

# IRON(III)-ORGANIC COMPLEXES DISSOLVED IN SEAWATER: CHARACTERIZATION OF IRON(III)-SUCCINATE AND IRON(III)-MALATE COMPLEXES IN AQUEOUS SOLUTION

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## Abstract

Iron(III), as an essential element and one of the most important element -for biochemical processes in the marine environment, is bioavailable only in dissolved form. By complexing with succinic and malic acid, intermediates in the citric acid cycle, iron(III) forms soluble complexes in aqueous solutions. Each organic acid form with Fe(III) several complexes, depending on acids concentration and pH (4.5 – 11). All investigated complexes showed stability for rather long period of time (weeks to years).

**Keywords:** Trace Elements, Phytoplankton, Electrochemistry

## Introduction

Dissolved iron(III) is very important element for marine organisms (for their biochemical and physiological functioning). Despite its abundance in the environment, dissolved  $\text{Fe}^{3+}$  in the oceans is present at low concentrations,  $<10^{-9}$  mol  $\text{L}^{-1}$  (>99%), mostly in organic complexes. Low solubility of  $\text{Fe}^{3+}$  under oxidizing conditions is caused due to the formation of insoluble Fe(III)-hydroxides and oxides and that is why Fe(III) is a limiting factor for primary production [1]. Bioavailable forms of iron(III) are, among others, complexes with succinic and malic acid [2]. Therefore, these complexes are possible candidates in the iron fertilization experiments in high-nutrient low-chlorophyll (HNLC) areas of the Oceans.

## Results and discussion

Measurements were performed by square wave voltammetry (SWV) and by UV-Vis spectrophotometry [3].

Iron(III) with different concentrations of succinic acid (0.04 - 0.5 mol  $\text{L}^{-1}$ ) in pH range 5.2 – 7.4, measured by SWV, gave redox responses of two Fe(III)-succinate complexes (Figure 1. A). Within  $C_{\text{suc}}$  from 0.04 to 0.12 mol  $\text{L}^{-1}$ , Fe(III)-succinate (I) reduction peak at the potential  $\approx -0.22$  V was registered, and with  $C_{\text{suc}} \geq 0.12$  mol  $\text{L}^{-1}$ , Fe(III)-succinate (II) complex at  $\approx -0.37$  V. The formation kinetics of both complexes was slow, Fe(III)-succinate complex (I) was equilibrated within 17 h, and Fe(III)-succinate complex (II) in about 15 h. However, after equilibration period, complex (I) was stable in the solution for about a week, and complex (II) for about 10 h. Analysis of UV-Vis spectra under same experimental conditions were processed by multivariate non-linear least-square fitting program Specfit [3]. The model, taking into account obtained iron(III) complexes by SWV, presumed that stoichiometry ratio of Fe(III):succinate complexes (I) and (II) was 1:2 and 1:3, respectively.

Three iron(III) - malate reduction peaks were detected in the pH range from 4.5 to 11, with malic acid concentration  $C_{\text{mal}} = 0.1$  mol  $\text{L}^{-1}$ . By SWV first complex reduction was registered at about -0.1 V (pH from 4.5 to 6.5), second one at about -0.35 V (pH = 6.5 - 9) and third at about -0.6 V (pH = 8.5 - 11) (Figure 1. B). Formation kinetics of this complexes was fast, and equilibrium was reached within 30 minutes. Fe(III)-malate complexes were much more stable than complexes with succinic acid, since they were detected in the solution even after one year. By UV-Vis spectrophotometry in the pH range from 1.5 to 8 three complexes were registered, as well, with two isosbestic points at 310 and 392 nm. Changes in spectra were detected in the pH range from 1.5 to 6.5, but at pH > 6.5 spectra remained almost unchanged. Principal Component Analysis (PCA) of spectra gave three spectrally distinguishable Fe(III)-malate complexes. Combination of voltammetric and UV-Vis results presumed stoichiometry of complexes: in the pH range from 1.5 – 3 exist complex Fe(mal) (with undissociated hydroxyl group at the second carbon atom in malic acid molecule); Fe(mal) and Fe(mal)<sub>2</sub> complexes (with dissociated hydroxyl group) in the pH range from 3.5 to 6.5 and these complexes gave reduction peak 1 in Fig.1B. In the pH range from 6.5 to 9 exists complex Fe(mal)<sub>2</sub>(OH)<sub>x</sub> (peak 2) and in the pH range from 8.5 to 11 complex Fe(mal)<sub>2</sub>(OH)<sub>y</sub> (peak 3) is present.

## Conclusion

Obtained results showed that succinic and malic acids form stable dissolved  $\text{Fe}^{3+}$  complexes in the pH range from 4 to 11 that remain in the solution for rather long period of time. The addition of relatively small amount of described iron complexes to the phytoplankton culture (*Dunaliella* sp.) in laboratory conditions resulted in increased production of phytoplankton biomass.

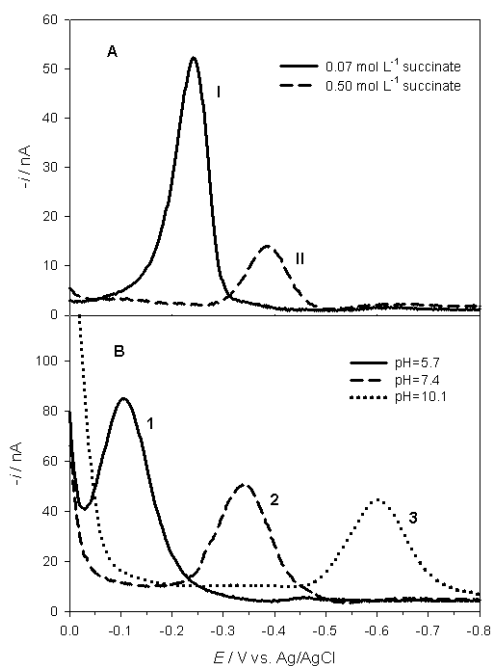


Fig. 1. A) SW voltamograms of Fe(III)-succinate complexes in 0.55 mol  $\text{L}^{-1}$  NaCl with  $C_{\text{Fe}} = 4 \times 10^{-5}$  mol  $\text{L}^{-1}$ , pH=6.00 and  $C_{\text{suc}}$ : (I) 0.07 and (II) 0.5 mol  $\text{L}^{-1}$ .

B) SW voltamograms of Fe(III)-malate complexes in 0.55 mol  $\text{L}^{-1}$  NaCl with  $C_{\text{Fe}} = 4 \times 10^{-5}$  mol  $\text{L}^{-1}$ ,  $C_{\text{mal}} = 0.1$  mol  $\text{L}^{-1}$  and pH: (1) 5.7, (2) 7.4 and (3) 10.1.

## References

- 1 - Hiemstra T. and van Riemsdijk W. H., 2006. Biogeochemical speciation of Fe in ocean water. *Mar. Chem.*, 102 (3-4): 181-197.
- 2 - Puskarić S. And Mortain-Bertrand A., 2003. Physiology of diatom *Skeletonema costatum* (Grev.) Cleve photosynthetic extracellular release: evidence for a novel coupling between marine bacteria and phytoplankton. *J. Plankton Res.*, 25(10): 1227-1235.
- 3 - Cmuk P., Piantanida I. And Mlakar M., 2009. Iron (III)-complexes engaged in the biochemical processes in seawater. I. Voltammetry of Fe(III)-succinate complexes in model aqueous solution, *Electroanalysis*, 21(23): 2527-2534.