

Voltammetric Studies of Zn(II) Interaction with the Humic Substances in Natural Waters

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Summary: The interaction of Zn(II) with humic substances extracted from some marine and estuarine sediments was studied by voltammetry in filtered samples of sea and lake water. The complexation capacity of these naturally occurring ligands in comparison with the synthetic ones is discussed.

Résumé: L'interaction de Zn(II) avec les substances humiques extraites de quelques sédiments marins et estuarien a été étudiée par voltammétrie d'échantillons filtrés de l'eau de mer et de l'eau des lacs. La force de complexation de ces ligands naturels en comparaison aux ligands synthétiques est discutée.

Investigations of Zn(II) complex formation with humic substances of different origin were performed in filtered sea and lake water at the natural concentration level of Zn(II) to deduce the significance of dissolved humic substances as the complexing agents for heavy metal traces in natural waters.

The humics were isolated from marine (HAL = humic acid from Limski Canal, Adriatic Sea (1) and HAN from the Norwegian Sea) and estuarine sediments (HAM from Mahakam, Borneo and FAM = fulvic acid). They were characterized according to the elementary composition, visible spectra, infrared spectra, molecular weight and the metal content. The results indicate high molecular weight products. Molecular weight, hydrophobicity and the content of aliphatic groups increase from FAM, HAM, HAL to HAN. The lowest molecular weight of 20000 was determined for FAM.

Measurements of the Zn(II) complex formation were performed in the same water type with two types of ligands, i.e. the synthetic (NTA = nitrilotriacetic acid, EDTA = ethylenediaminetetraacetic acid) and the natural humic substances. Concentrations of ionic Zn(II) (i.e. all labile complexed forms of Zn(II)) were measured without ligand and in the presence of various ligand concentrations on the hanging mercury drop electrode (HMDE) by anodic stripping voltammetry in the differential pulse mode (DPASV). From the reaction of Zn(II) with the synthetic ligands, the side reactions with the macroconstituents of the water types, the rate of complex formation, and, in general, the mechanism of trace metal complex formation in water had been deduced (2-4). From the dependence of the measured respective ionic Zn(II) concentration for respective adjusted

concentrations of the organic ligand $[L]_{tot}$ follows the respective concentration of the complex $[ZnL]$. As the monomeric synthetic ligands are to be compared with the polymeric humics, having a number of complexation sites, for this comparison the $mg\ dm^{-3}$ scale in Table 1 has to be used.

The results show the following features. The monomeric ligands NTA and EDTA have higher complexation power for Zn(II) in lake than in sea water. The reason is the strong competition by the in sea water in higher excess present Ca(II) and Mg(II) ions (2-4). The polymeric humic substances have a significantly lower complexation power than the synthetic monomeric ligands NTA and EDTA, as is evidenced by the respective required concentrations in $mg\ dm^{-3}$. The fulvic acid FAM has a very low complexation power for Zn(II) reflecting that ligands rich in acidic functional groups are unsuitable for heavy metal complexation. While HAM and HAN show only smaller differences of complexation power in sea and lake water, the elevation in complexation power for HAL and FAM in lake water is rather substantial.

In sea water as well as in lake water complexation of Zn(II) by the studied humic ligands can be observed, however, only at levels above $1\ mg\ dm^{-3}$ for these ligands. Yet in the open sea the concentration of dissolved humics is usually an order of magnitude lower. Therefore dissolved humics will play in the sea no significant role for the speciation of Zn, Cd and Pb. The situation may become different in certain coastal waters or estuaries and in certain inland waters where locally levels of dissolved humics above $1\ mg\ dm^{-3}$ can occur.

Table 1 Complexation of Zn(II) in various natural water types

The data refer to a 50 % complexation of the total Zn(II), where $[Zn]_{ion.} = [ZnL]$

Water sample	pH	Ligand (L)	Molecular weight	$[ZnL]_{-3}$ mol. dm^{-3}	$mg. dm^{-3}$	$[L]_{tot}$ mol. dm^{-3}
Ligurian sea	7.8	NTA	235	9.9×10^{-8}	0.52	2.2×10^{-6}
	7.8	EDTA	358	9.8×10^{-8}	0.10	2.8×10^{-7}
Adriatic sea	7.6	FAM	20000	2.1×10^{-7}	54.0	2.7×10^{-6}
Ligurian sea	8.2	HAM	>20000	1.2×10^{-7}	6.3	$< 3.2 \times 10^{-7}$
	8.1	HAL	>20000	1.4×10^{-7}	4.9	$< 2.5 \times 10^{-7}$
	8.2	HAN	>20000	1.6×10^{-7}	4.7	$< 2.4 \times 10^{-7}$
Ontario lake	7.5	NTA	235	2.1×10^{-7}	0.13	5.5×10^{-7}
	7.8	EDTA	358	2.0×10^{-8}	0.08	2.2×10^{-7}
	8.2	FAM	20000	3.6×10^{-7}	13.0	6.5×10^{-7}
	8.2	HAM	>20000	1.1×10^{-7}	5.1	$< 2.6 \times 10^{-7}$
	8.3	HAL	>20000	1.3×10^{-8}	2.8	$< 1.4 \times 10^{-7}$
	8.5	HAN	>20000	9.8×10^{-8}	4.2	$< 2.1 \times 10^{-7}$

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"Voltammetric studies of Zn(II) interaction with the humic substances in natural waters"

Paper presented by B. Raspor (Yugoslavia)

Discussion

V. Žutić:

To understand the interaction with humic material in natural water it would be important to make the same experiments with the humic material of lower molecular weight, which is likely to be present in sea water. As it is difficult to isolate such material, it would be important to understand the active sites on the humic material and the effect of molecular weight on the complexing ability. Could you comment on that?

B. Raspor:

There is no straightforward relation between the molecular weight and the complexing ability of the substance. The predominant and prevalent role plays the coordination chemistry of the complex formed. Our experimental data indicate that lower molecular weight humic substance, i.e., fulvic

acid, has low capacity for complexing zinc, due to higher content of carboxylic groups. The higher molecular weight substances, like two humic acids isolated from marine sediments, which are rich in alyphatic groups have higher capacity to bind zinc. Beside having higher alyphatic groups content, these humic acids have higher nitrogen content, as well. Therefore, it might be postulated that zinc will be bound by humic substances if the conditions for the formation of chelate ring, of the type existing in EDTA and NTA complexes, are fulfilled.