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Aqueous oxidation of iron monosulfide (FeS) in the presence of glycine

Mădălina I. Duinea[a,b], Ana M. Sandu[a], Mihaela A. Petcu[a], Irina Dăbuleanu[a], Geta Cârâc[b], Paul Chiriță[a,*]

[a] University of Craiova, Department of Chemistry, Calea Bucuresti 107I, Craiova 200478, Romania
[b] "Dunarea de Jos" University of Galati, Department of Chemistry, Physics and Environment, 47 Domneasca Street, Galati 800081, Romania

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ABSTRACT

The effect of glycine on the aqueous oxidation of FeS was evaluated in the range of 0.1–1.0 mM at pH 2.5 and 25 °C by electrochemical techniques (potentiodynamic polarization and Electrochemical Impedance Spectroscopy) and Density Functional Theory (DFT) computations. Our findings show that the inhibition efficiency of glycine in controlling the oxidative dissolution of FeS increases when the glycine concentration increases up to 0.5 mM. Further increase of glycine concentration up to 1 mM produces the decrease of the corresponding inhibition efficiency. The results of our study indicate that the inhibiting effect of glycine on the oxidative dissolution of FeS is produced by the glycine adsorption on the ferric iron formed by the oxidation of the FeS surface.

1. Introduction

Iron monosulfide phases (pyrrhotite, troilite and mackinawite) are among of the most reactive of the sulfide minerals [1–4], and their oxidative dissolution is of high importance to understanding acid mine drainage, remediation of mine wastes or mineral processing. The products of their complete oxidation by dissolved oxygen are ferric iron, protons and sulfate [2–4]. Because the oxidative dissolution may not be complete, the mineral surface accumulates elemental sulfur and polysulfide species [2,4–16]. When the pH of the dissolution medium is higher than 3, on the mineral surface precipitate ferric oxyhydroxides [2,4]. Elemental sulfur, polysulfide species and ferric oxyhydroxides can influence the overall oxidative dissolution of iron monosulfide [12–14,17–19]. At low pH values, the formed ferric iron can dissolve other mineral sulfides releasing toxic species which contribute to the phenomenon of acid mine drainage [4,20]. An effective method to control the oxidative dissolution of iron monosulfide supposes the coating of the mineral surface with a substance that prevents the oxidant attack. Cai et al. [1] have found that triethylenetetramine (TETA) inhibits the oxidative dissolution of pyrrhotite ($Fe_{1-x}S$; $0 < x \leq 0.125$). The probable mechanism of the inhibition is based on the capacity of TETA to hinder the oxidant attack and, respectively, on its property to consume the formed protons. At pH ≤ 5 and 25 °C, the oxidation of troilite (FeS) with dissolved oxygen is controlled by the organic ligands of the Fe^{2+} [21,22]. At low concentration of the organic ligands (2,2′-bipyridine or 1,10-phenanthroline), the rate of the oxidative dissolution decreases because the organic molecules adsorb on the mineral surface and hinder the electron transfer from FeS to oxidant. Increasing the ligand concentration, the rate of the oxidative dissolution increases as the result of the promotion of the ferrous iron release from the mineral surface. It is thought that a high ligand concentration labializes the Fe—S bonds increasing the rate of the electron transfer from mineral to oxidant.

It is known that amino acids (organic compounds containing heteroatoms such as O, N, P or S) are effective inhibitors of the iron corrosion [24]. The presence of iron into the iron monosulfide lattice makes the amino acids potential inhibitors of the oxidative dissolution of this kind of minerals. Because the iron monosulfide oxidative dissolution is an electrochemical process [15,22,23], it can be successfully investigated by electrochemical techniques. The goal of the present work was therefore to investigate the effect of glycine (the simplest amino acid) on the troilite (the stoichiometric iron monosulfide) oxidative dissolution in air-equilibrated HCl solutions by electrochemical techniques (potentiodynamic polarization and Electrochemical Impedance Spectroscopy). The reactivity of glycine was evaluated by quantum chemical calculations.

2. Experimental

2.1. Materials

Synthetic FeS (troilite) purchased from Merck was used in this

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[*] Corresponding author.
E-mail address: paul.chirita@chimie.ucv.ro (P. Chiriță).

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study. Its composition ($Fe_{1.00 \pm 0.01}S_{0.99 \pm 0.02}$) is consistent with the expected stoichiometry of troilite [18]. X-ray diffraction analysis of the material confirmed the presence of troilite [18]. All solutions were prepared with chemicals of reagent grade purity and distilled water.

2.2. Electrochemical measurements

The electrochemical measurements were performed with a Zahner Zennium electrochemical workstation. The working electrode consisted of a rectangular piece of FeS with the exposed surface of 1 cm^2. The FeS electrode was first polished successively with SiC abrasive paper of increasing finesses up to 3000 grits, and then sonicated for 10 min in ethanol. A platinum sheet and a saturated calomel electrode (SCE) were used as counter electrode and, respectively, reference electrode.

The volume of air-equilibrated solution used in the experiments was 250 mL, the pH was 2.50, and the temperature 25 °C. Glycine ($NH_2{-}CH_2{-}COOH$) was added in the desired concentration. Potentiodynamic polarization measurements were carried out from − 250 mV to + 250 mV *versus* open circuit potential (OCP) at a rate of 1 mV/s. The frequency interval of Electrochemical Impedance Spectroscopy (EIS) measurements was from 100 kHz to 10 mHz and the AC signal amplitude was 10 mV. Tales software was used to fit the impedance data. All experiments were carried out in triplicate. The representative measurements are presented in graphical and tabular form.

2.3. Batch dissolution experiment

Four-hour dissolution experiment was performed in an Erlenmeyer flask. The sample loading was 10 g/L of FeS in air-equilibrated solution of 1.00 mM glycine at pH 2.50 and 25 °C. At the ending of the experiment the reacted FeS particles were separated, washed with distilled water and dried in an evacuated desiccator.

2.4. Fourier transform infrared (FTIR) spectroscopy measurements

FTIR analysis of the initial FeS and reacted FeS was done using KBr technique with a Bruker Alpha spectrometer. The infrared spectra of the analyzed samples were collected in the range 375–4000 cm^{-1} with the resolution 4 cm^{-1}.

2.5. Fe^{2+} (or Fe^{3+}) - glycine reaction

The reaction between Fe^{2+} (or Fe^{3+}) (0.25 mM) and glycine (0.75 mM) in aqueous medium was analyzed by UV–vis spectroscopy using a PG Instruments T70 UV–vis spectrophotometer [25].

2.6. Density functional (DFT) calculations

A series of DFT calculations were performed with the scalar relativistic zeroth order regular approximation (ZORA) formalism implemented in the Amsterdam Density Functional (ADF) 2016.104 code [26,27]. Calculations for glycine were carried out with the PW91 functional proposed by Perdew et al. [28] and the core double-zeta polarized basis set (DZP). Large frozen core was used for the optimization. Quantum calculations for both FeS bulk and FeS (001) surface used the local density approximation (LDA), the core double-zeta basis set (DZ) and the Large frozen core. The program default settings are the convergence criteria of our calculations.

3. Results and discussion

3.1. Potentiodynamic polarization results

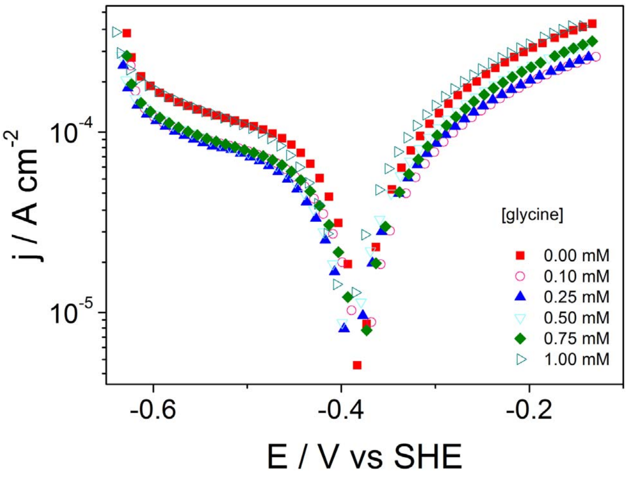

Fig. 1. Potentiodynamic polarization curves for FeS in air-equilibrated solution with different concentrations of glycine at pH 2.5 and 25 °C.

Table 1

Electrochemical parameters and inhibition efficiency (IE_j) for FeS electrode immersed in aqueous solutions of glycine with concentrations between 0 and 1 mM. Experimental conditions: pH 2.50 and 25 °C. $IE_j = (1 - j_{ox}/66)\cdot 100$; where j_{ox} is the current density of FeS oxidation computed in the presence of glycine, and 66 is the current density in the absence of glycine. The maximum standard deviation in the observed E_{ox} and j_{ox} is ± 2.4% and, respectively, 7.5%.

[Glycine]/mM	E_{ox}\V	j_{ox}/μA cm^{-2}	ba/mV dec^{-1}	bc/mV dec^{-1}	IE_j/%
0.00	− 0.378	66.0	274	− 558	–
0.10	− 0.383	48.5	312	− 572	26.5
0.25	− 0.388	42.2	276	− 490	36.1
0.50	− 0.381	38.7	215	− 426	41.4
0.75	− 0.385	46.7	264	− 521	29.2
1.00	− 0.387	60.7	244	− 465	8.0

Fig. 1 shows a series of potentiodynamic polarization curves of FeS electrode in air-equilibrated solutions at initial pH 2.5 and 25 °C. Electrochemical parameters of FeS electrode (Table 1) were evaluated by Tafel method. Because FeS is not a metal, we will use the term oxidative dissolution instead of the term corrosion which describes the oxidation of the metals [25]. The addition of glycine in the concentration range 0.1–1 mM does not significantly change the oxidation potential (E_{ox}). This finding suggests that glycine acts as a mixed inhibitor [29]. In the glycine concentration range 0–0.5 mM the oxidation current density (j_{ox}) decreases from 66 μA cm^{-2} down to 38.7 μA cm^{-2}. Increasing the concentration of glycine up to 1 mM, j_{ox} increases up to 60.7 μA cm^{-2}. Such a variation indicates that up to approximately 0.5 mM, glycine gradually adsorbs on the mineral surface producing a decrease of the current density associated with the oxidative dissolution of FeS in air-equilibrated solutions (j_{ox}), while at higher concentrations, glycine leaves the FeS surface, facilitating the electron transfer from mineral to oxidant (dissolved O_2) and increasing the values of j_{ox}. The inhibition efficiencies (IE_j) of glycine in controlling the oxidative dissolution of FeS computed using j_{ox} values are presented in Table 1. As is normal, the IE_j variation is in a reverse relation to the j_{ox} variation. Up to 0.5 mM glycine concentration IE_j increases, while at higher glycine concentrations, it decreases.

3.2. Electrochemical impedance spectroscopy

The experimental impedance behaviors of the FeS in HCl solutions at pH 2.5, with and without glycine, and at OCP are presented in Fig. 2. The Nyquist plots obtained in the absence and, respectively, the presence of glycine show an incomplete capacitive loop at high frequency region and a complete capacitive semicircle at low frequencies. The incomplete capacitive loop is attributed to the surface layer formed by the elemental sulfur, polysulfide species and ferric oxyhydroxides