

Jerzy A. MIELCZARSKI\*, Ela MIELCZARSKI\*

## **MONITORING MINERAL SURFACE PHENOMENA BY INFRARED REFLECTION SPECTROSCOPY**

*Received March 15, 2005; reviewed; accepted May 15, 2005*

Determination of the mineral surface composition and structure at molecular and atomic levels and understanding adsorption mechanisms and kinetics are crucial to perform efficient separation processes for mineral beneficiation. This understanding is a fundamental requirement to make possible the prediction and control of the macroscopic surface properties that govern the efficiency of separation technologies. The developed infrared external reflection technique has a unique ability to study interface phenomena at a molecular level on heterogeneous substrates. The variety, precision and reliability of information about interface phenomena delivered by this technique are superior to other single techniques. The experiments are fast and non-destructive. High sensitivity (part of monolayer), *in-situ* collected information in a multiphase system even in the region of a strong absorption of substrate, makes this technique a very valuable experimental tool. The complexity of the recorded reflection spectra, their sensitivity to any variations of the optical properties of all bulk and surface components and their spatial distribution in the system under investigation, are in fact the major strength of the technique. In this paper a few examples of application of this multidagnostic technique for monitoring surface modifications of sulphide and semisoluble minerals for selective flotation are overviewed in detail.

*Key words: adsorption of flotation reagents, surface monitoring, reflection spectroscopy*

### **INTRODUCTION**

Selective separation of mineral components from ore is achieved by addition of specific collectors, activators, depressants or modifiers and manipulation of solution conditions (pH, Eh, aeration). The flotation behaviour of each component of ore depends on the nature and structure of produced surface species. The possibility of monitoring surface phenomena at the interfaces of natural minerals contacted with aqueous solution is vitally important for the understanding of the processes responsible for selective and efficient separation.

---

\* "Laboratoire Environnement et Minéralurgie". U.M.R. 7569 du C.N.R.S. INPL/ENSG  
15 Avenue du Charmois, BP 40, Vandoeuvre-lès-Nancy 54501, Cedex, France  
Tel.: 33 3 83 59 62 83, Fax: 33 3 83 59 62 55 e-mail:jerzy.mielczarski@ensg.inpl-nancy.fr.

Infrared spectroscopy is particularly well suited to determine surface composition at a molecular level. The infrared spectroscopy is functional group selective, so it is particularly well suited to detect small changes of the molecular microenvironmental properties as those emerging at the interfaces. Experiments can be performed *in-situ* in both gas-mineral and aqueous solution-mineral interfaces. There is only very gentle interaction of the infrared beam with the examined sample with an energy level lower than 0.3 eV. The recent instrumental development of infrared spectroscopy is contributing significantly to the increased emphasis being placed on nanoscale surface characterization. To perform the proper interpretation of reflection spectra for a more detailed picture of the interfacial structure, it is vitally important to combine spectroscopic measurements with a spectral simulation technique. The importance of such combination is reinforced by the anticipated sensitivity of surface infrared absorbance not only to surface concentration but also to adsorbate structure, molecular orientation, surface distribution, lateral interaction, surface diffusion, molecular recognition, and so-called optical effects. Some of them are overviewed in this paper.

Single reflection spectra from any mineral surface at three chosen incident angles and two polarizations are sufficient to propose a reliable three dimensional « picture » of the nature and structure of mineral surface layer. All solid minerals with known optical property could be examined. The unique advantages of the developed method are discussed on examples of sulphide and semi-soluble minerals.

## EXPERIMENTAL

### MATERIALS

The natural mineral samples of chalcocite and apatite (procured from Ward's Natural Science) with dimensions of about of 13 x 20 mm<sup>2</sup> were used in these studies. Ethyl xanthate was synthesized from CS<sub>2</sub>, KOH and ethyl alcohol, and then purified by crystallization from acetone and petroleum ether. More than 98% pure sodium oleate (sodium salt of cis-9-octadecenoic acid), supplied by Aldrich-Chemie, was used. Other reagents used were all of an analytical grade. Distilled water from the Millipore (Milli-Qplus) system was used throughout the experiments.

### ADSORPTION STUDIES

The mineral samples were polished with emery paper and alumina powder. The final polishing was made with the use of 0.05 µm alumina and the polished sample was washed with water. Typically the mineral sample was immersed in 200 ml of collector solution at different pH for a period of 5 s to 20 h. The solution concentration varied from 2·10<sup>-6</sup> to 5·10<sup>-4</sup> M. Immediately after contact with collector solution, the sample was immersed in pure water for about 1 s and then placed instantly in an FTIR spectrophotometer to record the reflection spectra.

## INFRARED ANALYSIS

The infrared reflection spectra of slab samples were recorded with a Bruker IFS55 FTIR spectrometer equipped with a MCT or DTGS detector and a reflection attachment (Seagull). A wire-grid polarizer was placed before the sample and provided p- or s-polarized light. These accessories were from Harrick Scientific Co. For each adsorption layer sample usually three reflection spectra were recorded by the use of s- and p-polarized light and different angles of incidence. An optimized optical reflection system permits to detect adsorbed amounts as low as about 20% of a statistical monolayer of ethyl xanthate on a chalcocite surface, which is equivalent to a 0.2 nm thick uniform layer of copper ethyl xanthate. The unit of intensity was defined as  $-\log(R/R_0)$ , where  $R_0$  and  $R$  are the reflectivity of the systems without and with the investigated adsorbed layer, respectively. Both sample and reference spectra are averaged over the same number of scans, from 200 to 2000 scans, depending on energy throughput.

## DEVELOPING THE INFRARED EXTERNAL REFLECTION TECHNIQUE

During extensive studies the infrared external reflection technique was developed that let to overcome experimental problems and collect reliable data to monitor and understand surface phenomena at a molecular level. A schematic diagram of the interaction of electromagnetic waves with a simple three-phase system is presented in Fig.1.

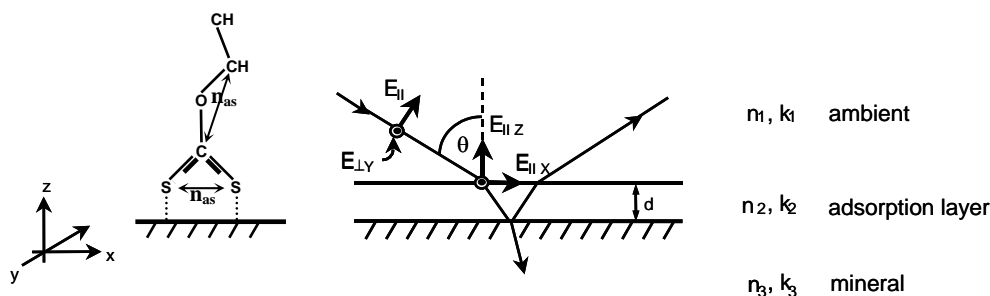


Fig. 1. Schematic diagram of the interaction of electric field vectors in three directions with a simple three phase system. There is also presented ethyl xanthate molecule with marked dipole transition moments of the asymmetric stretching vibrations of the SCS group (parallel to interface) and of the asymmetric stretching vibrations of the COC group (almost vertical to interface)

For polarization perpendicular to the plane of the incident beam (s - polarization) there is only one electric field vector,  $E_{\perp Y}$ , parallel to substrate plane. Hence, only molecular groups of the adsorbed species having a dipole transition moment parallel to the interface in y direction can interact with the incident radiation and produce an absorbance band  $A_{\perp Y}$ . For example, in the case of the adsorption of xanthate molecule

involving both sulphur atoms with the same distance from interface (Fig.1) and assuming a uniaxial system (no difference in orientation in x - y plane), it is expected that the absorbance assigned to the asymmetric vibration of the SCS group,  $A_{\perp Y}$ , will show the highest value. This results from the most favourable configuration for interaction of the asymmetric stretching vibration of the SCS group and electric field vector  $E_{\perp Y}$ . For a molecule inclined to interface the interaction is lower and the recorded absorbance will decrease depending on the orientation of this molecular group versus interface. No interaction and obviously no absorbance band due to the asymmetric stretching vibration is observed when the SCS group is turned  $90^\circ$  from the position presented in Fig.1 when the dipole transition moment of the asymmetric vibration of the group becomes vertical to interface.

For parallel polarization (p - polarization) there are two electric field vector components at the interface, one parallel  $E_{\parallel X}$  and one perpendicular  $E_{\parallel Z}$  to the substrate plane (Fig.1). Therefore, for p - polarization the molecular groups showing dipole transition moments parallel and vertical to interface in x and z directions can produce absorbance bands. Using the example of SCS group of xanthate molecules at the surface presented in Fig.1 two absorbance bands: the  $A_{\parallel X}$  for the asymmetric stretching vibration of the SCS group and the  $A_{\parallel Z}$  related to the asymmetric stretching vibration of the COC group will be presented in the recorded spectrum. It is also possible to distinguish these two components because they show reverse absorbance, whereas one produces positive absorbance the second one is negative, depending on the angle of incidence. The intensities of the absorbance band recorded for the two polarizations  $A_{\perp}$  and  $A_{\parallel}$ , depend on the nature of the vibration of the particular molecular group, the amount of surface species, the angle of the incident beam and the orientation of molecules in the surface layer. These together allow determining orientation of each molecular group of the adsorbed collector based on the recorded two spectra at different conditions. The type of the produced surface species and their orientation at interface determine the level of hydrophobicity that governs the selectivity of flotation process (Mielczarski, 1993; Mielczarski et al. 1996 a,b; 1998 a,b; 1999 a,b; 2002 a,b).

The incident infrared beam reflected from mineral surface carries all the information about surface composition and structure. With proper manipulation of the experimental optical conditions (incident angle and polarization) it is sufficient to record three spectra which together give a three dimensional "picture" of the species present at the mineral surface. The technique is based on the comparison of the experimental spectra with the simulated spectra of the hypothetical surface layer with the assumed composition and structure as will be shown later. The good agreement (fitting) between all recorded experimental spectra and the simulated ones allows us to evaluate qualitatively and quantitatively the investigated surface structure.

It is also important to underline that the simulation of isotropic adsorbed layer on natural minerals could be performed before any experiments are carried out (for example: Mielczarski and Yoon 1991; Mielczarski, 1993; Mielczarski and

Mielczarski, 1995; 1999 Mielczarski et al., 1995; 1996 a,b; 1997; 2002b), allowing to predict the best experimental conditions that ensure optimal spectral sensitivity and the maximum confidence in the interpretation of experimental results. This also significantly speeds up the experimental procedure.

The developed technique has unique properties compared with other known infrared techniques such as transmission, diffuse reflectance, attenuated total reflection, or photoacoustic. This technique supported by the spectral simulation of surface species allows obtaining almost all the details about the mineral-aqueous solution interactions, including:

- the nature of the adsorbed products (by which functional group adsorption takes place),
- the adsorbed quantities of different surface products (starting from 20% of monolayer),
- the surface distribution of the adsorbed species (uniform layer or patches with determined thickness),
- molecular orientation of the adsorbed species (orientation of particular functional groups),
- molecular recognition (selective adsorption on specific surface sites),
- dynamic phenomena such as kinetics of adsorption/desorption, stability of surface products, surface mobility of the adsorbed species.

The method provides information on mechanisms and dynamics of surface phenomena and the proposition of surface modifications for numerous applications where mineral surface properties play important roles. This multidagnostic technique shows important advantages in the study of the surface phenomena on solids:

- the prediction of the most efficient experimental conditions,
- the investigation can be carried out *in-situ*, which is particularly important when the produced surface species are not stable after removal of the sample from aqueous solution and drying,
- any type of mineral sample can be investigated; there is no limitation, from the transparent to non-transparent for infrared radiation,
- it is very easy to distinguish the absorbance bands of substrate from the bands due to the adsorption layer; they are, at certain optical conditions, positive and negative, respectively,
- the technique shows the ability to study mechanisms of the formation of monolayers on substrates showing very strong absorbance in the region of the characteristic vibration of the surface species, for example carboxyl group interactions with a calcite surface. This ability could be very helpful to study other very complex systems, for example biological ones,
- the surface distribution of the adsorbed species in multicomponent and heterogeneous mineral systems was successfully investigated (spatially resolved spectroscopic analysis). It was demonstrated that it is possible to determine

exactly the type of mineral on which adsorption takes place even if the same product is formed on different mineral components. This unique advantage can find a wide application for studying the interfacial properties at a molecular level for multicomponent and heterogeneous mineral samples.

All of the mentioned features were experimentally evaluated in our original studies. Examples of optical considerations and spectra simulations for different multilayer stratified systems on solid substrate can be found in several papers (Yen and Wong, 1989; Mielczarski and Yoon, 1989; Parikh and Allara, 1992; Mielczarski, 1993; Mielczarski and Mielczarski, 1995; 1999a; Mielczarski et al., 1995; 1996a,b; 2002b; Hoffmann et al., 1995; Brunner et al. 1997. This multidagnostic technique has been applied extensively to study of interaction of different minerals such as semisoluble minerals (Mielczarski and Mielczarski, 1995; 1999a Mielczarski et al., 1998a,b; 1999a; 2002a; and sulfides (Mielczarski et al., 1995; 1996a,b; 1997; 1998b) with various aqueous solutions.

## RESULTS AND DISCUSSION

### ETHYL XANTHATE INTERACTION WITH CHALCOCITE

Adsorption of ethyl xanthate on copper(I) sulfide has been performed at open circuit potential (OCP) using solutions with different concentrations and pHs. The reflection spectra were recorded at angles of incidence of 70 and 85° for p-polarization and 20° for s-polarization (Fig. 2a).

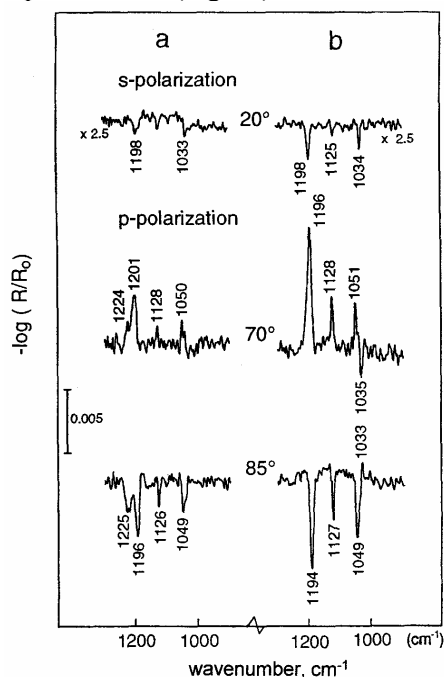


Fig. 2. Reflection spectra of ethyl xanthate adsorbed on chalcocite from solution of  $5 \times 10^{-5}$  M at pH 9.2. a - spectra recorded immediately after adsorption, b - sample (a) after 30 min immersion in water

These are the optical conditions, which ensure the determination of all the possible vibrations characteristic for the adsorbed molecules and appropriate spectral sensitivity. As expected the spectra recorded from the same sample at various optical conditions are very different. There are strong changes in absorbance intensities as well as “negative” or “positive” peaks are observed. These experimental spectra were compared to the simulated spectra of the copper(I) sulfide with assumed one nanometer thick adsorbed cuprous ethyl xanthate layer (Fig.3).

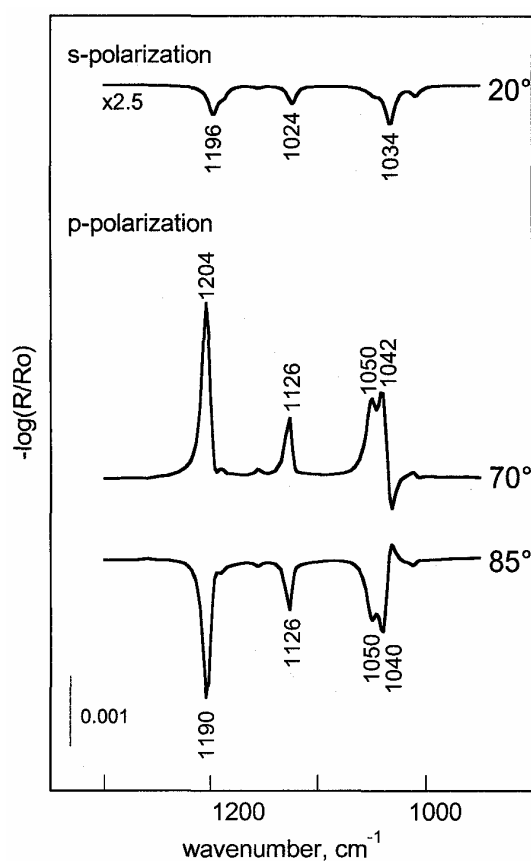


Fig. 3. Simulated reflection spectra of an isotropic 1 nm copper(I) ethyl xanthate on chalcocite for s-polarization and 20° and p-polarization and incident angles of 70° and 85

The comparison shows that the major features of the experimental spectra such as relative intensity, band shapes and positions could be predicted by theoretical calculation and explained by changes of three electric field components within the adsorbed nanolayer. The similar features of the spectra indicate that the adsorbed product is cuprous ethyl xanthate and the adsorbed molecules are not well organized at the chalcocite surface because the spectral calculation was performed with the assumption of an isotropic surface structure of cuprous xanthate. Nevertheless, important differences are also observed that cannot be explained by optical effects. One of the major differences is

the presence of the band at about  $1225\text{ cm}^{-1}$  in the spectra of all samples after a short adsorption time, when a close to monolayer coverage was produced. The results obtained (Figure 2a) clearly show that the band at about  $1225\text{ cm}^{-1}$  is related to the formation of a surface product limited to a submonolayer coverage. This band practically disappears from the reflection spectra after longer adsorption when multilayer coverage is produced (spectra not shown). Furthermore, since the band is observed at the incident angles of  $70^\circ$  and  $85^\circ$  at p-polarization and practically negligible at s-polarization (Figure 2a), it is due to the molecular dipole moment oriented almost vertical to the surface.

Very interesting changes in the structure and composition of the adsorbed layer were observed after holding the copper(I) sulfide sample with the adsorbed xanthate layer in water over a period of about 30 min (Figure 2b). It can be seen that the band at  $1225\text{ cm}^{-1}$  disappeared. At the same time the absorbance bands characteristic of the cuprous xanthate complex became sharp and more intensive, and a negative band at  $1035\text{ cm}^{-1}$  in the spectrum recorded at  $70^\circ$  and p-polarization is found. These observations indicate that the already adsorbed xanthate molecules undergo surface diffusion and reorganization on the surface of cuprous sulfide forming a well-ordered structure. The performed quantitative evaluation enables the determination of the average orientation of the molecular groups of xanthate molecules, i.e. COC and SCS, in the adsorption layer. The results of the calculation are presented in Figure 4.

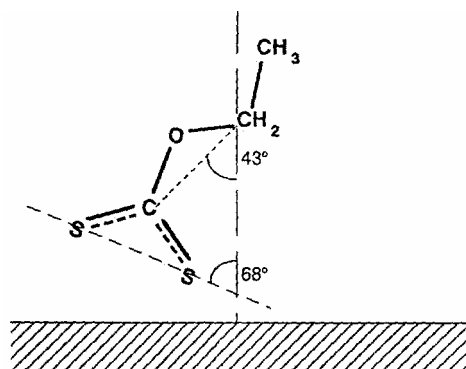


Fig. 4. Determined molecular arrangement of adsorbed ethyl xanthate molecules on chalcocite

The calculated average thickness of this adsorption layer is 2.0 nm, which is about two oriented monolayers. A quantitative evaluation of the sample presented in Figure 2a gives a value of about 1.8 nm. The good agreement between surface coverage found for the same sample, before and after immersing in water, supports the conclusion about surface diffusion of adsorbed copper(I) xanthate molecules and their reorganization in a well-organized structure, with simultaneous removal of the surface product characterized by the band at  $1225\text{ cm}^{-1}$ .

These results indicate that the first step of the formation of the self-assembled cuprous xanthate layer is governed by a very high affinity between xanthate ions and copper(I) sulfide and the formation of the surface product with a band at  $1225\text{ cm}^{-1}$ , both of which



hamper the formation of the ordered surface layer. The surface product with the band at  $1225\text{ cm}^{-1}$  can act as an impurity, which disturbs the formation of the organized surface structure. Removal of this product and reorganization of the structure of the xanthate molecules at the copper(I) sulfide surface required certain conditioning time to be successfully completed with creation of a well-ordered structure. This can be achieved by immersing the copper(I) sulfide with adsorption layer in water or, even better, in a low-concentration xanthate solution. The band at  $1225\text{ cm}^{-1}$  is assigned to surface decomposition product(s) that are produced at a very early stage of xanthate adsorption when the most energetic surface sites interact with xanthate molecules. Monothiocarbonate is a possible product at this step of surface reaction.

#### *In-situ* SPECTROELECTROCHEMICAL STUDIES

In-situ measurement is more complicated than *ex-situ* but is the only way to furnish information about all of the produced surface species including those less stable after sample emersion from aqueous solution. A special experimental cell has to be constructed with a window transparent for infrared beam holding a layer of aqueous solution at mineral interface. A minimum five-phase system: air-window-solution layer-adsorption layer-mineral has to be considered. In fact in the performed experiments a two-component adsorption layer was determined which increase the number phase to six. It was already demonstrated (Mielczarski et al 1995) that optical properties of window material and the thickness of aqueous solution have to be carefully chosen to obtain optimal experimental sensitivity and, equally as important, the maximum of confidence in the interpretation of experimental spectra. They are two major factors which determine the optimal optical configuration of the designed in situ spectroelectrochemical cell.

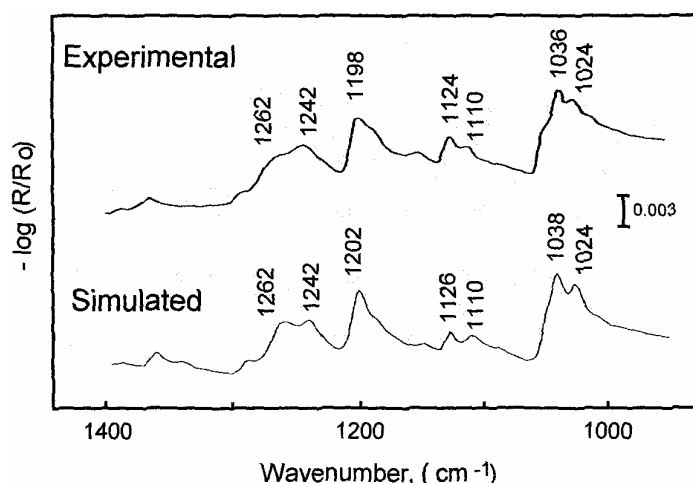


Fig. 5. Experimental reflection spectrum of chalcopyrite contacted with ethyl xanthate solution of  $1.6 \times 10^{-4}\text{ M}$  at a potential of 370 mV, and simulated spectrum of a 5.2 nm isotropic layer of copper(I) ethyl xanthate and a 6.9 nm layer of liquid form of dixanthogen on chalcocite

The complex experimental in-situ spectroelectrochemical configuration, and the produced multicomponent surface coverage of mineral at controlled potential were successfully simulated (Mielczarski et al 1996b). An example of the results obtained are presented in Figure 5 showing the recorded in-situ experimental spectrum of the adsorbed layer of ethyl xanthate ( $\text{CH}_3\text{CH}_2\text{OCS}_2^-$ ) on chalcocite ( $\text{Cu}_2\text{S}$ ) and the simulated spectrum calculated for the experimental configuration with assumed surface composition and surface structure. They show a very good agreement between them. This allows to conclude that there are two surface products, i.e., cuprous ethyl xanthate complex (band at  $1198\text{ cm}^{-1}$ ) and dimer - ethyl dixanthogen (doublet at  $1242, 1262\text{ cm}^{-1}$ ) produced by dimerization of ethyl xanthate ion. The dimer is not very stable on mineral surface after the removal of mineral sample from solution but its presence is crucial for increasing mineral hydrophobicity. The in-situ studies allow to determine accurately the electrochemical conditions of dixanthogen formation. The cuprous xanthate complex is formed directly on mineral surface at mineral potential above  $15\text{ mV}$  (SHE), while the dixanthogen is produced at a potential higher than  $200\text{ mV}$ , and it is spread on the surface as the upper layer. The average thickness of cuprous amyl xanthate is  $5.2\text{ nm}$ , while dixanthogen forms a  $6.9\text{ nm}$  thick layer. The produced dixanthogen is in its liquid form which significantly enhances a lateral diffusion of this very hydrophobic product on mineral surface.

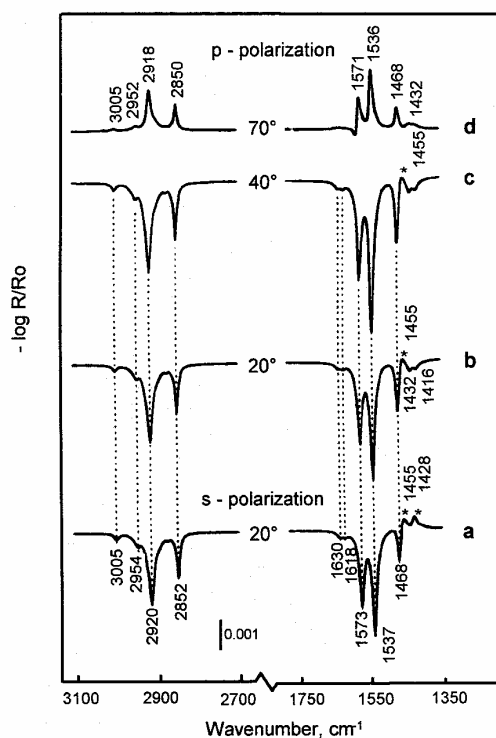


Fig. 6. Simulated reflection spectra of isotropic adsorbed calcium oleate,  $2.1\text{ nm}$  layer on apatite

## COMPOSITION AND STRUCTURE OF THE ADSORBED LAYER OF OLEATE ON APATITE

When in the experimental spectra of the adsorption layer (the band positions and shapes) are similar to simulated ones, as presented in Figure 6, it would indicate that the adsorbed product is calcium oleate surface complex and the produced layer has an isotropic structure. However, any difference between the simulated and the experimental spectra indicates specific orientation or composition changes with regards to the nature and structure of the adsorbed layer assumed for calculation.

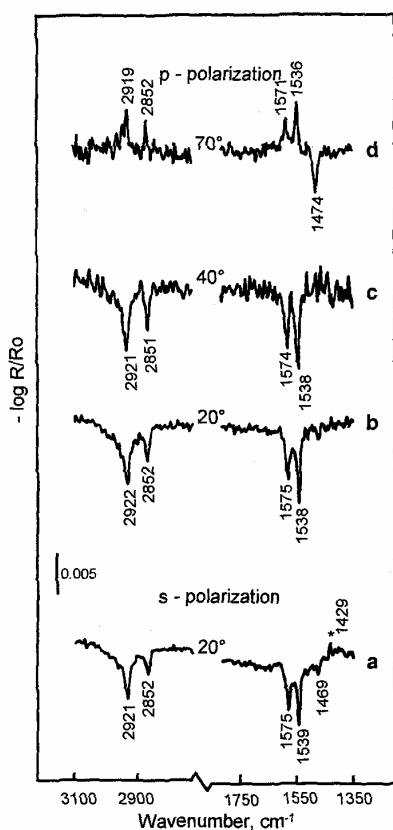


Fig. 7. Experimental reflection spectra of self-assembled layer of oleate produced on apatite after adsorption from  $3.3 \times 10^{-5}$  M oleate solution at pH 10 for 10 min

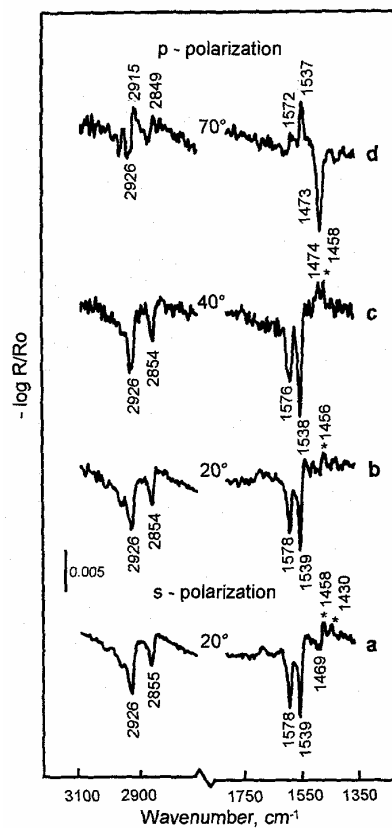


Fig. 8. Experimental reflection spectra of self-assembled layer of oleate produced on apatite after adsorption from  $3.3 \times 10^{-5}$  M oleate solution at pH 10 for 1 h

The reflection spectra of two adsorbed layers of oleate on apatite after 10 min and 1 h of adsorption are presented in Figures 7 and 8, respectively. Almost the same positions and shapes of the two absorbance bands assigned to the asymmetric stretching vibration of the  $\text{COO}^-$  groups are observed in the simulated spectra (bands

at 1573 and 1537  $\text{cm}^{-1}$ , Figure 6) and the experimental spectra (bands at 1575 and 1539  $\text{cm}^{-1}$ , Figure 7). This indicates that calcium oleate surface complex is produced at the mineral interface. The reflection spectra recorded at 20° and both polarizations are almost exactly the same indicating that the uniaxial model can be used for calculation of molecular orientations of the adsorbed species.

The experimental spectra (Figures 7 and 8) are different from the simulated spectra (Figure 6) in the observed relative intensity of absorbance bands, suggesting organization of the adsorbed molecules at the interface. The most striking difference is a negative band at 1474  $\text{cm}^{-1}$  in the spectra recorded at 70° and p - polarization (Figures 7 and 8, spectra d) whereas the simulated spectrum shows a positive band. This band is characteristic of the symmetric stretching vibration of the  $\text{COO}^-$  group and its negative value indicates that the dipole moment of carboxylate group is preferentially oriented in z direction. The specific orientation of carboxylate groups can be calculated applying the equations for uniaxial orientation model presented in the reported work (Mielczarski and Mielczarski, 1995). After 10 min of adsorption carboxylate groups form two conformations: bidentate and unidentate with orientation angles  $\phi_1$  of 83° and 62° (Figure 9).

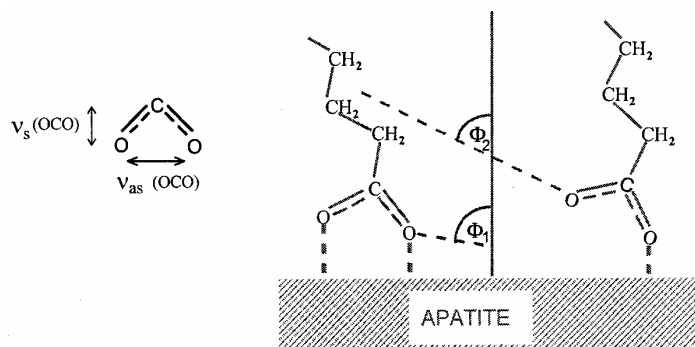


Fig. 9. Two molecular conformations: a – bidentate, b – unidentate of adsorbed oleate molecules on apatite

The same calculation for the adsorption layer produced after 1 h of adsorption indicates orientation angles 50° and 60°. The latter results could suggest close to random orientation structure because they are approaching a value of 54.7°, so-called magic angle, which is equivalent of randomly oriented structure. This effect is caused by the nature of aliphatic chain in oleate, which has the cis-double bond in the middle of the chain. Even for the all-trans conformations these two parts of polymethylene chains have two chain axes with an angle of 112°. Hence, whereas the head ended aliphatic part will have a position almost vertical to interface, as can be deduced from the orientation angle of carboxylate group (83°) the second part of the chain will be oriented nearly parallel to the interface. This will result in an average orientation angle close to the magic angle characteristic for a randomly oriented population. In fact this situation is observed experimentally for aliphatic molecular groups.

## CONCLUSIONS

The developed infrared external reflection technique has a very unique ability to study interface phenomena at a molecular level for heterogeneous and multicomponent substrates such as natural minerals or biominerals. The variety, precision and reliability of information about interface phenomena delivered by this technique is incomparable to other single techniques. The obtained results of fundamental and applied work show clearly that it is difficult to find another surface characterization technique that is able to furnish so much detailed information about surface phenomena which can help to predict, control and modify surface properties in a complex system by controlling a few key parameters of the solution.

## REFERENCES

- BRUNNER, H, MAYER, U AND HOFFMANN, H, 1997. *External reflection infrared spectroscopy of anisotropic adsorbate layers on dielectric substrates*. Appl. Spectrosc, 51: 209-217.
- FINKELSTEIN, N P, 1989. *Review of interactions in flotation of sparingly soluble calcium minerals with anionic collectors*. Trans. Inst. Min. Metall. 98: C157 – C177.
- HOFFMANN, H, MAYER, U AND KRISCHANITZ, A, 1995. *Structure of alkylsiloxane monolayers on silicon surfaces investigated by external reflection infrared spectroscopy*. Langmuir 11: 1304-1312.
- MACPHAIL, R A, STRAUSS, H L, SNYDER, R G AND ELLIGER, C A, 1982. *C-H stretching modes and the structure of n-alkyl chains. I. Long, all-trans chains*. J. Phys. Chem. 88 : 334-341.
- MIELCZARSKI, J A AND YOON, R H, 1989. *FTIR external reflection study of molecular orientation in spontaneously adsorbed layers on low-absorption substrates*. J. Phys. Chem. 93: 2034-2038.
- MIELCZARSKI, J A AND YOON, R H, 1991. *Spectroscopic studies of the structure of the adsorption layer of thionocarbamate. II. On cuprous sulfide*. Langmuir, 7 : 101-108.
- MIELCZARSKI, J A, 1993. *External reflection infrared spectroscopy at metallic, semiconductor and nonmetallic substrates. I. Monolayers films*. J. Phys. Chem. 97 : 2649-2663.
- MIELCZARSKI, J A and MIELCZARSKI, E, 1995. *Determination of molecular orientation and thickness of self-assembled monolayers of oleate on apatite by FTIR reflection spectroscopy*. J. Phys. Chem. 99 : 3206-3217.
- MIELCZARSKI, J A, MIELCZARSKI, E, ZACHWIEJA, J AND CASES, J M, 1995. *In situ and ex situ infrared studies of nature and structure of thiol monolayers adsorbed on cuprous sulfide at controlled potential*. Langmuir, 11 : 2787-2799.
- MIELCZARSKI, J A, MIELCZARSKI, E AND CASES, J M, 1996a. *Interaction of amyl xanthate with chalcopyrite, tetrahedrite and tennantite at controlled potentials. Simulation and spectroelectrochemical results for two component adsorption layers*. Langmuir, 12 : 6521-29.
- MIELCZARSKI, J A, XU, Z AND CASES, J M, 1996b. *Qualitative and quantitative evaluation of heterogeneous adsorbed monolayers on mineral electrodes by infrared reflection spectroscopy*. J. Phys. Chem. 100 : 7181-7184.
- MIELCZARSKI, J A, MIELCZARSKI, E AND CASES, J M, 1997. *Infrared evaluation of composition and structure of ethyl xanthate monolayers produced on chalcopyrite, tetrahedrite and tennantite at controlled potentials*. J. Coll. Inter. Sci. 188 : 150-161.
- MIELCZARSKI, E, MIELCZARSKI, J A AND CASES, J M, 1998a. *Molecular recognition effect in monolayer formation of oleate on fluorite*. Langmuir, 14 : 1739-47.
- MIELCZARSKI, J A, MIELCZARSKI, E AND CASES, J M, 1998b. *Influence of chain length on adsorption of xanthates on chalcopyrite*. Int. J. Miner. Proc. 52 : 215-231.
- MIELCZARSKI, J A AND MIELCZARSKI, E, 1999a. *Infrared external reflection spectroscopy of adsorbed monolayers in a region of strong absorption of substrate*. J. Phys. Chem. 103 : 5852-5859.

- MIELCZARSKI, J A, MIELCZARSKI, E and CASES, J M, 1999b. *Dynamic of fluorite - oleate interactions*. Langmuir, 15 : 500-508.
- MIELCZARSKI, J A and MIELCZARSKI, E, 1999c. *Infrared external reflection spectroscopy of adsorbed monolayers in a region of strong absorption of substrate*. J. Phys. Chem, 103 : 5852-5859.
- MIELCZARSKI, E, MIELCZARSKI, J A, CASES, J M, RAI, B and PRADIP. 2002a. *Influence of solution conditions and mineral surface structure on the formation of oleate adsorption layers on fluorite*. Colloids and Surfaces, 205 : 73-84.
- MIELCZARSKI, E, DUVAL, Y and MIELCZARSKI, J A, 2002b. *Spectroscopic characterization of the nature and structure of adsorbed organic monolayers on quartz in the region of very strong absorption of substrate. Reverse surface selection rule*. J. Phys. Chem. B, 106 (46) : 11985-11992.
- PARIKH, A N. and ALLARA, D L. 1992. *Quantitative determination of molecular structure in multilayered thin films of biaxial and lower symmetry from photon spectroscopies. I. Reflection infrared vibrational spectroscopy*. J. Chem. Phys. 96 : 927-945.
- SNYDER, R G, STRAUSS, H L and ELLIGER, C A, 1982. *C-H stretching modes and the structure of n-alkyl chains. I. Long, disordered chains*. J. Phys. Chem. 86 : 5145-5150.
- YEN, Y S and WONG, J S, 1989. *Infrared reflectance properties of surface thin films*. J. Phys. Chem., 93: 7208-7216.

**Mielczarski J.A., Mielczarska E.,** *Monitorowanie zjawisk powierzchniowych za pomocą refleksyjnej spektroskopii w podczerwieni*, Physicochemical Problems of Mineral Processing, 39 (2005) 33-46 (w jęz. ang).

Poznanie składu powierzchni minerału oraz struktury cząsteczek i atomów na tej powierzchni a także zrozumienie mechanizmów i kinetyki adsorpcji na powierzchni, stanowią istotne elementy potrzebne dla osiągnięcia efektywnej separacji w procesach wzbogacania minerałów. Jest to podstawowy warunek, który musi być spełniony, aby móc przewidzieć i kontrolować właściwości powierzchniowe minerałów, które to właściwości rządzą efektywnością procesów separacyjnych. Rozwój techniki spektroskopii w podczerwieni stwarza ogromne możliwości dla badania zjawisk na granicy faz na poziomie molekularnym, które zachodzą na heterogennych powierzchniach. Różnorodność, precyzja i niezawodność uzyskiwanych informacji o zjawiskach na granicy międzyfazowej sprawia, że techniki spektroskopowe przewyższają inne proste techniki badawcze. Pomiary wykonywane tą techniką są szybkie i nie powodują zniszczenia badanej próby. Wysoka czułość (dochodząca do monowarstwy) w zbieraniu informacji w sposób in situ w układzie wielofazowym nawet w obszarze o silnej adsorpcji substartów powoduje, że ta technika jest cennym eksperymentalnym narzędziem. Złożoność rejestrowanego widma refleksyjnego, jego czułość na wszelkie zmiany we właściwościach optycznych zarówno związków będących w roztworze jak i na powierzchni międzyfazowej oraz ich dystrybucja w badanych układach, są faktyczną siłą tej techniki badawczej. W pracy dokonano przeglądu, na podstawie wybranych przykładów, możliwości tej techniki badawczej w monitorowaniu modyfikacji właściwości powierzchniowych siarczków i minerałów typu sole, pod kątem ich selektywnej flotacji.