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

Xiaofang Yang^{a,b,*}, Payman Roonasi^a, Allan Holmgren^a

^a Division of Chemistry, Department of Chemical Engineering and Geosciences, Luleå University of Technology, SE-97187 Luleå, Sweden

^b Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

The sorption of sodium silicate by synthetic magnetite (Fe_3O_4) at different pH conditions (pH 7–11) and initial silicate concentrations (1×10^{-3} and $10 \times 10^{-3} \text{ mol L}^{-1}$) was studied using in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The analysis of infrared spectra of sodium silicate in solution as well as adsorbed on magnetite nano-particles clearly showed the evolution of different silicate species depending on pH and silica concentration. The silicate concentration studied ($10 \times 10^{-3} \text{ mol L}^{-1}$) contained polymeric or condensed silicate species at lower pH as well as monomers at high pH, as evident from infrared spectra. Condensation of monomers resulted in an increased intensity of absorptions in the high frequency part ($>1050 \text{ cm}^{-1}$) of the spectral region, which contains information about both silicate in solution and sorbed silicate viz. 1300 cm^{-1} – 850 cm^{-1} . In the pH range studied, infrared spectra of sorbed silicate and sorbed silicate during desorption both indicated the presence of different types of surface complexes at the magnetite surface. The sorption mechanism proposed is in accordance with a ligand exchange reaction where both monodentate and bidentate complexes could exist at low surface loading level, the relative proportion of the complexes being due to both pH and concentration in solution. Oligomerization occurred on the magnetite surface at higher surface loading.

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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 sur-

faces 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 $1.3 \times 10^{-3} \text{ mol L}^{-1}$ 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 ($1.3 \times 10^{-3} \text{ mol L}^{-1}$). Gong et al. concluded that the role of sodium silicate (10^{-3} to $10^{-2} \text{ mol L}^{-1}$) 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} ($2.4 \times 10^{-4} \text{ mol L}^{-1}$) to 500 g t^{-1} ($4 \times 10^{-4} \text{ mol L}^{-1}$) 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

* Corresponding author at: Division of Chemistry, Department of Chemical Engineering and Geosciences, Luleå University of Technology, SE-97187 Luleå, Sweden. Fax: +46 0 920 491199.

E-mail address: xiaofang.yang@ltu.se (X. Yang).

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 $\text{SiO}_2\text{:Na}_2\text{O}$ 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 $\text{SiO}_2\text{:Na}_2\text{O}$ ratio and higher SiO_2 concentration. In alkaline and diluted solutions ($\text{SiO}_2\text{:Na}_2\text{O} < 1.65$, 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 existing in sodium metasilicate solutions and claimed that silicate monomers predominated in $0.2\text{--}3 \text{ mol L}^{-1}$ 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_4SiO_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 1.0×10^{-4} to $1.0 \times 10^{-3} \text{ mol L}^{-1}$ solutions using a modified surface complex model (CD-MUSIC distribution model) [21]. They concluded that a bidentate surface complex ($\equiv\text{Fe}_2\text{O}_2\text{Si}(\text{OH})_2$) is favoured at low surface loading while at high surface loading polymerized species are more likely. Jordan et al. [22] used titration and sorption data along with the Fiteql 4.0 code to model the surface complexes formed when dilute silicate solutions ($< 2.0 \times 10^{-4} \text{ mol L}^{-1}$) were sorbed on three different iron oxides, viz. goethite, hematite, and magnetite. Their results indicated the formation of two types of monodentate surface complexes, $\equiv\text{FeH}_3\text{SiO}_4$ and $\equiv\text{FeH}_2\text{SiO}_4^-$.

Attenuated total reflection Fourier transformed infrared (ATR-FTIR) spectroscopy has been proven to be a powerful in situ technique to study solid-liquid interface reactions, where various inorganic anions (such as arsenate, sulfate, phosphate) and organic compounds interacts with metal oxides and minerals [23–26]. Although there are some IR, XPS and EXAFS studies on the interaction of silicate with iron oxides or polymers [27,28], no in situ spectroscopy study monitoring the sorption of silicate from dilute solutions, viz. the concentrations used in mineral flotation ($< 10 \text{ mmol L}^{-1}$), onto the surface of magnetite could be found in the literature. The one most closely resembling our study is an investigation by Gong et al. who applied ATR-IR spectroscopy to study silicate solutions and used XPS to analyse the adsorbed species on hematite after drying. Their results show that polymerized silicate species were formed at the hematite surface [6].

Therefore, in the present paper, the ATR-FTIR technique was used to obtain molecular information about sodium silicate in solution as well as adsorbed onto magnetite particles in situ. The effects of pH and concentration of silicate in solution on silicate species distribution and adsorption characteristics 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. Experimental

2.1. Materials

Two types of sodium silicates were used. Stock solutions of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) from J.T. Baker were prepared with Milli-Q water as solvent. Silicate3.25 was an industrial water glass reagent with a $\text{SiO}_2\text{:Na}_2\text{O}$ weight ratio of 3.25 and obtained from Luossavaara–Kirunavaara AB (LKAB) in Kiruna, Sweden. The pH of the stock solutions was > 11.5 and sample solutions were prepared just before the in situ measurements. To avoid the ionic strength effects, no extra ionic medium was used. 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. Preparation of magnetite films

Magnetite films were prepared from the colloidal dispersion of fresh made magnetite which was synthesized by coprecipitation of Fe(II) and Fe(III), a method described by Julivet et al. and Kim et al. [29,30]. Briefly, 5 mL deoxygenated FeCl_2 and FeCl_3 solution (molar ratio 1:2) at a total iron concentration of 1.2 mol L^{-1} was added to 40 mL 0.9 M NH_4OH solutions. All solutions were carefully kept under argon atmosphere at room temperature, and vigorously stirred. The precipitation was separated from the supernatant by decantation after stirring for 20 min, and then rinsed 4 times with deoxygenated Milli-Q water. Finally, the resulting magnetite paste was dispersed again and kept in a closed vessel. Although all possible precautions were taken to avoid the oxidation of the magnetite particles, a partial oxidation of the particle surfaces to maghemite cannot be completely excluded.

Powder XRD pattern confirmed the crystal structure as magnetite and the broad lines indicated small particle size. TEM images showed aggregated spherical particles with an average size of 10 nm. The specific surface area estimated from particle size was around $115 \text{ m}^2 \text{ g}^{-1}$ ($\rho_{\text{Fe}_3\text{O}_4} = 5.2 \text{ g cm}^{-3}$), and the BET surface area was $97.7 \text{ m}^2 \text{ g}^{-1}$. By spreading certain amount of magnetite suspension 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° , $50 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$) with totally 25 internal reflections mounted in a $\sim 3.5 \text{ mL}$ 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 $\sim 4.7 \text{ mL min}^{-1}$.

A calculated amount of silicate stock solution was added to the MilliQ-water after solvent (water) background spectrum was

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

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 discussion

3.1. Spectra of aqueous sodium silicate

Fig. 1 shows the spectrum of 10 mmol L⁻¹ sodium metasilicate in aqueous solution at different pH. 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. For a 10 mmol L⁻¹ solution at pH 11.5, spectrum showed two prominent absorption bands at 885 and 1023 cm⁻¹, and 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 to higher frequency upon lowering the pH indicates the formation of polymeric species.

Although there are a number of studies on the assignments of vibration 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 mol 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.

Table 1

Speciation model of dilute silicate aqueous solution based on the reaction: $\text{pH}^+ + q\text{Si}(\text{OH})_4 \rightleftharpoons \text{H}_p(\text{Si}(\text{OH})_4)_q^{p+}$. Formation constants from Felmy [35]. $\log K_{sp}(\text{SiO}_2, \text{am}) = -2.71$ [34]

<i>p</i>	<i>q</i>	Chemical formula	$\log(K_{p,q})$
-1	1	$\text{SiO}(\text{OH})_3^-$	-9.82
-2	1	$\text{SiO}_2(\text{OH})_2^{2-}$	-23.27
-1	2	$\text{Si}_2[-]$	-8.50
-2	2	$\text{Si}_2[2-]$	-19.4
-3	3	$\text{Si}_3[3-](\text{cyclo})$	-29.3
-3	3	$\text{Si}_3[3-](\text{linear})$	-29.4
-4	4	$\text{Si}_4[4-](\text{linear})$	-39.1
-4	4	$\text{Si}_4[4-](\text{cyclo})$	-39.2
-4	4	$\text{Si}_4[4-](\text{sub})$	-39.1
-4	4	$\text{Si}_4[2-]$	-15.6
-6	6	$\text{Si}_6[6-]$	-61.8

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.

In the modelling 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 >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 0.01 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 mmol L⁻¹ (the solubility limit of amorphous silica [34]), 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. 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 mmol L⁻¹ solution, more dimers and trimers

Fig. 3. Results from curve fitting of spectra in Fig. 1. The integrated absorbance of each component band resolved from spectra of 10 mmol L⁻¹ sodium metasilicate solution in Fig. 1 is plotted vs wavenumber. It shows the effect of pH on the infrared absorption in the 1200 cm⁻¹–875 cm⁻¹ region.

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 mmol L⁻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 Na₂SiO₃·9H₂O at pH > 13 [18]. The spectral features of 0.05 mol L⁻¹ Na₂SiO₃ were similar to our spectrum of a 0.01 mol L⁻¹ solution at pH 11.5 where bands at ~1020 and ~890 cm⁻¹ are the most prominent ones. They assigned these two bands to the fully dissociated SiO₂(OH)₂²⁻ species. However, according to the distribution diagram in Fig. 2, the prominent species in 10 mmol L⁻¹ solution at pH 11.5 is SiO(OH)₃⁻ rather than SiO₂(OH)₂²⁻. Accordingly, the bands observed here at 1020 and 890 cm⁻¹ are assigned to SiO(OH)₃⁻ species. Apparently, this assignment seems also to be consistent with the spectra reported by the same authors concerning a 0.2 mol L⁻¹ solution of Na₂SiO₃·9H₂O. However, when the alkaline condition changed by adding NaOH to the latter system (0.2 mol L⁻¹ Na₂SiO₃, 0.4 mol L⁻¹ NaOH), the two bands at 1020 and 890 cm⁻¹ shifted to 1001 and 934 cm⁻¹ caused by undissociated Na-silicate species, although a shoulder still appeared at 890 cm⁻¹. In another study, Bass and Turner also observed a similar shift of infrared bands from 1020 and 890 cm⁻¹ to 1000 and 930 cm⁻¹, respectively (0.4 mol L⁻¹ sodium silicate solution), when the ratio of silica to alkali decreased from 3.3 to 0.2 [17]. Considering the two main factors determining the properties of sodium silicate solutions, namely silica to alkali ratio and silicate concentration, a solution with lower ratio of silica to alkali should imply a higher pH value. Thus, it seems clear that the bands at ~1000

Fig. 4. Sorption and desorption of sodium silicate as a function of pH and time. Filled circles, integrated absorbance of adsorbed silicate per mg magnetite; open circles, integrated absorbance of residual silicate adsorbed on magnetite during desorption; lines, solution pH during sorption (filled circles) and desorption (open circles). Infrared spectra were integrated between 1300 cm⁻¹ and 800 cm⁻¹.

and ~930 cm⁻¹ correspond to partly undissociated SiO₂(OH)₂²⁻. Since the concentration of silica in the present study is much lower (10 mM), the effect of undissociated sodium silicate species can be omitted indicating that the wavenumber distance between these two bands become larger when SiO₂(OH)₂²⁻ anions are forming SiO(OH)₃⁻ species through protonation.

Based on the fractional distribution of silicate anions in aqueous solution (Fig. 2), analysis of our infrared spectra, and comparison with previous studies, the infrared bands at ~890 and 1020 cm⁻¹ could be assigned to Si–O stretching vibration of SiO(OH)₃⁻ 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 solutions, 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.

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. 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 of Fig. 4.

Fig. 5. Infrared spectra of silicate adsorbed on magnetite from (a) 10 mmol L⁻¹, (b) 1 mmol L⁻¹ aqueous sodium metasilicate solutions, and (c) 1 mmol L⁻¹ aqueous Silicate3.25 solutions at different pH. Spectra are plotted in the same order as the indicated pH values.

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 Silicate3.25 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 oxyhydroxides 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 ($\text{SiO}(\text{OH})_3^-$) and neutral $\text{Si}(\text{OH})_4$ 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 SiO-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 Silicate3.25 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-

Fig. 6. Results from curve fitting of spectra in Figs. 5a, 5b and 5c. The figure shows the integrated absorbance of each component band resolved from spectra of (a) 10 mmol L⁻¹, (b) 1 mmol L⁻¹ sodium metasilicate solution, and (c) 1 mmol L⁻¹ Silicate3.25 solution.

parent increase in the intensity of the band at 1120 cm⁻¹ can be observed. When pH was decreased from 8.3 to 7.0, there was no remarkable change in the lines-shape. Similarly, spectra of sorbed Silicate3.25 on magnetite (Fig. 5c) at pH 9.9 to 6.6, were dominated by a sharp band centred at 1020 cm⁻¹ with shoulders on each side viz. at ~930 and ~1120 cm⁻¹.

The broad absorption at pH 11.1 (Fig. 5a) 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. The only experimental difference 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 results shown in Fig. 2. 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 dimerized silicate monomers and possibly the dimerization is enhanced at the magnetite surface.

Thus these clear spectral changes upon sorption indicated a strong and specific 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 1 mmol L⁻¹ silicate solutions, the position of component bands was similar as shown in Figs. 6b and 6c, even though pH was changed. Figs. 6b and 6c also show that the absorbance at ~1020 cm⁻¹ is the most intense band in the pH range 10–7. In

contrast to the situation in solution, this band continued to be the strongest one also at low pH.

The possible surface complexes can be postulated to be ≡Fe–OSi(OH)₂OX or (≡FeO)₂–Si(OH)OX for the reactions between silicate monomers and the magnetite surface. The following ligand-exchange reactions are proposed:

or/and

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 ~950 cm⁻¹ in the present work would be related to the FeO–Si stretching in the bidentate surface complex (≡FeO)₂–Si(OH)OX. Therefore, at high pH and low surface concentration, the SiO(OH)₃⁻ species in solution should be sorbed onto magnetite although the magnetite surface at this pH is negatively charged resulting in a bi-dentate complex, (≡FeO)₂–Si(OH)OX, whilst 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. 6a shows the pH effect on the frequency positions and intensities of resolved bands obtained upon sorption from a 10 mmol L⁻¹ silicate solution. The sharp band at ~1030 cm⁻¹ (pH 11.1) is the most intense band in the pH range studied. A comparison of the spectral intensity of resolved bands for sorbed silica in the 1100 cm⁻¹–1200 cm⁻¹ region (Fig. 6a) with those obtained for aqueous silicate solution in the same region (Fig. 3) shows a similar tendency i.e. increasing intensity with decreasing pH. All resolved bands of silicate sorbed at pH 11.1 shifted to higher frequency with lower pH, which indicate that silicate species sorbed onto the magnetite surface take part in polymerization reactions forming a three dimensional framework such as amorphous silica [40]. It is therefore suggested that the strong broad band growing with decreasing pH at high frequency (1100–1200 cm⁻¹, Fig. 6a) and appearing with much lower intensity when sorbing from a 1 mmol L⁻¹ solution (Figs. 5b 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

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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