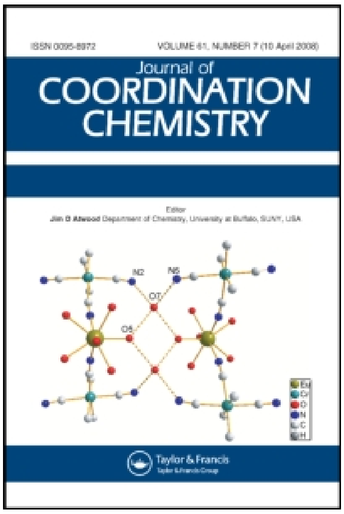

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REVIEW

ADSORPTION OF IONS AND MOLECULES TO SOLID SURFACES IN CONNECTION WITH FLOTATION OF SULPHIDE MINERALS

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Valuable sulphide minerals are separated and concentrated from the crude ore by means of flotation. One fundamental step in this process is the selective hydrophobation by a collector of certain sulphide mineral surfaces. The most commonly used collectors are alkylxanthate (*O*-alkyldithiocarbonate) ions, $R\text{-}O\text{-}CS_2^-$, *O,O*-dialkyldithiophosphate ions, $(RO)_2\text{-}PS_2^-$, and *N,N*-dialkyldithiocarbamate ions, $R_2N\text{-}CS_2^-$. The adsorption mechanisms of these collectors on the sulphide minerals sphalerite (ZnS), galena (PbS), chalcocite (Cu_2S), acanthite (Ag_2S), covellite (CuS), chalcopyrite ($CuFeS_2$), pyrite (FeS_2), marcasite (FeS_2), pentlandite ($(Fe, Ni)_9S_8$), pyrrhotite (FeS_{1-x}), troilite (FeS), millerite (NiS), molybdenite (MoS_2), realgar (AsS), orpiment (As_2S_3) and arsenopyrite (FeAsS). A strong correlation between the structure of the sulphide mineral and the adsorption mechanism is found. The studied collectors are adsorbed to the mineral surface according to one or two of the following adsorption mechanisms: a) the collector is oxidized to a very hydrophobic compound physisorbed to the surface, b) the mineral surface is oxidized and the metal ions are dissolved from the surface, which in presence of collector precipitates on the mineral surface as a hydrophobic solid metal collector salt, and c) the collector forms surface complexes chemisorbed to specific atoms/ions in the mineral surface through covalent interactions. The crystal structure of sulphide minerals and some metal collector salts are presented. The most commonly used techniques to study ions and molecules adsorbed on solid surfaces are presented and evaluated.

KEYWORDS: adsorption, sulphide minerals, flotation, alkylxanthate, *O,O*-dialkyldithiophosphate and DRIFT (Diffuse Reflectance Infrared Fourier Transformation)

CONTENTS

1. INTRODUCTION

Flotation is the main technique used in the mineral processing industry for separation and concentration of valuable minerals from the crude ore. The fundamental steps in the flotation process are grinding, conditioning and flotation. The crude ore is ground wet in large mills into such a fine powder that each individual mineral particle in principle consists of only one compound. This slurry of ground ore is poured into a water basin, and the resulting slurry of ca. 25 weigh% ore is called a flotation pulp. The basic idea of the conditioning step is to selectively modify the surfaces of the desired mineral particles in such a way that they become hydrophobic. A wide range of chemicals are added to the flotation pulp in the conditioning step to make the flotation step as effective as possible. These chemicals are divided into the following categories depending on the function: collectors, depressants, frothers, activators and modifiers. In the flotation step small gas bubbles, normally air, are blown in at the bottom of the flotation pulp. The hydrophobated particles in the flotation pulp are caught by the uprising bubbles. Frothers, usually bulky alcohols as methyl-isobutyl-carbinol, polypropylene glycol ethers or pine oil terpenols are added to the pulp to chemically and mechanically stabilize the bubbles. This results in the formation of a mineralized froth on top of the aqueous slurry phase. This froth, containing the desired mineral particles, is mechanically separated from the rest and the desired mineral concentrate is obtained.

This article will summarize and critically evaluate the chemical mechanisms proposed for the adsorption of the collector ions/molecules on sulphide mineral surfaces, and the methods used to obtain information about adsorption processes on solid surfaces. The far most used collector for hydrophobation of sulphide minerals is the alkylxanthate (*O*-alkyldithiocarbonate) ion, $R\text{-}O\text{-}CS_2^-$, and the following discussion will mainly be focused on this collector. Other collectors used in flotation of sulphide minerals are *O,O*-dialkyldithiophosphate ions, $(RO)_2PS_2^-$, which will be discussed briefly in this article, and *N,N*-dialkyldithiocarbamate ions, $R_2N\text{-}CS_2^-$.

Several mechanisms have been proposed over the years for the adsorption of these sulphur donating collectors/ligands in particular and of ligands in general to sulphide mineral surfaces. Each mineral will be discussed individually as the sulphide minerals have different chemical properties and structures. The main emphasis will be put on the adsorption of alkylxanthate ions as this collector type is the most widely used in mineral processing, and as the adsorption mechanisms of alkylxanthate ions can also be applied to the *O,O*-dialkyldithiophosphate and *N,N*-dialkyldithiocarbamate ions. The relationship between adsorption mechanism and structure of the sulphide minerals will be discussed for a more general understanding of the possible adsorption reactions/reaction mechanisms taking place on sulphide mineral surfaces in particular and on solid surfaces in general.

2. CHEMICAL SORPTION PROCESSES

The deposition of chemical species to a solid surface may be termed a ***sorption process***.[1] Three principal sorption processes can be distinguished: a) precipitation, b) adsorption, which can be divided into the subgroups chemisorption and physisorption, and c) absorption.

Precipitation is characterized by the formation of a solid phase with a three-dimentional lattice. This solid precipitation can either be grown directly on the underlying lattice as a continuation of that lattice or on some species which is adsorbed to the underlying lattice. A precipitation mechanism can be initiated by either homogeneous or heterogeneous nucleation. The latter may involve the formation of a solid mixture either by inclusion or by coprecipitation, or may take place on the surface of a preexistent solid phase.[1-3]

The ***adsorption*** is defined by a concentration of species on the surface of a solid particle but without the formation of a three-dimentional lattice. An absolute adsorption involves a two-dimentional arrangement of molecules or ions on a solid surface, including 'two-dimentional solid solutions'. 'Multilayer adsorption' must, with the definition given above, mean that each molecule or ion layer is arranged independently of the arrangement of the underlying layers. Adsorption can be divided into two groups, *chemisorption* and *physisorption*, depending on the kind of chemical interaction the adsorbed species, the adsorbate, forms to the solid surface, the adsorbent or the substrate, or underlying adsorbate.

In ***physisorption*** the dominating interaction between the adsorbate and the adsorbent is the van der Waals force of a similar kind as between molecules. The van der Waals force is a weak long-range interaction and the energy released when a species is physisorbed is of the same order of magnitude as the heat of condensation. Typical values of heat of physisorption are in the range 20–60 kJ mol^{-1} adsorbated molecules or ions. This energy is insufficient for breaking of bonds in the adsorbate, which means that physisorbed molecules or ions retain their identity, although it might be slightly distorted on account of the presence of the surface.[4,5] The physisorption process is generally reversible.

In ***chemisorption*** the adsorbate species are chemically bound to specific ions, molecules or atoms in the surface. This interaction has a covalent character, and the chemisorption process must be exothermic as no entropy loss takes place in this process or only a small positive entropy effect is seen if the coordination sites of interest are hydrated (solvated). As the translational freedom of the adsorbate is reduced at the chemisorption the entropy of adsorption (translation) term, $\Delta S_{\text{ad,transl}}$, becomes negative. An additional positive entropy of adsorption (desorption) term, $\Delta S_{\text{ad,desorp}}$, must be added if the chemisorption process involves a substitution of a more weakly chemisorbed species as e.g. water in an aqueous solution; solid surfaces are indeed hydrated (solvated in other solvents than water).[4,5] The heat of chemisorption is 5–10 times larger than the heat of physisorption, which means that this energy is large enough to break bonds in the adsorbate. The total heat of adsorption can however sometimes be endothermic because if one or several bonds in the adsorbate are broken the translational entropy of the products can be larger than the heat of adsorption of the incoming molecule. However, the ΔH_{ad} term must be exothermic otherwise the adsorbate will not be chemisorbed to the surface. The size of the heat of adsorption can be used to distinguish chemisorption from physisorption. Processes with heats of adsorption less negative than -25 kJ mol^{-1} are regarded as physisorption, and values more negative than -40 kJ mol^{-1} as chemisorption.[4,5]

Absorption is characterized of penetration/diffusion of molecules or ions into a solid phase.[2,3] The absorption process has no importance for the hydrophobation of minerals and surface modifications of solids, and will not be further presented here.

3. OVERVIEW OF METHODS FOR THE STUDY OF SORPTION PROCESSES ON SOLID SURFACES

A wide range of physical and analytical techniques has been applied to study the adsorption of ionic and molecular species on solid surfaces. A short presentation of the techniques mainly used in the studies of adsorption on solid surfaces is given below.

3.1 Kinetic Methods

The presence of an electric charge on the surface is a source of kinetic stability of small or colloidal particles. Ions of opposite charge tend to cluster nearby, and an 'ionic atmosphere' is formed. Two regions of charge on surfaces are distinguished, an immobile layer of ions and water molecules (in aqueous solution) tightly stuck to the surface and the 'free' ions and water molecules in the aqueous bulk. The radius of the sphere capturing the inner immobile layer is called the *radius of shear*. This radius is the most important factor determining the mobility of the particles. The electric potential at this radius of shear relative to the value in the bulk medium is called the *ξ-potential* or the *electrokinetic potential*.[5,6] Electrokinetic phenomena have often been used to obtain information about the properties of electrical double layers at solution-solid interfaces. This requires introduction of a model of the double layer, either of Helmholz or Stern type.[4] The value of the dielectric constant ε in the double layer is probably not the same as the value of ε in the bulk. The ξ-potential is the result of a rather brutal averaging process applied to a double layer in a non-equilibrium state. The ξ-potential is approximately equal to the total potential fall in the double layer. Measurements of the capacitance of the double layer by a-c-bridge techniques are often used to obtain experimental data about the double layer including the ξ-potential.[6]

Specific adsorption of anions will cause that the surface becomes more negative, while specific adsorption of cations will cause a more positively charged surface. Specific adsorption of an ion may result in blocking of the surface and the reaction rate will decrease. The blocking of a surface increases with increasing size of e.g. R groups, $-CH_3 < -C_2H_5 < -C_4H_9$. It has also been stated that the ξ-potential can be correlated to adsorption of ionic or molecular species on mineral surfaces, and thereby also their flotation behaviour.[6] Hunter has written an extensive summary of theory and determination of the ξ-potential in colloidal systems.[6]

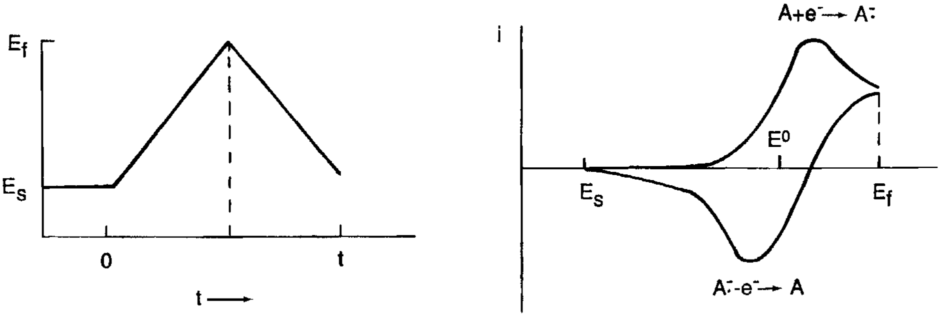
3.2 Thermodynamic Methods

3.2.1 Rest potential measurements

At the rest potential, the rate of the anodic and cathodic reactions is the same giving a zero current. By comparing this potential with the thermodynamic redox potentials of possible reactions, it is possible to postulate what kind of electrochemical reaction that may occur. When the rest potential is far from the thermodynamic potential of the system, one might expect that the surface is covered by any adsorbed compound. By measuring the rest potential as a function of time, slow transformations of a surface can be detected. It has been claimed that there is a good correlation between the rest potential and the flotability of minerals.[7]

3.2.2 Cyclic voltammetry

In a cyclic voltammetry experiment one or several reactions of the type oxform $+ n\,e^- \rightleftharpoons$ redform are studied with an electrode in solution where semi-infinite linear diffusion is assumed. Initially, the electrode is held at a potential E_i, where no reaction occurs at the electrode. The potential is then swept linearly at v (V/sec) until a predetermined potential E_{max} is obtained. From there the potential is immediately swept back at $-v$ (V/sec) to the initial potential E_i see Fig. 1. This cycle can then be repeated if wanted. It is assumed that the rate of electron transfer is so



(a) (b)

Figure 1 (a) Cyclic potential sweep and (b) resulting cyclic voltammogram.

rapid at the electrode surface that the concentrations of the oxform and the red-form of a species are immediately adjusted to the radio dictated by the Nernst equation $f(t) = C_{\text{oxform}}/C_{\text{redform}} = \exp[(nF/RT)\cdot(E(t)\text{-}E^\circ)]$, where E° is the thermodynamic standard electrode potential. This shows that the ratio $C_{\text{oxform}}/C_{\text{redform}}$ is a function of time, see Fig. 1. The advantage of cyclic voltammetry is that also non-equlibrium processes, such as adsorption, can be studied. An excellent description of the theory of cyclic voltammetry is given by Bard and Faulkner.[8]

3.2.3. Potentiometric sweep (PDS)

In potentiometric sweep experiments the electrode potential is slowly changed by a certain velocity, and the current is measured as a function of the potential. The change in potential must allow the formation of a steady state or equilibrium condition. It is well-known that a linear relationship between the logarithmated current and the potential is obtained, the so called Tafel region for an irreversible electron transfer process under activation control. The Tafel behaviour is an indicator of totally irreversible kinetics.[8] From the Tafel slope and the dependence on ions in solution a reaction mechanism may be deduced.

3.2.4 Solubility measurements

Adsorption phenomena are in some cases studied by measuring the change in concentration of a certain species in an aqueous solution before and after addition of an adsorbing solid material. This gives of course no indication of type of reaction, adsorption mechanism or if the species studied has undergone any chemical reaction. The amount disappearing from the solution phase is expected to be adsorbed on any specific surface. Adsorption isotherms can be calculated by knowledge of the total surface of the solid (powder). This kind of solubility measurements has only occasionally been used to study the adsorption of alkylxanthate collectors on mineral surfaces. Sposito has given a good critical overview of solubility methods in the study of adsorption of chemical species on solid surfaces.[1]

However, some of the sulphide minerals, especially galena (and chalcopyrite), are easily oxidized to species that are substantially more soluble than the sulphide mineral itself. It is therefore very important to determine the total amount of metal species dissolved from sulphide mineral surfaces treated in different ways under varying oxidizing conditions. The total amount of a certain metal is preferably determined by using an atomic spectroscopic technique as e.g. atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), atomic fluorescence spectroscopy (AFS) or inductively coupled plasma spectroscopy (ICP), which allow the determination of extremely low concentrations in a solution.[9]

3.2.5 Potentiometry

Potentiometric measurements are carried out by determining the potential between a reference half cell and a half cell where the concentration of the species under study defines the potential of the half cell. A glass electrode is normally used for determination of H^+, and ion selective electrodes are available for a relatively large number of inorganic ions for the determination of the free concentration of the particular ion. The measuring cell can be written: Ref | | M^{n+} (Ionic medium) | M(s). Such electrodes must be calibrated over the concentration range under study.

In potentiometric experiments the potential between two half-cells is a function of the concentration of one species in the measuring half-cell when no current flows between the half-cells. Since no current flows in the experiment, no net faradic reaction takes place. The obtained potential is normally showing the thermodynamic property of the system. Many variables in the electrochemical experiments such as electrode area and geometry and mass transfer do not affect the potential.[8]

Potentiometric measurements must be performed in the solution phase, and a major drawback of potentiometric methods is that it is extremely difficult to do potentiometric measurements sufficiently close to a surface.

3.2.6 Calorimetry

In calorimetrical experiments the heat evolved or consumed in a chemical reaction is determined. Two calorimetric techniques can be distinguished in the study of adsorption of collectors on mineral surfaces, titration and ampoule (or wetting) calorimetry. In titration calorimetrical experiments a solution containing the species to be adsorbed is added portionwise to a mineral slurry, normally an aqueous one. By adding portions containing smaller amounts of adsorbate than corresponding to one monolayer on the solid surfaces adsorption isotherms may be determined. Adsorption processes are not always momentary and a new registration technique has been developed recently where reaction processes as long as 15–20 minutes can be studied.[10] An important disadvantage with this technique is that the mineral powder has been in contact with water for several hours before the first addition of adsorbate. The mineral surfaces can e.g. be oxidized and thereby modified. Furthermore, the added ligand (adsorbate) may react with the metal ions or complexes dissolved from the surface after an oxidation, and a different reaction than that under study may occur.

In an ampoule calorimetrical experiment mineral powder is enclosed in a glass ampoule, which is smashed in pure water or in an aqueous solution containing an adsorbing ligand/collector. If an adsorption shall be studied calorimetrically it is very important that the mineral surfaces are unoxidized, which requires extraordinary precautions against oxidation for several sulphide minerals, e.g. galena, and that the water and the aqueous solution are free from oxygen and other oxidizing agents which can oxidize the mineral surfaces. In the ampoule calorimetrical experiments the heat of wetting determined in the pure solvent must be subtracted from the heat of adsorption in order to get the heat of adsorption of the mineral surface.

The titration and ampoule calorimetric techniques were originally described by Sunner and Wadsö[11] and later improved by Ots *et al.*[12,13] The automation of the titration calorimeter has been reported by Persson *et al.*[10,14]

3.3 Vibration Spectroscopic Methods

Several vibration spectroscopic techniques for the study of compounds, ions and complexes adsorbed on solid surfaces are available e.g. transmission infrared (IR) spectroscopy, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, attenuated total reflection (ATR) spectroscopy and infrared total reflection-absorption spectroscopy (IRAS).

The DRIFT technique requires almost always the sample as a powder. The quality of the DRIFT spectra is enhanced with decreasing particle size (the surface area/weight increases), decreasing range of the particle size and by dilution with a non-absorbing matrix, e.g. potassium bromide. However, the particle size must be larger than the wavelength of the infrared light, otherwise interference patterns will arise and the signal will not obey the theory of the diffuse reflectance, see below. The ATR technique can be applied on both powders and planar polished surfaces. However, the DRIFT technique has lower detection limits than the ATR technique and is therefore to prefer for powders. IRAS can be applied for studying adsorption on planar metal surfaces. A combination of studies on both powders and planar surfaces should give the best information about the adsorption processes on a surface. At the study of natural minerals it can be very difficult to obtain sufficiently planar surfaces for good IRAS or ATR measurements and the best choice is usually DRIFT measurements on powders.

Transmission IR was the most widely used technique until the more recently developed surface sensitive techniques became generally available. At the study of a surface using transmission IR spectroscopy, it is very important that the sample has a very large area/volume ratio as an average spectrum of the entire sample is obtained with this technique. The compounds on the surface must therefore be detectable from the rest if it shall be possible to extract information.

DRIFT Spectroscopy. When electromagnetic radiation reaches a solid surface it can be completely or partially absorbed and/or reflected depending on the optical properties of the solid material.[15] The reflection can either be specular, where the angles of incidence and reflection are equal, or diffuse, where electromagnetic radiation is reflected, ideally, in all directions. The phenomenon of diffused reflected electromagnetic radiation has been known since the beginning of this century, but a complete theory, which in a correct way relates the absorption of a sample to its concentration, does not exist. The most widely used theory for studies in the infrared region is the continuum or Kubelka-Munk theory.[16,17] The Kubelka-Munk equation for an 'infinitely thick' layer is given by $f(R_\infty) = (1-R_\infty)^2/2R_\infty = k/s$, where R_∞ is the absolute diffuse reflectance of a layer, k is the molar absorption coefficient, which is predicted to be proportional to the peak value of $f(R_\infty)$ for each band with constant scattering coefficient, s, which is dependent on particle size and range, and the way the sample is loaded in the sample cup. The k and s terms must be held as constant as possible in a series of experiments. The term absolute diffuse reflectance is not valid in practice since no perfect diffuse reflection standard exists. The R_∞ term is replaced by R'_∞, where $R'_\infty = R'_{\infty\text{sample}}/R'_{\infty\text{reference}}$, where $R'_{\infty\text{sample}}$ is the single beam reflectance spectrum of the sample, and $R'_{\infty\text{reference}}$ is the single beam spectrum of a non-absorbing reference with high diffuse reflectance and without absorption bands in the frequency region of interest. No significant difference between Kubelka-Munk units and log $R_{\text{reference}}/R_{\text{sample}}$ units, i.e. absorbance units, was found at a comparison of alkylxanthate species on sulphide mineral surfaces.[16] Excellent descriptions of the DRIFT technique are given by Fuller and Griffiths[17,18] and by Griffiths and de Haseth.[19]

3.4 Ellipsometry

Ellipsometry, a light scattering technique, determines the thickness of an inhomogeneous region on a surface, and the index of refraction and the absorption coefficient of this region can be determined as a function of the wavelength. Plane polarized light impinging onto a surface from some angle can be resolved into components parallel to and perpendicular to the plane of incidence. The two components are reflected differently, and, as a consequence, the reflected beam becomes elliptically polarized. When the angle of incidence is the Brewsterian angle, $\tan^{-1}n$ where n is the index of refraction of the substrate medium, only the perpendicular component will be reflected, assuming that the surface between the medium and air is absolutely sharp (reflected unpolarized light will under these conditions be completely plane polarized). Ellipsometry is very sensitive and allows detection of films of an average thickness of 0.2 Å or about 0.05 of a monolayer. More details about apparatus and measuring technique used in ellipsometric studies are given by Smith.[20]

3.5 X-ray Spectroscopic Methods

X-ray spectroscopic techniques such as X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Fine Structure (XAFS) can be used to study compounds and complexes on solid surfaces. However, such studies are difficult to perform when alkylxanthates are adsorbed on sulphide minerals as it is very difficult to distinguish between sulphide and xanthate sulphurs. Brown *et al.* have recently written a review on the general possibility to use X-ray spectroscopic techniques in the study of adsorption on solid surfaces.[21]

3.6 Comments

The adsorption reactions to be studied take place at a solid-liquid interface. At this phase boundary it is experimentally very difficult to do *in-situ* identification of the species adsorbed as well as to distinguish between processes in the liquid phase and on the surface. The only spectroscopic technique allowing *in-situ* measurements is ATR. However, the sensitivity of the ATR technique is lower at *in-situ* than at *ex-situ* measurements as the solvent hamper the signal more than the air. Most of the *in-situ* studies use electrokinetic, electrochemical or calorimetrical techniques to determine a thermodynamic property of the system. Evaluation of a thermodynamic result requires knowledge of the absolute composition of the system. A severe drawback of thermodynamic investigations of phase boundaries is that the composition and/or the concentration of neither the ultimate surface layer nor the molecular layer of the solution phase close to the surface is known or can be determined with sufficient accuracy to be used for evaluation of thermodynamic studies. It is therefore very difficult/impossible to draw conclusions from such studies.

The other way to study adsorption processes is to analyse surfaces and liquid phases separately both before and after treatment. The *ex-situ* measurements also have drawbacks such as the possibility to side reactions at the separation step and at sample preparation of the solid. It must be assumed that no such side reactions take place. A large number of vibration spectroscopic studies has however indicated that there is no or a very limited influence of possible side reactions.

With the present knowledge of the chemical and physical composition of surfaces, analytical and structural methods, e.g. different kinds of spectroscopic techniques, are to be preferred. Thermodynamic methods are less informative as long as we do not know with sufficient accuracy the kind of species and its concentrations responsible for the determined thermodynamic effect at the adsorption processes. This is obvious when electrochemical techniques such as cyclic voltammetry are used. A reaction which is not previously known, e.g. reactions of adsorbates at the phase boundary, must be assumed; the stated reaction is assumed, *not* proven. Such claimed reactions and reaction mechanisms must therefore be proven independently by a non-thermodynamic technique before such a postulation can be accepted.

To sum up, three levels of understanding of adsorption processes on solid surfaces in solution can be distinguished: a) the analytical chemical composition of the surface and the adsorbate, which can be divided in (1) precipitation, (2) chemisorbed surface complexes and (3) physisorbed species, b) the structure of the ultimate surface layer and the structural arrangement of the adsorbate relative to the underlying surface and c) the thermodynamics of the adsorption process. It has been found that DRIFT is a very informative technique at the study of semiconducting materials such as the sulphide minerals. Methods for detailed structural characterization of surfaces and adsorbates are available, e.g. grazing incident reflEXAFS and fluorescence yield EXAFS. However, so far these methods have only been applied on metals, and oxide and clay mineral surfaces.[20] To be able to understand thermodynamic results, the points *a* and *b* above must be known. So far, no thermodynamic results have been reported on surfaces sufficiently characterized for a complete thermodynamic understanding.

4. OVERVIEW OF THE CRYSTAL STRUCTURES OF SULPHIDE MINERALS

Knowledge of the crystal structures of the sulphide mineral studied is very important in order to understand the mechanism of hydrophobation with sulphur donor collectors. If a chemisorption process shall be possible there must be metal ion coordination sites available in the surface. The crystal structure can also imply possible oxidation products at grinding in the presence of oxygen and other oxidizing agents, and thereby also the easiness to oxidation. The structures can be divided into three main groups depending on the type of sulphur in the compound: compounds with a) disulphide ions, S_2^{2-}, b) sheets or clusters of sulphur atoms with sulphur-sulphur distances in the range 3.1–3.4 Å, and c) sulphide ions, S^{2-}, as different products and amounts of these products are formed upon oxidation of sulphur in these compounds. The crystal structures of some of the most important sulphide minerals are given below.

Galena, PbS, has a rocksalt type structure with lead and sulphide ions in place of the sodium and chloride ions, respectively.[22] Each lead ion is surrounded by six sulphide ions in an octahedral fashion, and each sulphide is octahedrally surrounded by six lead ions. The galena structure is given in Fig. 2. Crystallographic data: cubic, $Fm\bar{3}m$ (No. 225), $a = 5.9315$ Å and $Z = 4$.

Pyrite, FeS_2, has a cubic structure built up of iron(II) and disulphide, S_2^{2-}, ions. Pyrite has a modified rocksalt structure, where the iron(II) and disulphide ions are

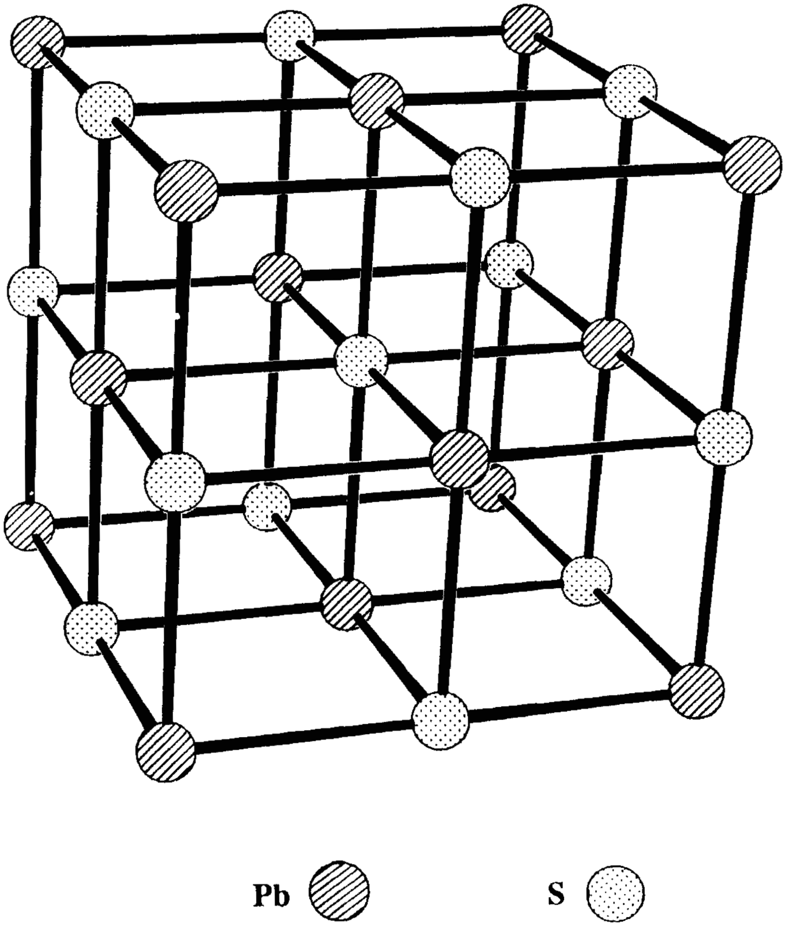


Figure 2 Crystal structure of galena.

in the positions of the sodium and chloride irons, respectively.[23-26] The iron(II) ions are surrounded by six sulphur atoms in an octahedral fashion, and each sulphur is surrounded by another sulphur and three iron(II) ions in a distorted tetrahedral configuration. The structure of pyrite is given in Fig. 3. Crystallographic data: cubic, $Pa\bar{3}$ (No. 205), a = 5.4179 Å and Z = 4.

Sphalerite, ZnS, has a structure similar to that of diamond. One half of the carbon atoms is replaced by zinc ions, and the other half by sulphide ions, in such a way that each ion is tetrahedrally surrounded by four counterions.[27] The sphalerite structure is given in Fig. 4. Crystallographic data: cubic, $F\bar{4}3$m (No. 216), a = 5.4033 Å and Z = 4.

Chalcopyrite, $CuFeS_2$, crystallizes in a structure very similar to sphalerite, where half of the zincs are replaced by copper, and the other half iron.[28-30] Chalcopyrite

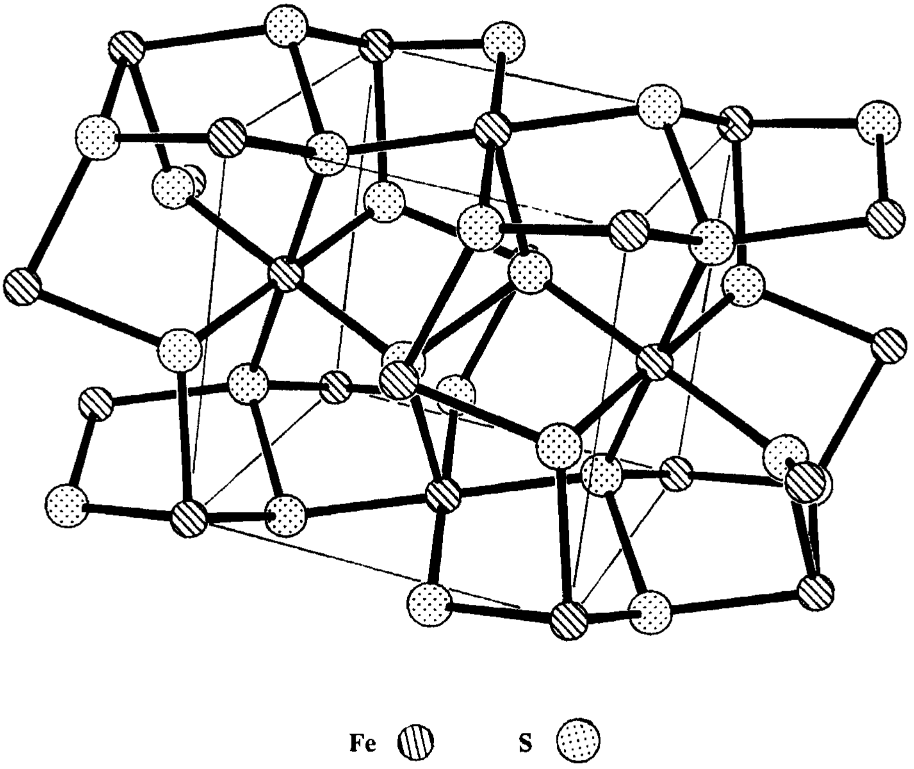


Figure 3 Crystal structure of pyrite.

contains only sulphide ions, and due to the tetrahedral configuration around the metal ions it is expected that metal ion coordination sites are available in the surface. The structure of chalcopyrite is given in Fig. 5. Crystallographic data: tetragonal, $I\bar{4}2d$ (No. 122), $a = 5.289$ Å, $c = 10.423$ Å and $Z = 4$.

Chalcocite, Cu_2S, undergoes a phase transition at 104°C. Above this transition point chalcocite has a small hexagonal unit cell containing two formula units, in which the sulphide ions are arranged in a nearly perfect hexagonal closest packing. It has been shown that the coppers are distributed throughout the interstices, almost as in a fluid state, with only partial concentration at the tetrahedral, triangular as well as two-coordinated sites.[31,32] The electrical conductivity and the diffusion coefficient for copper in this phase are unusually large.[31,32] Crystallographic data: hexagonal, $P6_3/mmc$ (No. 194), $a = 3.89$ Å, $c = 6.88$ Å and $Z = 2$.

An extremely complicated structure is formed below the transition point, 'low chalcocite', where each unit cell contains 48 formula units. The structure consists of hexagonal close packed sulphide ions, in which one third of the coppers occupies triangular interstices within the close packed sulphide layers to form triangular sheets. The remaining coppers occupy triangular sites between the close packed sulphide layers.[33,34] The coordination chemistry of copper(I) is characterized by

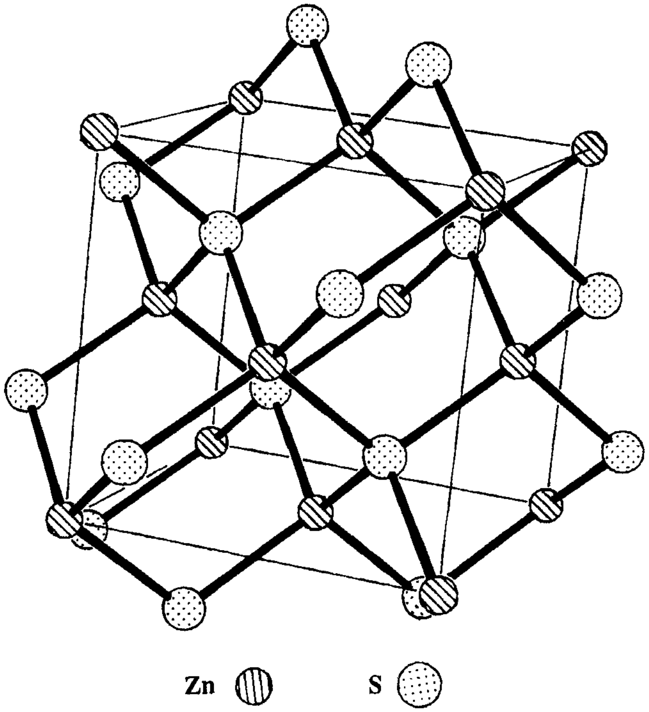


Figure 4 Crystal structure of sphalerite.

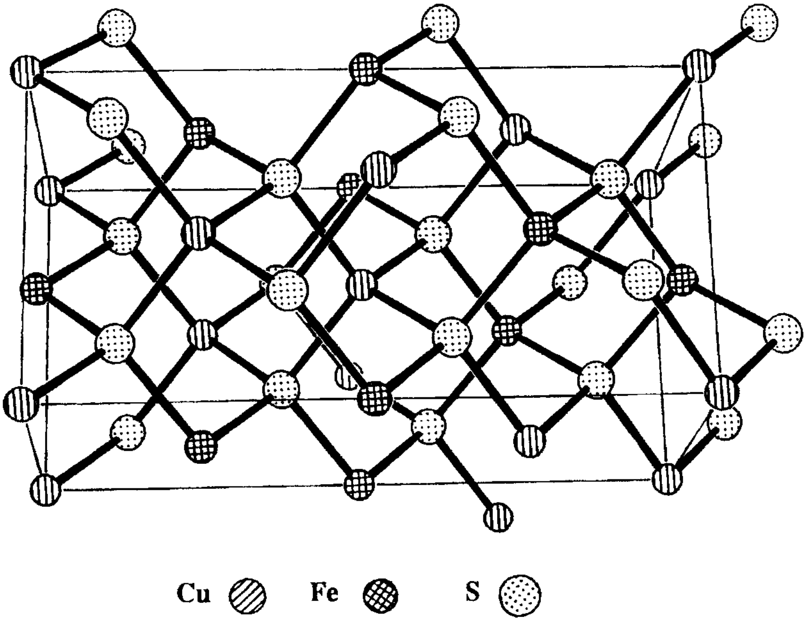


Figure 5 Crystal structure of chalocopyrite.

two- (linear), three- (trigonal) and four- (tetrahedral) coordination. This means that there may only be few free coordination sites available, at one vertex of tetrahedrally coordinated copper, for formation of chemisorbed complexes without structural rearrangements on the surface. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 15.246 Å, b = 11.884 Å, c = 13.494 Å, β = 116.35° and Z = 48.

Acanthite, Ag_2S, contains an arrangement of approximately body-centered sulphide ions. The silver ions in the lattice are either linearly coordinated or three-coordinated in a flattened trigonal pyramid.[35] Acanthite undergoes a phase transition at 173°C to a cubic form, in which a body-centered sulphide lattice builds up the structure, and where the silver ions are distributed among three different types of interstices.[36] Crystallographic data: monoclinic, $P2_1/n$ (No. 14), a = 4.231 Å, b = 6.930 Å, c = 9.526 Å, β = 125.48° and Z = 4.

Covellite, CuS, has a rather complex crystal structure containing two types of sulphide anions, sulphide, S^{2-}, and disulphide, S_2^{2-}, and both copper(I) and copper(II) cations.[37–39] A better formula for covellite may be $Cu_2S \cdot CuS_2$. The structure of covellite shows copper(II) cations in the triangular interstices and copper(I) ions in the tetrahedral interstices. The tetrahedra share corners to form a continuous layer, and the copper(II) ions in the trigonal interstices build a planar CuS layer. The resulting structure thus consists of a sheet of CuS_3 triangles sharing corners, sandwiched between a double layer of CuS_4 tetrahedra. Disulphide ions link the layers. The structure of covellite is given in Fig. 6. Crystallographic data: trigonal, $P6_3/mmc$ (No. 194), a = 3.976 Å, c = 16.382 Å and Z = 6.

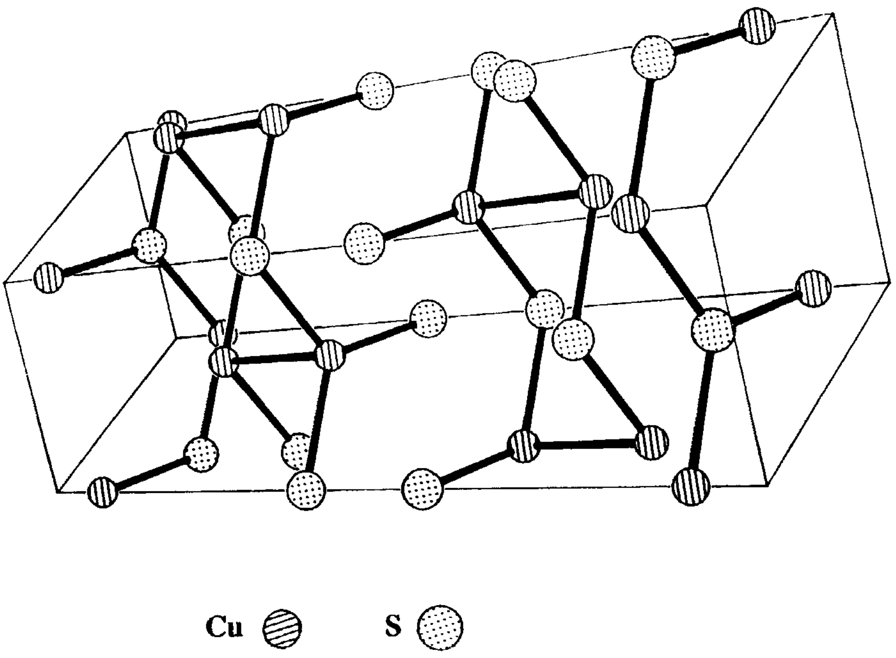


Figure 6 Crystal structure of covellite.

Marcasite, FeS_2, is an ortorhombic polymorph of pyrite.[40–42] The nearest neighbour configuration in marcasite is the same as in pyrite. The structure of marcasite is given in Fig. 7. Crystallographic data: ortorhombic, *Pnn*2 (No. 34), a = 4.4431 Å, b = 5.4245 Å, c = 3.3871 Å and Z = 2.

Arsenopyrite, FeAsS, has a structure very similar to that of marcasite.[43–45] The replacement of one half of the sulphurs by arsenics leads to that the unit cell has the double volume compared to marcasite, see structure of arsenopyrite in Fig. 8. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 5.744 Å, b = 5.675 Å, c = 5.785 Å, β = 112.17° and Z = 4.

Troilite, FeS, has a NiAs type structure, where each iron(II) ion is surrounded by six sulphide ions in a somewhat irregular octahedron; the Fe-S bond distances vary in the range 2.36–2.72 Å and the S-S distances vary in the range 3.348–3.750 Å.[46] Troilite contains sulphur only as isolated sulphide ions even though some S-S distances are significantly shorter than in structures of close-packed sulphide ions. Crystallographic data: hexagonal, $P\bar{6}2c$ (No. 190), a = 5.962 Å, c = 11.750 Å and Z = 12.

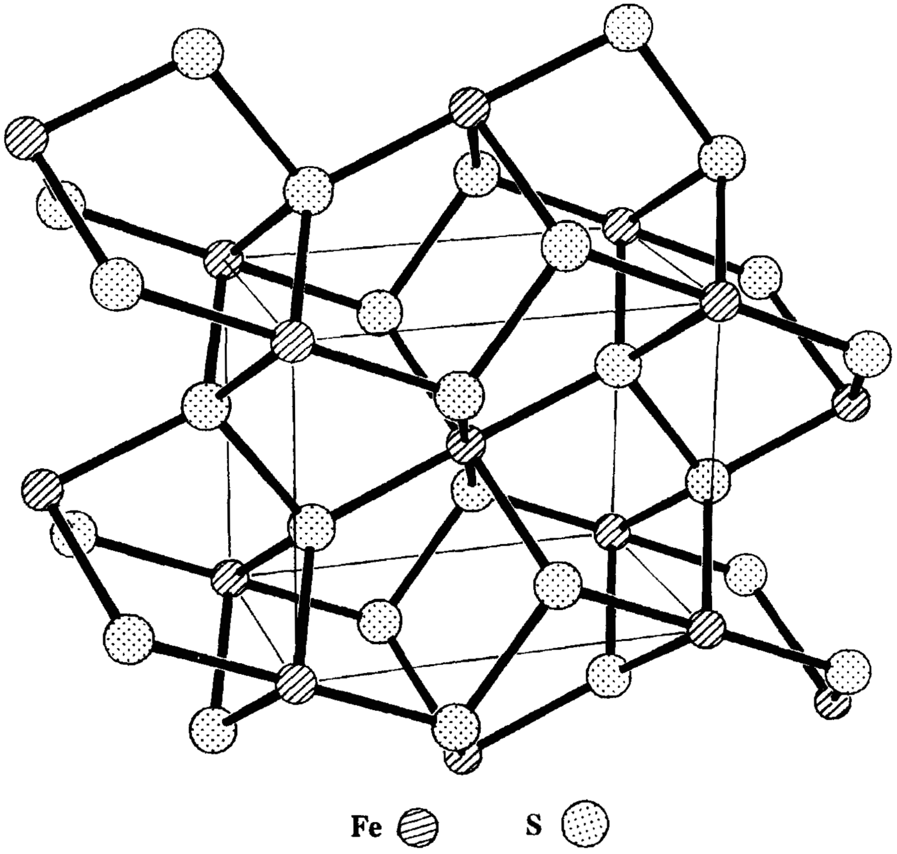


Figure 7 Crystal structure of marcasite.

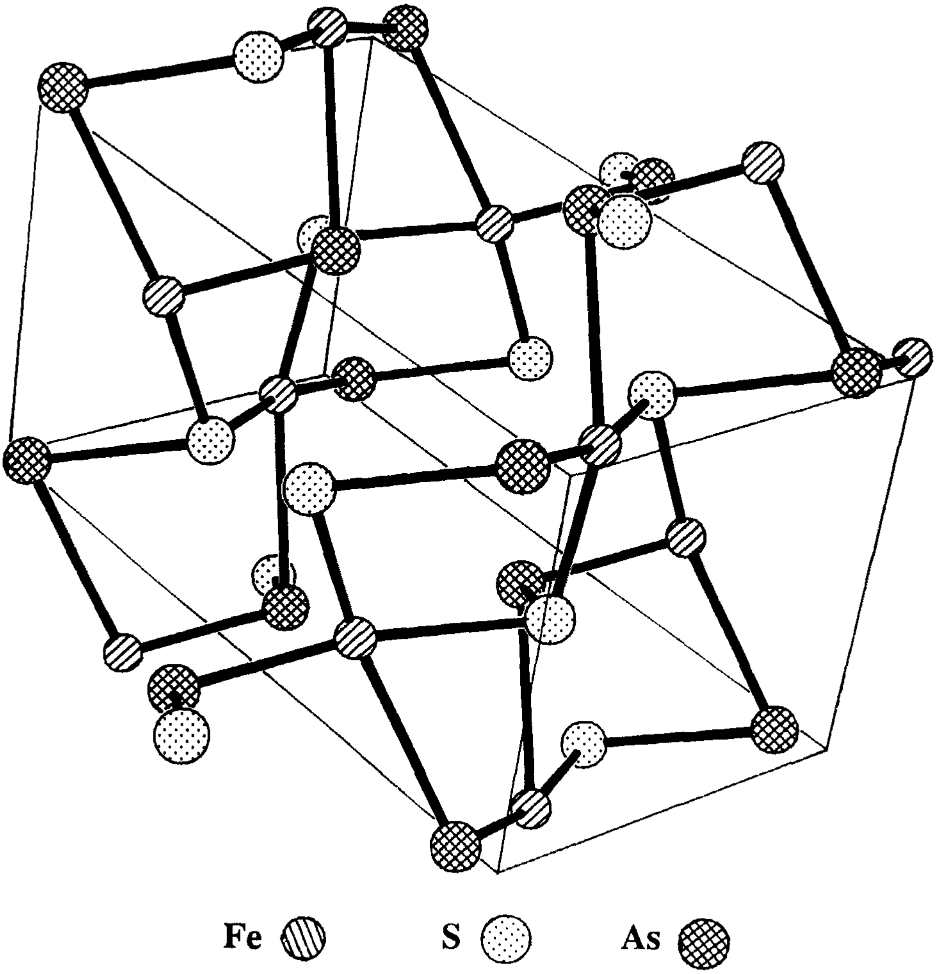


Figure 8 Crystal structure of arsenopyrite.

Pentlandite, (Ni, Fe)$_9$S$_8$, has a complicated face-centered cubic structure. Each unit cell contains 32 sulphide ions, and totally 36 irons and nickels occupy 4 octahedral and 32 tetrahedral interstices.[47–50] The tetrahedrally coordinated irons and nickels are clustered eight and eight in cubic groups. The shortest S-S distance in pentlandite is 3.36 Å and the metal-metal distances in the tetrahedral sites are as short as 2.5 Å, which is comparable to the metal-metal distances in metallic iron and nickel. Crystallographic data: cubic, $Fm\bar{3}m$ (No. 225), a = 9.977, 10.038, 10.044 Å (depending on sample) and $Z = 4$.

Pyrrhotite, FeS_{1-x}, has a very complicated structure based on the NiAs type structure.[51–53] The shortest S-S distance in pyrrhotite is 3.39 Å. Crystallographic data: four-dimensional space group W^{Pna2_1}, a = 11.952 Å, b = 6.892 Å, c = 5.744 Å;

it can also be expressed as ortorhombic, *Ccmm* (No. 63), a = 5.976 Å, b = 3.446 Å, c = 5.744 Å and Z = 4.

Millerite, NiS, has a rhombohedral structure in which both nickel and sulphur have fivefold coordination.[54,55] The sulphurs are arranged in triangles, which form trigonal prismatic columns. The nickels are also aranged in triangles, about the sides of these prisms, which gives a distorted square pyramidal configuration around nickel. The shortest S-S distance is 3.24 Å, and the Ni-Ni distance in millerite is also short, 2.534 Å, which is to be compared with the corresponding distance in metallic nickel, 2.492 Å. The millerite structure is given in Fig. 9. Crystallographic data: trigonal, *R3m* (No. 160), a = 9.610 Å, c = 3.1499 Å and Z = 9.

Molybdenite, MoS_2, has a sheet structure where a sheet of molybdenum is sandwiched between two sheets of sulphurs. The S-S distances within the sulphur sheets are short, 3.15 Å.[56] The molybdenite structure is given in Fig. 10. Crystallographic data: hexagonal, $P6_3/mmc$ (No. 194), a = 3.166 Å, cgonal = 18.41 Å and Z = 3.

Realgar, AsS, is built up of cagelike As_4S_4 molecules, where each of the four independent arsenics is bonded to another arsenic and two sulphurs, and each sulphur coordinates two arsenics.[57] The shortest S-S distance within the cage is 3.35 Å. The realgar structure is given in Fig. 11. Crystallographic data: monoclinic, $P2_1/n$ (No. 14), a = 9.325 Å, b = 13.571 Å, c = 6.587 Å, β = 106.38° and Z = 4.

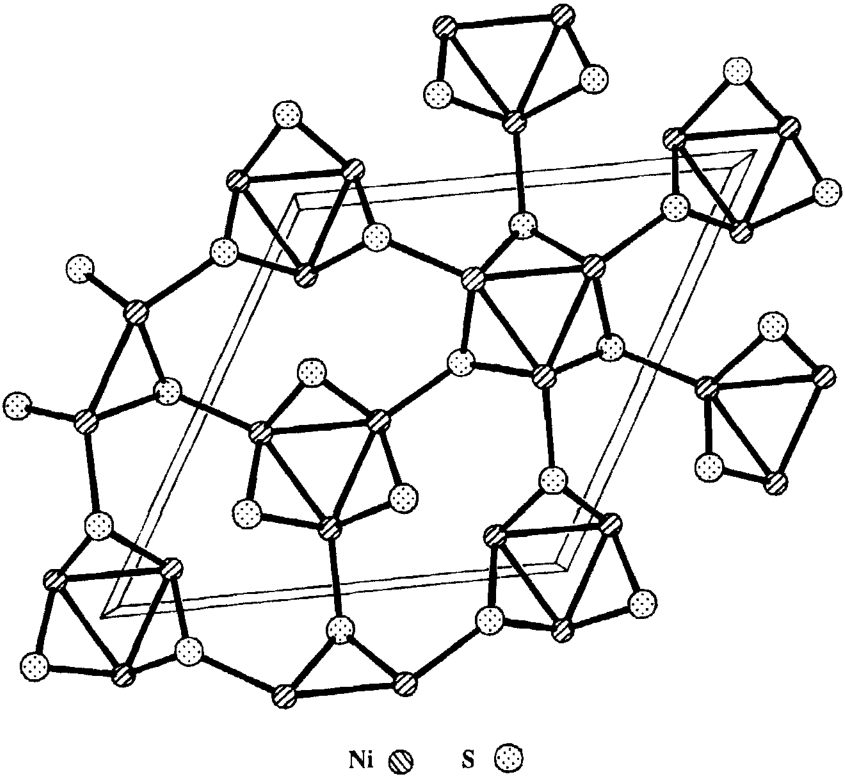


Figure 9 Crystal structure of millerite.

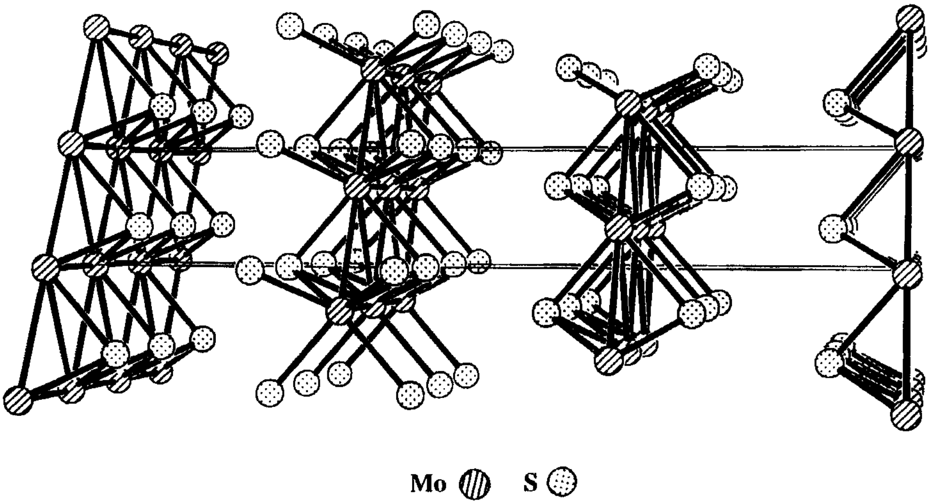


Figure 10 Crystal structure of molybdenite.

Orpiment, As_2S_3, contains trigonal pyramidal AsS_3 units, which share corners to form sixmembered rings in a corrugated layer.[57,58] The shortest S-S distance is 3.242 Å in this structure. The orpiment structure is given in Fig. 12. Crystallographic data: monoclinic, $P2_1/n$, $a = 11.475$ Å, $b = 9.577$ Å, $c = 4.256$ Å, $\beta = 90.68°$ and $Z = 4$.

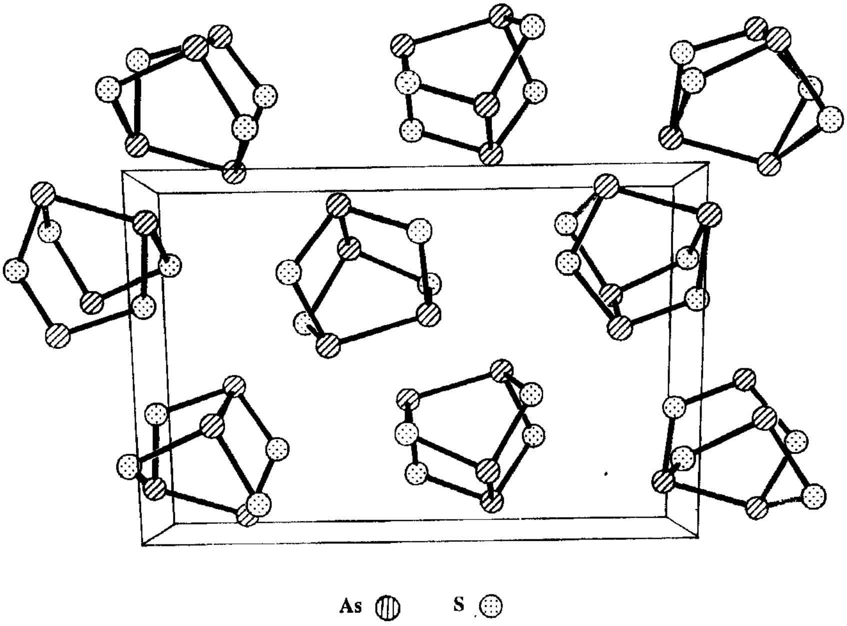


Figure 11 Crystal structure of realgar.

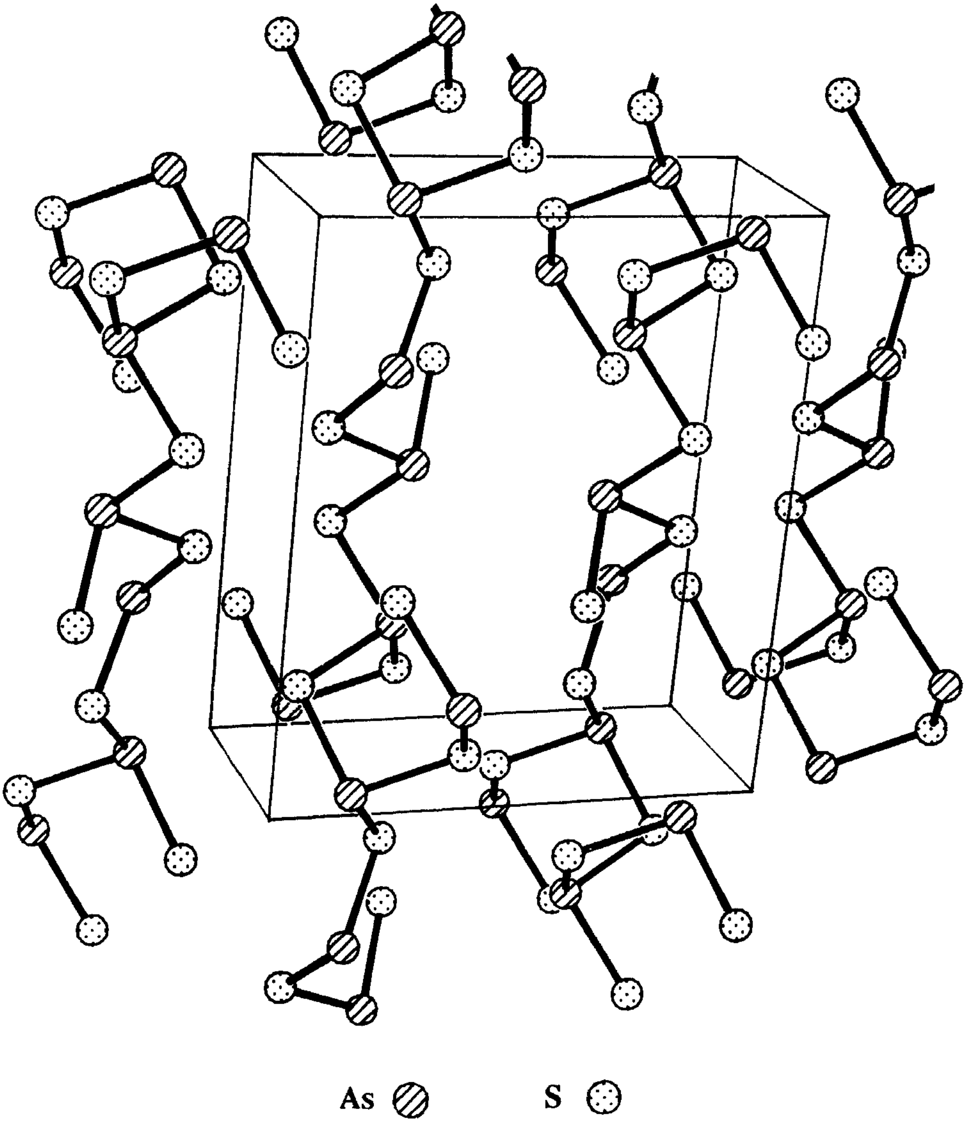


Figure 12 Crystal structure of orpiment.

5. OVERVIEW OF THE CRYSTAL STRUCTURES OF METAL ALKYLXANTHATES, *O,O*-DIALKYLDITHIOPHOSPHATES AND *N,N*-DIALKYL DITHIOCARBAMATES

A short overview of some structures of metal complexes with bidentate ligands coordinating through two sulphur atoms will be given in this section to show the coordination properties in a sulphur surrounding of the metal ions present in the minerals discussed above. The structures of metal alkylxanthate, *O,O*-diethyldithiophosphate and *N,N*-dialkyldithiocarbamate complexes in the solid state will be presented. These ligands/anions have a monovalent negative charge, and the two C-S bonds are equal in bond strength and distance. The electron donating properties increase slightly in the order *O,O*-diethyldithiophosphate < *N,N*-dialkyldithiocarbamate < alkylxanthate.[59] More detailed review articles of the coordination chemistry of metal alkylxanthates[60] and dialkyldithiocarbamates[61,62] were presented around 1980.

5.1 Zinc

Zinc ethylxanthate, $Zn(S_2COC_2H_5)_2$. Each ethylxanthate ion is bridging between two zinc ions and each zinc coordinates four different ethylxanthate ions forming an infinite two-dimentional lattice.[63] The average Zn-S bond distance is 2.36 Å, and the S-Zn-S angles are in the range 104.9–114.8°. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), $a = 18.278$ Å, $b = 5.700$ Å, $c = 11.381$ Å, $\beta = 101.47°$ and $Z = 4$.

Zinc isopropylxanthate, $Zn(S_2COCH(CH_3)_2)_2$. The structure is built up of tetramers forming 16-membered rings where half of the isopropylxanthate ions bridge between two zinc ions and the other half act as bidentate ligands.[64] The Zn-S bond distances are in the range 2.307–2.408 Å. Crystallographic data: triclinic, $P\bar{1}$ (No. 2), $a = 10.915$ Å, $b = 13.167$ Å, $c = 10.393$ Å, $\alpha = 100.89°$, $\beta = 100.42°$, $\gamma = 101.33°$ and Z = 4.

Zinc diethyldithiophosphate, $Zn(S_2P(OC_2H_5)_2)_2$. One diethyldithiophosphate ion is bridging between two zinc ions, and the other diethyldithiophosphate ion is bidentately coordinated to one zincc.[65] The coordination figure around zinc is a distorted tetrahedron. The Zn-S bond distances are found in the range 2.337–2.401 Å. Crystallographic data: monoclinic, $P2_1/a$ (No. 14), $a = 12.084$ Å, b = 19.840 Å, $c = 8.463$ Å, $\beta = 113.99°$ and Z = 4.

Zinc diisopropyldithiophosphate, $Zn(S_2P(OCH(CH_3)_2)_2)_2$. The complex is dimeric, where each zinc coordinates four sulphurs in a distorted tetrahedron.[66] One of the dithiophosphate ions are bidentately coordinated to zinc, and the other is bridging between the to zinc in the dimer. The Zn-S bond distances are in the range 2.302–2.409 Å. Crystallographic data: monoclinic, $C2/c$ (No. 15), $a = 10.934$ Å, $b = 17.098$ Å, $c = 25.587$ Å, $\beta = 99.23°$ and Z = 8.

Zinc dimethyldithiocarbamate, $Zn(S_2CN(CH_3)_2)_2$. The structure consists of centrosymmetric dimers where two dithiocarbamate ions bridge between the two zinc ions and the other two are bidentately coordinated to zinc fulfilling a tetrahedral configuration around the zinc ions.[67] The Zn-S bond distances are 2.312, 2.333, 2.373 and 2.429 Å. Crystallographic data: monoclinic, $C2/c$ (No. 15), $a = 8.455$ Å, $b = 15.747$ Å, $c = 18.345$ Å, $\beta = 104.76°$ and $Z = 8$.

Zinc diethyldithiocarbamate, $Zn(S_2CN(C_2H_5)_2)_2$. This structure is built up in the same way as zinc dimethyldithiocarbamate.[68] Crystallographic data: monoclinic, $P2_1/c$ (No. 14), $a = 10.015$ Å, $b = 10.661$ Å, $c = 16.357$ Å, $\beta = 111.63°$ and $Z = 4$.

Zinc diisopropyldithiocarbamate, $Zn(S_2CN(CH(CH_3)_2)_2)_2$. This structure is isostructural with zinc diethyldithiocarbamate.[69] The four Zn-S bond distances are in the range 2.335–2.454 Å with a fifth Zn-S distance at 2.815 Å. Crystallographic data: monoclinic, $P2_1/a$ (No. 14), $a = 16.857$ Å, $b = 11.168$ Å, $c = 11.408$ Å, $\beta = 111.8°$ and Z = 4.

Tetraethylammonium tris(isopropyldithiocarbamato)zincate, $(C_2H_5)_4N[Zn(S_2COCH(CH_3)_2)_3]$. Zinc coordinates two monodentating and one bidentating ethylxanthate ions in a distorted tetrahedral fashion.[70] The Zn-S bond distances to the monodentate ethylxanthate ions are 2.299 and 2.312 Å, the Zn-S bond distances to the bidentating ligand is 2.422 and 2.457 Å. The S-Zn-S angle to the bidentate ligand is 73°, while the other S-Zn-S angles are close to the tetrahedral angle. Crystallographic data: ortorhombic, *Pbca* (No. 61), $a = 14.709$ Å, $b = 18.780$ Å, $c = 20.130$ Å and $Z = 8$.

5.2 Cadmium

Cadmium ethylxanthate, $Cd(S_2COC_2H_5)_2$. This structure is built up in the same way as the zinc ethylxanthate structure,[71] see above. The average Cd-S bond distance is 2.56 Å. Crystallographic data: monoclinic, *Pa* (No. 7), $a = 11.289$ Å, $b = 5.872$ Å, $c = 9.057$ Å $\beta = 90.28°$ and $Z = 2$.

Cadmium diisopropyldithiophosphate, $Cd(S_2P(OCH(CH_3)_2)_2)_2$. This structure is isomorphous with the corresponding zinc compound,[66] see above. The Cd-S bond distances are in the range 2.486–2.590 Å. Crystallographic data: monoclinic, *C2/c* (No. 15), $a = 10.964$ Å, $b = 16.906$ Å, $c = 26.490$ Å, $\beta = 99.91°$ and $Z = 8$.

Cadmium n-butylxanthate, $Cd(S_2COC_4H_9)_2$. Cadmium n-butylxanthate has the same kind of structure as the zinc and cadmium ethylxanthates,[72] see above. The tetrahedral coordination figure is fairly distorted in this structure with S-Cd-S angles in the range 95.3–121.5°. The average Cd-S bond distance is 2.59 Å. Crystallographic data: monoclinic, *P*2$_1$/*a* (No. 14), $a = 11.59$ Å $b = 5.84$ Å, $c = 25.7$ Å, $\beta = 101.73°$ and $Z = 4$.

Cadmium diethyldithiocarbamate, $Cd(S_2CN(C_2H_5)_2)_2$. This structure consists of dimers with four short, 2.536–2.644 Å and one long, 2.800 Å, Cd-S bond distances.[73] The configuration around cadmium is something between a tetragonal pyramid and a trigonal bipyramid. Crystallographic data: monoclinic, *P*2$_1$/*c* (No. 14), $a = 10.166$ Å, $b = 10.746$ Å, $c = 16.717$ Å, $\beta = 111.88°$ and $Z = 4$.

5.3 Lead

The reported solid state structures of lead(II) alkylxanthate, diethyldithiophosphate and dialkyldithiocarbamate complexes are build in the same way. Lead coordinates two ligands in a pyramidal fashion, where one of the sulphurs is stronger bonded than the other. The difference in Pb-S bond distance is generally 0.1 Å or more, and the angle S-Pb-S for the for strongly coordinated sulphurs is about 95°. There are two long Pb-S distances, hardly at bond distance, at about 3.5 Å completing a very distorted octahedron. In the following will only details of the structures be given.

Lead ethylxanthate, $Pb(S_2COC_2H_5)_2$. The Pb-S bond distances are 2.74 and 2.95 Å to one of the ethylxanthate ions, and 2.79 and 2.84 Å to the other.[74] Crystallographic data: monoclinic, *P*2$_1$/*c* (No. 14), $a = 13.267$ Å, $b = 4.301$ Å, $c = 22.722$ Å, $\beta = 109.27°$ and $Z = 4$.

Lead isopropylxanthate monopyridine, $Pb(S_2COCH(CH_3)_2)_2) \cdot NC_5H_5$. The Pb-S bond distances are 2.833 and 2.896 Å to one of the isopropylxanthate ion, and 2.722 and 3.057 Å to the other.[75] Perpendicular to the square-pyramid is a pyridine coordinated to the lead(II) ion at 2.55 Å. Crystallographic data: monoclinic, *P*2$_1$/*c* (No. 14), $a = 17.80$ Å, $b = 11.18$ Å, $c = 10.61$ Å, $\beta = 107.8°$ and $Z = 4$.

Lead n-butylxanthate, $Pb(S_2COC_4H_9)_2$. The Pb-S bond distances are 2.77 and 2.83 Å to one of n-butylxanthate ions, and 2.76 and 3.03 Å to the other.[76] Crystallographic data: monoclinic, *C2/c* (No. 15), a = 36.87 Å, b = 4.58 Å, c = 10.71 Å, β = 112.0° and Z = 4.

Tetraethylammonium tris(ethylxanthato)plumbate(II), $[(C_2H_5)_4N][Pb(S_2COC_2H_5)_3]$. Five sulphur atoms lie in an approximate plane, the sulphur and the lone pair forming the apex of an approximate pentagonal bipyramid.[77] There is a weak sulphur bridge between the $Pb(S_2COC_2H_5)_3^-$ anions indicating a possible dimeric association in the solid state. The average Pb-S bond distance is 3.02 Å and the average long Pb-S distance is 3.68 Å. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 11.07 Å, b = 19.3 Å, c = 15.1 Å, β = 112° and Z = 4.

Lead diethyldithiophosphate, $Pb(S_2P(OC_2H_5)_2)_2$. The Pb-S bond distances are 2.754 and 2.990 Å for one of the dimethyldithiocarbamate ions, and 2.790 and 3.022 Å for the other.[78] The long Pb-S distances are found at 3.469 and 3.471 Å. Crystallographic data: triclinic, $P\bar{1}$ (No. 2), a = 10.102 Å, b = 10.366 Å, c = 9.702 Å, α = 99.82 Å, β = 109.91°, γ = 86.17° and Z = 2.

Lead diisopropyldithiophosphate, $Pb(S_2P(OCH(CH_3)_2)_2)_2$. The structure is built up of polymeric chains.[79] Almost planar $Pb(S_2P)_2$ groups stack one above the other in a staggered arrangement joined by intergroup Pb-S bonds. These bonds may be considered as 'axial bonds' in the resultat sixfold coordination. The Pb-S bond distances are 2.766, 3.01 and 3.20 Å. Crystallographic data: monoclinic, $P2_1/n$, a = 25.290 Å, b = 10.067 Å, c = 9.335 Å, β = 95.97° and Z = 4.

Lead dimethyldithiocarbamate, $Pb(S_2CN(CH_3)_2)_2$. The Pb-S bond distances are 2.779 and 2.873 Å to both dimethyldithiocarbamate ions, and the long Pb-S distances are found at 3.361 and 3.859 Å.[80] Crystallographic data: ortorhombic, *Fdd2* (No. 43), a = 21.073 Å, b = 27.073 Å, c = 4.214 Å and Z = 4.

Lead diethyldithiocarbamate, $Pb(S_2CN(C_2H_5)_2)_2$. The Pb-S bond distances are 2.744 and 2.940 Å to one diethyldithiocarbamate ion, and 2.786 and 2.885 Å to the other.[81] The long Pb-S distances completing the distorted ocathedron are 3.445 and 3.554 Å. Crystallographic data: monoclinic, *Cc* (no. 9), a = 16.614 Å, b = 11.781 Å, c = 9.351 Å, β = 117.54° and Z = 4.

Lead diisoprophyldithiocarbamate, $Pb(S_2CN(CH(CH_3)_2)_2)_2$. The Pb-S bond distances are 2.673 and 2.843 Å to one of the diisopropyldithiocarbamate ions, and 2.681 and 2.859 Å to the other.[82] The long Pb-S distances are found at 3.513 and 3.541 Å. Crystallographic data: monoclinic, $P2_1/a$ (No. 14), a = 21.055 Å, b = 8.502 Å, c = 11.720 Å, β = 96.15° and Z = 4.

5.4 Copper

Any crystallographic determinations of copper(I) alkylxanthate structures have to my knowledge not been reported.

Copper(I) diisopropyldithiophosphate, $[CuS_2P(OCH(CH_3)_2)_2]_4$. Copper(I) diisopropyldithiophosphate exist as discrete tetramers in the solid state, where each tetramer contains a central tetrahedron of coppers.[83] Chelated to this tetrahedron through sulphur atoms are diisopropyldithiophosphate ions, where one of the sulphur atoms in the ligand bridges two coppers almost symmetrical at Cu-S bond distances of 2.256 and 2.272 Å. The other sulphur forms a bond with a third copper at 2.272 Å. Crystallographic data: ortorhombic, $P2_12_12_1$ (No. 19), a = 11.283 Å, b = 12.380 Å, c = 33.825 Å and Z = 4.

Copper(I) diethyldithiocarbamate, $[CuS_2CN(CH_3)_2]_4$. The structure is built up from discrete tetrameric molecules, $[CuS_2CN(CH_3)_2]_4$.[84] It comprises a central Cu_4-tetrahedron surrounded by four diethyldithiocarbamate ions. The average Cu-S bond distance is 2.26 Å, and the average Cu-Cu distance is 2.66 Å. Crystallographic data: tetragonal, $P\bar{4}2_1c$ (No. 114), a = 13.494 Å, c = 9.335 Å and Z = 2.

Copper(II) dimethyldithiocarbamate, $Cu(S_2CN(CH_3)_2)_2$. The structure is built up of discrete molecules, where the CuS_4 entity is planar.[85] The Cu-S bond distances in this planar entity are 2.309 and 2.319 Å. Two long Cu-S distances in the axial positions are found at 3.159 Å. Crystallographic data: monoclinic, $C2/c$ (No. 15), a = 15.243 Å, b = 9.538 Å, c = 8.086 Å, β = 101.31° and Z = 4.

Copper(II) diethyldithiocarbamate, $Cu(S_2CN(C_2H_5)_2)_2$. This structure is built up in the same way as the copper(II) dimethyldithiocarbamate,[86] see above. The Cu-S bond distances are 2.297, 2.301, 2.317 and 2.339 Å, and the long distances are 2.851 and 2.859 Å. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 9.907 Å, b = 10.627 Å, c = 16.591 Å, β = 113.87° and Z = 4.

Copper(II) diisopropyldithiocarbamate, $Cu(S_2CN(CH(CH_3)_2)_2)_2$. This structure is built up in the same way as the copper(II) dimethyldithiocarbamate,[87] see above. The Cu-S bond distances are 2.271, 2.283, 2.286 and 2.291, and the long distances are 3.15 Å. Crystallographic data: triclinic, $P\bar{1}$ (No. 2), a = 11.573 Å, b = 11.706 Å, c = 7.626 Å, α = 96.25°, β = 96.30°, γ = 88.72° and Z = 2.

5.5 *Silver*

Tetramethylammonium bis(diethyldithiophosphato)argentate(I), $(NH_4)_2[Ag(S_2P(OC_2H_5)_2)_2]_2$. The bis(diethyldithiophosphateargentate(I) ion is dimeric in this structure.[88] The silver ion is surrounded by four sulphurs in a distorted tetrahedral fashion. One sulphur is bridging between silver atoms, where one Ag-S bond distance, 2.679 Å, is significantly longer than the other one, 2.868 Å. The other sulphur atom of this diethyldithiophosphate ligand is coordinated to one silver at 2.728 Å. The other diethyldithiophosphate ion is monodentately coordinated to silver at 2.517 Å. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 12.966 Å, b = 16.159 Å, c = 12.898 Å, β = 106.0° and Z = 2.

Silver(I) dipropyldithiocarbamate, $[AgS_2CN(CH_3)_2]_6$. The structure is built up of from discrete hexameric molecules, $[AgS_2CN(CH_3)_2]_6$.[89] The silver atoms are situated in the central part of a hexamer and form a somewhat distorted octahedron with six comparatively short and six longer edges. The short edges correspond to silver-silver distances, somewhat longer than in metallic silver. The long edges form two centrosymmetrically related triangles in the silver octahedron. Outside each of the other six phases one dipropyldithiocarbamate ligand is situated. One of the sulphurs is coordinated to silver, and the other to two silvers. The silver coordination is three-fold but not planar. The average Ag-S bond distance is 2.49 Å, and the average Ag-Ag distance is 2.66 Å. Crystallographic data: triclinic, $P\bar{1}$ (No. 2), a = 11.374 Å, b = 12.375, c = 12.997, Å, α = 96.10°, β = 116.40°, γ = 83.24° and Z = 1.

5.6 *Iron*

Iron(III) ethylxanthate, $Fe(S_2CN(C_2H_5)_2\ )_3$. Three ethylxanthate ions are coordinated to iron, where the six sulphurs form a slightly distorted octahedron around iron.[90,91]

The Fe-S bond distances are 2.308 and 2.326 Å. Crystallographic data: trigonal, $R\bar{3}$ *(No. 148)*, a = 14.910 Å, c = 13.318 Å and Z = 6.

Iron(II) diethyldithiocarbamate, $Fe(S_2CN(C_2H_5)_2)_2$. The structure consists of dimers where iron is surrounded by five sulphurs.[92] The four short Fe-S bond distances are in the range 2.402–2.453 Å, and the fifth sulphur, perpendicular to four short Fe-S bonds is found at 2.613 Å. The coordination figure around iron is a distorted trigonal bipyramid. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 10.0540 Å, b = 10.6937 Å, c = 16.5824 Å, β = 112.6° and Z = 4.

Iron(III) dimethyldithiocarbamate, $Fe(S_2CN(CH_3)_2)_3$. The structure is built up of discrete iron(III) dimethyldithiocarbamate molecules, where six sulphurs surround the iron(III) ion in form of a slightly distorted octahedron.[93,94] The average Fe-S bond distance increases with increasing temperature; 2.303 Å (25 K), 2.339 Å (150 K), 2.396 Å (295 K) and 2.415 Å (400 K). Crystallographic data: ortorhombic, *Pbca* (No. 61); at 25 K: a = 17.288 Å, b = 19.947 Å, c = 9.998 Å and Z = 8, at 150 K: a = 17.419 Å, b = 20.272 Å, c = 10.060 Å and Z = 8, at 295 K: a = 17.569 Å, b = 20.518 Å, c = 10.118 Å and Z = 8, and at 400 K: a = 17.6961 Å, b = 20.7906 Å, c = 10.1630 Å and Z = 8,.

Iron(III) diethyldithiocarbamate, $Fe(S_2CN(C_2H_5)_2)_3$. The structure is built up of iron(III) diethyldithiocarbamate molecules where iron coordinates three diethyldithiocarbamate ions with the sulphurs in a slightly distorted octahedron.[95] A phase transition takes place on cooling iron(III) diethyldithiocarbamate, and the structure is reported at 297 and 79 K. The average Fe-S bond distance is 2.358 Å at 297 K and 2.306 Å at 79 K. Crystallographic data: 297 K: monoclinic, $P2_1/c$ (No. 14), a = 14.29 Å, b = 10.37 Å, c = 17.87 Å, β = 116.6°, Z = 4, and at 79 K, crystallographic data: monoclinic, *C2/n* (No. 15), a = 13.96 Å, b = 10.24 Å, c = 17.71 Å, β = 116.5° and Z = 4.

Iron(III) dibutyldithiocarbamate, $Fe(S_2CN(C_4H_9)_2)_3$. The structure is built up in the same way as iron(III) diethyldithiocarbamate.[96] The average Fe-S bonds distance is 2.367 Å. Crystallographic data: hexagonal, $P3_1/c$, a = 14.970 Å, c = 14.390 Å and Z = 2.

Iron(IV) tridimethyldithiocarbamate pentaiodide, $[Fe(S_2CN(CH_3)_2)_3]I_5$. The iron in tris(dimethyldithiocarbamato)iron(IV) ions coordinates three dimethylcarbamate ligands in a slightly distorted octahedron.[97] The average Fe-S bond distance is 2.299 Å, which significantly shorter than in the iron(III) dialkyldithiocarbamates, see above. Crystallographic data: triclinic, $P\bar{1}$ (No. 2), a = 17.41 Å, b = 10.197 Å, c = 10.184 Å, α = 74.71°, β = 73.29°, γ = 89.19° and Z = 2.

5.7 Nickel

The reported solid state structures of nickel(II) alkylxanthate, dialkyldithiophosphate and dialkyldithiocarbamate complexes show that they are all monomeric molecules, which are built up in the same way. Nickel coordinates two ligands where the NiS_4 entity is planar. In the following will only details of the structures be given.

Nickel ethylxantathate, $Ni(S_2COC_2H_5)_2$. The Ni-S bond distances are 2.23 and 2.24 Å, and the S-Ni-S angle is 79.5°.[98] Crystallographic data: ortorhombic, *Pbca* (No. 61), a = 7.57 Å, b = 7.23 Å, c = 20.92 Å and Z = 4.

Nickel ethylxantathate, $Ni(S_2COC_2H_5)_2$. A triclinic phase of nickel(II) ethylxanthate has also been reported.[99] Crystallographic data: triclinic, $P\bar{1}$ (No. 2, a = 8.835 Å, b = 10.299 Å, c = 8.143 Å, α = 91.81°, β = 122.33°, γ = 70.52° and Z = 2.

Nickel phenyl-4-isobutylxantathate, $Ni(S_2COC_6H_4C(CH_3))_2$. The average Ni-S bond distance is 2.215 Å.[100] Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 16.826 Å, b = 6.978 Å, c = 28.282 Å, β = 131.74° and Z = 4.

Nickel diethyldithiophosphate, $Ni(S_2P(OC_2H_5)_2)_2$. The Ni-S bond distances are 2.230 and 2.236 Å, and the S-Ni-S angle is 88.5°.[101] Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 10.493 Å, b = 10.300 Å, c = 8.76 Å, β = 102.59° and Z = 2.

Nickel dimethyldithiocarbamate, $Ni(S_2CN(CH_3)_2)_2$. The average Ni-S bond distance is 2.181 Å, and the S-Ni-S angle is 78.9°.[102] Crystallographic data: monoclinic, $P2_1/a$ (No. 14), a = 15.62 Å, b = 17.83 Å, c = 8.16 Å, β = 110.5° and Z = 4.

Nickel diethyldithiocarbamate, $Ni(S_2CN(C_2H_5)_2)_2$. The Ni-S bond distances are 2.195 and 2.207 Å, and the S-Ni-S angle is 79.18°.[103] Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 6.189 Å, b = 11.537 Å, c = 11.603 Å, β = 95.85° and Z = 4.

Nickel diethyldithiocarbamate, $Ni(S_2CN(C_2H_5)_2)_2$. A triclinic phase of nickel(II) diethyldithiocarbamate has also been reported.[104] Crystallographic data: triclinic, $P\bar{1}$ (No. 2), a = 6.521 Å, b = 6.798 Å, c = 7.633 Å, α = 67.21°, β = 67.34°, γ = 85.79° and Z = 1.

Nickel diisopropyldithiocarbamate, $Ni(S_2CN(CH(CH_3)_2)_2)_2$. The Ni-S bond distances are 2.179, 2.181, 2.182 and 2.183 Å, and the S-Ni-S angle is 79.2°.[105] Crystallographic data: monoclinic, $P2_1/a$ (No. 14), a = 15.62 Å, b = 17.83 Å, c = 8.16 Å, β = 110.5° and Z = 4.

5.8 Molybdenum

Molybenum(IV) diethyldithiocarbamate, $Mo(S_2COC_2H_5)_4$. Molybdenum coordinates four diethyldithiocarbamate ions with the sulphurs forming a square antiprismatic/triangular dodecahedron around molybdenum.[106] Crystallographic data: monoclinic, $C2/c$ (No. 15), a = 17.928 Å, b = 10.362 Å, c = 17.418 Å, β = 92.10° and Z = 4.

Tetrakis(diethyldithiocarbamato)molybenum(V) chloride, $[Mo(S_2COC_2H_5)_4]Cl$. Molybdenum coordinates four diethyldithiocarbamate ions with the sulphurs forming a dodecahedron around molybdenum.[107] The average Mo-S bond distances is 2.519 Å. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 18.543 Å, b = 8.387 Å, c = 15.870 Å, β = 101.05° and Z = 2.

5.9 Arsenic

Arsenic(III) ethylxanthate, $As(S_2COC_2H_5)_3$. This structure consists of molecules where the ethylxanthate ions are monodentately coordinated to arsenic at 2.28 Å.[108] The other sulphur in the ethylxanthate ion is found at 2.94 Å from arsenic. These six sulphurs forms a very distorted octahedron around arsenic. The S-As-S angle is 129.5°, and S-As-S angle with sulphurs from the the same ethylxanthate ion is 92.° Crystallographic data: trigonal, $R\bar{3}$ (No. 148), a = 10.04 Å, α = 102.67° and Z = 2.

Arsenic(III) diethyldithiocarbamate, $As(S_2CN(C_2H_5)_2)_3$. The structure consists of arsenic(III) diethyldithiocarbamate molecules were arsenic coordinates the diethyldithiocarbamate ligands through one of the sulphurs.[109] The average As-S bond distances are 2.349 Å, and the average of the other three As-S distances are 2.845 Å. The configuration around iron is a distorted octahedron. Crystallographic data: monoclinic, $P2_1/c$ (No. 14), a = 18.543 Å, b = 8.387 Å, c = 15.870 Å, β = 101.05° and Z = 2.

6. REACTION MECHANISMS FOR THE HYDROPHOBATION OF SULPHIDE MINERALS WITH ALKYLXANTHATE ION

6.1 Sphalerite, ZnS, and Synthetic Zinc Sulphide

Sphalerite, natural zinc(II) sulphide, is the most important zinc mineral. Sphalerite always contains some amount of iron (0.5–10%) and it can also contain lead and other metals. Sphalerite and galena are often associated in the same ore. This means that relatively large amounts of other metals in sphalerite may influence its properties, and thereby the possibility to separate it from other minerals in the same ore. Sphalerite has several unique properties compared with most of the other sulphide minerals of commercial importance, especially in connection with alkylxanthate flotation. Sphalerite and synthetic zinc sulphide surfaces are not readily oxidized, and the amount of soluble zinc compounds on the surfaces is low also at oxidizing conditions.[110] Sphalerite surfaces seem to be more inert in course of time, most probably due to formation of oxide compounds on the surfaces. It has however not been possible to detect and analyse these possible oxides by DRIFT technique. Zinc alkylxanthates have a much higher solubility in water than most of the other transition and heavy metal alkylxanthates,[111,112] (See Table 1). This means that the possibility to precipitation of zinc alkylxanthate on sphalerite surfaces does not exist when sphalerite powders are treated with dilute solutions of short-chained potassium alkylxanthates.

It is impossible to precipitate zinc alkylxanthate on sphalerite surfaces in aqueous slurries at the submillimolar concentrations of alkylxanthate used in industrial flotation processes when short-chained alkylxanthates are used as only small amounts of zinc are dissolved from the sphalerite surfaces. However, zinc(II) forms comparatively stable complexes with sulphur donor ligands,[111] and it has been shown that alkylxanthate complexes can be formed on sphalerite and synthetic zinc sulphide surfaces.[120,121]

It has been shown that sphalerite becomes flotable when it is treated with an aqueous solution of potassium dodecylxanthate.[122] This alkylxanthate ion with a long carbon chain can be attached to the sphalerite surfaces as solid zinc dodecylxanthate (the solubility of metal alkylxanthates in water decreases with increasing size of the alkyl group), and/or as a surface complex where the xanthate group in the dodecylxanthate ion is chemisorbed to the sphalerite surface. If a chemisorbed surface complex is formed, the dodecyl group is most probably large (long) enough to make contact with an air bubble in the flotation process. Sphalerite can also be made of flotable by activation with e.g. copper(II) ions before treatment of alkylxanthate ions.[123,124] It has been claimed both that only solid copper(I) alkylxanthate,[125] and that a mixture of dialkyl dixanthogen and copper(I) alkylxanthate[124] is present on copper activated sphalerite after treatment with

Table 1. Solubilities, s/M, and solubility products, K_s, of some lead(II), zinc, iron(II), iron(III), silver, copper(I) and nickel(II) salts in water.

Compound	s	K_s
PbS[a]	$5.6 \cdot 10^{-17}$	$3.2 \cdot 10^{-33}$
$PbCO_3$[b]	$3.8 \cdot 10^{-7}$	$1.4 \cdot 10^{-13}$
$PbSO_4$[b]	$1.0 \cdot 10^{-4}$	$1.1 \cdot 10^{-8}$
PbS_2O_3[b]	$3.0 \cdot 10^{-2}$	$9.0 \cdot 10^{-4}$
$Pb(C_2H_5COCS_2)_2$[c]	$1.7 \cdot 10^{-6}$	$2.1 \cdot 10^{-17}$
$Pb(C_5H_{11}COCS_2)_2$[d]	$6.3 \cdot 10^{-9}$	$1.0 \cdot 10^{-24}$
$Pb((C_2H_5O)_2PS_2)_2$[b]	$4.5 \cdot 10^{-5}$	$3.6 \cdot 10^{-13}$
ZnS[a]	$3.5 \cdot 10^{-15}$	$1.3 \cdot 10^{-20}$
$ZnCO_3$[b]	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-4}$
$Zn(C_2H_5COCS_2)_2$[c]	$1.1 \cdot 10^{-3}$	$4.9 \cdot 10^{-9}$
$Zn(C_5H_{11}COCS_2)_2$[d]	$7.4 \cdot 10^{-5}$	$1.6 \cdot 10^{-12}$
$Zn((C_2H_5O)_2PS_2)_2$[c]	$2.7 \cdot 10^{-3}$	$7.6 \cdot 10^{-8}$
Cu_2S[a]	$2.2 \cdot 10^{-18}$	$4.0 \cdot 10^{-53}$
$CuC_2H_5COCS_2$[c]	$2.3 \cdot 10^{-10}$	$5.2 \cdot 10^{-20}$
$Cu(C_2H_5O)_2PS_2$[c]	$7.9 \cdot 10^{-6}$	$6.3 \cdot 10^{-11}$
Ag_2S[a]	$1.3 \cdot 10^{-18}$	$8.8 \cdot 10^{-54}$
Ag_2CO_3[b]	$1.2 \cdot 10^{-4}$	$6.2 \cdot 10^{-12}$
$AgC_2H_5COCS_2$[c]	$7.1 \cdot 10^{-10}$	$5.0 \cdot 10^{-19}$
$Ag(C_2H_5O)_2PS_2$[c]	$3.5 \cdot 10^{-8}$	$1.2 \cdot 10^{-15}$
FeS_2[a]	$3.2 \cdot 10^{-26}$	$1.0 \cdot 10^{-51}$
$Fe(C_2H_5COCS_2)_2$[c]	$2.7 \cdot 10^{-3}$	$8.0 \cdot 10^{-8}$
$Fe(C_2H_5COCS_2)_3$[f]	$2.8 \cdot 10^{-7}$	$1.6 \cdot 10^{-25}$
NiS[a]	$7.1 \cdot 10^{-13}$	$5.0 \cdot 10^{-25}$
$NiCO_3$[b]	$9.3 \cdot 10^{-3}$	$8.6 \cdot 10^{-5}$
$Ni(C_2H_5COCS_2)_2$[c]	$7.0 \cdot 10^{-5}$	$1.4 \cdot 10^{-12}$
$Ni(C_2H_5O)_2PS_2)_2$[e]	$2.6 \cdot 10^{-3}$	$7.4 \cdot 10^{-8}$

[a] Ref. 113. [b] Ref. 114. [c] Refs. 115 and 116. [d] Ref. 117. [e] Ref. 118. [f] Ref. 119.

alkylxanthate ions. As sphalerite always contains other metals, the properties of synthetic zinc sulphide free from other metals and sphalerite containing only small amounts of iron, <0.5 %, will be discussed first. Synthetic zinc sulphide was prepared in both an excess and a deficit of sulphide ions. Powder X-ray diffraction measurements showed that the very same crystalline phase is obtained independent of stoichiometry at the preparation.[120] However, DRIFT spectra show that the surfaces have different composition, see Fig. 13. This shows that the composition of the surfaces is very sensitive to the conditions at the preparation.[120] It has not been possible to assign the bands in these spectra to any expected compounds such as zinc oxide, sulphate or carbonate, even though it seems very likely that some kind of aqua and/or hydroxo species is present on the surfaces, as a broad intense O-H band was found around 3500 cm^{-1}.[120] The DRIFT spectrum of synthetic zinc sulphide prepared in an excess of sulphide ions is dramatically changed after washing with water while no such change was observed after washing with acetone. The samples of sphalerite and of synthetic zinc sulphide prepared in an excess of zinc ions were not affected by the washing with either water or acetone. No or very small amounts of ethylxanthate species are adsorbed on the surfaces of synthetic zinc sulphide pretreated with or precipitated in an excess of sulphide ions after treatment with aqueous and acetone solutions of potassium ethylxanthate. On the other hand, on the surfaces of sphalerite and of zinc sulphide prepared in an excess of zinc(II) ions relatively large amounts of ethylxanthate species are adsorbed after

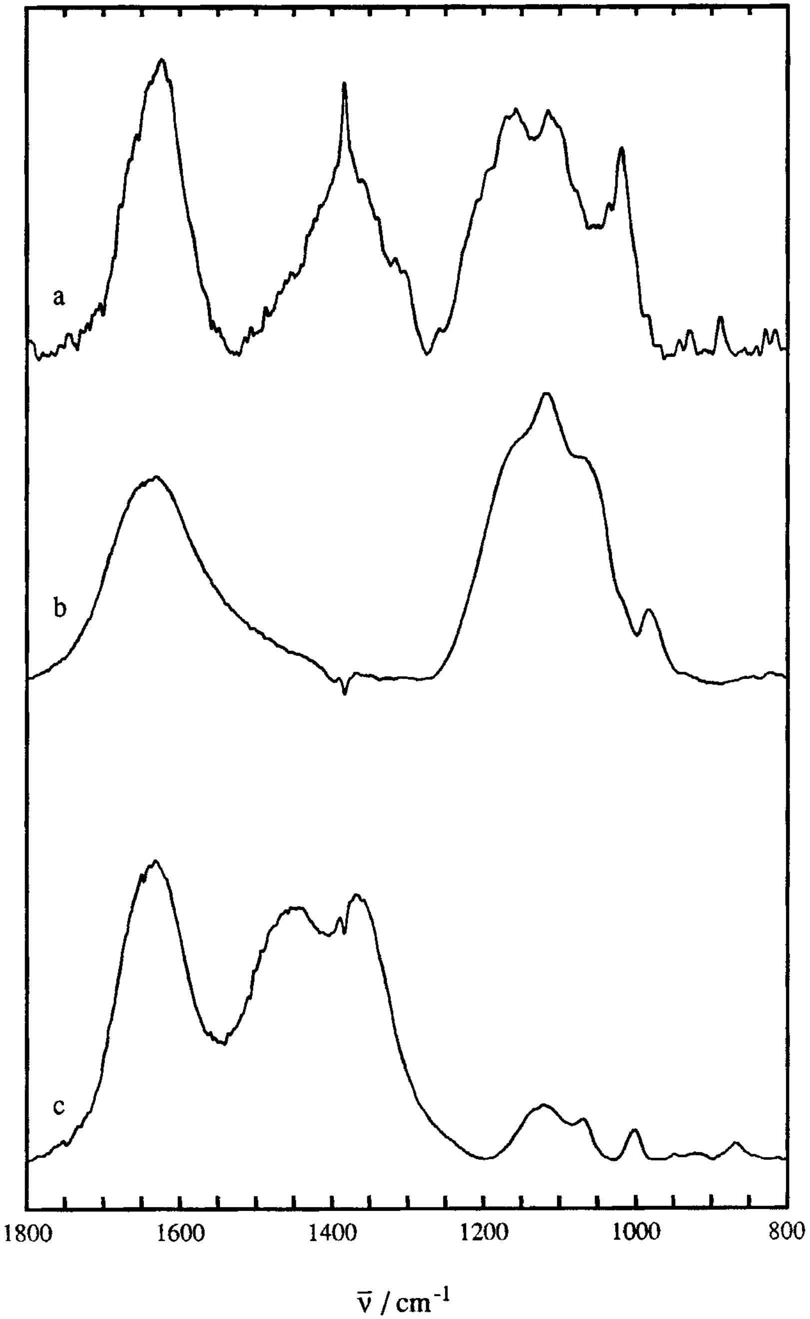


Figure 13 DRIFT spectra of (a) dryground sphalerite containing 0.5% iron, (b) synthetic zinc(II) sulphide precipitated in an excess of zinc(II) ions and (c) synthetic zinc(II) sulphide precipitated an excess of sulphide ions. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

the same treatment.[120] The DRIFT spectra of zinc sulphide and sphalerite with low iron content treated with potassium ethylxanthate are almost identical independently of solvent used.[120] The obtained DRIFT spectra of the ethylxanthate treated zinc sulphide and sphalerite surfaces differ markedly from the DRIFT spectrum of solid zinc(II) ethylxanthate, see Fig. 14. This shows very clearly that the ethylxanthate ions are adsorbed to the surfaces as chemisorbed surface complexes. One of the features in the DRIFT spectra of these adsorbed ethylxanthate species differing from the DRIFT spectrum of solid zinc(II) ethylxanthate is a band at 1290 cm^{-1}. This band is only observed in chemisorbed ethylxanthate complexes and in liquid diethyl dixanthogen, thus where the ethyl group has freedom to move and rotate.[120] The chemisorbed ethylxanthate species on sphalerite surfaces shows an upward shift of 15 cm^{-1} and a downward shift of 10 cm^{-1} of the bands found at 1 033 and 1127 cm^{-1} in solid zinc(II) ethylxanthate, respectively, and a broadening of the band at 1210 cm^{-1}. An ethylxanthate species with these special features is referred to as type

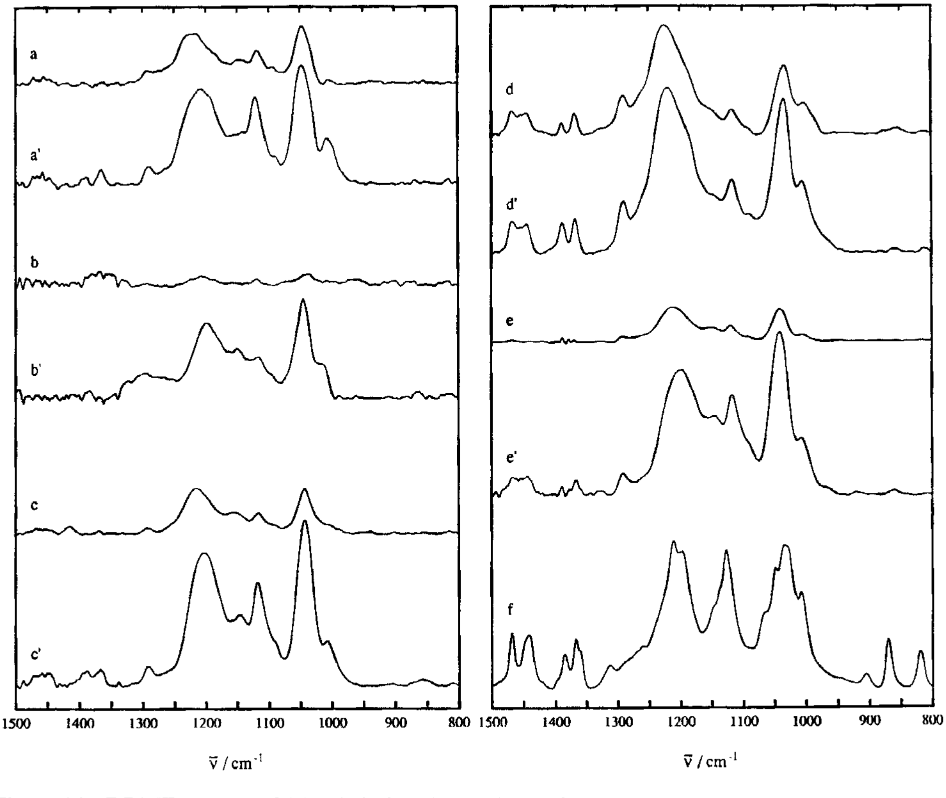


Figure 14 DRIFT spectra of (a) sphalerite, (b) synthetic zinc(II) sulphide precipitated in an excess of sulphide ions, (c) synthetic zinc(II) sulphide precipitated in an excess of zinc(II) ions pretreated with a 10 mM aqueous EDTA solution, (d) synthetic zinc(II) sulphide precipitated in an excess of zinc(II) ions and (e) synthetic zinc(II) sulphide precipitated in an excess of sulphide ions pretreated with a 10 mM aqueous solution EDTA solution after subtraction with the spectrum obtained before treatment with a potassium ethylxanthate solution. Spectra (a)-(e) are all after treatment with 5.0 mM potassium ethylxanthate in aqueous and (′) acetone solutions. Solid zinc(II) ethylxanthate (f) is given as reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is identical for the spectra (a)-(e).

1.[120] Another kind of chemisorbed ethylxanthate surface complex is formed on the surfaces of zinc(II) sulphide prepared in an excess of zinc ions. This ethylxanthate species, referred to as type 2, has a different splitting of the band at 1033 cm^{-1}, a downward shift of 10 cm^{-1} and an upward shift of 15 cm^{-1} compared with the bands at 1127 and 1210 cm^{1} in solid zinc(II) ethylxanthate, respectively,[120] see Fig. 14. The stabilities of ethylxanthate species of types 1 and 2 have been studied by washing the zinc sulphide and sphalerite surfaces with these surface complexes with water and acetone.[120] The surface complexes of type 1 is not affected by acetone while it is completely removed from the surfaces of zinc sulphide prepared in excess of sulphide ions and sphalerite with successive washings with water. The ethylxanthate species of type 2 is only partially removed from the zinc sulphide surfaces by successive washing with water. These results show that the ethylxanthate species of type 2 is more stable than that of type 1 if these ethylxanthate species are true chemisorbed surface complexes. Surface complexes of alkylxanthate ions are also formed on other surfaces of zinc salts with a similar structure as zinc sulphide. It has been shown that ethylxanthate species of type 1 is formed on the zinc(II) oxide surfaces. The conditions for the formation of ethylxanthate species of type 1 and 2, the shifts of the bands in the DRIFT spectra in comparison with solid zinc(II) ethylxanthate and the different stabilities in water and acetone in comparison with the solubilities of solid zinc(II) ethylxanthate in water and acetone strongly indicate that these ethylxanthate species are chemisorbed complexes coordinated to the zinc sites in the ultimate surface layer. It is reasonable to believe that the surfaces of zinc(II) sulphide prepared in an excess of sulphide ions are enriched with sulphide ions. The adsorbed sulphide ions hamper or make the zinc sulphide surface inert to adsorption of ethylxanthate ions. This shows that sulphide ions are chemisorbed to the zinc sulphide surfaces, and that the number of zinc sites in the surface available for further coordination is very low; sulphide ions are indeed used as a depressing agent in flotation of sulphide minerals.[112] This shows that zinc(II) ions must be present in the ultimate surface layer of the metal sulphide, and that the metal ions must be available for coordination if ligands shall be chemisorbed to a metal sulphide surface.

The donating oxygen atom in the acetate ion is relatively hard, thus forming mainly electrostatic interactions. The acetate ion is therefore expected to form only weak chemisorbed complexes, if such complexes are formed at all on solid surfaces of zinc salts. Zinc sulphide prepared in an excess of zinc(II) ions was treated with a concentrated, 1.0 M, aqueous sodium acetate solution, and the recorded DRIFT spectrum of the zinc sulphide surface did not show any sign of acetate species on the surface.[120]

It seems that the chemisorbed surface complexes to sulphide minerals are only formed when the ligand has a soft character, i.e. the formed bond has some covalent character. It is well-known that sulphur donor ligands have soft electron donor properties.[126] A preliminary study has shown that ethylxanthate ions are strongly coordinated to mercury in the mercury(II) bromide ethylxanthate complex, $HgBr_2(C_2H_5OCS_2)_2$.[120] This shows that the ethylxanthate ion has soft donor properties corresponding to a high D_s value.[126] The acetate ion is on the other hand a hard donor ligand, and it has been experimentally shown that acetate ions are neither coordinated to zinc sulphide surfaces nor to mercury(II) halides in aqueous solution in spite of the fact that high concentrations of acetate ion have been used.

Alkylxanthate ions display several types of coordination in the solid state. The alkylxanthate ion acts as a bidentate ligand in complexes of e.g. iron(III), cobalt(III) and nickel(II), while it is mono- *and* bidentately coordinated in tin(IV) ethylxanthate and tris(*O*-ethylxanthato)cadminumate(II) complexes.[127] In many alkylxanthate complexes in the solid state one of the sulphur atoms is strongly coordinated while the other atom is more weakly coordinated at a bond distance 0.1–0.2 Å further out.[127] The different kinds of interactions are clearly reflected in the vibrational spectra of the metal alkylxanthates. By comparison with DRIFT spectra of solid metal ethylxanthate complexes it is assumed that the ethylxanthate species of type 1 and 2 are chemisorbed mono- and bidentate surface complexes, respectively. The kind of surface complex formed depends most probably on the local structure around the metal ion in the surface. Zinc is tetrahedrally coordinated in zinc sulphide, and it can be assumed that zinc maintains this coordination geometry also in the surface through solvation or complex formation. Monodentate and bidentate ethylxanthate complexes should therefore be formed when the metal ion is coordinated to three and two sulphur atoms in the sulphide lattice, respectively.

Sphalerite often contains large amounts of iron and lead. DRIFT spectra of three sphalerite samples are given in Fig. 15. The two samples with low iron content, less than 1 % iron, denoted I and II, show only weak features, while the sample with 7 % iron and 1 % lead, denoted III, has relatively strong bands in the region 800–1200 cm^{-1}, see Fig. 15. The total concentrations of metals dissolved at slurrying in water are given in Table 2. This Table shows that large amounts of zinc, iron *and* lead are dissolved from sample III, while relatively small amounts of metal ions are dissolved from the samples with low iron content. The DRIFT spectrum of sample III after treatment with a 1.0 mM aqueous potassium ethylxanthate solution shows that the dominating ethylxanthate species on the surface is lead(II) ethylxanthate,[110] see Fig. 16. Sphalerite containing large amounts of lead will act as galena and the hydrophobation mechanism will be the same as for galena, see section 6.2 below. It will therefore be impossible to separate galena from lead containing sphalerite with alkylxanthate flotation.

As it is impossible to effectively flotate sphalerite with alkylxanthate ions with short alkyl groups sphalerite is activated with metal ions such as copper(II) or lead(II) to be flotable. Zinc(II) ions in the sphalerite surface are replaced by copper(II) ions or copper(II) ions are adsorbed on the sphalerite surface when sphalerite is treated with an aqueous solution of copper(II) ions.[122] Copper(II) ions react with alkylxanthate ions through a redox reaction to form dialkyl dixanthogen and solid copper(I) alkylxanthate in aqueous solution. There has been some controversy whether both of these alkylxanthate species or only solid copper(I) alkylxanthate is formed on the copper(II) activated sphalerite surfaces after treatment with an aqueous potassium alkylxanthate solution.[122,123] DRIFT spectra of copper(II) activated sphalerite before and after treatment with ethylxanthate and

Table 2. Total concentration, C_M/μM, of zinc, iron and lead in the aqueous phase of sphalerite slurries.

	C_{Zn}	C_{Fe}	C_{Pb}
Sphalerite I	3.5	–	–
Sphalerite II	6.9	2.1	–
Sphalerite III	32.7	7.2	1.4

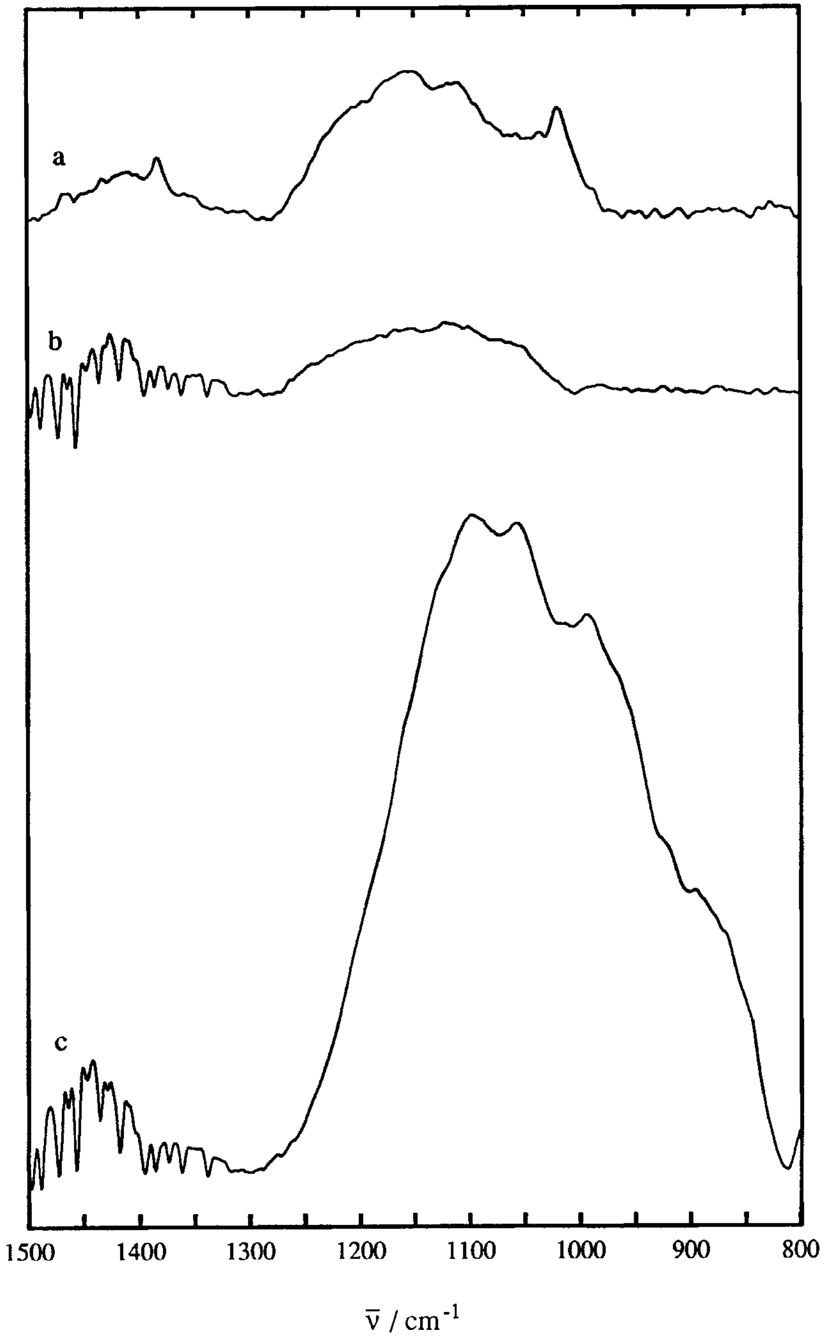


Figure 15 DRIFT spectra of dry ground (a) sphalerite I, (b) sphalerite II and (c) sphalerite III. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is the same for all spectra.

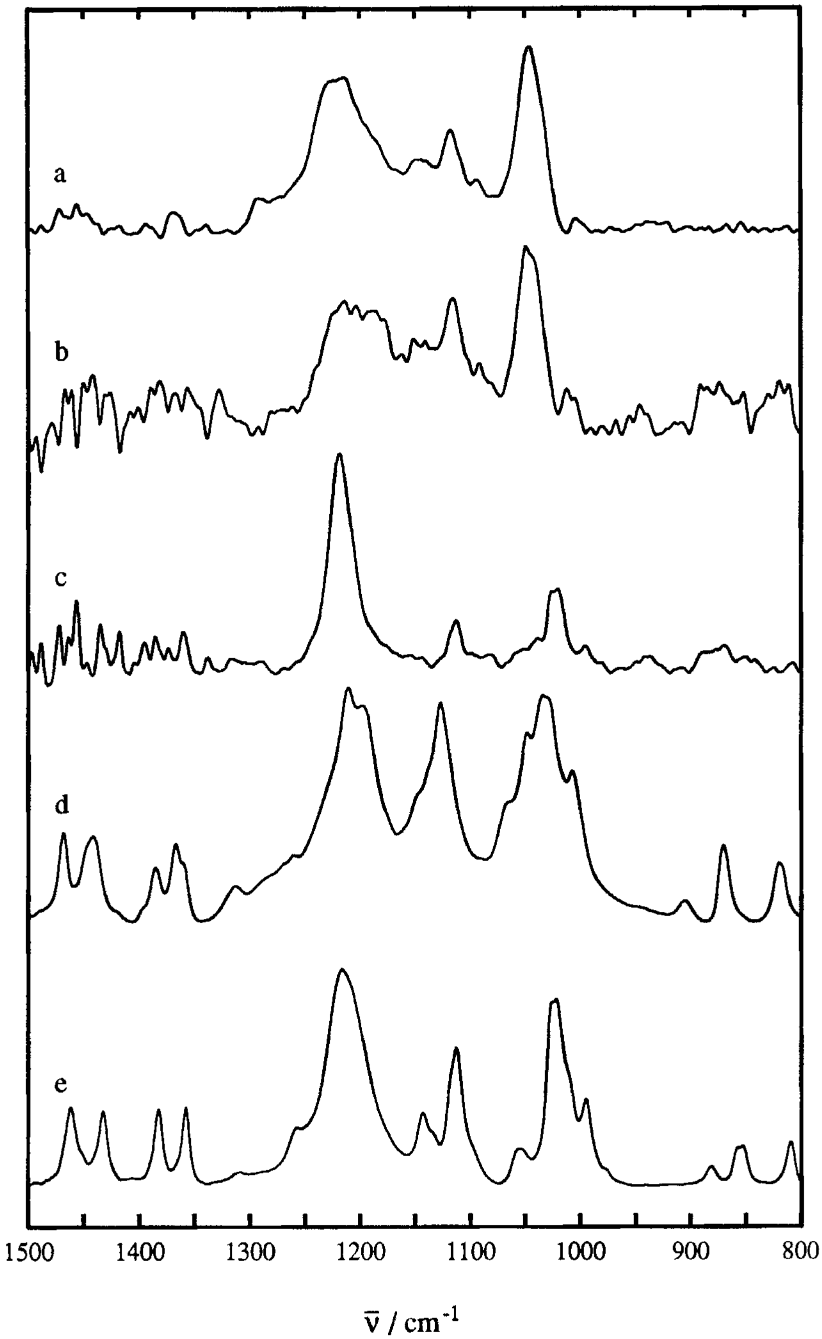


Figure 16 DRIFT spectra of (a) sphalerite I, (b) sphalerite II and (c) sphalerite III treated with a 1.0 mM potassium ethylxanthate aqueous solution after subtraction with the spectrum obtained before treatment with a potassium ethylxanthate solution, and of (d) solid zinc(II) ethylxanthate and (e) solid lead(II) ethylxanthate. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary. The spectra (a)-(c) have the same ordinate scale for easy comparison.

n-decylxanthate ions, as well as DRIFT spectra of solid copper(I) ethyl- and *n*-decylxanthate and diethyl and di-*n*-decyl dixanthogen are given in Fig. 17. It is seen in this figure that both solid copper(I) alkylxanthate *and* dialkyl dixanthogen are present on copper(II) activated sphalerite surfaces after treatment with an aqueous solution of alkylxanthate;[110] this is most clearly seen for *n*-decylxanthate. This shows that the copper present on the copper(II) activated sphalerite surface has the oxidation state + 2, and that copper(II) ions are accessible to react with alkylxanthate ions. The copper(II) ions in the surface or in solution after a dissolution process react through a redox process to form both solid copper(I) alkylxanthate and dialkyl dixanthogen, and both products are adsorbed on the surface in aqueous media. Lead(II) activated sphalerite behaves most probably as lead containing sphalerite, thus as a galena.

6.2 Galena, PbS, and Synthetic Lead(II) Sulphide

The galena-alkali alkylxanthate system in aqueous solution is one of the most thoroughly investigated mineral-collector systems. It is well-known from many years of practical flotation of galena with alkali alkylxanthate as collector that alkylxanthate ions effectively hydrophobate galena surfaces. A large number of studies using a wide range of experimental techniques has been performed in order to get chemical information for the understanding of the molecular mechanism of the hydrophobation of galena. Furthermore, the sensitivity of the hydrophobation effect to external factors such as pH, redox potential and the presence of oxidizing agents such as oxygen at the grinding and at the flotation has been studied extensively. Several review articles on the reaction between galena and alkali alkylxanthates in aqueous solution have been published.[127–129] The references given below are a selection of some of the most important studies for the recently proposed reaction mechanisms of the hydrophobation of galena, and some recent works not previously reviewed.

The most important information needed for the understanding of the hydrophobation mechanism of galena is a qualitative analysis of the compound(s) present on the galena before *and* after treatment with an aqueous alkali alkylxanthate solution. Galena is very easily oxidized, and extreme precautions must be taken to avoid partial oxidation of galena surfaces. It has been shown that also extremely small amounts of oxygen in water are able to oxidize galena surfaces.[10,130–135] However, there is always an induction time before the oxidation reaction attains full rate.[130]

An early electron diffraction study reported a slow oxidation of galena surfaces in air at room temperature, while it was rapid and extensive during wet grinding.[131,132] The only oxidation products confirmed to be present on the galena surfaces were lead(II) sulphate and basic lead(II) sulphate. The solubility of these oxidation products in water is substantially higher than of galena, and the main part of these is dissolved at slurrying in water. When oxidized galena was treated with an aqueous solution of alkali alkylxanthate a thin layer of an alkylxanthate species was detected on the surface. It was proposed that alkylxanthic acid was adsorbed on the galena surfaces.[131,132] An infrared spectroscopic study on synthetic lead(II) sulphide has reported that the amount and the kind of oxidation products on the surfaces vary with the sample treatment.[133] After treatment with potassium ethylxanthate in aqueous solution solid lead(II) ethylxanthate was found to be present on the lead(II) sulphide surfaces. Most of the lead(II) ethylxanthate was

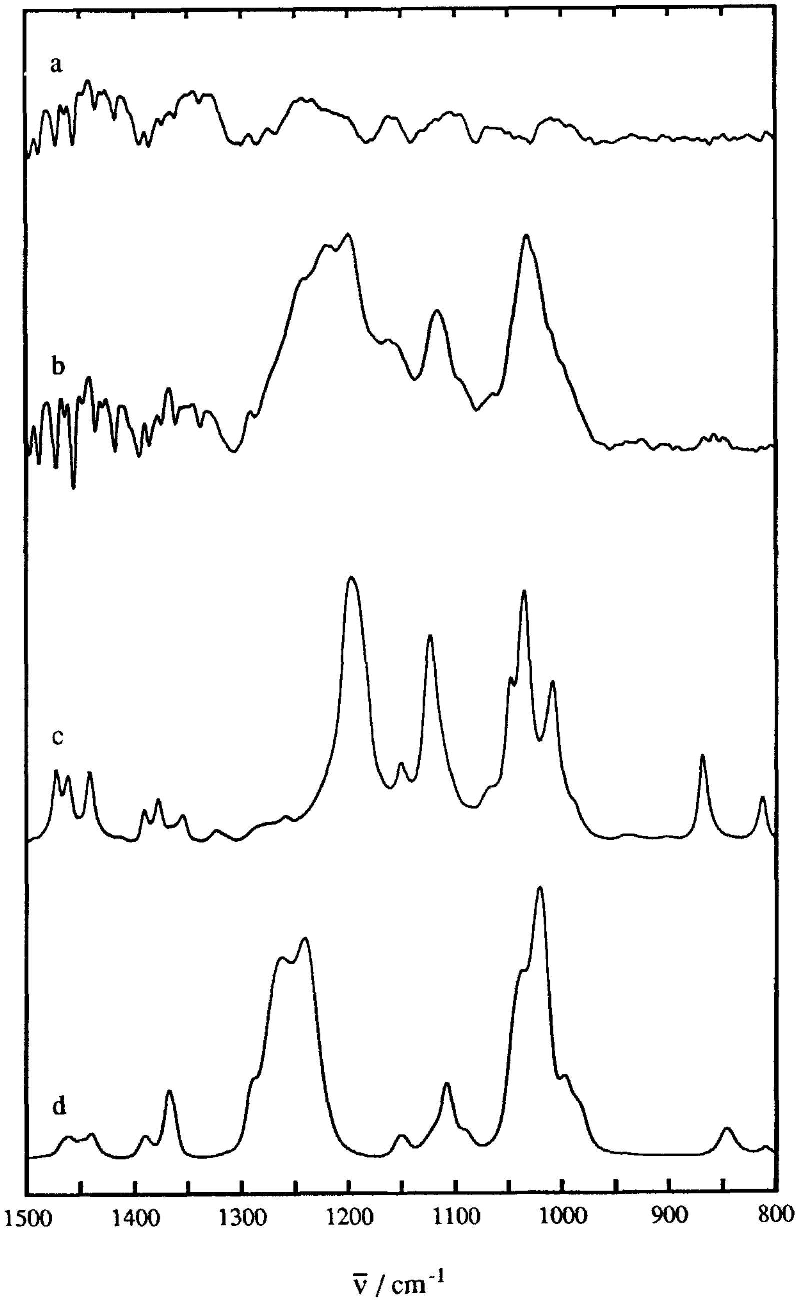


Figure 17a DRIFT spectra of (a) copper(II) activated sphalerite I, (b) copper(II) activated sphalerite I treated with a 1.0 mM aqueous potassium ethylxanthate solution after subtraction with the spectrum obtained before treatment with a potassium ethylxanthate solution, (c) solid copper(I) ethylxanthate and (d) liquid diethyl dixanthogen. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

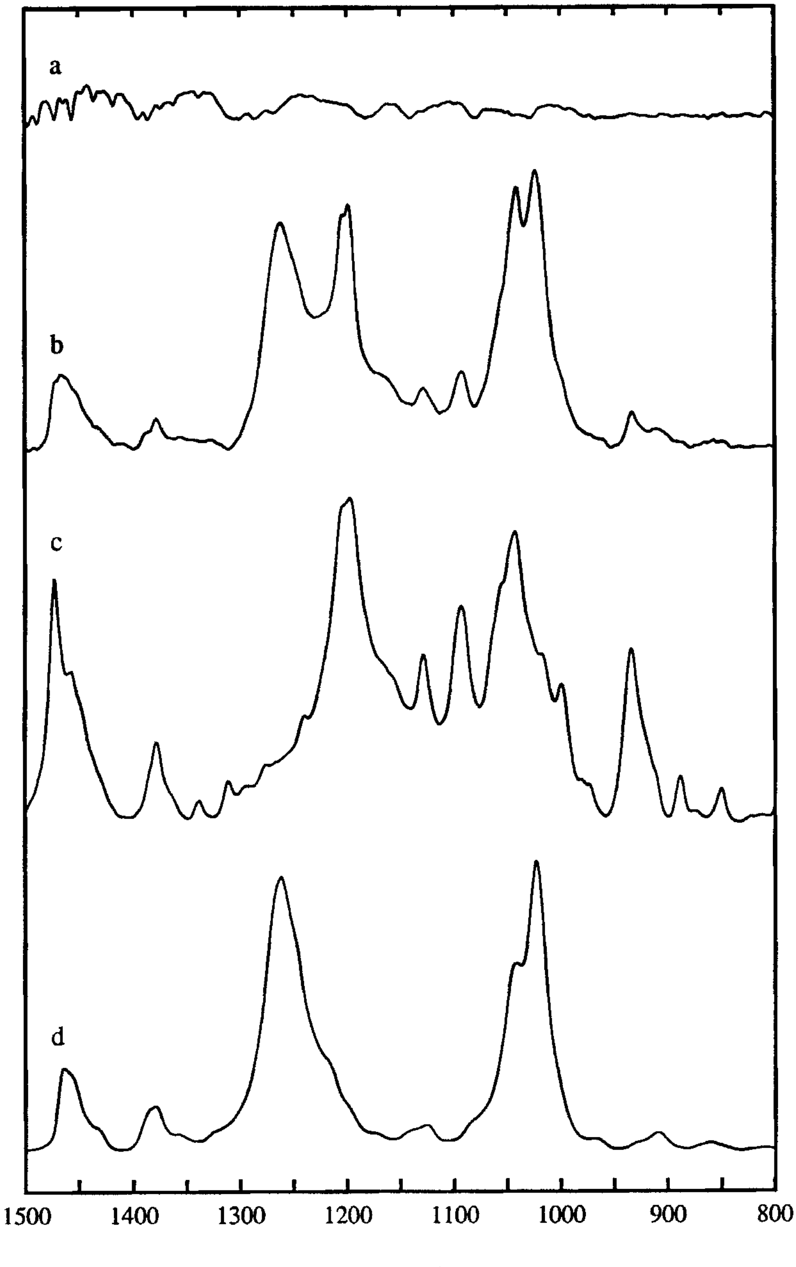


Figure 17b DRIFT spectra of (a) copper(II) activated sphalerite I, (b) copper(II) activated sphalerite I treated with a 1.0 mM aqueous potassium *n*-decylxanthate solution after subtraction with the spectrum obtained before treatment with potassium *n*-decylxanthate solution, (c) solid copper(I) *n*-decylxanthate and (d) liquid di-n-decyl dixanthogen. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

readily removed from the surface by washing with acetone. It was suggested that a 1:1 lead(II) ethylxanthate surface complex remained on the surface.[133] Based on these observations it was concluded that alkylxanthate ions form strong covalent bonds to the lead(II) ions in the lead(II) sulphide surface.

The adsorption of ethylxanthate on vacuum deposited films of lead(II) sulphide has been studied by means of infrared multiple reflectance spectroscopy.[134] Ethylxanthate ions are not adsorbed on non-oxidized lead(II) sulphide surfaces under reducing conditions. On the other hand, diethyl dixanthogen is reported to react with non-oxidized lead(II) sulphide surfaces to form a proposed monomolecular layer of a lead(II) ethylxanthate complex. The infrared spectrum of the formed complex closely resembles the spectrum of solid lead(II) ethylxanthate. It can therefore be concluded that dialkyl dixanthogen is able to oxidize galena and lead(II) sulphide surfaces and the corresponding lead(II) alkylxanthate is formed. Lead(II) sulphide was slowly oxidized to lead(II) thiosulphate when small amounts of oxygen were let into the infrared vacuum cell. Treatment of oxidized galena surfaces with an oxygen-free aqueous potassium ethylxanthate solution, and of unoxidized galena surfaces with an air-saturated aqueous potassium ethylxanthate solution yielded bulk precipitation of lead(II) ethylxanthate on the surfaces. A major part of the lead(II) ethylxanthate could be removed by subjecting it to high vacuum for a couple of days or washing it with an organic solvent, e.g. diethyl ether, in which the solubility of lead(II) alkylxanthate is high. The infrared spectrum of the remaining ethylxanthate species on the galena surfaces is slightly different compared with the infrared spectrum of solid lead(II) ethylxanthate. This result was interpreted as desorption of lead(II) ethylxanthate from a galena surface leaving a 1:1 lead(II) ethylxanthate complex identical with that reported by Greenler[133] on the surface.[134]

The bands at about 1210 and 1050 cm^{-1} for lead(II) alkylxanthates have been assigned to a stretching vibration of the C-O-C group and the C-S bond, respectively.[134] It has later been shown that these bands and most of the other bands of the alkylxanthate ion are highly coupled.[16,136,137] The band at 1210 cm^{-1}, assigned as solid lead(II) ethylxanthate on the galena surface, has shifted to 1195 cm^{-1} in the proposed 1:1 monolayer complex. This downward shift was interpreted as a change in the coordination of the alkylxanthate ion from one and a half dentate in solid lead(II) ethylxanthate to monodentate in the 1:1 monolayer complex.[134] This interpretation was based on a study of the shifts of this band in a number of solid alkylxanthates of mono- and divalent metal ions.[138]

The surfaces of galena powder unprotected against oxidation have been reported to consist of lead(II) sulphate and carbonate and of small amounts of lead(II) thiosulphate.[139] Solid lead(II) pentylxanthate was detected on the galena surfaces after treatment with an aqueous solution of potassium pentylxanthate. After some months of storage, the band at 1220 cm^{-1}, considered as solid lead(II) pentylxanthate, had shifted to 1190 cm^{-1}. This was interpreted as sublimation of lead(II) pentylxanthate in course of time leaving a 1:1 monolayer complex of the same kind as proposed previously.[134]

Another more recent infrared spectroscopic study has strongly indicated that the reaction between oxidized galena and an aqueous potassium ethylxanthate solution yields only lead(II) ethylxanthate on the galena surfaces, and that no traces of diethyl dixanthogen were detected.[140] A thermochemical study has proposed that lead(II) thiosulphate and/or basic thiosulphate are the major oxidation products on naturally oxidized galena surfaces.[141] A comparison of the reactions between an aqueous ethylxanthate solution and naturally oxidized galena on one hand, and bulk lead(II) thiosulphate, sulphate and carbonate on the other hand shows a similar heat of reaction. It was concluded from these results that the adsorption of alkylxanthate ions on oxidized galena surfaces takes place through an ion exchange mechanism where the anions of the oxidation product of galena are exchanged for ethylxanthate ions.[141] No particular difference in the properties of dry and wet ground galena was observed.[141] Another calorimetric study has claimed that alkylxanthate ions were adsorbed along two different mechanisms, chemisorption, which is time-independent, and a time-dependent precipitation of lead(II) alkylxanthate.[142] The chemisorption mechanism was found to disappear when the pH was increased.

Cases *et al.* have in several papers reported studies on the galena-alkylxanthate system. They claim that the alkylxanthate species formed is very much dependent on pH. One of the main products is dialkyl dixanthogen, besides lead(II) alkylxanthate and alkylxanthate monolayer complexes (non-stoichiometric lead alkylxanthate).[139,143–145] However, the formation of dialkyl dixanthogen has only been reported in old studies which are reviewed in ref. 60 and not confirmed by any other recent study. They used a particle size <5 or 15 μm, which means a risk that the particles may be of the same size as the wavelength and interference patterns may occur which disturb the spectrum. Furthermore, they did not use a non-absorbing matrix, an omission decreasing the sensitivity substantially. The measurements have in some cases been performed in pH ranges where the alkylxanthate ion decomposes. The results reported by Cases *et al.* do not seem to be reliable and they will not be further discussed in this article.

It has been shown that non-oxidized surfaces do not react with oxygen-free aqueous solutions of potassium ethylxanthate in the pH-range 7–11.[145] The reaction between galena surfaces free from oxidation products and oxygen containing aqueous solutions of potassium ethylxanthate initially showed an induction period where practically no reactions took place, but after this period the ethylxanthate ions started to react with the galena surface. On the other hand, oxidized galena surfaces reacted immediately with an aqueous potassium ethylxanthate solution independent of the solution was oxygen-containing or oxygen-free.[145] It was proposed that oxidized galena surfaces adsorb alkylxanthate ions by an ion exchange mechanism[135] similar to that proposed by Mellgren.[141]

The oxidation of ethylxanthate ions has been studied on polished gold, platinum and galena electrodes.[146] Addition of potassium ethylxanthate to aqueous solutions containing a neutral salt changes the redox properties of the electrodes. This implies that ethylxanthate ions are adsorbed to the electrode surfaces, replacing preadsorbed water molecules and hydroxide ions. Oxidation of galena is inhibited by small amounts of ethylxanthate or lead(II) ions, while addition of sulphide ions was not found to influence the oxidation of galena.[147]

A large number of electrochemical studies of galena electrodes in aqueous alkali alkylxanthate solutions has been reported. A controversy in the literature concerning the possible oxidation of ethylxanthate ions to diethyl dixanthogen at the galena surface in diluted oxygenated potassium ethylxanthate solutions has in detail been reviewed by Finkelstein and Poling.[129] A majority of the reported studies claims that the rest potential of the galena electrode in aqueous potassium ethylxanthate solution is lower than the redox potential for the ethylxanthate ion/diethyl dixanthogen couple. This means that diethyl dixanthogen cannot be formed at galena surfaces in the presence of ethylxanthate ions and oxygen.[129] It has also been shown that galena becomes flotable at significantly lower potentials than the redox potential of the couple ethylxanthate ion/diethyl dixanthogen,[148] which means that lead(II) ethylxanthate must be the hydrophobating agent.[129]

Several reaction mechanisms of the adsorption of alkylxanthate ions on metal and mineral surfaces have been proposed from electrochemical studies. However, the proposed intermediates and products formed on the electrode surfaces have not been confirmed by other analytical techniques, and the results are not in agreement with results obtained in non-electrochemical studies.[129]

These results show a split view of the adsorption of alkylxanthate species on galena surfaces. It can however be concluded that galena surfaces are very easily oxidized to lead(II) sulphate, thiosulphate and carbonate, and extreme precautions must be taken to avoid oxidation. In practical flotation it can be taken for certain that the galena surfaces are oxidized when the mineral powder/slurry is poured into the flotation pulp in spite of grinding in iron mills. The following discussion of adsorption of alkylxanthate ions to galena surfaces must be divided into two parts, oxidized and non-oxidized galena surfaces, as they obviously behave very differently.

Bulk precipitation of lead(II) alkylxanthate on galena surfaces is yielded when oxidized galena is treated with an aqueous solution of alkali alkylxanthate. The formation of a 1:1 monolayer complex has been proposed by several authors.[133,134,139] This proposal was based on a downward shift of the band at 1210 cm^{-1} as described above. However, the other bands from the alkylxanthate ion in the proposed complex remain unshifted, which is surprising since all bands of the -COCS$_2$-unit are expected to shift and not only a single band. A very recent study using DRIFT spectroscopy has critically examined the existence of the 1:1 monolayer complex.[10] Lead(II) oxosulphur compounds have a strong broad absorption band just below 1200 cm^{-1}. It has been shown that a mixture of lead(II) ethylxanthate and sulphate yields an infrared spectrum very similar to that of the proposed 1:1 monolayer complex.[10] Furthermore DRIFT spectra of oxidized galena treated with diluted, 0.1 and 0.2 mM, potassium ethylxanthate solutions are also very similar to the proposed 1:1 monolayer complex. A difference between these spectra, 0.2 mM–0.1 mM, yields however a spectrum similar to that of solid lead(II) alkylxanthate,[10] see Fig. 18. This shows that the coexistence of lead(II) alkylxanthate and lead(II)oxosulphur compounds causes a downward shift of the band found at about 1210 cm^{-1} in solid lead(II) ethylxanthate. The size of the shift is dependent on the distribution of lead(II) alkylxanthate and oxosulphur compounds; more details are given in ref. 10.

The solubilities and solubility products of lead(II) sulphide, carbonate, sulphate and thiosulphate and some lead(II) alkylxanthate, show that the lead(II) oxosulphur compounds are considerably more soluble than the lead(II) alkylxanthates, see Table 1; the solubility of lead(II) sulphide and galena is extremely low in neutral and alkaline solutions. In order to get bulk precipitation of lead(II) alkylxanthate on a galena surface, concentrations of lead(II) ions of 10–100 μM must be present close to the surface if the concentration of alkylxanthate ion is in the range 0.1–1.0 mM, which is the usual concentration in the flotation pulp. The only reasonable origin of these lead(II) ions is oxidation products of galena with sufficient solubility. Washing experiments of oxidized galena surfaces using DRIFT spectroscopy have shown that lead(II) oxosulphur salts are more readily washed off the surface than lead(II)

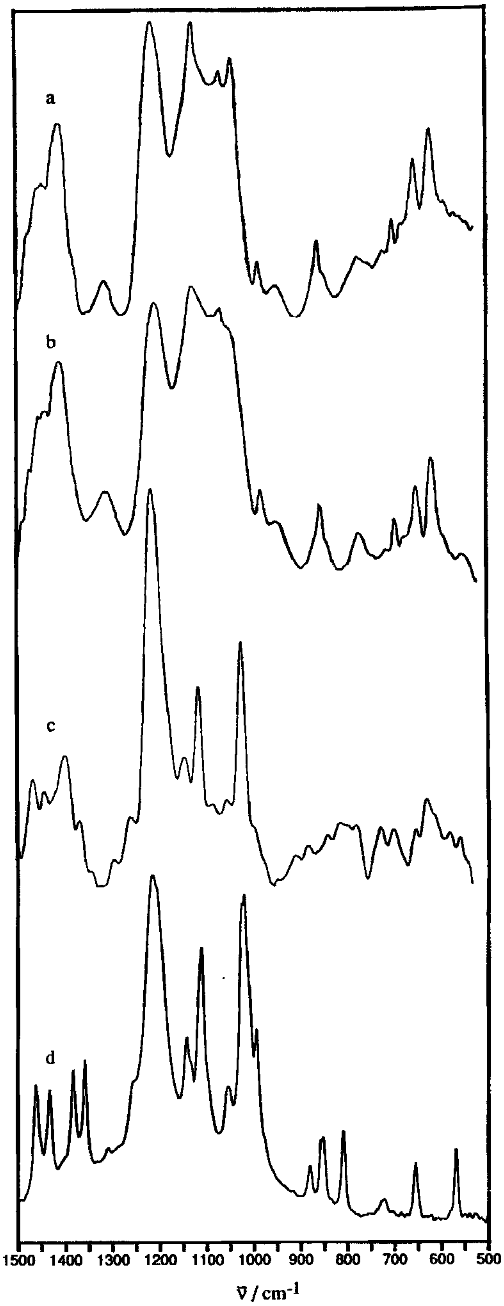


Figure 18 DRIFT spectra of galena powders treated with (a) 0.2 mM and 0.1 mM potassium ethylxanthate solutions. The difference between spectra (a) and (b) yields spectrum (c). The spectrum of solid lead(II) ethylxanthate (d) is given for comparison. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

carbonate,[10] which is in accordance with the solubilites, see Table 1. Another favourable point for precipitation on the galena surfaces is that the lead(II) ions have their origin from the surface, which means that a concentration gradient is obtained around the galena particles during the dissolution process. This means that the solubility product of the lead(II) alkylxanthate is first exceeded very close to the galena surface, and that the solid surface can be used as nuclei of crystallisation. Based on these and previous observations[10,130–133,135,141] the following mechanism for the hydrophobation of oxidized galena surfaces by alkylxanthate ions was proposed:[10] 1) The galena surfaces are easily oxidized in the presence of air or other oxidizing agents when galena is ground into a fine powder. These oxidation products are fairly soluble in water, and they are partly dissolved when an aqueous slurry is prepared. A concentration gradient of lead(II) ions will most probably be obtained the galena particles at the initial stages of the dissolution of these compounds from the galena surfaces. 2) By the presence of alkylxanthate ions in the aqueous phase when preparing the galena slurry, the solubility product of lead(II) alkylxanthate is first exceeded in close vicinity of the galena surfaces and small islands of solid lead(II) alkylxanthate are formed on the oxidized galena surface. The degree of coverage of lead(II) alkylxanthate on the oxidized galena surfaces increases with increasing concentration of alkylxanthate ions and degree of oxidation of the galena surface. Practical flotation shows that there is an initial concentration gradient of lead(II) ions or complexes around the galena particles, otherwise the flotation process should be markedly less selective. Too high alkylxanthate concentrations in the pulp will most probably result in that precipitation of lead(II) alkylxanthate takes place also in solution and on non-galena surfaces. At low alkylxanthate concentrations the solubility production will only be exceeded very close to the galena surfaces, where the highest lead(II) concentration is found.

Lead(II) alkylxanthates have pronounced hydrophobic properties, even when the carbon chain in the alkylxanthate is short.[149–151] The formation of islands of lead(II) ethylxanthate on oxidized galena surfaces is most probably enough to make the galena particles sufficiently hydrophobic to be attached to an air-bubble, and thereby flotable. The formation of small islands of lead(II) alkylxanthate on oxidized galena surfaces has been beautifully demonstrated in an experiment where radioactively labelled alkylxanthate ions have been used.[152] It can be assumed that the degree of coverage of hydrophobic compounds on the galena surface necessary for flotation increases with increasing particle size and weight.

It is extremely important to distinguish between reactions taking place on oxidized and non-oxidized galena surfaces. The precipitation of solid lead(II) alkylxanthate will predominate over other possible reactions on the galena surface. On the other hand, non-oxidized galena surfaces interact with alkylxanthate ions and other ligands with soft donor atom(s) by forming chemisorbed surface complexes. Some of the reported studies on non-oxidized or slightly oxidized galena surfaces will be presented below. However, it must be borne in mind that in practical flotation of galena, the galena surfaces are doubtless heavily oxidized, and that studies of non-oxidized galena have no relevance to practical flotation.

The dissolution of lead(II) sulphide has been studied as a function of pH, light intensity and concentration of oxygen in the aqueous phase.[153] The results have shown that the dissolution reaction is pH dependent, enhanced by dissolved oxygen and slightly affected by photoirradiation. The amount of dissolved lead(II) species decreases when pH increases pH from 2.5 to 9.0. No lead(II) sulphide was dissolved at all at pH >9.0. The extent of lead(II) sulphide dissolution was found to increase slightly with increasing light intensity under both aerobic and anaerobic conditions. The surface protonation was considered as the initial reaction step in the dissolution process. Under photoir radiation a considerable amount of sulphate was detected in the solution. This was attributed to the oxidation of sulphide by incipient oxygen production from the water oxidation on the lead(II) sulphide surfaces.[153] It has been proposed from electrophoretic measurements, coagulation and solution equilibria studies, that surface dissolution can be followed by readsorption or "interfacial precipitation" of lead hydroxy species on the galena surface.[154]

Potentiometric titrations and solubility studies of freshly precipitated lead(II) sulphide have shown that protons are adsorbed on galena surfaces in oxygen-free acidic aqueous solutions. The lead concentration in slightly acidic solutions therefore becomes quite high due to a proposed ion exchange reaction between protons and lead(II) ions in the galena surface under strict anaerobic conditions.[155] It has also been shown that the hydrated galena and synthetic lead(II) sulphide surfaces have acid-base behaviour with the acidity constants $pK_{a1} = 7.15$ and $pK_{a2} = 10.2$ for galena and $pK_{a1} = 7.11$ and $pK_{a2} = 10.0$ for synthetic lead(II) sulphide.[156] The logarithmated equilibrium constant for the ion exchange reaction $\text{▨}Pb + 2\ H^{+} \rightleftharpoons 2\text{▨}H + Pb^{2+}$ has been determined to 10.21 and 9.48 for galena and synthetic lead(II) sulphide, respectively, in the pH range 4.5–7.0; ▨ denotes solid galena surface. It has also been reported that alkylxanthate ions are chemisorbed to galena surfaces with a stability constant of $3.5 \cdot 10^{4}$ M.[156] It is important to stress that also under strict anaerobic and slightly acidic conditions lead(II) will be transferred from the galena surfaces to the solution phase, which may result in a precipitation of lead(II) alkylxanthate at the addition or in the presence of alkylxanthate ions.

In order to study chemisorption of alkylxanthate ions on mineral surfaces it is preferable to use a solvent where the alkylxanthate compounds are soluble, e.g. acetone and acetonitrile.[157] Two separate ethylxanthate species have been distinguished on galena and synthetic lead(II) sulphide surfaces after treatment with potassium ethylxanthate in acetone solution.[157] These chemisorbed ethylxanthate species are characterized by features in the DRIFT spectra different from those of solid lead(II) ethylxanthate, see Figs. 19 and 20, and by their solution chemistry behaviour. The two types of chemisorbed ethylxanthate species are denoted I and II. The ethylxanthate species of type I is only slightly soluble in water and acetone. It is assumed that the bond between lead in the galena and lead(II) sulphide surfaces and the ethylxanthate ion in type I complexes has a substantial covalent character, since the DRIFT spectrum of this chemisorbed surface complex shows spectral characteristics similar to the more covalent ethylxanthates of transition and heavy metals but none of the spectral features of the ionic alkali ethylxanthates.[157,158] The ethylxanthate surface species of type II is only formed in poorly solvating solvents such as acetone and acetonitrile.[157] The ethylxanthate species of type II is not possible to extract from the surface with acetone, while it is easily extracted with water. How the ethylxanthate ion in the surface complexes of type II is coordinated to the surface is not understood as the spectrum of type II species does not show any resemblance to any known alkylxanthate species, and no relevant references are therefore available. A possible explanation is an electrostatic interaction of the alkylxanthate ions to the surface if the mineral particle is charged. Measurements

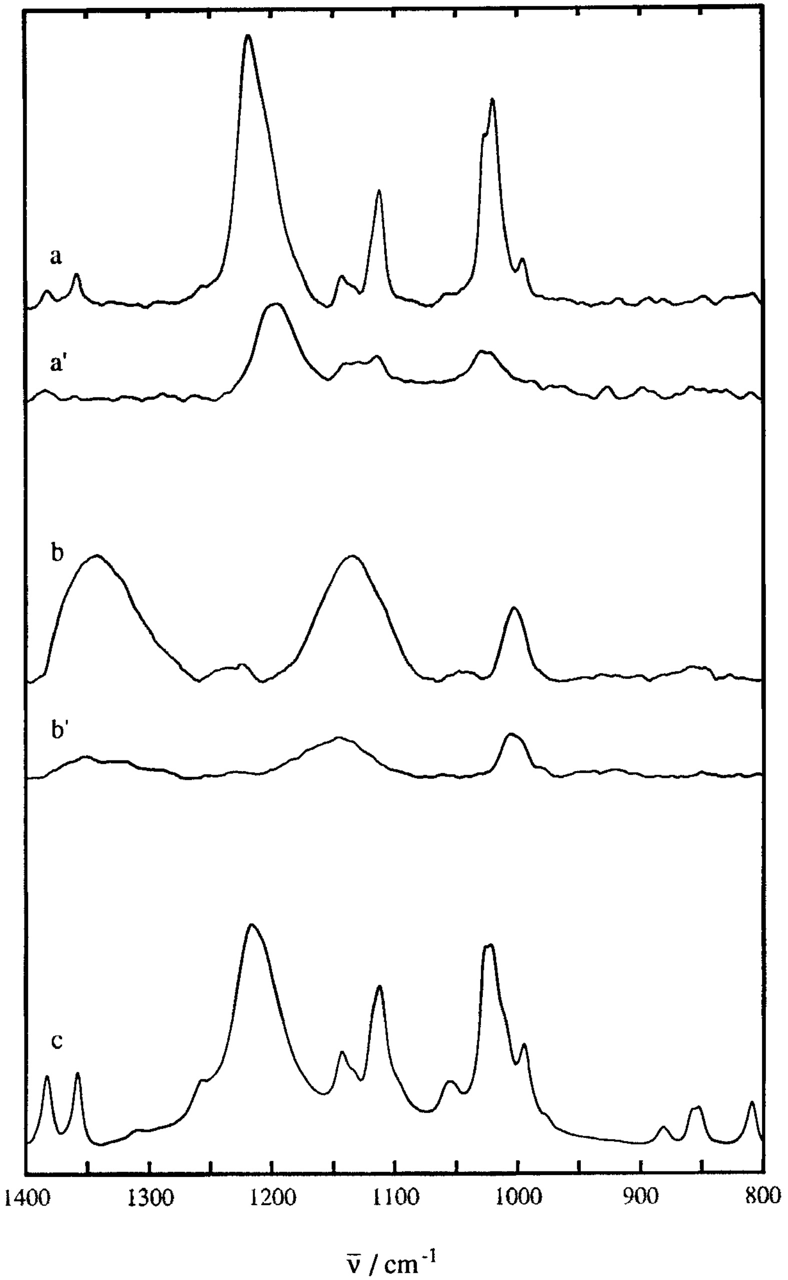


Figure 19 DRIFT spectra of galena and galena pretreated with a 10 mM EDTA solution ('). (a) treated with a 5.0 mM aqueous of potassium ethylxantahte, after subtraction with the spectrum obtained before treatment with a potassium ethylxanthate solution. Solid lead(II) ethylxanthate is given as reference. The ordinate scale is in (R_{ref}/R_{sample}) units, and it is identical for the spectra of the galena samples treated in aqueous and acetone solutions.

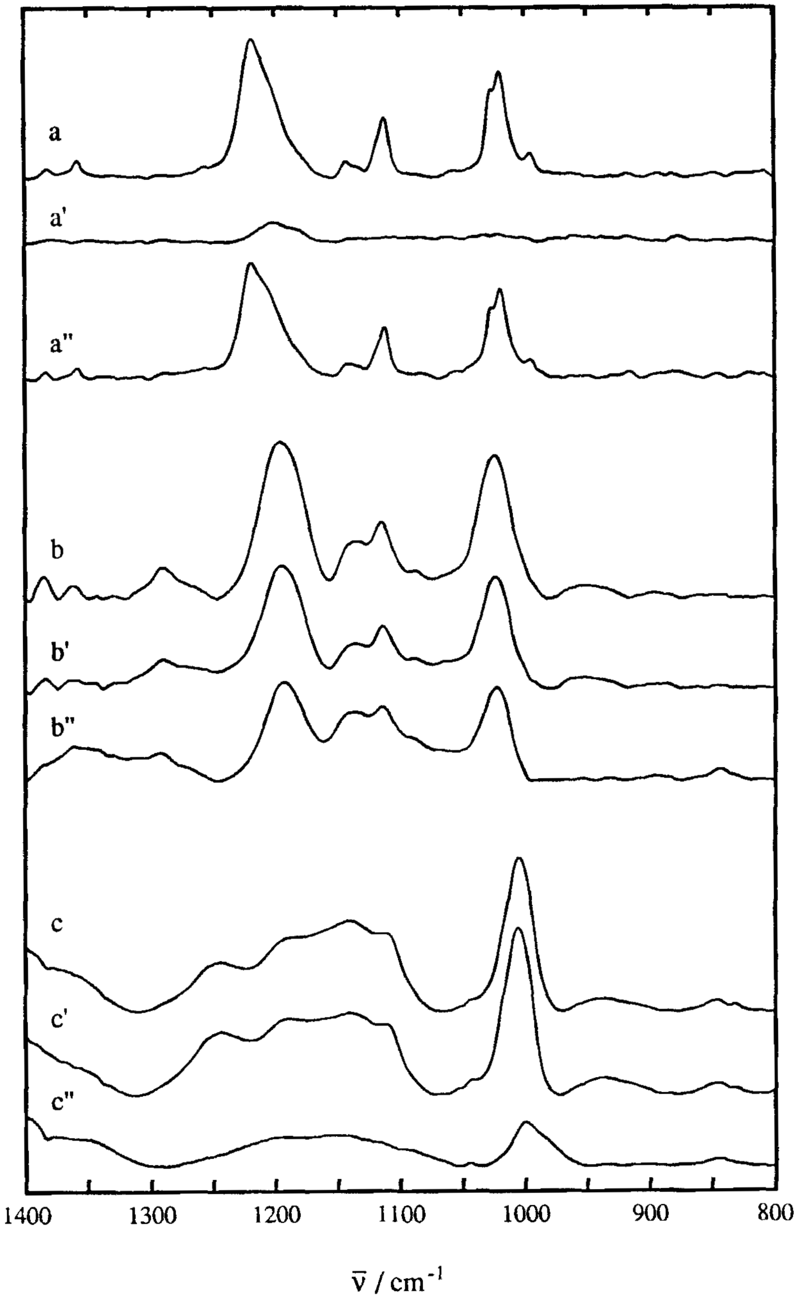


Figure 20 DRIFT spectra of (a) galena treated with a 5.0 mM aqueous solution of potassium ethylxanthate, (b) lead(II) sulphide prepared in an excess of lead(II) ions, pretreated with a 10 mM EDTA solution and treated with a 5.0 mM acetone solution of potassium ethylxanthate and (c) lead(II) sulphide prepared in an excess of lead(II) ions treated with a 5.0 mM acetone solution of potassium ethylxanthate, and after a single washing (′) with acetone and with water (″) after subtracting with the spectrum obtained before treatment with a potassium ethylxanthate solution. The ethylxanthate species is washed off the surfaces after successive washings. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is identical for the (a), (b) and (c) spectra, respectively. The (b) and (c) spectra represent type I and II complexes, respectively.

of the ζ-potential at varying pH in aqueous solution have shown that galena particles are charged, and that this charge is a function of pH and the concentration of lead(II) and alkylxanthate ions in the aqueous phase.[159,160] Acetone and acetonitrile, which have low dielectric constants, will only poorly neutralize any charge of mineral particles and stable electrostatically coordinated surface complexes of e.g. alkylxanthate ions may therefore be formed. This cannot take place in aqueous solution as water has a high dielectric constant and will much more effectively neutralize any particle charge, and the alkylxanthate ion is most probably more strongly solvated in water than in acetone and acetonitrile.[157]

6.3 Chalcocite, Cu_2S, and Acanthite, Ag_2S

It has been shown that very small amounts of copper are dissolved when chalcocite powder is slurried in water.[161,162] This means that chalcocite surfaces either are resistant to oxidation and/or that the oxidation products of chalcocite have a low solubility in water. Yoon *et al.* have from IRAS (infrared reflectance absorption spectroscopy) measurements proposed that a monolayer of alkylxanthate ions is chemisorbed on chalcocite surfaces, and that solid copper(I) alkylxanthate is formed on top of this monolayer at treatment with an aqueous alkali alkylxanthate solution.[163,164] However, the bands in these works have been assigned as pure assigned as pure vibrations, which is known to be incorrect,[136,137] and no proofs for the proposed reaction mechanism are given. A similar adsorption mechanism has been proposed for thiocarbamate.[165] Kapylov *et al.* have reported that copper(I) alkylxanthate is the sole alkylxanthate species on chalcocite surfaces treated with an aqueous solution of potassium alkylxanthate.[166]

Mielczarski and Suoninen have used XPS in the study of adsorption of alkylxanthate ions on chalcocite surfaces.[167] Their results support a reaction mechanism proposed by Clifford *et al.*,[168] which states that 1) Preadsorbed groups such as water and hydroxide ions the surface are replaced by alkylxanthate ions resulting in a random orientation of the alkylxanthate ions on the surface, 2) Larger preadsorbed aggregates such as hydrocarbons are replaced by alkylxanthate ions from the solution leading to a considerably increasing degree of order of alkylxanthate ions on the surface, 3) This process is terminated by the formation of a close-packed well-oriented monolayer, 4) After creation of a complete monolayer of alkylxanthate ions, the adsorption continues by addition of essentially randomly oriented copper(I) ethylxanthate molecules. It has also been proposed that dialkyl dixanthogen can be formed on chalcocite surfaces through a redox reaction where oxygen adsorbed on mineral surfaces oxidizes alkylxanthate ions to dialkyl dixanthogen.[169] However, it has been recently shown that adsorbed oxygen on sulphide mineral surfaces cannot oxidize alkylxanthate ions to dialkylxanthogen.[170]

The DRIFT spectrum of chalcocite shows that the surfaces are almost free from oxidation products, although the grinding of chalcocite was performed without protection against oxidation, see Fig. 21. The previous observations that only small amounts of copper ions are released from chalcocite in water are therefore most probably a result of resistance to surface oxidation. Treatment of chalcocite powder with an aqueous solution of potassium alkylxanthate yields only very small amounts of ethylxanthate species on the surfaces, see Fig. 21. Since there is no evidence for chemisorption of alkylxanthate ions on chalcocite surfaces, the alkylxanthate species on the chalcocite surfaces is most probably solid copper(I) alkylxanthate. When the same alkylxanthate treatment is performed with synthetic copper(I) sulphide rela-

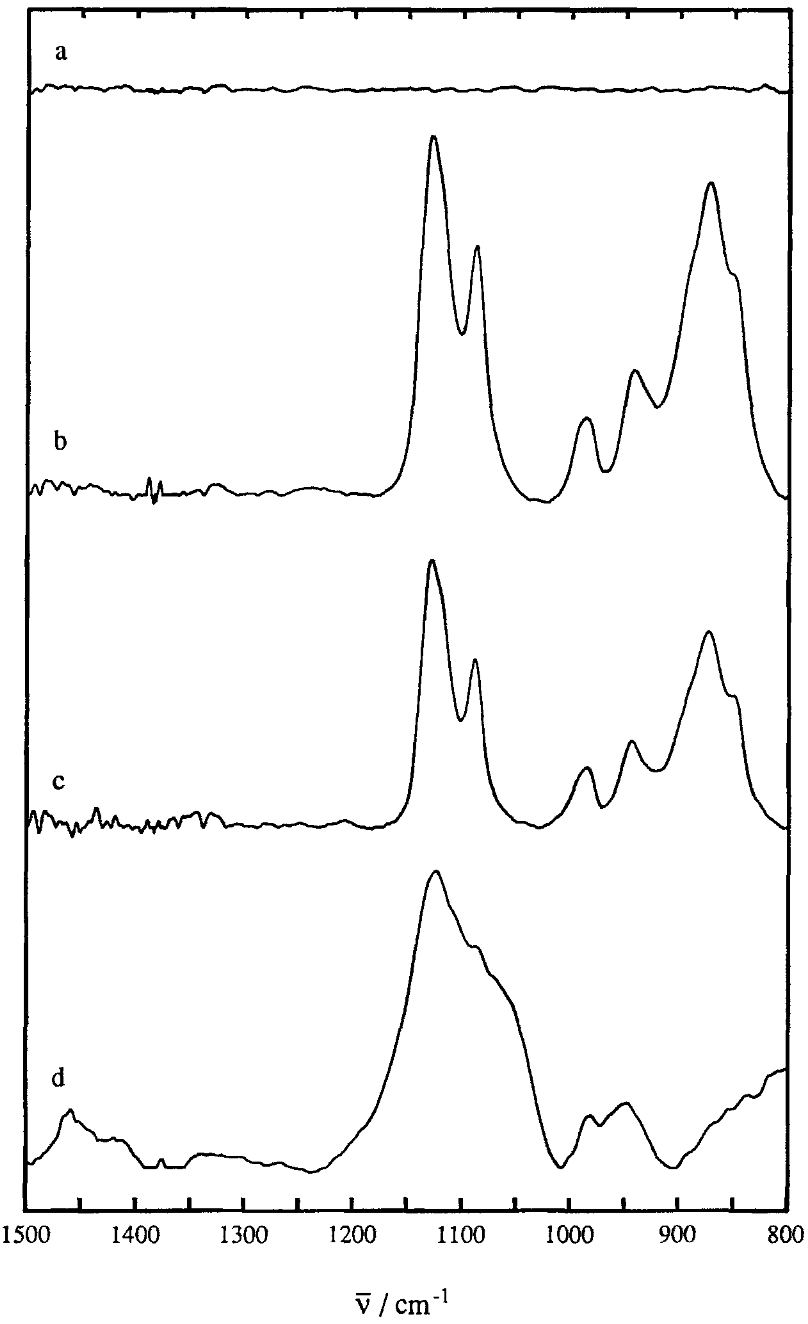


Figure 21a DRIFT spectra of (a) chalcocite, (b) copper(I) sulphide prepared in an excess of copper(I) ions, (c) copper(I) sulphide prepared in an excess of sulphide ions and (d) solid copper(I) oxide. The ordinate scale is in long (R_{ref}/R_{sample}) units and it is arbitrary.

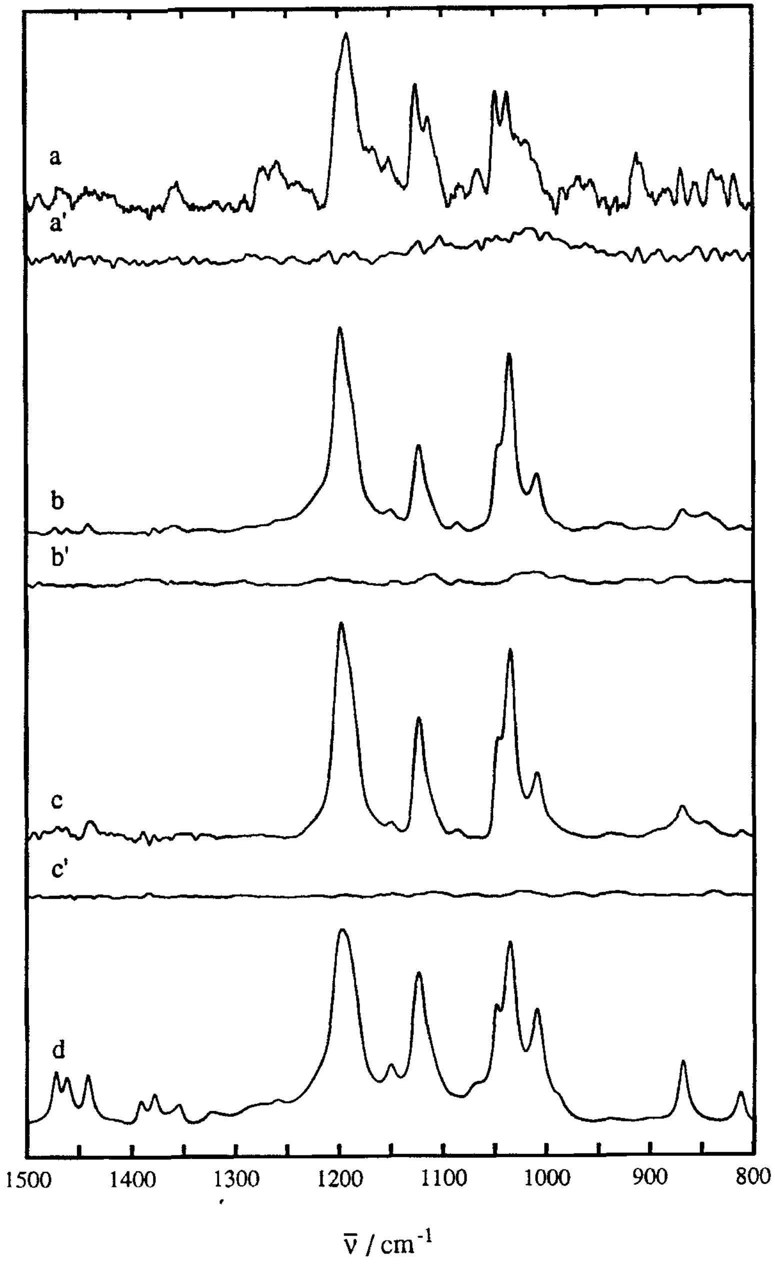


Figure 21b DRIFT spectra of (a) chalcocite, (b) copper(I) sulphide prepared in an excess of copper(I) ions, (c) copper(I) sulphide prepared in an excess of sulphide ions treated with 5.0 mM aqueous and (′) acetone solutions of potassium ethylxanthate after subtraction with the spectrum obtained before treatment with the potassium ethylxanthate solution. The spectrum (d) of copper(I) ethylxanthate is given as reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is identical for the spectra (a)-(c), respectively.

tively large amounts of copper(I) alklyxanthate precipitate on the surfaces, and there are no traces of dialkyl dixanthogen. This shows that no copper(II) ions are present in the outermost surface layers, since the reaction between copper(II) and alkylxanthate yields copper(I) alkylxanthate *and* dialkyl dixanthogen. This proves that copper remains in its lower oxidation state even though the surfaces of synthetic copper(I) sulphide are oxidized.

It has been proposed that a monolayer of alkylxanthate ions is chemisorbed on copper(I) sulphide surfaces, and that copper(I) alkylxanthate is formed on top of this layer.[163,164] Chemisorbed species should be formed also in solvents where the access to soluble copper(I) ions and complexes is low and the copper(I) sulphide surface only weakly solvated. The spectra in Fig. 21 clearly show that no alkylxanthate species is adsorbed on surfaces of copper(I) sulphide in acetone slurries. The fact that alkylxanthate ions do not adsorb on copper(I) sulphide in acetone slurries strongly indicates that alkylxanthate species do not form chemisorbed surface complexes on copper(I) sulphide and chalcocite surfaces.

The DRIFT spectra of acanthite and synthetic silver(I) sulphide are very different in spite of their identical X-ray diffractograms.[162] The stoichiometry at the preparation of the synthetic silver(I) sulphide seems to be very important for the surface composition and properties of silver(I) sulphide, see Fig. 22. Treatment of synthetic silver(I) sulphide and acanthite with an aqueous or acetone solution of potassium ethylxanthate yields solid silver(I) ethylxanthate on the surfaces.[162] This shows that silver(I) ions are accessible in the surfaces of oxidized synthetic silver(I) sulphide and acanthite, which is in contrast to the observations for chalcocite. The obtained DRIFT spectra give no indication of chemisorbed ethylxanthate complexes on the surfaces. However, the amount of silver(I) ethylxanthate is significantly smaller on acanthite surfaces. This depends probably on different inclinations to oxidation and impurities in the surface. The principles for hydrophobation of chalcocite and acanthite are very similar, and the amount of solid metal alkylxanthate on the surfaces depends on the accessibility of soluble copper(I) and silver(I) ions, respectively. Synthetic silver(I) sulphide reveals more silver(I) ions/complexes from the surface than acanthite. Synthetic copper(I) sulphide and especially chalcocite reveal only very small amounts of copper(I) ions/complexes. Chemisorbed alkylxanthate complexes do not seem to be formed on either chalcocite, synthetic copper(I) sulphide, acanthite or synthetic silver(I) sulphide surfaces. This is somewhat unexpected since both copper(I) and silver(I) are regarded as soft electron acceptors and are known to strongly coordinate ligands with soft donor atoms in solution.[111] The reason for the absence of chemisorbed complexes is probably that the copper(I) and silver(I) ions in the studied minerals and synthetic sulphides have linear or trigonal coordination in the surfaces, which means that if further ligands are to be coordinated a structural rearrangement around the metal ions in the surface is necessary; such a rearrangement is very energy consuming. The energy possible to gain at the formation of a chemisorbed surface complex will not exceed the energy necessary for a structural rearrangement in the surface, and no chemisorption to chalcocite and acanthite surfaces will therefore occur.

6.4 Covellite, CuS

Relatively few studies have been reported on the interaction between covellite and alkali alkylxanthates. This is probably due to the fact that covellite is of minor

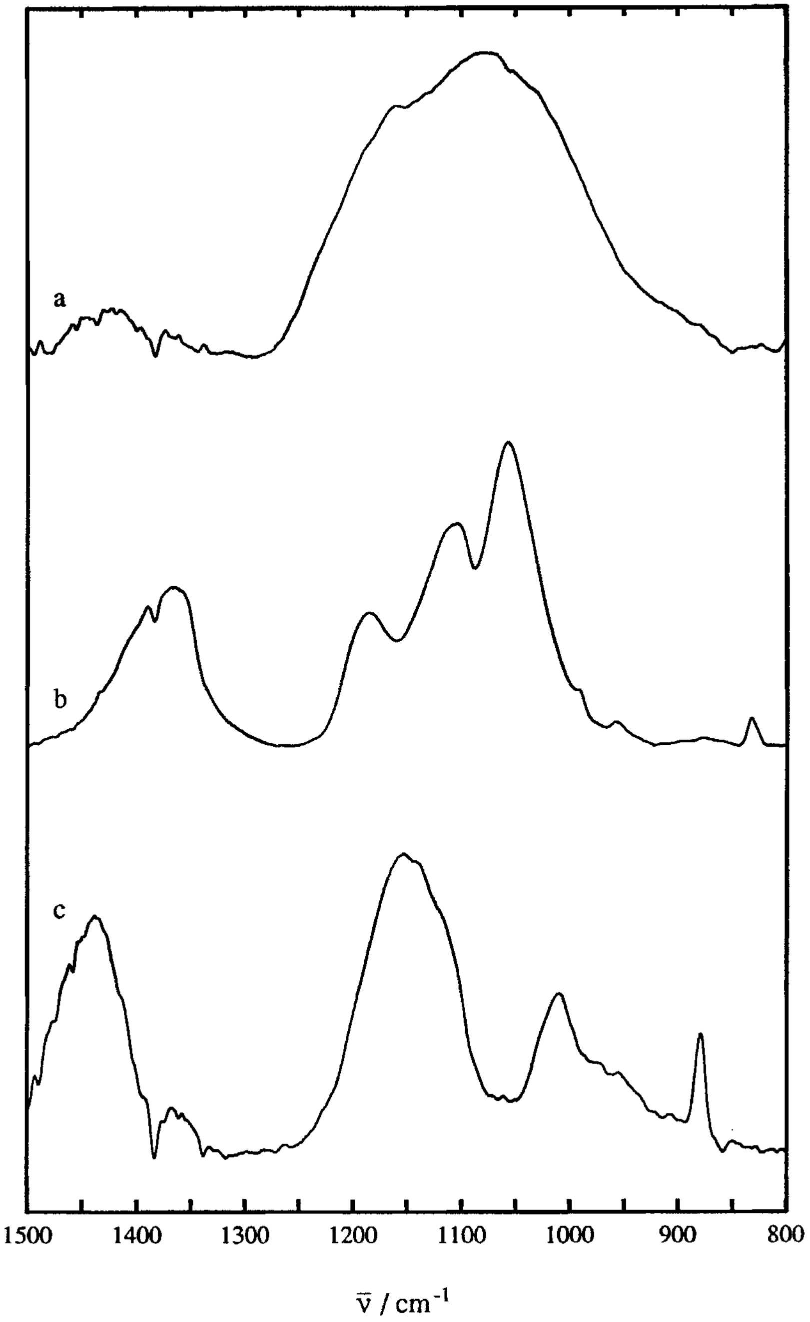


Figure 22a DRIFT spectra of (a) acanthite, (b) silver(I) sulphide prepared in an excess of silver(I) ions and (c) silver(I) sulphide prepared in an excess of sulphide ions. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

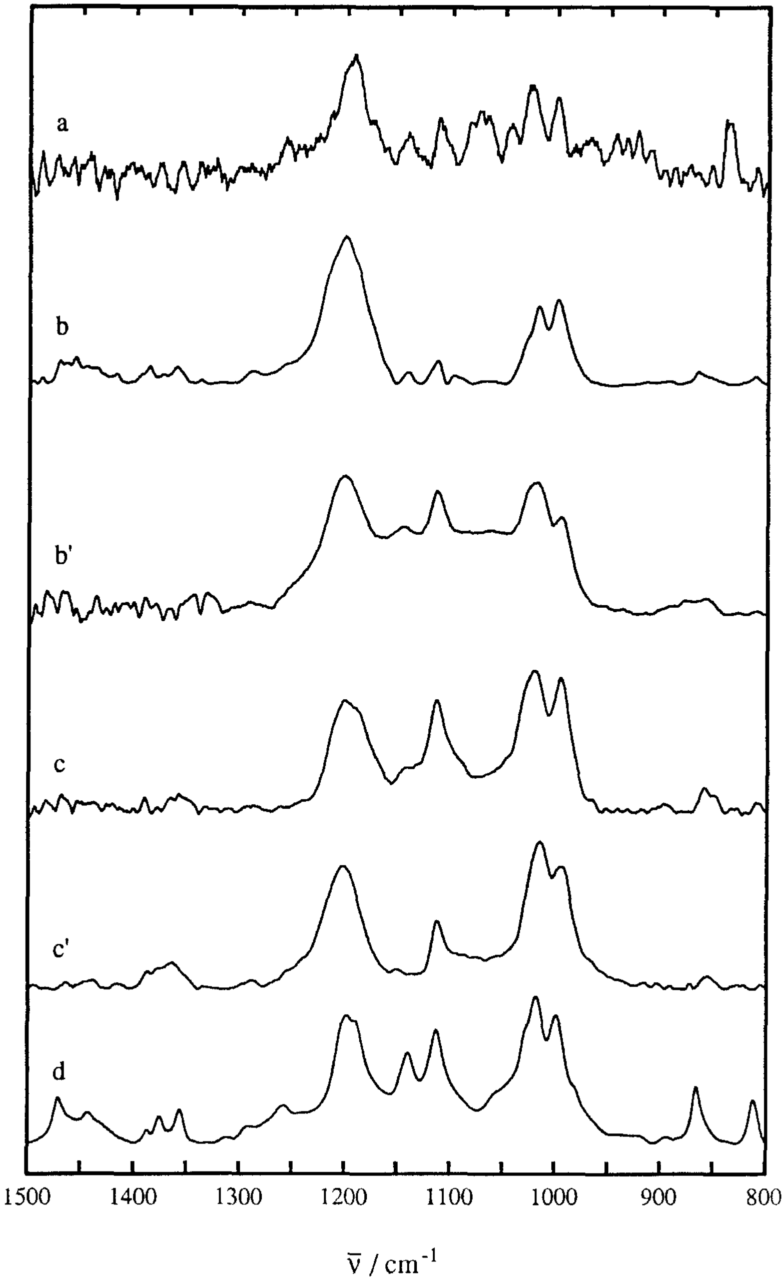


Figure 22b DRIFT spectra of (a) acanthite, (b) silver(I) sulphide prepared in an excess of silver(I) ions and (c) silver(I) sulphide prepared in an excess of sulphide ions treated with 5.0 mM aqueous and (′) acetone solutions of potassium ethylxanthate after subtraction with the spectrum obtained before treatment with the potassium ethylxanthate solution. The spectrum of (d) silver(I) ethylxanthate is given as reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

commercial importance. Covellite has the formula CuS, but it is *not* copper(II) sulphide. A better formula for describing the complex structure should be $CuS_2 \cdot Cu_2S$, see section 4. The structure contains both sulphide and disulphide ions as well as both copper(I) and copper(II) ions. This makes a large number of reactions with alkylxanthate ions possible.

Gaudin *et al.* reported early that copper(I) pentylxanthate, dipentyl dixanthogen and elemental sulphur had been extracted from covellite treated with potassium pentylxanthate, and it was proposed that copper(II) ions in covellite had reacted with pentylxanthate ions.[171] Allison *et al.* have treated covellite with alkali alkylxanthate solutions and the alkylxanthate species formed on the covellite surfaces were extracted with carbon disulphide. For alkylxanthates with a relatively long (large) alkyl chain both dialkyl dixanthogen and copper(I) alkylxanthate were found, while for alkylxanthates with a short alkyl chain only copper(I) alkylxanthate was identified on the surfaces.[172] An ESCA study of covellite before and after treatment with alkali alkylxanthates and sodium, *O,O*-diethyldithiophosphate has shown the characteristics of a copper(I) spectrum with peaks in the region 932.5–934.7 eV.[168] Ackerman *et al.* have shown by means of infrared spectroscopy that copper(I) isopropylxanthate is present on covellite surfaces and diisopropyl dixanthogen is present in the solution after treatment of covellite with potassium isopropylxanthate in aqueous solution.[173,174] They also observed that copper(II) ions were dissoved from the covellite surfaces, and that the copper(II) ions oxidize alkylxanthate ions to dialkyl dixanthogen in a rapid process. The mechanism for the hydrophobation of covellite with alkali alkylxanthate has been discussed by Fuerstenau *et al.*[175] and by Rao and Patel.[176] They have claimed that copper(II) alkylxanthate was formed, but due to its low stability it decomposes instantaneously into copper(I) alkylxanthate and dialkyl dixanthogen. The degree of oxidation of the covellite surface will not affect this process. Attempts have been made to oxidize covellite surfaces by storing a covellite sample in oxygen atmosphere for 24 hours at 40°C, and another covellite sample in air at room temperature for nine months. No oxidation products were found on the covellite samples after these treatments.[177] An atomic absorption spectrophotometric study of aqueous slurries of covellite both in the absence and in the presence of alkylxanthate ions has shown that large amounts of copper are dissolved from the covellite surfaces, also at relatively high concentrations of alkylxanthate ions,[177] see Table 3. The amounts of copper found in the solution after treatment with potassium alkylxanthate are surprisingly high in relation to the solubility product of copper(I) ethylxanthate, 5.2.

Table 3. Concentration of copper in the solution, $C_{Cu}/\mu M$, after treatment of covellit with potassium ethylxanthate solution of varying concentration, $C_{KEX}/\mu M$.

C_{KEX}[a]	C_{Cu}
0	58.23
1.0	19.83
3.0	14.00
4.0	8.65
5.0	7.71
10.0	2.83

[a] KEX = Potassium ethylxanthate.

10^{-20} M^2.[115,116] This indicates that the copper(I) species are strongly stabilized in some way. As it is known that thiosulphate ions are an oxidation product of sulphide minerals and that the thiosulphate complexes of copper(I) are very stable, it is reasonable that the increased solubility of copper(I) is caused by the formation of dithiosulphatocuprate(I) complexes.

A DRIFT spectroscopic study of covellite surfaces after treatment with potassium ethylxanthate in aqueous solution has shown that solid copper(I) ethylxanthate is the only ethylxanthate species present on the surface.[177] No diethyl dixanthogen could be detected on the surface. The amount of copper(I) ethylxanthate formed on the covellite surfaces seems to be proportional to the concentration of ethylxanthate ions at treatments with alkylxanthate concentrations lower than 3.0 mM, while the amount seems to be fairly constant at higher alkylxanthate concentrations,[177] see Fig. 23. This shows that only a limited amount of copper is available on the covellite surfaces. A DRIFT spectrum of a covellite sample treated with a 1.0 mM potassium ethylxanthate solution in dry acetone did not show any differences from a spectrum obtained from a covellite sample washed with water or acetone.[177] This shows that neither solid copper(I) ethylxanthate nor chemisorbed surface complexes are formed on covellite surfaces in acetone solution.

A parallel study was performed with potassium decylxanthate. The DRIFT spectra of decylxanthate treated covellite show the presence of both copper(I) decylxanthate and didecyl dixanthogen on the surfaces.[177] The reason for finding didecyl dixanthogen and not diethyl dixanthogen on covellite surfaces is most certainly due to higher solubility and lower detection limit by the DRIFT technique of the latter. It can be assumed that small amounts of diethyl dixanthogen may be present on ethylxanthate treated covellite surfaces and that the remaining diethyl dixanthogen is present in the aqueous phase. The formation of copper(I) alkylxanthate and very small amounts dialkyl dixanthogen on the covellite surfaces after treatment with alkylxanthate ions in aqueous solution has been proven. XPS measurements of pure covellite give a peak typical for copper(I) compounds strongly indicating that copper dissolves from covellite surfaces as copper(I) complexes. The hydrophobation of covellite by copper(I) alkylxanthate follows the same mechanism as galena and chalcocite, where copper(I) complexes are dissolved from the surfaces and surfaces and a concentration gradient is obtained around the mineral particles. The formation of dialkly dixanthogen on covellite surfaces shows the presence of strong oxidizing agents in/on the surfaces of covellite. The oxidizing agents are most probably oxidation products of the disulphide ions in covellite, $S_2O_8{}^{2-}$ and/ or $S_2O_7{}^{2-}$ ions. However, it can not be ruled out that also copper(II) may act as an oxidizing agent in this case. The dialkyl dixanthogen is physisorbed to the covellite surfaces in fairly weak interactions; see section 5.6 below for a more detailed description of the hydrophobation mechanism of dialkyl dixanthogens.

For comparison, malachite, natural $Cu_2CO_3(OH)_2$, has also been treated with alkylxanthate ions in aqueous solution.[177] In this case, only copper(II) ions are present in the mineral surface. The DRIFT spectrum of malachite treated with an aqueous solution of potassium ethylxanthate shows that both copper(I) ethylxanthate and diethyl dixanthogen are formed on the malachite surfaces as expected, see Fig. 24. This shows that both copper(I) alkylxanthate and dialkyl dixanthogen are formed on the mineral surfaces when copper(II) is present.

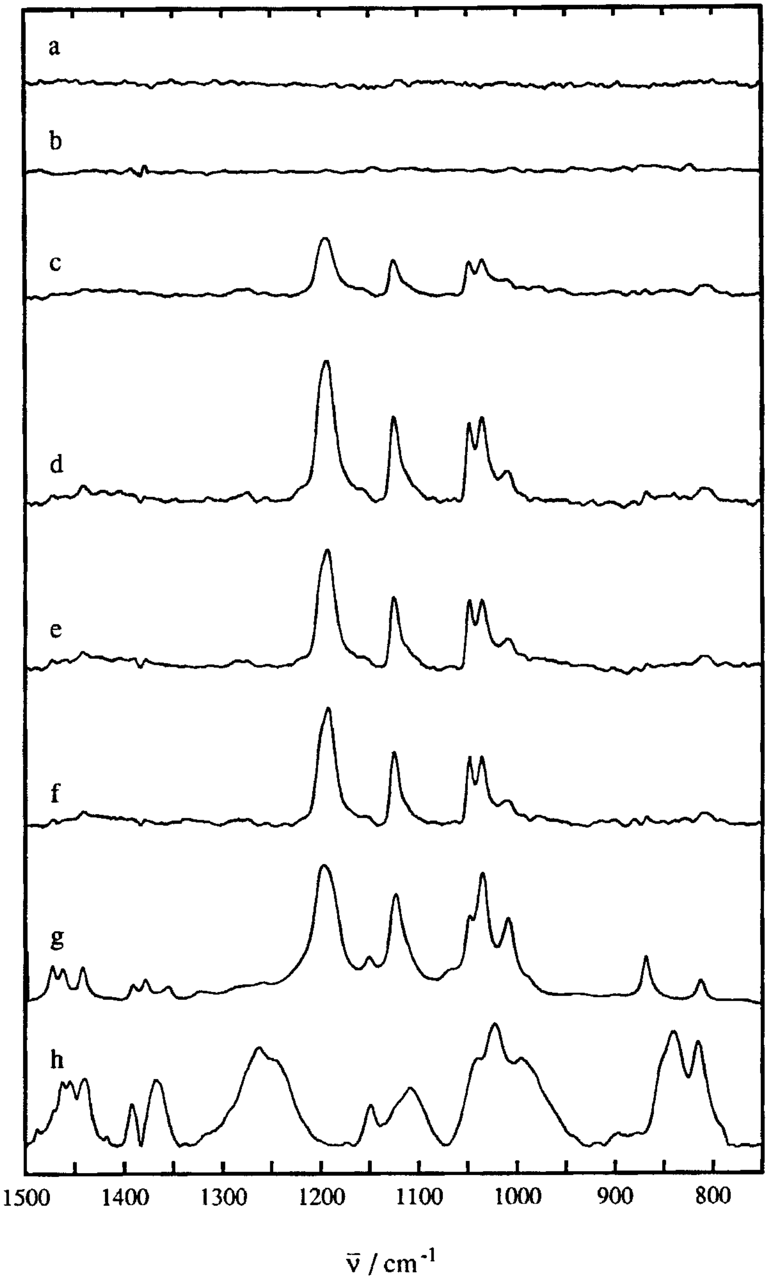


Figure 23 DRIFT spectra of (a) covellite, (b) covellite treated with water, (c) covellite treated with aqueous solutions of potassium ethylxanthate, 1.0 mM, (d) 3.0 mM, (e) 5.0 mM and (f) 10.0 mM. The spectra of (g) solid copper(I) ethylxanthate and (h) liquid diethyl dixanthogen are given for comparison. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary. The spectra a-f have the same ordinate scale.

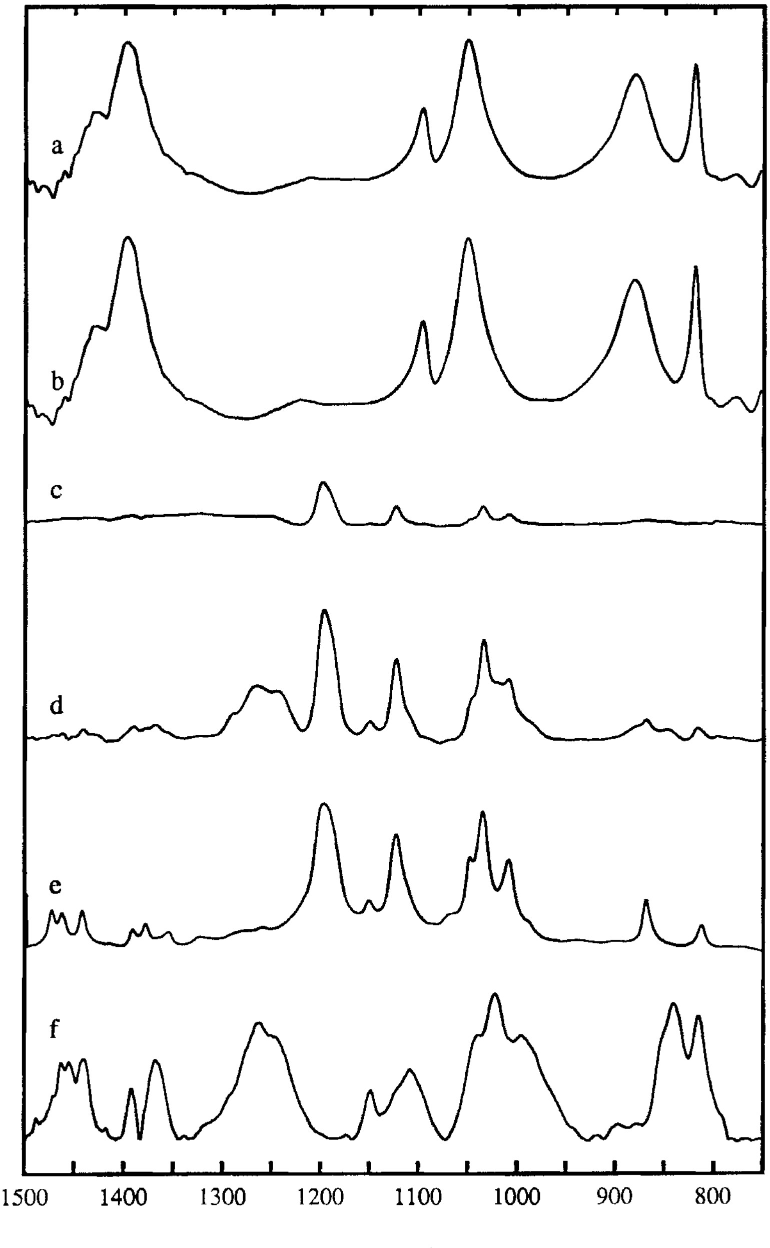


Figure 24 The DRIFT spectra of (a) malachite, (b) malachite treated with water, (c) malachite treated with aqueous solutions of potassium ethylxanthate 1.0 mM and (d) 10.0 mM. The spectra of (e) solid copper(I) ethylxanthate and (f) liquid diethyl dixanthogen are given for comparison. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary. The spectra a-d have the same ordinate scale.

6.5 Chalcopyrite, $CuFeS_2$

The structure of chalcopyrite is built up of copper(I), iron(III) and sulphide ions in such a way that each copper(I) and iron(III) ion is tetrahedrally surrounded by four sulphide ions, and the sulphide ions are tetrahedrally surrounded by two copper(I) and two iron(III) ions. This means that the chalocopyrite structure is much more closely related to the chalcocite structure than to the pyrite structure, see section 4.

It has been reported that both copper(I) alkylxanthate and copper(I) thioperoxydicarbonate are formed as hydrophobic coating on chalcopyrite after treatment with potassium alkylxanthate solutions at oxidizing conditions.[166] An IR spectroscopic study has reported that basic copper(I) isopropylxanthate is formed on chalcopyrite surfaces after treatment with an alkaline potassium isopropylxanthate solution, and that selective flotation was most effective in the pH range 7.5–9.5.[178] Leppinen *et al.* have reported from ATR studies that dialkyl dixanthogen is initially formed on chalcopyrite surfaces and that copper(I) ethylxanthate is then formed on top of the dialkyl dixanthogen at higher potentials.[165,179] This seems however very unlikely as it should require higher potentials to form copper(I) ethylxanthate than diethyl dixanthogen. Roos *et al.* have also reported that copper(I) alkylxanthate species and dialkyl dixanthogen are responsible for the hydrophobation of chalcopyrite surfaces after treatment with aqueous solutions of potassium alkylxanthate.[180] Ackerman *et al.* have previously found only dialkyl dixanthogen on the chalcopyrite surface by extraction from the surface by carbon disulphide.[173,174] Metal methylxanthates have low solubility in carbon disulphide, which might be the reason for the absence of copper(I) alkylxantahte.

The only alkylxanthate species adsorbed on the chalcopyrite surfaces after treatment with an aqueous potassium alkylxanthate solution is solid copper(I) alkylxanthate, shown by its characteristic bands at 1035, 1120 and 1200 cm^{-1} in the DRIFT spectrum of ethylxanthate treated chalcopyrite surfaces,[181] see Fig. 25. No dialkyl dixanthogen or iron(III) alkylxanthate have been detected on the chalocopyrite surfaces, see Fig. 25. This is in agreement with an XPS study where it has been found that the copper in chalcopyrite surfaces is present as copper(I).[168] This shows that there is no sufficiently strong oxidizing agent on the chalcopyrite surfaces for the oxidation of alkylxanthate ions to dialkyl dixanthogen. The amounts of copper and especially iron dissolved from the chalcopyrite surfaces are very large, see Table 4. It can also be seen in this Table that the copper concentration decreases markedly also at the addition of small amounts of alkali alkylxanthate, which is in accordance with the formation of solid copper(I) alkylxanthate on chalcopyrite surfaces and that no stabilizing complexing agents are present in the system, as it obviously is in the covellite system, see section 6.4 above. The solubility of iron(III) alkylxanthate

Table 4. Total concentration of copper, C_{Cu}/μM, and iron, C_{Fe}/μM, in aqueous solution, after treatment of chalcopyrite with potassium ethylxanthate solutions of varying concentration, C_{KEX}mM.

C_{KEX}	C_{Cu}	C_{Fe}
0	36.6	262.5
0.2	3.09	209.7
1.0	0.20	148.4
3.0	0.32	31.2
5.0	0.40	15.7
10.0	0.69	12.7

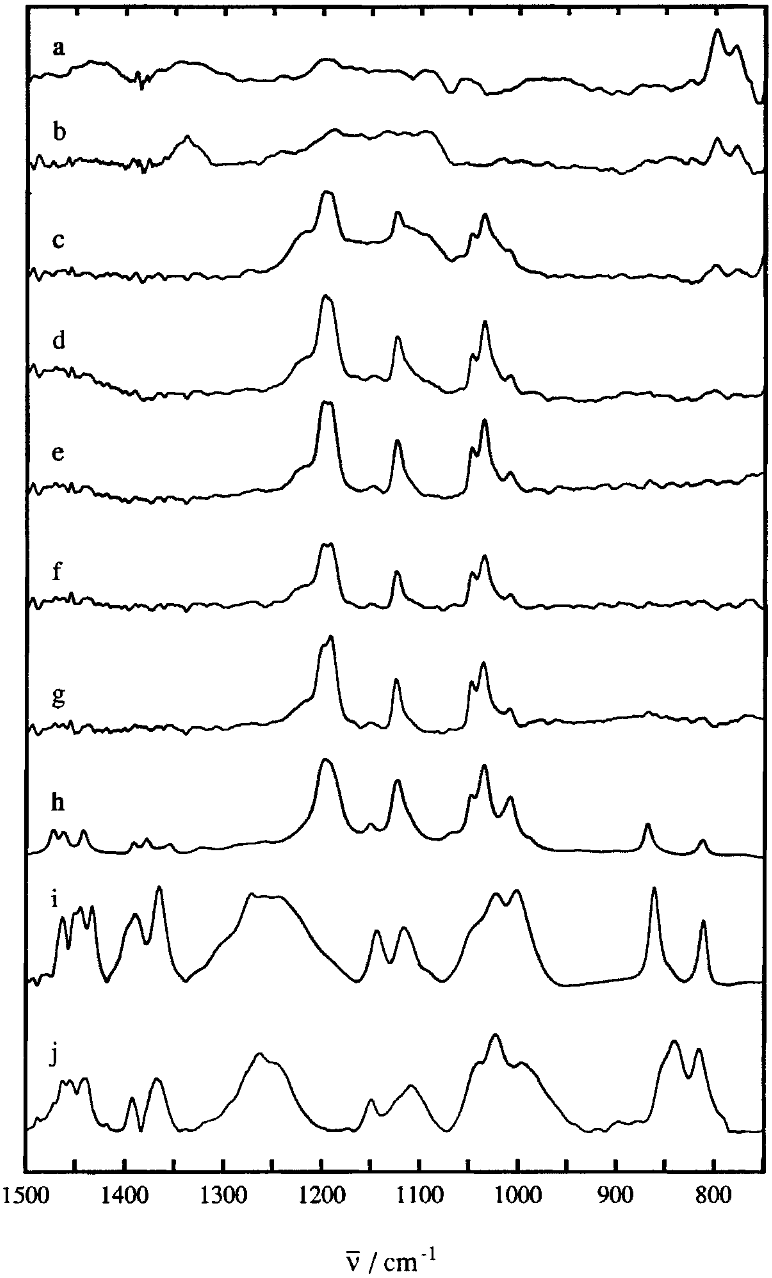


Figure 25 DRIFT spectra of (a) chalcopyrite, (b) chalcopyrite treated with water, (c) chalcopyrite treated with aqueous solutions of potassium ethylxanthate, 0.2 mM, (d) 1.0 mM, (e) 3.0, (f) 5.0 mM and (g) 10.0 mM. The spectra of (h) solid copper(I) ethylxanthate, (i) solid iron(III) ethylxanthate and (j) comparison. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary. The spectra a-g have the same ordinate scale.

species is fairly high in aqueous solution, see Table 1, and it is not likely that iron(III) alkylxanthate will precipitate on the chalcopyrite surfaces at the alkylxanthate concentrations used in flotation processes. The hydrophobation mechanism is thus identical with that of chalcocite and galena.

6.6 Pyrite, FeS_2, and Marcasite, FeS_2

Pyrite, natural iron(II) disulphide, is one of the most common sulphide ores, and it is often present together with smaller amounts of valuable minerals such as chalcopyrite. Pyrite is the raw material in the production of sulphuric acid and is therefore of large economical importance. Pyrite must therefore be depressed at the floation of chalcopyrite and separated from gangue minerals at its flotation. The pyrite-alkylxanthate ion system is therefore one of the most thoroughly investigated mineral-collector systems. Several mechanisms for the hydrophobation of pyrite with alkylxanthate ions have been proposed during the years, and some of them are summarized below.

Marcasite is a polymorph of pyrite much less common than pyrite. A limited number of papers concerning the marcasite-alkylxanthate ion system has been reported.[182,183] The chemical properties of marcasite are identical with those of pyrite. Pyrite and marcasite will therefore be discussed together. Taggart *et al.* early proposed that pyrite is hydrophobated by oxidation of iron in the pyrite surface to an iron(III) compound and a subsequent precipitation of iron(III) alkylxanthate.[184] The presence of dialkyl dixanthogen was also observed on pyrite surfaces after treatment with aqueous alkali alkylxanthate solutions. Gaudin found also that alkylxanthate treatment in aqueous solution of pyrite yields dialkyl dixanthogen coated pyrite surfaces.[185] Cook has claimed that the active alkylxanthate species in the hydrophobation of pyrite is the alkylxanthic acid, and that the flotation response is governed by the conditions controlling the presence of alkylxanthic acid.[186] Gaudin later reported that pyrite coordinates alkylxanthate ions up to monolayer when oxidation is prevented during the exposure of pyrite to aqueous solutions of potassium alkylxanthate.[187] In the presence of oxygen, the amount of coordinated alkylxanthate species adsorbed on the pyrite surface largely exceeds a monolayer. This study also reported the presence of oily droplets in the aqueous phase after treatment with ethylxanthate ions, but any formation of diethyl dixanthogen was not mentioned. Fuerstenau has reported that alkylxanthate ions appear to be chemisorbed on pyrite surfaces in oxygen-free systems, while dialkyl dixanthogen is formed in the presence of oxygen.[117]

It has been concluded from spectroscopic, electrokinetic and electrochemical measurements[188-191] and from practical flotation[187] that dialkyl dixanthogen is the alkylxanthate species responsible for the hydrophobation of pyrite surfaces. Dialkyl dixanthogen is proposed to be formed by an anodic oxidation of alkylxanthate ions on the surface of pyrite coupled with a cathodic reduction of adsorbed oxygen.[188-191] The overall reaction is said to occur thermodynamically to about pH 11, but above this pH the alkylxanthate ion is the most stable alkylxanthate species. It has been suggested that dialkyl dixanthogen formed on pyrite surfaces is strongly bound to the surface, but the kind of interaction present between the pyrite surface and the dialkyl dixanthogen molecules was not mentioned.[164] This observation is in contradiction to previous observations, where it has been shown that dialkyl dixanthogen is physisorbed to mineral surfaces, which means that the interaction is weak.

It was first suggested that alkylxanthate ions were oxidized to dialkyl dixanthogen by oxygen.[192] It was later suggested that ion(III) irons or iron(III) hydroxide are the oxidizing agents at the formation of dialkyl dixanthogen in an electrochemical reaction. Rao and Patel have reported that iron(III) salts were found to enhance the oxidation of butyl- and pentylxanthate ions in the presence of oxygen,[193] and Allison has reported that oxidation of alkylxanthate ions by oxygen to dialkyl dixanthogen is catalysed by iron(III) species.[194] Tipman and Leja have claimed in contradiction to previous reports that a more powerful oxidizing agent than dissolved oxygen was necessary for the formation of dialkyl dixanthogen.[195] X-ray emission spectroscopic measurements have shown that oxygen containing species on pyrite surfaces consist of iron oxides rather than adsorbed oxygen molecules.[196] Sheikh and Leja have reported that below pH 3.5 iron(III) ethylxanthate is obtained regardless of whether iron(II) or iron(III) reactants were used in the presence of air.[197] Iron(II) ethylxanthate was obtained only in highly concentrated solutions at neutral pH and under reducing conditions.[197] Iron(III) does not oxidize alkylxanthate ions to dialkyl dixanthogen in aqueous solution as e.g. copper(II). Dialkyl dixanthogen has been detected as a product of the decomposition of iron(III) alkylxanthate at high pH.[197]

A calorimetric study has claimed that dipentyl dixanthogen is adsorbed on marcasite surfaces in an electrochemical reaction at the treatment of marcasite with potassium pentylxanthate in aqueous solution.[182] It was proposed that oxygen, adsorbed on marcasite and pyrite surfaces, oxidizes alkylxanthate ions to dialkyl dixanthogen. Mielczarski has proposed from ATR measurements that a monolayer of iron(III) alkylxanthate is formed on marcasite surfaces as an initial stage.[183] In a second step a multilayer coverage of dialkyl dixanthogen is formed on the marcasite surfaces. Large amounts of iron are dissolved from pyrite surfaces at slurrying, and the amount of dissolved iron increases in course of time, and it is dependent on the concentration of oxygen in the aqueous phase,[170] see Table 5. This shows that pyrite surfaces are oxidized in aqueous solution to water soluble iron compounds.

Diethyl dixanthogen was the only product found on the pyrite surfaces as identified by DRIFT spectroscopy,[170,181] when pyrite and marcasite powders, not protected against oxidation, were treated with aqueous solutions of potassium ethylxanthate of varying concentrations, 0.2–10.0 mM, see Fig. 26. At the treatment with low concentrations of ethylxanthate ions, 0.2–3.0 mM, the amount of diethyl dixanthogen on the pyrite and marcasite surfaces was proportional to the concentration of potassium ethylxanthate, while the amount of diethyl dixanthogen formed

Table 5. The total amount of iron, in mg Fe g^{-1} pyrite powder, in the aqueous phase after slurrying pyrite in water and in an aqueous solution of potassium ethylxanthate, 10.0 mM, as a function of time.

Time	Water	$KC_2H_5OCS_2(aq)$
15 min	2	0.3–0.5
2 h	10	a
48 h	10	a
48 h	6[b]	a

[a] Not determined
[b] Deairated water

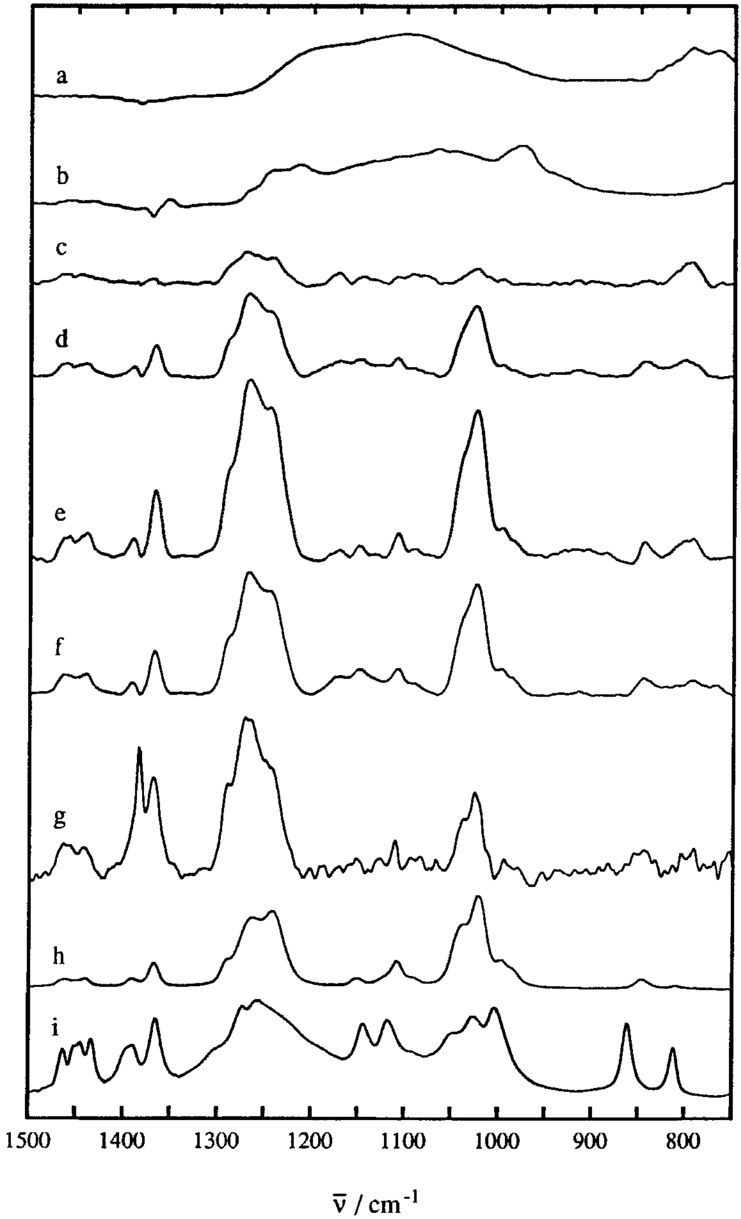


Figure 26 DRIFT spectrum of (a) dry-ground pyrite, (b) dry ground pyrite treated with an aqueous solution of potassium ethylxanthate, (c)-(f) pyrite after treatment with an aqueous solution of potassium ethylxanthate of concentration 0.2 mM, 1.0 mM, 3.0 mM and 10.0 mM, respectively, (g) wet-ground pyrite treated with a 1.0 mM solution of potassium ethylxanthate, after subtraction with the spectrum of the untreated pyrite. The spectra of (g) diethyl dixanthogen (transmission data) and (h) solid iron(III) ethylxanthate (DRIFT data) are given for comparison. The ordinate scale is in log ($R_{\text{ref}}/R_{\text{sample}}$) units and it is arbitrary. The spectra (c)-(f) have the same ordinate scale.

seems to be constant at potassium ethylxanthate concentrations higher than 3.0 mM, see Fig. 26.

The role of oxygen as oxidizing agent, whether an oxidized pyrite surface is necessary for the sole formation of diethyl dixanthogen on pyrite and marcasite surfaces and if the oxidation reaction takes place at the surface or in the solution in close vicinity of the surface have been studied in a series of experiments.[170,181] Pyrite, not protected from oxidation, was slurried in water, and potassium ethylxanthate was added to the aqueous phase after filtration. As no precipitate and no diethyl dixanthogen were formed, it was concluded that the species responsible for the oxidation of ethylxanthate ions are bound to the pyrite surface in its active form.[170] Pyrite and marcasite powders were washed for one hour with a 0.10 M aqueous solution of ethylenediiminobis(2-hydroxy-4-methyl-phenyl)acetate, which is an extraordinarily strong complexing agent for iron(III),[198] in order to dissolve and remove all iron containing oxidation products from the pyrite and marcasite surfaces. Treatment of pyrite and marcasite, pretreated with ethylenediiminobis(2-hydroxy-4-methyl-phenyl)acetate, with a 1.0 mM potassium ethylxanthate solution yeilds diethyl dixanthogen on the pyrite and marcasite surfaces but in substantially smaller amounts than on the surfaces of ordinarily treated pyrite and marcasite powders, see Fig. 27. This shows that another compound than pyrite and marcasite on the mineral surfaces plays an important role at the oxidation of ethylxanthate ions.

Ethylenediiminobis(2-hydroxy-4-methyl-phenyl)acetate pretreated pyrite and marcasite powders were stored in hydrogen atmosphere at room temperature for 24 hours in order to reduce possible remaining oxidation products on the pyrite and marcasite surfaces. These pretreated and reduced powders were then treated with an oxygen-free aqueous solution of potassium ethylxanthate, 1.0 mM. This experiment was repeated with an air-saturated potassium ethylxanthate solution. Neither diethyl dixanthogen nor iron(III) ethylxanthate were found on the pyrite and marcasite surfaces after these treatments, see Fig. 27. Pyrite and marcasite powders, ground dry in air, were treated with the same oxygen-free potassium ethylxanthate solution as used in the experiment described above. Large amounts of diethyl dixanthogen were found on the pyrite and marcasite surfaces after this treatment, see Fig. 27. These experiments show that oxygen in the aqueous solution is *not* the oxidizing agent at the formation of dialkyl dixanthogen on pyrite and marcasite surfaces. This means that the only remaining sufficiently strong oxidizing agents on oxidized pyrite and marcasite surfaces are oxidation products of the disulfide ions in the minerals. Possible oxidation products of the disulfide ion with sufficiently high oxidation potentials are the $S_2O_x^{2-}$ ions, $x = 3$–8. The part of the oxidation products which are sufficiently strong oxidation agents to oxidize alkylxanthate ions is most probably small. It has been shown that alkylxanthate ions are oxidized to dialkyl dixanthogen by $S_2O_8^{2-}$ and $S_2O_7^{2-}$ anions,[199] while no oxidation takes place with the $S_2O_5^{2-}$ and $S_2O_4^{2-}$ anions.[170] It has however so far not been possible to establish the oxidizing agent(s) responsible for the oxidation of alkylxanthate ions to dialkyl dixanthogen on pyrite and marcasite surfaces. In an other experiment pyrite was treated with 1.0 mM aqueous solutions of potassium ethylxanthate with varying pH in order to study the pH dependence of the formation of dialkyl dixanthogen on pyrite surfaces. It was found that only diethyl dixanthogen was formed, and the amount seems to be independent of pH, see Fig. 28. This indicates that the mechanism for the formation of dialkyl dixanthogen on

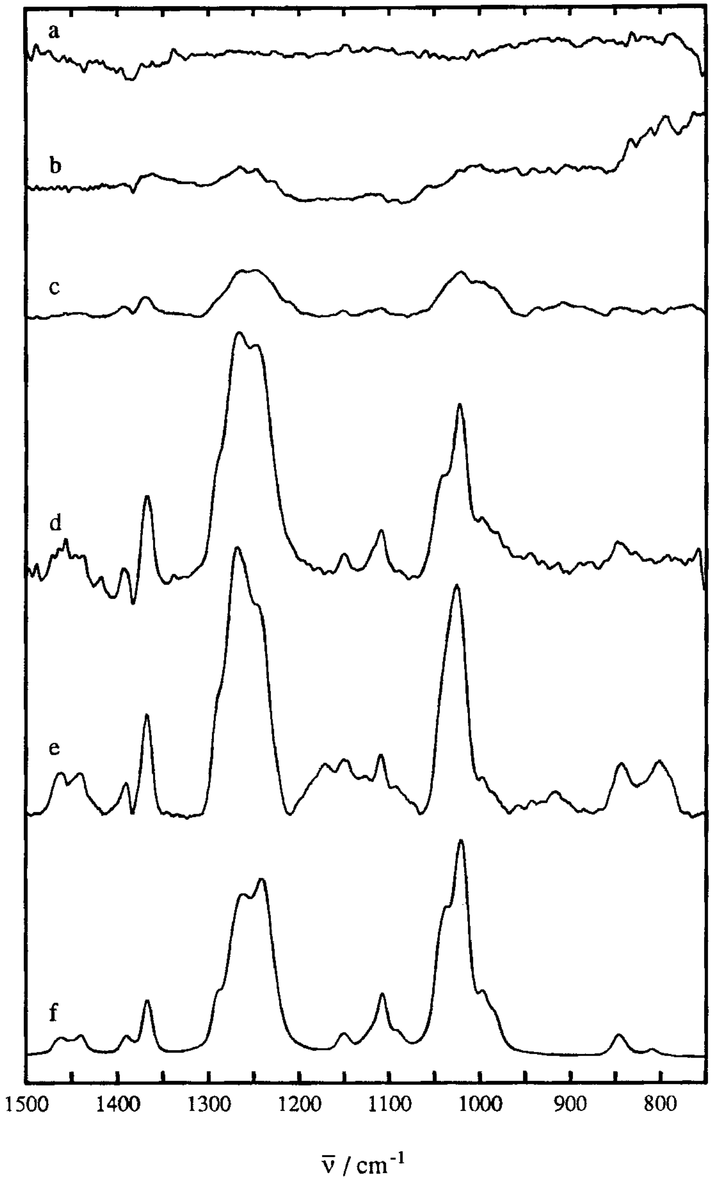


Figure 27 DRIFT spectra of (a) pyrite pretreated with ethylenediimobis(2-hydroxy-4-methylphenyl)acetate and reduced with hydrogen after treatment with an oxygen-free and (b) an air-saturated aqueous solution of potassium ethylxanthate, 1.0 mM, (c) pyrite pretreated with ethylenediimobis(2-hydroxy-4-methlyphenyl)acetate after treatment with an air-saturated aqueous solution of potassium ethylxanthate, 1.0 mM, and of (d) oxidized pyrite after treatment with an oxygen-free, and (e) an air-saturated aqueous solution of potassium ethylxanthate, 1.0 mM, after subtraction with the spectrum obtained before treatment with a potassium ethylxanthate solution. The transmission spectrum of (f) liquid diethyl dixanthogen is given as reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary. The spectra a-c have the same ordinate scale.

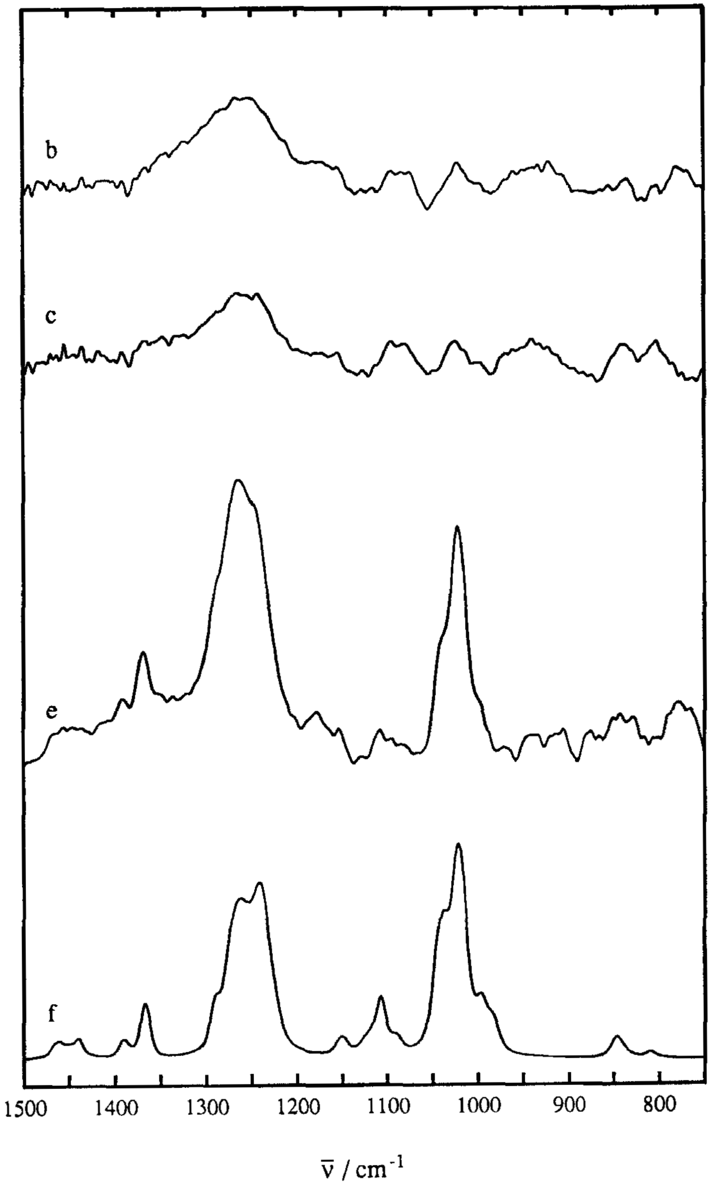


Figure 27b DRIFT spectra of (b) marcasite pretreated with ethylenediimobis(2-hydroxy-4-methyl-phenyl)acetate and reduced with hydrogen after treatment with an air-saturated aqueous solution of potassium ethylxanthate, 1.0 mM, (c) marcasite pretreated with ethylenediiminobis(2-hydroxy-4-methyl-phenyl)acetate, 1.0 mM, and (e) an air-saturated aqueous solution of potassium ethylxanthate, 1.0 mM, *after subtraction with the spectrum obtained before treatment with a potassium ethylxanthate solution.* The transmission spectrum of (f) liquid diethyl dixanthogen is given as reference. The ordinate scale is in long (R_{ref}/R_{sample}) units and it is arbitrary. The spectra a-e have the same ordinate scale.

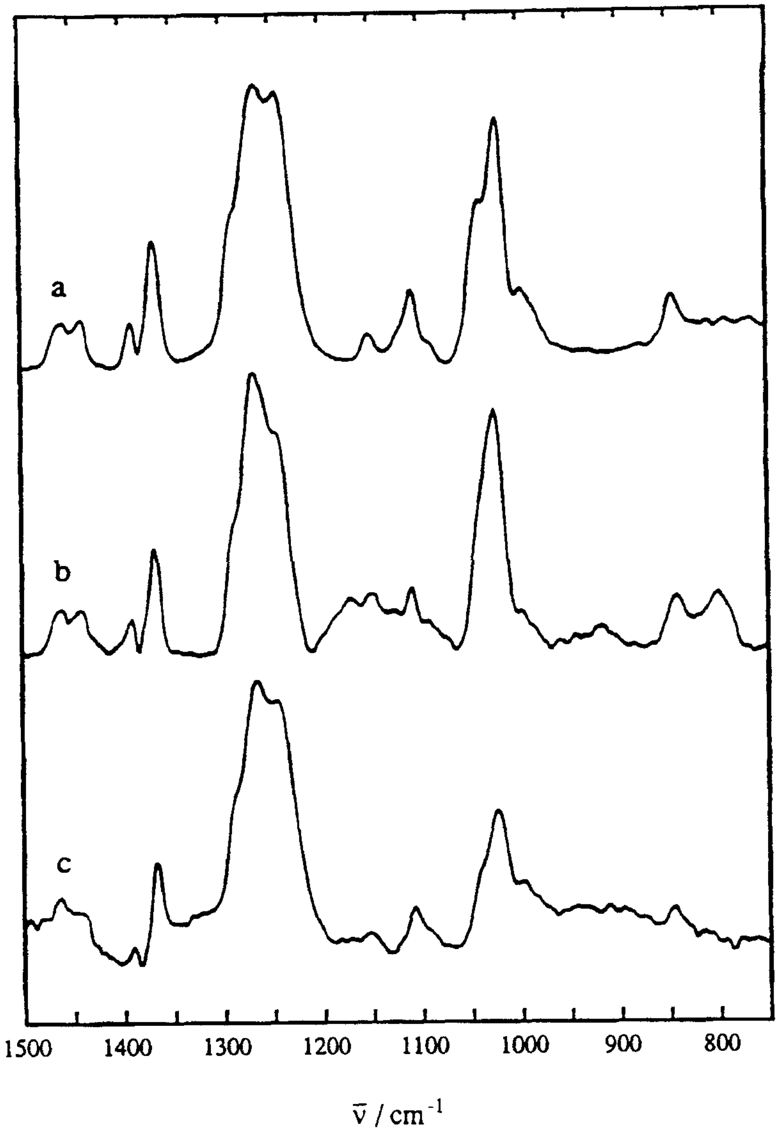


Figure 28 DRIFT spectra of (a) pyrite treated with aqueous solutions of potassium ethylxanthate, 1.0 mM at pH 4.6, (b) pH 7.0 and (c) pH 10.2 after subtraction with the spectrum of the untreated marcasite. The ordinate scale is in log (R_{ref}/R_{sample}) units and all spectra have the same arbitrary ordinate scale.

pyrite surfaces is the same in the pH region 4.6–10.2. This is in accordance with an oxidation with $S_2O_x^{2-}$ species, x = 7 or 8, while the stable iron(III) and alkylxanthate species vary in this pH range.

Flotation in a laboratory flotation cell has shown that the highest recovery of pyrite, when alkylxanthate ions are used as collectors, is found at pH 4 and 10, and with a minimum at pH 7.[116] The physical properties of the surface are of importance for the binding of dialkyl dixanthogen to the pyrite surface as dialky dixanthogen is physisorbed on the pyrite surface. A measurement of the ζ-potential of pyrite surfaces has shown that the ζ-potential is zero at pH 7,[188] which might be the reason for weaker physisorption at this pH.

These experiments have clearly shown that dialkyl dixanthogen is the hydrophobating alkylxanthate species on pyrite and marcasite as reported previously. No formation of iron alkylxanthate species has been found on the pyrite and marcasite surfaces independent of pretreatment and conditions at the treatment with alkylxanthate ions. In contradiction with most of the previous postulations it has now been shown that neither oxygen nor iron(III) species are oxidizing agents at the formation of dialkyl dixanthogen on the pyrite surfaces. Instead it has been shown that oxidation products of the disulphide ion, e.g. $S_2O_8^{2-}$ and/or $S_2O_7^{2-}$, are most probably the oxidizing agent(s). These are known to be strong oxidizing agents, and they oxidize alkylxanthate ions fast to dialkyl dixanthogen in aqueous solution. This reaction between alkylxanthate and peroxodisulphate ions has indeed been used for preparation of pure dialkyl dixanthogen.[199] The mechanism for the hydrophobation of oxidized pyrite and marcasite surfaces can therefore be summarized as follows: 1) The disulfide ion in the mineral must partly be oxidized to an oxosulphur anion with a high oxidation potential; most probably $S_2O_8^{2-}$ and/or $S_2O_7^{2-}$ ions. This oxidation product is probably not dissolved from the surface before the reaction with alkylxathate ions. 2) The alkylxanthate ions are oxidized to dialkyl dixanthogen by this oxidition agent in or on the surface. 3) The highly hydrophobic dialkyl dixanthogen is physisorbed on the pyrite and marcasite surfaces.

Pyrite is depressed by fairly large amounts calcium hydroxide at about pH 10.5. It is reasonable to believe that gypsum, $CaSO_4.nH_2O$, precipitates as a hydrophilic agent on the pyrite surfaces; the disulphide ions in pyrite is fairly easily oxidized to a variety of oxosulphur anions with sulphate and thiosulphate as the predominating ones. However, it has not been possible to prove the presence of gypsum on pyrite surfaces after treatment with calcium ions. On the other hand, precipitation of solid barium sulphate has been established at the treatment with barium ions.[170] This shows that sulphate ions are presence in close vicinity of the pyrite surfaces in aqueous slurries, and that the formation of gypsum is possible. The lack of evidence of gypsum on the pyrite surfaces may lay in that two small amounts are formed to be detected by the DRIFT and FT-Raman spectroscopic techniques used.

6.7 *Pentlandite, $(Fe,Ni)_9S_8$, Pyrrhotite, FeS_{1-x}, and Troilite, FeS*

Pentlandite and pyrrhotite have complicated structures where some of the S-S distances are fairly short, less than 3.4 Å.[47–53] The troilite structure is built up of close-packed sulphide ions with iron(II) in the octahedral interstices where the S-S distances vary in the range 3.35–3.75 Å. These S-S distances are substantially longer than those in the disulphide ion, 2.2 Å, but significantly shorter than the S-S distances in structures with close-packed sulphide ions where the S-S distances normally are longer than 3.7 Å. It can therefore be expected that hydrophobation mechanisms for these iron containing sulphide minerals are different from those of pyrite and galena, respectively.

Hodgson and Agar have reported from electrochemical studies that dialkyl dixanthogen is chemisorbed to the nickel sites in pentlandite, while no chemisorption of alkylxanthate ions takes place on pyrrhotite surfaces.[200] Instead the pyrrhotite surfaces were rendered hydrophobic by dialkyl dixanthogen which was formed as part of a mixed potential reaction involving the normal oxidiation process.[200] Rao and Finch have reported that pyrrhotite is hydrophobated by dialkyl dixanthogen.[201] They propose that the pyrrhotite-alkylxanthate ion reaction follows a charge transfer mechanism where an electron is transferred from the alkylxanthate ion to oxygen dissolved in water as proposed by Hodgson and Agar.[200] In the presence of nitrogen instead of air no dialkyl dixanthogen is formed, which should imply the importance of oxygen for the oxidation of alkylxanthate ions at pyrrhotite surfaces. No studies on the interaction between troilite and alkyxanthate ions in aqueous solution has to my knowledge been reported.

Pentlandite and pyrrhotite have been treated with aqueous solutions of potassium ethylxanthate and decylxanthate. DRIFT spectra of these alkylxanthate treated minerals show that didecyl dixanthogen is present on both pentlandite and pyrrhotite surfaces, while the samples treated with ethylxanthate have no detectable amounts of ethylxanthate species on the surfaces,[181] see Fig. 29. The amounts of didecyl dixanthogen formed on pentlandite and pyrrhotite surfaces are relatively small in comparison with those obtained on pyrite and marcasite surfaces.[182] The reason why diethyl dixanthogen is not observed on these mineral surfaces, while didecyl dixanthogen is, depends certainly on different solubilities in aqueous solution and not on chemical differences; diethyl dixanthogen is substantially more soluble in water than didecyl dixanthogen.[202] This shows that small amounts of an oxidizing agent(s), strong enough to oxidize alkylxanthate ions to dialkyl dixanthogen, are present on oxidized pentlandite and pyrrhotite surfaces. If the amount of dialkyl dixanthogen formed on pentlandite and pyrrhotite surfaces is sufficient to flotate these mineral surfaces is uncertain. Pentlandite and pyrrhotite are hydrophobated according to the same hydrophobation mechanism as pyrite and marcasite, described above, even though the amount of a strong oxidizing agent on the surfaces is markedly less than on pyrite and marcasite. This is most probably due to that the S-S distances in pentlandite and pyrrhotite are longer than the corresponding distances in pyrite and marcasite. The relative amounts of the oxidation products of sulphur in sulphide minerals, non-oxidizing ones as the sulphate, SO_4^{2-}, and thiosuphate, $S_2O_3^{2-}$, ions, and oxidizing ones as the peroxodisulphate, $S_2O_8^{2-}$, and disulphate, $S_2O_7^{2-}$, ions are dependent on the sulphur-sulphur distance, and the relative amount of oxidizing species seems to increase with decreasing S-S distance in the mineral structure.

No alkylxanthate species has been detected by means of DRIFT spectroscopy on troilite surfaces after treatment with an aqueous potassium alkylxanthate solution.[181] The reason to this behaviour can be summarized as follows: a/ only sulphide ions are present in the troilite structure, and neither sulphide ions nor their oxidation products react with alkylxanthate ions, b/ both iron(II) and iron(III) ions are hard electron acceptors, which have no or only a very weak ability to form covalent interactions, thereby being unable to form chemisorbed alkylxanthate

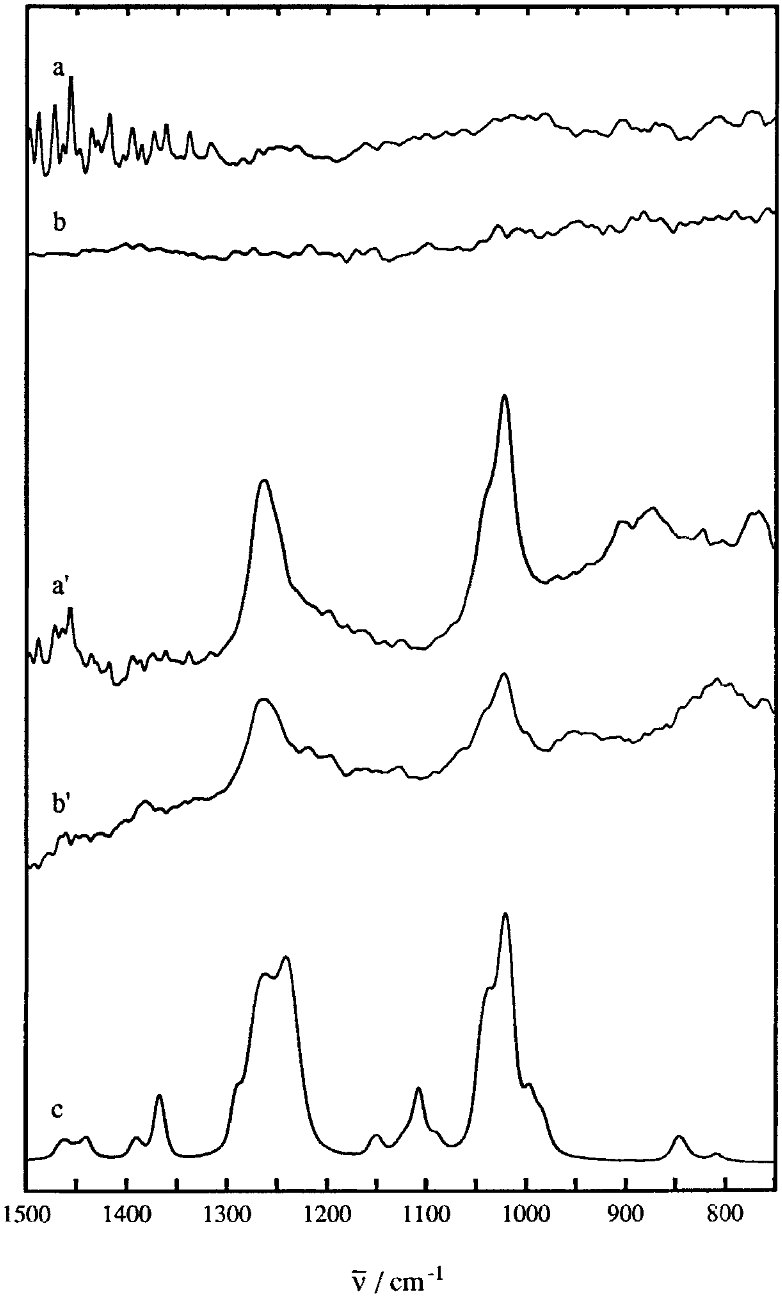


Figure 29 DRIFT spectra of (a) pentlandite and (b) pyrrhotite treated with a 1.0 mM aqueous solution of potassium ethylxanthate and (′) decylxanthate after subtraction with the spectrum of the untreated mineral. The DRIFT spectrum of diethyl dixanthogen is given as reference (c). The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

complexes on a troilite surface, and c/ the concentration of dissolved iron is not high enough to exceed the solubility product of iron(III) alkylxanthate.

6.8 *Millerite, NiS, and Molybdenite, MoS_2*

The sulphurs in the millerite structure are arranged in triangles where the shortest S-S distance is 3.24 Å.[54,55] Molybdenite has a sheet structure where the S-S distances within the sulphur sheets are 3.15 Å.[56] The S-S distances in millerite and molybdenite are roughly the same as in pentlandite and pyrrhotite, and one may expect that the hydrophobation mechanism of millerite and molybdenite is the same as for pentlandite and pyrrhotite.

DRIFT spectra of millerite and molybdenite treated with aqueous solutions of potassium ethylxanthate and decylxanthate show that dialkyl dixanthogen is the sole alkylxanthate species formed on the surfaces,[203] see Fig. 30. This shows that oxidized millerite and molybdenite contain small amounts of a highly oxidizing agent(s) in the surfaces. The amounts of dialkyl dixanthogen formed on millerite and molybdenite surfaces are somewhat larger than on pentrandite and pyrrhotite but substantially smaller than on pyrite and marcasite. This may indicate that the somewhat shorter S-S distances in millerite and molybdenite than in pentlandite and pyrrhotite may be the cause of the formation of larger amounts of highly oxidizing species are formed on the surfaces.

6.9 *Realgar, AsS, Orpiment, As_2S_3, and Arsenopyrite, FeAsS*

The shortest S-S distances in realgar, orpiment and arsenopyrite are 3.295, 3.242 and 3.197 Å, respectively.[43–45,57,58] These arsenic containing sulphide minerals are therefore expected to have the same hydrophobation mechanism with alkylxanthate ions in aqueous solution as pentlandite, pyrrhotite, millerite and molybdenite.

It has been shown that dialkyl dixanthogen is the main alkylxanthate species formed on the arsenopyrite surfaces after treatment with aqueous solutions of potassium alkylxanthate.[204] It has been proposed that alkylxanthate ions are coordinated to iron sites in the arsenopyrite surfaces, where the alkylxanthate ion is fast converted to dialkyl dixanthogen.[205] It is however very doubtful if this reaction mechanism is correct as previous studies have shown that the implied oxidizing agent iron(III) does not oxidize alkylxanthate ions to dialkyl dixanthogen in aqueous solution.

DRIFT spectra of realgar, orpiment and arsenopyrite powders treated with an aqueous solution of potassium decylxanthate show that both didecyl dixanthogen and arsenic(III) decylxanthate are present on the surfaces, while no ethylxanthate species are observed after treatment with an aqueous potassium ethylxanthate solution,[203] see Fig. 31. The reason for the absence of ethylxanthate species is certainly due to that the solubilities of diethyl dixanthogen and arsenic(III) ethylxanthate in water are substantially higher than the corresponding decylxanthate compounds. Fairly small and almost equal amounts of didecyl dixanthogen and arsenic(III) decylxanthate are formed on the surfaces of realgar and arsenopyrite; the amounts of dialkyl dixanthogen formed is about the same as on pentlandite, pyrrhotite, millerite and molybdenite. On the other hand, large amounts of arsenic(III) decylxanthate are formed on the orpiment surfaces, while the amounts of didecyl dixanthogen formed on the orpiment surfaces are about the same as on the other arsenic containing sulphide minerals, see Fig. 31. These results

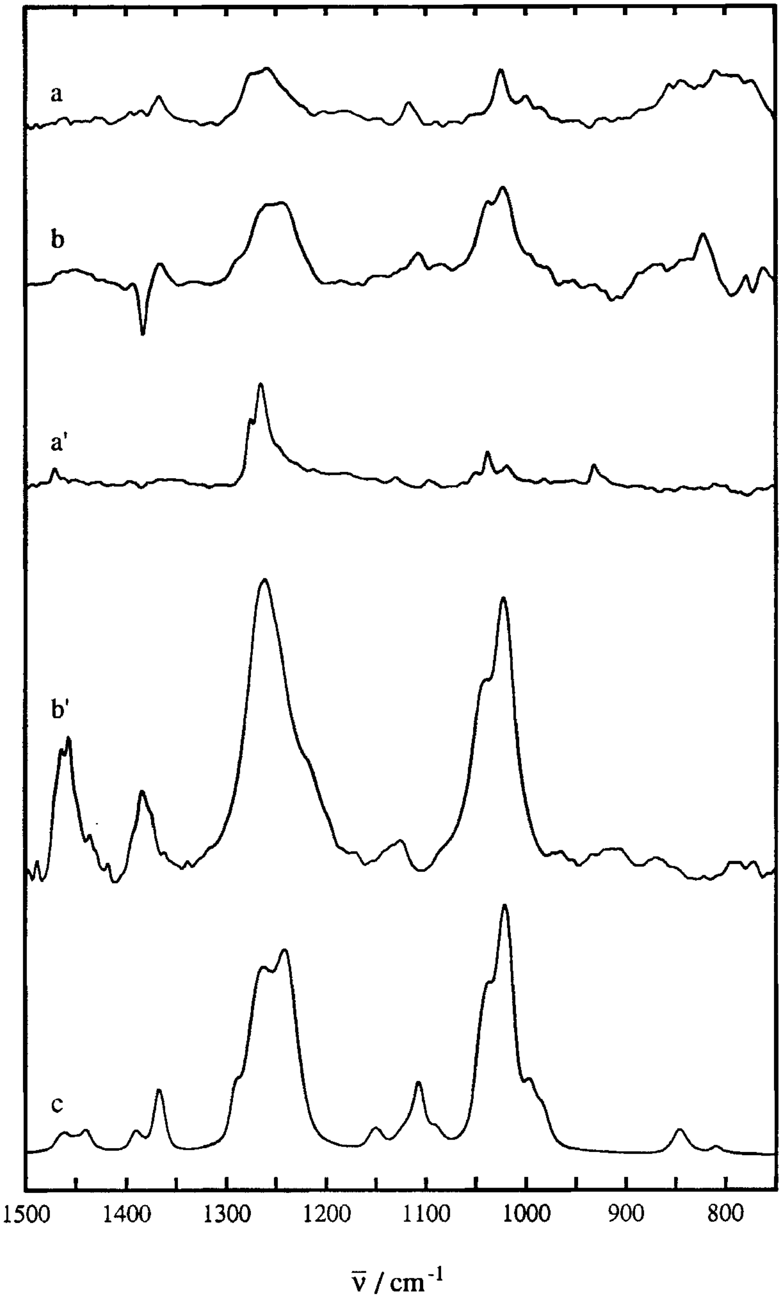


Figure 30 DRIFT spectra of (a) millerite and (b) molybdenite treated with 1.0 mM aqueous solutions of potassium ethylxanthate and (′) decylxanthate after subtraction with the spectrum of the untreated mineral. The DRIFT spectrum of diethyl dixanthogen is given as reference (c). The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

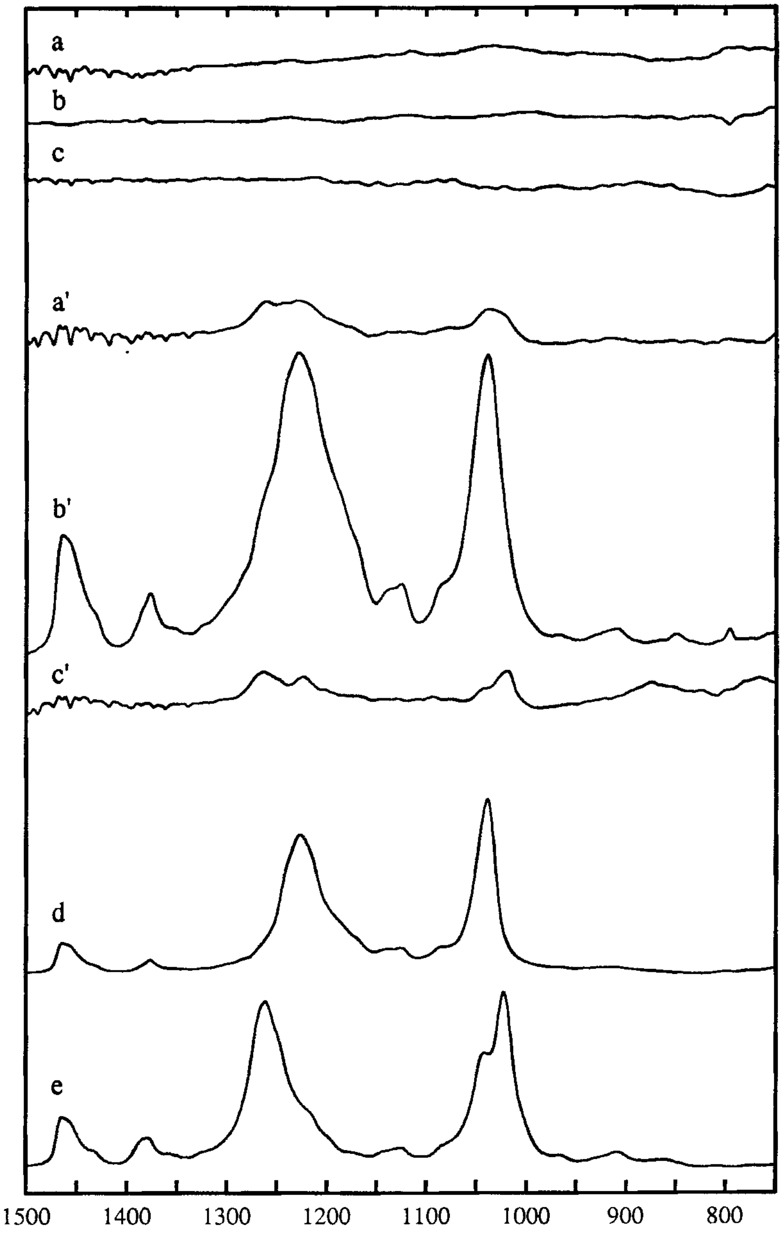


Figure 31 DRIFT spectra of (a) realgar, (b) orpiment and (c) arsenopyrite treated with 1.0 mM aqueous solutions of potassium ethylxanthate and (′) decylxanthate after subtraction with the spectrum of the untreated mineral. The DRIFT spectra of d) arsenic(III) decylxanthate and (e) didecyl dixanthogen are given as references. The ordinate scale in log (R_{ref}/R_{sample}) units and it is arbitrary.

show that small amounts of a highly oxidizing compound is formed on the surfaces of arsenic containing sulphide minerals as expected as the shortest sulphur-sulphur distance in these minerals is in the range 3.2–3.3 Å. Furthermore, arsenic is transferred to a fairly water soluble arsenic(III) compound. Large amounts of this compound are formed on orpiment surfaces, while the amounts are substantially smaller on the realgar and arsenopyrite surfaces. This shows that the surfaces of these arsenic containing sulphide minerals are hydrophobated by dialkyl dixanthogen in the same way and to the same extent as pentlandite and pyrrhotite. In addition, a water soluble arsenic(III) compound is formed at oxidation of the mineral, which leads to that arsenic(III) dissolves from the mineral surface at the slurrying and a concentration gradient of arsenic(III) is formed around the mineral particles. At the presence or addition of decylxanthate ion, the solubility product of arsenic(III) decylxanthate is exceeded in close vicinity of the particle and arsenic(III) alkylxanthate precipitates on the mineral surface in a dissolution-precipitation mechanism similar to that described for galena above; the solubilities of arsenic(III) alkylxanthates indicate that the carbon chain in the alkylxanthate ion cannot be too short if precipitation of arsenic(III) alkylxanthate shall occur, see Table 1.

7. REACTION MECHANISMS FOR THE HYDROPHOBATION OF SULPHIDE MINERALS WITH *O,O*-DIETHYLDITHIOPHOSPHATE IONS

The chemistry of *O,O*-dialkyldithiophosphate ions is in many respects very similar to that of the alkylxanthate ions. They follow in principal the same mechanisms as the alkylxanthate ions in the hydrophobation of mineral surfaces, a) formation of solid metal *O,O*-dialkyldithiophosphates on the mineral surfaces, and b) formation of oxidation products such as bis(*O,O*-dialkyldithiophosphoryl) disulphide through a redox reaction with highly oxidizing ions in the mineral surface such as copper(II) and $S_2O_8^{2-}$ ions. However, no formation of chemisorbed *O,O*-dialkyldithiophosphate complexes has so far been found; the alkylxanthate ions have on the other hand shown that they can form chemisorbed surface complexes to sphalerite surfaces, see section 5.1. This is due to that sulphur atoms in the *O,O*-diethyldithiophosphate ion are weaker electron donors than the sulphurs in the alkylxanthate ions.[59,120]

Solid copper(I) *O,O*-diethyldithiophosphate is formed on the surfaces of the copper containing minerals covellite, calcocite and chalcopyrite at the treatment with an aqueous solution of sodium *O,O*-diethyldithiophosphate as determined by DRIFT spectrosocopy,[206] see Fig. 32, which is in accordance with previous results.[169,173,207–209] XPS measurements have shown that the copper in these minerals is present as copper(I),[168] and that the copper dissolved from the mineral surfaces reacts with *O,O*-diethyldithiophosphate ions to form only copper(I) *O,O*-diethyldithiophosphate. The hydrophobation mechanism of chalcocite, covellite and chalcopyrite with *O,O*-diethyldithiophosphate ions is the same dissolution-precipitation mechanism as described above for the galena and copper sulphide mineral-alkylxanthate systems. Small amounts of bis(*O,O*-dialkyldithiophosphorye) disulphide are formed as well on covellite surfaces. Bis(*O,O*-dialkyldithiophosphoryl) disulphide is in this case most probably a product of the reaction between oxidized disulphide ions and *O,O*-diethyldithiophosphate ions.

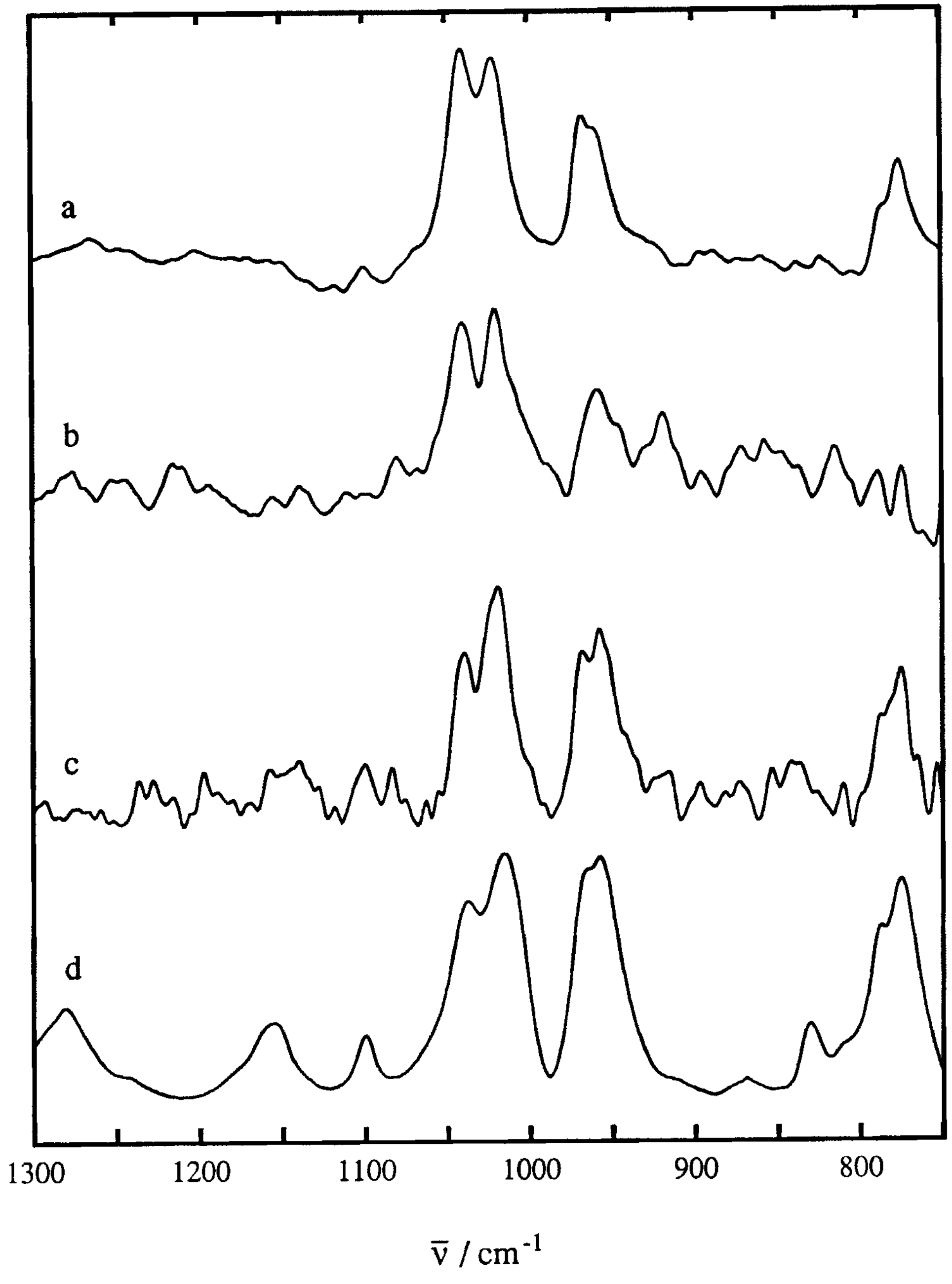


Figure 32 DRIFT spectra of (a) covellite, (b) chalcocite and (c) chalcopyrite treated with a 1.0 mM aqueous solution of sodium *O,O*-diethyldithiophosphate after subtraction with the spectrum of the untreated mineral. The DRIFT spectrum of (d) solid copper(I) *O,O*-diethyldithiophosphate is given as reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

The reactions of the iron containing sulphide minerals with *O,O*-diethyldithiophosphate ions are not as uniform as for the copper containing minerals, and each mineral will therefore be looked upon individually. The reaction between oxidized pyrite or marcasite and sodium *O,O-diethyldithio- phosphate yields as expected bis(O,O*-diethyldithiophosphoryl) disulphide.[117,169,173,207] This has been confirmed by a recent DRIFT spectroscopic study which clearly shows that bis(*O,O*-diethyldithiophosphoryl) disulphide is the sole hydrophobation agent on pyrite and marcasite surfaces after treatment with an aqueous solution of sodium *O,O*-diethyldithiophosphate,[206] see Fig. 33. A single study has reported that pyrite is hydrophobated with iron(III) *O,O*-diethyldithiophosphate.[208] However, the solubility of iron(III) *O,O*-diethyldithiophosphate is estimated to be fairly high[210] and it does not seem likely that iron(III) *O,O*-diethyldithiophosphate can be precipitated at the *O,O*-diethyldithiophosphate concentrations used in flotation processes. The hydrophobation mechanism of pyrite and marcasite with *O,O*-dialkyldithiophosphate ions is the same as that described for the hydrophobation of these minerals with alkylxanthate ions, see section 6.6.

DRIFT spectra of pentlandite and pyrrhotite treated with an aqueous solution of sodium *O,O*-diethyldithiophosphate show that small amounts of bis(*O,O*-diethyldithiophosphoryl) disulphide are formed on pyrrhotite surfaces while no *O,O*-diethyldithiophosphate species was detected on the pentlandite surfaces,[206] see Fig. 33. This shows that *O,O*-diethyldithiophosphate ions hydrophobate pyrrhotite in the same way as alkylxanthate ions, see section 6.7.

The DRIFT spectrum of troilite treated with an aqueous solution of sodium diethyldithiophosphate shows no *O,O*-diethyldithiophosphate species on the surfaces,[206] see Fig. 33. Too small amounts of iron are dissolved from the troilite surface to allow the formation of any solid iron *O,O*-diethyldithiophosphate compound, which all are fairly soluble in water,[210] and it seems that no highly oxidizing agents are formed on the troilite surfaces, see section 6.7. Troilite is therefore not likely to be hydrophobated by *O,O*-diethyldithiophosphate ions.[206]

DRIFT spectra of millerite and molybdenite treated with an aqueous solution of sodium *O,O*-diethyldithiophosphate show that small amounts of bis(*O,O*-diethyldithiophosphoryl) disulphide are formed on the surfaces,[206] see Fig. 34. This shows that *O,O*-diethyldithiophosphate ions hydrophobate millerite and molybdenite in the same way as alkylxanthate ions and this result confirms that the amount of highly oxidizing agents on the millerite and molybdenite surfaces is larger than on the pentlandite an pyrrhotite surfaces, see also section 6.7.

Solid lead(II) *O,O*-diethyldithiophosphate is formed on galena surfaces after treatment with an aqueous solution of sodium *O,O*-diethyldithiophosphate,[206] see Fig. 35. The *O,O*-diethyldithiophosphate ions are most certainly a less effective collector of galena than the alkylxanthate ions, as the solubility of lead(II) *O,O*-diethyldithiophosphate is higher than of lead(II) ethylxanthate,[207] see Table 1. Galena treated with sodium *O,O*-diethyldithiophosphate in acetone did not show any reaction products in the galena surface,[189] see Fig. 35, which implies that no chemisorbed surface complexes are formed. This implies that *O,O*-dialkyldithiophosphate ions form weaker covalent interactions than the alkylxanthate ions, which is in accordance with a previous study on the donor properties of alkylxanthate and *O,O*-diethyldithiophosphate ions toward mercury(II) bromide.[59,120]

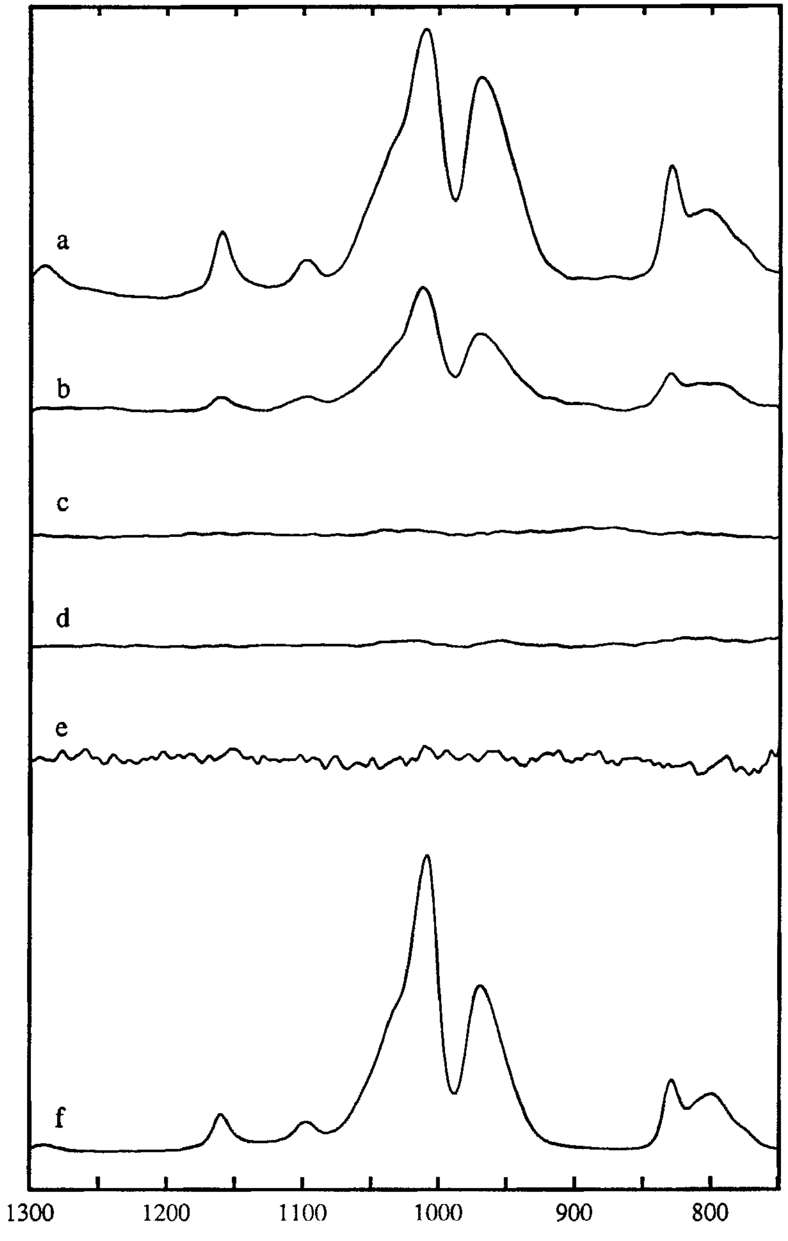


Figure 33 DRIFT spectra of (a) pyrite, (b) marcasite, (c) pentlandite, (d) pyrrhotite and (e) troilite treated with a 1.0 mM aqueous solution of solution *O,O*-diethyldithiophosphate after subtraction with the spectrum of the untreated mineral. The DRIFT spectrum of (e) bis(*O,O*-diethyldithiophosphoryl) disulphide is given as reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

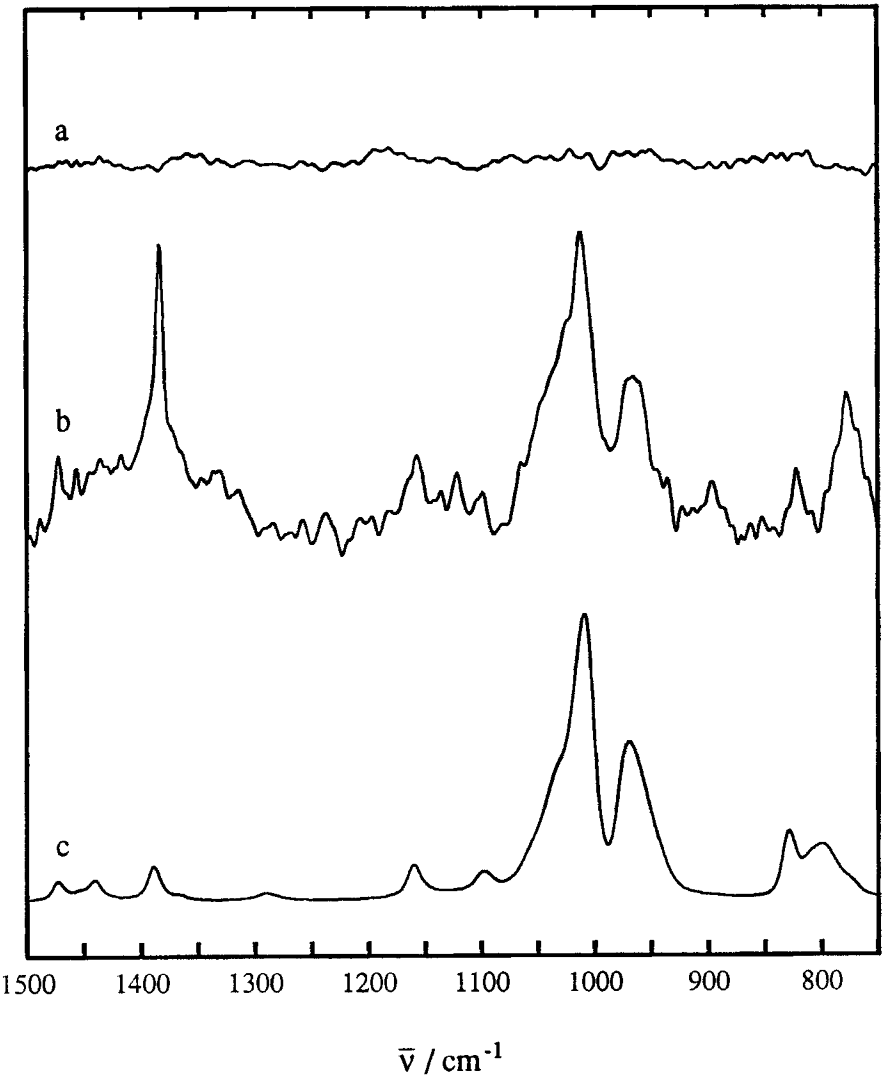


Figure 34 DRIFT spectra of (a) millerite and (b) molybdenite treated with a 1.0 mM aqueous solution of sodium *O,O*-diethyldithiophosphate after subtraction with spectrum of the untreated mineral. The DRIFT spectrum of bis(*O,O*-diethyldithiophosphoryl) disulphide is given as a reference. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

Neither solid zinc *O,O*-diethyldithiophosphate nor chemisorbed surface complexes are formed on sphalerite surfaces after treatment with a 10 mM aqueous solution of sodium *O,O*-diethyldithiophosphate,[206] see Fig. 35.

The hydrophobation mechanisms are the same independent of the use of alkylxanthate or *O,O*-diethyldithiophosphate ions and most probably also *N,N*-dialkyldithiocarbamate ions. Highly oxidizing species are formed under oxidizing conditions in the surfaces of sulphide minerals which contain disulphide ions, e.g.

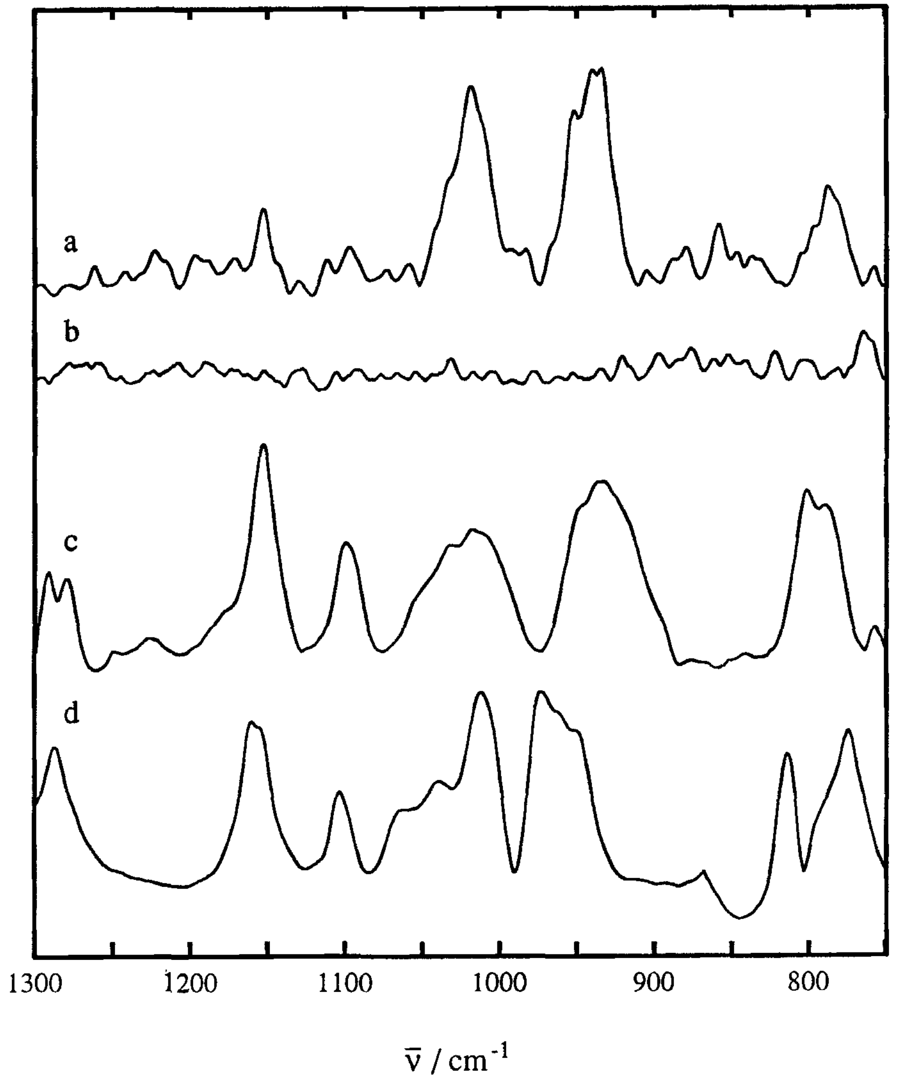


Figure 35 DRIFT spectra of (a) galena and (b) sphalerite treated with 1.0 mM and 10.0 mM aqueous solutions of sodium *O,O*-diethyldithiophosphate, respectively, after subtraction with the spectrum of the untreated mineral. The DRIFT spectra of (c) solid lead(II) *O,O*-diethyldithiophosphate and (d) solid zinc *O,O*-diethyldithiophosphate are given as references. The ordinate scale is in log (R_{ref}/R_{sample}) units and it is arbitrary.

pyrite, marcasite and covellite, and bis(*O,O*-diethyldithiophosphoryl) disulphide will be formed at addition of *O,O*-diethyldithiophosphate ions. Small amounts of bis(*O,O*-diethyldithiophosphoryl) disulphide are formed on millerite, molybdenite and pyrrhotite as small amounts of a strongly oxidizing agent is formed in the surfaces of these minerals where the shortest S-S distance is in the range 3.1–3.4 Å. If only sulphide ions are present in the mineral structure, the corresponding metal

O,O-diethyldithiophosphate will be formed on the mineral surface if the solubility is sufficiently low. The *O,O*-diethyldithiophosphate ion has so far not been found to form chemisorbed surface complexes to any of the minerals studied implying that the *O,O*-diethyldithiophosphate ion is a weaker electron-pair donor than the alkylxanthate ion.

8. RELATIONSHIP BETWEEN ADSORPTION MECHANISM OF ALKYLXANTHATE AND *O,O*-DIETHYLDITHIOPHOSPHATE IONS TO AND CRYSTAL STRUCTURE OF SULPHIDE MINERALS

The structures of sulphide minerals can be divided into three classes, minerals with (a) disulphide ions, S_2^{2-}, (b) clusters or sheets of sulphur atoms with S-S distances shorter than 3.4 Å, and (c) close-packed sulphide ions with S-S distances longer than 3.7 Å. When class (a) and (b) sulphide minerals are oxidized at e.g. the grinding, a powerful oxidizing agent is formed on the surfaces of the minerals. This oxidizing agent(s) has not yet been characterized, but most probably it is $S_2O_8^{2-}$ and/or $S_2O_7^{2-}$. These ions are both possible oxidation products of the disulphide ion and known to be able to oxidize alkylxanthate ions to dialkyl dixanthogen, and *O,O*-diethyldithiophosphate ions to bis(*O,O*-diethyldithiophosphoryl) disulphide. Only the $S_2O_x^{2-}$ ions with $x \geqslant 7$ have sufficiently high oxidation potential (in aqueous solution) to oxidize alkylxanthate and *O,O*-diethyldithiophosphate ions. This reaction overrules all other possible reactions between alkylxanthate or *O,O*-diethyldithiophosphate ions with species on or in the surface. Of the minerals in this study pyrite, marcasite and covellite belong to class (a), and millerite, molybdenite, pyrrhotite, pentlandite, realgar, orpiment and arsenopyrite belong to class (b).

Sulphide minerals with isolated sulphide ions, class (c) sulphide minerals, may undergo two kinds of reactions during the mineral processing, a) the sulphide mineral may be oxidized to relatively soluble metal sulphate and/or thiosulphate at e.g. grinding, and a subsequent precipitation of a metal collector salt can take place if this compound has a sufficiently low solubility and b) chemisorbed alkylxanthate surface complexes may be formed at the treatment of an aqueous alkali alkylxanthate solution, where the metal ions in the mineral surface form a specific covalent bond to the ligand. The oxidation products of a mineral are substantially more soluble than the mineral itself, and a solid metal alkylxanthate or *O,O*-diethyldithiophosphate is formed on the surface of the mineral at the treatment with a collector if the solubility of this compound is sufficiently low. The minerals galena, chalcocite, acanthite and chalcopyrite are hydrophobated by the corresponding metal collector salt. Formation of chemisorbed surface complex has been shown for the sphalerite-alkylxanthate system under conditions similar to those in practical flotation, while chemisorption of the *O,O*-diethyldithiophosphate ion to sulphide mineral surfaces has so far not been proven. The precipitation reaction overrules in most of the cases the formation of a chemisorbed surface complex.

9. CONCLUSIONS

The length of the shortest S-S distance in the sulphide mineral determines whether the formation of dialkyl dixanthogen and bis(*O,O*-diethyldithiophosphoryl) disulphide at the treatment of alkylxanthate and *O,O*-dialkyldithiophosphate ions, respectively, is possible or not. A powerful oxidizing agent is formed on the mineral surfaces at grinding under oxidizing conditions if the S-S distances are shorter than 3.4 Å. (See Table 6.)

Substantially larger amounts of this highly oxidizing agent are formed on the surfaces of minerals containing disulphide ions compared with the minerals with clusters or sheets of sulphur atoms where the S-S distance is in the range 3.1–3.4 Å. This powerful oxidizing agent is most probably $S_2O_8^{2-}$ and/or $S_2O_7^{2-}$ ions. These ions oxidize alkylxanthate and *O,O*-dialkyldithiophosphate ions to dialkyl dixanthogen and bis(*O,O*-dialkyldithiophosphoryl) disulphide, respectively, in aqueous solution.

The copper(II) ion is also a sufficiently strong oxidizing agent for the oxidation of alkylxanthate or *O,O*-dialkyldithiophosphate ions. Dialkyl dixanthogen and bis(*O,O*-dialkyldithiophosphoryl) disulphide hydrophobate mineral surfaces effectively. These compounds are physisorbed to the mineral surfaces in relatively weak interactions. Pyrite and marcasite are hydrophobated, and surfaces of covellite, pentlandite, pyrrhotite, millerite, molybdenite, realgar, orpiment and copper(II) activated sphalerite can be modified by the formation of dialkyl dixanthogen or bis(*O,O*-dialkyldithiophosphoryl) disulphide at the treatment with aqueous solutions of alkali alkylxanthate and *O,O*-dialkyldithiophosphate, respectively.

Sulphide minerals with solely isolated sulphide ions can only be oxidized to the corresponding metal sulphate and thiosulphate, and no powerful oxidizing agents can be formed. When the metal sulphide is oxidized to the corresponding sulphate and/or thiosulphate, the solubility of metal species at the mineral surface increases markedly. The majority of the metal alkylxanthates and *O,O*-

Table 6. S-S distances in some sulphide minerals, and the product expected and obtained at the treatment of oxidized sulphide minerals with aqueous solutions of potassium alkylxanthate and sodium *O,O*-diethyldithiophosphate. X denotes alkylxanthate and *O,O*-diethyldithiophosphate ions, respectively, and X_2 denotes dialkyldixanthogen and bis(*O,O*-dialkyldithiophosphoryl) disulphide.

Mineral	Formula	Shortest S-S Distance	Product $ROCS_2^-$		Product $(RO)_2PS_2^-$	
			Expected	Observed	Expected	Observed
Acanthite	Ag_2S	4.135	AgX	AgX	AgX	AgX
Arsenopyrite	FeAsS	3.197	X_2	AsX_3, X_2	X_2	b,c
Chalcocite	Cu_2S	3.710	CuX	CuX	CuX	CuX
Chalcopyrite	$CuFeS_2$	3.685	CuX	CuX	CuX	CuX
Covellite	CuS	2.084, 3.757	CuX, X_2	CuX, X_2	CuX, X_2	CuX, X_2
Galena	PbS	4.194	PbX_2	PbX_2	PbX_2	PbX_2
Marcasite	FeS_2	2.223	X_2	X_2	X_2	X_2
Millerite	NiS	3.244	X_2	X_2	X_2	X_2
Molybdenite	MoS_2	3.154	X_2	X_2	X_2	X_2
Orpiment	As_2S_3	3.242	X_2	AsX_3, X_2	X_2	b,c
Pentlandite	$(Fe,Ni)_9S_8$	3.362	X_2	X_2	X_2	b,c
Pyrrhotite	FeS_{1-x}	3.390	X_2	X_2	X_2	X_2
Pyrite	FeS_2	2.177	X_2	X_2	X_2	X_2
Realgar	AsS	3.295	X_2	AsX_3, X_2	X_2	b,c
Sphalerite	ZnS	3.821	a,b	a	X_2	b,c
Troilite	FeS	3.348	X_2	b,c	X_2	b,c

[a] Chemisorbed complex
[b] See text for comment
[c] No product observed

dialkyldithiophosphates has very low solubility in aqueous solution, see Table 1. At the slurrying of oxidized sulphide minerals in aqueous solutions containing alkylxanthate or *O,O*-dialkyldithiophosphate ions, the soluble metal compounds in the surface will dissolve, a concentration gradient of metal ions will be formed around the mineral particle, and the solubility product will therefore first be exceeded in close vicinity of the mineral particle and the corresponding metal alkylxanthate or *O,O*-dialkyldithiophosphate will precipitate at the mineral surfaces. As the metal alkylxanthates or *O,O*-dialkyldithiophosphates are very hydrophobic, the mineral particles will be hydrophobated also at partial coverage of the mineral surface. Galena, acanthite, chalcocite, chalcopyrite, covellite and orpiment are hydrophobated according to this mechanism, and sphalerite, realgar and arsenopyrite may also be hydrophobated according to this mechanism if long-chained alkylxanthates are used.

The last hydrophobation mechanism is chemisorption of alkylxanthate ions to a mineral surface. It has been shown that alkylxanthate ions can be chemisorbed to sphalerite and synthetic zinc and cadmium sulphide[120] surfaces in aqueous solution also under oxidizing conditions. Sufficient hydrophobation through chemisorption of mineral surfaces is obtained only with long-chained alkylxanthates. Practical flotation experiments have shown that the alkyl group must contain at least five carbons, otherwise the mineral particles cannot make contact with uprising air-bubbles. It has so far not been proven that *O,O*-dialkyldithiophosphate ions can be chemisorbed to sulphide mineral surfaces.

The same chemical species are formed on the mineral surfaces independent of dry or wet grinding of the mineral. The only difference is that smaller amounts of collector species are present on the surfaces after wet grinding as some reacting species on the mineral surface is washed off the surface at the grinding.

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