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Dissolved Organic Matter in Seawater and the Electric Charge of Immersed Surfaces

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ABSTRACT

Changes in the electrical charge that occur on the surfaces of test particles of quartz, germanium, and an anion-exchange resin when they are exposed to natural and artificial seawater have been studied by means of microelectrophoresis. Although the materials all assumed surface charges in a moderately electronegative range when immersed in natural seawater, they showed pronounced differences in charge consistent with their inherent chemical nature when exposed to seawater pretreated with ultraviolet irradiation to photo-oxidize organic matter. The characteristic surface charge exhibited by solids in seawater thus appears to be due to adsorbed organic constituents. The possibility that minor inorganic constituents of seawater might play a significant role in determining the surface charge of solids in natural seawater is unlikely because the surface charges were nearly the same in photo-oxidized seawater and in an artificial seawater of the same salinity containing only major inorganic components.

Introduction. The surfaces of solids in the sea are the sites of phenomena of geochemical, ecological, and economic importance. The formation, aggregation, sedimentation, and flotation of particulate matter (Krauskopf 1967, Breger 1970, Carlucci and Williams 1965), the colonization of surfaces by periphytic organisms (ZoBell 1946, Meadows and Anderson 1968), and the deterioration of immersed materials through fouling and corrosion (Wood 1965, Butler and Ison 1966) are all affected by processes occurring at solid-liquid interfaces. To gain a better understanding of these matters it appears particularly important to define the earliest events that take place on immersion of a material in seawater, since these may mediate or direct subsequent processes. It is with this objective that we have studied the changes in surface electrical charge occurring on solid surfaces after contact with seawater.

In an earlier study we found by electrophoresis that the mobilities (and therefore surface charges) of a wide variety of materials that ranged from strongly positive to strongly negative in artificial seawater converged to a narrow range.  

1. Received 1 May 1973; revised 7 July 1973.
of moderately negative mobilities in natural waters from several coastal sources (Neihof and Loeb 1972). This range was similar to that of natural particulate matter such as bacteria, small algae, and detritus. These results suggested that the characteristic charge of surfaces in seawater may be due to the adsorption of dissolved electronegatively charged constituents. The additional finding from dialysis experiments, that a significant fraction of the adsorbing material was of high molecular weight, suggested that organic matter might be involved. This possibility is strongly supported by the results of numerous other kinds of experiments showing that organic substances collect at interfaces in seawater (Harvey 1941, ZoBell 1943, Bader et al. 1960, Chave 1965, Parker and Barsom 1970).

To evaluate the contribution of organic matter to the surface charge of materials immersed in seawater it is necessary to have a control seawater that is free of organics. Artificial seawater as normally prepared is not satisfactory for this purpose because of traces of surface-active material present in reagent grade salts (Jarvis and Scheiman 1968, Wallace et al. 1972). It is also conceivable that differences in minor inorganic constituents of artificial as compared with natural seawater might be sufficient to cause differences in the charge on immersed surfaces. An attractive alternative to artificial seawater lies in the use of the ultraviolet photo-oxidation procedure of Armstrong et al. (1966), which has been shown to eliminate most of the dissolved organic matter in seawater without apparent change in inorganic composition. In this investigation we have used this technique to determine the extent to which dissolved organic matter in seawater from diverse sources is responsible for the characteristic surface charge acquired by solid materials of inherently different charge type.

Materials and Methods. The apparatus and methods for making electrophoresis measurements have been described elsewhere in detail (Neihof 1969, Neihof and Loeb 1972). Briefly stated, the procedure consisted in observing with a microscope the velocity of particles moving in a flat quartz cell under a known gradient of electrical potential. Thermostatting to avoid thermal convection (25.0°C) and a palladium electrode system that eliminates gas bubble generation (Neihof and Schuldiner 1960) made possible the use of the high currents necessary in media of high conductivity such as seawater. The electrophoretic mobility, $M$, in $(\mu m/sec)/(V/cm)$ was computed from the formula:

$$M = \frac{DKA}{TI},$$

where $T$ is the time in seconds required for a particle to traverse a distance $D$ in $\mu m$, $K$ is the specific conductance of the suspending medium in ohm$^{-1}$cm$^{-1}$, $I$ is the current in amperes, and $A$ is the cross-sectional area of the electrophoresis cell in cm$^2$. 
Test particles of quartz, germanium, and a strong-base ion-exchange resin carrying quaternary ammonium groups (Dowex 21 K) were chosen because of their widely differing surface properties. Quartz and germanium are also amenable to rigorous cleaning procedures and are suitable for optical studies that are in progress. The materials were powdered in suitable mortars and the particles fractionated by differential sedimentation to retain those with diameters in the range of about 0.5 to 5 µm. Quartz particles were cleaned in several changes of hot concentrated nitric acid, washed thoroughly in distilled water, and ignited overnight at 600°C. Germanium particles were heated overnight at 600°C in an atmosphere of purified hydrogen. The ion-exchange resin was washed several times in triple-distilled water. Contact of cleaned particles with the laboratory atmosphere and other possible sources of contamination was minimized.

All glass and Teflon ware that was to contact seawater was cleaned in a mixture of hot concentrated nitric and sulfuric acids and rinsed thoroughly in distilled water. Teflon containers were also steamed for 30 to 60 minutes before use.

Seawater samples were obtained from two sources: the Chesapeake Bay off Patuxent Naval Air Station, Maryland (collected at the surface at high tide 3 May, 1972, salinity 9.0%/o, pH 7.9) and the Gulf of Mexico about 350 km WNW Key West, Florida (collected 29 March, 1972, salinity 35.4%/o, pH 8.1). The latter sample was taken about one meter below the surface through well-flushed Nytex and polyethylene tubing by suction into 20-l carboys and was received in the laboratory two days later. Both samples were filtered through 300-µm Nylon plankton netting at the time of collection and stored at 3°C in Pyrex or Teflon FEP containers. Before use, water samples were centrifuged for 30 min at 18,000 g in 150 ml Corex bottles to free them of natural particulate matter.

The artificial seawater contained reagent grade salts nominally contributing only the seven major ions in seawater in the relative amounts given by Lyman and Fleming (1940). The concentration of the solution was adjusted so that its conductivity matched that of the natural seawater under comparative study.

The ultraviolet photo-oxidation procedure of Armstrong et al. (1966) was amended in this investigation to provide more rigorous oxidation conditions by irradiating for 24 hours and adding 2 drops of 30% hydrogen peroxide per 120-ml quartz container at three or four intervals during the irradiation. Artificial-seawater as well as the natural-seawater samples were so treated.

The dissolved organic carbon content of the water samples was determined by the method of Menzel and Vaccaro (1964).

In a typical experiment, particles were suspended initially at a density of about $3 \times 10^7$ particles/ml in 5 to 25 ml of seawater in a centrifuge tube; subsequently they were exposed to successive fresh 25-ml portions of seawater by centrifugation and resuspension. In order to keep particles well dispersed, it was occasionally necessary to irradiate the suspensions ultrasonically with a
Figure 1. Electrophoretic mobilities of particles in artificial and Gulf of Mexico seawater. Artificial seawater: germanium, circles; quartz, open squares; anion-exchange resin, open triangles. Gulf water: germanium, dots; quartz, solid squares; anion-exchange resin, solid triangles.

metal probe shielded from direct contact with the seawater by a glass test tube partially filled with water; mobilities were not detectably affected by this treatment. For mobility measurements, aliquots of suspension were removed from the centrifuge tube and diluted to about 2 ml with the appropriate seawater to obtain a concentration of about \(0.4 \times 10^7\) particles/ml. The mean mobility of 20 particles was routinely taken to characterize a suspension; standard deviations of ±0.05 to ±0.10 (µm/sec)/(volt/cm) were typical.

Results and Discussion. The results of experiments pertaining to Gulf of Mexico and Chesapeake Bay seawater are summarized in Figs. 1 and 2, respectively.

In photo-oxidized seawater the model particles exhibited widely different mobilities (Figs. 1A and 2A). Anion exchange resin and quartz carry pronounced positive and negative charges, respectively, as would be expected from the nature of the dissociable groups on their surfaces. The negative mobility of germanium in photo-oxidized Bay water is consistent with ionization of surface germanic acid groups (Sparnaay 1960), but it is relatively low; in the higher-salinity Gulf water it is reduced to zero. No significant changes in mobilities occurred with exposure to increasing volumes of photo-oxidized water.

As shown in Figs. 1A and 2A, the mobility of each kind of particle in each of the two concentrations of artificial seawater agreed well with that in photo-oxidized seawater of the same salinity. Thus it appears that in photo-oxidized seawater the seven major ions were sufficient to determine the surface charge on these solids. It can be concluded that the role of minor inorganic constituents in producing the changes in surface charge observed when the particles are transferred to untreated natural seawater must be insignificant except for
the possible coincidence that trace inorganic impurities in the reagent salts of artificial seawater affect mobilities in the same way as the trace constituents of the natural seawater.

The higher mobilities of a given kind of particle in water of 9.0‰ salinity (Bay water) compared with those in water of 35.4‰ salinity (Gulf water) are largely attributable to the well-known ionic strength effect that results in a more expanded ionic double layer outside the surface of shear around the particle in water of lower electrolyte concentration (Abramson et al. 1942).

After equilibration in untreated seawater (Figs. 1C and 2C), model particles can assume mobilities that are greatly different from those exhibited in the photo-oxidized water. The range of mobilities was 0 to –0.6 for Gulf water and –0.55 to –0.9 for Bay water. This constriction of the mobility range confirms previous results obtained with other materials and other water samples (Neihof and Loeb 1972). Such behavior is readily explained by the adsorption of soluble organic constituents from seawater since it is well known that an adsorbed coating dominates the electrophoretic behavior of particles with different underlying surfaces (Abramson et al. 1942).

In untreated seawater, all model particle surfaces equilibrated rapidly (in less than 0.5 hour) with a given volume of water. However, the total volume of water to which the particles were exposed in order to obtain a final mobility that did not change on subsequent exposure to a fresh portion of water varied for the different materials. With quartz and germanium surfaces, coverage by
adsorbed material was apparently complete during the first contact of particles with the smallest volume of water used (5 ml), and no significant changes in mobility occurred with increasing volumes of either sample of natural seawater. With particles of ion-exchange resin, however, there was an indication of less than equilibrium coverage with exposure to small quantities of Bay water, and in Gulf water, exposure to about 250 ml was required before a constant surface charge was reached. The greater volume required for equilibration of the resin is probably due to its porosity and high density of ion-exchange groups that increase its capacity for interaction with seawater constituents compared with the relatively smooth nonporous surfaces of glass and germanium. The larger volume of Gulf water than of Bay water required by the resin to reach a constant surface charge is inversely correlated with the content of dissolved organic matter: 0.75 mg C/l for Gulf water compared with 2.3 mg C/l for Bay water. The failure of the ion-exchange resin mobilities to approach the mobilities of quartz and germanium as closely in Gulf water as in Bay water may be due to incomplete surface coverage after equilibration with the water sample of lower organic content, but other causes cannot be ruled out.

The results of transferring particles that had been exposed to repeated changes of photo-oxidized seawater (Figs. 1A and 2A) to untreated seawater are shown in Figs. 1B and 2B. In all cases there was a change in mobility after comparable exposure to the values obtained by direct immersion of fresh particles in untreated seawater (compare with Figs. 1C and 2C). Thus, exposure to photo-oxidized seawater produces no irreversible surface charge changes on any of the model particles.

An assessment of the difficulty of removing adsorbed constituents was made by washing particles, previously equilibrated with untreated seawater, in photo-oxidized seawater. After the particles had been washed in eight 25-ml portions over a period of a day, the mobility of the ion-exchange resin was unchanged, and the mobilities of quartz and germanium remained much closer to the values obtained in natural water than to those obtained in photo-oxidized water: a strong retention is thus indicated. Such behavior is characteristic of macromolecular substances carrying multiple binding sites that bind cooperatively (Silberberg 1962).

The results of this study show that materials with electropositive or strongly electronegative surface charges are unlikely to exist in natural seawater; this is consistent with the findings of an earlier study on naturally occurring particulate matter (Neihof and Loeb 1972). Materials that are capable of exhibiting extreme surface charges in water containing only the inorganic constituents of seawater assume moderately negative charges when exposed to natural seawater. This occurs as a result of a rapid interaction with dissolved organic substances. In view of the variety of materials on which such adsorption has been shown to occur, we suggest that it may take place on all surfaces at least to some extent. Dissolved polymeric substances in particular have the required
properties for this interaction. Proteins, humic acids, and other substances derived from the degradation of natural products of marine and terrestrial origin are surface-active polymers carrying a net negative charge at the pH of seawater and are therefore attractive candidates (Duursma 1965).

Although the similar charge assumed by the different model particles in seawater, especially the estuarine sample, suggests that similar constituents are being adsorbed, there is no certainty that they are the same. Different solid substrates are known to show specific adsorptive selectivities for the various dissolved constituents in seawater, and it would not be surprising if such specificities existed among the substrates used in this investigation. Spectral studies now in progress may help to elucidate these and other questions.

**Acknowledgments.** We thank Robert Lamontagne and Gene Bugg of the Ocean Sciences Division for the organic carbon analyses and E. M. Swiggard and W. J. Moore of the Solid State Division for cleaning the germanium powder.

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