ARTICLE IN PRESS

Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Inhibitory effect of three phenacyl derivatives on the oxidation of sphalerite (ZnS) in air-equilibrated acidic solution

Paul Chiriţă[a,*], Mădălina I. Duinea[a,b], Ana M. Sandu[a], Lucian M. Bîrsă[c], Laura G. Sârbu[c], Mihaela Baibarac[d], Florinel Sava[d], Mihai Popescu[d], Elena Matei[d]

[a] Department of Chemistry, University of Craiova, Calea Bucuresti 107I, Craiova, 200478, Romania
[b] Faculty of Sciences and Environment, “Dunarea de Jos” University of Galati, 111 Domneasca Street, Galati, 800201, Romania
[c] Department of Chemistry, "Al. I. Cuza" University of Iasi, 11 Carol I Blv., Iasi, 700506, Romania
[d] Lab Optical Processes in Nanostructured Materials, National Institute of Materials Physics, P.O. Box MG-7, Bucharest, R077125, Romania

ARTICLE INFO

Keywords:
Sphalerite oxidation
Oxygen
Inhibition
Potentyodynamic polarization
Quantum chemical calculations

ABSTRACT

Three phenacyl derivatives have been investigated as potential inhibitors for the aqueous oxidation of sphalerite (ZnS) in air-equilibrated solutions of HCl (pH 2.5 and 25 °C) using potentyodynamic polarization, aqueous batch experiments, scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) analysis, Fourier transform infrared (FTIR) spectroscopy, Raman scattering and quantum chemical calculations. Findings show that the studied phenacyl derivatives are inhibitors of sphalerite aqueous oxidation. Quantum chemical calculations indicate that the adsorption of phenacyl derivatives on ZnS is energetically favorable and accounts for the observed inhibiting effects.

1. Introduction

Sphalerite (ZnS) is the main zinc sulfide mineral and is usually associated with pyrite, chalcopyrite, galena, and other sulfides [1,2]. Zn can be substituted by different metals within the sphalerite structure. The most common metals substituting Zn into sphalerite are Fe (from 0 to 32 wt.%), Cd and Mn [3]. Ferric iron or dissolved oxygen in the presence of protons oxidize the mineral producing sulfuric acid and releasing zinc and metals that substitute zinc in the sphalerite lattice [4,5]. The released species can pollute rivers and oceans [4]. Hence, it is important to know the factors that control the oxidative dissolution of sphalerite and identify effective solutions for its inhibition.

Numerous studies focused on the aqueous oxidation of companion minerals of sphalerite [6–19] and only a few studies [3–5,20–24] investigated sphalerite oxidative dissolution. Acero et al. [21] found that the rate of the oxidative dissolution of sphalerite in the presence of oxygen is independent of oxidant concentration and increases when pH decreases. X-ray photoelectron spectroscopy (XPS) investigation of reacted samples indicates the development of a sulfur rich layer on the mineral surface during dissolution. According to Acero et al., [21] the formed sulfur rich layer does not exert an inhibiting effect on the sphalerite oxidative dissolution. Weisner et al. [23,24] found that polysulfide species (formed during the initial rapid leaching period) decrease sphalerite leaching rate (i.e., are inhibitors) and only elemental sulfur (formed after prolonged leaching periods) does not affect the aqueous oxidation rates of sphalerite at pH 1 in O_2-purged $HClO_4$ from 25 to 85 °C. Because the non-oxidative leaching of sphalerite is fast, at least in the first 24–30 h [3,25], the first of the conclusions must be regarded with prudence as long as the non-oxidative release of Zn is not subtracted from the overall amount of dissolved Zn.

A solution to inhibit the sphalerite oxidative dissolution could be the pretreatment of the mineral with organic compounds. Thus, the electrons transfer to the oxidant is hindered by the organic molecules that adsorb to the sulfide surface through heteroatoms and multiple bonds in the structure [26,27]. This mechanism of inhibition is similar to that responsible for the inhibition of metal corrosion [28–31].

In this work, the potential inhibitory effect of three phenacyl derivatives (4-(2-hydroxyphenyl)-2-(morpholin-4-yl)-1,3-thiazole (**Pr02**), 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxoethan-2-yl-*N*,*N*-diethyldithiocarbamate (**Pr04**) and 1-(5-bromo-2-hydroxy-3-methylphenyl)-1-oxoethan-2-yl-*O*-ethyl xanthate (**Pr06**)) on the oxidative dissolution of sphalerite was examined conducting potentiodynamic polarization measurements. The three phenacyl derivatives incorporate heteroatoms and multiple bonds which would facilitate the adsorption on the surface of sphalerite. The uninhibited and inhibited surfaces were characterized using scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) analysis, Fourier transform infrared (FTIR) spectroscopy and Raman scattering. A quantum chemical method was

---

[*] Corresponding author.
E-mail addresses: paulxchirita@gmail.com, paul.chirita@chimie.ucv.ro (P. Chiriţă).

https://doi.org/10.1016/j.corsci.2018.04.017
Received 17 December 2016; Received in revised form 7 April 2018; Accepted 8 April 2018

Please cite this article as: Chiriță, P., Corrosion Science (2018), https://doi.org/10.1016/j.corsci.2018.04.017

employed to investigate the correlation between the inhibitory effect and the **Pr02**, **Pr04** and **Pr04** structures. Thus, we have registered the potentiodynamic polarization curves of sphalerite oxidation in the absence and presence of the three phenacyl derivatives and characterized the interaction between mineral surface and organic molecules. This would be helpful in predicting the rate determining step which controls ZnS oxidation and, respectively, reaction intermediate(s) involved in the rate determining step.

2. Experimental

2.1. Materials

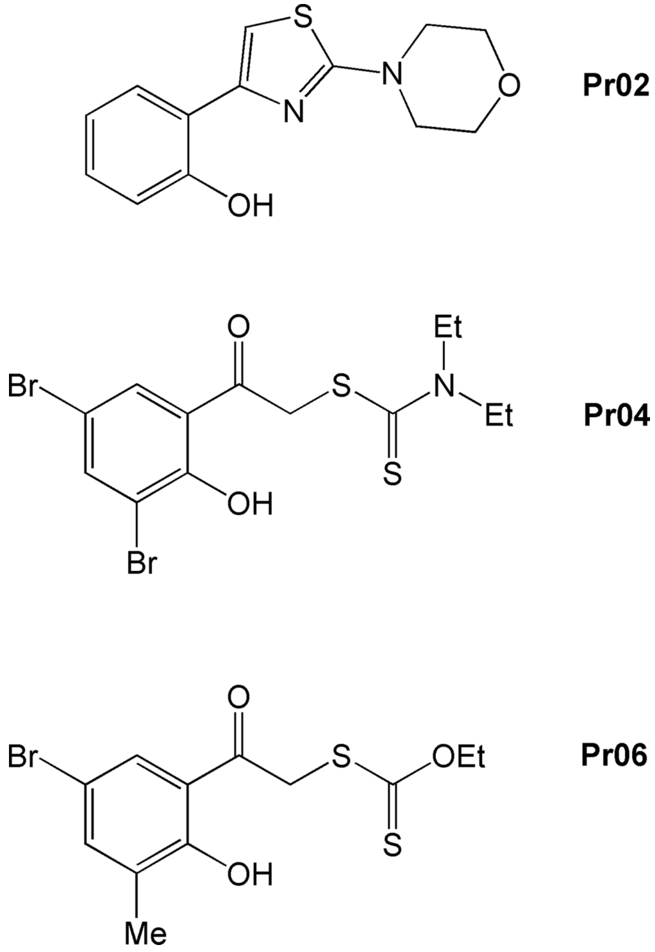
A natural ZnS sample was used in the present study. X-ray diffraction analysis confirmed the sample to be face-centered cubic ZnS phase (sphalerite) (Fig. S1 of the Supplementary content). Its chemical composition is: 58.0 wt.% Zn, 35.2 wt.% S and 5.3 wt.% Fe. Minor amounts (approximately 1.5 wt%) of Cd, Al and Si were determined.

The acid solutions (pH 2.50) were prepared from reagent grade purity HCl. Appropriate concentration of acid was prepared by using distilled water.

The molecular structures of the three organic compounds (**Pr02**, **Pr04** and **Pr06**) are depicted in Scheme 1. These compounds were synthesized according to the following experimental procedures.

2.1.1. 4-(2-Hydroxyphenyl)-2-(morpholin-4-yl)-1,3-thiazole (Pr02)

To a solution of 2-thiocyanato-1-(2′-hydroxyphenyl)-1-ethanone (0.895 g, 5 mmol) [32] in acetone (25 mL), morpholine (0.52 mL, 6 mmol) was added. After 24 h at room temperature the formed precipitate was filtered, washed with methanol and dried. Recrystallization from 50 mL ethanol gave white crystals of **Pr02**, 1.06 g (η = 81%); mp 189–190 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.37 (4H, m, CH_2—O—CH_2), 3.78 (4H, m, CH_2-N-CH_2), 690 (1H, m, Har-5), 6.97 (1H, d, Har-3), 7.50 (1H, m, Har-4), 7.84 (1H, s, H-5), 7.95 (1H, m, Har-6), 12.10 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 43.8 (CH_2), 50.8 (CH_2), 51.8 (CH_2), 118.4 (Car), 118.9 (Car), 122.7 (Car), 125.3 (Car), 128.7 (Car), 130.9 (C), 133.8 (C), 137.4(CH), 154.8 (Car) ppm; IR (ATR): ν = 3400, 2956, 1604, 1441 cm^{-1}; MS (ESI): *m/z* = 262 (M^+).



Scheme 1. Structures of **Pr02**, **Pr04** and **Pr06**.

2.1.2. 1-(3,5-Dibromo-2-hydroxyphenyl)-1-oxoethan-2-yl-N,N-diethyldithiocarbamate (Pr04)

To a solution of 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone (3.73 g, 10 mmol) in acetone (40 mL), a solution of sodium *N,N*-diethyldithiocarbamate trihydrate (2.25 g, 10 mmol) in acetone-water (1:1, 20 mL) was added. The reaction mixture was refluxed for 10 min and then poured into water. The precipitate was filtered, dried and recrystallized from ethanol (40 mL) to give the pure product **Pr04**; yield 3.6 g (82%). The analytical and spectral data are in accordance with those previously reported [33].

2.1.3. 1-(5-Bromo-2-hydroxy-3-methylphenyl)-1-oxoethan-2-yl-O-ethyl xanthate (Pr06)

To a solution of 1.54 g 2-bromo-1-(5-bromo-2-hydroxy-3-methylphenyl)ethan-1-one (5 mmol) [33] in 50 mL acetone, a solution of 0.8 g potasium *O*-ethylxantogenate (5 mmol) in 10 mL water-acetone (1:1) was added. The reaction mixture was refluxed for 10 min, cooled and then poured into 200 mL water. The precipitate was filtered, washed with water, and dried. Recrystallization from 50 mL ethanol gave yellow pale crystals of **Pr06**, 1.55 g (89%); mp 132–133 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, ^3J = 5.4 Hz, CH_3), 3.76 (q, ^3J = 5.5 Hz, CH_2), 4.98 (s, CH_2), 7.48 (d, ^4J = 2.3 Hz, Har-4), 7.93 (d, ^4J = 2.3 Hz, Har-6), 12.21 (s, 1 H, OH) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 12.9 (CH_3), 17.6 (CH_3), 44.8 (CH_2), 52.6 (CH_2–O), 111.1 (Car), 127.7 (Car), 129.8 (Car), 130.9 (Car), 131.4 (Car), 157.0 (Car), 190.9 (C), 196.6 (C) ppm; IR (ATR): ν = 3440, 2932, 1642, 1469, 1244, 1125, 958, 654 cm^{-1}; MS (ESI): *m/z* = 347.94 (M^+, $C_{12}H_{13}{}^{79}BrO_3S_2$).

2.2. Construction of carbon paste electrodes (CPE)

For the construction of carbon paste electrodes (working electrodes), ZnS sample was ground under ethanol, dried and sieved. Particles smaller than 125 μm in diameter were divided into four portions. A portion was immersed for 4 h in ethanol, while the other three portions were immersed for 4 h in 1 mM ethanolic solutions of **Pr02**, **Pr04** and **Pr06,** respectively. After pretreatment, each solid phase was separated and dried in an evacuated desiccator. The pretreated powders were used for the construction of the carbon paste electrodes (Fig. 1) using a modified version of the procedure described by Almeida and Giannetti [34]. An isolated Cu wire with a diameter of 4 mm was immersed in a mixture of 2.0 g graphite and 2.4 g paraffin wax heated at 75 °C. Thereafter, 0.02 g of powdered sphalerite was placed in a Teflon cavity with a diameter of 5 mm and the extremity of the wire covered with the hot mixture of graphite/paraffin was immediately pressed on the ZnS particles placed in the cavity. The result was a hemisphere with a diameter of nearly 5 mm formed from the mixture of graphite/paraffin covered by a very stable ZnS bed. The isolation prevents the contact between the Cu wire and the solution.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a three-electrode cell that consists of a working electrode (CPE), a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode, using a ZAHNER ZENNIUM electrochemical workstation.