

## SOLUBILITY OF Fe(III)-GLYCINE-NTA COMPLEXES IN AQUATIC SYSTEMS

Vlado Cuculic\* and Marko Branica

Center for marine and environmental research, Rudjer Boškovic Institute, Bijenicka 54, 10001 Zagreb, Croatia

\*cuculic@rudjer.irb.hr, branica@rudjer.irb.hr

### Abstract

Solubility of iron(III)-glycine-NTA mixed complex in aquatic solution was measured by cathodic voltammetry with static mercury drop electrode. Experimental determined Fe(III) retention time in soluble phase at pH = 8.1 in 0.1 mol L<sup>-1</sup> NaClO<sub>4</sub> was found to be more than 18 hours. It was achieved by addition of NTA to the iron(III)-glycine water solution. Under these conditions, iron(III) hydrolysis was sufficiently suppressed.

**Keywords:** aquatic system, iron(III), mixed complex, glycine, nitrilotriacetate, voltammetry.

### Introduction

Iron is one of the most abundant metal on the earth's crust with a great biogeochemical importance in natural aquatic systems. It is an essential element whose key chemical and biological functions involve oxidation/reduction processes and interactions with oxygen (1). However, its strong tendency toward hydrolysis and precipitation is limiting factor for iron occurrence in soluble phase in natural aquatic systems (2). Soluble form of Fe(III) is necessary for phytoplankton growth. Iron is thought to be an element that regulates ecosystem structure and rate of primary production in large areas of the ocean (3). Dissolved iron concentrations in the surface waters of the Pacific area are < 0.1 nM, so rate of input of bioavailable iron must exert a strong influence on ocean productivity in these systems (3,4). The major source of iron in the ocean is deposition of atmospheric dust particles. However, iron oxyhydroxide particles and iron colloids are not directly available to phytoplankton due to their insolubility (4). Ionic iron must be in soluble form during sufficient period of time in order to be available to the phytoplankton. It is mainly achieved by organic complexation of iron(III) (1).

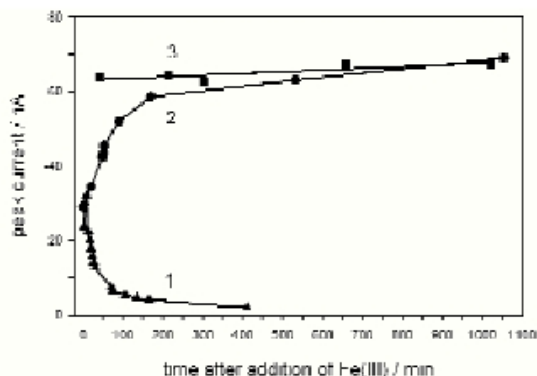
### Methods and materials

μAUTOLAB analyzer (ECO Chemie, Utrecht, NL) and an electroanalytical quartz cell (20 ml) were used in experiments. The working electrode was a standing mercury drop electrode (SMDE), Ag/AgCl as reference electrode and counter electrode was platinum wire. The stock solutions of 10<sup>-2</sup> mol L<sup>-1</sup> of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (p.a., Kemika, Croatia), 10<sup>-2</sup> mol L<sup>-1</sup> of disodium nitrilotriacetate (Na<sub>2</sub>NTA) (Sigma-Aldrich Chemie, Germany), 1 mol L<sup>-1</sup> of glycine and 7.13 mol L<sup>-1</sup> of the NaClO<sub>4</sub> (p.a., Fluka Chemie, Switzerland) with bidistilled, Milli-Q water were prepared.

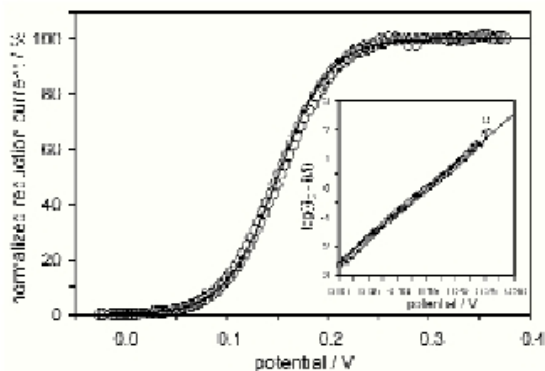
### Results and discussion

The electrochemical measurements were performed in a 0.1 mol L<sup>-1</sup> NaClO<sub>4</sub> water solution at pH = 8.1. Figure 1 shows differential pulse Fe(III) reduction peak current dependence on the time of the experiment. In figure 1, curve 1 shows reduction currents of the Fe(III) - glycine complex without NTA added. Advanced hydrolysis after only few minutes since Fe(III) addition is observed. This complex is very unstable at pH = 8.1 (natural seawater pH) and hydrolysis prevails over formation of Fe(III)-glycine complex. In figure 1, curve 2 shows Fe(III) reduction where NTA was added about 50 minutes after preequilibration of iron(III) and glycine. Before the addition of NTA, Fe(III)-glycine complex was formed, which has very strong tendency toward hydrolysis (5). After NTA addition, gradually formation of mixed Fe(III)-glycine-NTA complex takes place. After about 8 hours, mixed complex peak current achieves constant values. It is clear that presence of the both ligands, glycine and NTA, stabilizes iron(III) in soluble phase because peak current (Fig. 1, curve 2) was constant over 18 hours. When NTA was added into glycine water solution prior to addition of iron(III) ions, Fe(III) mixed complex was formed instantaneously (Fig. 1, curve 3). So, addition of NTA in Fe(III)-glycine water solution results in formation of the highly stabilized Fe(III)-glycine-NTA mixed complex that keeps iron(III) in soluble phase more than 18 hours.

Figure 2 shows d.c. polarogram of the Fe(III)-glycine-NTA reduction and logarithmic dependence of the reduction currents on potential (insert). Logarithmic analysis of the polarogram gives us a slope value 58.8±0.04 mV. Number of electrons in reaction depends on slope as follows: slope = 0.059V / n, for reversible electrode reaction. That clearly shows that oxidation/reduction reaction of the Fe(III)-glycine-NTA mixed complex is one-electron, reversible electrode reaction.



**Fig. 1.** DP reduction peak current dependence on the time of the experiment. 1: Fe(III)-glycine reduction; 2: Fe(III)-glycine-NTA reduction, NTA added after 50 min.; 3: Fe(III)-glycine-NTA reduction; c(Fe<sup>3+</sup>) = 2.5×10<sup>-5</sup> mol L<sup>-1</sup>; 0.2 mol L<sup>-1</sup> glycine; 5×10<sup>-4</sup> mol L<sup>-1</sup> NTA; 0.1 mol L<sup>-1</sup> NaClO<sub>4</sub>; pH = 8.1; DE = 2 mV; a = 25 mV; t<sub>pulse</sub> = 0.05 s; τ<sub>drop</sub> = 0.2 s.



**Fig. 2.** D.C. polarogram of the Fe(III)-glycine-NTA reduction and logarithmic dependence of the reduction current on potential (insert). c(Fe<sup>3+</sup>) = 2×10<sup>-4</sup> mol L<sup>-1</sup>; 0.02 mol L<sup>-1</sup> glycine; 5×10<sup>-4</sup> mol L<sup>-1</sup> NTA; 0.1 mol L<sup>-1</sup> NaClO<sub>4</sub>; pH = 8.1; drop time = 0.5 s; E = 2 mV.

### References

- 1-Sunda, W.G., Huntsman, S.A., 1995. Iron uptake and growth limitation in oceanic and coastal phytoplankton. *Mar. Chem.*, 50: 189-206.
- 2-Crumbliss, A.L., Garrison, J.M., 1988. A comparison of some aspects of the aqueous coordination chemistry of aluminum(III) and iron(III). *Comments Inorg. Chem.*, 8: 1-26.
- 3-Martin, J.H., Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature*, 331: 341-343.
- 4-Liu, X., Millero, F.J., 2002. The solubility of iron in seawater. *Mar. Chem.*, 77: 43-54.
- 5-Cuculic, V., 2003. Electrochemical reactions of iron ions and complexes in water solutions. Doctoral Thesis, University of Zagreb.