

Voltammetric Studies on the Potentialities of Cd(II)-Chelate
Formation in Sea Water

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Summary: The general conditions for chelation of Cd(II) with the model ligand NTA in sea water have been determined at the realistic trace level of 3×10^{-9} M by voltammetric measurements.

Résumé: Les conditions générales pour la chélation de Cd(II) avec l'NTA comme ligand modèle dans l'eau de mer sont déterminées par voltammetrie à une concentration totale du Cd(II) de 3×10^{-9} M.

One prerequisite for a detailed understanding of the speciation of toxic trace metals dissolved in the sea is to establish the conditions under which trace metals are chelated by those components of dissolved organic matter (DOM) having chelator properties. As the uptake by marine organisms at the phytoplanktonic level depends strongly on the chemical nature of the dissolved toxic metal species its nature has immediate significance for the entrance into the marine food chain at this trophic level.

Intercorrelated key parameters for the tendency of trace metal chelation by suitable components of DOM are the conditional stability constants of the chelates to be formed and the corresponding ligand concentration required to chelate a certain percentage of the total dissolved trace metal concentration. Both parameters are strongly influenced in a specific manner by the major components of sea water salinity as has been shown previously¹⁾. Although the actual nature of the chelating components of DOM is still largely unknown, the general conditions and limitations for chelation of respective trace metals can be quantitatively established using as typical chelator organic compounds with well defined coordination chemistry properties in model solutions of the sea water salinity components and in natural sea water, which contains negligible amounts of DOM.

As chelating ligand with defined properties nitrilotriacetic acid (NTA) and as toxic trace metal Cd(II) have been selected. NTA is to be expected also as pollutant in coastal waters of countries where it is used as substitute for phosphates in detergents to exclude algae eutrophication of rivers. Although those studies on the typical general conditions and physicochemical parameters of trace metal chelation by organic ligands can be performed conclusively at elevated and thus more convenient trace metal levels¹⁾, it is for several reasons desirable to have even the potentiality to measure also at or close to the actual total ultra trace level

at which usually toxic metals are dissolved in the sea. Such potentialities provides the application of a highly sensitive advanced voltammetric method as differential pulse anodic stripping voltammetry (DPASV) in a very satisfactory and reliable manner. At a total Cd(II)-level of 0.27 $\mu\text{g}/\text{l}$ corresponding to 3×10^{-9} M the chelation degree obtained by adjusted amounts of NTA was determined by monitoring the amount of Cd(II) which remained unchelated in various media (0.59 M NaCl, artificial sea water - both at pH of about 8 and an overall ionic strength of 0.7 - and natural Adriatic sea water). Besides the major salinity components, particularly Ca(II) and Mg(II), at this low Cd(II)- level also the competition of the Zn(II)-traces, for the chelating ligand NTA becomes manifested. Due to the accumulative action of all these competing effects in natural sea water a 10^3 times higher NTA-concentration amounting to the substantial ligand concentration of about 1.0×10^{-4} M NTA is required to achieve a chelation of 20% of the total Cd(II) concentration (3×10^{-9} M). Such high concentrations of chelating organic material are hardly to be expected in the open sea. Thus, if there occurs chelation of Cd(II) by components of DOM to any noticeable extent these natural organic ligands must form stronger chelates with several orders higher common conditional stability constants than $[\text{CdNTA}]^-$ for which $\lg K$ is about 9.0. This rules out any Cd(II)-chelation by dissolved humic material in the open sea and renders it even in estuaries improbable according to the stability constant range determined for various Cd-humates recently by Mantoura et al. ²⁾.

References

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DISCUSSION

Questions and comments:

1. Under the conditions of pH and Cl^- of sea water which part of Cd_{Tot} is present as Cd^{2+} ? (Lj. MUSANI, Yugoslavia)
 - About 2% of dissolved Cd_{Tot} in sea water is present as Cd^{2+} .

2. This 2% of Cd^{2+} can change strongly in contaminated sea water and upwelling zones or not? (A. BALLESTER, Spain)
 - Taking into account the fact that in open ocean water the concentration of dissolved Cd_{Tot} is around 10^{-10}M , the probability that 2% of this 10^{-10}M will be appreciably effected with higher concentration of DOM (like it is in contaminated and upwelling zones) is small, due to the presence of higher concentrations of other cations in sea water which are able to form complexes with the DOM. Our experimental determinations of Cd(II)-NTA formation in sea water at $3 \times 10^{-9}\text{M}$ Cd(II), showed that even at the total concentration of $1 \times 10^{-4}\text{M}$ NTA (which is rather high concentration of ligand Cd^{2+} remains within 1 and 2%.

