

KINETICS OF XANTHATE ADSORPTION ON METAL SULPHIDES

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ABSTRACT

In sulphide mineral flotation a sufficient hydrophobicity of the mineral surfaces is obtained by the adsorption of collector chemicals at the metal sulphide/aqueous interface. This surface modification is of fundamental and applied interest. In an ongoing study, financed by Agricola Research Centre, attenuated total reflection infrared spectroscopy (ATR-FT-IRS) has been shown possible to use in monitoring the adsorption kinetics and the orientation of heptyl xanthate (HX) when adsorbed onto synthesized solid surfaces - zinc sulphide and lead sulphide *in-situ*. The choice of using the ATR technique is because it is very suitable when working with water as solvent.

In the study of surface reactions the substrate is of vast importance, implying that the chemistry of the surface has to be well characterised. This work is utilizing different spectroscopic methods (XPS, ATR-FT-IR) in the characterisation of the surfaces.

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1. INTRODUCTION

In the year 2001, a research programme started at the department of chemical and metallurgical engineering at Luleå University of Technology, funded by SSF, LKAB and Boliden AB. A better understanding of the important surface reactions going on at mineral surfaces exposed to water is one of the goals the research programme has to achieve. This study is a contribution to the programme area, "Mineral surface reactions and chemical modelling", and is focused on the kinetics of collector adsorption at metal sulphide/solution interfaces.

A thin inorganic layer covering the attenuated total reflection (ATR) element used in combination with infrared spectroscopy is a prerequisite for the adsorption studies. Among a variety of such possible ATR elements we selected germanium because of its high refractive index. A high refractive index implies that the penetration depth of the totally reflected infrared radiation outside the germanium surface becomes small and therefore interacts less with the bulk solution. Its high refractive index also facilitates total internal reflection by being higher than the refractive index of many of the inorganic materials intended to be synthesised on the germanium surface.

Using the ATR technique it is possible to monitor the adsorption rate by recording infrared spectra of adsorbed species, from which information about adsorption kinetics and the orientation of the adsorbed species can be obtained.

1.1 Infrared spectroscopy

Chemical analysis is an important application of infrared spectroscopy. The vibrational spectrum of fundamental modes of different atomic groups in a molecule is rather similar to the spectrum of these groups in some other molecule. The identity of the molecule or the atomic groups within the molecule can consequently often be established by examining the infrared spectrum and referring to a table of characteristic vibrational frequencies (table 1).

Table 1. Characteristic frequencies¹

Vibrating mode	Wavenumber [cm^{-1}]	Example
C-H stretch	2800-3300	
C-H bend	1300-1500, 500-900	
R-O-(C=S)-S-X	1250-1200	Dialkyl xanthates, dixanthogens
	1140-1110	and copper and zinc xanthates
	1070-1020	
C-O-C stretch	1190-1175	Sodium and Potassium xanthates
CS ₂ stretch	1064-1021	
O-H stretch	3100-3800	
O-H bend	1200-1600	

1.1.1 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FT-IRS)

ATR-FT-IRS is a special infrared technique utilizing total reflection in an optical medium. When IR radiation undergoes multiple internal reflections in an IR element, see Fig. 1, the evanescent field established at the IRE surface can be used for infrared analysis.

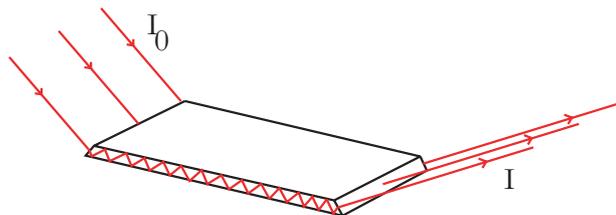


Figure 1. Infrared light internally reflected through an infrared transparent material

¹ Colthup, Daly and Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3ed, Academic Press, 1990

The propagating wave creates an electromagnetic disturbance with exponentially decaying intensity normal to the surface, and into the lower refractive index medium. This exponentially decaying electric field is called an evanescent wave. The wave is reduced or attenuated upon interaction with the absorbing medium just outside the interface of the internal reflection element (IRE), schematically illustrated in Fig. 2. Multiple reflections and the possibility to vary the penetration depth, d_p , makes the ATR method very surface sensitive and suitable for the study of different interfacial phenomena occurring in water as solvent.

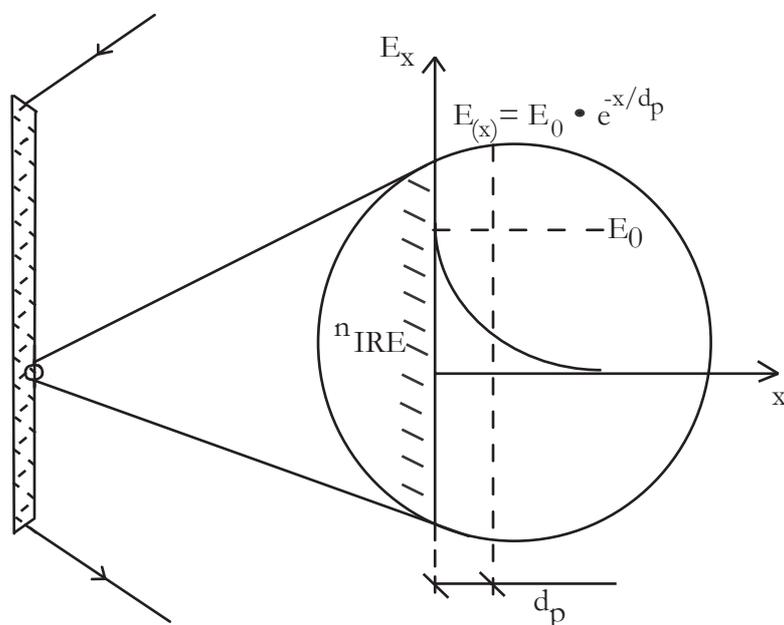


Figure 2. Schematic picture of penetration depth

ATR-FT-IR with polarized light

A combination of polarized light with the ATR technique can reveal information about the absorbing species when it is interacting with the evanescent energy field. The degree of interaction is dependent on the plane of polarization of the wave relative to the plane in which the transition moments lie in. This relationship between plane of polarization and the transition moment makes it possible to determine the preferred orientation of the absorbing species.

1.2 Model system

In this study, a surface-active reactant is adsorbed at a metal sulphide surface. This can be described by a simplified picture as in Fig. 3. At $t = 0$, the surfactants are in the solution, and none is adsorbed. At $t = t$, some of the surfactants has adsorbed, and some are still in the solution. For longer reaction times, equilibrium between the molecules at the surface and in the solution is established.

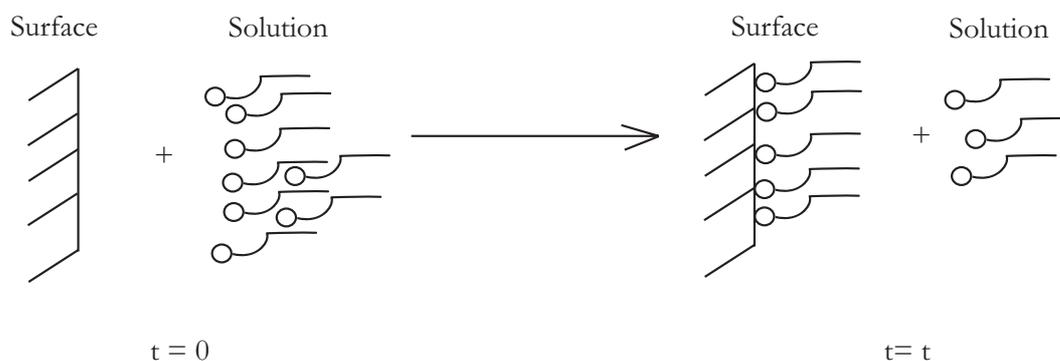


Figure 3. Schematic picture of the adsorption of a surfactant at a surface

To our experience, the surface excess of adsorbate is proportional to the measured intensity of methylene (CH₂) and methyl (CH₃) stretching vibrations in the wavenumber region 2800-3000 cm⁻¹. This is also an experience encountered by other authors².

2. EXPERIMENTAL

2.1 Chemical bath deposition

In the beginning of this study, different deposition methods were tested. Simplicity and inexpensiveness has been the guidelines for the selection of the final method. The method, Chemical Bath Deposition^{3,4,5,6,7}, was used because the chemical environment is relatively simple to control and it is adequately good for making thin films.

2.2 X-ray Photoelectron Spectroscopy (XPS)

The XP results were collected with a Kratos Axis Ultra electron spectrometer using monochromatic Al K α radiation (1486.6 eV). The analyzing pass energy was 160 eV, with a step size of 1 eV for the survey scans, and to separate photoelectron lines a pass energy of 20 eV was used, with a step size of 0.1 eV. The pressure in the analyzing chamber during measurements was 5×10^{-9} torr and no pre-cooling was used. To compensate for surface charging, a low-energy electron gun was used. The binding energy (BE) scale was referenced to the C1s line of aliphatic carbon, set at 285.0 eV.

2.3 Infrared Attenuated Total Reflection Measurements

Infrared spectra were recorded with a Bruker IFS 113V (pressure ~ 1 mmHg) spectrometer equipped with a MCT detector. In order to get a sufficiently good signal to noise ratio, background and sample spectra were recorded using more than 1000 scans. Spectra recorded during the adsorption process were obtained by co-adding scans during some minutes at a resolution of 4 cm⁻¹. When p- and s-polarized radiation was used, a polarizer was placed before the internal reflection element. The internal reflection elements have the size of 50 x 20 x 2mm³, with a trapezoidal form (45°), see Fig. 1.

The *in-situ* heptyl xanthate (HX) adsorption onto the metal sulphide covered elements was performed in a cell where the element was sealed to the cell with a viton gasket (Fig. 4). Aqueous solutions of HX (pH ~ 5) were circulated with a constant flow rate through the cell (17.5ml/min). The experimental set-up is shown schematically in Fig. 4.

The germanium crystals with deposited metal sulphides were thoroughly washed with acetone, ethanol and water, before starting the adsorption experiments.

2.3.1 Heptyl xanthate adsorption onto ZnS and PbS

The concentration of the HX solutions used varied between 10^{-5} M and 10^{-3} M. The adsorption experiments were carried out with different volumes of the solutions, and milliQ water was used as solvent.

² W.H Jang and J.D Miller; Langmuir, 9, pp.3159-3165, 1993

³ Nair, P. K., and Nair, M. T. S., *Semicond. Sci. Technol.*, 7, 239-244, 1992

⁴ Nair, P. K., Nair, M. T. S., García, V. M., Arenas, O. L., Peña, Y., Castillo, A., Ayla, I. T., Gomezdaza, O., Sánchez, A., Campos, J., Hu, H., Suárez, R., and Rincon, M. E., *Solar Energy Materials and Solar Cells*, 52, 313-344, 1998

⁵ M.Froment and D.Lincot, *Electrochimica Acta*, vol.40, no10, 1995

⁶ Chopra, KL. Kainthla, RC et al, *Physics of thin films*, vol 12, pp 201-, 1982

⁷ Johnston, D. A., Carletto, M. H., Reddy K. T. R., Forbes, I., and Miles, R. W., *Thin Solid Films*, 403-404, 102-106, 2002

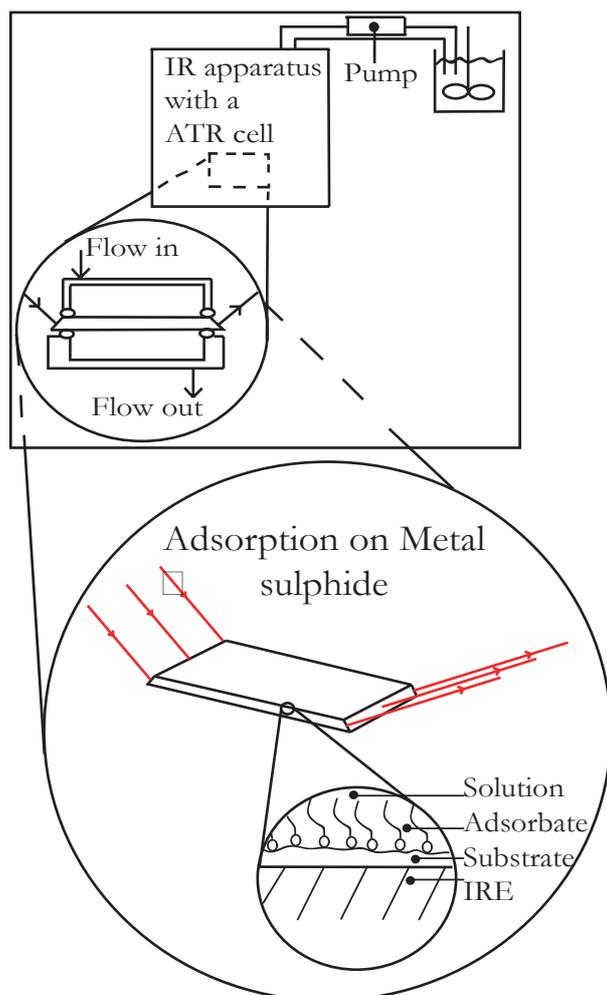


Figure 4. Schematic experimental set-up for the total internal reflection measurements.

3. RESULTS

3.1 Surface Characterization (XPS)

It has been established by the use of XPS that the layers studied contain the synthesized metal sulphide, and impurities. These impurities can be oxidized forms of the metal sulphide, species related to the deposition method, and carbon containing species at the surface.

3.2 Heptyl xanthate adsorption

Fig. 5 shows two representative infrared spectra of heptyl xanthate vibrations from the fingerprint region. According to Mielczarski et al.⁸ the band at 1200 cm^{-1} is mainly due to the asymmetric stretching vibration of C-O-C, and the band between $1064\text{--}1021\text{ cm}^{-1}$ has a strong involvement of the asymmetric S-C-S stretch⁹. A clear difference is seen between the adsorbed species on ZnS, compared with adsorbed species on PbS. Heptyl xanthate adsorbed onto PbS has a shift to lower frequency for the characteristic xanthate vibration bands. For the stretching vibrations lower frequencies indicate a stronger bond to the metal sulphide surface.

⁸ Mielczarski, J and Leppinen, J. Surf. Sci, 187, 526, **1987**

⁹ Colthup, N.B, Porter Powel, L, Spectrochim. Acta, 43A(3), 317, **1987**

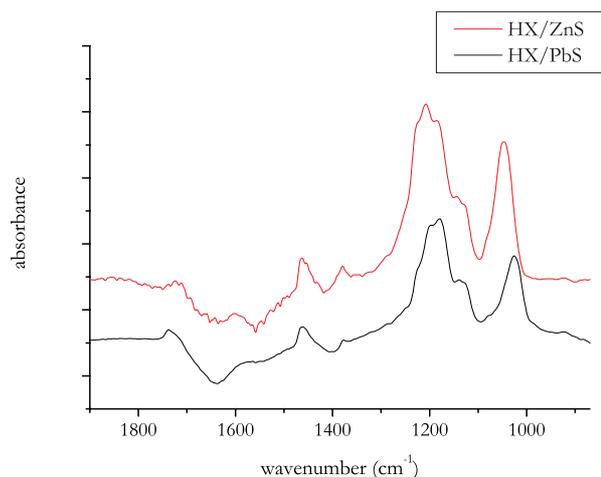


Figure 5. Fingerprint region for HX/ZnS and HX/PbS

3.2.1 Adsorption rate

The adsorption rate is possible to monitor by analyzing the evolution of the asymmetric methylene stretching band around 2926 cm^{-1} , as in Fig. 6. If the peak height of the asymmetric methylene stretching vibration band is plotted versus time in a Cartesian coordinate system, an adsorption kinetic curve is obtained (Fig. 7).

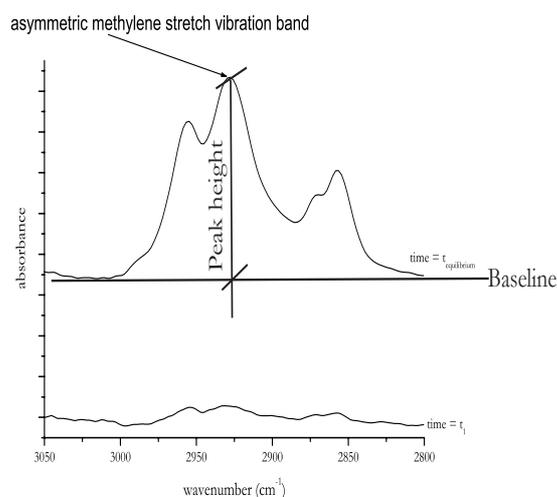


Figure 6. CH_2 stretch vibrations monitored with time of HX adsorbed onto ZnS (in-situ)

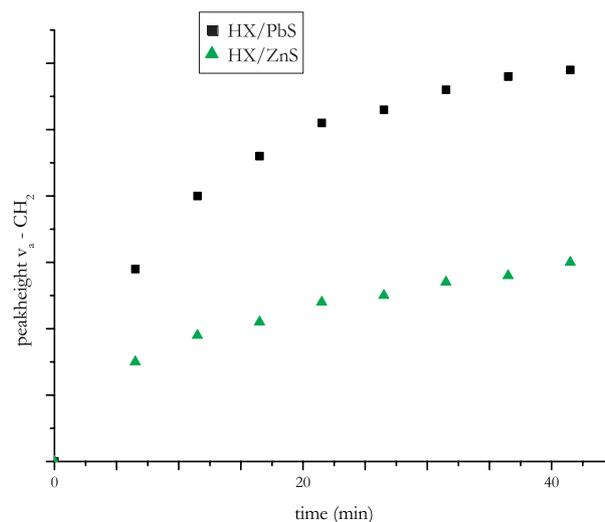


Figure 7. Heptyl Xanthate adsorption onto ZnS and PbS (in-situ)

The rate of heptyl xanthate adsorption *in-situ* onto the zinc sulphide and the lead sulphide is compared with each other in Fig. 7. According to Fig. 7 the adsorption of heptyl xanthate onto lead sulphide is more rapid than onto zinc sulphide.

3.2.2 Polarized infrared measurement

From a polarized infrared study a dichroic value (A_s/A_p) can be calculated and used in the calculations of the orientation of the alkyl chain in heptyl xanthate. The polarized infrared study shows a dichroic value becoming lower with higher concentrations. In Fig. 8 polarized spectra from heptyl xanthate adsorbed onto zinc sulphide is shown.

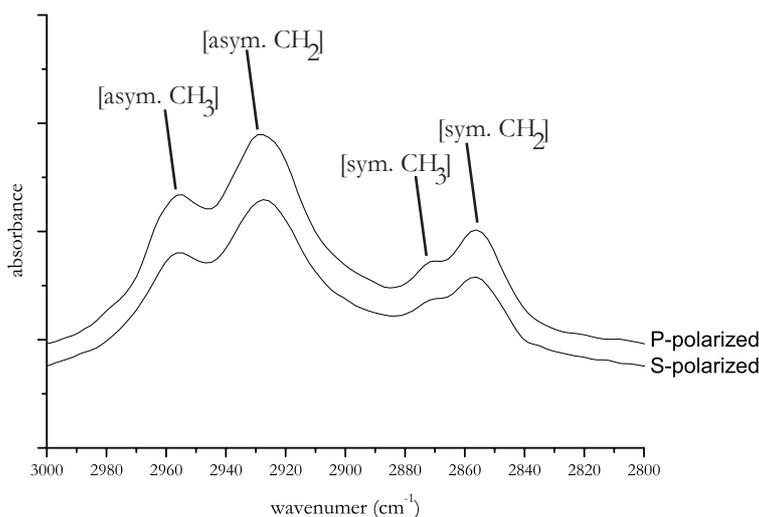


Figure 8. Polarized spectra of adsorbed HX on ZnS (in-situ)

4. CONCLUSIONS

We have shown that chemical bath deposited thin layers of metal sulphides on a germanium internal reflection element offers the possibility to study the adsorption behaviour of these thin films using *in-situ* IR-ATR spectroscopy. The metal sulphide layers obtained have small elements of different impurities, but the reproducibility of the layers is good. In general the possibility of controlled synthesis of thin films on ATR elements opens up new possibilities to study various materials *in-situ*.

We have also shown that using polarized infrared radiation to study the adsorption of heptyl xanthate onto synthesised metal sulphide layers offers a possibility to gain information about the orientation of the adsorbed collector chemical.

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