# The Colloidal State and Surface Phenomena – Group Report

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## INTRODUCTION

Seawater contains particles, both inorganic and biologically produced, ranging in size from colloidal to those which will settle under gravity. The concentration of particulate matter in any part of the oceans depends on the proximity and magnitude of inputs of solid material. Such sources can be both external (atmosphere, land masses, marine sediments) and internal, which includes particles formed biologically as well as those produced by bubbling, precipitation, etc. Solid-liquid interfaces provided by the particles are sites for a wide variety of chemical and biological interactions. Similarly, wind-induced bubbling near the sea surface gives gas-liquid interfaces which are also highly reactive. In the absence of interfaces of both sorts, the types and rates of processes occurring in the marine environment would be very substantially reduced. Of paramount importance to surface chemistry are synergistic effects (a) between compounds (surface chemical interactions between lipids and proteins); (b) between disciplines (organic coatings on inorganic particles); and (c) between kingdoms (biota grazing at surfaces). Such interactions add greatly to the interest (and difficulty) of marine surface chemistry.

## ELECTRON TRANSFER REACTIONS

Electron transfer in aqueous media occurs either homogeneously or at surfaces. To the marine chemist the surface can be either a natural solid particle or the "dirty piece of platinum" (Sillén) sometimes used to measure the oxidation potential of seawater. Whether the electron exchange is homogeneous or heterogeneous makes little basic difference in the statistical theory of these reactions developed by Marcus (this volume), because the surface may be regarded simply as an additional reagent in the reaction mixture. There is good agreement between the Marcus model and results of laboratory experiments on "pure" solutions, except in the case of Co(III), for which considerable discrepancies occur.

Although the theory is statistical, this should not produce problems in applying it to seawater, where the concentration of many transition metal ions is of order $10^{-9}$ M. Even at these low concentrations, there will be about $10^{14}$ species per liter, and since statistical fluctuations are proportional to $N^{-1/2}$ (where N is the species concentration), such perturbations will be negligible. In the case of a biological system, a single event may produce a whole chain of reactions, each of which would have to be treated separately. Rates of electron transfer reactions for low reactant concentrations are generally not subject to diffusion control, unless the reaction itself is very rapid. For example, if hydrated electrons can be formed in surface seawater (see "Photosynthesis" section), then, because they exhibit extremely fast kinetics, there would probably be diffusion control of the reaction rate. Application of the model to seawater is complicated somewhat by the large number of competing reactions, but even greater problems are likely to arise because of the current lack of knowledge concerning the speciation of many elements in seawater.

## TECHNIQUES FOR COUNTING PARTICLES IN SUSPENSIONS AND SCATTERING PROPERTIES OF SEAWATER

Light-scattering is a technique widely used in oceanography for the study of particles in suspension (Jerlov, 1968). In seawater, a light beam will experience scattering from three components: the water, the dissolved electrolytes, and the particles in suspension. The first two are well understood, but because the particles have widely differing shapes, sizes, refractive indices, and internal structures, their light-scattering properties are extremely complex. The applicability of the Mie theory for spherical isotropic particles (Kerker, 1969) to the assemblage of particles found in seawater is of unknown reliability at present. In spite of this, oceanographers (as well as other scientists) regularly use scattering techniques to look at suspended particles.

Another technique widely used for studying marine solid phases is the Coulter counter (Strickland and Parsons, 1972) which measures the change in solution conductance produced by the presence of particles. This instrument suffers from the deficiency that only a part of the spectrum of particle sizes can be examined at any one time, and what is really measured is not the particles themselves, but a complicated function of the relative conductivities of the particles and the solution.

The most promising novel experimental technique for particle size analysis, counting of particles, and studies of colloidal stability of particulates is to use single particle scattering counters (Kratohvil, personal communication). These devices, which use laser sources, are already applied to various hydrosols and aerosols. Further research should be conducted on model particles, spherical and nonspherical, of sizes as found in seawater (up to 100 $\mu$m) in order to establish the calibration procedure.

Another novel technique worth exploring is the effect of an electric field on light-scattering by suspended particles (Jennings, 1972). In the case of clay suspensions, the quantities derived from such measurements (dipole moment, rotatory diffusion

coefficients, particle mass, radius of gyration) can help in deducing the possible mode or modes of aggregation of clay particles (Schweitzer and Jennings, 1971).

The exchange of ions on clay particles is known to change their stability and hence scattering properties, a topic worth pursuing further with seawater clays (Kratohvil, personal communication).

Except for the soluble macromolecular substances, the application of laser scattering spectroscopy (Chu, 1975) to seawater particulates will probably be limited to the determination of their electrophoretic mobility from the shift of the broadened Rayleigh line caused by the applied electric field (Ware, 1974; Uzgiris and Costaschuk, 1973).

Aggregation-disaggregation of particles at high pressures can also be followed by light-scattering, and instrumentation for working at pressures up to 1500 atm has been described (Schulz and Lechnor, 1970).

In respect to studies of light penetration in the sea, less reliance on the theoretical computed Mie scattering functions is recommended. What is needed are absolute measurements of scattering radiance, as well as polarization and turbidity, in the single and multiple scattering regimes (Querfeld et al., 1972) on model suspensions consisting of particles of well-defined geometrical shapes.

## ELECTRICAL PROPERTIES OF PARTICLES

A hydrophobic particle immersed in an aqueous solution will generally carry an excess surface charge. This can be acquired by dissociation of surface groups, uptake of ions such as $H^+$ or $OH^-$ from the water or may be a property of the solid structure, e.g., isomorphous substitution in clays leading to an excess negative charge or unsatisfied valencies at the edges of crystal matrices. Whatever its cause, such surface charge will produce polarization

of the water and electrolyte ions close to the particle. Immediately adjacent to the charged surface there will be a thin layer of ions of charge opposite to that of the particle, and further out a more diffuse region of counter ions. Together these constitute the electrical double layer. The magnitude of the voltage drop across the outer part of the layer ( the $\zeta$ potential) is important in determining particle stability. In weak or dilute electrolytes the number of counter ions in the inner part of the double layer will be small, leading to a relatively large $\zeta$ potential. If there are nearby particles having similarly large $\zeta$ potentials, electrostatic repulsion between them will inhibit aggregation. In seawater, one would predict that due to the high electrolyte concentration, most of the excess charge on particles will be neutralized in the inner part of the double layer. This will lead to small values for the $\zeta$ potential and consequent destabilization by compression of the double layer and coagulation of unprotected colloidal particles. The coagulation process should be particularly dramatic in estuaries where the charged particles experience rapid changes in electrolyte concentration.

Through the above approach it is possible to understand why some ions are adsorbed by particles more strongly than other ions, and to explain trends in adsorption within groups of elements in the periodic table. Such properties can also be thought of in terms of particular reactions, such as ion exchange and coordinate bonding, in which ions are held at specific sites rather than by more general electrostatic forces. For instance, using a coordinate model for the uptake of trace metals by silica particles, it has been possible to account for the observed residence times of these metals in the oceans (Schindler, 1974). There is no real conflict between the double layer and specific interaction approaches. The former is more useful in describing ion adsorption and the latter in explaining ion exchange reactions. Neither theory seems able to explain the changes in composition of marine sediment pore waters found when the water is squeezed from the sediment at different temperatures. Perhaps

particle-particle interactions (see next section) are important in explaining such effects.

Application of double layer theory to solids in the real ocean is made complex because particles in the marine environment are coated with organic material which will provide steric stabilization and thus greatly alter their electrical properties. For example, it has been shown that estuarine particles, examined by the streaming current method, have surprisingly large $\zeta$ potentials, and the sign of the charge can reverse with increase in water salinity (Pravdic, 1970). Organic coatings obviously modify very considerably the predictions of double layer theory and enable particles to remain discrete in spite of the high salt content of the water.

The chemical composition of organic coatings on particles in the ocean is largely unknown, but such coatings are probably reworked by marine bacteria and other microorganisms. Within the sediments, polychaete worms will also be of great importance both in coating particles with organic material and in mixing bottom deposits. Organic layers are difficult to remove by mild chemical treatment (dilute HCl), implying that once coated, a particle is likely to remain so, except possibly in the sediments where there is some evidence for degradative breakdown.

## CHARACTERIZATION OF SEDIMENTS

The interaction between sediment and solution is important in determining the composition of seawater. Particle-particle interactions are important in understanding the nature of pore solutions, mass transport through the sediments, and pore-water content. The pore structure will also depend on the kind of particle (e.g., silica, kaolinite, montmorillonite), their shape and size distribution, as well as pressure and the chemical composition of the pore water. For example, at atmospheric pressures montmorillonite particles form a gel, but at higher pressures, ca. 10 atm, the clay platelets become aligned in parallel arrays. On the other hand, at atmospheric pressures kaolinite

particles can form "card-house" structures because the edges and faces of the clay platelets are of opposite electrical charge. The application of high pressures, e.g., about 60 atm, can crush the "card-houses" and cause the platelets to take on some degree of alignment.

Little appears to be known about the arrangement of clay particles coated with marine organic matter, and this may be a controlling feature in understanding particle interaction in marine sediments. Therefore, it is important to study how natural samples of coated clay particles pack under pressure and to measure pore volumes, surface areas and pressure-volume responses (packing structure), and electrokinetic properties. Of the various methods available, surface area measurements may be most immediately accessible.

Methods of measuring the surface areas of solid particulate material can be broadly divided into two categories:

(1) examination of the material in the dry state;
(2) examination in the "wet" state, e.g., as far as possible that of the natural environment of the particles.

An approach commonly used for dried material is the BET method in which the adsorption of $N_2$ or Kr is determined at liquid nitrogen temperatures. In the case of dried sea sediments, this would include salt crystals formed in the drying process. A further problem is that in the case of clay minerals, only the external surface is detected by $N_2$ molecules. The adsorption of water vapor, however, can be used to determine the internal surface of clays. For the "wet" state, the adsorption of dye ions, surface active ions, and some nonionic molecules can be used. These methods, however, need to be carefully checked on standard samples, and the influence of organic matter present on the particles in marine sediments will have to be taken into account. In some samples, e.g., sands, manganese nodules, the porosity of the particles will also need to be investigated.

Newly developed flow microcalorimetric methods (Templer, 1972) offer both the sensitivity and the capability of studying marine sediments without pretreatment, with respect to determining the specific surface area and energetics of adsorption of a variety of naturally occurring and man-made organic compounds.

## NATURE AND STRUCTURE OF SOLID PHASES

Zeolites are aluminosilicate minerals having a framework structure whose ion exchange properties are due to the presence of aluminum. These properties are well characterized and can be understood in terms of crystal structure. Zeolites vary greatly in internal porosity and in Si/Al atom ratio (from 1/1 to 5/1). Ion exchange selectivity is a function of both the porosity of the structure (and therefore water content) and Si/Al atom ratio. There are only two zeolites or groups of zeolites reported to be present in marine sediments, namely phillipsite and clinoptilolite. Phillipsite in marine sediments is derived from alteration of basic glass, while clinoptilolite is an alteration product of silicic volcanic ash. Based on general selectivity rules, phillipsite with Si/Al ratio of about 1.5/1 should prefer alkaline earth to alkali metal cations and potassium over sodium, and clinoptilolite with a Si/Al atom ratio of 5/1 should prefer sodium to calcium ions and potassium over sodium. Literature data indicate that this statement is correct. Most trivalent cations do not diffuse into the naturally occurring zeolites at any measurable rate at ambient temperatures because of the necessity of stripping the hydration envelopes from these cations, and because of the strong interactions that occur with framework oxygen atoms within the zeolite structure. In the case of hydrolyzed trivalent ions (e.g., polymeric hydrolyzed oxides), exchange is further inhibited by physical blocking due to their large size. The rate of ion exchange reactions is either solid phase or liquid phase diffusion controlled. Which of these two resistances to mass transfer is rate controlling in the poorly stirred marine sediments depends on both particle size and the value of the ionic diffusion coefficient. For those zeolites with extremely dense structures and very small diffusion

coefficients, diffusion in the solid phase may be rate controlling. In open zeolite structures, liquid film diffusion may become the slow step. Alkali metal and alkaline earth cation exchange in phillipsite and clinoptilolite should fall into the latter category.

The ion exchange properties of clays can be understood and interpreted using the same general principles elucidated for zeolites. There are, however, problems which are specific to clays; for example, their anion exchange properties and kinetic problems arising from close packing of layers in some structures.

Other groups of minerals (and synthetic materials) possessing ion exchange properties are hydrous oxides and phosphates of polyvalent metals. In the case of hydrous oxides, the exchange capacity stems from nonbridging hydroxyl groups on the surface. Both anions and cations are exchanged, and this exchange is pH dependent. The initial exchange reactions are sometimes followed by a second reaction which fixes the ions on the surface. Examples of fixation include phase formation, such as $CaSiO_3$ which may accompany exchange of $Ca^{++}$ on active silica surfaces, and olation and/or oxolation of basic metallic species to the surface. The formation and subsequent surface reactions of hydrous oxides in seawater needs further study. Coprecipitation phenomena accompanying hydrous oxide formation and their effects upon surface properties are still poorly understood. Also, almost nothing is known about the effect of organic coatings on ion exchange reactions.

For phosphates, exchange takes place by an initial surface reaction involving phosphate-OH groups. With some phosphates, such as those of Zr(IV) and Ti(IV), this initial reaction is followed by diffusion into the interior of the structure. In others, i.e., Fe(III) and Al(III), diffusion is not extensive and ion exchange may be considered to be a surface reaction.

In anoxic sediments, insoluble sulfides form and these can exchange or adsorb with dissolved species in the pore water.

Zirconium phosphate may find uses as a separation tool in marine analytical chemistry due to its ability to take up ions such as $NH_4^+$, $Ca^{++}$, $Mg^{++}$ from solutions rich in sodium chloride. Furthermore, because they exhibit very high selectivities, inorganic exchangers may be applicable to problems of concentration, separation, and identification of seawater metal species.

## THE FORMULATION OF MIXED SOLID PHASES IN THE OCEAN - THE MANGANESE NODULE PROBLEM

The formation of deep sea nodules consisting of layers of manganese oxides and ferric hyroxide colloids appears to be a common phenomenon. Whether this is a true epitaxial growth of one phase upon another, or heterogeneous nucleation, is not yet known, and there is a need for model studies of the growth of synthetic manganese nodules in the laboratory. Various nucleating substrates should be investigated in order to first determine the most efficient heterogeneous nucleation sites for the growth of $Fe(OH)_3$ and subsequent manganese oxides under simulated seawater conditions. The determination of the critical supersaturations of manganese oxides and $Fe(OH)_3$ in the presence of trace concentrations of the other components will be particularly important.

It is now possible to study the kinetics of formation of synthetic nodules in the laboratory in order to assess the influence of trace metal ions on the rate of the process. The conditions under which $Fe(OH)_3$ or manganese oxides will grow on the other substrate will be determined by the results of such studies. Inhibition or initiation of the growth of one phase by traces of metal ions, organic impurities, and organisms, coupled with minute changes of pH, may account for the rather well-defined change in the nature of the growing phase (e.g., layered manganese oxide-$Fe(OH)_3$). Available information on the growth of crystals from supersaturated solution shows clearly that it is not necessary to completely cover the growing surface in order to modify the rate of the process. The number of active growth

sites may be relatively small. Redox reactions involving Fe(II) and (III) and Mn(II) and (IV) can also be investigated by this method.

A biological model of the interaction of metal hydroxide polymers and organic molecules is ferritin. This substance consists of Fe(III) hydroxide phosphate micelles coated with protein (Harrison and Hoy, 1973). The model is undoubtedly very different from a marine system, but it may furnish some clues to marine chemists.

Natural manganese nodules should be studied by selective dissolution of the surface phase. Not only would kinetics of the process be important (here we should mention that there is considerable electrochemical literature dealing with the dissolution of $MnO_2$ electrodes, e.g., Kordesch, 1974; Heise and Cahoon, 1971; Malati, 1971) but also the structure and composition of the surface phases. Microscopic studies (SEM, electron microprobes, ion microprobe, etc.) should be made as a function of depth in order to identify the layered structure of the nodules and the presence of trace metal ions. Potentiometric titrations (which will be described later) of the nodules in artificial seawater will yield information on the nature of the surface phases. These potentiometric titrations could be made with metal ions as well as the hydrogen ions.

## PARTICLES IN ESTUARIES AND DELTAS

An estuary is the meeting place for waters of very different chemical composition and properties. It is here that seawater of ionic strength approximately 0.7 M mixes with river water of considerably lower salt content and often lower pH. The fresh water, however, may be more concentrated with respect to the plant nutrient elements P, N and Si derived from land drainage, and many of the transition metals. During the mixing process the water will be in contact with solid phases, including sediment on the estuary bed and particles in suspension. These latter are derived from the inflowing river and sea waters, as well

as by resuspension of bottom material under the action of tidal currents.

Due to the large change in physico-chemical environment experienced by estuarine particles, a wide variety of mineral-water reactions are possible. For example, ion exchange occurs when riverborne solids encounter saline water in the estuary. Where the inflowing river water is acidic, elements which form insoluble hydrous oxides at the pH of seawater are removed from the water. There is field evidence for the importance of such a process for iron, and laboratory results indicate that the removal is more likely to be by heterogeneous nucleation onto pre-existing solid particles, rather than by homogeneous flocculation (Aston and Chester, 1973). The formation of such hydrous oxide phases could lead to the scavenging of other species from solution, but there is little field evidence for this at the present time. In highly polluted estuaries, the enhanced levels of dissolved organic molecules may lead to release of some transition metals from particles via formation of soluble organo-metallic complexes. As well as these chemical interactions, particles also show considerable changes in potential with water salinity, as discussed previously.

The above discussion gives some idea of the large variety of solid-water reactions which are possible in estuaries. From our present knowledge it is difficult to know the relative importance of the various interactions and whether they occur in all estuaries. In such circumstances the development of new chemical techniques does not seem warranted at the present. It may be possible to get some leads from other environmental areas such as soil science, but the way ahead is probably to use existing techniques for field studies and laboratory experiments of various degrees of complexity, aimed at simulating estuarine chemical processes.

## THE AIR-SEA INTERFACE

### Introduction

Defining the thickness of water constituting the surface layer of the oceans is a problem on a par with deciding the hydration number of an ion in solution or the size of a particle suspended in an aqueous medium. The thickness of the sea surface microlayer can be derived in a number of ways: (a) by harvesting a sample of water from the interface (methods for doing this are discussed below); (b) by measuring the level at which some physical property of the water near the interface begins to diverge from its value in the bulk water; and (c) from conceptual models of the interface, e.g., assume it is covered by a monolayer or interpret the kinetics of air-sea gas exchange in terms of a laminar film model. It is hardly surprising that these various approaches yield layer thicknesses spanning six orders of magnitude.

Most currently available field data have been obtained using surface samples which collect a slice of water approximately 200 $\mu$m thick. The results show that relative to subsurface water, the interfacial material is enriched in dissolved and particulate organics, trace metals bound to dissolved organic and particulate phases, bacteria and other microorganisms, DDT and PCBs. With such enrichments the interfacial layer has obvious importance in the transfer of matter and energy across the air-sea interface.

### Sampling Techniques

The available microlayer samplers are categorized in Table 1. While all of these samplers except the Baier slide may transport surfactants from underlying water to the surface, this problem is most serious for the bubbling techniques.

Three identifiable needs with respect to sampling are:

- better definition of the "surface" collected;
- comparison experiments to determine collection efficiencies for various classes of surfactant;
- methods for collecting larger quantities of the surfactant organic material.

TABLE 1 - Examples of microlayer samplers

| Sampler | Thickness sampled | Comments |
|---|---|---|
| Screen<br>Garret (1965)<br>Sieburth (1965) | ~200 μm | Quantitative for lipids, probably not for proteins. Good for neuston. |
| Skimmer<br>Harvey (1966) | ~200 μm | Probably as for screen |
| Bubble-microtome<br>MacIntyre (1968) | ~0.001 bubble diameter | Collects inner surface of bubble rather than air/sea interface |
| Germanium slide<br>Baier (1970) | molecular | Allows direct IR analysis of collected material |
| Foam fractionation<br>Lemlich (1972) | ~2 μm | Prefers most surface-active materials |

The use of polytetrafluoroethylene materials (Fluon and Teflon) should be carefully examined since these are not necessarily chemically inert. These materials are frequently prepared, prior to fabrication, by emulsion polymerization and hence the surfaces can contain chemical groups, e.g., carboxyl, which could bind metal ions. Bulk polymerized materials, e.g., FEP, are preferable, but again these should be checked for surface groupings.

Foam fractionation is a useful method of rapidly stripping milligram quantities of surfactant from the upper layers. Well known to surface chemists both as a preparative technique and as a way of removing surfactant contaminants from water, it has received little attention from oceanographers and appears to be a most promising technique. It consists of blowing air or nitrogen

through the system in order to create a foam, i.e. a large interfacial area with a small volume. Removal of the foam from the surface of the bulk phase thus yields a high concentration of the most surface-active materials.

## Trace Metals

The affinity of certain surfactants for trace metals ensures a high concentration of these biologically active materials at the molecular surface of the sea. Metals reach the sea surface either by atmospheric fallout of terrigenous or anthropogenous material, or by attachment to rising bubbles and spend appreciable time at the interface. Since the surface layer represents a high-energy food source utilized by a special biota, this material is directly available to the food chain in concentrated form. Since bubbles selectively eject near surface water, this material is also available for concentrated re-injection into the atmosphere.

The interfacial chemistry of these metals is largely unknown, and two identifiable problems with environmental repercussions are:

(a) the nature of "binding" of trace metals to the interface - whether inorganic particulate, biogenic particulate, or chemical binding to identifiable organic ligands of surfactant material;

(b) the processes which regulate trace metals in the microlayer. The sources, sinks, and transfer rates are still mostly conjectural.

## Photochemistry

The surface microlayer is the only region of the ocean in which ultraviolet photochemistry may be important, and studies exist for both iodine and hydrocarbons. However, such fundamental information as the wavelength-vs-depth spectrum of actinic light within the microlayer seems to be unavailable. The possibility exists of generating, however briefly, a photochemically induced hydrated electron within the microlayer, and thence direct reduction of an available electron acceptor. It is of some interest to put better limits on microlayer photochemistry.

## Physico-Chemical Hydrodynamics

The physico-chemical hydrodynamics of the microlayer dominates the transfer of particles from sea to air, and affects the transport kinetics of water, gases, heat, and momentum. Identifiable problems in this area include:

(a) The chemical nature of organic material in the microlayer. Despite considerable work, our understanding is best described as rudimentary, and agreement between methods (of collection and analysis) leaves much to be desired.

(b) Glycoproteins (proteins with sugar sidechains, of which a bacterial cell membrane is a typical single-molecule example) may be the most important member of the interfacial chemical family. It is important to verify the identification of these compounds and to develop (or import) methods for studying them.

(c) The rheological nature of the microlayer - its viscosity, surface tension, elasticity, etc. - is particularly important with respect to interfacial transport, but is largely unknown. Part of the problem may be that existing information on the surface chemistry of proteins is underutilized by oceanographers. Specific data on the rheology of microlayer constituents is nonexistent, but can be obtained using the traditional tools of the surface chemist: static and dynamic measurements of surface tension, potential, and viscosity.

(d) Bubble-bursting is demonstrably the most important sea-to-air transfer mechanism for both particles and electric charge. The dynamics of the process remain elusive, and we do not know, for instance, the changes in transfer resulting from changes in surface tension or viscosity. There is evidence that the gas composition of the bubble can influence transfer, but no theory to suggest reasons for such influence

## NOVEL TECHNIQUES FOR USE IN STUDIES OF MARINE INTERFACES

### Separation of Particulate and Dissolved Fractions

The most popular method of separation currently in use, namely that of using a filter membrane having a pore diameter of approximately 0.5 $\mu$m, is open to question:

(a) on the basis that the separation between various particle sizes is arbitrary and that colloidal material and macromolecular material will pass through the filter;

(b) that microorganisms can be damaged by the filtration process and so alter the composition of the aqueous phase.

For collection and partial fractionation of the suspended material prior to examination, the use of centrifugation could prove valuable in giving fractions as a function of the size and density of the particles. Modifications of the centrifuge technique are possible in that separations can be achieved by variation of the centrifugal field. In addition, a continuous flow centrifuge can be used for the treatment of large volumes of material. This technique has already proved useful in collecting particulate material from seawater (Chester et al., 1974).

For more detailed examination of the colloidal fractions, both lyophobic (particulate) and lyophilic (macromolecular) dialysis could be used to remove the seawater electrolytes. While accepting that this could cause long term changes in the system removal of salts would be necessary for the most advantageous application of some techniques, e.g., electrophoresis. Short term dialysis, e.g., against $10^{-3}$ M saline, could be achieved by about three changes of dialysate of two hours each with the colloidal fractions contained in the dialysis bag.

## Microelectrophoretic Examination

It appears probable that much of the material in the dialysis bag will be of an organic nature, and this can be used as a starting point for qualitative investigations of its nature. One possible approach is to adsorb the material on to carrier particles of known size and surface properties which can then be examined by microelectrophoresis. The reversal of electrophoretic charge by various inorganic ions falls into well-defined patterns depending on the nature of the chemical groups on the surface - the so-called reversal of charge spectra (Kruyt, 1952). Establishment of the ion-binding sequence for cations with the organic matter from seawater would give useful clues as to the nature of its composition.

## Potentiometric and Thermometric Titrimetry

Potentiometric titration is a relatively simple technique that can probably be carried out on board ship. For well-defined model systems it has been used as a tool to obtain information on the number of charged groups on the surface, sometimes also on their nature and ion-binding. Although the situation in seawater is obviously far more complex, it seems that the expertise available with model systems can be helpful as a tool of characterization in addition to the existing ones.

Titrations can be performed with any dispersed matter, whether colloidal or suspended. The material may be marine sediments (crushed or original), particulate matter, manganese nodules, material taken from the sea surface, both organic and inorganic materials, or mixtures of them. Fractionation and/or concentration as a first stage is required to obtain a large enough adsorbing area. How much is actually needed depends on the surface area of the material, or, for that matter, on the amount of available titratable groups. Perhaps it is of the order of a few hundred milligrams.

The classical titration is a pH-titration which can be carried out in situ. It gives the number of groups that at a given pH are protonated. In the most ideal systems (isolated polyelectrolytes or proteins) it is sometimes, but not always, possible to distinguish between different groups (carboxyl, $\varepsilon$-amino, etc.). However, in the case of seawater, we might expect to obtain a composite overall curve which would be relatively uninformative. Hence, it seems more appropriate to apply the titration technique in conjunction with dialysis and fractionation so that information can be obtained on the influence of salts (nature and concentration) on the various components of the mixture to be investigated. For this reason, dialysis down to about $10^{-3}$ M should precede the titration.

Once the material is available in $10^{-3}$ M electrolyte, preferably in fractionated form, it can be titrated with $H^+$ or $OH^-$ ions

(preferably in two directions to analyze the extent of pH reversibility) as a function of the concentration of deliberately added electrolytes. Electrolytes "screen" any charge on the material to be titrated, thereby reducing the mutual electrostatic repulsion between adjoining charged groups. Consequently, more groups become dissociated at given pH and upon titration. This is measured in that more acid or base (depending on the direction of titration) is needed over a particular pH range. It is here that ion specificity enters; the stronger a given cation binds to a given negative group, the higher the titratable negative charge. By the same token, the stronger an anion binds, the higher the positive charge. By carrying out titrations with different electrolytes (NaCl, LiCl, $CaCl_2$, $MgCl_2$, $MgSO_4$, $Na_2SO_4$, etc.) it should be possible to obtain at least a semiquantitative insight into the relative ion-binding on the various fractions.

Inference of ion binding can also be obtained from the shift of the point of zero charge, assuming that there is one. The stronger a cation binds, the more it shifts to a lower pH (and conversely for anions). This shift is just opposite to that of the iscelectric point, measured by electrophoresis. In view of this, it seems feasible to carry out titrations at fixed electrolyte concentration. Ion-selective electrodes may be useful in this respect. Information is now available in the literature on various oxidic materials, polyelectrolytes and proteins, so that comparison of the curves obtained against these well-characterized molecules is possible.

The technique of thermometric titration as applied to seawater has been described by Millero et al.(1974). It has been used on suspended natural clay minerals and humic material to distinguish groups that protonate as well as some of the major functional groups. Application of this technique is made possible because of the large differences in the heats of protonation of phenolic and carboxylic groups.

By combining various separation techniques, thermometric titration may prove to be very useful in studying colloidal material

suspended in seawater, as well as other particulate material.

## Approaches to Metal-Organic Binding

The organic-like metal ion binding material in the sea undoubtedly consists of a variety of species, and it would be useful to have some overall characterization. Direct chemical analysis, for example, will yield information about the amounts of heavy metal ions (e.g., Fe, Ni, etc.), but not the nature of their coordination. There are also unbound ligands attached to the organic residues offering potential binding atoms of differing degrees of polarizability or "hardness". It is well known in coordination chemistry that "hard" and "soft" metal ions preferentially bind ligand atoms of similar polarizability. To determine the approximate character of the potential binding sites in the organic residues, potentiometric titration with metal ions can be utilized. Thus, the "hard" alkaline earth cations will be expected to be taken up by ligand molecules offering oxygen-coordination sites while the more polarizable transition metal ions will be bound by -N and other "soft" ligand atoms. In this manner, it will be possible to compare the nature of the binding sites in different organic fractions.

Characterizing the material with respect to already bound cations and with respect to unbound ligands serves the useful purpose of determining potentially exchanging or reactive sites for heavy metal ions. Study of the number of and redox potentials of the bound heavy metal cations (Fe, Co, etc.) should serve to help understand the overall redox processes. Because of the slow diffusion rate toward an electrode of any large organic species containing these ions, it may be desirable to use redox mediators (dissolved small redox active molecules) to bring the heavy metal cations into redox equilibrium with the electrode.

To some extent it may be necessary to introduce new concepts in dealing with this material containing such a wide distribution of species. In dealing with simple materials, the chemist purifies and provides a detailed characterization. In dealing with

the next stage of complication (a system of polymer molecules of a variety of sizes), one introduces parameters and measurements to characterize the distribution of molecular size and weight rather than measuring each molecule individually. Similarly, in the present system one may have to introduce the notion of a distribution of redox potentials and of binding sites.

## Enzyme Analysis

Enzyme analysis is a potentially valuable technique in characterizing organic coatings on particles. It has been used with success in the study of bacterial cell surfaces and is just beginning to be applied to the study of animal cell surfaces. There is a large arsenal of enzyme systems which could assist in identifying the nature of these organic coatings.

## Ion Microprobe - Ion Microscopy

One of the most exciting techniques for the study of solid surfaces involves ion-sputtering mass spectrometry. It is possible to determine the compositional distributions of any element on an inorganic surface with a spatial resolution of 1 $\mu$m. It is also possible to perform compositional depth profiles of various elements from less than 1 $\mu$m down to several tens of microns. This technique should be applied to the study of the various phases that can be isolated from the marine environment including sediment particles, manganese nodules, phosphorites, etc. The technique greatly extends the amount of information presently obtained by the electron microprobe technique. It is much more sensitive and is applicable to all elements (and isotopes) including the elements of low atomic number.

In the ion microscopy mode the technique can be used to study surface compositional distribution which can then be correlated with morphological microscopic techniques such as light microscopy, electron microscopy, SEM.

## ESCA ("Electron Spectroscopy for Chemical Analysis")

In addition to the ion microprobe, there are a number of surface techniques that have been used with considerable success for the study of metals, minerals, airborne particulates, etc. These obviously should be investigated for their applicability to marine surfaces. They include ESCA, Auger, and ion-scattering spectrometry. ESCA has been used to provide information on the chemical form of inorganic compounds of sulfur, phosphorus, nitrogen, etc. For the most effective characterization of surfaces, the various techniques should be used in combination.

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