

The influence of surface active substances on metal ions (Cd,Cu,Pb,In and TI) speciation in NaCl solutions

Marta PLAVSIC and Bozena COSOVIC

"Rudjer Boskovic" Institute, Center for Marine Research, ZAGREB (Croatia)

The speciation of metal ions in natural waters is governed by the presence of inorganic and organic ligands as well as particulate matter (BRULAND, 1983). A part of organic matter with surface active properties is very important as it influences the distribution between heavy metal species in the bulk of solution as well as their fractionation at different phase boundaries (COSOVIC, 1990).

Electrochemical methods (differential pulse voltammetry and alternating current voltammetry in phase and out of phase) were used to study adsorption processes at the electrode/solution interface as well as complexation in the solution.

General scheme of the applied methodology is presented in Fig.1. For studying reduction processes the electrode is pretreated at the potential more positive than the standard redox potential by formation of the adsorbed layer of organic molecules. After the absorption period the reduction process of metal ion is measured at the modified electrode surface during the scan in negative direction. For studying oxidation processes the electrode is kept at the potential more negative than standard redox potential while simultaneously adsorption of organic molecules and reduction of metal ions occur. After the accumulation time period the reoxidation of metal is measured during the potential scan in positive direction. However this process takes place at the electrode which is modified by the adsorbed layer of organic molecules.

The comparison is made between the influence of humic acid(HA) and nonionic surfactant Triton-X-100 on the cathodic and/or anodic waves (PLAVSIC and COSOVIC, 1991; PLAVSIC *et al.*, 1991) of heavy metal ions (Cu,Cd,Pb,In and TI). Triton-X-100 is a typical neutral nonionic surface active substance which absorbs strongly at the mercury electrode and affects charge transfer processes at the electrode/electrolyte interface. HA is at the same time surface active and complexing agent. The complexing capacities of HA for Cu,Cd,Pb,In and TI were measured in the bulk of solution by direct titration with heavy metal ions (PLAVSIC *et al.*, 1982).

At lower pH values (pH=1.6) the cathodic and anodic waves of metal ions (Cd,Pb,In) decrease with increasing the amount of SAS (both HA and Triton-X-100) and follow the adsorption isotherm of the particular SAS. The same behaviour was also observed for Triton-X-100 at higher pH values (pH=6.4). At higher pH values the predominant reaction of Cd, Pb and In with HA will be complexation reaction, usually enhanced at the electrode surface due to the higher amount of HA present in the interfacial region.

The hydrophobic/hydrophilic effects and dehydration step of aqua complexes of metal ion play an important role in the interfacial region especially for indium ions.

For Cu the predominant reaction with HA will be complexation even at low pH values (pH=1.6) TI-ions are not influenced by the presence of SAS due to a small size and a low tendency for forming complexes.

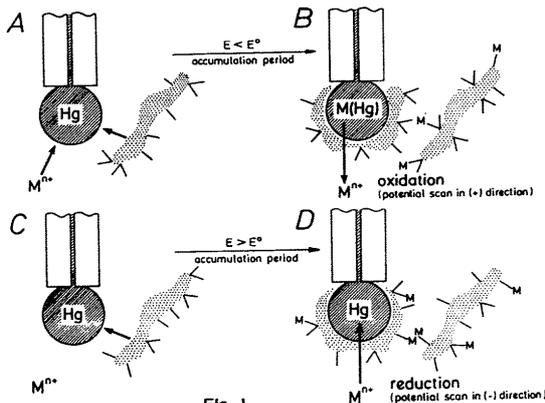


Fig. 1

Our experiments demonstrated that by relatively simple electrochemical method, following the influence of different organic substances on the oxido-reduction processes of different heavy metal ions and adsorption properties of natural and synthetic organic matter some conclusions regarding heavy metal ion speciation (preference for complexation in the bulk of solution, enrichment on the phase boundaries) as well as the nature of the organic matter (adsorbability at the electrode, interaction in the bulk of solution, preference for certain metal ion) can be drawn. The results obtained can be applied to the natural water systems.

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Nutrient enrichment and deep chlorophyll maximum along the Algerian current.

P. RAIMBAULT and B. COSTE

Centre Océanologique de Marseille, Campus de Luminy, MARSEILLE (France)

The *Médiprod VI* cruise was performed in June 1990 to obtain hydrological, chemical and biological data in the Algerian current between 1°E and 5°E with a high space resolution. The main objective was to understand what dynamical processes bring nutrients in the euphotic zone and explain the high values of chlorophyll concentrations encountered near the basis of the photic zone.

From an hydrological point of view, the surface waters are characterized by two different water bodies separated by a strong salinity gradient: near the coast was de Modified Atlantic Water (MAW) with salinities lower than 36.60 and, at about 60 km off the coast, the Surface Mediterranean Waters (SMW) with salinities ranging from 36.80 to 36.90. The boundary of the "Atlantic jet" appears to be the 36.60 isohaline.

Main features of the nutrient field (nitrate) (fig. 1) are:

1/ below the nitracline, the vertical nitrate distribution shows a tongue-like distribution with superposition of minima and maxima.

2/ the presence near the coast of a relatively nitrate-rich water (4-5 µM) of deeper origin along the 27.5 isopycne and of a nitrate-poor layer (< 3 µM) along the 27.5 isopycne, associated to high levels of dissolved oxygen (> 5.0 ml.l⁻¹) and to chlorophyll concentrations greater than 0.2 mg.m⁻³, showing its subsurface origin.

3/ in the offshore area, it can be noted successively the presence of a nitrate-rich layer (> 5 µM) crossing the isopycnals and of a nitrate-poor layer (< 3 µM) which do not follow an isopycnal level.

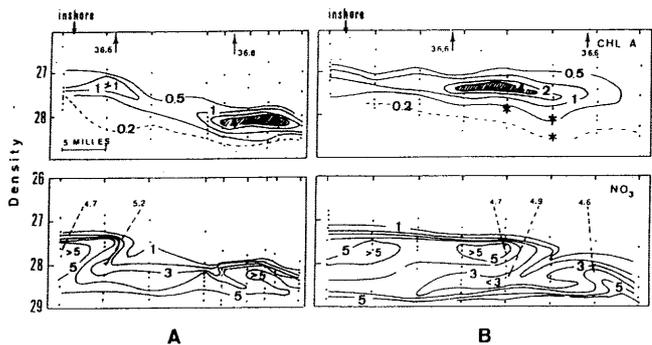


Figure 1: Chlorophyll and nitrate concentrations along the 1°10' E transect (A) and the 3°10' E transect (B). Chlorophyll concentrations greater than 4 mg.m⁻³ have been shaded. Some oxygen values (ml.l⁻¹) are reported on the nitrate diagrams.

The surface chlorophyll concentrations are less than 0.10 mg.m⁻³ over the whole area. Higher concentrations from 2 to more than 15 mg.m⁻³ occurred as a Deep Chlorophyll Maximum (DCM) in a narrow band between 15 to 30 miles off the coast line. This DCM has a width of 10 to 15 meters at a depth of 50-65 meters; it is associated with nitrate concentrations higher than 1 µM and with low light intensity (1 to 3% of the surface irradiance). On each side of the narrow band with high chlorophyll values the DCM is characterized by concentrations ranging from 0.5 to 1 mg.m⁻³ and a sharp gradient.

DCM was correlated to density values of 28.0-28.1 on the western part of the studied area while eastward it was associated to densities of 27.4.

DCM was always located just above the sharp nitrate gradient associated to intrusions of nitrate-rich waters.

These observations can be explained by nutrient inputs into the photic zone resulting of the cross-frontal circulation: 1/ on the inshore side of the current the nutrient enrichment would originate in isopycnal vertical motions as proposed by YENTSCH (1974), FASHAM *et al.* (1985), PRIEUR (1986) and BOUCHER *et al.* (1987); 2/ on the offshore side, the nutrient intrusion would be due to diapycnal mixing according to the scheme proposed by TANG (1983).

Thus the DCM in this area can be explained as resulting of an equilibrium between nutrient fluxes, light availability and water stability.

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