



PHYSICAL CHEMISTRY 2016

*13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Proceedings
Volume I*

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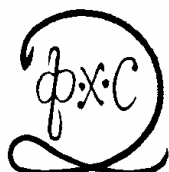
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Organized by

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Serbia*

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and

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STABILITY OF LEAD ETHYL XANTHATE ON GALENA SURFACE

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ABSTRACT

The stability of lead ethyl xanthate (ethyl xantate ion $C_2H_5OCS_2^-$, EX^-) on galena (PbS) surface in an alkaline medium (pH=9-12) was investigated using ATR-IR and UV spectrophotometric methods. The prolonged time of mineral treatment with ethyl xanthate solution up to 4 hours, at pH=9.2, did not affect the surface adsorbed ethyl xanthate. However, within pH range 10-12, the decomposition of surface layer occurs. The ethyl monothiocarbonate ion EMTC⁻ (monothiocarbonate CO_2S^{2-}) is an intermediate product of lead ethyl xanthate decomposition.

INTRODUCTION

Much of the research was focused on the action of hydrophobic xanthate-type surfactants ($ROCS_2M$; R = alkyl group; $M^+ = Na^+, K^+$) as flotation reagents (collectors) on sulphide minerals. Different mechanisms have been suggested in literature to explain how xanthates can render hydrophobic the surface of minerals [1,2]. It is generally accepted that galena floats well with K-ethyl xanthate at pH 9 [1-4] due to the formation both forms of lead ethyl xanthate, monolayer of -Pb-EX (-Pb- surface site; chemically adsorbed EX^-) and physically adsorbed stoichiometric $Pb(EX)_2$, as well as a small amount of ethyl dixanthogen, $(EX)_2$.

Several authors have lately suggested the decomposition of lead xanthate in alkaline solutions [5,6].

The purpose of this work was to study the effect of alkaline aqueous solutions (pH=9-12) on the stability of the surface ethylxanthate on galena and degradation kinetics.

EXPERIMENTAL

Natural galena grains from a Stari Trg deposit, Serbia, were manually selected and ground in an agate mortar. The specific surface area of mineral ($4.00m^2/g$) was determined in a Culter Counter Model D Industrial. Chemical analysis

showed that galena contained Pb 85.6% and S 13.7%. Commercial grade potassium ethyl xanthate (KEX) was purified by multiple recrystallization from acetone, and then used as flotation collector (surfactant). Reflection infrared spectra were recorded using a Perkin Elmer Infrared Spectrophotometer with ATR-attachment and Ge crystal. The mineral suspension (0.250 g of the mineral and 0.025 dm³ of xanthate solution, concentration $1 \times 10^{-3} \text{ mol dm}^{-3}$) was stirred for 15 minutes or 4 hours at pH 9.2, 10.5 and 11.6. After filtration the xanthate-treated galena was washed with distilled water and placed in the Ge reflection element. For UV analysis the ethyl xanthate treated-galena for 15 minutes at pH 9 was filtered, washed and transferred into 15 ml of distilled water, at pH=9.2, 10.5 or 11.6. The concentrations of ethyl xanthate (301 nm) and lead xanthate decomposition product (221 nm) were determined using UV-VIS spectrophotometer UV-1800, Shimadzu.

RESULTS AND DISCUSSION

The -C-O-C- xanthate band, which appears at about 1200 cm^{-1} , was used for determination of the adsorbed form of Pb-ethyl xanthate on galena (Fig.1). The monolayer form of Pb-ethyl xanthate (-Pb-EX; chemically adsorbed EX^-), has a band below 1200 cm^{-1} .

The position band above 1200 cm^{-1} at pH=9.2 (Fig.1, a,b) indicates the prevailing presence of the multilayer, physically adsorbed $\text{Pb}(\text{EX})_2$. The prolonged contact time did not change the surface layer composition (Fig.1, b).

At pH 10.5, the -Pb-EX is only formed on galena surface (Fig.1, c). A four-hour treatment leads to a decrease of the amount of the chemisorbed EX^- (Fig.1, d). When galena was conditioned with KEX 15 min at pH 11.6 the observed absorption bands of EX^- were weaker intensities, indicating a small amount of chemisorbed xanthate (Fig.1,e). Surface ethyl xanthate was almost completely decomposed within 4 hours (Fig.1, f) and surface lead hydroxide was detected (Fig.2, a, b).

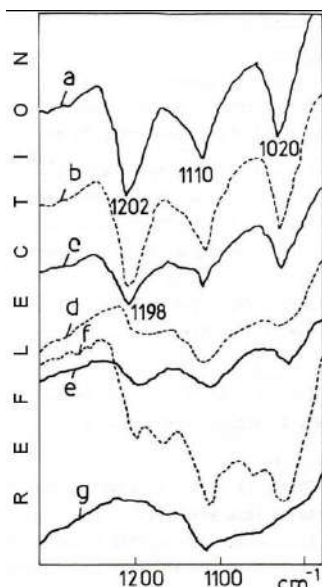


Figure 1. IR spectra of KEX treated galena at: pH=9.2, (a) 15 min, (b) 4h; pH=10.5, (c) 15 min, (d) 4 h; pH=11.6, (e) 15 min, (f) 4 h; (g-galena, pH 9.2).

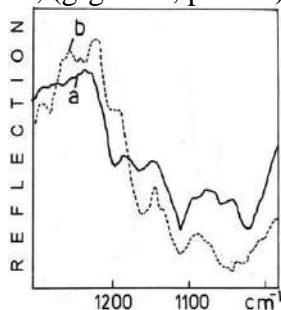


Figure 2. IR spectra of: a) KEX treated galena at pH=11.6, 4 h (Fig.1, f); b) Precipitated Pb(OH)₂.

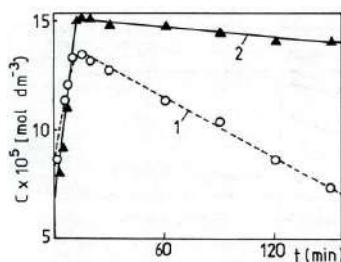


Figure 3. EX⁻ (1) and EMTC⁻ (2) concentrations as a function of time, pH 11.6

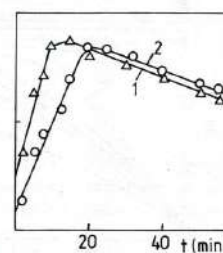
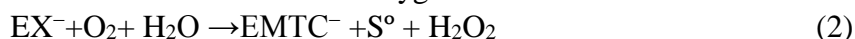


Figure 4. EX⁻ concentrations at pH 10.5 (2) and 11.6 (1) as a function of time

UV results showed the presence of ethyl xanthate and ethyl monothiocarbonate ions, EMTC⁻, in a high alkaline aqueous solution (pH 10.5 and 11.6) as a decomposition products of surface lead ethyl xanthate (Figs.3 and 4). The rates of EX⁻ and EMTC⁻ formation were high at the beginning (Fig.3). The EX⁻ ion concentration reached its maximum in 15 min at pH 11.6 and in 20 min at pH 10.5 (Fig.4). Further, concentrations of both EX⁻ and EMTC⁻ ions decreased (Fig.3). These kinetic data can be explained according to the lead xanthate decomposition mechanism proposed by Harris and Finkelstein [5]:



Because the decomposition test was carried in air, ethyl xanthate concentration fell in the reaction with oxygen



Further abstraction of EMTC^- from the solution (Fig.3, curve 2) is caused by its decomposition. The ethyl monothiocarbonate ion is obviously an intermediate product of lead ethyl xanthate decomposition.

The surface lead ethyl xanthate at 9.2 is stable. The EX^- and EMTC^- concentrations in the solution were below $1 \times 10^{-5} \text{ mol dm}^{-3}$.

CONCLUSIONS

The surface ethyl xanthate on galena (chemically and physically adsorbed) is stable within the agitation time of four hours at pH 9.2. The prolonged contact (4 hours) at pH 10.5 leads to a decrease of the amount of the chemisorbed EX^- .

When galena was conditioned with KEX^- 15 min at pH 11.6 the observed absorption bands of EX^- were very weak. Surface ethyl xanthate was almost completely decomposed within 4 hours and surface lead hydroxide was detected. The ethyl monothiocarbonate ion is an intermediate product of the ethyl xanthate decomposition. The decomposition rate of surface ethyl xanthate in pH range 10-12 is very high at the beginning.

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REFERENCES

- [1] J. Leppinen, J. Mielczarski, Int. J. Miner. Process., 1986, **18**, 3-20.
- [2] N. P. Finkelstein, Int. J. Miner. Process., 1997, **52**, 81-120.
- [3] R. Woods, J. Phys. Chem., 1971, **75**, 354-362.
- [4] D. R. Vučinić, P. M. Lazić, A. A. Rosić, Colloids Surf. A: Physicochem. Eng. Aspects, 2006, **279**, 96-104.
- [5] P. J. Harris, N. P. Finkelstein, Int. J. Miner. Process., 1975, **2**, 77-100.
- [6] X. Chen, Y. Hu, H. Peng, X. Cao, J. Cent. South. Univ., 2015, **22**, 495-501.