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Synthesis of 2-ethyl-2-hexenal oxime and its flotation performance for copper ore

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ABSTRACT

A novel collector 2-ethyl-2-hexenal oxime was synthesized from 2-ethyl-2-hexenal and hydroxylamine hydrochloride. The yield of oxime was 78.05% under the optimum experimental conditions. The oxime was characterized by elemental analysis, infrared spectrum, mass spectrum, ^{1}H NMR and ^{13}C NMR spectroscopy. The results of ultraviolet spectrum showed that the oxime exhibited stronger reaction affinity with Cu^{2+} than with Ni^{2+} or Fe^{3+}, etc. Infrared spectroscopic analysis implicated that the oxime bound to Cu^{2+} through both the C=C and C=N groups. Microflotation tests of pure malachite mineral and chalcopyrite mineral indicated that the recovery of chalcopyrite was 91.16% under the flotation condition of rougher pH 10 and collector concentration of 200 mg/L, and the recovery of malachite reached 90.56% under the flotation condition of rougher pH 11.5 and collector concentration of 250 mg/L. The results of flotation tests of sulfide–oxide copper from Dexing copper mine showed that 2-ethyl-2-hexenal oxime achieved an excellent mean concentration containing 4.52% Cu with 79.54% Cu recovery, and the Cu average recovery increased by 2.35% compared to that of butyl xanthate.

1. Introduction

Oximes are applied in synthesis of various intermediates, such as amines (Li et al., 2009), amides (Chandrasekhar and Gopalaiah, 2001), nitriles (Anand et al., 2007; Mendelsohn et al., 2009), nitro compounds (Olah et al., 1992), isoquinolines (Parthasarathy and Cheng, 2009; Too et al., 2010) and isooxazolines (Pohjakallio and Pihko, 2009; Shotter et al., 1975). Hydroxy substituted oximes and hydroximic acids have characteristic group of —C=N—OH and multiple coordinating atoms, they are important copper solvent extraction agents in mineral processing (Agrawal et al., 2008; Gouvea and Morais, 2010; Sridhar and Verma, 2011) and excellent collectors in mineral flotation field (Bralurna and Charkraburtty, 1981; Fuerstenau and Herrera-Urbina, 2000; Desaraju and Winston, 1986), respectively. Since industrial ore deposits at present are fine and complex, and the grade of minerals becomes gradually lower and lower, it is necessary to consider the impact of collectors' chemical structures on flotation properties such as selectivity, collecting ability and frothiness.

2-Ethyl-2-hexenal oxime has two structural features: conjugated olefinic and ethyl substitution on the α-carbon. It has particular characteristics: high taste intensity and significant degrees of sweetness (Acton et al., 1970); good foaming properties in the flotation of copper ores (Miroslaw et al., 1978). However, the systematic studies on the preparing of 2-ethyl-2-hexenal oxime have seldom been reported. Due to π–π conjugated system between carbon–carbon and carbon–nitrogen double bonds in the molecular structure of 2-ethyl-2-hexenal oxime, it may form complexes with metal atoms at mineral surface. So this compound may be a new type of high-efficiency collector for the retrieval of minerals. To our best knowledge, there is no report using this kind of compound to retrieve minerals.

In this study, we aimed to develop an approach to synthesize 2-ethyl-2-hexenal oxime under organic solvent-free conditions. The two-phase reaction between 2-ethyl-2-hexenal and hydroxylamine was easy to perform and afforded 2-ethyl-2-hexenal oxime in good yield. The interactions between oxime and metal ions such as Cu^{2+}, Ni^{2+}, Fe^{3+}, Ag^{+}, Co^{2+} and Zn^{2+} were also studied by UV spectrum, and the coordination compound of 2-ethyl-2-hexenal oxime reacting with Cu^{2+} was analyzed using infrared spectroscopy in this paper. Furthermore, flotation tests of pure malachite mineral, chalcopyrite mineral and sulfide–oxide copper from Dexing copper mine were also carried out.

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2. Experimental methods

2.1. Reagents and instruments

n-Butyraldehyde was of chemical purity grade, and the other chemicals were of analytical grade. The elemental analysis of oxime was carried out with Element Vario EL III analyzer, Germany. IR was used to analyze oxime and copper–oxime complex. It was recorded with AVATAR370 infrared spectrophotometer from Nicolet, USA. The KBr pellet method was used for the IR sample preparation. The mass spectrometry of oxime was surveyed by GCMS-QP2010 analyzer from Japan. The ^{1}H NMR and ^{13}C NMR spectra of oxime were obtained by an INOVA-400 (400 MHz) spectrometer from USA in $CDCl_3$. UV was used to analyze the oxime solutions before and after the addition of metal ions. It was gained by a UV-2100 UV–VIS spectrophotometer from UNICO.

2.2. Synthesis of 2-ethyl-2-hexenal oxime

2-Ethyl-2-hexenal oxime was synthesized by two steps (Scheme 1).

The preparation of 2-ethyl-2-hexenal (**2**) was carried out according to literature (Ding, 2007). An accurate amount of hydroxylamine hydrochloride dissolved in 50 mL deionized water was taken in a 100 mL three-neck round bottom flask with a magnetic stirrer. Some sodium carbonate was added to adjust the pH value of solution. When the solution was heated to the desired temperature, 2-ethyl-2-hexenal (**2**; 12.62 g, 0.10 mol) was added dropwise. After the addition was finished, the mixture had been stirred for several hours. The oily layer was separated, treated with saturated $NaHCO_3$ solution, then washed with distilled water to pH value of 7, dried thoroughly over anhydrous sodium sulfate, distilled in vacuo (b.p.82–84 °C/1.862 kPa) to yield 2-ethyl-2-hexenal oxime (**3**).

2.3. Evaluation of reaction between 2-ethyl-2-hexenal oxime and metal ions

Solutions (4×10^{-5} mol/L, in methanol) of Cu^{2+}, Ni^{2+}, Fe^{3+} and Zn^{2+} were prepared from the corresponding chloride salts, Ag^+ from corresponding nitrate salt and Co^{2+} from corresponding sulfate salt. Solution (4×10^{-5} mol/L, in methanol) of 2-ethyl-2-hexenal oxime was prepared for the following experiments, too. Mixing 10 mL of one metal ion solution with 10 mL of the oxime solution, sufficient oscillation and several hours of standing were required before measuring the absorbance of the supernatant against the metal ion's blank.

2.4. Batch flotation tests

2.4.1. Flotation tests of pure malachite mineral and chalcopyrite mineral

Hand-picked malachite mineral and chalcopyrite mineral were obtained from Shilu Copper Mine of Guangdong Province and Dexing Copper Mine of Jiangxi Province in China respectively. They were drily ground to fine particles by using an agate mortar and pestle and the −0.076 mm mineral particles were selected for flotation experiments. The purity of malachite particles and chalcopyrite particles were 95.93% and 94.28% respectively based on mineralogical analysis, X-ray diffraction, and chemical analysis. In the microflotation tests, we just treated them as pure minerals.

The microflotation experiments were conducted in XFG flotation cell whose volume for rougher flotation was 40 mL. 2 Grams of pure malachite mineral or chalcopyrite mineral were taken into the flotation tank at every experiment, the pH of the pulp slurry was pre-adjusted to any desired value by the addition of effective amounts of sodium hydroxide solution or hydrochloric acid solution, and then the slurry had been agitated at about 1650 rpm for 2 min. At the end of the 2 min conditioning, effective amounts of 2-ethyl-2-hexenal oxime (in sodium hydroxide solution) were added to the slurry while agitating for a period of 2 min, then the froth flotation was continued for about 5 min during which froth products were collected. The froth products were dried, weighted and the recoveries were calculated.

2.4.2. Flotation tests of porphyry copper ores

The samples for flotation were porphyry copper ores from the Dexing Copper Mine of Jiangxi Province in China. Among the ore, the copper-bearing minerals were chalcopyrite, chalcocite, digenite, tetrahedrite, tennantite and malachite, etc. The main iron-bearing minerals were pyrite and marcasite. The molybdenum form was molybdenite and the gold forms were native gold and electrum. The significant amounts of non-sulfide gangue minerals were quartz, sericite, chlorite, illite and biotite. Undressed ore contains copper 0.38%, sulfur 1.42% and the oxidation ratio was 13.42%. The flotation flowsheet was illustrated in Fig. 1.

The ore (1 kg, crushed to −2 mm during sampling) was ground to 65% passing 74 μm in a closed steel ∅200 × 400 mm XMB ball mill at a pulp density of 62.5% by weight. The bench-scale flotation tests were conducted in a XFD-63 flotation cell (self-aeration) whose volume for rougher flotation was 3.0 L, using 1 kg ore at every turn to obtain a Cu rougher concentrate.

2.5. pK_a calculation

Calculation on pK_a value of 2-ethyl-2-hexenal oxime was made using ACD/Labs pK_a DB program (product version 11.02, provided by Advanced Chemistry Development, Inc.).

3. Results and discussions

3.1. Characterization of 2-ethyl-2-hexenal oxime

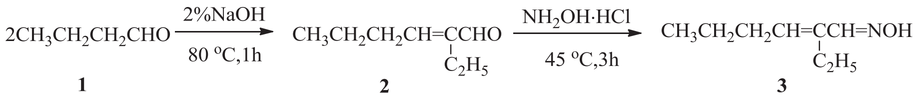
Physical and representative spectral data of 2-ethyl-2-hexenal oxime were demonstrated below.

The oxime was a creamcolored liquid at room temperature. It crystallized into white needle crystal at low temperature (m.p. 21–23 °C). It could dissolve in common organic solvents, but had poor solubility in water.

The elemental content was as follows: Analysis (Calcd for $C_8H_{15}NO$, %): C 68.04, H 10.71, N 9.92. Found: C 67.86, H 10.93, N 9.84.

The IR spectroscopy and NMR were used to characterize the 2-ethyl-2-hexenal oxime as shown in Tables 1 and 2.

EI-MS of 2-ethyl-2-hexenal oxime (m/z,%): 141 (M+, 80), 124 (100), 112 (65), 96 (75), 80 (90), 67 (85), 55 (65), 41 (93), 39 (60).



$$2CH_3CH_2CH_2CHO \xrightarrow[80\ ^{\circ}C,1h]{2\%NaOH} CH_3CH_2CH_2CH{=}\underset{C_2H_5}{C}CHO \xrightarrow[45\ ^{\circ}C,3h]{NH_2OH\cdot HCl} CH_3CH_2CH_2CH{=}\underset{C_2H_5}{C}CH{=}NOH$$

1 **2** **3**

Scheme 1. Synthetic route for 2-ethyl-2-hexenal oxime.