MEASUREMENTS OF CD-NTA-EDTA INTERACTIONS WITH D.C., D.P., AND PULSE POLAROGRAPHY

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SUMMARY: The effect of various polarographic techniques on the distribution of cadmium species between the bulk of solution and the electrode surface was investigated. The model system used was Cd-NTA, Cd-EDTA, and their mixture.

RESUME: L'effet des techniques polarographiques différentes sur la distribution d'espèces de cadmium parmi le bulk de la solution et la surface d'électrode a été examiné. On a employé comme système modèle la Cd-NTA, Cd-EDTA et leur mixture.

Interactions between trace metals and organic ligands in the natural aquatic system as well as in the polluted waters influence the metal species distribution the result of which are various geochemical pathways. Electrochemical methods are very valuable for trace metal speciation. However, their application must be performed cautiously because of very specific sensitivity of the electrode reaction to the different groups of heavy metal species. At the same time possible redistribution of species at the electrode surface with respect to the bulk of the solution must be taken into account.

This study will show the effect of various polarographic techniques on a well-known model system (Cd-NTA and EDTA) (1-3). Each of compared polarographic modes (direct current - D.C., differential pulse - D.P., and pulse - (P) polarography) has its own characteristics which must be known for the interpretation of the given response. Copper complexing

capacity has been previously studied with the model and natural type of ligands (4). Cadmium complexing capacity in the presence of the NTA and EDTA mixtures was determined by polarography. Therefore, by polarographic measurements of this model system in seawater (S=38.3‰ and pH=8) as an electrolyte, with all techniques applied (D.C., P.P., and D.P.P.), well separated polarographic waves corresponding to the reduction were obtained:

1) "free" cadmium ions ($E_{1/2}$ = -o.6 V),
2) Cd-NTA ($E_{1/2}$ = -o.9 V vs. ZKE)
3) Cd-EDTA ($E_{1/2}$ = 1.2 V vs. ZKE)

A polarographic wave of "free" cadmium was analysed from experimentaly obtained data, and Cd-NTA and Cd-EDTA interaction was analysed by using a method based on the current decrease of the first wave (5,6), the one corresponding to the supposed decrease in "free" cadmium concentration because of the inert complex formation. By this method it is shown that it is a question of 1:1 complexes of one metal (Cd) and two ligands (NTA and EDTA). In fact, the analysis of the results obtained by pulse and differential pulse polarography is in accord with the theory, while the results obtained by d.c. polarography are not compatible with the method proposed. This can be explained by a kinetic effect which is prominent in d.c. polarography with the dropping time applied (t=1s). In order to avoid a kinetic effect in further calculations of constants and complexing capacity, results obtained by pulse polarography were used.

Apparent stability constants (4) for Cd-NTA and Cd-EDTA were calculated according to the data obtained from the analysis of the first, the second and the third catodic wave. The average values for the apparent stability constants in seawater (S=38.3‰ and pH=8) are: Cd-NTA = 1.o4 x $1o^4 M^{-1}$ and Cd-EDTA = 1.8 x $1o^5 M^{-1}$ at 293°K.

References:

1. Maljković, D., Branica, M. (1971): Polarography of sea water. II. Complex formation of Cd with EDTA Limnol. Oceanogr., 16, 779-785.
2. Raspor, B., Branica, M. (1973): Polarographic study of cadmium-ethly-diaminotetraacetate chelate at pH=8, J. Electroanal. Chem. 45, 79-88.
3. Raspor, B., Branica, M. (1975): Polarographic reduction of Cd(II)-nitrilotriacetic acid chelate in chloride solutions of pH about 8, J. Electroanal. Chem. 59, 98-1o9.

4. Plavšić, M., Krznarić, D., Branica, M. (1982): Determination of the apparent copper complexing capacity of seawater by anodic stripping voltammetry, Marine Chemistry, 11, 17-31.
5. Ružić, I. (1982): Theoretical aspects of the direct titration of natural waters and its information yield for trace metal speciation, Anal.Chim.Acta, 14o, 99-113.
6. Ružić, I., Nikolić, S.(1982): The influence of kinetics on the direct titration curves of natural water systems - theoretical considerations, Anal.Chim. Acta, 14o, 331-334.