

Chemical Oceanography

The Kinetics of Cd(II)-Chelate Formation in Sea Water

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Summary: The significant typical influences of the macrocomponents of sea water on the kinetics of the chelation of heavy metal traces have been studied with the model chelate Cd(II)EDTA.

Resumée: Les effets dominants typiques des composantes majeures de l'eau de mer sur la cinétique de chelation des traces des métaux lourds sont étudiés pour la chelate Cd(II)EDTA comme modèle.

The chelation of heavy metals dissolved at normal or pollution levels in sea water with suitably structured soluble organic compounds is in several aspects a complicated problem of high significance in marine chemistry, for instance with respect of uptake and thus toxic action of heavy metals on marine organisms or concerning interactions with and incorporations in marine sediments. The rate and mechanism of chelation are expected to be influenced by various components of sea water. To get more insight into the general typical features of this involved problem model studies on the chelation rate of Cd(II) with EDTA have been performed in the rather low concentration range 10^{-5} to 10^{-7} M for both reactants. The adopted method for the determination of the operational rate constant k_f of chelation was to monitor after addition of the ligand EDTA the time dependence of the concentration decrease of unchelated Cd(II) with conventional anodic stripping voltammetry in the differential mode at two synchronized slowly dropping mercury electrodes (SDME, controlled drop time 51 s). At low concentration levels of both reactants the chelation is a 2nd order reaction. To elucidate the influences of the macro components of sea water systematic measurements have been made as well in model solutions containing the respective individual macro component (NaCl, CaCl₂ and MgCl₂) as in artificial and in natural sea water from the North Sea. The ionic strength of natural sea water (0.7) was adjusted in the model solutions

by corresponding addition of NaCl and a pH of about 8 with a borate buffer. The results are summarized in the table. A significant decrease in the rate of Cd(II)-EDTA formation is caused by the competitive chelate formation of the excess of Ca^{2+} and Mg^{2+} . Their EDTA-chelates are formed with a high rate as they are present as free hydrated Ca^{2+} and Mg^{2+} ions. But the stability of their chelates is significantly lower than that of Cd(II) EDTA. Thus, in sea water the formation of Cd(II) EDTA is essentially due to the rate of ligand exchange from the earth alkali chelates with Cd(II) present as chloro-complexes, i.e. $\text{M(II)EDTA} + \text{Cd(II) Cl}_n \rightarrow \text{Cd(II)EDTA} + n\text{Cl}^- + \text{M}^{2+}$. Due to the lower stability of Mg(II)EDTA the ligand exchange with Cd(II) is more complete and rapid than from the more stable Ca(II)EDTA. The nearly identical rate constants k_f in artificial and natural sea water suggest the fundamental conclusion that only the studied macro components of sea water affect in a significant manner the chelation rate of heavy metal traces with soluble organic matter being present at a similar concentration level and having chelating properties analogue to EDTA.

Rate constant of Cd(II)-EDTA formation

Electrolyte	k_f in $\text{M}^{-1} \text{s}^{-1}$
0.59 M NaCl	unmeasurably fast
0.0536 M MgCl_2 (I=0.7)	2.78×10^3
0.01 M CaCl_2 (I=0.7)	4.21×10^2
Artificial seawater	3.26×10^2
North Sea (Helgoland)	$(3.58 \pm 0.5) \times 10^2$

5×10^{-7} M Cd(II), 5×10^{-7} M EDTA, pH 8

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DISCUSSION

Question and comment:

1. What would be the effects of other trace metals present in sea water on the Cd-chelate formation kinetics?
(D. ZAFIROPOULOS, Greece).
- The influence of the other trace metals present in sea water on the kinetics of the Cd(II)-chelate formation will depend on the relative concentration ratio and the stability constants of the respective chelates. In the case when the concentration of the trace metal is higher than the one of Cd(II) as well as when the stability constant of the chelate is higher than the one from Cd-(II)-chelate, due to unavailability of the ligand, the rate of the Cd(II)-chelate formation will be slower or hardly measurable with the applied technique.

