Interactions between Iron Oxides and Silicates

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Abstract

Silicates such as sodium silicate and bentonite are of great importance in the flotation of magnetite and in the balling of green pellets, respectively. Sodium silicate, also known as ‘water glass’, serves mainly as a dispersing agent in the flotation process, whereas bentonite has binding properties keeping the agglomerating magnetite particles together in the pelletizing process. Both processes are of utmost importance to the Swedish iron ore industry, the first one reducing the phosphorous content of the pellets whereas the second process is vital for the strength of the green pellets. Since the flotation precedes the green pellet balling, the surface modifications of magnetite particles by adsorbing ions or molecules during flotation may influence their properties in the agglomeration process. In addition to silicate from water glass, the iron oxide surfaces may also be modified by the collector used as well as by ions present in the process water and probably fines from gangue minerals that could not be washed off properly before pelletizing.

The main objective of this Licentiate thesis was to acquire a better understanding of the mechanisms involved in the sorption of dissolved silicate from aqueous solutions onto iron oxide surfaces by using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy and subsequently to develop a method to monitor the orientation of bentonite platelets settling onto the bare iron oxide using polarized ATR-FTIR technique. Accordingly, this thesis encompasses the study of the interaction between dissolved silicate in aqueous solution and magnetite (Fe₃O₄) as well as maghemite (γ-Fe₂O₃) surfaces at low silicate concentrations and various pH values including those used in the flotation process. Both the kinetics of sorption and desorption were studied. Maghemite was included because there is always questioned whether the surface of the magnetite particles, which may have been exposed to air, represents magnetite or if they are to some extent oxidized to maghemite and whether this oxidization affects the sorption behavior.

The infrared spectra show that the silicate concentration and pH both determine the species of sorbed silicate on the surfaces. A maximum sorption of silicate onto magnetite was observed in the pH range 9.5-7.0, close to pH 8.5. Molecular deposition (sorption) of silicate onto magnetite and maghemite seems to take place in a similar manner. However, the sorbed amount of silicate is different due to the difference in surface reactive sites. At high pH (>9.5) or low silicate concentration (≤ 0.1 mM), the dominant surface species was a bidentate monomeric surface complex assigned to the infrared band at 950 cm⁻¹. Decreasing pH or
increasing the concentration of silicate implies more of oligomeric surface silicate species assigned to the infrared absorption ranging from 1000 cm$^{-1}$ to 1050 cm$^{-1}$. The shift of this band implied information about the degree of surface polymerization. Moreover, a 3-dimensional silica framework structure, which was assigned to the band at $\sim$1120 cm$^{-1}$, was observed on the iron oxide surface with the evolution of silicate polymerization on surface. Desorption of sorbed silicate from the surface showed a comparatively slow overall desorption rate, suggesting that polymerized species had a stronger affinity for the iron oxide surface as compared to monomeric species.

In the last part of this thesis, the orientation of bentonite platelets on a ZnSe ATR crystal as well as on a layer of magnetite particles deposited on the crystal was analyzed with polarized horizontal ATR-FTIR Spectroscopy. For a dry bentonite film deposited from aqueous dispersion onto the ZnSe crystal at room temperature, the (001) surface (basal plane) of the platelets was preferentially oriented perpendicular to the surface normal of the ATR crystal. This was also true for a dry bentonite film settled on a thin layer of magnetite particles deposited on the ZnSe crystal, but the magnetite particles contributed to an increased order (lower tilt angle). For a wet film, the tilt angle of the bentonite platelets was considerably larger indicating that the swelled bentonite layer above the ZnSe crystal contained platelets that tended to form so called card house structures. All settling experiments were performed using aqueous bentonites dispersions at pH 5.6.
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List of papers

This thesis is based on the following papers, referred to in the text by Roman number.

I. A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy
   Xiaofang Yang, Payman Roonasi, Allan Holmgren
   Accepted for publication in *J. Colloid Interface Sci.*, in press.

II. Kinetics of silicate sorption on magnetite and maghemite. An in-situ ATR-FTIR study
    Xiaofang Yang, Payman Roonasi, Rickard Jolsterå, Allan Holmgren

III. A polarized Fourier transform infrared spectrometry attenuated total reflection study of bentonite settled onto magnetite.
    Allan Holmgren, Xiaofang Yang
    Accepted for publication in *J. Phys. Chem. C*, in press.
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APPENDED PAPERS
1. Introduction

1.1 Background

Magnetite (Fe₃O₄) is the main iron oxide constituent of the Luossavaara-Kiirunavaara AB (LKAB) Kiruna ore. After the apatite was remove by flotation from the finely ground iron ore, the purified magnetite concentrates then were ready for balling, where water and binder such as sodium bentonite were added to facilitate the growth as well as control the strength of green pellets. Magnetite contains both divalent and trivalent iron, Fe²⁺ only occupy octahedral sites whereas Fe³⁺ distributes in both octahedral and tetrahedral sites, as shown in Figure 1.1. Maghemite, named from magnetite-hematite, has a structure similar to magnetite, but all or most of Fe²⁺ are oxidized to trivalent state [1]. Accordingly, the unit cell volume of maghemite is reduced as compared with magnetite resulting from the oxidation of the Fe (II) atoms. Both magnetite and maghemite are strongly magnetic.

![Figure 1.1 Ball-and-stick model of the magnetite structure.](image)

A silicate can represent soluble silicate anions or species in solution, and also can be a group of the most important and abundant minerals containing silicon and oxygen in tetrahedral units of SiO₄. Soluble sodium silicates, also known as ‘water glass’, are probably one of the oldest and most widely used industrial chemicals [2]. Among a wide variety of applications, sodium silicate is used as a deflocculation agent in clay mining processes and ore flotation because of its surface charge modifying ability. In ore flotation, sodium silicate
is often used as depressant or dispersant to improve the selectivity in the flotation of salt-type minerals such as apatite, calcite and fluorite, from sulfides and oxides, siliceous minerals, and also other salt-type minerals [3]. However, the mechanisms explaining the variation in the activity and efficiency of sodium silicate in flotation depending on the mineral system and the silicate dosage is still not well understood [4-6]. Thus, the knowledge about the reaction between soluble silicate and metal oxide is of great importance to better understand the behavior of silicate in flotation process and other industrial applications such as the synthesis of zeolites and iron oxide-silicate composites as well as the interfacial reactions in the environmental systems.

A silicate mineral with 2:1 silicon tetrahedral and aluminum octahedral structure may form swelling clay. Sodium bentonite, consisting mostly of montmorillonite (structure as shown in Figure 1.2), exhibits swelling property and is frequently used as a binder to improve the green pellets strength of valuable mineral such as magnetite [7-9]. It is already known that the water absorption capacity (swelling property) and particle size of bentonite are the most important factors to evaluate the binding performance of bentonite. Moreover, the chemical environment of the magnetite particles in the pelletizing process and the mixing conditions will also influence the binding perperties of bentonites and these factors are sometimes crucial for the final result [10]. However, the mechanism by which bentonite works as a binder in magnetite green pellets is still not very well established, although it is reasonable to assume that the cohesive forces, water-bridge and capillary forces which are closely related to the delamination of bentonite should be the main binding forces [9].
1.2 Internal reflection spectroscopy (IRS)

In IRS as in other types of FTIR measurement, such as transmission and diffuse reflectance spectroscopy, to detect signals of infrared radiation probed molecules or species, a transition dipole moment upon excitation by infrared radiation is necessary. Thus the measured absorbance, $A_i$, of the IRS signals of the probed molecules or species can be expressed as

$$A_i \propto (M_i \cdot E_i)^2$$

where $A_i$ represents the absorbance of each of the vibrational modes, $M_i$ is the transition dipole moment of that mode, and $E_i$ is the electrical field amplitude that the mode is exposed to. Moreover, the absorbance of an infrared spectrum where the recorded absorbance is measured relative to a suitable reference obeys Beer-Lambert’s law,

$$A_i = \log \frac{I}{I_0} = \varepsilon \cdot c \cdot l$$

where $I$ is the recorded intensity caused by the absorbing system, $I_0$ is the intensity of the reference, $l$ is the path length through the medium containing the probed system, $c$ is the concentration of the probed species, and $\varepsilon$ is the molar absorption coefficient which depends on the degree of interaction between the infrared light and the vibrational mode and is a function of the wavelength of the radiation.

Using internal reflection infrared spectroscopy, the optical spectrum of a sample that is in contact with an optically denser but transparent medium is recorded and the wavelength dependence of the reflectivity of this interface is measured by introducing infrared light into the denser medium in which the propagating wave of radiation undergoes total internal reflection [11]. The existence of evanescent wave in the medium of lower index of refraction is the basis of the internal reflection spectroscopy. This evanescent wave is an exponentially decayed electromagnetic field from $E_0$ at the surface of the rarer medium to value $E$, at a distance $Z$ from the surface, according to the equation expressed as follows,

$$E = E_0 \exp \left[ -\frac{2\pi}{\lambda_1} \left( \sin^2 \theta - n_2^2 \right)^{\frac{1}{2}} \cdot Z \right]$$
where $\lambda_i = \lambda/n_1$ is the wavelength of the radiation in the denser medium, $\lambda$ is the wavelength in free space, $n_{21} = n_2/n_1$, where $n_1$ and $n_2$ are the refractive indices of the optically denser and rarer medium, respectively, $\theta$ is the incident angle, and $Z$ is the distance from the rarer medium surface. It is worth to point out here that the evanescent wave is a nontransverse wave, which means that it has vector components in all spatial orientations and allows the interaction between all these vector components and dipoles in all orientations. A single reflection IRS arrangement is illustrated in Figure 1.3.

![Figure 1.3. Schematic diagram of the internal reflection spectroscopic arrangement.](image)

Accordingly, as shown in Figure 1.3 the penetration of the exponential field normal to the surface into the sample (rarer medium) is defined as the depth of penetration $d_p$, at which the evanescent wave field decays to a value of $E_0 \cdot \exp(-1)$. Thus the $d_p$ can be expressed as,

$$d_p = \frac{\lambda}{2 \pi n_1} \cdot \frac{1}{(\sin^2 \theta - n_{21}^2)^{1/2}}$$

(4)

This equation illustrates one of the possibilities inherent in IRS, namely the possibility to vary the depth of penetration by changing the angle of incidence ($\theta$) or by choosing an appropriate IRE since $n_{21}$ is the ratio between the refractive index of the rarer medium and the crystal itself ($n_2/n_1$). It also should be noticed that the depth of penetration is wavelength-dependent, a fact that should be accounted for if absorbencies at different wavenumber are compared.
Moreover, since in practice the incident infrared radiation will be adsorbed at the sample-IRE interface, the propagating light becomes attenuated. For multiple reflections, the total reflectance of the attenuated radiation is expressed as follows,

\[ R^N = (1 - \alpha \cdot d_e)^N \]  

(5)

where \( N \) is the number of reflections, \( d_e \) is the effective sample thickness, and \( \alpha \) (cm\(^{-1}\)) is the absorption coefficient of the sample. The effective sample thickness \( d_e \) is defined as the thickness of sample that would give the same absorbance for transmission at normal incidence as that obtained in a single reflection IRS measurement. The effective sample thickness is important because it provides a relationship between transmission and internal reflection spectroscopy by permitting the direct compassion of spectral contrasts in the transmission and internal reflection spectra. This attenuated-multiple-reflection is the basic idea of the attenuated total reflectance (ATR) technique.

1.3 Attenuated total reflection (ATR) technique

ATR is a widely used internal reflection spectroscopy sampling tool nowadays since the pioneering work of Harrick and Fahrenfort in 1960s [12], by which the adsorbed species on surfaces as well as some other chemical phenomena at the solid-liquid interfaces can be monitored in-situ. An ATR spectroscopic measurement is carried out by placing the sample in contact with an internal reflection element (IRE) of high refractive index and propagating infrared radiation through the IRE, radiation that is allowed to interact with the sample. Accordingly, it is interesting and important to know if the whole sample layer is probed and to be aware of the experimental factors, such as refractive indices (RIs) of IRE and sample, incident angle, and chemical properties of IRE and so on.

Generally three methods are used to make the sample in contact with the IRE: (1) spreading a concentrated suspension or paste or slurry onto the ATR crystal surface [13-17], (2) in-situ synthesizing a sample layer on the crystal surface [18,19], or (3) coating the IRE with colloidal particles from a suspension (by spreading, or dip-coating, or spinning) to form a thin film, which is stable if the film is subjected to a flow of solution [20-23]. In the present work, the third method was used, i.e. a trapezoidal-shaped ZnSe ATR crystal was coated with a thin film of the particles by spreading the particle suspension. In combination with the flow-cell
technique [20,22], the interfacial reactions occurring at the film-liquid interface could be monitored in situ.

1.4 Polarized horizontal ATR-FTIR spectroscopy

ATR technique in combination with polarized radiation (polarized ATR) has been proved to be a convenient technique to study the spatial orientation and structure of different species close to the sampling crystal surface. This technique is based on the fact that the absorption of the infrared light by a certain probed vibrational modes becomes maximal when the transition dipole moment is parallel to the electric field component of the incident light. However, so far, much of the attention has been focused on the orientation of surfactant molecules or biological membranes (double layers) [24-26]. The applications of this technique to study the orientation of mineral such as clay particles is much more scant and the orientation of bentonites platelets on a magnetite surface, reported in this thesis and the appended Paper III, represents a unique contribution to the scientific community.

The polarized light in the plane of the crystal surface is defined as s-polarized (As), and the infrared light passing through the plane of incidence is p-polarized (Ap). In the model describing the orientation of molecules adsorbed on an ATR crystal, the tilt angle of the molecule with respect to the crystal surface is defined as the angle between the molecular axis and the surface normal of the crystal, and can be calculated from the dichroic ratio, D.

\[
D = \frac{A_s}{A_p}
\]

In a layer of alkyl chain molecules on an ATR crystal, for example, the molecular axis is commonly assumed to be uniaxially distributed with respect to the normal of the crystal surface, and the transition dipole moments within the molecule are also symmetrically distributed around this axis with a certain angle \(\alpha\) with respect to the molecular axis. This is illustrated in Figure 1.4.
Figure 1.4. Schematic diagram showing the polarized radiation through an IRE and axially symmetric distributions of adsorbed molecules on IRE. The molecular axis is uniaxially distributed around the surface normal of the IRE and the transition dipole moment is uniaxially distributed around the molecular axis with angle $\alpha$.

The measured absorptions of polarized radiation ($A_s$ and $A_p$) are proportional to the square of the vector product expressed in Eq. 1, namely proportional to the square of the vector product between the electric field vector ($E$) of the evanescent field and the transition dipole moment ($M$). For a molecule that has a uniaxially symmetric distributed molecular axis around the $z$-axis, the absorbance can be expressed as [27]

$$A_i = \int \int M_i^2 \cdot E_i^2 \cdot N(\alpha, \gamma) d\alpha d\gamma$$  \hspace{1cm} (7)

where $i$ represents the $x$, $y$ or $z$ direction, $M_i$ and $E_i$ are the projection of the vectors $M$ and $E$ along the $i$-direction, and $N(\alpha, \gamma)$ is the orientation distribution function of the transition dipole moments. The angles $\alpha$ and $\gamma$ are as shown in Figure 1.4.

The component vectors of the electric field depend on the refractive indices of the crystal, the sample on crystal and the medium outside the sample as well as on the angle of incidence. The equations used to calculate the $x$, $y$, and $z$ components of the electric field are described by Harrick and Mirabella [28] as well as in a number of publications [24,27,29]. The electric field components in a three-layer refractive index model can be expressed as,
In Eqs. 8-10, $\theta$ is the angle of incidence, $n_{31} = n_3/n_1$ and $n_{32} = n_3/n_2$, where $n_1$, $n_2$, and $n_3$ are the refractive indices of the IRE, second layer (sample) and outside medium, respectively.

Thus the dichroic ratio of the absorption from an orientated molecule of which the angle between the transition dipole moment and the molecular axis is 0° can be calculated using the following equation

\[
D = \frac{A_s}{A_p} = \frac{E_s'^2 \cdot \sin^2 \gamma}{E_s'^2 \cdot \sin^2 \gamma + 2E_s'^2 \cdot \cos^2 \gamma}
\]  

where $\gamma$ is the average tilt angle between the molecular axis and the IRE surface normal.

Solving Eq. 11 for $\gamma$ gives Eq. 12,

\[
\gamma = \arcsin \left( \frac{2DE_s'^2}{D(2E_s'^2 - E_x'^2) + E_y'^2} \right)^{1/2}
\]  

This equation was used to calculate the average tilt angle of bentonite platelets in the present study.

1.5 Scope of the present work

The scope of the present work is to study the interactions between iron oxides (viz. magnetite and maghemite) and silicates, including sodium silicate anions and bentonite clay.
In the first part, the sorption behaviour of sodium silicate onto magnetite and maghemite was studied by in situ ATR-FTIR spectroscopy. The effects of pH, silica concentration, and time on silicate sorption and polymerization at the iron oxide-water interface were examined. In the second part, the polarized HATR-FTIR spectroscopy was used to investigate the orientation of delaminated bentonite platelets settled onto a thin magnetite film.
2. Materials and Methods

2.1 Chemicals and Materials

Two different sodium metasilicate (Na₂SiO₃·9H₂O) were used as metasilicate (SiO₂/Na₂O weight ratio of 1) source. The sodium metasilicate from J.T. Baker was used in the work presented in Paper I, and another fresh Na₂SiO₃·9H₂O from Sigma was used in the work presented in Paper II. The preparation procedure for sodium silicate stock solution was the same for the two sources of metasilicate, namely dissolution into Milli-Q water and dilution to 0.5 M. Silicate3.25 was an industrial water glass reagent with a SiO₂/Na₂O weight ratio of 3.25 and was obtained from the flotation plant at Luossavaara-Kiirunavaara AB (LKAB) in Kiruna, Sweden. The pH of the soluble silicate stock solutions was > 11.5 and sample solutions were prepared just before the in-situ measurements. No extra ionic medium was used in sodium silicate sorption measurements.

The clay mineral Bentonite, originally from Milos in Greece, was obtained from Minelco and ion exchanged using 0.6 M NaCl. Briefly, in the ion exchange procedure bentonite was mixed with 50 mL 0.6 M NaCl solution and stirred for about 3 hours. After stirring, the bentonite settled at the bottom of the beaker because of particle coagulation due to the high NaCl concentration and the supernatant was substituted for another 50 ml of NaCl solution. This was repeated three times and finally the suspension was allowed to settle at elevated temperature (60 °C) for 1 hour. The ion exchanged bentonite was then redispersed in 200 ml Milli-Q water (pH=5.6) under stirring for 8 hours, then centrifuged at 20 000 rpm for 30 minutes and this procedure was repeated until the water contained no chloride ions according to an AgNO₃ test. This bentonite sample has a BET surface area of 53.8 ±0.3 m²/g. The particle size distribution was narrow with peak intensity at 340 nm, as measured by a Zeta Plus instrument (Brookhaven Instruments Corporation). The average size of the particles indicated that the clay mineral was well delaminated. The chemical composition of the ion exchanged Milos bentonite in weight-% was as follows: 59.6 (SiO₂), 21.9 (Al₂O₃), 4.6 (Fe₂O₃), 3.1 (MgO), 3.1 (Na₂O), 0.5 (K₂O), 0.8 (TiO₂), 0.1 (CaO), 0.4 (Tot C). The analyses were performed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) [30].

Magnetite and maghemite used in this work were synthesized. Magnetite was synthesized from Fe (II) and Fe (III) chlorides using a coprecipitation method described by Julivet et al. [31] and Jarlbring et al. [32]. Briefly, Fe(II) / Fe(III) chloride salt mixture (1: 2 molar ratio)
made from deoxygenated Milli-Q water was hydrolyzed using NH\textsubscript{4}OH, purified also with deoxygenated Milli-Q water, and stored under argon atmosphere. Maghemite was prepared by heating the synthetic magnetite in an oven at 240 °C overnight. The BET surface area of magnetite and maghemite was 97.7 m\textsuperscript{2}·g\textsuperscript{-1} and 87.3 m\textsuperscript{2}·g\textsuperscript{-1}, respectively.

All other reagents were of analytical grade, and all solutions were prepared from Milli-Q water as solvent. NaOH and HCl solutions were used for pH adjustments.

2.2 Film preparation

The iron oxide (magnetite and maghemite) film used in the sodium silicate sorption experiments was made from the corresponding oxide suspension by spreading a certain amount of suspension over the IRE and evaporating the water solvent in a vacuum desiccator. After rinsing with Milli-Q water and dried, the weight of the film was calculated from the weight difference between the crystal with and without iron oxide layer.

The basis of the polarized ATR measurements was the assumption that the bentonite platelets and the magnetite particles form a thin film which could be entirely penetrated by the evanescent field. This was also experimentally verified. The magnetite films were prepared in a similar way as described above and the thickness of the bentonite films could be easily controlled by using diluted suspensions or different settling time. The thickness of film deposit on the ZnSe crystal for polarized ATR analysis was estimated using transmission IR spectroscopy. The transmission spectra of deposited bentonite film were recorded at four different equally spaced spots along the ZnSe crystal viz. at 1, 3, 5, and 7 cm from one of the cut edges of the crystal.

2.3 In situ sorption ATR-FTIR measurements

All in-situ ATR-FTIR spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a vertical ATR accessory. The vertical ATR accessory consisted of a trapezoidal-shaped ZnSe IRE (45°, 50 mm × 20 mm × 2 mm, RI~2.4) with totally 25 internal reflections mounted in a ~3.5mL flow-through stainless steel cell. The setup of in-situ ATR measurements was shown in Figure 2.1. The spectra of aqueous silicate and of silicate sorbed on iron oxides were recorded by averaging 100-200 scans at a resolution of 4 cm\textsuperscript{-1}. Data evaluation and spectra simulation were performed with OPUS software from Bruker Optics.
The spectra of sorbed silicate were recorded with ZnSe, magnetite deposit and water as background. After the background spectrum had been recorded, sodium silicate was added to the reaction vessel and adjusted to the desired pH before the adsorption experiments were commenced. The effect of lowering pH on sorption was measured by collecting spectra of silicate sorbed on magnetite at each pH step during 30 min. Desorption experiments were performed by flushing the flow-cell with Milli-Q water at desired pH. All experiments were performed under ambient temperature (22 ± 1°C).

Figure 2.1. Schematic diagram of the in situ ATR-FTIR spectroscopy setup.

2.4 Polarized HATR-FTIR measurements

A horizontal ATR trough crystal plate mount was used in these measurements. The IRE fixed to the plate mount was a ZnSe crystal plate (80 mm × 10 mm × 3 mm, 45°, RI~2.4) with 13 reflections on one side. All spectra were recorded under room temperature and normal pressure using the double-side forward-backward acquisition mode. The single beam background spectrum of ZnSe with a layer of magnetite was recorded under argon atmosphere. 256 scans were recorded and signal-averaged at an optical resolution of 4 cm⁻¹. Polarization of the infrared beam was achieved with a rotatable grid polarizer of aluminium.
deposited on BaF₂, placed in front of the HATR accessory. The setup of polarized HATR was illustrated in Figure 2.2.

Figure 2.2. Schematic diagram of the polarized HATR-FTIR spectroscopy setup.

The calculation of tilt angle of bentonite platelets settled onto bare ZnSe crystal or magnetite deposited crystal is based on the model illustrated in Figure 2.3. In this model, the molecular axis in Figure 1.4 is defined as the normal of the (001) surface of bentonite platelets. Meanwhile, a uniaxial distribution of transition dipole moments parallel to the (001) surface normal of the bentonite platelets is assumed.

Figure 2.3. Schematic diagram of polarized HATR-FTIR technique. The tilt angle of a delaminated bentonite platelet with respect to the surface normal of the ZnSe crystal or the magnetite deposited ZnSe, is denoted by γ.
3. Results and Discussion

3.1 Spectra of sodium silicate in aqueous solution (Paper I)

The spectra of 10 mmol·L⁻¹ sodium metasilicate in aqueous solution at different pH are shown in Figure 3.1. Due to the transmission limit of the ZnSe crystal and the strong absorption of water, the infrared absorption bands of sodium silicate are shown between 1300 cm⁻¹ and 850 cm⁻¹. It can be seen from Figure 3.1 that at pH 11.5, two absorption bands at 885 and 1023 cm⁻¹ were prominent, the latter band having a shoulder at ~1060 cm⁻¹. Lowering the pH to 9.7, the bands at 885 and 1023 cm⁻¹ decreased in intensity whereas the shoulder at 1060 cm⁻¹ grew in intensity accompanied by a new broad band emerging at higher frequency. In addition, a weak band emerged with peak frequency at 945 cm⁻¹. At the lowest pH studied (~7.5), the line shape of the spectrum was similar to the spectrum at pH 8.6 with the dominant band at 1122 cm⁻¹ and shoulders at 1090 and 1175 cm⁻¹. As expected, the spectra show that the distribution of silicate species is pH dependent. The shift of band at ~1020 cm⁻¹ to higher frequency upon lowering the pH indicates the formation of polymeric species.

![Figure 3.1. Infrared spectra of 10 mmol·L⁻¹ aqueous sodium metasilicate solutions in the pH range 7.5-11.5.](image)

To assign the infrared vibrational bands, the distribution of silicate species with pH and concentration in solution need to be evaluated. A silicate speciation model was then set up using the formation constants from Felmy et al. [33] and the WinSGW program [34]. The formation constants and the chemical formula of each species used in the modelling are compiled in Table 3.1 and the calculated thermodynamic equilibrium distributions are plotted.
in Figure 3.2. Below 2 mmol·L⁻¹ (the solubility limit of amorphous silica [35]), the monomers \( \text{SiO}_2(\text{OH})_2^{2-}, \text{SiO}(\text{OH})_3^- \), and \( \text{Si}(\text{OH})_4^- \) are dominant with protons transferred between different species as pH was changed (as shown in Figure 3.2a). The distribution of silicates becomes more complex when the concentration of silicate in solution increases, dimers, trimers, oligomers and higher aggregates will form by condensation of monomers at high concentration, and even silica precipitates under the thermodynamic equilibrium. In 10 mmol·L⁻¹ solution, more dimers and trimers and even tetramers and polymers are formed between pH 9 to 11, and at low pH colloidal SiO₂ might be formed. However, these oligomeric species are not seen in the thermodynamic equilibrium distribution plot as shown in Figure 3.2b.

![Figure 3.2. Distribution diagram of silicate anions as a function of pH in (a) 1 mmol·L⁻¹ and (b) 10 mmol·L⁻¹ aqueous sodium metasilicate solution.](image)

Curve fitting of the absorption bands was utilized in an attempt to distinguish the spectral features of the various silicate anions from each other. Each spectrum was resolved into six or seven component bands using the OPUS program. It is clear that the variation of spectral features in the wavenumber region 1250-850 cm⁻¹ can be explained by the change in relative contributions from component bands at different pH.
Based on the fractional distribution of silicate anions in aqueous solution (Fig. 3.2), analysis of our infrared spectra, and comparison with previous studies [36-38], the infrared bands at ~890 and 1020 cm\(^{-1}\) could be assigned to Si-O stretching vibration of SiO(OH)\(_2^−\) species. The band at ~945 cm\(^{-1}\) seems to mainly involve the stretching of Si-OH in Si(OH)\(_4^−\) monomers, since it appears at low pH, whereas the band at 1070 cm\(^{-1}\) may originate from stretching vibrations involving the Si-O-Si entity. With decreasing pH of the silicate solution, the SiO(OH)\(_3^−\) anions tend to be protonated and possibly further condensed since more OH function groups are available. Hence the bands appearing in the 1050-1200 cm\(^{-1}\) range and showing an increased intensity upon lowering the pH are assigned to stretching vibrations involving the Si-O-Si entities. However, it should be stressed here that these assignments are to large extent based upon comparison with previous experimental studies, since not so much quantum chemical calculations such as density functional theory modelling of silicate species are available in the literature. Although the assignments above are judged to be plausible, the contribution from for example SiO-H bending vibrations to the assigned frequencies is still unclear.

Table 3.1. Speciation model of dilute silicate aqueous solution based on the reaction: pH\(^+\) + qSi(OH)\(_4^−\) ⇌ H\(_q\)(Si (OH)\(_4^−\))\(_q^p^+\). Formation constants from A. Felmy [33]. LogK\(_{sp(SiO_2,am)}\) = -2.71 [35].

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>Chemical formula</th>
<th>log (K(_{sp}^p,q))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>SiO(OH)(_3^−)</td>
<td>-9.82</td>
</tr>
<tr>
<td>-2</td>
<td>1</td>
<td>SiO(_2^−)(OH)(_2^−)</td>
<td>-23.27</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>Si(_2^−)[-]</td>
<td>-8.50</td>
</tr>
<tr>
<td>-2</td>
<td>2</td>
<td>Si(_2^−)[-]</td>
<td>-19.4</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>Si(_3^−)(3-cyclo)</td>
<td>-29.3</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>Si(_3^−)(linear)</td>
<td>-29.4</td>
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<td>Si(_4^−)(sub)</td>
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</tr>
<tr>
<td>-6</td>
<td>6</td>
<td>Si(_6^−)[-]</td>
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3.2 Factors influencing silicate sorption and desorption (Papers I, II)

3.2.1 The effect of pH on silicate sorption and desorption behavior

The effect of pH and silicate type on the amount of silicate sorption and desorption at magnetite-water interface was investigated using in situ ATR-FTIR spectroscopy. In this study, the integrated intensity of infrared absorbance between 1300 and 800 cm\(^{-1}\) was used to evaluate the surface loading of silicate. As a first approximation, it may be assumed here that the integrated absorbance in the 1300-800 cm\(^{-1}\) region is proportional to the amount of adsorbed silicate. This assumption is reasonable as long as surface species formed at different pH are similar or exhibit transition dipole moments of similar numerical value. If not so, there is no simple linear relation between the integrated absorbance at different pH and the amount of adsorbed species. However, this difficulty does of course not exclude qualitative interpretations in the following analysis.

![Figure 3.3](image_url)

Figure 3.3. Sorption and desorption of sodium silicate as a function of pH and time. Filled symbols, integrated absorbance of sorbed silicate per mg magnetite; open symbols, integrated absorbance of residual silicate sorbed on magnetite during desorption; lines, solution pH during sorption and desorption.
The amount of sorbed sodium silicate from 1 mmol·L⁻¹ silicate solutions but different types, viz. metasilicate and Silicate3.25, onto magnetite was firstly compared. As shown in Figure 3.3, the amount of silicate sorbed from 1 mmol·L⁻¹ metasilicate and Silicate3.25 solutions were about the same. It indicates that at least for dilute silicate solutions the pH value seems to be a more useful parameter rather than the silica to alkali ratio of silicate that could reveal information about the silicate species distribution. A considerable increase in the intensity was observed from pH 11 to 9, whereas decreasing pH from 9 to 7 only contributed a minor change in spectral intensity. Comparing the results obtained for 10 mmol·L⁻¹ metasilicate solution (not shown) with 1 mmol·L⁻¹ solutions, the surface loading of silicate on magnetite is about 4-5 times larger at the higher silicate concentration. In the current measurements, the maximum sorption of silicate expected around pH 9 [39-42] was not observed. This might be because of the observed sorption already has passed its maximum when reaching pH 7. However, subsequent desorption at pH 7 for 30 min was not enough to desorb the silicate from the surface as the silicate sorption was expected to be reduced at this pH value. Probably this is reflecting a non-equilibrium situation where both the silicate species sorbed at the magnetite surface and the protonation state of the surface itself must change as pH is lowered. Accordingly, the residual amount of silicate after flushing with Milli-Q water at different pH indicates that more of the surface species were desorbed at higher pH and the desorption curve exhibits an initial fast decrease followed by a slower desorption step.

To better assess the pH dependence of silicate sorption on magnetite, a series of ATR spectra were recorded from 1mM sodium metasilicate solution contacting with magnetite at the pH values 10.8, 9.5, 8.5, and 7.0. In Figure 3.4, a clear pH dependent sorption behavior can be seen. From pH 10.8 to pH 8.5, the integrated intensity of sorbed silicate increased with decreasing pH. However, when pH was lowered to 7.0 the integrated intensity decreased implying that between pH 9 and 7 there is a maximum in the amount of sorbed silicate. Moreover, the corresponding desorption curves clearly indicate that the sorbed silicate is more easily desorbed at high pH.
Figure 3.4. Sorption of silicate from 1 mM sodium metasilicate aqueous solution at different pH onto magnetite followed by desorption. Filled symbols, integrated absorbance of sorbed silicate per mg magnetite; open symbols, integrated absorbance of residual silicate on surface during desorption.

To determine the pH effect at different silicate concentration, the spectra recorded after 30 min of reaction at each pH value (as shown in Figure 3.3a, 1 mmol·L⁻¹ sodium metasilicate) were compiled in Figure 3.5a, and corresponding spectra from 10 mmol·L⁻¹ sodium metasilicate solution were plotted in Figure 3.5b. The significant increase in spectral intensity compared with those of silicate in solution indicated a strong affinity of magnetite for silicate. It can be seen in Figure 3.5 that the line shape of spectra obtained from 10 mmol·L⁻¹ and 1 mmol·L⁻¹ solutions are very different. In Figure 3.5a, the broad absorption at pH 11.1 is apparently composed of three broad bands at ~955, 1029, and ~1120 cm⁻¹ with the most intense band at 1029 cm⁻¹ shifting to 1060 cm⁻¹ as pH was decreased to 7. Simultaneously, the infrared band at 1120 cm⁻¹ became much stronger. However, in Figure 3.5b, at pH 11.2, the maximum absorbance is located at 955 cm⁻¹ and the peak frequency remained constant in position with decreasing pH. When pH was lowered to 9.3, the band at ~1020 cm⁻¹ increased in intensity becoming the strongest band in the spectral region (800-1300 cm⁻¹) and simultaneously an apparent increase in the intensity of the band at 1120cm⁻¹ can be observed. When pH further decreased from 8.3 to 7.0, there was no remarkable change in the lineshape.

At high pH and low silicate concentration, the SiO(OH)₃⁻ species in solution could be sorbed onto magnetite and formed bidentate surface complexes which exhibits a band at 950
cm⁻¹ [43,44]. To higher silicate concentration, the condensation of silicate monomers especially at low pH is much faster [45,46]. It is therefore reasonable to suggest that the increase in intensity at 1120 cm⁻¹ and 1060 cm⁻¹ is due to the sorption of low polymeric silicate species and possibly the polymerization is enhanced at the magnetite surface. Thus the strong infrared absorbance in the wavenumber region 1050-1200 cm⁻¹ is related to the polymeric species, and the appearance of band at ~1120 cm⁻¹ could be an infrared spectral evidence for the formation of a 3D framework silica structure on surface.

Figure 3.5. Infrared spectra of silicate sorbed on magnetite from (a) 10 mmol·L⁻¹ and (b) 1 mmol·L⁻¹ aqueous sodium metasilicate solutions at different pH. Spectra are plotted in the same order as the indicated pH-values.

3.2.2 Effect of silicate concentration on sorption

In Figure 3.6 (a, b) the integrated intensity due to silicate sorbed from aqueous solution at pH 8.5 onto magnetite (a) and maghemite (b) is shown. Different silicate concentrations were used in order to determine the effect of silicate concentration on sorbed species. The results in Figure 3.6 show that high silicate concentration gives high surface loading on iron oxide adsorbents and that the sorption capacity of two iron oxide samples for silicate is different. After flushing the silicate sorbed surface for 2 h, it is clear that the silicates sorbed from low concentration solution were more easily to be desorbed than from high concentration solution (5 mM). However, it is more interesting to compare how the sorption and desorption spectra recorded at different concentration varies with time (Figures 3.7 and 3.8). The line shape of spectra collected from same concentration for magnetite and maghemite is rather similar,
although the spectral intensity is much larger for former. At the lowest concentration (0.1 mM, Figure 3.7), the spectra showed a dominant band at 950 cm\(^{-1}\), where the spectra recorded from 1mM silicate solution at pH 10.8 (Figure 3.5b) had the predominant band, is due to the bidentate monomeric surface species. The appearance of a shoulder of this band at 1000 cm\(^{-1}\) indicates the formation of oligomeric species. At 5 mM, the dominant band at \(\sim\)1020 cm\(^{-1}\) for a 1 mM solution shifted to \(\sim\)1050 cm\(^{-1}\) upon increased surface loading. This may be explained as an increased polymerization of oligomeric silicate species at the magnetite surface but may simultaneously reflect a change of the structure of the oligomers since infrared spectra are well-known to be sensitive to changes in molecular structure. Similar spectral features were observed upon sorption from a 10 mM solution (Figure 3.5a), where the increased absorbance at 1120 cm\(^{-1}\) implies that a three dimensional silica framework structure eventually will form a silica layer, which infrared spectrum is similar to the spectrum of amorphous silica colloidal particles. Accordingly, the formation of polymeric species should be the explanation to the different desorption behaviour observed in Figure 3.6.

Figure 3.6. Sorption and desorption of sodium silicate at pH 8.5 and different initial silica concentration, (a) magnetite and (b) maghemite. Filled symbols, integrated absorbance of sorbed silicate per mg magnetite; open symbols, integrated absorbance of residual silicate on surface during desorption. Infrared spectra were integrated between 1300-800 cm\(^{-1}\).
Figure 3.7. ATR-FTIR spectra showing the time dependence of silicate sorption on magnetite at pH 8.5 and different silicate concentrations.

Figure 3.8. ATR-FTIR spectra showing the time dependence of silicate sorption on maghemite at pH 8.5 and different silicate concentrations.
3.3 Comparison of magnetite with maghemite (Paper II)

Another interesting question addressed in this study was the possible difference between magnetite and maghemite concerning their sorption behaviour. Evidently, magnetite exhibits a considerably higher affinity for the silicate species, as shown in Figure 3.6.

Both iron oxides have about the same point of zero charge as determined by Sun et al. [47] and Jarlbing et al. [48] using zeta potential measurements on iron oxide samples prepared by applying a similar synthesis routine as here, viz. at about pH 6.0 for magnetite and at about pH 6.2 for maghemite. The measured BET areas are also rather similar viz. 98 m²/g for magnetite and 87 m²/g for maghemite. However, the unit cell volume of maghemite is slightly smaller because of the oxidation of the Fe (II) atoms. The number of measured proton active adsorption sites by potentiometric titrations is about 0.8 sites/nm² for maghemite [48] and 5.2 sites/nm² for magnetite [47]. It is therefore proposed here that the number of active surface sites is the main reason for magnetite being a more effective sorbent for silicate species than maghemite. It should be noticed that in neither of these two cases, a sorption equilibrium plateau value was reached.

3.4 Orientation of Bentonite platelets (Paper III)

3.4.1 Estimation of film thickness

The intensity of the ν(Si-O) band at 1040 cm⁻¹ was utilized to estimate the film thickness by using an already measured absorption coefficient for Wyoming montmorillonite (3.60 × 10⁴ cm⁻¹) [49] and the equation below,

\[ \alpha = \left( \frac{\ln 10}{d} \right) A_{\text{max}} \]  

(13)

where \( A_{\text{max}} \) is the peak absorbance of the Si-O band, \( \alpha \) is the absorption coefficient, and \( d \) is the film thickness [50]. In our experiments, the thickness of bentonites film on ZnSe crystal varied between 53 and 79 nm, and the thickness of films settled onto magnetite within 5h varied between 9 and 10 nm. These values are far below the depth of penetration (\( d_p \)) of the infrared radiation.
3.4.2 Orientation of Bentonite Platelets on ZnSe

A p-polarized infrared spectrum of a dry thin (10 nm) film of bentonite on the ZnSe crystal is shown in Figure 3.9. The most intense bands of bentonite are located in the spectral region 1150-900 cm\(^{-1}\). Due to the large Napierian absorption coefficient of Si-O stretching vibrations, the bands in this region are very strong although the bentonite film is very thin. By simulating the spectrum with component bands, four \(\nu\text{(Si-O)}\) bands are obtained, viz. at 1115, 1085, 1040, and 1010 cm\(^{-1}\). Additionally, three weak bands from bending vibration of the metal-OH entities in the bentonite structure are detected, at 919, 810, and 843 cm\(^{-1}\).

Figure 3.9. A p-polarized infrared spectrum of a thin (10 nm) film of bentonite on the ZnSe ATR crystal showing the spectral region 1150-840 cm\(^{-1}\). The peak positions of the curve fitted sub bands (dashed lines) are indicated, except for two weak bands at 880 cm\(^{-1}\) and 843 cm\(^{-1}\). The absorbance spectrum was obtained using the p-polarized single beam background spectrum of the ATR crystal.

From previous studies \([49,51-55]\), the band at \(\sim1080\) cm\(^{-1}\) is caused by a transition dipole moment perpendicular to the (001) surface of the clay mineral (out-of-plane vibrations), and the band at \(\sim1040\) cm\(^{-1}\) is due to having a transition dipole moment perpendicular to the surface normal of the (001) surface (in-plane vibrations). In the present work, the band assigned to out-of-plane vibrations is used to determine the orientation of bentonite platelets settled onto the surface of the ZnSe ATR crystal or onto the magnetite particles deposited on the crystal.
It can be seen in Figure 3.10 that the spectra of bentonite are sensitive to the polarization of the incident infrared radiation. The intensity of the band at ~1080 cm\(^{-1}\) in the p-polarized spectrum \((A_p)\) is much higher than in the s-polarized spectrum. By curve fitting the \(A_s\) and \(A_p\) spectra in Figure 3.10, the integrated intensity of the absorption band at 1082 cm\(^{-1}\) is obtained. The measured dichroic ratio \((A_s / A_p)\) is 0.26. According to the refractive index of bentonite at 1084 cm\(^{-1}\) \((n_2 = 1.15)\) and Eqs 8-10, and 12, the average tilt angle of bentonite platelets with respect to the normal of ZnSe surface was calculated. The tilt angle obtained \((\gamma = 34^o)\) indicates that the platelets are oriented with their basal planes preferentially parallel to the ATR crystal.

Figure 3.10. Infrared spectra of bentonite in the Si-O stretching region, showing the p-polarized spectrum and the s-polarized spectrum. The absorbance spectra were obtained using single beam background spectra of the ATR crystal.

However, the bentonite film as well as the magnetite film deposited on ZnSe contained small amount of water which will influence the refractive indices of the films according to the equation [56],

\[
n_2 = F_v \cdot n_{par} + (1 - F_v) \cdot n_{water}
\]

where \(F_v\) is the volume fraction of particles in the film, \(n_{par}\) is the refractive index of the pure particles, and \(n_{water}\) is the refractive index of pure water. If \(n_2 = 1.248\) (pure water at 1084 cm\(^{-1}\))
was used in the calculation, the tile angle then reduced to 30°. Therefore, it is reasonable to suggest that the true value of the angle should be in the range between 30 and 34°.

3.4.3 Orientation of bentonite platelets on magnetite

To estimate the orientation of bentonite on magnetite deposited on the ZnSe crystal, the evaluation of the refractive index of the bentonite/magnetite layer in the Three-Layer refractive index model needs to be taking into account. An effective refractive index of the combined magnetite/bentonite layer should be between the indices for “dry” bentonite (1.15) and the maximum value for a thin porous layer of spherical magnetite particles (1.73). However, since an accurate value of refractive index \( n_2 \) was not available for the combined magnetite/bentonite layer, the dependence of the average tilt angle on \( n_2 \) was calculated from the measured dichroic ratio for a room temperature dried magnetite/bentonite film (\( A_s/A_p = 0.30 \)) as well as a film covered by the aqueous suspension (\( A_s/A_p = 0.46 \)). As shown in Figure 3.11, the tilt angle decreases from 36° to 19° upon increasing the refractive index from 1.15 to 1.7 indicating the platelets to be oriented with their basal planes preferentially parallel to the surface of the ATR crystal. Without having an exact value of the refractive index, the average value (1.425) was preferred resulting in a tilt angle of 25° between the surface normal of the ATR crystal and the normal to the (001) plane of the platelets.

![Figure 3.11](image-url)

Figure 3.11. The calculated tilt angles vary with the refractive index of the magnetite/bentonite film (\( n_2 \)). The two curves are calculated using \( A_s/A_p \) values at 1080 cm\(^{-1}\) for a dry (0.30) and a wet (0.46) film, as obtained from curve fitting of the measured absorption bands.
The average tilt angle can be used to calculate the order parameter, $S$, frequently used for stretched polymer films and lamellar liquid crystalline systems [26,57],

$$S = 1.5 \times \cos^2 \gamma - 0.5$$  \hspace{1cm} (15)

From these experiments it may be concluded that the magnetite particles contributed to an increased order of the settled bentonite particles since the average tilt angle was smaller for a magnetite covered crystal as compared with the bare crystal. The positively charged magnetite particles (pH 5.6) on the ZnSe surface is expected to increase the affinity of the surface for the first layer of clay particles contributing to their preferential orientation.

Figure 3.12. Curve fitting of the p-polarized Si-O stretching region of bentonite after four hours of settling. The single beam background spectrum was recorded with a layer of magnetite on the ATR crystal.

The orientation of the platelets also changed with the settling time. Figure 3.12 shows the p-polarized spectrum of bentonite and its simulated component bands after 4 h of settling. The 1080 cm$^{-1}$ band in the water evaporated film was shifted to 1072 cm$^{-1}$; The calculated dichroic ratio ($A_p / A_o$) is 0.46. The tilt angle calculated using $n_1 = 1.244$ for water at 1072 cm$^{-1}$ and $n_2 = 1.425$ for the magnetite/bentonite layer was 45° ($S = 0.25$) for the wet film. This higher value as compared to the dry bentonite film indicates that the bentonite platelets still dispersed in suspension were less order at the magnetite surface than the platelets already settled.
Considering the swelling property of bentonite, the excess water between the platelets seems to induce not only a broader distribution of orientations but also a higher average tilt angle. Another reason for the increased tilt angle obtained when water is both outside and in between the platelets may be that the bentonite platelets exhibit so-called card house structures when they are about to settle on the magnetite layer. In card house structures, the edge of one platelet is interacting with the basal (001) plane of another platelet. Such an arrangement should imply larger tilt angles. One and half hour before the film was dry (4.5 h of settling) the corresponding tilt angle was reduced to 31° (S = 0.60).
4. Conclusions

In situ ATR-FTIR spectroscopy was used to monitor the silicate species in aqueous solution as well as sorbed on synthetic magnetite and maghemite surfaces. The spectral changes observed for sodium silicate solutions at different pH showed the variation of dominating silicate anions in solution. As evident from infrared spectra, in the silicate solution at 10 mmol·L⁻¹ polymeric or condensed silicate species formed when decreasing pH.

The sorption of silicates onto magnetite was pH dependent and fast. From the infrared absorption of silicate species versus time it was concluded that a maximum absorption appeared between pH 7.0 and pH 9.5. Below pH 9.5, a sorption equilibrium value could not be reached within 2 hours. The infrared spectra of sorbed silicate indicated the presence of different types of surface species, which were dependent on pH and silicate concentration. At high pH or low silicate concentration, the dominant surface species was a bidentate monomeric surface complex assigned to the infrared band at 950 cm⁻¹. Decreasing pH or increasing the concentration of silicate implies more of oligomeric surface silicate species assigned to the infrared absorption range between 1000 cm⁻¹ and 1050 cm⁻¹. The shift of this band to higher wavenumber revealed interesting information about the degree of surface polymerization. Moreover, a 3-dimensional silica framework structure was assigned to the band at ~1120 cm⁻¹. This absorption band was most clearly observed and becoming dominant on the iron oxide surface when the silicate concentration increased to 5 mmol·L⁻¹.

The corresponding desorption experiments of sorbed silicate indicated a strong attachment of silicate to magnetite and maghemite surfaces. However, a higher pH could promote the desorption. Oligomeric and polymeric species were more strongly sorbed on surfaces than monomeric species.

Magnetite exhibits a higher silicate sorption capacity than maghemite because of the larger number of active surface sites.

The orientation of bentonite platelets on a ZnSe ATR crystal as well as on a layer of magnetite particles deposited on the crystal was analyzed with polarized horizontal ATR-FTIR Spectroscopy. For a bentonite film dried on the ATR crystal at room temperature, the (001) surface (basal plane) of the platelets was preferentially oriented perpendicular to the surface normal of the ATR crystal. This was also true for a dry bentonite film settled on a thin layer of magnetite particles deposited on the ZnSe crystal, but the magnetite particles contributed to an increased order (lower tilt angle). For a wet film, the tilt angle of the
bentonite platelets was considerably larger indicating that the swelled bentonite layer above the ZnSe crystal contained platelets that tended to form so called card house structures at pH 5.6.
5. Future work

All the suggestions listed below for future work are not in chronological order but are ideas that should be effected in order to further elucidate the agglomeration properties of magnetite particles.

- In the present study, ATR-FTIR spectroscopy proved to be a suitable technique to differentiate between silicate in solution and silicate sorbed on iron oxide surfaces and also to detect differences in silicate polymerization on the iron oxides. However, because of the complexity of vibration modes of silicate species, the interpretation of infrared spectra from silicate species could be substantially improved by theoretical calculations such as DFT modelling. Comparison between calculated and experimentally obtained vibration frequencies should therefore contribute to a deeper understanding of what kind of species that are actually detected on the iron oxide surfaces.

- A combination of different experimental techniques usually could reveal more information of the system investigated. Combining Solid NMR and potentiometric titrations with the ATR-FTIR technique, within the present study, would certainly not be an exception. Since Fluor-apatite has already been detected on iron oxide without line broadening using NMR spectroscopy, despite the magnetic properties of iron oxide, the ultimate challenge would be to cover magnetite particles with silicate and use $^{29}$Si-NMR to reveal information about sorbed silicate species. Moreover, it would also be interesting to apply NMR spectroscopy on a non-magnetic model system, for example silicate sorbed alumina, with the aim to get more information on the distribution of silicate species on iron oxides. This approach would also be combined with DFT calculations.

- The present study increased the understanding of sorption and desorption properties of silicate on magnetite and maghemite. To further explain the effect of sodium silicate on the flotation efficiency and on the properties of green pellets, the presences of mainly Ca$^{2+}$, Mg$^{2+}$, and phosphate ions as in process water need to be considered in the subsequent experiments.
• The orientation of bentonite platelets on magnetite and/or maghemite at more alkaline and higher ionic strength condition (real conditions in pelletization) need to be done to complete the model of the interactions between bentonite and magnetite.

• The effect of surface properties of magnetite on the orientation of bentonite platelets is very important considering the strength of green pellets. The iron oxide surface will be modified with sodium silicate with or without the presence of calcium and/or other ions.

• As a complement to support the studies orientation suggested above, it would be really nice to have access to cryovitrification/ cryo-TEM to possibly verify the experimental results obtained from ATR-FTIR measurements.
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Paper I

A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy

Xiaofang Yang, Payman Roonasi, Allan Holmgren

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A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy

Xiaofang Yang, Payman Roonasi, Allan Holmgren

1. Introduction

Soluble sodium silicates are probably one of the oldest and most widely used industrial chemicals. Because of its unique chemical properties, e.g. buffering ability, surface charges modifying ability, heat and chemical stability, polymerizing capability, and viscosity regulating ability, sodium silicates have been used as cleaners and detergents, modifying reagents in flotation, and binders in agglomeration just to name a few applications [1,2]. Among a wide variety of applications where these properties are utilized, an important one is the use of sodium silicate as a deflocculation agent in clay mining processes and ore flotation. In ore flotation, sodium silicate is often used as depressant or dispersant to improve the selectivity in the flotation of salt-type minerals such as apatite, calcite and fluorite, from sulfides and oxides, siliceous minerals, and also other salt-type minerals [3]. It is already known that in the flotation process soluble sodium silicates, also known as ‘water-glass’, can adsorb onto the target particle surfaces and disperse the agglomerates into fine particles by charging the surfaces. However, sodium silicates showed different selectivity, dispersing activity, and efficiency depending on the mineral system and silicate dosage. In the flotation of apatite from calcite, Rao et al. [4] found for example that at pH 8 and 9 sodium silicate at concentrations higher than 1 × 10⁻³ mol L⁻¹ exhibited a certain depression effect on calcite, but had no such effect at lower concentration. At higher pH values, however, polymeric silicates selectively adsorbed onto calcite surfaces rather than on apatite even at this low silicate concentration (1 × 10⁻³ mol L⁻¹). Gong et al. concluded that the role of sodium silicate (10⁻³ to 10⁻⁴ mol L⁻¹) in the selective flotation of apatite from iron oxides was attributed to the adsorption of moderately polymerized silicate species, which were responsible for the depression of the iron oxide [5,6]. However, in the reversed flotation of apatite from magnetite, Su et al. observed that the selectivity of sodium silicate as depressant decreased when the dosage increased from 300 g t⁻¹ (2.4 × 10⁻⁴ mol L⁻¹) to 500 g t⁻¹ (4 × 10⁻⁴ mol L⁻¹) resulting in a less efficient dephosphorization of magnetite fines and proposed that the dispersion effect of sodium silicate played a key role at such a low concentration rather than the depressant effect [7]. Knowledge about silicate–metal oxide reactions is of course also important to better understand other industrial applications than
flotation such as the synthesis of zeolites and iron oxide-silicate composites as well as interfacial reactions in environmental systems [8–10].

During the past decades, a lot of experimental work was performed to specify silicate anion species in aqueous solution. These efforts were based on potentiometric titrations as well as infrared, Raman and \(^{29}\)Si NMR spectroscopy [11–17]. From these studies, it became clear that aqueous silicate solutions is a mixture of anions and that the distribution of various silicate species mainly depended on the SiO\(_2\)/Na\(_2\)O ratio, SiO\(_2\) concentration, pH, temperature and aging. Combining results from \(^{29}\)Si NMR and infrared spectroscopy, Bass et al. [17] confirmed that more of polymeric silicates were present in the silicate solutions at higher SiO\(_2\)/Na\(_2\)O ratio and higher SiO\(_2\) concentration. In alkaline and diluted solutions (SiO\(_2\)/Na\(_2\)O < 1.65, 0.4 mol L\(^{-1}\)), monomer, dimer, and cyclic trimer silicate species are dominant. Quit recently, Halasz et al. assigned the infrared and Raman bands for the silicate species in existing in sodium metasilicate solutions and claimed that silicate monomers predominated in 0.2–3 mol L\(^{-1}\) aqueous metasilicate solutions [18].

Many publications about the adsorption of silicate anions on iron oxides have used batch experiments and ex situ spectroscopy methods. Stumm and colleagues were among the pioneers, who elaborated a ligand-exchange model to explain and predict the adsorption of H\(_4\)SiO\(_4\) on goethite [8]. Other authors [10,19,20] have used but also developed this ligand-exchange model. Very recently, Hiemstra et al. modelled silicate sorption onto goethite from 1 to 10 mmol L\(^{-1}\) aqueous metasilicate solutions [18].

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They concluded that a bidentate surface complex (≡<\(\leq\)\(\geq\)), onto the surface of magnetite could be found around 115 m\(^2\) g\(^{-1}\). By spreading certain amount of magnetite suspensions over the substrate with a pipette, magnetite was evenly deposited onto the ZnSe crystal and subsequently dried in a vacuum desiccator. After rinsing the deposit with Milli-Q water and allowing it to dry again, the weight of deposited magnetite was calculated from the weight difference.

### 2.3. ATR-FTIR measurements

All spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer equipped with a DTGS detector and a vertical ATR accessory. The vertical ATR accessory consisted of a trapezoidal-shaped ZnSe IRE (45°, 50 mm × 20 mm × 2 mm) with totally 25 internal reflections mounted in a ~3.5 mL flow-through stainless steel cell. Spectra of aqueous silicate and of silicate adsorbed on magnetite were recorded by averaging 200 scans at a resolution of 4 cm\(^{-1}\). Data evaluation and spectra simulation were performed with OPUS software from Bruker Optics.

### 2.4. Spectra of sodium silicate in solution and on magnetite

In situ ATR infrared measurements were performed using the flow cell technique described elsewhere [23,24,26]. The pH of the reaction solutions were monitored by a combined pH electrode and adjusted when needed. A peristaltic pump was used to pump reaction solution through the flow cell at a flow rate of ~4.7 mL min\(^{-1}\). A calculated amount of silicate stock solution was added to the MilliQ water after solvent (water) background spectrum was monitored. Possible interfacial reactions and formed surface complexes were analyzed by comparing the spectra of silicate adsorbed on the magnetite particles with those of silicate in solution.

### 2.5. Materials

Two types of sodium silicates were used. Stock solutions of sodium metasilicate (Na\(_2\)SiO\(_3\)·9H\(_2\)O) from J.T. Baker were prepared with Milli-Q water as solvent. Silicate3.25 was an industrial wa-

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recorded. The diluted silicate solution was then adjusted to desired pH using NaOH. All experiments were commenced at pH > 11. After the spectrum of silicate in solution at a desired pH has been collected, the pH was lowered to next level by addition of HCl, and the spectrum at the new pH was recorded.

Spectra of adsorbed silicate were recorded with ZnSe, magnetite deposit and water as background. After the background spectrum had been recorded, sodium silicate was added to the reaction vessel and adjusted to highest pH studied before begin the adsorption experiment. The effect of pH on sorption was measured by collecting spectra of silicate sorbed on magnetite at each pH step during about 30 min. All experiments were performed under ambient temperature (22 ± 1°C).

3. Results and discussions

3.1. Spectra of aqueous sodium silicate

Fig. 1 shows the spectrum of 10 mmol L⁻¹ aqueous sodium metasilicate solutions in the pH range 7.5-11.5. The infrared absorption bands of silica solids, glasses and gels [31,32], the assignments related to the distribution of anionic species in sodium silicate solution, especially very dilute solutions, are still unclear and some even incompatible [16-18]. To obtain the distribution of silicate species with pH and concentration, a silicate speciation model was set up using WinSGW program [33]. Formation constants are given by Sjöberg et al. [34] for dilute solution ([Si] = 48 × 10⁻³ mmol L⁻¹) and also by Felmy et al. [35]. Constants given by Sjöberg et al. are valid at 25°C and 0.6 M NaCl medium but since the silicate speciation is influenced by ionic strength, the thermodynamic constants given by Felmy et al. were preferred.

![Fig. 1](images/fig1.png)

Fig. 1. Infrared spectra of 10 mmol L⁻¹ aqueous sodium metasilicate solutions in the pH range 7.5-11.5.

<table>
<thead>
<tr>
<th>pH</th>
<th>p</th>
<th>Chemical formula</th>
<th>log K_{pq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>Si(OH)₄</td>
<td>-27.27</td>
</tr>
<tr>
<td>-2</td>
<td>2</td>
<td>Si₃[2-]</td>
<td>-23.27</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>Si₂[3-] (cyclo)</td>
<td>-23.3</td>
</tr>
<tr>
<td>-4</td>
<td>4</td>
<td>Si[4-] (cyclo)</td>
<td>-29.1</td>
</tr>
<tr>
<td>-5</td>
<td>5</td>
<td>Si[5-] (cyclo)</td>
<td>-39.1</td>
</tr>
<tr>
<td>-6</td>
<td>6</td>
<td>Si[6-]</td>
<td>-61.8</td>
</tr>
</tbody>
</table>

3.2. Formation of amorphous silica

In the modelling of the precipitation of amorphous silica under thermodynamic conditions was included. In this context it should be mentioned that the kinetics of the formation of silica precipitate is rather slow especially at high pH, low ionic strength, and low silica concentration, as shown by Icopini et al. [36]. The half-life of molybdate-reactive silica was about 2700 h at a silica concentration of 4.2 mM at pH 8-9 and silicate concentration of 12.5 mM at pH 11 with ionic strength of 6.01 M. Starting at pH 11, would therefore imply that the formation of amorphous silica precipitate during the period of solution spectra collection or sorption can be ignored. The formation of nanocolloidal silica is strongly limited at high pH although at pH 7 and 10 mM silicate concentration about 10% of the silicic acid could be formed to nanocolloidal silica after 1 h [36], since the solution becomes supersaturated when pH is lowered [13]. Equilibrium protonation/deprotonation parameters and the formation constants are shown in Table 1 along with the chemical formula of each species and the calculated equilibrium distributions are plotted in Fig. 2. Below 2 mM L⁻¹ (the solubility limit of amorphous silica [34], the monomers SiOH(OH)₃⁻, SiOH₂⁻, and Si(OH)₄⁻ are dominant with protons transferred between different species as pH was changed. The distribution of silicates becomes more complex when the concentration of silicate in solution increases, because dimers, trimers, oligomers and higher aggregates will form by condensation of monomers at high concentration. In 10 mM L⁻¹ solution, more dimers and trimers form.

![Fig. 2](images/fig2.png)

Fig. 2. Distribution diagram of silicate anions as a function of pH in (a) 1 mmol L⁻¹ and (b) 10 mmol L⁻¹ aqueous sodium metasilicate solution.

Table 1: Speciation model of dilute silicate aqueous solution based on the reaction: pH⁻ + Si(OH)₄ ⇌ K_{sp}Si(OH)₄.pH. Formation constants from Felmy [35]. log K_{pq} = \text{constant}.

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but even tetramers and polymers are formed between pH 9 to 13, and at low pH colloidal SiO2 might be formed. The distribution diagram in Fig. 2 is a support in our interpretation of infrared spectra of silicate species in solution.

Curve fitting of the absorption bands was utilized in an attempt to distinguish the spectral features of the various silicate anions from each other. Considering the spectral intensity and signal to noise problems at low concentrations only spectra in Fig. 1 (10 mmolL−1) were curve fitted using the OPUS program (Fig. 3). Each spectrum was resolved into six or seven component bands. It is clear that the variation of spectral features in the wavenumber region 1250–850 cm−1 can be explained by the change in relative contributions from component bands at different pH. As shown in Fig. 3, the most intense component band at 1020 cm−1 (pH 11.5) together with the band at ~890 cm−1 decreased in intensity with decreasing pH, whilst the intensity of the bands at ~1065, 1122, and 1180 cm−1 showed a significant increase becoming the three most intense bands at low pH. An additional band showed up at 945 cm−1 as pH was changed to lower values than 9.7.

Halasz et al. reported infrared spectra of sodium silicate solutions dissolved from Na2SiO3 and Na2SiO3− species, although a shoulder still appeared at 890 cm−1 and 1180 cm−1. Thus, it seems clear that the bands at 1020 and 890 cm−1 caused by undissociated Na-silicate anions tend to be protonated and possibly further condensed since more OH function groups are available. Hence the bands appearing in the 1050–1200 cm−1 range and showing an increased intensity upon lowering the pH are assigned to stretching vibrations involving the Si–O–Si entities.

3.2. The effect of pH on sorption and desorption of the silicates

The effect of pH on the amount of silicate adsorbed on magnetite is shown in Fig. 4, where the integrated intensity of the absorbance from 1300 to 800 cm−1 was plotted versus pH and time. As a first approximation, it may be assumed here that the integrated absorbance in the 1300–800 cm−1 region is proportional to the amount of adsorbed silicate [37]. This assumption is reasonable as long as surface species formed at different pH are similar or exhibit transition dipole moments of similar numerical value. However, this difficulty does of course not exclude qualitative interpretations of Fig. 4.

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As evident from Fig. 4, the adsorption equilibrium was not reached after 30 min independent of pH value although the increase in intensity per minute was considerably lowered with time. However, there was no significant change in the spectral line shape with time, which implies that the same types of surface complexes are formed at a certain pH. Therefore, only the last spectrum at each pH value is shown in Fig. 5 and used in the following discussion about formed surface complexes on magnetite at different pH, but at constant silicate concentration in solution. As shown in Fig. 4, the integrated intensity for silicate adsorbed from 1 mmol L\(^{-1}\) metasilicate and Silicate\(3.25\) solutions (Figs. 4b and 4c) were about the same, whilst the adsorption from 10 mmol L\(^{-1}\) metasilicate solution was 4 to 5 times larger. A considerable increase in the adsorption of silicate occurred from pH 11 to 9, whereas a decrease in pH from 9 to 7 only contributed a minor change in spectral intensity. It is well known that silicate sorption onto iron oxhydroxides has a maximum at a pH value around 9 [8,10,21,22], but this is not reflected in our spectra. The observed sorption should already have passed its maximum when reaching pH 7. However, sorption at pH 7 for 30 min was not enough time to desorb the silicate from the surface. Probably this is reflecting a non-equilibrium situation where both the silicate species sorbed at the magnetite surface and the protonation state of the surface itself must change as pH is lowered.

In the pH range 11–9, the magnetite surface should be dominated by both negatively charged surface sites and neutral surface hydroxyl groups as the point of zero charge of magnetite is about 6 [38]. In solution silicate exists as negatively charged anions. Despite this, the silicate anions are readily adsorbed at the magnetite surface, as evident from the fast and large increase in the surface concentration of silicate. At lower pH values, neutral surface hydroxyl groups become predominant on the magnetite surface and neutral silicate species begin to dominate in solution as well (pH < 9.5). Therefore, the negatively charged silicate anions (Si(OH)\(3^-\)) and neutral Si(OH)\(4\) species both are active adsorbate species. The observed pH dependent adsorption properties are consistent with the ligand exchange of protonated as well as deprotonated surface hydroxyl groups with Si-O-H groups having Lewis base properties [39].

To further assess the properties of the adsorbate, desorption experiments were performed by flushing the flow-cell with Milli-Q water at a certain pH. It can be seen from Fig. 4 that the extent of silicate desorption from magnetite was influenced by pH. Higher pH implied that more of the surface species were desorbed and the desorption curve exhibits an initial fast decrease in spectral intensity followed by a slower desorption step. A higher desorption rate and extent of desorption under alkaline conditions is reasonable considering the nature of a ligand-exchange reaction. Even after long desorption time, it was a significant amount of surface species left. This indicates that a certain amount of surface species are firmly attached to the magnetite surface by covalent bonds implying that inner-sphere complexes are formed between magnetite and silicate species.

3.3. Spectra of sodium silicate at the magnetite surface

Figs. 5a, 5b, and 5c show the spectra of silicates on magnetite sorbed from 10 mmol L\(^{-1}\) and 1 mmol L\(^{-1}\) sodium metasilicate solution (Figs. 5a and 5b) and 1 mmol L\(^{-1}\) Silicate\(3.25\) solution (Fig. 5c) at different pH. A comparison of the spectra of sorbed silicates with those of silicate in aqueous solution (Fig. 1) shows that the absorbance of the surface species is significantly higher. This is because of the strong affinity of magnetite for the silicate species resulting in a higher concentration of these species at the magnetite surface. The spectral line-shape for silicates sorbed from 1 mmol L\(^{-1}\) solutions (Figs. 5b and 5c) is rather similar, whilst the line-shapes obtained from 10 mmol L\(^{-1}\) solution are clearly different changing with pH (Fig. 5a).

It can be seen from Figs. 5b and 5c that the spectra of sorbed silicate from 1 mmol L\(^{-1}\) sodium silicate solutions are similar although they have different silica to alkali ratio. In Fig. 5b, at pH 11.2, the maximum absorbance is located at 955 cm\(^{-1}\) and the peak frequency remained constant in position with decreasing pH. However, as solution pH was lowered to 9.3, the band at ∼1020 cm\(^{-1}\) increased in intensity becoming the strongest band in the spectral region (800–1300 cm\(^{-1}\)) and simultaneously an ap-
between Figs. 5a and 5b is the concentration of the aqueous silicate solution. A higher concentration should facilitate the condensation of silicate monomers at low pH, as supported by the infrared spectral changes observed in the 1000–1200 cm⁻¹ region (Fig. 5a) and appearing with much lower intensity when sorbing 1 mmol L⁻¹ silicate solution. The sharp band at ~1020 cm⁻¹, an assignment that is supported by thermodynamic modelling [21].

Thus these clear spectral changes upon sorption indicated a strong surface reaction implying the formation of inner-sphere surface complexes. Depending on sorption conditions, viz. pH and adsorbate concentration, the formed surface-silicate complexes varies from monomers to dimers or possibly polymers.

3.4. Surface complexation of silicate on magnetite

Fig. 6 shows the resolved component bands from spectra of sorbed silicate on magnetite. Each spectrum of sorbed silicate was curve fitted using a minimum of component bands. For the two sorbed silicate solutions admitted the assignments of spectral absorption bands in the 1100 cm⁻¹–1200 cm⁻¹ region (Fig. 6a) and appearing with much lower intensity when sorbing from a 1 mmol L⁻¹ solution (Figs. 5a and 5c), should at least partly be due to the surface polymerization of sorbed silicate. The results here show that the pH value and the concentration of silicate in solution are very important parameters determining the type of complexes that will be formed on the magnetite surface and if polymeric species should be expected.

4. Conclusions

In situ ATR-FTIR spectroscopy was used to monitor the silicate species in solution as well as sorbed on magnetite surfaces. The spectral changes observed for sodium silicate solutions at different pH were analyzed in detail and showed the variation of dominating silicate anions in solution. As evident from infrared spectra, the silicate concentration studied (10 × 10⁻³ mol L⁻¹) contained polymeric or condensed silicate species. Infrared spectra of the aqueous silicate solutions admitted the assignments of spectral absorption regions to monomers as well as oligomers. The information obtained for the silicate solutions was then used to facilitate the interpretations of spectra recorded for silicate species sorbed on a thin layer of magnetite nano-particles. Within a reaction time of 30 min, the sorption of silicate onto magnetite from 1 × 10⁻³ and 10 × 10⁻³ mol L⁻¹ solutions was significant at each pH step from 11 to 9. At lower pH, the reaction slowed down and only a minor amount of additional silicate species were attached to the magnetite surface. In the pH range studied (11–7), infrared spectra of sorbed silicate indicated the presence of different types of surface complexes that will be formed on the magnetite surface and if polymeric species should be expected. The possible surface complexes can be postulated to be $\equiv$Fe–OSi(OH)₂–X or $\equiv$FeO–Si(OH)X for the reactions between silicate monomers and the magnetite surface. The following ligand-exchange reactions are proposed:

$$\equiv$Fe–OX + H–OSi(OH)₂–X $\leftrightarrow$ $\equiv$Fe–OSi(OH)₂OX + HO–X (1)

or/and

$$2(\equiv$Fe–OX) + (H–O)₂Si(OH)X $\leftrightarrow$ (≡Fe–O)₂Si(OH)XOX + 2HO–X, (2)

where X represents a negative charge or proton. Comparing with FTIR and EXAFS data on the iron(III)-silica coprecipitate [9,28], the infrared band at ~955 cm⁻¹ shifting to 1060 cm⁻¹ can be assigned to the FeO–Si stretching in the bidentate surface complex ($≡$FeO)₂–Si(OH)X. Therefore, at high pH and low surface concentration, the Si(OH)₄ species in solution should be sorbed onto magnetite surface. At lower pH oligomeric surface species should be formed. The latter species corresponds to the increase in intensity of the infrared band observed at ~1020 cm⁻¹, an assignment that is supported by thermodynamic modelling [21].

Fig. 6 shows the resolved component bands from spectra of sorbed silicate on magnetite. Each spectrum of sorbed silicate was curve fitted using a minimum of component bands. For the two sorbed silicate solutions admitted the assignments of spectral absorption bands in the 1100 cm⁻¹–1200 cm⁻¹ region (Fig. 6a) and appearing with much lower intensity when sorbing from a 1 mmol L⁻¹ solution (Figs. 5a and 5c), should at least partly be due to the surface polymerization of sorbed silicate. The results here show that the pH value and the concentration of silicate in solution are very important parameters determining the type of complexes that will be formed on the magnetite surface and if polymeric species should be expected.
species at the magnetite surface, whereas desorption of sorbed silicate indicated species firmly attached to the magnetite surface. At least for dilute silicate solutions, the value of pH seems to be a more useful parameter rather than the silica to alkali ratio in order to reveal information about species distribution facilitating the interpretation of infrared spectra. The adsorption mechanism proposed is in accordance with a ligand exchange reaction where both monodentate and bidentate complexes could exist simultaneously at low surface loading level. Subsequent polymerization occurred on surface with pH lowering and further surface accumulation.

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References

Paper II

Kinetics of silicate sorption on magnetite and maghemite. An in situ ATR-FTIR study

Xiaofang Yang, Payman Roonasi, Rickard Jolsterä, Allan Holmgren

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Abstract

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to monitor the in situ sorption of sodium metasilicate from aqueous solution onto synthesized magnetite and maghemite particles in the pH range 10.8-7.0 using silicate concentrations between 0.1 mM and 5 mM. The spectral data showed that both pH and silicate concentration had great influence on the interfacial reaction between soluble silicate and the iron oxide surfaces, regarding the amount adsorbed per unit mass of iron oxide and the surface species formed. A pH dependent sorption of silicate on iron oxides was observed, implying that a maximum sorption took place in the pH range of 9.5 – 7.0. All experiments showed a fast initial increase in the absorption intensity followed by a slower sorption stage which was strongly dependent on the concentration of silicate in solution and the pH value. The amount of sorption onto magnetite was 3 to 5 times larger than onto maghemite, but there was no significant difference in the line shape of corresponding absorption bands. At pH 8.5 and low concentration (≤ 0.1mM), the silicate monomers dominate in solution and on the iron oxide surface also monomeric species were dominating as evident from the infrared band at 950 cm⁻¹. However, at higher concentration (0.4-5.0 mM), the dominating absorption band at about 1000 cm⁻¹ shifted to higher frequency during the sorption indicating that oligomeric surface silicate species were formed on the iron oxide surface. Desorption of silicate from the surface of the iron oxides was easier to accomplish at low silicate concentration, whilst the highest concentration showed a comparatively low relative amount of desorbed silicate, suggesting that polymerized species had a stronger affinity for the iron oxide surface as compared to monomeric species.

Keywords: Silicate sorption, magnetite, maghemite, in-situ ATR-FTIR
Introduction

Interfacial reaction between soluble silicates and iron oxide surfaces is of great importance in the natural environment considering the content of dissolved silicate in natural waters from mineral weathering [1-3] as well as in industrial applications, e.g., flotation of salt-type minerals from metal oxides and other salt-type minerals where sodium silicate is usually used as dispersion or depressant agent [4]. Concretely, in the dephosphorizing flotation of magnetite particles, sodium silicate with modulus 3.25 (weight ratio of SiO₂ to NaO₂) is used mainly to disperse the agglomerated particles [5], whereas in the flotation of apatite from hematite sodium silicate may be utilized as a selective depressing agent to reduce the flotation of the gangue mineral (hematite) [6]. It is well known that the concentration, modulus, and pH of sodium silicate solutions are the main factors determining selective silicate sorption on mineral surfaces and that the properties of the modifying agent is strongly influenced by the distribution of silicate species in solution viz. monomers, oligomers, higher polymers, and colloidal silica [6-9].

During the past decades, the study of interaction between silicate and iron oxides as well as other minerals was mainly carried out by batch adsorption experiments, modeling methods, and ex-situ spectroscopy techniques [1,3,7,10,11,12]. However, there are very few if any in-situ studies on the sorption of silicate species onto magnetite showing the formation of surface complexes with time. Another topic is the often appearing question whether the surface of the magnetite particles, which during experimental handling may be exposed to air, represents magnetite or to some extent are oxidized to maghemite although the structure of the two iron oxides is similar both representing a spinel structure with tetrahedral and octahedral sites [13]. In maghemite, all or most of the octahedral Fe (II) in magnetite are oxidized to trivalent implying a Fe(II)-deficient structure with a slightly smaller unit cell volume as compared with magnetite. From a surface chemical point of view, the important question is whether the
sorption behavior of sodium silicate onto the two mentioned iron oxides are the same or if the oxidization state of the iron atoms has a significant influence on the affinity of the surfaces for silicates. Moreover, a molecular level investigation of silicate species sorbed on iron oxide surfaces and especially the time-dependence of the sorption is critical in industrial processes with limited conditioning times but also important in geochemical systems.

Accordingly, in the present study attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was utilized to monitor the sorption of sodium silicate onto a thin layer of synthetic magnetite (Fe₃O₄) nanoparticles as compared with the sorption onto a corresponding layer of synthetic maghemite (γ-Fe₂O₃). The study encompassed different pH and silicate concentration. Of special interest here was the possible change of sorbed species at the iron oxide surfaces with time and the possible difference in the amount sorbed under similar experimental conditions. In addition, desorption of the already adsorbed silicate species was studied, possibly revealing the type of surface complexes formed and the affinity of different silicate species for the surfaces.

2. Experimental

2.1 Chemicals and Materials

Sodium metasilicate (Na₂SiO₃·9H₂O) from Sigma was dissolved in Milli-Q water and prepared as a stock solution (0.5M, pH >11.5). Magnetite used in this study was synthesised based on a coprecipitation of Fe (II) and Fe (III) chlorides method described by Julivet et al. and Jarlbring et al.[14,15]. Briefly, Fe(II) / Fe(III) chloride salt mixture (1: 2 molar ratio) was hydrolyzed using NH₄OH, purified with deoxygenated Milli-Q water, and stored under argon atmosphere. Maghemite was prepared by heating magnetite in an oven at 240 °C overnight. The BET surface area of magnetite was 97.7 m²·g⁻¹ and of maghemite was 87.3 m²·g⁻¹.
All other reagents were of analytical grade, and all solutions were prepared from Milli-Q water as solvent. NaOH and HCl solutions were used for pH adjustments.

2.2 FTIR measurements

Spectral data were acquired with a Bruker IFS 66v/S FTIR spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a vertical ATR accessory. The vertical ATR accessory consisted of a trapezoidal-shaped ZnSe internal reflection element (45°, 50mm × 20mm × 2mm, totally 25-reflections) and a single-chamber (~3.5mL) flow-through stainless steel cell. Spectra of silicate sorbed on iron oxide were recorded by averaging 100-200 scans at a resolution of 4 cm⁻¹. All spectral data evaluations were performed with the OPUS program from Bruker Optics.

2.3 Preparation of iron oxide films on the ATR crystal

A visually evenly distributed magnetite or maghemite film was deposited on one side of the ATR crystal by spreading a certain amount of the iron oxide dispersion on the crystal surface and subsequently evaporate the dispersion medium in a desiccator under vacuum. After rinsing the deposited film gently with Milli-Q water and let it dry in the desiccator again, the mass of deposited film was weighted. Since the dispersion was allowed to stand for a while after stirring to let the larger particles settle down, the concentration of the dispersion dispensed using a pipettor varied to a certain extent. Thus the mass of the film was not exactly controlled but only weighted and amounted to generally less than 1 mg. Accordingly, the bulk silicate concentration can be assumed to effectively constant during the experiments.

2.3 ATR-FTIR spectra of sorbed silicate
In situ ATR infrared measurements were performed using the flow cell technique described by Peak and others [16,17]. The pH of the silicate solution was monitored by a combined pH electrode and adjusted when needed. The solution (100 mL) was pumped from a beaker into the flow-cell by a peristaltic pump at a flow-rate of ~ 4.7 mL·min⁻¹. Single beam background spectra of the solvent (MilliQ water) were recorded at each pH. Sodium silicate was added into the vessel at a desired concentration and pH adjusted with NaOH / HCl. Spectra of sorbed silicate were recorded as a function of time. Desorption experiments were carried out by flushing flow-cell with MilliQ water at desired pH. All experiments were performed under ambient temperature (22 ± 1°C).

3. Results and Discussion

3.1. pH dependent silicate sorption / desorption kinetics onto magnetite

The pH dependence of silicate sorption from 1mM sodium silicate solution onto magnetite was determined by collecting ATR-FTIR spectra of sorbed silicate with time at the pH values; 10.8, 9.5, 8.5, and 7.0 (Fig.1). In Figure 1, the infrared absorbance caused by silicate was integrated between 1300 cm⁻¹ and 800cm⁻¹ and divided by the mass of magnetite deposited as a thin layer on the ATR crystal and then this ratio was plotted versus the reaction time. It can be clearly seen that from pH 10.8 to pH 8.5, the integrated intensity of sorbed silicate increased with decreasing pH. However, when pH was lowered to 7.0 the integrated intensity decreased implying that there is a maximum in the amount of sorbed silica. This pH dependent silicate sorption behavior of magnetite is consistent with previous studies [1,7,11,12]. The measured absorbance of the infrared spectrum is proportional to the square of the vector product between the electric field vector of the evanescent field (E), which mainly depends on the thickness of the iron oxide layer in the present case, and the transition dipole
moment (M), which should relate to the structure of formed surface silicate species. Using an equation proposed by Dobson et al. [18], the absorption may be described as,

\[ A_i = \varepsilon_i \cdot \Gamma_i \cdot \frac{d_i}{t} \]  

(1)

where \( A_i \) is the measured absorbance of the i-species, \( \varepsilon_i \) is the molar absorption coefficient of sorbed silicate species, \( \Gamma_i \) is the apparent surface loading concentration, \( t \) is the thickness of the deposited layer on the crystal, \( d_i \) is the effective path length determined by the refractive indices of the internal reflection element and the medium outside, by the thickness of the layer, angle of incidence, and the wavelength of the infrared radiation.

As a first approximation, it is assumed that the molar absorption coefficients of sorbed silicate species formed at different pH are not changing with the amount sorbed or are experienced to the same relative change. This assumption is reasonable, at least for pH 9.5-7.0, considering the similarities in line shapes of the infrared spectra of sorbed silicate within this pH range (not shown). Except at extremely high pH (pH 10.8), showing a different line shape, the spectral line shapes recorded at pH 7.0, pH 8.5, and pH 9.5 were very similar indicating similar silicate species on the iron oxide surface at each pH value and that the relative amount of these species were also similar. Between different series of spectral data at a certain pH, the mass of the deposited magnetite layer varied from 1mg to 0.3mg. For the experiments at pH 7.0 and pH 8.5, the mass of the magnetite layer was close to 0.3 mg, and at pH 9.5 and pH 10.8 the amount of magnetite was close to 1mg. However, the integrated intensity of infrared absorption should be proportional to the mass of the magnetite layer and it turned out to be so. The ratio between the integrated absorbance and the mass of magnetite was very close to 1, as calculated for the pH 7.0, pH 8.5, and pH 9.5 series. Accordingly, despite of the uncertainty of the \( d/e/t \) ratio in Eq.1 that restricted the application of accurate quantitative comparison between different experimental series, the time dependent trend of
silicate sorption onto magnetite, as shown in Fig. 1, should be true in this pH range. It should be noticed that the line shape and peak frequency position of the absorption bands at pH 10.8 is different from the ones at lower pH (Fig. 2) and therefore a direct comparison of sorbed amounts between high (10.8) and low (9.5 – 7.0) pH values in Fig. 1 is more uncertain. However, it seems still plausible to suggest that the highest pH value imply a lower amount of sorbed silica, which is also supported by results from others [1,7,11,12].

Desorption experiments carried out directly after sorption at a certain pH were used to assess the sorption affinity of silicate for the magnetite surface. The residual silicate on the magnetite surface was monitored during the time the flow-cell was flushed with MilliQ water. ATR-FTIR spectra are shown in Fig. 2 and desorption results are plotted in Fig. 1. During the desorption time used here (~2h) it is clear that silicate is more easily desorbed at high pH than at low pH. This might be caused by the formation of oligomeric surface silicate species at low pH. Formation of such species would imply stronger interaction with the magnetite surface since each species may offer many Fe-O-Si bonds with the surface and therefore it takes longer time to desorb these species. Although the desorption rate seemed to be higher in the beginning of the desorption reaction, an equilibrium plateau value was not reached within 2 hours.

According to Figs. 2a and b, infrared spectra recorded upon sorption from a 1 mM silicate solution at pH 10.8 is quite different from corresponding spectra at pH 8.5. At pH 10.8 the strongest absorption had its peak position at 952 cm\(^{-1}\) with a shoulder at ~1020 cm\(^{-1}\). This shoulder is hardly detected at the beginning of the sorption reaction but grows in intensity with the time of reaction. At this pH value, the dominant species in solution is SiO(OH)\(_3\)\(^-\) (Fig. 3) [19] and the magnetite surface should be negatively charged since its point of zero charge is ~6.0 [20]. Comparing the sorption and the desorption it also seems that the absorbance at ~1020 cm\(^{-1}\) upon sorption increases faster relative to the 952 cm\(^{-1}\) band than the
absorbance at ~1020 cm\(^{-1}\) decreases relative to the 952 cm\(^{-1}\) band during desorption. These spectral changes indicate that two different surface complexes appear at the magnetite surface during sorption. These in-situ ATR-FTIR results were compared with EXAFS results of Pokrovski et al.[21] on iron(III)-silica co-precipitate, strongly indicating that the 952 cm\(^{-1}\) band should be assigned to the bidentate monomeric surface species, (\(=\text{FeO})_2\text{-Si(OH)}\text{OH}\) or (\(=\text{FeO})_2\text{-Si(OH})\text{O}^-, whilst the shoulder at ~1020 cm\(^{-1}\) should be assigned to oligomeric surface silicate species.

At pH 8.5, it is interesting to notice that the oligomeric species is dominating already at the beginning of the sorption reaction although the peak frequency of the absorption band appears at lower wavenumber (1000 cm\(^{-1}\)). This might indicate a difference in the degree of oligomerization with fewer monomer units in the oligomer at the beginning of the sorption reaction. Since these oligomers do not dominate in aqueous solution at this low concentration (1 mM, Fig.3), it further indicates that the polymerization occurs at the magnetite surface. This latter suggestion is in accordance with results from the literature [2, 7], showing that polymerization of silicic acid on an iron oxide surface is promoted at low pH. At longer sorption times, it is also evident from the experiments at pH = 8.5 that an infrared absorption at wavenumbers > 1100 cm\(^{-1}\) evolves. This absorption band is consistent with a three dimensional framework such as amorphous silica [22] and would imply that the polymerization of silica occur at the magnetite surface also at this low concentration of silica in solution (1 mM).

3.2. Effect of silicate concentration on sorption.

In Figs. 4 and 5, the sorption of silicate from aqueous solution onto magnetite (Fig. 4) and maghemite (Fig. 5) is shown at pH 8.5 and different silicate concentration. Clearly, the concentration as well as pH is important for the type of surface complexes formed. At the
lowest concentration (0.1 mM, Fig. 4), the recorded spectra reminds very much of spectra recorded at pH 10.8 but for a higher silicate concentration (1 mM, Fig. 2a). Accordingly, the 950 cm\(^{-1}\) band is due to bidentate monomeric surface species, whilst the shoulder at the high frequency side of this band demonstrates the formation of oligomeric species. At the highest silicate concentration (5 mM), the dominant band at ~1020 cm\(^{-1}\) for a 1 mM solution is shifted to ~1050 cm\(^{-1}\) upon increased surface loading. This is an interesting spectral shift because a higher silicate concentration is expected to result in more of polymeric species. Accordingly, the shift from 1020 cm\(^{-1}\) to 1050 cm\(^{-1}\) is an indication of increased polymerization at the magnetite surface resulting in oligomeric species with a higher degree of polymerization but may simultaneously reflect a change of the structure of the oligomers since infrared spectra are well-known to be sensitive to changes in molecular structure. Sorption from a 5mM aqueous silicate solution also imply a much higher intensity at 1100 -1150 cm\(^{-1}\), which was assigned to a three dimensional framework such as amorphous silica. However, the broadness of this band is significantly larger than the half-width of a spectrum of amorphous silica particles (not shown) although the peak frequency is almost the same. This might imply that the three dimensional silica framework structure eventually will form a silica layer which infrared spectrum is similar to the spectrum of amorphous silica particles. It might be speculated that the appearance of such a broad band in this region could be due to the number of Si-O-Si units exposed to different environments such as in cyclic trimers, mono-substituted cyclic tetramers, cyclic tetramers, bridged cyclic tetramers etc. If these units represent slightly different vibrational potentials with low activation energy between them, the result should be a broadening of the absorption band caused by Si-O vibrations.

Fig. 5 shows that vibrational spectra of silicate sorbed on a maghemite surface at pH 8.5 are very similar to the corresponding spectra for silicate on magnetite. Spectra recorded for sorption from a 1 mM solution are similar in line shape compared to corresponding spectra
obtained for magnetite (Fig. 4). The surface species assigned for magnetite are also valid for maghemite and they appear at almost the same peak frequencies for the two iron oxide surfaces. However, for silicate sorbed from a 5 mM solution, the absorbance ratio $A_{1150}/A_{1020}$ is somewhat larger for the maghemite/silicate system than for silicate on magnetite suggesting that the three dimensional silica phase is more readily formed on maghemite as compared with magnetite.

The experiments involving maghemite were also encompassing sorption from a 0.4 mM silicate solution (Fig. 5). At this silicate concentration, being in between 1mM and 0.1 mM (Fig. 4), the band at 950 cm$^{-1}$ had slightly higher intensity in the beginning of the sorption reaction, relative to the absorption at ~1000 cm$^{-1}$. The latter band shifts gradually to 1020 cm$^{-1}$ and increases in intensity as the sorption reaction proceeds. These findings are in accordance with the spectral results discussed above, showing that monomeric silicate species dominates at low silicate concentration whereas oligomeric species become more frequent at higher concentration and at longer reaction times.

3.3 A comparison between sorption onto magnetite and maghemite.

Another interesting question addressed in this study was the possible difference between magnetite and maghemite concerning their sorption behaviour. The results so far have shown that their qualitative sorption behaviour is rather similar. However, comparing the amount of silicate species sorbed on the two iron oxide surfaces (Figs. 4, 5, and 6), the difference is apparent. The amount of silicate sorbed on magnetite is higher by a factor of 3-5 as compared with maghemite although the structure of the two iron oxides is similar both representing a spinel structure with tetrahedral and octahedral sites. The main physical difference between the two is the unit cell volume being slightly smaller for maghemite caused by the oxidation of the Fe (II) atoms. Both minerals have about the same point of zero charge as determined by
Sun et al. and Jarlbing et al. using zeta potential measurements on iron oxide samples prepared by applying a similar synthesis routine as here, viz. at about pH 6.0 for magnetite and at about pH 6.2 for maghemite [15,20]. The measured BET areas are also rather similar viz. 98 m\(^2\)/g for magnetite and 87 m\(^2\)/g for maghemite, at least partly due to the similarities between the particle size of the two synthesized iron oxides. However, the number of measured proton active adsorption sites is very different for the two iron oxides. As determined by potentiometric titrations, the number of proton active surface sites is about 0.8 sites/nm\(^2\) for maghemite and 5.2 sites/nm\(^2\) for magnetite [15,20]. It is therefore proposed here that the number of active surface sites is the main cause of magnetite being a more effective sorbent for silicate species than maghemite. According to Figs. 6a and b, about 3 times more is sorbed at 5 mM silicate concentration and 5 times more at 1 mM silicate concentration after the iron oxide have been exposed to the silicate solutions for about 2 hours. It should be noticed that in neither of these two cases, a sorption equilibrium plateau value was reached.

Conclusions

The sorption of silicate from aqueous solution onto magnetite and maghemite was monitored by in-situ ATR-FTIR spectroscopy. From the infrared absorption of silicate species versus time it was concluded that a maximum absorption appeared between pH 7.0 and pH 9.5. Below pH 9.5, a sorption equilibrium value could not be reached within 2 hours. Desorption of already sorbed silicate on a magnetite surface was easier to accomplish at high pH (10.8) than at low pH (9.5 – 7.0). One reason could be the more extensive formation of oligomeric surface silicate species at low pH. At high pH or low silicate concentration, the dominant surface species was a bidentate monomeric surface complex assigned to the infrared band at 950 cm\(^{-1}\). Decreasing pH or increasing the concentration of silica implies more of oligomeric surface silicate species assigned to the infrared absorption at 1000 cm\(^{-1}\) to 1050
cm⁻¹. At the highest silicate concentration (5 mM) this band shifted from 1020 cm⁻¹ to 1050 cm⁻¹ as the surface loading increased with the time of reaction. Simultaneously, a broad band at 1150 cm⁻¹ grew in intensity, a band that was assigned to a three dimensional silica framework. The gradual shift from 1000 cm⁻¹ to higher frequency indicated that the degree of polymerization increased with the sorption time and silicate concentration.

The main difference between magnetite and maghemite concerning silicate sorption was the amount sorbed. The amount of silicate sorbed onto Magnetite was 3-5 times larger than the corresponding sorption onto maghemite.

Acknowledgments

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References


Figure captions

Figure 1. Sorption of silicate from 1 mM sodium metasilicate aqueous solution at different pH onto magnetite followed by desorption. Filled circles, integrated absorbance of sorbed silicate per mg magnetite; open circles, integrated absorbance of residual silicate on surface during desorption. Infrared spectra were integrated between 1300 and 800 cm⁻¹.

Figure 2. ATR-FTIR spectra of silicate sorbed onto magnetite from 1mM sodium metasilicate aqueous solutions. The time dependence of the sorption is shown for (a) pH 10.8 and (b) pH 8.5.

Figure 3. The diagram shows the distribution of silicic acid/ silicate anions in aqueous solution as a function of pH. The total silica concentration was 1mM and the thermodynamic equilibrium constants are listed in Table 1.

Figure 4. ATR-FTIR spectra showing the time dependence of silicate sorption on magnetite at pH 8.5 and different silica concentration.

Figure 5. ATR-FTIR spectra showing the time dependence of silicate sorption on maghemite at pH 8.5 and different silica concentration.

Figure 6. Sorption and desorption of sodium silicate at pH 8.5 and different silica concentration; a) magnetite, and b) maghemite. Filled circles; integrated absorbance of sorbed silicate per mg magnetite; open circles, integrated absorbance of residual silicate on surface during desorption. Infrared spectra were integrated between 1300 and 800 cm⁻¹.
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Table 1. Speciation model of dilute silicate aqueous solution based on the reaction:

\[ \text{pH}^+ + q\text{Si(OH)}_4 \rightleftharpoons H_p(\text{Si(OH)}_4)_q^{+q}. \]

Formation constants from A. Felmy [19].

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Paper III

A polarized Fourier transform infrared spectrometry attenuated total reflection study of bentonite settled onto magnetite

Allan Holmgren, Xiaofang Yang

Journal of Physical Chemistry C

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Sodium bentonite in aqueous suspension was allowed to settle onto a layer of magnetite, and the orientation of the bentonite platelets was monitored using the Fourier transform infrared spectrometry-attenuated total reflection technique. This study is the first reported use of polarized IR to study the in situ settling of delaminated bentonite platelets onto a thin layer of magnetite nanoparticles. The experiment was performed at a pH value (pH 5.6) close to the point of zero charge for the edge surfaces of the bentonite platelets in order to possibly enhance the probability for the (001) surface of bentonite to adhere to the positively charged magnetite particles. The order parameter (S) of the platelets was calculated both for the dry film and the film formed during water evaporation. These results were compared with the orientation of bentonite platelets on the internal reflection element (ZnSe) without magnetite particles, a system where the three layer model is valid. During settling of the bentonite, the tilt angle of the normal to the (001) surface of the platelets decreases and reaches a minimum value for the dry film. When the film is still covered by a layer of water, the tilt angles indicate the film to be at least partly built up of so-called card-house structures, implying that the edge surfaces of the platelets are at least partly adhering to the basal (001) surfaces.

Introduction

Minerals composed of silicon oxide tetrahedrals combined with aluminum oxide octahedrals are very common in nature. Clay minerals belong to these types of structures, which exhibit swelling and nonswelling properties in water depending on the organization of their tetrahedral and octahedral layers. If the silica tetrahedra and the alumina octahedra stick together as one unit, the mineral is nonswelling, as in kaolinite, whereas a structural unit with Si–Al–Si layers forms swelling clays.1,2 The structure of bentonite, commonly constituting ~80% montmorillonite, is shown in Figure 1. The (001) plane, perpendicular to the surface normal of the bentonite platelets is always negatively charged due to atomic substitution in the octahedral sheet, whereas the surface of the silica tetrahedra is, therefore, not sensitive to pH changes since the charge is due to atomic substitution, whereas the edge surface of the platelet, which consists of metal hydroxide groups, is sensitive to this experimental parameter. There are investigations suggesting that the point of zero charge of the edge surfaces is close to pH ≈ 7.3,4 whereas the magnetite particles are positively charged up to pH ≈ 5.9.5 At pH values lower than 6, so-called card-house structures may form due to electrostatic attraction between positive and negative charges, implying that the edges of the bentonite platelets may adhere to the 001 surfaces of other platelets.2 If these card-house structures are formed, they will certainly affect the dichroic ratio of the Si–O vibrations with transition moments perpendicular and parallel to the surface normal of the platelets and, consequently, the average orientation of bentonite particles on the particulate magnetite substrate. Swelling clays imply the possibility of water intercalation between the Si-layers of adjacent structural units, such as in bentonite. The latter types of clays are very popular as adsorbents since they offer the possibility to intercalate anions, cations, and organic molecules such as proteins, in addition to water. Furthermore, the layered structure may cause bentonite to delaminate under shear stress. Because of these properties and because of its abundance in nature, this type of clays has become very popular as adsorbents in a variety of applications, such as in wine purification, as a component in kitty litter, and in water treatment but also as a sealing agent in nuclear waste.

Figure 1. The structure of montmorillonite platelets showing the three layers of the platelet viz. the two silica tetrahedra on each side of the alumina or magnesia (Me) octahedra. Between these platelets there are exchangeable cations and water molecules. The ideal composition may be written: (Na,Ca)1/3(Al5/3,Mg1/3)Si4O10(OH)2. The thickness of the platelets is ~1 nm, and in the bentonite studied here, a fraction of the Me-atoms are substituted for, e.g., Fe(II) atoms.
deposition, in geotechnical engineering, and as lubricant in drilling. Bentonite is also frequently used as a binder in pelletizing plants, where it seems to facilitate the agglomera-
tion of valuable mineral particles such as magnetite into mechanically strong green pellets, partly due to its swelling
ability. The mechanism by which bentonite acts as a binder in
green pellets is not very well-known, although it is reasonable
to assume that its negatively charged silicate surfaces and their
possibility to adhere to less negatively charged magnetite
particles should affect the wettability of the system, and therefore
the capillary forces being one of the forces keeping the magnetite
particles together. Upon mixing magnetite with bentonite,
expanded or delaminated bentonite grains may also form a sort
of fibrous structure between the magnetite particles during or
before agglomeration.

To obtain information about the orientation of bentonite
platelets on magnetite, polarized infrared spectroscopy was a
natural choice. Much of the attention in prior and recent IR
studies has focused on the behavior of species adsorbed at
mineral surfaces, including clay minerals. This technique has also recently been utilized to study the orientation of
monolayers of clay minerals on different ATR substrates as well as
dye molecules adsorbed on the mineral surface. The clay
film had been formed. In this context it might be clarified that
the first layer is electrostatically interacting with another mineral,
such as magnetite, has not been reported so far. This became
the challenge of the present study.

This study was, therefore, devoted to the orientation of
bentonite particles on the magnetite surface under both wet and
dry conditions, since the orientation caused by mineral–metal
oxide interaction is believed to be important for the strength of
the green pellets, that is, pellets before sintering at elevated
temperature. Of special interest was the interaction at very low
water contents, where the magnetite–bentonite system is
approaching natural dryness. Fourier transform infrared (FTIR)
spectroscopy with s-polarized and p-polarized incident radiation
in combination with the attenuated total reflection (ATR)
technique admitted the orientation of bentonite platelets settles
from a water suspension onto magnetite particles to be examined,
as well as the orientation of the platelets after a “dry” film had been formed. In this context it might be clarified that
settled particles may be regarded as being in aqueous suspension
when they are separated by water molecules, but they constitute
a settled aqueous suspension as opposed to the bulk suspension.

Materials and Methods

The Clay Mineral. The clay mineral bentonite, originally
from Milos in Greece, was obtained from Minelco and was ion
exchanged using 0.6 M NaCl. The bentonite obtained was
claimed to be ion exchanged already, so doing it again was
rather a precautionary measure. In the exchange procedure, 1 g
of the bentonite was mixed with 50 mL of the sodium chloride
solution, and the suspension was stirred for about 3 h. After
stirring, the bentonite settled at the bottom of the beaker because
of particle coagulation due to the high sodium chloride
concentration, and the clear solution was substituted for another
50 mL of aqueous sodium chloride. This was repeated three
times, and finally the suspension was allowed to settle at elevated
temperature (60 °C) for 1 h. The ion-exchanged product was
then redispersed in 200 mL of Milli-Q water (pH = 5.6) under
stirring for 8 h. Some larger particles settled rather quickly, whereas the smaller ones were dispersed for days. This pH was
used for reasons explained later, although the used clay
plants is usually between 8 and 10. The suspension so obtained was
then centrifuged at 20 000 rpm for 30 min, and this procedure
was repeated until the water contained no chloride ions
according to an AgNO₃ test. These bentonite particles had a
BET surface of 53.8 ± 0.3 m²/g. The particle size distribution
was narrow with peak intensity at 340 nm, as measured by a
Zeta Plus instrument from Brookhaven Instruments Corporation.
The average size of the particles indicated the clay mineral to
be very well-delaminated. The chemical composition of the iron-
exchanged Milos bentonite in wt %: 59.6 (SiO₂), 21.9 (Al₂O₃),
4.6 (Fe₂O₃), 3.1 (MgO), 3.1 (Na₂O), 0.5 (K₂O), 0.8 (TiO₂), 0.1
(CaO), 0.4 (Tot C). The analyses were performed using
inductively coupled plasma-atomic emission spectrometry (ICP-
AES). The Magnetcite Particles. The synthesis of magnetite was
carried out by controlled coprecipitation of Fe(II) and Fe(III)
when added to an aqueous alkaline solution. Fe(II) and
Fe(III) chloride solutions were prepared by dissolving the salts
in deoxygenated Milli-Q water. A 5 mL portion of the mixture
(molar ratio 1:2; 1.2 M total iron chloride concentration) was
added dropwise (0.5 mL/min) to a reaction vessel containing
40 mL of 0.9 M NH₄OH solution. The reaction mixture was kept
under argon atmosphere at room temperature and was vigorously
stirred. After addition of the iron salts, the mixture was stirred
for another 20 min, and then the precipitated magnetite was
separated from the supernatant by decantation under argon.
The solid was washed 4 times with deoxygenated Milli-Q water
and separated by decantation. The magnetite particles formed
had a diameter of about 20 nm and were then allowed to settle onto
an ATR crystal during evaporation of the dispersion medium
(water).

Film Preparation. The magnetite film on the ATR crystal
was accomplished by evaporating a freshly synthesized aqueous
dispersion of the magnetite particles (0.15 mg/mL). Because
small particles of magnetite have a tendency to oxidize to form
hematite or maghemite, especially at elevated temperature, a
freshly prepared magnetite suspension was used. The magnetite
film was formed during evaporation of the water medium under
reduced atmospheric pressure (~700 mBar) and by tilting the
length direction of the ATR crystal about 5°. This arrangement
allowed the water meniscus to move along the crystal surface
and resulted in a smooth and evenly distributed film of the
magnetite particles. The magnetite film so formed was allowed
to dry in vacuum. Shortly before the IR measurements, 1.25
mL of a dispersion of bentonite (0.0125 wt %) was added to
the magnetite film on the ATR crystal. The pH of this dispersion
was measured to be 5.6, in good accordance with pH of the
Milli-Q water used as dispersion medium. The low pH is due to
the proton exchange during ion exchange of the water. Then,
the bentonite particles were allowed to settle onto the magnetite
surface, and the orientation of the settled platelets were measured
in situ by polarized FTIR.

Infrared Spectroscopy. The ATR internal reflection element
was a ZnSe crystal plate (New Era Enterprises, Inc.) with the size
80 (l) × 10 (w) × 3 mm (t) and a face angle of 45° (13 reflections
on one side, refractive index 2.41). A horizontal ATR (HATR)
trough crystal plate mount was used in these experiments. Infrared
spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer
equipped with a DTGS detector. All spectra were recorded at room
temperature (23 °C) and normal pressure using the double-side
forward–backward acquisition mode. The single beam background
A Polarized FTIR-ATR Study of Bentonite on Magnetite

The measured absorptions \( A \) and \( A_p \) are proportional to the square of the vector product between the electric field vector of the evanescent field \( E \) and the transition dipole moment \( M \). This may be written according to eq 1,

\[
A = (E \cdot M)^2
\]

where \( A \) is the absorbance.

The components of the electric field vector \( E \) are described by Harrick and Mirabella\textsuperscript{26,29} as well as in a number of publications.

\[
E_i^2 = \frac{4 \cos^2 \alpha (\sin^2 \alpha - n_i^2)}{(1 - n_i^2)(1 + n_i^2)\sin^2 \alpha - n_i^2}
\]

(2)

\[
E_p^2 = \frac{4 \cos^2 \alpha}{1 - n_i^2}
\]

(3)

\[
E_s^2 = \frac{4 \cos^2 \alpha (\sin^2 \alpha) n_i^2}{(1 - n_i^2)(1 + n_i^2)\sin^2 \alpha - n_i^2}
\]

(4)

In eqs 2–4, \( \alpha \) is the angle of incidence, \( n_{31} = n_1 n_i \) and \( n_{32} = n_i n_2 \), where \( n_1 \) is the refractive index of the ATR crystal, \( n_2 \) is the refractive index of the inorganic layer (magnetite and bentonite), and \( n_i \) is the refractive index of the medium outside this layer (water or air). In addition to the angle of incidence of the infrared radiation, the electric field components are described by three refractive indices (the three layer model).

If the second layer is composed of alkyl chain molecules adsorbed onto the ATR crystal, then a molecular axis is commonly defined with transition dipole moments in the molecules forming an angle \( \theta \) with respect to the molecular axis. A weakness of this model is that alkyl chains can exhibit trans-gauche conformers, implying that the molecular axis is rather a curve than a straight line. On the other hand, an all-trans conformation of the alkyl chains may imply a biaxial distribution of the molecular axis around the surface normal of the ATR crystal. However, in the present case a uniaxial distribution of transition dipole moments parallel to the (001) surface normal of the bentonite platelets is considered. This model is similar to the one used in polarized infrared transmission spectroscopy of lamellar liquid crystalline phases, except that in the latter experiments the molecular system has to be tilted in order to measure a dichroic ratio.\textsuperscript{30}

The average angle between the transition moment and the surface normal of the ATR crystal is probed by the ratio between the absorption of s-polarized and p-polarized infrared radiation and can be calculated by the following equation,

\[
D = \frac{A_s}{A_p} = \frac{E_s^2}{E_p^2} \sin^2 \gamma + \frac{2E_s^2}{E_p^2} \cos^2 \gamma
\]

(5)

where \( \gamma \) is the average tilt angle.

In the derivation of eq 5, the average angle between the transition dipole moment \( M \) and the normal to the (001) surface of bentonite is assumed to be \( \theta = 0^\circ \). Solving eq 5 for \( \gamma \) gives eq 6,

\[
\gamma = \text{arcsin} \left( \sqrt{\frac{2DE_s^2}{D(2E_s^2 - E_p^2) + E_p^2}} \right)^{1/2}
\]

(6)

Equation 6 was used to calculate average tilt angles for bentonite platelets settled on the magnetite particles, which were deposited on the ZnSe internal reflection element.

Results and Discussion

The theory briefly described above and used in the estimation of the orientation of bentonite platelets on magnetite particles relies on the assumption that the bentonite platelets including the magnetite particles form a thin film on the substrate. This may be accomplished by using a sufficiently diluted suspension of bentonite or by interrupting the settling of the dispersed...
bentonite platelets at an appropriate time. The latter method also serves as an evidence for attractive electrostatic interaction between the thin layer of magnetite particles on the crystal and bentonite platelets settled on this layer. Interrupting the settling process after half an hour and gently washing the crystal with distilled water resulted in only a minor decrease in the measured absorbance of the bentonite film covered with water. A minor decrease might be expected since bentonite platelets still in suspension are now not detected. However, the concentration of bentonite at the surface of the crystal is much higher than in the suspension, at least for diluted suspensions, which explains the observed minor decrease in absorbance.

1. Estimation of Film Thickness. The thickness of the bentonite deposit on the ZnSe crystal was estimated using transmission IR spectroscopy. The transmission spectra of deposited bentonite films were recorded at four different equally spaced spots along the ZnSe crystal viz. at 1, 3, 5, and 7 cm from one of the cut edges of the crystal. The intensity of the ν(Si–O) band at 1040 cm\(^{-1}\) was utilized to estimate the film thickness by using an already measured absorption coefficient for Wyoming montmorillonite. Although the bentonite used here is only about 80% montmorillonite, the absorption coefficient for Wyoming montmorillonite is assumed to be sufficiently good to make an estimation of the thickness of the bentonite film. The absorption coefficient is defined by eq 7,

\[
\alpha = \frac{\ln 10}{d} A_{\text{max}} \tag{7}
\]

where \(A_{\text{max}}\) is the peak absorbance of the Si–O band, and \(d\) is the film thickness.\(^{23}\) According to Johnston et al.,\(^{22}\) the experimentally determined absorption coefficient for the Si–O band at about 1040 cm\(^{-1}\) is 3.60 × 10\(^{-3}\) cm\(^{-1}\) (Wyoming montmorillonite). In our transmission experiments concerning bentonite on magnetite, the absorbance at 1040 cm\(^{-1}\) varied between 0.0824 and 0.126. According to eq 7, this implies that the thickness of the bentonite film varied between 53 and 79 nm. In corresponding experiments with bentonite settling on a ZnSe crystal without magnetite particles, the settling was interrupted after 5 h, implying a film thickness varying between 9 and 10 nm, that is, about 10 layers of bentonite platelets. These thicknesses of the bentonite film are far below the penetration depth of the infrared radiation, which could easily be checked since a spectrum of water above the thicker bentonite film resulted in an absorbance of 0.67 for the H\(_2\)O bending mode (\(A_\nu\)). Using a Beer’s law expression for the absorbance of a water and a molar absorptivity of 22.1 L mol\(^{-1}\) cm\(^{-1}\) for the bending mode of water at 1635 cm\(^{-1}\),\(^{34}\) the effective penetration depth into water was calculated to be 420 nm, taking the 3 reflections on one side of the ATR crystal into account. A Gibbs’ surface excess of water at the bentonite surface was not considered since it has been shown that this quantity is negligible even if the sorptivity of interfacial water would be 10 times larger than in bulk water.\(^{25}\) The penetration depth for p-polarized light is considerably larger (\(A_\nu = 1.36\)). Thus, the thickness of the bentonite deposit is clearly much less than the penetration depth, so the thin-film approximation seems reasonable.

2. FTIR-ATR Spectra of Bentonite. In the mid-infrared region, the most intense bands of dry bentonite are located in the wavenumber region 1150–900 cm\(^{-1}\) (Figure 3.1). The dominant band in this region is very strong, even if the bentonite is a thin film, due to the large Napierian absorption coefficient of Si–O stretching vibrations. However, if the clay film is thin enough, then a water layer in contact with the clay exhibits even stronger absorptions, especially in the OH-stretching region (not shown in Figure 3). The OH-stretching and OH-bending absorptions of water on and within the bentonite film are observed at 3230 cm\(^{-1}\) and 1636 cm\(^{-1}\), respectively. In addition, the water association band due to the combination of the bending vibration and the hindered rotation of water molecules is observed at 2121 cm\(^{-1}\). It is well-known that the OH stretching vibration of water is normally located at about 3420 cm\(^{-1}\) in transmission spectra. However, in ATR spectra of water the peak frequency is generally observed at a lower frequency. This is due to the anomalous dispersion of water, as shown in a publication by Mehmet Hancer et al.\(^{35}\) The absorption maximum of water varied considerably with the refractive index of the ATR element used. Thus, it was shown that internal reflection elements with refractive indices 3.43, 2.00, and 1.71 implied absorption maxima at 3370, 3280, and 3205 cm\(^{-1}\). Accordingly, an absorbance maximum at 3230 cm\(^{-1}\) would indicate that water is in contact with the ZnSe crystal (refractive index 2.41), or more likely, since the bentonite film is firmly attached to the magnetic particles on the ZnSe crystal, the position of the OH stretching vibration of water is also affected by the refractive index of the magnetite/bentonite layer at 3320 cm\(^{-1}\).

Upon drying the film in air, the OH stretching and bending bands of water eventually disappear almost completely, and in the OH-stretching region there is only one weak band at 3620 cm\(^{-1}\) remaining. This band has been ascribed to the OH-stretching of a metal atom hydroxyl in the clay structure.\(^{36}\) The Si–O stretching bands of bentonite were located to the spectral region 1200–960 cm\(^{-1}\). Four ν(Si–O) bands are detected, viz. at ∼1115, ∼1085, ∼1040, and ∼1010 cm\(^{-1}\). In addition, weak bands are observed below 1000 cm\(^{-1}\) due to bending vibration of the metal–OH entities within the bentonite structure.\(^{37}\) The peak frequencies of the latter absorption bands are at 919, 880, and 843 cm\(^{-1}\).

However, the most important assignments for polarized infrared measurements are the directions of the dipole moments caused by Si–O vibrations. From previous studies,\(^{12,22,29–30}\) it seems clear that the band observed at ∼1080 cm\(^{-1}\) is caused by a transition dipole moment perpendicular to the (001) surface of the clay mineral and that absorption at a lower frequency, viz. at ∼1040 cm\(^{-1}\), is due to vibrations having a transition dipole moment perpendicular to the surface normal of the (001) surface (in-plane vibrations). In the present work, the assignment of the out-of-plane mode is utilized to determine the orientation of bentonite platelets settled onto the surface of the ATR crystal or onto the magnetic particles deposited on the internal reflection element (ZnSe).
A Polarized FTIR-ATR Study of Bentonite on Magnetite

3. The Orientation of Bentonite Platelets on ZnSe.

The FTIR-ATR spectra of bentonite particles settled on the internal reflection element are sensitive to the polarization of the incident infrared beam (Figure 4). The p-polarized spectrum was obtained with the IR beam polarized parallel to the plane of incidence, while the s-polarized spectrum was obtained with the beam polarized perpendicular to the plane of incidence. The most prominent difference between the two directions of polarization is the significantly higher intensity of the band at 1082 cm$^{-1}$ in the $A_p$ spectrum. This implies a low dichroic ratio ($A_p/A_s$) and consequently indicates that the bentonite platelets are oriented on the ZnSe crystal with their (001) planes preferentially parallel to the surface of the ATR crystal. A curve fit of the two band shapes in Figure 3 was accomplished by using component bands with peak frequencies at 843, 880, 919, 1010, 1039, 1084, and 1114 cm$^{-1}$. The residual rms error of the curve fit was 0.001. According to this curve fitting, the dichroic ratio of the 1082 cm$^{-1}$ band was 0.26. With the refractive index of bentonite at 1084 cm$^{-1}$ ($n_2 = 1.15$), the tilt angle of the normal to the (001) surface could be calculated using eqs 2–4, and 6.

The tilt angle obtained ($\gamma = 34^\circ$) indicates that the platelets are oriented with their basal planes preferentially parallel to the ATR crystal. The dichroic ratio would have been 0.675 in order to imply randomly oriented bentonite platelets. According to IR spectra, the "dry" film contained very small amounts of water that should affect the refractive index of the film. Using $n_2 = 1.248$ (pure water at 1084 cm$^{-1}$), the tilt angle became 30$^\circ$, so the true value should be in the range between 30 and 34$^\circ$. However, this tilt angle is considerably larger than the angle obtained by Johnston et al. in a similar investigation on the orientation of a monolayer of Wyoming montmorillonite on ZnSe, viz. 12$^\circ$. The lower value obtained for Wyoming montmorillonite may be due to the film preparation method used, where the platelets were predialyzed at the water/air interface using a cationic amphiphile and subsequently compressed at various surface pressures in a Langmuir–Blodget trough before deposition on the ZnSe crystal. The settling method used here should admit more card-house-type structures in the bentonite multilayers.

4. The Orientation of Bentonite Platelets on Magnetite.

Tilt angles for bentonite settled on a magnetite deposit were obtained by Johnston et al. in a similar investigation on the refractive index of magnetite. However, this tilt angle is considerably larger than the angle obtained assuming a three layer model to be valid, that is, three refractive indices are describing the components of the E-vector of the evanescent field (eqs 2–4 and 6). However, in the experiments with a maghemite film on the internal reflection element there are actually four refractive indices, since the refractive index of magnetite should be different from the corresponding index for bentonite. As can be seen from eqs 2–4, the electric field components in x and y directions are independent of the refractive index of the deposited layer (magnetite and bentonite), whereas the z-component is strongly influenced by the value of $n_2$. In the dichroic ratio, $A_1$ (absorbance measured with y-polarized light) is equal to $A_s$, and $A_p$ (measured by light polarized in the x-y plane) is equal to $A_p + A_s$. Accordingly, a precise determination of the orientation of the bentonite platelets on magnetite using the three layer model (eq 6) demands an accurate value of $n_2$. However, in the present study the aim was primarily to determine the preferred orientation of the platelets and not an exact value of the tilt angle.

To estimate a refractive index for the thin and porous magnetite layer, the refractive index of magnetite powder and the volume fraction of empty space between the magnetite particles are needed. However, as far as we know there is no refractive index of magnetite particles reported at 1080 cm$^{-1}$. According to Handbook of Chemistry and Physics, the refractive index of magnetite powder is 2.42 (sodium line, 5893 Å). The corresponding value for hematite is 3.22. In a recent study of optical properties of thin iron oxide films on steel, it was shown by ellipsometric measurements that the index is 1.9 at 1200 nm with a declining optical dispersion (d$\rho$/d$\lambda$). The corresponding value for a hematite film thermally grown on steel was 2.35. In this context it is interesting to compare the latter value with an investigation of combustion-synthesized hematite aggregates consisting of 50 nm Fe$_2$O$_3$ particles, showing that the refractive index increased from 1.81 to 1.98 as the aggregation number increased from 3 to 7. Experimental data were analyzed at 488 nm.

Since reported index values for hematite are larger than the values for maghemite, it is assumed here that the refractive index of magnetite particles should not exceed 1.9. Provided the magnetite nanoparticles are close-packed spheres on the ZnSe crystal, it is straightforward to calculate the fraction of space occupied by the spheres, which is 0.740. With water ($n = 1.248$ at 1084 cm$^{-1}$) in the empty space between the particles, the refractive index of the porous layer was estimated to be 1.73, assuming a linear relationship. In case the particles are not close-packed on the ZnSe surface but have a larger fraction of empty space between them, the refractive index will be even lower. The refractive index of the wet bentonite film is also expected to be strongly influenced by the index of water since sodium bentonite is swelling clay. If the two indices are similar, then the three layer model should be valid.

Accordingly, an effective refractive index of the combined maghemite/bentonite layer should be between the indexes for "dry" bentonite (1.15) and the maximum value for a thin porous layer of maghemite particles (1.73).

Because an accurate value of $n_2$ was not available for the combined magnetite/bentonite layer, the dependence of the tilt angle on the refractive index $n_2$ was calculated (Figure 5) at the experimentally obtained dichroic ratio for a "dry" maghemite/bentonite film ($A_p/A_s = 0.30$) as well as for a film covered by the aqueous suspension ($A_p/A_s = 0.46$).

As shown in Figure 5, the tilt angle decreases from 36 to 19$^\circ$, upon increasing the refractive index from 1.15 to 1.7, that is, all indices in this range indicate the platelets to be oriented with their basal planes preferentially parallel to the surface of the ATR crystal. Without having an exact value of the refractive index, the average value (1.425) was preferred, resulting in a tilt angle of 25$^\circ$ between the surface normal of the ATR crystal and the normal to the (001) plane of the platelets.
resulted in a dry film, which was obtained after 7 h, the 1080 cm\(^{-1}\) band after 4 h is shown. Before the water evaporation had time. In Figure 6, the curve fitting of the infrared absorption spectrum was recorded with a layer of magnetite on the ATR crystal.

The calculated tilt angles vary with the refractive index of the magnetite/bentonite film \((n)\). The two curves are calculated using \(A/I_A\) values at 1080 cm\(^{-1}\) for a dry (0.30) and a wet (0.46) film, as obtained from curve fitting of the measured absorption bands.

Moreover, the calculations indicate that the magnetite particles larger the true refractive index is, the smaller the tilt angle. The orientation of the platelets also changed with the settling time. In Figure 6, the curve fitting of the infrared absorption spectrum was recorded with a layer of magnetite on the ATR crystal.

Figure 5. The calculated tilt angles vary with the refractive index of the magnetite/bentonite film \((n)\). The two curves are calculated using \(A/I_A\) values at 1080 cm\(^{-1}\) for a dry (0.30) and a wet (0.46) film, as obtained from curve fitting of the measured absorption bands.

The average tilt angle can be used to calculate the order parameter, \(S\), frequently used for stretched polymer films and liquid crystals \((S = 1.5 \cos^2 \gamma - 0.5)\) and originally defined by R. S. Stein.\(^4\) An average tilt angle of 25° gives \(S = 0.72\). The positively charged magnetite particles on the ZnSe surface is expected to increase the affinity of the surface for the first layer of clay particles, contributing to their preferential orientation. On the other hand, the magnetite layer is certainly not completely smooth and would therefore contribute to larger tilt angles since the clay particles might adapt to the topography of the underlying surface.

It is interesting to notice that the three layer model used here in the calculation of the tilt angle give reasonable values, although a four layer model, if available, would have been the natural choice. Irrespective of the refractive index in the range 1.15–1.7, the bentonite platelets are evidently oriented with their (001) surface almost parallel to the magnetite film, that is, the band characters were either Gaussian or Lorentzian (Figure 6). Settling times closer to apparent dryness was not possible to probe because the water film was not evenly evaporated, but part of the surface along the edges of the trough began to dry. However, it seems clear that the tilt angle is lowest for the dry film and is higher if the film is covered by a water suspension of the platelets.

Conclusions

The orientation of bentonite platelets on the internal reflection element (ZnSe) as well as on a layer of magnetite particles deposited on the internal reflection element was analyzed with polarized FTIR-ATR spectroscopy. A thin layer of the clay particles was accomplished by settling from a diluted suspension. The dichroic ratio of the out-of-plane Si–O stretching vibration differed significantly from the ratio for a random distribution of the platelets. For a dry bentonite film on ZnSe, the (001) surface (basal plane) of the platelets was preferentially oriented perpendicular to the normal of the ATR crystal. This was also true for a “dry” bentonite film settled on a thin layer of magnetite particles deposited on the ZnSe crystal, but the magnetite particles contributed to an increased order (lower tilt angle). For a wet film, the tilt angle of the bentonite platelets was considerably larger indicating that the swollen bentonite layer above the ZnSe crystal contained platelets that tended to form so-called card-house structures at this pH (5.6).

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References and Notes
