



## Competition between sodium oleate and sodium silicate for a silicate/oleate modified magnetite surface studied by in situ ATR-FTIR spectroscopy

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### ABSTRACT

Attenuated Total Reflection (ATR) IR spectroscopy was utilized to monitor adsorption of sodium oleate and sodium silicate onto synthetic magnetite at pH = 8.5, both individually and in a competitive manner. Oleate was adsorbed within a concentration range of 0.01–0.5 mM. It was observed that adsorption of oleate increased linearly with increasing concentration of oleate in solution up to a concentration of 0.1 mM. The infrared spectrum of oleate showed a broad single band at  $1535\text{ cm}^{-1}$  assigned to the asymmetric stretching vibration of carboxylate, implying chemisorption of oleate to the magnetite surface. The kinetics of oleate adsorption followed a pseudo first-order reaction with an apparent rate constant of  $k_1 = 0.030 \pm 0.002\text{ min}^{-1}$ . Competitive adsorption of silicate and oleate was performed either by adding silicate solution to a magnetite film initially equilibrated with 0.1 mM oleate or adding oleate solution to magnetite treated with silicate solutions in the concentration range 0.1–5 mM. It was shown that silicate, within reasonable time, had only minor effect on the amount of oleate already adsorbed on magnetite. On the other hand, oleate did not efficiently compete with silicate if the latter substance was already adsorbed on the iron oxide.

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### 1. Introduction

The agglomeration of finely ground iron ore concentrates into magnetite pellets is a complex surface chemical process involving a mixture of various components such as magnetite, bentonite, water-glass, olivine, as well as ions dissolved in the process water. In addition it may be necessary to use a collector for reversed flotation of apatite from magnetite, as is the case at Luossavaara-Kirunaavaara AB (LKAB) in Sweden. This reagent is applied to minimize the apatite content by froth flotation, but a small amount of the collector may also adsorb at the magnetite particle surfaces and such a wetting modification was recently shown to affect the strength of the green pellets formed in the pelletizing process [1]. Thus, it is important to reduce the adsorption of this collector in order to further improve the strength of the pellets. Although the chemical structure of the collector is unspecified by the manufacturer, from NMR and IR spectra of this compound it was clear that the collector contains a number of carbonyl groups, double bond(s), methyl ( $\text{CH}_3$ ) and methylene ( $\text{CH}_2$ ) entities. In this study we have used sodium oleate as a model collector molecule. Oleate, which is a well known surfactant and collector, consists of a carboxylate head group, a hydrocarbon chain, and a double bond at

the C:9 position of the C 18 alkyl chain. Attenuated Total Reflection (ATR) infrared spectroscopy was utilized, a technique that has been widely applied to study surface adsorption from aqueous solution onto finely dispersed solids including metal oxides e.g. [2–8]. ATR spectroscopy has also been used to study surface reactions related to flotation [9–15]. Especially the in situ method is advantageous since it admits the adsorbed species to be monitored while the mineral is in contact with the solution. This advantage not only allows one to acquire information regarding the nature of the species, but also the rate of adsorption can be studied in situ i.e. in real time [3,8–10].

The aim of the present study was primarily to investigate the adsorption properties of oleate on the magnetite particle surfaces including the adsorption kinetics and the competition between oleate and sodium silicate for the magnetite surface. Silicate species adsorbed at magnetite will make the iron oxide surface hydrophilic, which is advantageous for the particle agglomeration process, whilst adsorbed collector would have the opposite effect. Sodium silicate (known as water-glass) is one of the mostly used modifying reagents in flotation. It is well known that the speciation of silicate species in aqueous solution depends on  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio,  $\text{SiO}_2$  concentration, pH, temperature, and aging [16–20]. These parameters therefore play a significant role in its application in surface modification processes. Here pH was adjusted to intermediate value (8.5), close to the pH of the process water at LKAB. Poly-

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merization of silicate is known to be more extensive at intermediate pH values than at higher pH [20].

## 2. Materials and methods

### 2.1. Materials and reagents

Magnetite was synthesized as previously described [3,20,21]. The small magnetite particles implied a high surface area ( $97.7 \text{ m}^2/\text{g}$ ), which is advantageous for spectroscopic measurements and these particles were used as a model system for magnetite from the iron ore.

Sodium oleate (~99%) was obtained from Sigma. Fresh solutions of oleate were prepared by dissolving sodium oleate in water. Water-glass reagent with a modulus ( $\text{SiO}_2/\text{Na}_2\text{O}$  ratio) of 3.3 was used as the silicate solution source. The water-glass solutions were diluted to a desirable concentration just before the experiment. Analytical grade of NaOH and HCl were used for pH adjustment. Milli-Q water (Millipore Corp.) was used in all stages for preparation of sodium oleate and water-glass solutions and adsorption measurements.

### 2.2. ATR-FTIR measurements

#### 2.2.1. Instrumentation and experimental set up

The internal reflection element (IRE) was thoroughly rinsed with ethanol and Milli-Q water before deposition of a magnetite layer. The magnetite particles were deposited over the ZnS-IRE ( $50 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$ ) by evenly spreading a few drops of an as-synthesized magnetite suspension over the crystal and drying it in a vacuum desiccator. A single sided rectangularly shaped flow through cell, made of stainless steel, was used. The cell was connected to a 250 ml reservoir containing 150 ml solution via Viton tubings and the solutions were circulated through the cell at a rate of 5 ml/min (for further details, see Ref. [3]). All experiments were performed at room temperature and the reservoir was protected from air by a flow of argon. The pH value was probed during the experiment using a glass electrode. The IR spectra were recorded on a Bruker IFS 66v/S equipped with a DTGS detector and typically 350 co-added scans were recorded at a resolution of  $4 \text{ cm}^{-1}$ . Data acquisition as well as data processing and analysis were carried out by means of the OPUS software.

#### 2.2.2. Adsorption measurements

**2.2.2.1. Oleate adsorption.** Milli-Q water at pH = 8.5 was continuously circulated through the cell for 30 min before the background spectrum was collected. Afterwards, a known volume of the freshly prepared sodium oleate solution was added to the reaction vessel to acquire the desired spectra. The sample spectra were recorded using the repeated measurements facility until no significant increase in intensity of the C–H stretching frequency was observed. This was assumed to represent the adsorption maximum at the given concentration. The same procedure was repeated for oleate concentrations between 0.01 mM and 0.5 mM. Although the reported critical micellization concentration (CMC) of aqueous sodium oleate solutions varies a lot in the literature (0.7–4.8 mM), [22,23] the concentration range used should be below the CMC value.

A new magnetite film was deposited on the IRE for each kinetic experiment and after the background spectrum had been recorded. The background solution (Milli-Q water at pH = 8.5) was then replaced by oleate solution (further details can be found in Ref. [3]).

Experiments were also performed using aqueous oleate solutions in the concentration range 0.05–0.5 mM and a bare ZnS crystal (without deposited magnetite) to make sure the observed intensity was not due to oleate adsorbed onto the bare ZnS-IRE

or from oleate in aqueous solution. Only negligible IR absorption, due to oleate, was detected in these experiments.

**2.2.2.2. Adsorption of water-glass on oleate modified magnetite.** The effect of water-glass on oleate adsorption at the magnetite surface was performed as follows:

An aqueous solution of 0.1 mM oleate was equilibrated with the magnetite surface and spectra were recorded until adsorption equilibrium (*ca.* 80 min), in the same way as described in Section 2.2.2.1. Then, a given amount of water-glass was added to obtain a silicate concentration of 0.01 mM and subsequently spectra of adsorbed silicate were monitored with time. The experiment was continued by increasing the concentration of silicate to 0.06 mM, 0.2 mM, 1 mM, and 5 mM. Spectra were recorded 75 min after each addition. The pH of the aqueous solutions (Milli-Q water) was 8.5.

**2.2.2.3. Adsorption of oleate on silicate modified magnetite.** A 0.1 mM aqueous silicate solution was prepared (pH = 8.5). This silicate solution was circulated for 100 min in contact with the magnetite surface while the spectra were collected in the same way as described under Section 2.2.2.1. Subsequently, sodium oleate was added to this solution to obtain a 0.1 mM solution with respect to oleate. This procedure was repeated with initial silicate concentrations of 0.4 mM, 1 mM, and 5 mM before adding sodium oleate (0.1 mM). The latter sequence of silicate/oleate addition is natural since silicate work both as a depressor and as a dispersing agent.

## 3. Results and discussion

### 3.1. Adsorption of oleate onto magnetite

Fig. 1 shows IR spectra of oleate adsorbed on magnetite at different concentrations and Fig. 2 depicts the plot of integrated absorbance in C–H stretching region ( $2800\text{--}3000 \text{ cm}^{-1}$ ) versus equilibrium oleate concentration in solution. As evident from Figs. 1 and 2, the adsorption increased nearly proportional to oleate

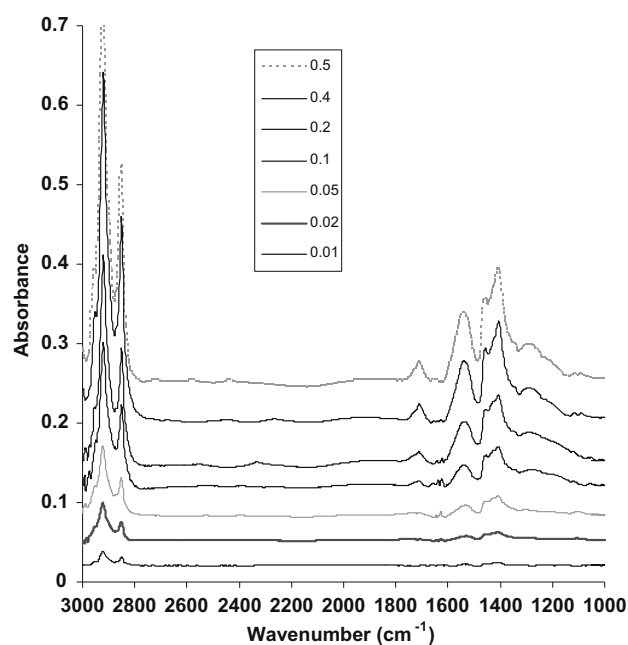


Fig. 1. Infrared spectra of oleate adsorbed on magnetite from 0.01–0.5 mM aqueous oleate solutions. The insert shows the bulk oleate concentration in mM and spectra were shifted along the absorbance axis for clarity.

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