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Oxidation of Copper(I) in Seawater at Nanomolar Levels

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Abstract

The oxidation and reduction of copper in air-saturated seawater and NaCl solutions has been measured as a function of pH (7.17-8.49), temperature (5-35ºC) and ionic strength (0.1-0.7 M). The oxidation rate was fitted to an equation for sodium chloride and seawater valid at different pH and media conditions:

$$\log\ k_{(NaCl)} = 5.221 + 0.609\,pH\text{-}1915.433/T\text{-}1.818\sqrt{I} + 0.408I$$

$$\log\ k_{(sw)} = 5.036 + 0.514\,pH\text{-}1764.915/T\text{-}1.101\sqrt{I} + 0.233I$$

The reduction of Cu(II) was studied in both media for different initial concentration of copper(II). When the initial Cu(II) concentration was 200 nM, the copper(I) produced was 20% and 9% for NaCl and seawater, respectively. Considering the copper(I) reduced from Cu(II), the speciation and the contribution of these species to the kinetic process was studied. The Cu(I) speciation is dominated by the $CuCl_2^-$ species. On the other hand, the neutral chloride CuCl species dominates the Cu(I) oxidation in the range 0.1 M to 0.7 M chloride concentrations.

Keywords *Kinetic · copper · oxidation · reduction · seawater · oxygen*

Introduction

The study of redox reactions for Cu(I) and Cu(II) in the marine environment is important because copper redox chemistry determines the copper speciation in natural waters and the interactions with biological process. In addition, copper is an essential redox-active transition metal, which acts as a structural element in regulatory proteins and participates in photosynthetic electron transport, mitochondrial respiration, oxidative stress responses and cell wall metabolism (Yruela 2005). At elevated concentrations, copper becomes toxic to plants and alters membrane permeability, chromatin structure, protein synthesis, enzyme activities, photosynthesis and respiratory processes (Marschner 1995; Yruela 2005). Copper toxicity may result from an intracellular reaction between copper and reduced glutathione, although copper also inhibits the enzyme catalase and reduces the cell defence mechanism against hydrogen peroxide and oxygen free radical (Sunda 1989).

The oxidation of Cu(I), at micromolar levels, in seawater and in NaCl solutions had been studied by different authors (Moffett and Zika 1983; Sharma and Millero 1988a,b,c). The rate constant k (kg $mol^{-1}min^{-1}$) for the oxidation of Cu(I) was defined by the Eq. 1:

$$d[Cu(I)]/dt = -k[Cu(I)][O_2] \qquad 1$$

In the conditions of excess oxygen, the system followed a pseudo-first order kinetic (k') being k determined from $k=k'/[O_2]$. These authors found the

Cu(I) oxidation rate constant depends of the speciation in the solution. The Cu(I) oxidation of Cu(I) is mainly controlled by the Cl$^-$ concentration. At lower Cl$^-$ concentration, the Cu(I) oxidation is much faster and the back reaction of Cu(II) becomes more important. The most reactive species for the oxidation of Cu(I) are Cu$^+$ and CuCl (Moffett and Zika 1983; Sharma and Millero 1988a,b,c).

In seawater, Cu(I) can be formed from Cu(II) due to the photoxidation of dissolved organic matter (Sharma and Millero 1988b), according to the sequence (Equations 2-5).

$$org \xrightarrow{h\upsilon} org^+ + e^- \tag{2}$$

$$e^- + O_2 \rightarrow O_2^- \tag{3}$$

$$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \tag{4}$$

$$Cu^{2+} + O_2^- \rightarrow Cu^+ + O_2 \tag{5}$$

Redox cycling between Cu^{2+} and Cu$^+$ catalyzes production of hydroxyl radicals from superoxide and hydrogen peroxide (Elstner et al. 1988) by the Haber-Weiss reaction and thus enhances the production of reactive oxygen species. These reactions for oxidation and reduction of copper are expressed in the Equations 6-11 (Barb et al. 1951; Gray 1969; Haber and Weiss 1934):

$$Cu^+ + OH \rightarrow Cu^{2+} + OH^- \qquad \text{Slow} \tag{6}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH + OH^- \qquad \text{Fast} \tag{7}$$

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \qquad \text{Fast} \tag{8}$$

$Cu^{2+} + HO_2^- \rightarrow Cu^+ + HO_2$ Slow 9

$HO_2 \leftrightarrow H^+ + O_2^-$ Fast 10

$Cu^{2+} + O_2^- \rightarrow Cu^+ + O_2$ Fast 11

Copper forms organic complexes with algal exudates and this leads to a great variety in organometallic species which can affect the free ionic copper concentration. In addition, primary photochemical processes, such as the Ligand to Metal Charge Transfer reactions of Cu(II) complexes, could result in Cu(I) formation (Zika 1981) (Eq. 12).

$$\left[Cu(II)Ln\right] + h\upsilon \xrightarrow{LMCT} Cu(I) + (nL)^- \tag{12}$$

In fact, copper exists primarily as complexes with organic ligands in seawater (Moffett and Zika 1987; Sunda and Hanson 1987; van den Berg 1984), leaving only around 1% of the total copper as free copper, which is considered to be available or toxic (Allen and Hansen 1996). Trace metals chemistry is affected by phytoplankton in natural and oceanic waters by surface reactions and metal uptake or production of extracellular organic matter with metal complexity properties (González-Dávila 1995). The release of extracellular organic appears to be a major source of labile substrate into the dissolved organic matter pool in the open ocean (Duursma 1961; Wangersky 1978; Zhou and Wangersky 1989).

In this work, the oxidation of copper (I) is studied at nanomolar levels, three order of magnitude lower than works done before (Moffett and Zika 1983; Sharma and Millero 1988a,b,c). In addition, we have not added any complexing agent into the reaction vessel in order to enable the Cu(I) formation from Cu(II) reduction. Reduction of Cu(II) has been studied because it could be responsible for the decrease in the oxidation velocity due to Cu(I) formation for seawater samples. We have studied the oxidation of copper(I) in seawater and sodium chloride solutions as a function of the initial copper concentration, pH, temperature, sodium bicarbonate and ionic strength. We have also calculated the speciation of Cu(I) and the contribution of each species to the kinetic rate. These results allow us to improve our knowledgement about the biogeochemical cycle of copper in natural waters.

Experimental

Chemicals

Stock solutions of Cu(I) ($4\cdot10^{-4}$ M) were daily prepared using analytical grade copper(I) chloride (Aldrich). The solutions were acidified at pH 2 with Suprapur HCl and bubbled with N_2 before and after the copper was added. The initial concentration of Cu(I) was kept at 200 nM in the reaction cell except for the studies at different concentrations.

Stock solutions of Cu(II) ($4\cdot10^{-4}$ M) were prepared using copper(II) chloride (Aldrich) and the initial concentrations were 200 and 400 nM in the reaction cell.

The experiments in sodium chloride were done in 0.7 M NaCl and 2 mM $NaHCO_3$. All the chemicals used for the copper determination were trace analytical grade.

The seawater used in this study was collected in the Northwest of Gran Canaria (The Canary Islands) at the European Station for Time Series in the Ocean (ESTOC). The salinity determined by using a salinometer (Portasal, 8410A) was 36.691. For the salinity studies, dilutions were done with Milli-Q ion exchange water (18 MQ). All the water samples were filtered by 0.1 μm.

pH Measurements

Tris-(hydroximethyl)aminomethane(Tris)-artificial seawater buffers (Millero 1986) were used to calibrate the electrode in the free hydrogen ion scale, $pH_F = -\log[H^+]$. The buffers were prepared with 0.005 $mol\cdot kg^{-1}$ Tris and Tris-HCl in artificial seawater. The pH was measured with an Orion pH meter using a combination electrode (Ross Combination, glass body). The effect of temperature and salinity on the pK^* of the Tris-buffers was considered in this study (Millero 1986).

Oxidation and Reduction Experiments

The oxidation and reduction kinetics of copper in seawater were studied in a 250 ml glass thermostated reaction cell following the disappearance and the formation of Cu(I), respectively. The temperature was controlled to ±0.02ºC with a refrigerated bath RB-5A in the range of 5-35ºC. Oxygen saturated solutions were prepared by bubbling pure air for half an hour. The pH was adjusted to the desired value with the addition of small amounts of 1 M HCl and 1 M NaOH. The addition of the Cu(I) stock solution to the samples corresponds to the zero time of reaction. Change in pH along the study was kept below 0.01 units.

Copper Analysis

The Cu(I) concentrations were determined spectrophotometrically using a modified version of the bathocupreine method (Moffett et al. 1985) in order to analyse copper at nanomolar concentrations. At selected times during the experiment, 10 mL of the samples was added to a 25 mL vessel which contained $2\cdot 10^{-5}$ M bathocupreine (bathocupreinedisulfonic acid, disodium salt hydrate) and 10^{-4} M ethylendiamine reagent. The bathocupreine and the Cu(I) forms a complex absorbing at 484 nm. The ethylendiamine forms strong complexes with copper (II) and removes possible interferences in the Cu(I) determination.

The Cu(I) at nanomolar concentration was measured using an UV detector USB2000 (Ocean Optics^{TM}) connected to a 5 m long waveguide capillary cell (LWCC) from World Precision Instruments.

A lineal relationship between the absorbance and the concentration of Cu(I) was found for the range 0-336 nM in sodium chloride and seawater solutions, respectively (Equations 13 and 14).

$$Absorbance = 6.59{\cdot}10^{-4} + 2.38{\cdot}10^{-3}\left[Cu(I)\right] \qquad 13$$

$$Absorbance = -1.26{\cdot}10^{-2} + 2.30{\cdot}10^{-3}\left[Cu(I)\right] \qquad 14$$

with a molar absortivity, ε, of 4464 $M^{-1}cm^{-1}$ in seawater and 4767 $M^{-1}cm^{-1}$ in NaCl.

Results and Discussion

The oxidation of Cu(I) at nanomolar concentration in air saturated solutions followed a pseudo first order kinetic. In Table 1, the half-live times ($t_{1/2}$) for the oxidation kinetics of Cu(I) in 0.7 M NaCl – 2 mM $NaHCO_3$ and seawater solutions at nanomolar and micromolar concentrations are shown. As pH decrease, an increase in $t_{1/2}$ is obtained being similar in both media. The $t_{1/2}$ comparison between the studies done at nanomolar and micromolar Cu(I) concentration shown differences as can be observed in Table 1. These differences have also been found for the iron kinetic studies (Santana-Casiano et al. 2005). Values for the Cu(I) oxidation from Sharma and Millero (1988a) are also included in Table 1. The $t_{1/2}$ obtained by theses authors are lower than those observed in this study. However, a difference exists between both experiments. Sharma and Millero introduced EDTA in the reaction cell in order to avoid any further Cu(II) reduction. In this study, no complexing agents were introduced in the reaction cell. The ethylendiamine was added together with the bathocupreine in the external vessels before the analysis of Cu(I) to avoid any interference with the Cu(II) when Cu(I) was measured.

To elucidate the effect of initial copper(I) concentration on the oxidation of Cu(I) in natural waters and the further effect of the Cu(II) back reaction, the experiments were made in 0.7 M NaCl and 2 mM $NaHCO_3$ solutions with a Cu(I) concentration in the range 50 to 385 nM (Table 2). There is not a measurable effect due to change in the initial Cu(I) concentration. The average value of log k'_{obs} is -1.31 ± 0.02. The result for 200 nM as initial copper(I) concentration can be extrapolated at low concentrations as 50 nM. The overall rate constant k (kg $mol^{-1}min^{-1}$) for seawater and NaCl can be computed considering $k = k_{obs}' / [O_2]$ from Eq. 1. The values of $[O_2]$ were determined from solubility equation by Benson and Krause (1984) and Millero et al. (2002).

The effect of bicarbonate concentration was studied in 0.7 M NaCl and $NaHCO_3$ solutions in the range 0 to 9 mM (Table 3). The results were fitted to a second polynomial equation (Eq. 15), with R^2 of 0.956 and a standard error deviation of 0.07 in the log k determination.

$$\begin{aligned}\log k_{(NaHCO_3)} = {} & 2.037(\pm 0.058) + 0.212(\pm 0.032)[NaHCO_3] \\ & -1.54 \cdot 10^{-2}(\pm 0.004)[NaHCO_3]^2\end{aligned} \qquad 15$$

The Cu(I) oxidation rate increased when $NaHCO_3$ was added until 5 mM, being constant from 5 mM to 9 mM and can be explained by the formation of complexes between the carbonate and Cu(I) (Equations 16 and 17). These complexes can even be more reactive than Cu(I) chloride complexes.

$$Cu^+ + HCO_3^- \rightarrow CuHCO_3 \qquad 16$$

$$Cu^+ + CO_3^{2-} \rightarrow CuCO_3^- \qquad 17$$

The stabilization at bicarbonate concentration higher than 5 mM is explained by considering the reaction of Cu(II) with carbonate and its reduction to Cu(I). In order to elucidate the effect of the back reaction from Cu(II), the reduction of copper(II) has been studied and will be discussed below.

The pH effect was studied in the pH range 7.17 to 8.49 in NaCl and seawater solutions (Fig. 1-2). The results were fitted to Equations 18 and 19 for NaCl and seawater at nanomolar levels and Eq. 20 for micromolar concentration in sodium chloride solution.

$$\mathbf{log}\, k_{(NaCl)} = -2.453(\pm 0.341) + 0.611(\pm 0.044)pH \qquad 18$$

$$\mathbf{log}\, k_{(sw)} = -1.484(\pm 0.266) + 0.489(\pm 0.034)pH \qquad 19$$

$$\mathbf{log}\, k_{(NaCl,\mu M)} = -4.244(\pm 0.585) + 0.839(\pm 0.074)pH \qquad 20$$

with a standard error of 0.03 ($R^2 = 0.98$).

The Cu(I) oxidation rate as a function of pH shows a slight effect indicating that acidic or basic species (CuOH and $CuClOH^-$) are not strongly involved in the oxidation of copper. In addition, the values are very close in both media indicating that similar complexes are involved and/or the effects due to different ionic interactions in seawater are compensated. Despite the weak dependence with the pH, the slope for micromolar concentration (0.839) is higher than the slope in nanomolar level (0.611). The effect of the pH is more important at micromolar level than at nanomolar. The differences could be due to the presence of intermediate agents such as superoxide or hydrogen peroxide produced in the process, playing a major role in the oxidation process at nanomolar concentrations and also due to the back-reaction from Cu(II) is more important at nanomolar scale, decreasing the rate constants.

The effect of ionic strength in the oxidation rate is presented in Fig. 3. Log *k* decreased with the increase of ionic strength from 0.1 to 0.7 M, due to the formation of copper(I) chloride complexes. This dependence is in agreement with previous studies (Moffet and Zika 1983; Sharma and Millero 1988a,b,c; Millero 1985). When ionic strength was lower than 0.4 M, the values in NaCl were higher than in seawater ($\Delta\log k = 0.2$), being similar at higher ionic strengths. The chloride copper complexes formation at high chloride concentrations accounts for the decrease in the rate of oxidation. The study of the ionic strength effect was done diluting the samples with Milli-Q water. However other experiments were done keeping constant the bicarbonate concentration (2 mM). The rates constant were higher when the bicarbonate concentration is kept constant (Fig. 3). At ionic strength 0.7 M, the rate constants in NaCl and seawater are similar. In both media, the main inorganic complexes of Cu(I) are the chloride ions and can be found as Cu^+, CuCl, $CuCl_2^-$ and $CuCl_3^{2-}$. When the ionic strength is lower, the effect of major ions in seawater can modify the rate constant, like Mg^{2+} and Ca^{2+} which can decrease the rate constant in seawater solutions. In addition, the back-reaction of Cu(II) is more important at lower Cl^- concentration (Sharma and Millero, 1988a). These processes can account the differences between NaCl and seawater solutions, at lower ionic strengths. The observed oxidation rates were fitted to Equations 21 and 22, where R^2 was 0.99 in NaCl and 0.98 in seawater.

$$\log k_{(I,NaCl)} = 3.67(\pm 0.18) - 1.83(\pm 0.66)\sqrt{I} + 4.16(\pm 0.57)I \qquad 21$$

$$\log k_{(I,sw)} = 3.23(\pm 0.16) - 1.11(\pm 0.56)\sqrt{I} + 2.45(\pm 0.47)I \qquad 22$$

The effect of temperature in the oxidation kinetic of Cu(I) in NaCl and seawater was studied from 5 to 35ºC and the results are shown in Fig. 4. In both media, the rate of oxidation increases with temperature. The plot of log *k* versus 1/T gives slopes very close, -1884 in NaCl and -1856 in seawater, inside the experimental error (Equations 23 and 24).

$$\log k_{(T,NaCl)} = 8.76(\pm 0.23) - 1884(\pm 66.90)/T \qquad 23$$

$$\log k_{(T,sw)} = 8.72(\pm 0.23) - 1856(\pm 65.92)/T \qquad 24$$

with a standard error of 0.02 and R^2 0.996 in both media.

The temperature studies allowed us to calculate the Energy of Activation (Ea), the Arrhenius parameter (A), enthalpy (ΔH^{Υ}) and entropy (ΔS^{Υ}) of activation (Millero 2001). The values in seawater media were: 35.54±1.26 $Kjmol^{-1}$, $5.2 \cdot 10^{8}$±1.7 min^{-1}, 33.10±1.25 $Kjmol^{-1}$ and -52.17±4.32 $Jmol^{-1}$, respectively.

The overall rate constants for the Cu(I) oxidation under different experimental conditions have been fitted to the Equations 25 and 26, considering the combination of all parameters studied at the same time.

$$\log k_{(NaCl)} = 5.221 + 0.609pH - 1915.433/T - 1.818\sqrt{I} + 0.408I \qquad 25$$

$$\log k_{(sw)} = 5.036 + 0.514pH - 1764.915/T - 1.101\sqrt{I} + 0.233I \qquad 26$$

with a standard error of estimation of 0.03 in seawater and NaCl. *k* is the rate constant (kg mol^{-1}min^{-1}), T is temperature (Kelvin) and I is the ionic strength. These equations are valid in the range studied for all these parameters.

Some experiments were done in NaCl and seawater solutions to study the formation of Cu(I) from Cu(II) (Fig. 5). The initial copper(II) concentration was 200 and 400 nM and the Cu(II) reduction was followed for times over 90 mins. The formation of Cu(I) increased with the initial concentration of Cu(II). At the same initial copper(II) concentration, the concentration of Cu(I) formed in NaCl is higher than in seawater, probably due to the presence of organic compounds that could complex Cu(II) decreasing the reactive Cu(II) species in seawater. At $[Cu(II)]_o$= 200 nM and after 20 mins of reaction, the Cu(I) concentration reaches a constant value of 9% of the initial copper(II) in seawater and 20% in NaCl solutions (Fig. 5). When the initial copper(II) concentration was 400 nM, the Cu(I) regenerated in NaCl reached 28% and 12% in seawater. When HCO_3^- increased to 9 mM and 200 nM of initial copper(II) concentration, the maximum concentration of Cu(I) was 16% in NaCl, instead of 20% in 2 mM HCO_3^-.The differences between 2 mM and 9 mM of HCO_3^- must be explained by the interaction between Cu(II) and carbonate (Eq. 27), being the reduction of Cu(II) lower in the presence of higher concentrations of sodium carbonate. When Cu(II) and ethylendiamine were initially added to the reaction vessel, the formation of Cu(I) was not observed, preventing the ethylendiamine the back reaction.

$$CuCO_3 + O_2^{\bullet -} \rightarrow Cu^+ + O_2 + CO_3^{2-} \qquad 27$$

The chemical reduction of Cu(II) to form Cu(I), trough reactions 27, 9 and 11, is shown to be important mechanism contributing to the presence of Cu(I) in surface seawater which also decreases the rate constant at nanomolar levels.

The experimental results were used to calculate the contribution of each specie to the overall rate constant for the Cu(I) oxidation in NaCl solutions. The overall oxidation rate is given by (Eq. 28):

$$k = \alpha_{Cu}k_0 + \alpha_{CuCl}k_1 + \alpha_{CuCl_2}k_2 + \alpha_{CuCl_3}k_3 \qquad 28$$

The formation of Cu(I) due to Cu(II) back reaction should be corrected in order to accurate the speciation of copper(I) in solution with more accurate. The Cu(I) formed from the reduction of Cu(II) has included in all the studies, by considering that after 20 mins the concentration was kept constant to 20% of the initial value. At time lower than 20 mins a linear dependence was applied following Fig. 5. The Cu(I) concentration must fulfil the next conditions (Equations 29-32):

$$[Cu(I)]_{meas} = [Cu(I)]_0 - [Cu(I)]_{ox} + [Cu(I)]_{reg} \qquad 29$$

$$[Cu(I)]_{reg} = [Cu(I)]_{ox} 0.20t/20 \qquad 30$$

$$[Cu(I)]_{ox} = \frac{[Cu(I)]_0 - [Cu(I)]_{meas}}{(1 - 0.20t/20)} \qquad 31$$

$$[Cu(I)]_{real} = [Cu(I)]_0 - [Cu(I)]_{ox} \qquad 32$$

where $[Cu(I)]_0$ is the initial concentration of Cu(I), $[Cu(I)]_{meas}$ is the Cu(I) measured. $[Cu(I)]_{ox}$ is the amount of Cu(I) that is oxidized. $[Cu(I)]_{reg}$ is the copper(I) regenerated. $[Cu(I)]_{reg}$ corrects the percentage of Cu(I) produced in the reduction process. $[Cu(I)]_{real}$ is the copper(I) concentration if only oxidation is taking place. The Eq. 30 allows us to subtract the Cu(I) regenerated from Cu(II) to those Cu(I) measured. In order to calculate the species contribution to the Cu(I) oxidation in NaCl, the rate constant are calculated as a function of the ionic strength.

The molar fraction α_i for the Cu(I) species can be determined by (Equations 33-36):

$$\alpha_{Cu} = (1 + \beta_1^*\left[Cl^-\right] + \beta_2^*\left[Cl^-\right]^2 + \beta_3^*\left[Cl^-\right]^3)^{-1} \qquad 33$$

$$\alpha_{CuCl} = \beta_1^*\left[Cl^-\right]\alpha_{Cu} \qquad 34$$

$$\alpha_{CuCl_2} = \beta_2^*\left[Cl^-\right]^2\alpha_{Cu} \qquad 35$$

$$\alpha_{CuCl_3} = \beta_3^*\left[Cl^-\right]^3\alpha_{Cu} \qquad 36$$

The stepwise association constants β_i are given by (Equations 37-39):

$$\beta_1 = ([\mathrm{CuCl}]/[\mathrm{Cu}^+][\mathrm{Cl}^-])(\gamma_{\mathrm{CuCl}}/\gamma_{\mathrm{Cu}}\gamma_{\mathrm{Cl}}) \qquad 37$$

$$\beta_2 = ([\mathrm{CuCl}_2^-]/[\mathrm{Cu}^+][\mathrm{Cl}^-]^2)(\gamma_{\mathrm{CuCl}_2}/\gamma_{\mathrm{Cu}}\gamma_{\mathrm{C}l_2}) \qquad 38$$

$$\beta_3 = ([\mathrm{CuCl}_3^{2-}]/[\mathrm{Cu}^+][\mathrm{Cl}^-]^3)(\gamma_{\mathrm{CuCl}_3}/\gamma_{\mathrm{Cu}}\gamma_{\mathrm{Cl}_3}) \qquad 39$$

where [i] and γ_i are, respectively, the concentrations and activity coefficients for each *i* species. $\beta_i^*=[CuCl_i^{-i+1}]/[Cu^+][Cl^-]$ is the stechiometric constant.

The equilibrium constants to calculate the speciation were the ones used by Sharma and Millero (1988c). The Pitzer parameters (Pitzer and Mayorga 1973) for the Cu(I) speciation in NaCl are given by (Equations 40-45):

$$Ln\gamma_M = Z_M^2 f^\gamma + 2I\cdot(B_{MCl} + IC_{MCl}) + I^2(Z_M^2 B'_{NaCl} + Z_M C_{NaCl}) \qquad 40$$

$$Ln\gamma_X = Z_x^2 f^\gamma + 2I\cdot(B_{NaX} + IC_{NaX}) + I^2(Z_X^2 B'_{NaCl} + Z_M C_{NaCl}) \qquad 41$$

where

$$f^\gamma = -0.392\left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + 1.67Ln(1+1.2\sqrt{I})\right] \qquad 42$$

$$B_{MX} = \beta_{MX}^0 + \frac{\beta_{MX}^1}{2I}\left[1-(1+2\sqrt{I})\exp(-2\sqrt{I})\right] \qquad 43$$

$$B'_{MX} = \frac{\beta_{MX}^1}{2I^2}\left[-1+(1+2\sqrt{I}+2I)\exp(-2\sqrt{I})\right] \qquad 44$$

$$C_{MX} = C_{MX}^\phi/(2\left|Z_M Z_X\right|^{1/2}) \qquad 45$$

The values of γ_{CuCl} can be estimated from (Eq. 46):

$$Ln\gamma_{CuCl} = AI \qquad 46$$

where A=0.132 is the salting coefficient for a neutral M^+X^- ion par.

In order to gain an insight into the role played by the different copper chloride species in the oxidation kinetic of Cu(I), the Cu(I) speciation in NaCl has been determined (Fig. 6). The speciation of Cu(I) is dominated by the $CuCl_2^-$ species, from 92% at 0.1 M to 72% at 0.7 M NaCl, while the $CuCl_3^{2-}$ species achieves a 29% at 0.7 M, following the results at micromolar studies by Sharma and Millero 1988a,b,c.

The contribution of the different Cu(I) species to the oxidation rate in oxygen saturated seawater is showed in the Fig. 7. The neutral chloride CuCl species dominates the Cu(I) oxidation in the range studied, 90% at 0.1 M and 55% at 0.7 M . $CuCl_2^-$ species increase with the ionic strength but is less important than CuCl at 0.7 M (56%). Free copper ions contribution is practically negligible, its contribution is 0.1% at 0.7 M and 0.7% at 0.1 M. Differences in the equilibrium constants can lead to both changes in the speciation and in the individual oxidation rates of Cu(I).

Conclusion

The results of this work show that the Cu(I) oxidation rate constant, as a function of pH, is slower at nanomolar levels than at micromolar concentration, being the intermediate species, generated in the solution, and the Cu(I) regenerated from Cu(II) reduction more important at this scale of concentration. The effect of pH shows a slight dependence indicating that acid or basic species are not strongly involved in the process. When the temperature increases, the oxidation rate also increases. The copper(I) oxidation rate constant increase with the bicarbonate concentration until 5 mM but is stabilized between 5-9 mM. The copper-carbonate complexes explain the effect of the bicarbonate concentration in the oxidation rate. The Cu(I) oxidation rate constant is similar in NaCl and seawater at ionic strength 0.7 M. At lower ionic strength, there are differences between NaCl and seawater. The rate constant is modified by the interaction with major ions, as Ca^{2+} and Mg^{2+}, and the back-reaction of Cu(II). The $CuCl_2^-$ is the specie which dominates the speciation of Cu(I) in sodium chloride. Neutral CuCl species dominate the Cu(I) contribution to the overall rate constant in the range between 0.1-0.7 M. The results of this work can be extrapolated at low concentration of copper (50 nM), because there are not a measurable effect of the initial copper(I) concentration.

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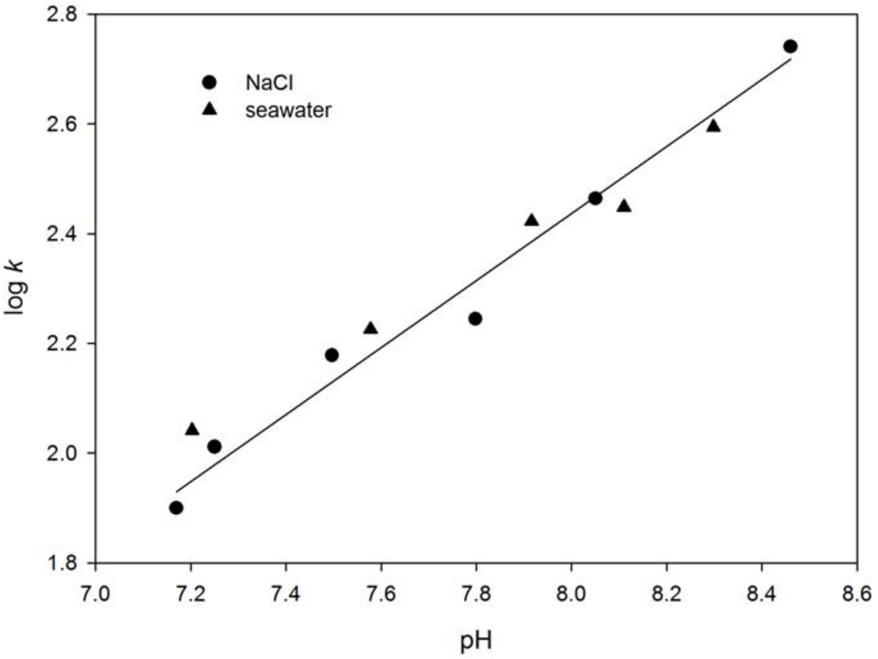

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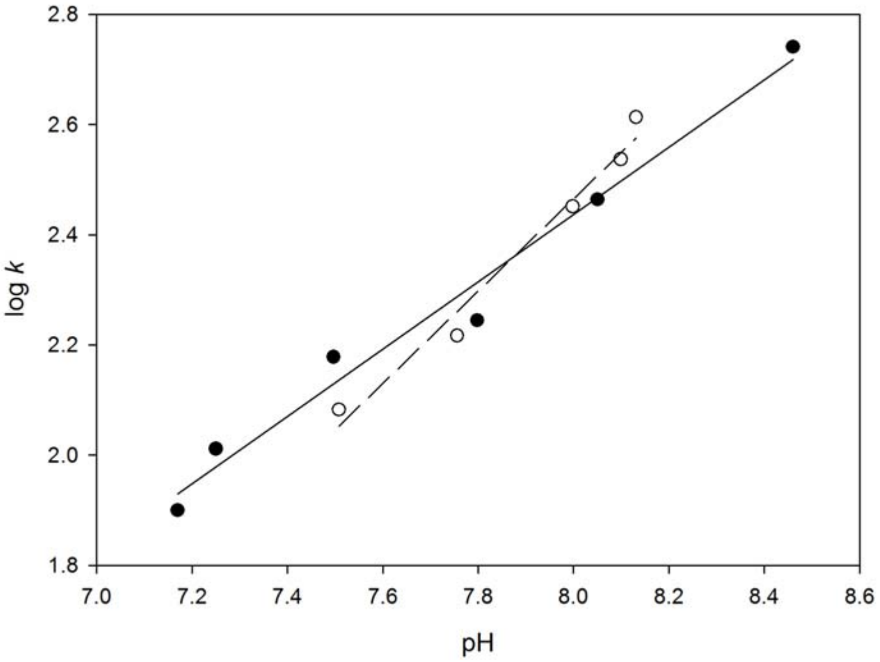

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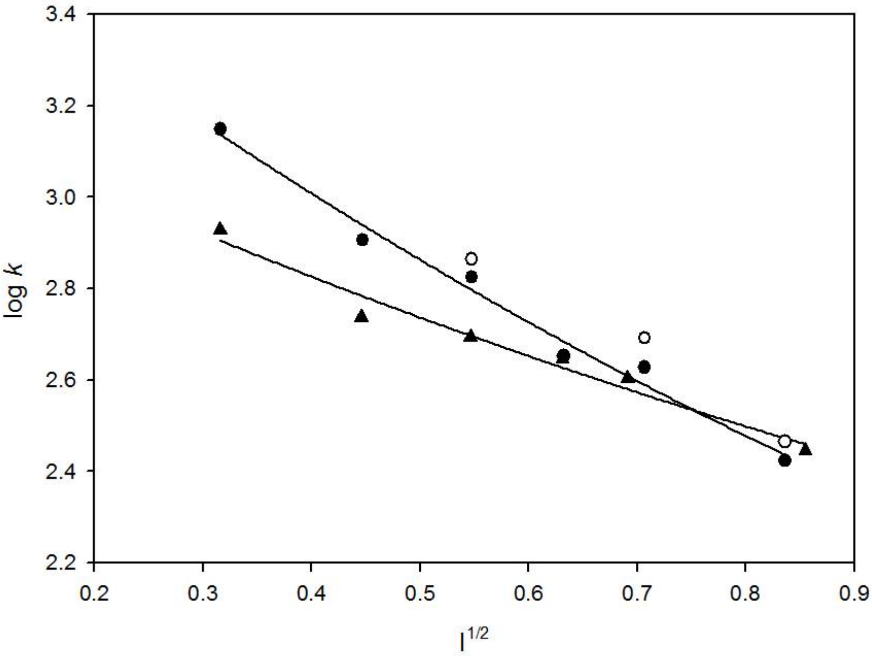

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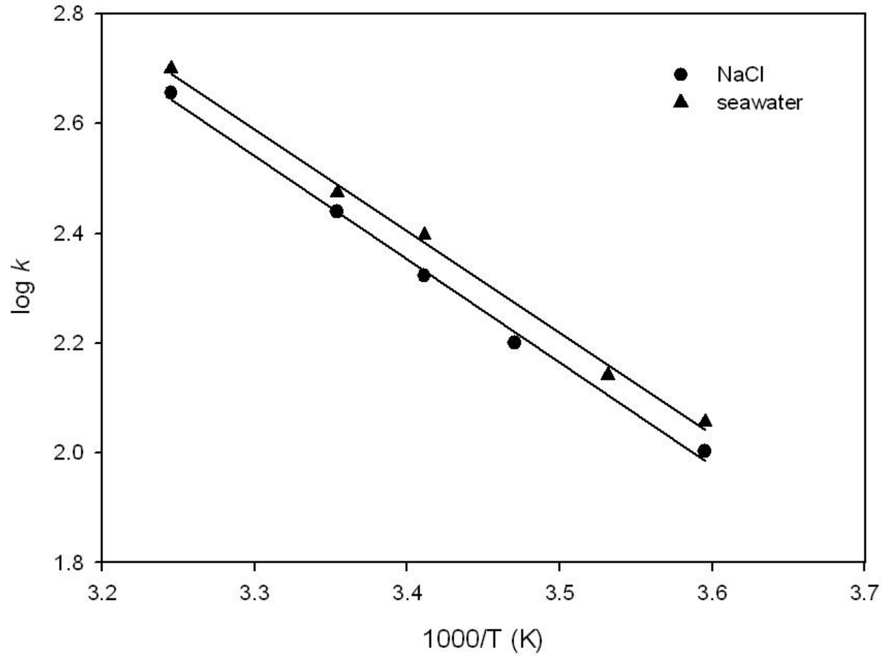

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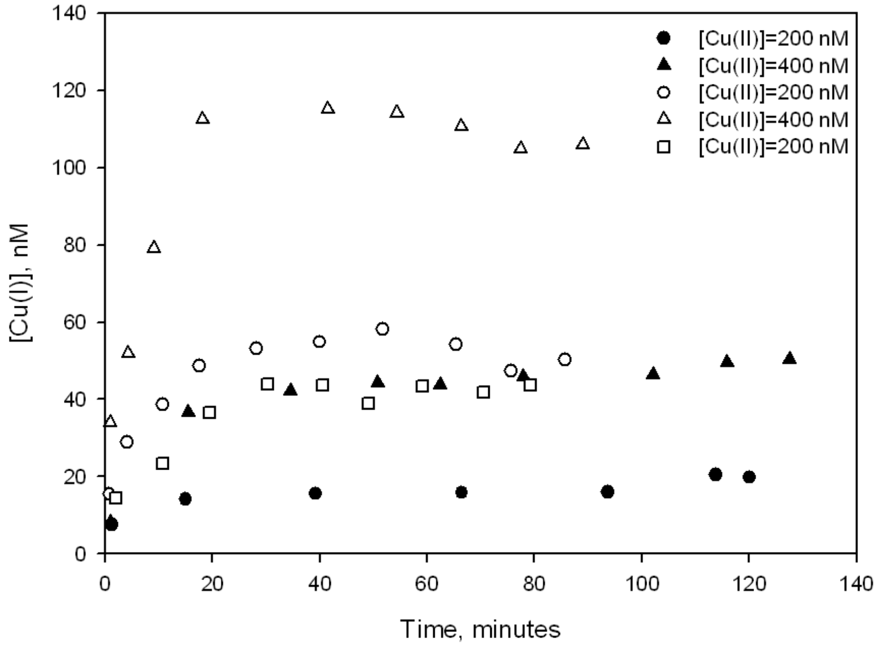

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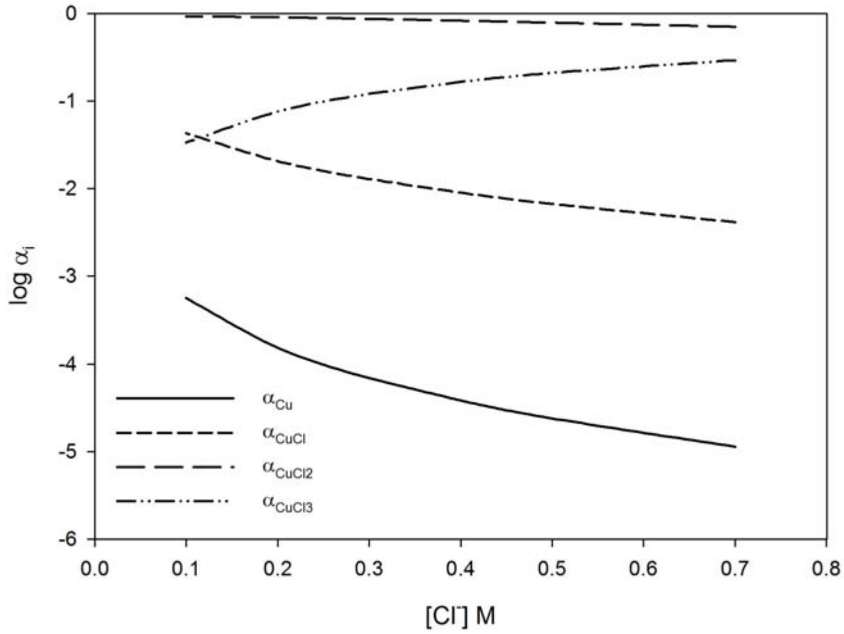

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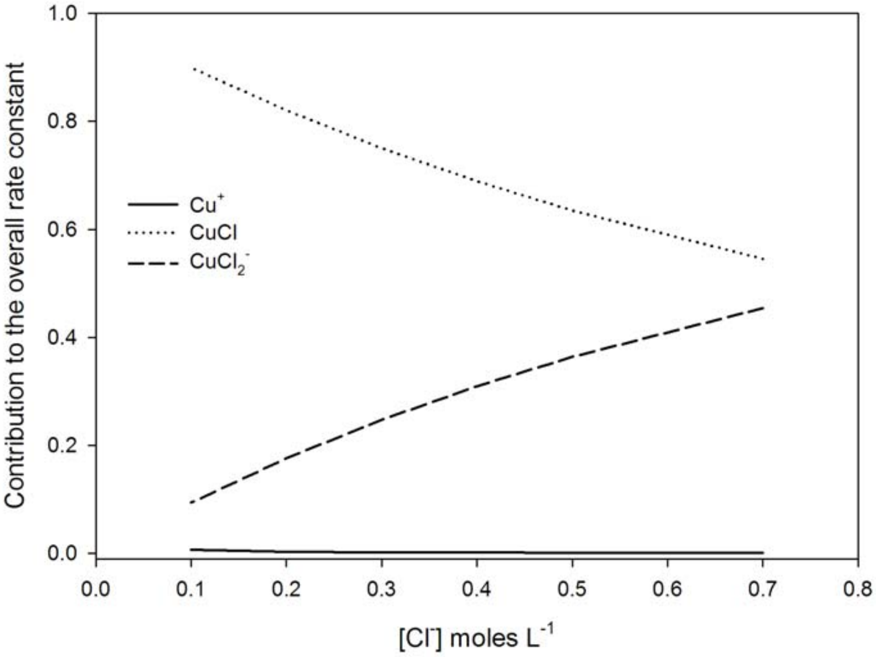

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Table 1 $t_{1/2}$ for the oxidation of Cu(I) in this study in NaCl and seawater for different pH and temperatures, compared with micromolar results from Sharma and Millero (1988a) and this study.

Media	**pH**	**Temperature (°C)**	**$t_{1/2}$ (minutes)**	
NaCl (0.7 M) and 2mM $NaHCO_3$	7.51	25	**27.15**	This study (µM)
	7.76	25	**19.93**	
	8.10	25	**9.53**	
	8.13	25	**8.00**	
	7.17	25	**42.25**	This study (nM)
	7.50	25	**22.25**	
	7.79	25	**16.29**	
	8.05	25	**11.52**	
Seawater (S=36.691)	7.20	25	**30.75**	
	8.01	25	**12.23**	
	8.11	25	**12.07**	
	7.97	5	**20.09**	
NaCl (1M)	8.00	25	**1.30**	Sharma and Millero (1988a)
Seawater (S=35)	8.00	25	**4.00**	
	8.00	5	**15.70**	

Table 2 Effect of initial copper(I) concentration on the apparent rate constant (min^{-1}) for the oxidation of copper (I) in NaCl 0.7 M and 2 mM $NaHCO_3$, pH 8.00 and temperature 25ºC.

Media	**$[Cu(I)]_0$ (nM)**	**log k'_{obs}**
NaCl 0.7 M and 2 mM NaHCO3	50	-1.28
	100	-1.33
	200	-1.34
	385	-1.30

Table 3 Effect of $NaHCO_3$ concentration on the rate constant (kg $mol^{-1}min^{-1}$), in NaCl 0.7 M. pH 8.00 and temperature 25ºC.

Media	**NaHCO3 (mM)**	**log *k***	**Standard deviation**
NaCl 0.7M	0	1.95	0.16
	1	2.30	0.15
	2	2.48	0.02
	4	2.60	0.05
	5	2.70	0.22
	7	2.73	0.04
	9	2.73	0.18