Investigation of Dialkyldithiophosphate

An In-situ ATR-FTIR, UV/Vis, Raman and Surface Chemical Study

KARIN LUNDSTEDT

MASTER OF SCIENCE PROGRAMME
Chemical Engineering

Luleå University of Technology
Department of Chemical Engineering and Geosciences
Division of Chemistry

2004-252 CIV • ISSN: 1402 - 1617 • ISRN: LTU - EX - - 05/252 - - SE
Investigation of Dialkyldithiophosphate
-An In-situ ATR-FTIR, UV/Vis, Raman and Surface Chemical Study.

Karin Lundstedt

Supervisors:
Doc. Allan Holmgren and Andreas Fredriksson

Division of Chemistry
Luleå University of Technology
SE-971 87 Luleå, Sweden

September 2005
This Master thesis has been performed within Agricola Research Centre (ARC) at the department of Chemical and Metallurgical engineering at Luleå University of Technology.

Flotation is an important mining industry process where the desired mineral is separated from the gangue. The aim of this process is to make the desired mineral hydrophobic in order for it to float to the surface. This is done by adding surface-active reactants, referred to as collectors. Although the flotation process has been used since the beginning of the last century there are still some uncertainties in the fundamental understanding of the reactions taking place at the surface of the mineral.

In this thesis the surface properties of two dialkyldithiophosphate collectors, namely diethyldithiophosphate and dibutyldithiophosphate are studied. The amount of adsorption of dialkyldithiophosphate onto germanium and onto zinc sulphide are studied in-situ with Attenuated Total Reflection (ATR) Infrared Spectroscopy. ATR is a surface sensitive method suitable when working with water as solvent.

While the expected adsorption of dialkyldithiophosphates onto germanium was not detected, adsorption was identified for dibutyldithiophosphate on zinc sulphide (the adsorption rates for this are presented in a kinetic plot). A comparison between the spectrum of dibutyldithiophosphate adsorbed on zinc sulphide to the precipitations of zinc and dibutyldithiophosphate is included in the discussion section.
ACKNOWLEDGEMENTS

First of all I would like to thank my supervisors Allan Holmgren and Andreas Fredriksson. Allan, for the discussion of the results and always having time to help me with non-working instruments in the lab. Andreas, for helping me with everything and anything from the first day of my thesis work till the last. It has been interesting to work with you and to get an insight in the world of surface chemistry.

I would also like to thank the professor of the department, Willis Forsling, for giving me the opportunity to go working in Australia for a few months through a STINT scholarship. It will be an everlasting experience.

Finally, I would like to thank my family and Patrik of course for always being there for me and believing in me.

Luleå, September 2005
Karin Lundstedt
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# NOMENCLATURE

*A list of symbols and abbreviations used in the thesis is given below.*

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflection</td>
</tr>
<tr>
<td>c</td>
<td>Velocity of light in vacuum; $2.997925 \times 10^{10}$ cm/s</td>
</tr>
<tr>
<td>C</td>
<td>Concentration of solution (mol L$^{-1}$)</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical Bath Deposition</td>
</tr>
<tr>
<td>db-dtp</td>
<td>Dibutyl dithiophosphate</td>
</tr>
<tr>
<td>de-dtp</td>
<td>Diethyl dithiophosphate</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Penetration depth</td>
</tr>
<tr>
<td>dtp</td>
<td>Dialkyl dithiophosphate</td>
</tr>
<tr>
<td>FT-IRS</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>Ge</td>
<td>Germanium</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant; $6.62608 \times 10^{-34}$ Js</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IRE</td>
<td>Internal Reflection Element</td>
</tr>
<tr>
<td>l</td>
<td>Path length (cm)</td>
</tr>
<tr>
<td>$n_{IRE}$</td>
<td>Refractive index of IRE</td>
</tr>
<tr>
<td>$n_{rare\ medium}$</td>
<td>Refractive index of sample</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>%T</td>
<td>Transmittance (%)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Molar absorption coefficient (L mol$^{-1}$ cm$^{-1}$)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency (Hz)</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>The critical angle (º)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of radiation (cm)</td>
</tr>
</tbody>
</table>
Agricola Research Centre is a research programme in mineral particle science and technology. The research program is carried out at the department of Chemical and Metallurgical engineering at Luleå University of Technology. This master thesis relates to one of the program areas, namely “Mineral surface reactions and chemical modelling”.

Flotation is an important mining industry process where the desired mineral is separated from the gangue. By bubbling air through a solution containing crushed ore, froth with a high concentration of minerals is formed. The aim of this process is to make the desired mineral hydrophobic in order for it to float to the surface. This is done by adding surface-active reactants, referred to as collectors. The flotation process has been used since the beginning of the last century, although, there are still some uncertainties in the fundamental understanding of the reactions taking place at the surface of the mineral.

In this thesis the surface properties of the potassium salt of two dialkyldithiophosphate collectors, namely 0, 0-diethyldithiophosphate (de-dtp) and 0, 0-dibutyldithiophosphate (db-dtp) are studied. Since both collectors are dialkyldithiophosphates (dtp) the aim is to examine how an increased length of the hydro carbon tail affects the surface properties. Dithiophosphates (dtp) together with xanthates are the most commonly used collectors in the flotation of sulphide minerals\(^1\) such as
galena, pyrite, chalcocite etc. For structural formula of dithiophosphate and xanthate see Figure 1.

![Structural formula of dithiophosphate and xanthate](image)

**Figure 1 Structures of the ions of heptylxanthate, 0, 0-diethyldithiophosphate and 0, 0-dibutyldithiophosphate, (from left to right)**

During the fifty years that dithiophosphates has been used as collectors some advantageous properties have been identified. Dithiophosphate can improve recovery in flotation, increase flotation rate and are more selective than most collectors used for similar applications. At a number of plants, dithiophosphate has replaced xanthates due to its economical and metallurgical advantages. However, the most profitable use of dithiophosphates is together with another collector type to enhance the collecting properties that each possesses.

*Attenuated total reflection (ATR) infrared spectroscopy* is a surface sensitive method used for, among others, obtaining spectra of species adsorbed on the surface of an infrared transparent crystal. In this thesis ATR spectroscopy is used to monitor adsorption of de-dtp and db-dtp, in water solution, onto a germanium (Ge) crystal and onto a Ge crystal coated with a zinc sulphide film.

To further examine the surface properties of de-dtp different analysing methods have been used, i.e. ultraviolet/visible spectroscopy, transmission infrared spectroscopy, Raman spectroscopy, surface free energy, and contact angle measurements.
2 THEORY

In this chapter the theory behind the methods used in the thesis are described.

2.1 A general introduction to spectroscopy

Spectroscopy is a widely used analytical method which is based on molecules’ interaction with electromagnetic radiation. A beam of radiation from a source is passed through, or reflected at a sample and the molecules in the sample can either cause the radiation to be absorbed, emitted or scattered. The final energy is analyzed in a detector and compared to the initial energy. The resulting interferrogram is usually mathematically processed, e.g. in vibrational spectroscopy the use of Fourier transform is normally practiced. The results are often presented in an absorption spectrum where the y-axis represents absorbance, or transmittance, and the x-axis energy, expressed as wavelength or wavenumbers.

The energy of a molecule consists of many different types of energy, e.g. rotational energy, vibrational energy and electronic energy. As an approximation these energies can be treated separately. The energies of molecules considered in this thesis are electronic energy, which gives rise to absorption in the ultraviolet and visible (UV/Vis) part of the electromagnetic spectrum, and molecular vibrations, which give rise to absorption in the infrared (IR) region. There are two major types of vibrational spectroscopy; Infrared (IR) and Raman.
The Electromagnetic Spectrum

A substance that is coloured absorbs light in the visible region and therefore the colour is detectable by the human eye. The visible radiation covers the range from approximately 400-800 nm and constitutes but a small part of the total electromagnetic spectrum, shown in Figure 2. The electromagnetic spectrum ranges from high energy gamma rays to low energy radio waves.

![Figure 2 The electromagnetic spectrum](image)

The Beer-Lambert law

The linear relationship between absorbance and concentration of an absorbing species is described by the Beer-Lambert law\(^3\),

\[
A = \varepsilon \cdot l \cdot [C], \tag{Equation 1}
\]

where \(\varepsilon\) is the molar absorption coefficient in L mol\(^{-1}\) cm\(^{-1}\), \(l\) is the path length in centimetres, \([C]\) is the concentration of the solution in mol L\(^{-1}\) and \(A\) is a dimensionless product called absorbance. For a schematic picture of the notations in Beer-Lambert’s law see Figure 3. The path length is the length the light travels through the sample, in Figure 3 a cuvette of path length, \(l\), is used as an example.
The absorbance, A, is related to the transmittance, T, of light according to;

\[ A = -\log T = \log \frac{I_0}{I}, \]

[Equation 2]

where \( I_0 \) is the incident intensity and I is the intensity of the radiation after passage through the cuvette. The transmittance is expressed in percentage, consequently, if all the light passes through the cuvette the absorbance is 0 and the transmittance is 100%.

When using the Beer-Lambert law, the absorbance is more often used than %T. The reason for this is that absorption is directly proportional to the other parameters as seen in Equation 1. A plot of absorbance against concentration gives a straight line through the origin as long as Beer-Lambert’s law is obeyed.

**2.2 Ultraviolet/Visible Spectroscopy**

Spectroscopy measurements of light absorption in the ultraviolet and visible part of the electromagnetic spectrum (see Figure 2) are used to detect bands corresponding to structural groups within the molecule.
Absorption of ultraviolet and visible radiation requires presence of certain functional groups within the organic molecule. These functional groups, named chromophores, contain valence electrons of low excitation energy. Of the six electronic excitations outlined in Figure 4, only the two lowest energy ones (coloured green) are achieved by the energies in the ultraviolet and visible spectrum\(^5\). In a resulting spectrum, absorption of ultraviolet and visible radiation at different wavelengths can be related to certain functional groups within the molecule.

![Diagram of electronic excitations](image)

**Figure 4** Electronic excitation that may occur in organic molecules

Table 1 lists some common chromophores with their approximate absorption maxima and type of electronic excitation. These data are only guidelines since the absorption maxima are affected by solvent and the structural details of the molecule containing the chromophore\(^6\).
Table 1 Light absorption characteristics of some common chromophores.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Example</th>
<th>Solvent</th>
<th>Excitation</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\epsilon_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>Ethene</td>
<td>Hexane</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>171</td>
<td>15000</td>
</tr>
<tr>
<td>C≡C</td>
<td>1-Hexyne</td>
<td>Hexane</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>180</td>
<td>10000</td>
</tr>
<tr>
<td>C=O</td>
<td>Ethanal</td>
<td>Hexane</td>
<td>$n \rightarrow \pi^*$</td>
<td>290</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\pi \rightarrow \pi^*$</td>
<td>180</td>
<td>10000</td>
</tr>
<tr>
<td>N=O</td>
<td>Nitromethane</td>
<td>Ethanol</td>
<td>$n \rightarrow \pi^*$</td>
<td>275</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\pi \rightarrow \pi^*$</td>
<td>200</td>
<td>5000</td>
</tr>
</tbody>
</table>

In Figure 5 the UV/Vis spectrum of isoprene is shown where an absorption peak at 222 nm is clearly distinguished.

![UV/Vis spectrum of isoprene](http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm)

**Figure 5** UV/Vis spectrum of isoprene in hexane solution, C=4 \times 10^{-5} M

(From http://www.cem.msu.edu/~reusch/VirtualText/Spektropy/UV-Vis/spectrum.htm, 2005-08-24)
2.3 Infrared Spectroscopy

Compared to the visible and ultraviolet radiation, the infrared radiation is lower in energy content (see Figure 2). The infrared region is usually divided into three parts based on wavelength, i.e. near (0.78 to 2.5 \( \mu \)m), mid (2.5 to 50 \( \mu \)m) and far-IR (50 to 1000\( \mu \)m).6

When infrared radiation interacts with a molecule it causes rotation among certain functional groups in the gas phase, and vibrations between atoms, within the molecule. Fourier Transform Infrared Spectroscopy (FT-IRS) is used to collect information about these vibrations assigned to certain frequencies. The amount of radiation absorbed is directly proportional to the amount of compound present, this will be further clarified later in the chapter, thereby, IR spectroscopy can be used for quantitative measurements as well as for qualitative measurements, i.e. identifying chemical compounds6.

In IR spectroscopy the incident radiation is changed continuously and the transmittance of the sample is measured. An IR spectrum is the absorbance or transmittance plotted against the incident frequency, usually expressed as wavenumbers (\( \text{cm}^{-1} \)). A linear wavenumber scale is directly proportional to energy and frequency as seen in Equation 3.

\[
E_{\text{photon}} = h \cdot \nu = \frac{h \cdot c}{\lambda},
\]

[Equation3]

where \( h \) is Planck’s constant, \( \nu \) the frequency, \( c \) the velocity of light in vacuum and \( \lambda \) the wavelength in centimetres. The wavenumber is represented by \( 1/ \lambda \) with the unity of \( \text{cm}^{-1} \).
Types of molecular vibrations

For a molecule to be infrared active the vibrational or rotational motion within the molecule must cause a net change in dipole moment. In a diatomic heteronuclear molecule the charge distribution is not symmetric because either of the atoms have a higher electron density, the molecule has a significant dipole moment and is said to be polar. Species such as $\text{O}_2$ and $\text{Cl}_2$ do not cause any net changes in dipole moment because of their homonuclear configuration, however, with a few exceptions, all molecular species do absorb infrared radiation.

The change in dipole moment is caused either by vibrational or rotational motion, which leads to a change in amplitude of the radiation interacting with the molecule. A change in rotational level requires the energy corresponding to radiation of 100 cm$^{-1}$. Rotational levels are quantized and absorption by gases gives discrete, well-defined lines, while liquids and solids cause broadening of the lines due to interactions and intramolecular collisions.

The molecular vibrations are divided into two categories, namely stretching and bending. The two possible stretching vibrations, asymmetric and symmetric, are shown at the left in Figure 6. Out of four possible bending vibrations, one example is shown at the right in Figure 6. The stretching vibrations cause a change in bond-length between two atoms while the bending vibrations change the angle between two bonds.

Figure 6 Asymmetric stretching vibrations, symmetric stretching vibrations and an example of bending vibrations, (from left to right)
Mid IR region

Of the three identified infrared regions (near, mid and far), the one most common with organic molecules is mid-IR. The wavenumber region of mid-IR radiation ranges from 4000 to 200 cm\(^{-1}\), however, the most used region is between 4000 and 670 cm\(^{-1}\). The mid-IR region is very information-rich and contains all the common vibrations for organic molecules and non-metallic inorganic species. In this wavelength region, reflection, absorption and emission spectra can be obtained for use in qualitative as well as quantitative analyses\(^6\).

In qualitative analysis of IR spectra the aim is to identify chemical compounds. This is done in two steps including examination of the group frequency region and the fingerprint region respectively. In the group frequency region (between 3600 and 1200 cm\(^{-1}\)) it is most likely to find absorption peaks corresponding to functional groups within the molecule. For the identification of chemical compounds, the fingerprint region (between 1200 and 600 cm\(^{-1}\)) is particularly useful since small differences in structure result in significant changes of the peaks in the absorption spectrum\(^6\). The name “fingerprint region” is commonly used with reference to the fact that chemical species have characteristic peaks within this region.

Attenuated Total Reflection (ATR) Infrared Spectroscopy

*Attenuated total reflection (ATR) Infrared Spectroscopy* is a surface sensitive spectroscopic method used for, among others, obtaining spectra of species adsorbed on the surface of an infrared transparent crystal. The ATR technique was developed independently by Harrick\(^8\) and Fahrenfort\(^9\) in the early nineteen sixties.

Figure 7 schematically shows an *Internal Reflection Element* (IRE) with the IR radiation internally reflected through the crystal. For the propagating wave of IR radiation to
undergo total internal reflection the medium in contact with the crystal has to be optically rarer than the crystal.

Figure 7 IR radiation internally reflected through an IRE

The IR radiation may extend slightly beyond the surface of the crystal, this electromagnetic field is called an *evanescent field* (see Figure 8). The intensity of this field is exponentially decaying in the sample media with distance to the surface of the IRE.

Figure 8 Schematic picture of the evanescent field established at the surface of the IRE

In order to establish an evanescent field and for total internal reflection to occur the angle of incidence have to exceed the critical angle ($\theta_c$). The critical angle is defined by Snell's law according to;

$$\theta_c = \sin^{-1}(n_2),$$  \hspace{1cm} [Equation 4]
\[ n_{21} = \frac{n_{\text{sample}}}{n_{\text{IRE}}} = \frac{\text{refractive index of the sample}}{\text{refractive index of the IRE}}. \]  

[Equation 5]

The penetration depth, \( d_p \), of the evanescent wave is defined as the distance from the sample/crystal interface to the depth where the intensity has dropped to \( e^{-1} \) (37%) of its starting value. The penetration depth is given by;

\[ d_p = \frac{\lambda}{2\pi \cdot n_{\text{IRE}} \sqrt{\sin^2 \theta - n_{21}^2}}, \]  

[Equation 6]

where \( \lambda \) is the wavelength of the IR radiation and \( \theta \) is the angle of incidence. From this equation it is easily seen the dependence of the penetration depth with changing IRE material, changing \( \theta \) and different wavelength of the radiation.

To achieve total internal reflection the crystal must have higher refractive index than the sample. A crystal with high refractive index minimizes the penetration depth of the evanescent wave and the interaction with the bulk solution is thereby reduced. There are many different IRE materials available with different properties and prices. In this thesis a germanium crystal is used because of its high refractive index.

Ever since Fahrenfort and Harrick presented their works, suggesting various applications of the ATR technique, the number of academic papers exploring a broad range of such applications has increased rapidly. Out of many applications of ATR a few of them are mentioned here; study of adsorbed species on semiconductor surfaces, membrane studies, determination of molecular spatial orientation and determination of optical constants. Sample contact is one of the hindrances in ATR spectroscopy but as long as it is sufficient a very wide range of solid substances can be analyzed by being placed or pressed against the surface of the IRE. Whereas there are several different accessories available for studying liquid samples only one is used in this thesis and the following section describes this particular one.
For a more complete description of the ATR-technique see internal reflection spectroscopy edited by Mirabella\textsuperscript{10}.

**Flow cell studies**

Flow cell studies involve an IRE mounted in a flow cell through which a solution containing the chemical compound of interest is pumped. Throughout the circulation of the solution a chemical with appropriate properties adsorbs or attaches to the surface of the IRE. Information about in-situ system at the aqueous/solid interface can be provided by ATR-IR spectroscopic flow cell studies. In situ study of a system gives real-time information of the chemical reactions.

The ATR technique has been applied to surface-active species for many years, although most studies are ex situ, however there are a few in situ studies published within this area during the last few decades\textsuperscript{11,12}.

**2.4 Raman Spectroscopy**

In Raman spectroscopy a sample is irradiated with a constant frequency laser source, usually in the visible part of the spectrum and the radiation scattered by the sample is analyzed by a spectrometer. Most of the radiation scattered by the sample have the same energy and wavelength as the incident radiation. This is called Rayleigh scattering; an elastic collision between the photon and the molecule. However, due to inelastic collisions with a molecule in the sample a small fraction (1 in \(10^7\)) of the incident photons changes in energy content through the scattering\textsuperscript{3}. This phenomenon is called the Raman effect, named after the Indian physicist C.V Raman who first observed it in 1928. If the photon looses energy through the scattering it gives rise to the “lower-frequency Stokes radiation”. If the photon gains energy it
emerges as the “higher-frequency anti-Stokes radiation”. The Rayleigh scattering is significantly more intense than either of the two other types.

Raman as well as infrared spectra involves vibrational and rotational energy levels, however, there are enough differences between the two techniques for them to be complementary rather than duplicates. In order for a molecular vibration to be Raman active, the vibration must be accompanied by a change in polarizability of the molecule. The polarizability can be seen as a deformation of the electron cloud of the molecule caused by an electrical field. For a molecule to be infrared active the vibrational mode of the molecule must change the dipole moment associated with it.

It is interesting to compare Raman and IR spectra for the asymmetric and symmetric stretching vibrations in a plane molecule, e.g. a carbon dioxide molecule. In the symmetric mode no change in dipole moment occur as the molecules move away from or towards the central atom, thus this mode is infrared inactive. During these fluctuations the molecular shape is alternately compressed and extended, i.e. the molecule is polarized and thus Raman active. In contrast, in the asymmetric mode the vibrations are infrared active and Raman inactive. The infrared activity arises from the dipole moment caused by the fluctuations in phase with the anti-symmetric vibrations. In contrast, the polarizability of one of the bonds increases as it lengthens while the other decreases by the same amount as is shortens which leads to no net change in polarizability.

However, there are molecules that yield the same peaks in both infrared and Raman spectrum, although, the shape and intensity of the peaks can differ since the energy transitions are different for the two mechanisms. An advantage with the Raman technique compared to IR is that water causes no interference, implying that aqueous solutions are suitable.
2.5 Surface free energy

Surface tension, or *surface free energy*, is the result of the interactions between molecules at an interface. Liquid molecules are attracted to each other at the surface and this leads to a net force pulling them together. A high value of the surface energy implies a strong interaction between molecules. One example of this is water that has a high degree of hydrogen bonding. Hydrocarbons, on the other hand, have low surface tension as a result of their weak dispersion forces.

The surface free energy has been measured using ‘the ring method’. A platinum ring is detached from the air/liquid interface and the detachment force required is measured by a du Noüy tensiometer. To ensure zero angle the platinum ring must be flamed before use to remove surface contaminants, kept circular in shape and in the same horizontal level as the liquid surface. To take account for the dimensions of the ring and the nature of the interface, correction factors have been calculated and tabulated by Harkins and Jordan\(^\text{13}\).

2.6 Contact angle

A drop of a liquid resting on a solid surface can either be wetting or non-wetting, a phenomenon described by the *contact angle* (see Figure 9). Wetting means that the liquid spreads easily over the solid and the contact angle is less than 90°. In contrast, non-wetting suggests that the liquid remains as a drop and the contact angle is greater than 90°. A non-wetting drop can be considered to rest in equilibrium by balancing three interfacial forces (see Figure 9), namely the interfacial tensions between solid and liquid (SL), solid and vapour (SV), and liquid and vapour (LV).
The central relationship describing contact angle is the Young equation\textsuperscript{14},

\[
\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}},
\]

[Equation 7]

where the contact angle, \( \theta \), is a function of the interfacial tensions.
3 EXPERIMENTAL

This section briefly describes the experimental set-up and laboratory work.

3.1 Stability of de-dtp

Always when working with water as solvent one has to consider the effect of hydrolysis. Many organic species are not stable in a water solution, thereby the stability of the de-dtp solution is an important property to measure. The de-dtp K-salt was dissolved in milliQ water to a concentration of 0.2 mM. The solution was analysed in an UV/Vis spectrometer in certain time ranges, where the dissolution of the salt in water was the starting point.

3.2 Surface free energy

The surface free energy was measured by the ring method. A reference measurement on milliQ water was performed to receive a correction factor for the instrument. The concentration of the de-dtp solution used was 1 mM, 10 mM and 0.1 M.

3.3 Contact angle

The contact angle measurements were performed in a FIBRO 1121/1122 DAT instrument equipped with a camera. A droplet of solution is put on a surface and the contact angle between the solid material and the liquid droplet is measured. Pieces of
a germanium crystal that fitted into the accessory of the analyzing instrument were used. Before the contact angle measurements the Ge crystals were washed with pure acetone. A reference value was measured between a water droplet and the clean Ge crystal. The clean germanium pieces were immersed into a de-dtp solution with a concentration of 1 mM up to 50 mM for half an hour. The pieces were dried and the contact angle was measured by putting a water droplet on the Ge surface.

3.4 ATR flow cell adsorption studies

The cleaning of the crystal was performed in three steps with a hold-up time of between 15 to 30 minutes in each washing solution. The first involved pure acetone, the second an ultrasonic bath with pure ethanol and finally in milliQ water. Following this cleaning process the crystal was dried in argon gas and then further dried in low pressure before the adsorption experiments were conducted. The flow cell was washed with ethanol and milliQ water.

The infrared spectrometer used for the adsorption studies was a Bruker 66 v/s equipped with a MCT detector. For a schematic picture of the experimental set-up see Figure 10. The adsorption studies were carried out in a flow cell where the IRE was mounted and sealed with viton gaskets. A continuous flow of solution through the cell (17.5 ml/min) admitted single side adsorption. The temperature in the bath was room temperature ($T \approx 22^\circ C$) and pH was as mixed.

The germanium IRE has the size of $50 \cdot 20 \cdot 2$ mm$^3$ with a trapezoidal shape with cut edges of 45°. This geometry of the IRE and an incident angle of the infrared light of 45° allow multiple internal reflections (>20).

The zinc sulphide film was deposited onto the germanium crystal by Chemical Bath Deposition (CBD). For a description of the method see reference 15.
Prior to the adsorption studies water was pumped through the system for one hour. A background of the water spectrum was recorded, the scan time was 15 minutes to get a good signal to noise ratio.
Figure 10 Experimental set-up for ATR spectroscopy measurements. A) Adsorption onto a Ge surface and B) Adsorption onto a ZnS surface. (A. Fredriksson, *Adsorption of Heptyl Xanthate at the metal Sulphide/Aqueous Interface*, Licentiate thesis, Luleå university of Technology, with permission.)
3.5 Spectroscopic studies of DTP

Raman, diffuse reflectance and transmission of de-dtp

The chemicals used in this thesis, potassium de-dtp and potassium db-dtp were delivered by Cheminova. The Raman spectroscopy measurement was performed in a NIR FT-Raman 1700X instrument on a de-dtp solution with a concentration of 50 mM. The diffuse reflectance sample contained 1% potassium de-dtp mixed together with KBr and the measurement was carried out in a Perkin Elmer 2000 FT/IR instrument at normal pressure. The transmission measurement was performed in a Bruker 66v/s spectrometer on a disc containing potassium de-dtp and KBr (1-3 mg de-dtp/300 mg KBr).

Zinc dialkyldithiophosphate salts

The precipitated zinc salts (de-dtp and db-dtp) were obtained by precipitation with dtp and ZnSO₄·7H₂O in a small quantity of water. The Zn de-dtp was easily precipitated as a solid sample while the Zn db-dtp had to be dissolved in ether to separate the solution formed. After drying in an excicator de-dtp was pressed into a disc together with KBr and solution of db-dtp was put onto the surface of a KBr disc. The precipitations were analyzed by transmission IR.

The zinc double salt (Zn₂(n-propyl-DTP)₄) was prepared by Dr. Anna-Carin Larsson at the division of Chemistry, Luleå University of Technology. Purification of the prepared species was done by washing with ether, acetone and MilliQ water. The recipes and discussion of the double salts can be found in references 16 and 17.

The oxidized form of db-dtp, also referred to as the disulfide, was produced following a simple reaction:
\[ 2\text{DTP}^- + I_3^- \rightarrow \text{dtp}_2 + 3\text{I}^- , \]  

[Equation 8]

where the water soluble triiodide ion, \( I_3^- \), was prepared by mixing iodine, \( I_2 \), with potassium iodide, KI.

\[ I_2 + I^- \rightarrow I_3^- . \]  

[Equation 9]

Purification of the non water soluble disulfide was preformed by reducing the remaining iodide ions with sodium disulfide, \( \text{Na}_2\text{S}_2\text{O}_5 \).
4 RESULTS

This section presents the result of the laboratory work.

4.1 Stability of de-dtp

The UV/Vis spectroscopy measurement on 0.2 mM de-dtp solution resulted in the spectrum in Figure 11. This spectrum represents a recording made 2 hours after the dissolution of the salt, however, the study shows that all spectra from 10 minutes after the dissolution of the salt up to 96 hours have the same appearance. If de-dtp would have been hydrolyzed one could expect changes in the spectrum. In sum this implies that de-dtp potassium salt is stable in water solution up to at least 96 hours. A peak at 226.3 nm is clearly distinguished. This peak arises from the delocalized double bond between P and S in the de-dtp molecule and these bonds are marked in red in Figure 12. The red marked delocalized bond is the only chromophore within the de-dtp molecule and consequently the absorption of UV/Vis radiation must be related to this bond.
Recall from the theory chapter on Beer-Lambert’s law that the absorbance is proportional to the concentration as long as the law is obeyed. In Figure 13 the absorbance, measured as peak height at 226.3 nm (see Figure 11), is plotted against the concentration in mM. The measure points can be adjusted to suit a straight line which shows that the law is obeyed within this concentration range.
4.2 Surface free energy

In Table 2 the surface free energy at different de-dtp concentrations is tabulated. The surface free energy decreases slightly as the de-dtp concentration is increased, this indicates that de-dtp has very low surface affinity and does not tend to form micelles.

Table 2 Surface free energy at different de-dtp concentrations

<table>
<thead>
<tr>
<th>De-dtp concentration</th>
<th>Surface free energy [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mM</td>
<td>71.5</td>
</tr>
<tr>
<td>10 mM</td>
<td>71.2</td>
</tr>
<tr>
<td>0.1 M</td>
<td>68.8</td>
</tr>
</tbody>
</table>

4.3 Contact angle

The result of the contact angle measurements is that there is no detectable difference between the clean Ge crystals and the crystals that has been immersed into the de-dtp solution. The reason for this is more thoroughly discussed later.
4.4 The CBD layer of ZnS

The chemistry of the precipitated ZnS layer can be found in reference 15.

4.5 ATR flow cell adsorption studies

The ATR adsorption studies of de-dtp and db-dtp onto a germanium crystal gave no detectable amounts of adsorption and can thus not be presented in spectra.

The spectra in Figure 14 shows the results of the ATR studies of db-dtp adsorbed onto ZnS. The spectra are recorded in certain time ranges and shown in the figure with increasing adsorption time. There are several wavenumber regions in the spectra in Figure 14 that should be studied to find out whether db-dtp adsorb on the ZnS surface or not. The region at higher wavenumbers (around 2900 cm\(^{-1}\)) corresponds to the asymmetric and symmetric stretching vibrations of CH\(_3\) and CH\(_2\). CH\(_3\) is higher in frequency (2960) than the CH\(_2\) group (2934). The CH\(_3\) and CH\(_2\) each give rise to a doublet separation of approximately 80 cm\(^{-1}\) according Colthup et al\(^7\). The higher frequency CH\(_3\) (2960) and the lower frequency CH\(_3\) (2874) vibrations in Figure 14 are separated by 86 cm\(^{-1}\) which is in good agreement with Colthup et al. The lower frequency CH\(_2\) is not visible due to low absorbance. The peak heights in this wavelength region are increasing with time as seen in see Figure 14, this indicates that db-dtp adsorb on the surface of ZnS.

In the region 1400-1500 cm\(^{-1}\) the CH\(_2\) scissors deformation and the CH\(_3\) asymmetrical deformation are found. These bands are near 1460 cm\(^{-1}\) in hydrocarbons\(^7\), which is in agreement with the peak in Figure 14 at 1466 cm\(^{-1}\).

The peaks in the fingerprint region (900-1800 cm\(^{-1}\)) are the characteristic peaks of the db-dtp molecule. As in the higher frequency region the peak heights are increasing in this region indicating that db-dtp adsorbs at the surface of ZnS. According to
reference 18 the peaks around 1040 are due to the P-O-C asymmetric stretch and C-C stretch. The other peaks above ~800 cm$^{-1}$ are probably also involving the P-O-C asymmetric stretch.

Figure 14 Absorbance spectra monitored with time for db-dtp adsorbed onto ZnS

**Kinetics**

The surface area between 2839 and 3000 cm$^{-1}$ in Figure 14 is calculated and plotted as a function of time which results in a kinetic plot, see Figure 15. The peak area is increasing with time which indicates that db-dtp adsorbs onto ZnS as a function of time. As seen from Figure 15 the adsorption rate is highest during the first minutes and equilibrium is reached after around 60 minutes.
Figure 15 Surface area, measured between 2839-3000 cm$^{-1}$, plotted against time in minutes

**Water spectrum**

Prior to the adsorption studies of dialkyldithiophosphate water was pumped through the ATR flow cell system for one hour to saturate the surface of the IRE with water molecules. Water absorbs strongly within the areas represented by peaks in Figure 16. The peak with highest intensity is due to OH stretching vibrations while the absorption around 1640 cm$^{-1}$ arises from bending vibrations of the water molecule.
4.6 Spectroscopic studies of DTP

Raman, diffuse reflectance and transmission

De-dtp was studied by different spectroscopic analyzing methods, see Figure 17. The blue line represents a solution analyzed in a Raman spectrometer, the black line is a transmittance spectrum and the red line is a diffuse reflectance spectrum. The wavenumber region around 2900 cm\(^{-1}\) is similar in the three spectra and corresponds to the asymmetric stretching vibrations of CH\(_3\) and CH\(_2\). The region around 1400 is the bending mode of CH\(_3\) groups and the peaks in the fingerprint region are the characteristic peaks of the db-dtp molecule.

In a symmetrical mode the vibrations are more intense in Raman compared to in IR spectroscopy. The peaks with higher intensity in the Raman spectrum (e.g. 2933 cm\(^{-1}\), 581 cm\(^{-1}\)) in Figure 17 can therefore be said to correspond to the symmetrical mode within the de-dtp molecule.
Comparison of potassium de-dtp and potassium db-dtp

In Figure 18 the transmission spectra of potassium de-dtp and potassium db-dtp analyzed in form of KBr discs are shown. It is not surprising that the spectra are similar to each other since the difference between the compounds’ chemical composition is small. However, the spectra differ from each other in the fingerprint region as this region is unique for each substance.
4.7 Dtp precipitations

In Figure 19 three precipitation spectra are presented and for comparison a transmission spectrum of potassium db-dtp analyzed in a KBr disc and an ATR spectrum of db-dtp recorded after 18 minutes of adsorption are shown. The red spectrum represents an oxidized disulphide of db-dtp ((db-dtp)$_2$), the magenta coloured a precipitation of the zinc double salt (Zn$_2$(n-Pr-dtp)$_4$) and the light green a precipitation of the basic zinc salt (Zn(db-dtp)$_2$). The reason for using propyl in stead of butyl in the magenta coloured spectrum is due to the complicated manufacturing procedure of Zn$_2$(n-bu-dtp)$_4$. Because of the similarity of the two compounds the spectrum of Zn$_2$(n-bu-dtp)$_4$ is assumed to be rather similar to that of Zn$_2$(n-Pr-dtp)$_4$ in the fingerprint region.
In the wavenumber region around 2900 cm\(^{-1}\) all five spectra have the similar appearance of the asymmetric stretching vibrations of CH\(_3\) and CH\(_2\). The higher frequency CH\(_3\) and CH\(_2\) and the lower frequency CH\(_3\) are visible in this region. The ATR spectra of adsorbed db-dtp have a broad peak corresponding to the H\(_2\)O bending in the region above 1600 cm\(^{-1}\), this because some of the water molecules near the surface of the IRE are detected. The ATR spectra can not be interpreted in the wavenumber region under about 900 cm\(^{-1}\), this because water absorbs strongly in this region. In the Zn\(_2\)(n-P-dtp)\(_4\) spectra a small peak corresponding to the water vibrations can be seen. This indicates that the sample contains some moist or incorporated H\(_2\)O in the salt structure. In the fingerprint area the spectrum of potassium db-dtp shows several splits of the peaks compared to the ATR spectra and the precipitation spectrum. The most intense peak on the Zn(db-dtp)\(_2\) precipitation spectra is at 975 cm\(^{-1}\), this is in good agreement with the results by Piras et al\(^{19}\) who got the most intense peak at 978 cm\(^{-1}\) in a transmission FT-IR spectra of commercial ZnDTP.
Figure 19 spectra of (db-dtp)$_4$, Zn$_2$(n-Pr-dtp)$_4$, Zn(db-dtp)$_2$, K-db-dtp, and db-dtp adsorbed on ZnS measured by ATR spectroscopy after 18 minutes (from top to bottom).
One primary assumption for this thesis was that de-dtp would adsorb onto the surface of a germanium crystal and that it would be detectable with ATR spectroscopy. This assumption was based on recent work done within ARC\textsuperscript{15,20} where xanthates, a chemical used for the same purpose and with similar molecular composition as DTP, has been adsorbed onto germanium. The first experimental work performed was the measurements of surface free energy and contact angle. De-dtp showed very low surface energy and the contact angle measurements could not detect any difference between the clean crystals and the once immersed into de-dtp. These first results implied that de-dtp might not adsorb onto the surface of germanium. The following adsorption studies of de-dtp onto germanium could not detect any adsorption. It was then assumed that a chemical with equal composition as de-dtp except for a longer hydrocarbon tail would be more surface active than de-dtp. Then again db-dtp showed the same result and did not adsorb on germanium. As a solution to this problem the germanium crystal was coated with a zinc sulphide film, which made it possible to detect adsorption of db-dtp, consequently successful adsorption experiments could be performed.

In infrared spectroscopy it is generally not too complicated to record spectra, the difficulty lies more in evaluating them. An evaluation problem with the ATR flow cell technique is that the solvent, i.e. the water molecules, give broad and intense peaks in the spectrum that can cover less intense vibrations. In the water spectrum in Figure 16 the broad peaks above 3000 cm\(^{-1}\) have a “tail” interacting with the region of
asymmetric and symmetric stretching vibration of CH\textsubscript{3} and CH\textsubscript{2} around 2900 cm\textsuperscript{-1}. To reduce this effect the ATR spectra have been corrected by an addition of a pure water spectrum to obtain a straight baseline in the region around 2900 cm\textsuperscript{-1}. This water correction appears to be quite complex since the water spectrum used for the addition is not the same as the water peaks that are reduced. The water spectrum in Figure 16, used for the addition to the db-dtp spectra, is recorded with water saturated at the surface of the IRE, in contrast to the water peaks in the db-dtp spectra that arises from the co-existing of the db-dtp and water in the solution and at the surface of the IRE. This water correction procedure is a necessary approach when monitoring the CH-region below 3000 cm\textsuperscript{-1}, although, an additional evaluation of the correction should, if possible, be made.

In order to find out what surface binding coordination that seems most likely to occur between the adsorbed db-dtp molecule and the ZnS film in the ATR studies the spectra in Figure 19 should be studied. Comparing the ATR spectrum of db-dtp adsorbed on ZnS with the precipitation spectra of Zn-db-dtp it is clear that Zn(db-dtp)\textsubscript{2} closely resemble the ATR spectrum. The bond type proposed would in this case be a terminal type of binding, where the dtp molecule has two bonds to the same Zn ion at the surface. This is in contradiction with recent NMR result\textsuperscript{21} which suggests a bridging type of bonding between synthetic sphalerite (ZnS) and dtp. This means that the dtp molecule binds to two different zinc ions at the surface. Since this thesis is in its beginning further experiments will give more understanding of the system and consequently the surface binding coordination.

ATR is a surface sensitive method where very small amounts of substances are detected. A clean surface is essential to be certain of what is detected. Despite a thoroughly cleaning procedure there may have been contaminations on the surface of the crystal that affects the results.
In this thesis de-dtp and db-dtp did not adsorb by a detectable amount onto germanium. However, when interpreting these results it should be kept in mind that the germanium surface might have been impure since the crystals were recycled from recent xanthate/germanium adsorption studies. The surface of germanium crystal can be oxidized in air, and water, which may cause the surface to be completely or partly covered with oxidation products, such as oxide, hydroxide, sulphate etc. If this was the case in the studies presented in this thesis it is possible that the crystal’s condition affected the presented results.
From the results of this thesis it is clear that db-dtp adsorb onto the surface of ZnS. Further experiments are though necessary to prove the repeatability of these results. Adsorption studies of de-dtp onto ZnS should be performed and be compared to the adsorption of db-dtp to see how the length of the hydro carbon tail affects the amount of adsorption and the adsorption rate. To examine how the external conditions affects the adsorption, experiments with varying pH, concentration, temperature, ionic strength etc. should be performed.

The Zn$_2$(n-Bu-dtp)$_4$ precipitation is not included in this thesis, thus it is an issue for future work to make and analyze the precipitation with IR transmission.

In this thesis the adsorption of de-dtp and db-dtp onto germanium was performed onto a recycled IRE. Further adsorption studies with unused germanium crystals should be performed to ensure that the same results are achieved.

The evaluation problems of the ATR spectrum originating from the intense water peaks should be further examined.
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