

Voltammetric Studies on the Speciation of Trace Metals by Amino  
Acids in Sea Water

P. Valenta and M. Sugawara<sup>+</sup>)

Chemistry Department, Institute of Applied Physical Chemistry,  
Nuclear Research Center, (KFA), Juelich, Federal Republic of Germany

Summary: Chelation of Cd(II) and Zn(II) with the amino acid L-aspartic acid has been determined at the realistic level of  $10^{-7}$  M in sea water by differential pulse polarography.

Résumé: La chélation du Cd(II) et du Zn(II) avec l'acide L-aspartique a été déterminée dans l'eau de mer par la polarographie différentielle impulsionnelle à une concentration totale du Cd(II) et du Zn(II) de  $4 \times 10^{-7}$  M.

One of the significant tasks in research on toxic trace metals in chemical oceanography and marine environmental chemistry is to elucidate their binding state and their distribution among their various chemical species. Polarographic and voltammetric methods are very useful to study the speciation of toxic metals in natural waters, e.g. sea water, at relevant low concentration levels corresponding to their base line values or to slight pollution<sup>1)</sup>. Among the potential complexing components of dissolved organic matter (DOM) in sea water, which could influence the uptake of toxic metals by marine organisms, are various amino acids. In this work the complexation with L-aspartic acid of Cd(II) and Zn(II) at a low overall level of  $4 \times 10^{-7}$  M has been studied by differential pulse polarography in model solutions of the major salinity components at an ionic strength of 0.7 M and in genuine sea water from various areas.

It was proved that these metals form with L-aspartic acid inert complexes and that under the given experimental conditions effects by the dissociation kinetics on the measured voltammetric response remain negligible<sup>2)3)</sup>. Therefore the equilibrium value of the concentration of Cd(II) or Zn(II) complexed by the respective adjusted concentration of the ligand L-aspartic acid can be determined in the following manner<sup>3)</sup>.

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After addition of certain amounts of L-aspartic acid to the investigated medium that fraction of the overall concentration of Cd(II) or Zn(II) which remains unchelated by this ligand is reduced at the respective reversible electrode potential and can be thus determined by differential pulse polarography. By this method<sup>3)</sup>, which was modified for 1:1 and 1:2 chelates, the chelation of Cd(II) or Zn(II), present at an overall concentration of  $10^{-7}$  M with L-aspartic acid has been studied in 0.59 M NaCl, 0.0536 M MgCl and 0.01 M CaCl<sub>2</sub> to elucidate the specific influence of the single major salinity components on this chelation. In all media the ionic strength had been adjusted to 0.7 by addition of NaClO<sub>4</sub>. Similar measurements in artificial sea water (filtrated through 0.45  $\mu$ m membrane filter) from the North Sea (Helgoland) and Ligurian Sea (La Spezia) revealed the cumulative specific influences of the major salinity components on the chelation of the studied trace metals with L-aspartic acid. No significant differences between the results in artificial sea water and genuine sea water were observed as usual in those studies<sup>3)</sup>.

For the measurements with Zn(II) a pH of 6.7 was adjusted in the model solutions of the single major salinity components by addition of NaHCO<sub>3</sub> and control of the CO<sub>2</sub> partial pressure in the nitrogen atmosphere hold over the solutions, because at pH 6.8 unchelated Zn(II) tends to form hydroxocomplexes yielding due to their irreversible electrode process a poor voltammetric response. Zn(II) forms a 1:1 and 1:2 chelate with L-aspartic acid in the studied range of the ligand concentration. Their conditional stability constants are  $\beta'_1 1.2 \times 10^2$  and  $\beta'_2 1.5 \times 10^4$ . These constants include specific and nonspecific influences and refer to sea water. The extrapolated common stability constants for an ionic strength of 0.7 M are  $\beta_1 2.7 \times 10^5$  and  $\beta_2 0.7 \times 10^{11}$ .

The most important net result for the chelation of  $10^{-7}$  M Zn(II) with L-aspartic acid in sea water, was, that for a chelation degree of 2 % a considerable concentration of this ligand of  $10^{-4}$  M is required.

Having an about ten times lower stability the Cd(II) chelate formed with L-aspartic acid requires an even considerably higher concentration above  $10^{-3}$  M to achieve any noticeable chelation.

Due to the ionization of L-aspartic acid at the pH of sea water and to the competition of the major salinity components the conditional stability constants of Zn(II) complexes are many orders lower than the common stability constants. The very good coincidence of the data for artificial sea water and natural sea water from two areas emphasizes that the stability on Zn- and Cd-L-aspartic acid complexes is significantly influenced only by the major salinity components, i.e.  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and by the pH of sea water.

From the obtained data for the required considerable concentrations of the ligand L-aspartic acid it is concluded that in the open sea among the chelating components of DOM L-aspartic acid is of negligible significance for the chelation of Cd(II) and Zn(II). Similar results have been obtained in a recent analogous study<sup>3)4)</sup> with the potential ligand glycine.

Yet in estuarine waters and interstitial water of sediments the often substantially higher DOM level might contain sufficient concentrations of both amino acids to achieve a certain degree of chelation of the dissolved trace metals Cd(II) and Zn(II)

#### References

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