Determination and application of the solubility product of metal xanthate in mineral flotation and heavy metal removal in wastewater treatment

Yun-Hui Zhang[a,b], Liu-Ming Wu[b], Pei-Pei Huang[c], Qi Shen[a], Zhong-Xi Sun[a,*]

[a] School of Chemistry and Chemical Engineering, University of Jinan, 250022 Jinan, China
[b] School of Water Conservancy and Environment, University of Jinan, 250022 Jinan, China
[c] Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, China

ABSTRACT

The reactions of ethyl and butyl xanthates with Pb^{2+}, Cd^{2+} and Zn^{2+} were investigated to determine the solubility products of metal xanthates using UV/Visible spectroscopic method and software WinSGW and MEDUSA. The effects of solution pH, chemical reactions and ionic strength on the determination of solubility products of metal xanthates were investigated. For a given metal, the solubility product of metal xanthate was found to decrease with the increase of the carbon chain length of the alkyl group. The determined solubility products of metal xanthates were in the order of $ZnX_2 > CdX_2 > PbX_2$ and $M(EX)_2 > M(BX)_2$. The accurate Ksp constant allowed more accurate calculation of the minimal concentration of xanthate ions for treating heavy metal-containing waste water to selectively separate metal ions, avoiding the potential presence of toxic xanthates in the treated water.

1. Introduction

Alkali xanthates are widely used as collectors in sulphide and oxide mineral flotation (Herrera-Urbina et al., 1998; Hosseini and Forssberg, 2006) as well as heavy metal removal from industry effluents (Aslan, 2012; Beyki et al., 2014; Reyes et al., 2012).

The solubility product constant (Ksp) of metal xanthate has been considered as an important physicochemical parameter of selective sulphide mineral flotation with xanthates as surfactants to explain the relative affinity of xanthates to different sulphide minerals (Taggart et al., 1930). Xanthates that form less soluble metal xanthates can adsorb more readily on the surface of metal sulphides. Therefore, the metal ions which form less soluble precipitates with xanthates such as lead ions have been used to activate the surface of sulphide (sphalerite) minerals for the effective flotation of otherwise difficult floated sulfide minerals. In addition, the Ksp value of metal xanthate has been also an important quantitative indicator for metal–xanthate interactions (Chen et al., 2012; Robledo-Cabrera et al., 2015). The low Ksp values and high stability constants of metal–xanthate complexes enable xanthates to be efficient candidates to selectively separate and remove different heavy metal ions from industrial effluents (Rao, 1971; Tare et al., 1992; Wing et al., 1974). The metal xanthate precipitation process produces less sludge than the metal hydroxide precipitation process because the generated metal-xanthate precipitates can be floated via froth flotation

readily (Beyki et al., 2014; Chang et al., 2002; Jiang et al., 2010). Moreover, xanthate can be economically produced on a large industrial scale and is convenient for large scale applications.

However, Ksp values of metal xanthate complexes currently in use remain those determined half a century ago. Only a few studies have been devoted to the Ksp determination of metal–xanthates. Kakovsky (1957) calculated theoretically Ksp values of metal xanthate compounds with a thermodynamic approach in 1957, and Du Rietz (1957a, 1957b, 1975) determined Ksp values by potentiometric titration. Since then, people used directly these Ksp values for various purposes without verifying their accuracy.

It is well known that the determination of Ksp values can be affected by various factors, such as solution pH, ionic strength as well as the presence of anions and organics. Taking a metal–xanthate system as an example, there are many chemical reactions taking place simultaneously, including metal ion hydrolysis, metal hydroxide precipitation and the formation of soluble metal xanthate complexes and carbonate (in an open system).

In a heavy metal–xanthate–water system, many chemical reactions occur at a given solution pH and redox potential. The general chemical reaction equilibria of species is considered to determine dominant reaction products. Therefore, it should be taken into account when evaluating chemical reactions in the system, i.e., metal ion hydrolysis, the formation of soluble metal xanthate complexes as well as simple

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* Corresponding author.
  E-mail address: chm_sunzx@ujn.edu.cn (Z.-X. Sun).

precipitation reaction of metal xanthates. In some cases, oxidation-reduction reactions in the solutions (Cheremisina and Larionov, 1971) may also be involved. Some main reactions are presented below:

(1) Metal xanthate precipitation

$$M^{2+} + 2\,X^- \Leftrightarrow MX_2(s) \tag{1}$$

where M^{2+} and X^- denote heavy metal ions and xanthate, respectively. This is the dominant chemical reaction in the metal–xanthate system. When heavy metal ions are mixed with xanthate ions, this precipitation reaction takes place immediately. In higher pH solutions, however, hydroxide ions may compete with xanthates for heavy metal ions, leading to the following metal hydrolysis reaction (2).

(2) Hydrolysis of metal ions

$$a\,M^{2+} + b\,OH^- \Leftrightarrow M_a(OH)_b^{2a-b} \tag{2}$$

The products of hydrolysis reactions include various soluble metal hydroxide species and metal hydroxide precipitates. In addition to the hydrolysis, some soluble metal xanthate complexes are also likely to be formed, which are shown in the reaction equation (3).

(3) Formation of metal xanthate complexes

$$n\,M^{2+} + m\,X^- \Leftrightarrow M_nX_m^{2n-m} \tag{3}$$

Previous studies (Cheremisina and Larionov, 1971; Nanjo and Yamasaki, 1969; Yamasaki and Nanjo, 1969) have confirmed that the existence of $M(EX)^+$ and calculated their formation constants (see S1 in Supporting information) for solutions of 1 M ionic strength at 25 °C.

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In acidic solutions or in the presence of oxidants, xanthate may be decomposed or oxidized through the following reactions (4)–(6).

(4) Decomposition of heavy metal xanthate salts

$$M_nX_m^{2n-m} + m\,H^+ \Leftrightarrow m\,ROH + m\,CS_2 + n\,M^{2+} \tag{4}$$
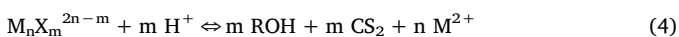
(5) Decomposition of xanthate ions (Iwasaki and Cooke, 1958)

$$X^- + H^+ \Leftrightarrow ROH + CS_2 \tag{5}$$

(6) Oxidation of xanthate ions (Iwasaki and Cooke, 1958)

$$2\,X^- + H_2O + 1/2\,O_2 \Leftrightarrow X_2 + 2\,OH^- \tag{6}$$

where R and X_2 denote non-polar alkyl group and dixanthogen, respectively. However, the influence of these factors, such as pH, ionic strength, complex chemical reactions and degassing, on the determination of Ksp values is largely unknown. Thanks to the fast development of the computer hardware and software in past decades, most of these chemical reactions can be taken into account when calculating Ksp values either theoretically or from experimental results.

In this study, batch experiments were conducted to measure the residual concentration of xanthates using UV–Vis spectrophotometric technique, and Ksp values of heavy metal xanthates were calculated and simulated using WinSGW (Eriksson, 1979; Karlsson and Lindgren, 2006; Sun et al., 2012) and MEDUSA (Baghdadi et al., 2015; Puigdomenech, 1999) software. Most possible solution chemical reactions of metal ions and xanthates were taken into account in the calculations.

2. Materials and methods

2.1. Materials

Pb (II), Cd (II) and Zn (II) were chosen as representative of typical heavy metals to study their interactions with xanthates. Stock solutions of heavy metals in distilled water were prepared from $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, purchased from Sinopharm Chemical Reagent Ltd. (Shanghai, China). The ethyl xanthate and butyl xanthate used in this study were synthesized by the reported method (Rao, 1971) and then purified three times by multiple recrystallization. Aqueous solutions of reactants were freshly prepared from analytical grade reagents in distilled water. After being vacuum dried at room temperature (RT) for 6 h, the purity of xanthates was determined to be greater than 99.8% by UV–Vis spectrophotometric technique. The dried xanthates were sealed in a small amber bottle in a refrigerator at 5 °C to minimize oxidation. The purity of xanthate was analyzed by UV–Vis spectrometer to make sure the purity was greater than 99.5% before use.

2.2. Batch precipitation experiments

Batch precipitation experiments were conducted under controlled aqueous conditions at RT to observe the effects of environmental conditions (such as pH, ionic strength, degassing, initial metal concentration, etc.) on the measurement of Ksp values. The pH of the sample solutions was adjusted to a desired range with diluted HNO_3 or NaOH solutions. Degassing of water was carried out by heating the distilled water to boiling, and then cooling down to RT prior to its use. The experiments using the degassed solution were performed in a closed system, i.e., with a lid on the test tube, to minimize the contact with the air. 0.001 M to 0.1 M $NaNO_3$ or Na_2SO_4 solutions were used to adjust ionic strength of xanthate solutions under the identical conditions as mentioned above.

The heavy metal solutions of predetermined concentrations were mixed with xanthate solutions of different concentrations at its natural pH. 0.05 mM BX was used for the Ksp determination of $Pb(BX)_2$ and $Cd(BX)_2$, and 5 mM BX, 0.05 mM EX, 0.5 mM EX and 5 mM EX were used for that of $Zn(BX)_2$, $Pb(EX)_2$, $Cd(EX)_2$ and $Zn(EX)_2$, respectively. The solutions were conditioned in a thermostatic oscillator at 25 °C for 3 h until the pH was stabilized. After the conditioning, metal xanthate precipitates were separated from the suspensions by centrifugation at 12,840*g* for 10 min. All tests were conducted in duplicate.

2.3. Analysis of residual xanthate concentrations

The concentrations of xanthate were determined by an ultraviolet and visible spectrophotometer (UV-2450, SHIMADZU, Japan). The absorption peak at 301 nm in the UV spectrum was used for the quantitative determination of xanthate ions. The blank tests were conducted to exclude the effects of natural decomposition of xanthates on the Ksp measurement.

2.4. Calculation of Ksp values

The software used in the data analysis includes WinSGW and MEDUSA. Most possible complex formation reactions were included in the calculation of Ksp values. The fitness of the experimental data with theoretical value was determined by comparing the theoretical distribution of soluble xanthate with measured values.

3. Results

3.1. Effect of degassing on Ksp determination of M(EX)₂

The degassing of aqueous solutions was performed in the Cd (II)–xanthate system as an example to judge the impact of oxygen on