

## ADSORPTION OF LEAD AND CADMIUM IONS ON CALCITE IN SEAWATER IN THE PRESENCE OF NONIONIC AND CATIONIC TENZIDES

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Immobilisation of dissolved trace metals by natural particulate matter and sediments in aqueous environment, together with possible remobilization influenced by different factors are determining the quality of an aquifer.

This work is a continuation of our adsorption studies on trace metal ions on calcite and bentonite (BILINSKI *et al.*, 1991; KOZAR *et al.*, 1992). In the present work the adsorption of lead and cadmium ions were studied on calcite added to seawater in the presence of model surface active substances (SAS), such as dodecyl pyridinium chloride (DPCI) and triton X-100 used respectively as positively and zero charged surfactants. Critical micellar concentrations (cmc) were determined in seawater medium from surface tension measurements.

Adsorption isotherms of the two tenzides were determined on calcite in seawater medium and in 0.55 mol NaCl l<sup>-1</sup> to get the surface coverage values. Adsorption of lead and cadmium ions was studied on coverage calcite surfaces.

Total concentrations of lead and cadmium ions were 2x10<sup>-7</sup> mol l<sup>-1</sup>. After adsorption solid phase was removed by filtration and lead and cadmium concentrations were measured by differential pulse anodic stripping voltammetry (DPASV).

The effects of the mentioned tenzides on immobilization or remobilization of cadmium and lead from calcite particles into water phase, are discussed.

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## INFLUENCE OF HYDROPHILIC AND HYDROPHOBIC SUBSTANCES ON PHYSICO-CHEMICAL PROPERTIES OF SURFACE FILMS

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Natural aquatic systems contain a large number of organic substances with different functional groups and different hydrophobic and hydrophilic properties. Surface active organic compounds which are released by phytoplankton as a product of its metabolism or are originating from decomposition and degradation processes of dead organisms form the surface microlayer (50-100 μm) which represents the interfacial region where many important bio-physico-chemical processes and flux of gases are taking place. Natural films are composed of free fatty acids, alcohols and hydrocarbons as well as of more oxygenated molecules of higher molecular weights such as glycopeptido-lipid-oligosaccharide complexes (DARRIGO, 1984). Although carboxydrates are water soluble compounds, they can form highly insoluble monolayer due to hydrogen binding and nonpolar interactions with lipid insoluble components. In the case of charged polyelectrolytes the interaction with functional groups of lipid films can be expected too. In adsorption at interfaces both hydrophobic and electrostatic (ionic) interactions determine the surface excess of solute species at natural boundaries. However, the hydrophobic fraction of surface active material was found more enriched in the surface microlayer collected at the natural air/seawater interface than were the total surfactants and total DOC (COSOVIC and VOJVODIC, 1989). Investigations of equilibrium and kinetic parameters of relevant interfacial processes can be carried out on real interfaces but very often it is more practical and convenient to use model interfaces. Two model interfaces, namely the air/water and the mercury electrode/solution interface are mostly used. Both interfaces are hydrophobic in nature and show similar adsorption effects for many organic substances (DAMASKIN *et al.*, 1971). The main advantage of the mercury electrode is its uniform, reproducible, renewable surface, smooth and energetically controlled, while monolayer techniques that are used for studies at air/water interface provide methods to organize appropriate molecules in a planned way and to study interactions at the interface under controlled conditions. There is also a possibility of transferring the film from the air/water interface to the mercury surface (PAGANO and MILLER, 1973; NELSON and BENTON, 1986; KOZARAC *et al.*, 1991). Lipid coated electrodes have interesting practical applications. Interactions of the lipid with various species in the bulk solution can be monitored electrochemically and ion and charge transfer across the film, as well as the interactions in the film can be detected. Lipid coated electrode represents also a very sophisticated system for the study of the structure and functioning of biological membranes.

Substances like long chain fatty acids and alcohols, polyoxyethylene and polysaccharides can be used as model for naturally occurring constituents which influence the physico-chemical processes at the air/water interface. Polysaccharide xantan is water soluble biopolymer (M<sub>w</sub>=2x10<sup>6</sup>) of microbial origin having polyelectrolyte properties. It has a five sugar repeat unit, two types of carboxyl groups and a cellulose backbone (RINAUDO and MILAS, 1982). It was used in this work as a model for hydrophilic big molecule which can interact with different more hydrophobic substances by ionic and hydrophobic bonds.

Here we present results of the adsorption studies of xantane at the mercury electrode surface and at the air/water interface, as well as its interaction with different lipid film forming material like oleic acid, phosphatidyl cholines, phosphatidic acid and others. Adsorption studies at the mercury electrode were performed by capacity current measurements using phase sensitive a.c. voltammetry. The structure and permeability of lipid layers were tested by using redox processes of cadmium as a probe for transport through the layer.

Studies at the air/water interface have been done by surface pressure and surface potential measurements. It was found that xantane being predominantly hydrophilic belongs to less adsorbable substances at the mercury electrode and is only slightly adsorbed at the air/water interface. It was also found that xantane interacts with both positively charged and uncharged lipid monolayers what can be clearly seen from surface pressure-area and surface potential-area isotherms. Lipid monolayers when, spread on xantane solution show the expansion of monolayer area and disappearance of the phase transition. Such a phenomenon indicates interaction of the solute xantane with the monolayer and may be interpreted as partially incorporation of polyelectrolyte molecule into the matrix monolayer.

Adsorbed layer of xantane at the mercury surface was found to be transparent for the transport of cadmium ions through it at the pH values of natural waters (pH=7-8). At lower pH (pH=2) the structure of polyelectrolyte changes and more compact layer of xantane was obtained.

Adsorbed layer of oleic acid inhibits the transport and redox processes of cadmium at the mercury electrode in both neutral and acidic media. The mixed adsorbed layer is formed if both substances, xantane and oleic acid are present in solution showing complex influence on transport processes.

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