an immersed solid material and seawater is the site of a number of processes affecting the behavior and performance of the material. The chemistry of these boundary processes is important in understanding such diverse phenomena as corrosion resistance, flotation and aggregation of particulates, consolidation of sediments, and the ecology of periphytic microorganisms and macro-fouling growths.

We have shown in previous publications that the surface electric charge on a variety of nonconducting materials immersed in seawater is very different from that found in seawaters containing only inorganic constituents and that the adsorption of dissolved organic materials present in natural seawater is responsible for the difference (Neihof and Loeb, 1972, 1974). We have now extended that study to an investigation of several properties of the surface film formed on a metal immersed in seawater by measurements of the rate of film formation, the change in surface charge, and changes in wettability due to the adsorbed film.

2. Experimental

Water samples were collected and stored using only Pyrex and Teflon bottles

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and tubing. All containers were cleaned with hot concentrated nitric-sulfuric acid and rinsed thoroughly with distilled water. Teflon ware was steamed for one-half hour before use. Water was collected at approximately 1 meter below the surface by suction through a Teflon tube into Teflon bottles in a vacuum chamber. Bottles were fitted with Teflon-lined screw caps. Samples were cooled to 4°C on return to the laboratory, centrifuged as soon as possible (within 24 hours) at 18,000 g for one-half hour to remove microorganisms and other particulate matter and finally stored at 4°C. During the course of the work, water samples were examined microscopically to insure that significant bacterial growth did not occur.

Samples of Chesapeake Bay water were collected off Patuxent Naval Air Station at various times from February to October. Salinities varied from 9.4‰ to 16.3‰ and pH from 7.7 to 8.2.

Removal of dissolved organic constituents from water samples was accomplished by ultraviolet photo-oxidation according to a procedure of Armstrong *et al.* (1966) described earlier (Neihof and Loeb, 1974). An irradiation period of 35-40 hours was used and oxygen was provided by 0.15 ml amounts of 30% hydrogen peroxide added initially and at three intervals thereafter.

The kinetics of the adsorption process on a platinum surface immersed in seawater were followed with an ellipsometer (Rudolph Research Type 43702-200E). A recent description of the ellipsometer and its use has been given by Rothen (1968). The instrument measures the elliptical polarization of light reflected from a specular surface. Changes which occur when the surface is modified serve as a sensitive indicator of adsorption. A Spectra-Physics He-Ne laser (Model 133) was used as the light source (wavelength 632.9 nm). Cells of 100 ml capacity with windows perpendicular to rays with 70° angle of incidence were constructed of fused quartz either in this laboratory or by Optical Cell Corporation, Brentwood, Maryland. The ellipsometer was in a temperature-controlled room at 23°C, and operated in the photoelectric detection mode. The procedure and computer program developed at the National Bureau of Standards were used as described by McCrackin and co-workers (1969).

A platinum plate 10 mm square and 1 mm thick, polished to a mirror surface, was washed and flamed just before immersion into the ellipsometer cell at the start of an experiment. The cell was filled with photo-oxidized seawater, the ellipsometer was aligned, and initial readings were made; readings taken during a 30-minute period were observed to remain constant. Then the cell was quickly emptied, rinsed, and refilled with seawater without moving the cell or platinum plate. Dur- all measurements the cell contents were stirred with a Teflon-covered magnetic stirrer. Readings were made within 2 minutes of sample contact with the platinum plate and at similar intervals thereafter. After the initial rapid change, readings were taken at greater intervals.

For contact angle measurements, specularly polished platinum plates were

flamed, immersed in photo-oxidized waters in covered Pyrex dishes, and the photo-oxidized water then exchanged for seawater samples. After 7 days in the seawater sample (40 ml per cm² of platinum) at 3 °C, the seawater was removed. The platinum plates were rinsed with three portions of photo-oxidized water followed by five portions of triple distilled water. The plates were dried in a desiccator over Drierite. Contact angles with methylene iodide and water were measured, as described by Zisman (1964). Plates were treated in quadruplicate and contact angles were reproducible to ± 1°C. As controls, 4 plates were subjected to the wetting and washing processes described using only photo-oxidized seawater and distilled water. In both of these measurements, it should be emphasized that the platinum mirror was always wet with photo-oxidized water while passing into the seawater sample. Similarly, on withdrawal from the sample, the mirror was immediately immersed into photo-oxidized water while still wet. This precaution eliminated the deposition of a film from the air-seawater interface onto the platinum surface.

Platinum particles for microelectrophoresis were prepared by repeatedly striking an arc between two flamed platinum wire electrodes immersed in triple distilled water following methods described by Bredig (1901) and Burton (1906). Direct current at 35-40 volts from storage batteries was used. Coarser particles were allowed to settle out for a few minutes and those which remained in suspension and could be sedimented by centrifuging for 10 minutes at 10,000 g were retained and washed twice in triple distilled water. Most of these particles were of a suitable size for electrophoresis (0.5-1.5 μm). Considerable care had to be exercised in preparing and handling platinum particles in order to exclude accidental contamination which lowered their characteristic positive mobility in photo-oxidzed seawater.

For microelectrophoresis, approximately 10^6 particles were equilibrated with three successive 20-ml portions of a water sample in centrifuge tubes at 5 °C during a period of about an hour. After each centrifugation the particles were resuspended in a fresh portion of water by brief treatment with an ultrasonic probe. Exposure of metal particles to more than 40 ml of untreated seawater gave no further change in electrophoretic mobilities. Mobility measurements were made on suspension concentrations of about 5×10^6/ml at 25 °C in apparatus previously described (Neihof, 1969). The velocity of each particle was determined from the time required to move a measured distance in a microscope field (400 ×) in both directions of a known electric field. The mean mobility of 20 particles was taken to characterize a suspension. These measurements afforded an additional opportunity to ascertain that the suspensions were free of microorganisms since previous studies have shown that bacteria may be seen with this optical system when present.

3. Results

When a freshly flamed platinum plate was immersed in freshly photo-oxidized seawater in the ellipsometer cell no changes with time were observed in the optical
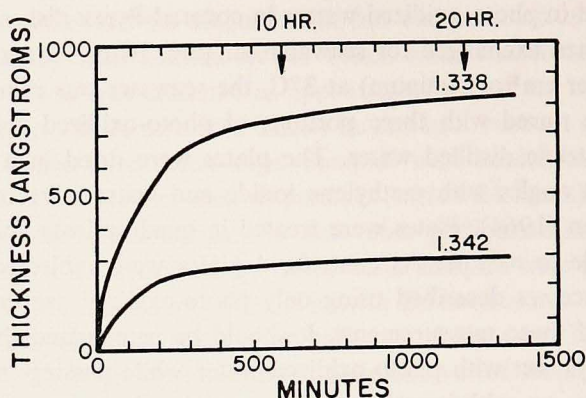
Figure 1. Ellipsometric observation of adsorption on polished platinum from Chesapeake Bay water (sample A, Table 2). Calculated thicknesses of the adsorbed film with different assigned values of the film refractive index (n) are plotted against immersion time.

properties of the surface. There was a small change in optical constants on changing from photo-oxidized seawater to distilled water which was instantaneously reversible and proportional to the ionic strength of the photo-oxidized water; this was interpreted as reflecting changes in the ionic atmosphere adjacent to the surfaces (Stedman, 1970).

When the photo-oxidized water was removed and replaced by raw seawater, an immediate change in optical properties occurred (Fig. 1); quite rapidly at first and continuing for about 20 hours at a progressively lower rate. Replacement of the seawater after 20 hours with a fresh portion did not lead to a significant change in rate, and replacement with photo-oxidized seawater arrested any further changes, i.e., the optical parameters remained constant. Similar results were obtained with two different water samples (A and D, Table 2).

Ellipsometric changes induced by raw seawater are consistent with formation of a surface film by adsorption of material from solution. Computation of both film refractive index and thickness is possible in principle under the assumption that the film is nonabsorbing at the wavelength used for observation. However, the refractive index of the film is so close to that of the seawater (immersion medium), most likely due to a high degree of solvation, that errors incurred in its determination lead to very large errors in calculated film thickness. Therefore, the values of film thickness given are derived from assumed values of the refractive index. The values chosen are both compatible with the experimental values of the ellipsometric data and also reasonable since they are intermediate between the refractive index of the solvent and that of biopolymers. (Serum albumin films, for example, present similar difficulties for ellipsometric analysis, Smith, L. E., personal communication). The

Table 1. Contact angles on known surfaces and on platinum exposed to seawater.

Sample	Contact angles with:	
	diiodomethane	water
Clean platinum	<10°	0°
Platinum after immersion in seawater		
from Chesapeake Bay (sample A, Table 2)	33°	45°
Nylon 2	30°	49°
Poly (methyl glutamate)	30°	49°
Polyethylene	52°	94°

values of film thickness will need to be corrected when the film index is accurately determined. The effects of nonhomogeneity of the film and the possibility of its being nonisotropic may also affect the calculated values of film thickness (Abeles, 1963; McCrackin and Colson, 1963). The kinetics of adsorption, however, are well represented by Figure 1. Although an equilibrium value may not have been reached after 20 hours with the volume of seawater used, prolongation of the experiment was not warranted in view of the risk of bacterial contamination and the lack of any change in rate on adding a fresh sample of seawater to the cell.

Table 1 shows the contact angles of diiodomethane and water on platinum exposed one week in photo-oxidized and natural seawaters and then washed in photo-oxidized and distilled water. For comparison, contact angles on several organic surfaces of known composition are also shown.

In theory a particle with high electrical conductance should have a very low electrophoretic mobility but, in practice, this occurs only when charge transfer processes across the solid-electrolyte interface can occur reversibly with little or no polarization (Henry, 1931; Overbeek, 1950). In commonly used electrolyte solutions, gold, silver and other metal particles behave electrophoretically as if they were insulators, probably because their surfaces are readily polarized and no appreciable current flows through the particle (Harrison and Elton, 1959; Benton and Sparks, 1966). In the present investigation platinum in seawater also appeared to behave in this way.

The photo-oxidized seawaters used showed no significant differences in their effect on platinum particle mobility, the mean value for all samples being 0.55 (Table 2). Constancy of the mobility of platinum in photo-oxidized seawater of different salinities is unexpected but has been confirmed over a much wider range of salinities than encountered here (Neihof and Loeb, 1976) and suggests an unusual interaction of platinum with the ions of seawater. pH changes in the range encountered in these waters had no appreciable effect on mobility.

In contrast to the results in photo-oxidized water, the mobilities of platinum particles in centrifuged raw seawater were always negative, i.e., their surface charge

Table 2. Electrophoretic mobilities of platinum particles in seawater.

| Sample | Salinity (‰) | Mobility (μm/sec)/(volt/cm) | |
		in raw seawater	in photo-oxidized seawater
A	9.4	-0.82 ± 0.02	
B	9.7	-0.80 ± 0.02	
C	10.5	-0.85 ± 0.04	$+0.55 \pm 0.06$
D	15.3	-0.67 ± 0.04	

was negative (Table 2). The mobilities also show the expected inverse correlation with salinity which was observed with other particles exposed to raw seawater (Neihof and Loeb, 1972).

The standard deviation of the means of different mobility determinations (20 particles each) for platinum in photo-oxidized waters was significantly larger than that for particles in raw seawater (see Table 2). This is likely to be due to the great sensitivity of clean platinum to traces of contamination which change the surface charge and the relative insensitivity to such contamination of the surface after it is covered with the film adsorbed from seawater.

4. Discussion

The results from the three different methods of investigating the interaction of platinum with seawater are consistent with the hypothesis that an organic film adsorbs on the metal surface.

By electrophoresis we find that clean platinum carries an electropositive charge in seawater depleted of organic matter, but it becomes electronegative on immersion in natural water. These results are similar to those obtained earlier with a wide variety of nonmetallic particles (Neihof and Loeb, 1972). Since similar surface charges were found in that study for all materials after immersion in seawater, whether positively or negatively charged in photo-oxidized waters, it was concluded that electrostatic interactions were not solely responsible for the adsorption. (Neihof and Loeb, 1972). There is also a similarity to the finding of Abramson that the mobilities of a variety of conducting and nonconducting particles were closely similar after an adsorbed film of protein had been allowed to form on their surfaces (Abramson, 1931).

After immersion of a mirror-smooth, platinum plate in photo-oxidized seawaters, drops of water and diiodomethane on the surface had very low contact angles (Table 1) as expected for clean metals (Zisman, 1964). After immersion of the plate in natural seawaters, however, the results were quite different. The much higher contact angles of water and diiodomethane indicate a less wettable, lower

energy surface consistent with the presence of an organic film. The angles suggest that the film has a closer similarity to the polar nonionic nylon and poly (methyl glutamate) materials than to the nonpolar polyethylene.

Similarly the ellipsometric measurements showed that the optical properties of the platinum surface in photo-oxidized seawater agreed with the accepted value for clean platinum (Barrett and Parsons, 1970) but changed on immersion in natural seawater in a manner consistent with formation of an organic film on the surface. A reasonable value for the film thickness is calculated if a refractive index compatible with the experimental data and corresponding to a reasonable biopolymer (Stromberg *et al.*, 1970) are assumed.

In principle the long term changes in optical properties of the film covered platinum surface (Fig. 1) could be interpreted as due to changes in film refractive index rather than film thickness. However, the electrophoretic mobility of platinum particles becomes constant within one hour of exposure to seawater which means that the coverage of the surface is complete in that time and that there is no further change in the surface charge density. The longer term ellipsometric changes are consistent with these electrophoretic results if interpreted as adsorption of additional material of the same composition and refractive index to yield a film of increasing thickness.

It should be pointed out that the decrease in apparent rate of build up of the film (Fig. 1) was not due to the depletion of adsorbable organic material in the seawater sample, since exposure of the platinum to a fresh portion of seawater did not affect the rate of change of the optical properties of the surface. This conclusion is reinforced by a calculation which shows that, with reasonable assumptions of film thickness and density, adsorption on all of the solid surfaces to which the sample was exposed would deplete the total dissolved organic matter in typical estuarine water by only a few percent.

It was noted that platinum particles equilibrated with raw seawater retained their anionic charge unchanged after five 10-ml washes in photo-oxidized seawater. No apparent changes in the thickness of the adsorbed film on platinum were detected by ellipsometry on immersing the surface in photo-oxidized seawater, and contact angles on platinum carrying an adsorbed film were markedly different from those on clean platinum after repeated washes in photo-oxidized seawater and distilled water. The film, once formed, is apparently held tenaciously. Since strong retention of an adsorbed film is characteristic of macromolecular adsorbates with multiple binding sites, these results are consistent with adsorption of high molecular weight material. Previous adsorption experiments with dialyzed seawater indicated that at least some component of the adsorbed film was macromolecular (Neihof and Loeb, 1972). The polymeric humic substances present in seawater have been suggested as likely candidates for adsorption and spectral data are consistent with their participation in films adsorbed from seawater (Loeb and Neihof, 1975).

The pertinence of the adsorbed film to biological surface growth, corrosion processes, and electrometric measurements is being investigated.

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