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Study of xanthate decomposition in aqueous solutions

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ABSTRACT

Xanthate is one of the commonly used collectors in froth flotation beneficiation of sulfide ores. It decomposes and generates toxic compounds such as carbon disulfide (CS_2) which is a concern in the mining industry. A vast body of literature exists for studies on xanthate/mineral interactions, but xanthate decomposition under various conditions (e.g., in solutions or flotation pulps) is not fully understood. We have undertaken detailed studies to fill this knowledge gap, and this paper shows our study of the xanthate decomposition in aqueous solutions in the absence of minerals. This condition has not been appropriately examined by past researchers, while decomposition under this condition is used as control to other complicated ones (e.g., in flotation pulps). A GC–MS based method was developed to directly measure the decomposition products in the gas phase. Decomposition kinetics was then established based on the generation of CS_2. Decomposition followed the first order kinetics, and the rate constant for Sodium iso-Butyl Xanthate (SIBX) at neutral pH level was determined to be $9.3 \times 10^{-4}\,h^{-1}$ at 25 °C, $1.7 \times 10^{-2}\,h^{-1}$ at 50 °C and $1.3 \times 10^{-1}\,h^{-1}$ at 70 °C. The effect of pH on decomposition behavior was examined in the pH range of 1.5–12.5. We determined experimentally a maximum in the extent of decomposition as a function of pH, which was predicted theoretically in literature. A mechanism involving multiple reactions that occurred in parallel or sequentially along with the decomposition was proposed to explain the observed change of xanthate decomposition over the entire pH range. These results offer valuable insights and can serve as the basis to mitigate the detrimental effects of xanthate decomposition in plant operations, for example, by modifying plant parameters to reduce xanthate decomposition without sacrificing its performance.

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1. Introduction

Xanthate (or alkyl dithiocarbonate, $R\text{-}OCS_2^-$) is a widely used collector in the flotation beneficiation of base metal (such as copper, nickel, zinc, and iron) sulfides and precious metal ores, besides its role as a reactant or additive in pesticide, rubber, cellulose, and pharmaceutical industries since the 18th century (Spottiswod and Kelly, 1982; Wills, 2006). It is also known to hydrolyze in aqueous solutions and flotation pulps to continually generate toxic species such as carbon disulfide (CS_2), which can accumulate in the flotation plants and thus present a significant hazard on the safety, health and environment (SHE). In recognition of the potential health impacts from the hazardous gases accumulating in the enclosed infrastructures and the chronic exposure to the decomposition products, regulatory bodies are limiting the permissible level of CS_2 in the ambient atmosphere. The permissible limit for CS_2 release has decreased from 10 ppm to 1 ppm in the US and Canada

(OSHA). Measures need to be taken to apply xanthate in a benign and sustainable manner in the flotation operations, reducing the negative SHE impacts. This requires a detailed understanding of the decomposition behavior of xanthate. While extensive studies have been conducted in the past eight decades to understand the interactions between xanthate and sulfide minerals as well as precious metals (Healy, 1984; Poling, 1976; Salamy and Nixon, 1953; Woods, 1976, 1984, 1996), the decomposition behavior remains poorly understood. To develop a more complete understanding of xanthate decomposition, we have taken steady investigations towards examining the decomposition behavior of xanthates under various conditions (e.g., in aqueous solutions in the absence of minerals and in ore pulps under flotation conditions). This paper focuses on Sodium iso-Butyl Xanthate (SIBX) decomposition in aqueous solutions in the absence of minerals, which is a control for other conditions.

Decomposition is defined as the breakup of the xanthate anion into fragments (such as carbon disulfide or carbonyl sulfide). Dimerization or oxidation of xanthate to dixanthogen (($R\text{-}OCS_2$)$_2$) is not included in the definition of decomposition, though it was

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included in some studies (Rao, 1971). There are a few published studies on xanthate decomposition in aqueous solutions in the absence of minerals (Rao, 1971; Report, 2000). In these studies, researchers applied a similar method called Stopped Flow Technique (SFT) developed by Tornell to investigate the decomposition (Tornell, 1966a,b, 1967). SFT employs UV–vis spectroscopy as the primary technique to track the decrease of xanthate in the aqueous solutions. The amounts of decomposition products generated were derived from the relationship of residual xanthate content as a function of time. This method suffered from several limitations in spite of adopting a meticulous protocol for preparing and measuring the concentrations of solution species. For example, decomposition products in the gas phase could not be identified directly and CS_2 had to be assumed to be the only product in the gas phase. The UV–vis band assignments for xanthate and its relevant compounds (such as xanthic acid or dixanthogen) were not unanimously agreed upon. SFT was not suitable for heterogeneous solutions containing minerals (i.e., flotation pulp). Last but not least, the decrease of xanthate in solution might not be solely due to decomposition. Despite the limitations of SFT, certain key findings have been reported.

Iwasaki and Cooke (1958), Finkelstein (1967) and Tipman and Leja (1975) indicated that oxygen did not affect decomposition in acidic and alkaline solutions. This permits studying xanthate decomposition under ambient conditions; i.e. exposure to air. Researchers have examined the impact of pH on decomposition more than that of any other factor. It was generally believed that decomposition is greater under acidic conditions than under alkaline conditions. However, in alkaline solutions, multiple reactions were associated with the xanthate decomposition process, in contrast to the dominance of a single step reaction in acidic solutions. For example, under acidic conditions, xanthate decomposes to CS_2, whereas under alkaline conditions it also forms dixanthogen (Pomianowski and Leja, 1963), perxanthate (Pomianowski and Leja, 1963; Sun and Forsling, 1997), monothio- and dithio-carbonates (Philip and Fichte, 1960), and trithiocarbonate (Report, 2000). With respect to kinetics, xanthate decomposition was reported to follow a first order law regardless of pH (Ballard et al., 1954; Finkelstein, 1967, 1977; Iwasaki and Cooke, 1958, 1959, 1964; Klein et al., 1960; Majima, 1961). Multiple reactions in parallel or sequentially (Report, 2000) accompanied the decomposition reaction, but the CS_2 generation was still found to obey the first order kinetics (Finkelstein, 1967, 1977). Nevertheless, it is unclear as to whether the decomposition reaction should be unimolecular (Ballard et al., 1954; Iwasaki and Cooke, 1958, 1959, 1964; Klein et al., 1960) or bimolecular (Majima, 1961). It remains uncertain as to whether there exists a maximum decomposition extent as a function of pH. Ballard et al. (1954), Klein et al. (1960) and Iwasaki and Cooke (1964) proposed such a maximum when pH reached a certain low level while others did not (Iwasaki and Cooke, 1958, 1959). Under alkaline conditions, Tipman and Leja (1975) found that decomposition remained almost unchanged with pH, while Finkelstein (1967, 1977) observed that it still decreased.

Although studies were found on xanthate decomposition in the literature, they are limited and provide inadequate methods and conflicting results. As explained above, the decomposition was not fully understood in aqueous solutions in the absence of minerals. It is, however, necessary to have sufficient knowledge of decomposition under this control condition so as to elucidate this behavior under other conditions. This paper reports the study of SIBX decomposition in aqueous solutions in the absence of minerals with a new method markedly different from the SFT. The method was adopted to analyze the decomposition products in the gas phase directly by GC–MS (Gas Chromatography-Mass Spectroscopy). SIBX decomposition was examined as a function of time,

xanthate concentration, and pH. One goal of the study was to determine whether the decomposition kinetics could be assessed by analyzing the decomposition products in the gas phase. A second goal was to examine whether or not a maximum decomposition extent exists. A third goal was to discuss and propose probable parallel and sequential reactions that may be responsible for the decomposition behavior across the acid-to-alkaline pH range.

2. Experimental

2.1. Materials

Sodium *iso*-Butyl Xanthate (SIBX, $(CH_2)_2CHCH_2OCS_2Na$) with $\geqslant 99\%$ purity was obtained from Cytec Industries. Fresh xanthate solutions were prepared right before each experiment. Reagent Grade CS_2 with $\geqslant 99.9\%$ purity was purchased from Fisher Scientific. A series of standard solutions of CS_2 with different concentrations in distilled water were prepared to develop a calibration curve for the estimation of the CS_2 generated upon SIBX decomposition. Water used was triple distilled (EC = $1.5\ \mu\Omega^{-1}$). Reagent Grade HCl and NaOH, obtained from Sigma Aldrich, were used to regulate the pH levels of the SIBX solutions.

2.2. Method

Our scheme to assess xanthate decomposition under various conditions (e.g., in solution in the absence of minerals or ore pulps under flotation conditions) is shown in Fig. 1.

A reactor where decomposition takes place is to simulate the desired conditions and accumulate decomposition products. The impact of factors can be examined by modifying the conditions in the reactor. The decomposition products in different phases can be either directly sent to the instrument for measurement, or collected and then subsequently sent for measurement. The instruments for measuring decomposition products in various phases include GC–MS, FTIR, UV–vis, and Raman.

Based on the scheme in Fig. 1, the experimental procedure to study decomposition in aqueous solution in the absence of minerals is shown in Fig. 2. The reactor is a 10 ml glass vial that can be crimped with an aluminum cap lined with a silicone septum. A Teflon film is deposited at the bottom of septum facing inside the vial. In each test, stock SIBX solution and distilled water were introduced into the vial to obtain a 1 ml SIBX solution at a desired concentration. The temperature was controlled by placing the vial in an incubator. 1 ml of the 9 ml headspace was extracted and transferred to the GC–MS for measurement after a given time. Each vial was used for only one measurement and the above procedure was repeated to prepare another vial for a new measurement.
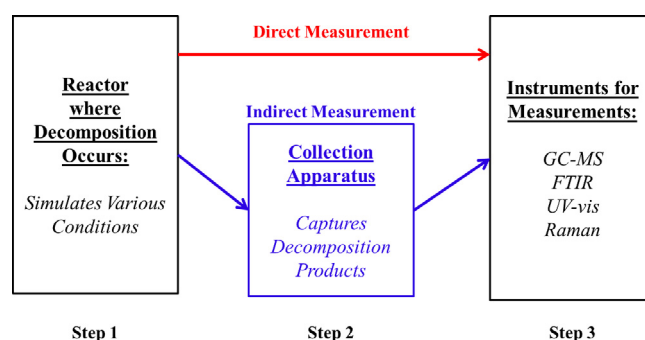

Fig. 1. General scheme for measuring decomposition products.