



## Solubility product and heat of formation of lead alkyl xanthates by microcalorimetric titration



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### ABSTRACT

Microcalorimetric titration of lead ions with various alkyl xanthate ions was used to determine the solubility product ( $K_{so}$ ) and the heat of formation ( $\Delta H^0$ ) of lead alkyl xanthates ( $PbX_2$ ). The titration was carried out at 25 °C in a 25 mL size isoperibol reactor containing lead aqueous solutions with an ionic strength of 0.01 M and pH 6. Sodium ethyl xanthate, potassium propyl xanthate, potassium butyl xanthate and potassium amyl xanthate were used in this study. A new relationship was found for the  $K_{so}$  and the number of carbon atoms (N) in the xanthate alkyl chain, namely  $\log K_{so} = -10.033 - 1.049 N$ . The relationship between  $\Delta H^0$  and N was found to be  $\Delta H^0 = -62.29 - 7.218 N$ , in kJ/mol  $PbX_2$ . The  $K_{so}$  and  $\Delta H^0$  values that were determined by microcalorimetry were compared to those theoretically calculated taking into account the transfer of the xanthate alkyl chain from the aqueous solution to the lead xanthate solid phase. There was an excellent agreement between theoretical and calorimetric  $\Delta H^0$ . Low deviation was found between theoretical and calculated  $K_{so}$ .

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### 1. Introduction

In the fundamental studies of the chemistry of sulfide flotation, knowledge of the solubility products ( $K_{so}$ ) of metal-collector compounds is important because it is used to delineate the adsorption mechanisms of collectors onto the sulfide. Kakovsky (1957) reported the  $K_{so}$  for various metal-collector compounds of interest in sulfide flotation. He used potentiometric and solubility techniques to determine the  $K_{so}$  of several metal alkyl xanthates and metal dialkyldithiophosphates. For lead alkyl xanthates, he reported a linear relationship between  $\log K_{so}$  and the number of carbon atoms (N) in the chain length of the collector, namely  $\log K_{so} = -14.2 - 1.21 N$ . The  $K_{so}$  values given by Kakovsky (1957) have been amply accepted by the scientific community in flotation to explain the interaction between collectors and lead sulfide surfaces. Based on these  $K_{so}$  values, conditions at which collectors chemisorb as monomers or precipitate as metal-collector have been established (Somasundaran and Wang, 2006; Fuerstenau et al., 2007).

For lead ethyl xanthate, the  $K_{so}$  given by Kakovsky is  $1.7 \times 10^{-17}$ . Other  $K_{so}$  values have been reported, however. Nanjo and Yamasaki (1969a,b) found a  $K_{so}$  of  $1.1 \times 10^{-15}$ , while Sheikh (1972) reported a value of  $1.56 \times 10^{-16}$ . They used the solubility method to determine  $K_{so}$ . As noted, the  $K_{so}$  values differ in one or two orders of magnitude from each other. Then, each  $K_{so}$  value will lead to distinct calculated solubility of lead ethyl xanthate as well as to different

lead ion-ethyl xanthate ion activity relationship for the formation of lead ethyl xanthate. Therefore, discrepancies will exist when thermodynamic analyses are conducted on the adsorption mechanisms of ethyl xanthate on galena (PbS), cerussite ( $PbCO_3$ ) and anglesite ( $PbSO_4$ ). For lead xanthates with more than 2 carbon atoms in the xanthate alkyl chain only the  $K_{so}$  values by Kakovsky (1957) have been reported.

Microcalorimetry is a technique through which the heat of a chemical reaction, taking place in an aqueous solution, can be accurately determined (Christensen et al., 1972; Eatough et al., 1972a, 1972b; Hansen, 2003). It is based on the in-situ measurement of the temperature change in the aqueous solution due to heat released or withdrawn by the chemical reaction. This technique has been used in the mineral field to study the adsorption of ethyl xanthate on galena (Mellgren, 1966; Partika et al., 1987; Persson and Persson, 1991), amyl xanthate on pyrite and marcasite (Haug and Miller, 1978), water adsorption on alumina (Griffiths and Fuerstenau, 1981) and recently of various sulfhydryl-type collectors on galena (McFadzean et al., 2014).

This work was aimed at the determination of the  $K_{so}$  of various lead alkyl xanthates at 25 °C through titration isoperibol calorimetry. Through this technique, first both the heat of formation ( $\Delta H^0$ ) of the lead alkyl xanthates and the equilibrium constant ( $K^0$ ) for the chemical reaction between lead and xanthate ions to form lead xanthate were determined. Then, the solubility product ( $K_{so}$ ) of the lead alkyl xanthate was calculated from the  $K^0$  value. The alkyl xanthates used in this work were sodium ethyl xanthate, potassium propyl xanthate, potassium butyl xanthate and potassium amyl xanthate.

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## 2. Experimental

### 2.1. Chemical reagents

All chemical reagents used in this work were analytical grade quality from JT Baker. The source of  $Pb^{2+}$  ions was  $Pb(NO_3)_2$ . Depending on the metal ion of the alkyl xanthate compound, sodium nitrate ( $NaNO_3$ ) or potassium nitrate ( $KNO_3$ ) was used to fix the ionic strength of aqueous solution at 0.01 mol/L. Sodium ethyl xanthate ( $C_2H_5OCS_2Na$ ), potassium propyl xanthate ( $C_3H_7OCS_2K$ ), potassium butyl xanthate ( $C_4H_9OCS_2K$ ) and potassium amyl xanthate ( $C_5H_{11}OCS_2K$ ) were synthesized from  $CS_2$  and their corresponding metal hydroxide and alcohol following the method developed by Foster (1928). These xanthates were purified threefold by dissolution in acetone and precipitation in ethylic ether. The purified xanthates were dried in vacuum at 25 °C and kept in a black-plastic bottle, which was placed in a glass desiccator with carbon dioxide adsorbent granules. All aqueous solutions were prepared with de-ionized water, obtained from passing distilled water through a Barnstead Easy pure II ion exchanger. Prior to its use for the preparation of the aqueous solutions, the de-ionized water was boiled and sparged with highly pure nitrogen gas to remove dissolved carbon dioxide and oxygen.

### 2.2. Equipment

An ISC 4300 isoperibol solution calorimeter was used for the microcalorimetric titration studies. Its temperature resolution and response time is 2  $\mu$ C and 0.5 s, respectively. The main components of the microcalorimeter are a 25 L water bath, a 2 mL microsyringe for the titrant (xanthate ions aqueous solution), a 25 mL glass-silver-plated-dewar reaction vessel for the titrate (lead ions aqueous solution), a calibration heater, a thermistor probe, a glass stirrer to stir the titrate in the dewar, an amplifier, a Wheatstone bridge circuit as an A/D converter and a computer for data acquisition and processing.

After each titration microcalorimetry test, the aqueous solution with the precipitated lead alkyl xanthate was centrifuged at 7000 rpm for 5 min using a Beckman Coulter Allegra 21R centrifuge. The supernatant solution was chemically analyzed for lead and xanthate ions. The former was determined by atomic absorption spectrometry using a Perkin Elmer 3110 spectrometer, while xanthate ions concentration was determined by UV/vis spectrometry using a Thermo Scientific Aquamate Plus apparatus and 1 × 1 cm quartz cuvette. The UV/vis absorption measurements were performed at 301 nm (Iwasaki and Cooke, 1959; Majima, 1961; Pomianowski and Leja, 1963; Leja, 1982). These concentrations were used to estimate an apparent equilibrium constant ( $K_{app}$ ) of the chemical reaction for the formation of the lead xanthates.

## 3. Microcalorimetric titration procedure

All microcalorimetric titration tests were carried out threefold. Before titration, the microsyringe and dewar with their aqueous solutions inside were kept within the calorimeter-water bath for at least 3 h for thermal equilibrium at 25 °C. Afterward, the energy equivalent ( $\epsilon_r$ ) of the dewar and content was determined. This was

accomplished by injecting electrical energy, through the calibration heater, equivalent to 2 cal ( $Q_E$ ) into the dewar. The temperature change ( $\Delta T$ ) was measured and the energy equivalent ( $\epsilon_r$ ) was calculated as follows:

$$\epsilon_r = \frac{Q_E}{\Delta T - (S_i + S_f) \left(\frac{t}{2}\right)} \quad (1)$$

where  $S_i$  and  $S_f$  are the initial and final rates of temperature rise, respectively, due to non-electrical heat contributions (stirring, radiation, conduction, etc.) and  $t$  is the time of injection of the electrical energy. With the value of  $\epsilon_r$  and the temperature change ( $\Delta T_c$ ) due to any chemical reaction, the gross heat ( $Q_c$ ) can be determined:

$$Q_c = \epsilon_r \Delta T_c \quad (2)$$

the performance and accuracy of the calorimeter was tested by measuring the molar enthalpy of protonation of tris-hydroxiaminomethane (THAM):



$\Delta H^0$  for this chemical reaction is  $47.55 \pm 0.06$  kJ/mol (Wilson and Smith, 1969). The chemical reaction was carried out by titrating 25 mL aqueous solution having 0.01 mol/L THAM with 2 mL HCl aqueous solution at a concentration of 0.1 mol/L HCl. From the temperature change, the gross heat ( $Q_c$ ) was calculated and corrected by the heat of dilution of HCl ( $-64.3$  J/mol; Lide, 2004) and the heat due to stirring. Next,  $\Delta H^0$  was determined and found to be  $-47.52 \pm 0.03$  kJ/mol. This value agrees well with the published data of  $47.55 \pm 0.06$  kJ/mol. The error was only 0.06%.

To quantify the heat of chemical reaction between lead and xanthates ions, the heat of dilution of ethyl, propyl, butyl and amyl xanthate ions had to be determined. The procedure involved the measurement of the heat evolved upon dilution of 2 mL aqueous solution with 0.1 mol/L xanthate in 25 mL water having an ionic strength of 0.01 mol/L. Table 1 presents the heat of dilution that was determined for each of the xanthates.

The heat of chemical reaction between lead ions and xanthate ions was determined by continuous titration of a lead aqueous solution (25 mL) having a concentration of  $2 \times 10^{-3}$  mol/L  $Pb^{2+}$ . The ionic strength of the lead ions aqueous solution was 0.01 mol/L and its pH 6. Under these conditions  $Pb^{2+}$  ions are predominant (Lopez-Valdivieso et al., 1986). Titration was carried out by injection of 2 mL aqueous solution having a concentration of  $8 \times 10^{-3}$  mol/L xanthate ions. This xanthate solution was injected at a constant delivery rate of 2 mL/min. A typical thermogram resulting from the titration is given in Fig. 1, where three regions are identified: a) a pre-reaction region where no titrant is added and the change of temperature with time is due to heating by stirring, b) a reaction period, in which the change of temperature of the titrate with time is largely the result of the reaction between lead ions and xanthate ions, and c) a post-reaction region, where no titrant is added and the change of temperature with time is again due to heating by stirring. In the Figure,  $x$  and  $y$  indicate the start and end of titration, respectively. This thermogram corresponded to the titration of lead ions with amyl xanthate ions in aqueous solution at an ionic strength of 0.01 mol/L. In Fig. 1, the energy equivalent ( $\epsilon_r = 28.237$  cal/°C) for the dewar and contents and the gross heat ( $Q_c = 0.186$  cal) due to the chemical reaction, heat of stirring and heat of dilution of xanthate ions are given.

**Table 1**  
Heat of dilution of ethyl, propyl, butyl and amyl xanthate ions in aqueous solutions at 0.01 M ionic strength and 25 °C.

Xanthate	Heat of dilution, KJ/mol
Ethyl	$-0.46 \pm 8.2 \times 10^{-5}$
Propyl	$-0.49 \pm 1.4 \times 10^{-3}$
Butyl	$-0.61 \pm 1.3 \times 10^{-3}$
Amyl	$-0.94 \pm 3.2 \times 10^{-2}$

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