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Adsorption mechanisms of glucose in aqueous goethite suspensions

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ABSTRACT

The adsorption of glucose and polysaccharides onto solid surfaces is important in several areas of science and engineering including soil chemistry and mineral processing. In this work we have studied the adsorption of D-glucose at the water–goethite (α-FeOOH) interface as a function of pH using batch adsorption measurements and a simultaneous infrared and potentiometric technique. Molecular orbital calculations were also performed in order to support interpretations of the infrared spectroscopic data. Infrared spectroscopy has shown that glucose adsorbs at the water–goethite interface with an intact ring structure and that the β-form is favored relative to the α isomer. The collective spectroscopic and macroscopic results were fully consistent with an adsorption mechanism where glucose interacts with goethite surface sites via hydrogen bonding interactions. Specific infrared peak shifts indicated that glucose primarily acts as a hydrogen bond donor and that it interacts with acceptor sites that become increasingly more prevalent as the surface is deprotonated. These results are in general agreement with the acid/base model for mono- and polysaccharide interactions at metal oxide surfaces, but contradict the inner sphere hypothesis that was proposed based on ex situ spectroscopic measurements.

1. Introduction

Almost all organisms use glucose as a fuel [1], and as a direct consequence of the importance of this molecule in nature glucose chemistry has been thoroughly studied. The aqueous solution chemistry of glucose has been investigated both by experimental spectroscopic methods and by theoretical approaches. As a result, it is well established that aqueous solutions of D-glucose contain two anomeric forms, α and β, that differ in the orientation of the hydroxyl group connected to the C_1 atom. At room temperature and normal pressure the ratio between the α anomer and β anomer is 36:64 [2]. Recent work has shown that glucose is solvated by intermolecular hydrogen bonding to water molecules, and that these solvent molecules interact with each glucose molecule via either H-donor or H-acceptor interactions [3,4]. The tendency of the β anomer to form more intermolecular H-bonds as compared to the α anomer explains the predominance of the former in solution whereas the latter is found to be more stable in gas phase [3].

Another area of interest is adsorption of glucose and polymers of glucose (polysaccharides) onto solid surfaces which has been the subject of several studies. For example, it has been shown that surface interactions with common soil constituents may reduce the bioavailability or alter the reaction pathways of glucose [5,6]. Thus, these interactions may partially protect glucose against degradation and reduce the efficiency as a carbon source for biomass production.

Adsorption of glucose and polysaccharides has also been exploited in a technical context where this phenomenon has been used in the flotation process to separate valuable ore from waste rock. In order to improve and optimize this process it is important to acquire a fundamental understanding of the adsorption reactions, and consequently a number of studies have been devoted to the molecular mechanisms behind glucose and polysaccharide adsorption onto mineral surfaces. In early studies the attractive forces were suggested to be primarily caused by hydrogen bonding, and that the comparatively large number of hydrogen bonding sites per glucose unit rendered stable surface species [7]. In addition, hydrophobic effects were also proposed to contribute to this stability [8]. The early view on these adsorption mechanisms was primarily based on macroscopic observations, but with the application of molecular probes (e.g. infrared spectroscopy) the hydrogen/hydrophobic bonding mechanisms have partly been dismissed in favor of a mechanism involving direct interactions between glucose oxygen atoms and surface sites [9–11].

In 2000 Liu et al. [10] proposed an acid/base model describing the interaction of polysaccharides with mineral surfaces. This model is founded on a key observation namely that polysaccharides interact with metal-hydroxylated species present at the mineral surfaces. Furthermore, the strengths of these interactions are correlated with the acidities of the metal-hydroxylated species and

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thus with the isoelectric points (IEPs) of the minerals; a lower acidity (higher IEP) results in a stronger interaction with the functional groups of the polysaccharide. Liu et al. [10] proposed that weak acid/base interactions, prevailing e.g. in systems with low-IEP minerals, are the result of hydrogen bonding whereas strong acid/base interactions are caused by chemical bonding (i.e. contact ion-pair or inner-sphere coordination) between the functional groups of the polysaccharide and metal ions present at the mineral surfaces. The latter type of interaction was supported by spectroscopic data [9,12]. Using IR spectroscopy Pavlovic and Brandao [13] also suggested that inner-sphere coordination was the predominating adsorption mechanism of not only polysaccharides but also of monomeric and dimeric sugar molecules on hematite.

A drawback of previous spectroscopic investigations of adsorption mechanisms of mono- and polysaccharides onto solid surfaces is the fact that most have been performed on dry, ex situ, samples. Potentially this may have an important influence on the bonding modes and may not reflect the true conditions at the water–solid interface. In the present study we circumvent this problem by applying a simultaneous infrared and potentiometric titration (SIPT) technique, which allows in situ studies of water–mineral interfaces [14], to a study of glucose adsorption. To our knowledge, this is the first time glucose adsorbed to mineral surfaces in an aqueous suspension has been characterized by means of in situ infrared spectroscopy. The mineral used in this study, α-FeOOH (goethite), was chosen for two main reasons: (1) It is a common soil mineral with a high reactivity towards organic molecules. (2) It has a high IEP (9.4) that should favor inner-sphere coordination. The infrared measurements were complemented with batch adsorption experiments in order to determine the pH-dependent glucose adsorption.

2. Experimental

2.1. Chemicals and solutions

Deionized (Milli-Q Plus) and boiled water was used to prepare all solutions and suspensions, and these were prepared at a background electrolyte concentration of 0.050 M Na(Cl) from NaCl (Merck, p.a.) dried at 180 °C. pH adjustments were made with NaOH (0.050 M) and HCl (0.050 M). A glucose solution was prepared by dissolving a weighed amount of D(+)-glucose (BDH AnalaR). The glucose solution and a 0.050 M Na(Cl) solution were sterilized by filtration using 0.2 μm Sarstedt filters (Filtropur S 0.2).

The synthesis and characterization of goethite (α-FeOOH) have been described by Boily et al. [15]. Briefly, goethite was prepared in polyethylene bottles by adding 2.5 M KOH (EKA, p.a.) to 10 L of 0.15 M $Fe(NO_3)_3$ (Merck, p.a.) at a rate of 10 mL/min. The precipitates were aged for 96 h at 60 °C and dialyzed for 2 weeks. The resulting particles were identified to be goethite by X-ray powder diffraction. Two batches of goethite were used in the experiments and the specific surface areas were determined to 104.9 m^2/g and 86.88 m^2/g using N_2 BET analysis. The suspension was diluted and NaCl added to give a NaCl concentration of 0.050 M.

2.2. Adsorption experiments

The adsorption experiment was carried out in batch mode with two replicates, in the pH range 4–10 and at a background electrolyte concentration of 0.050 M Na(Cl). The stock suspension of goethite was acidified to pH ~4 and purged overnight with $N_2(g)$. Each batch sample was prepared by transferring an aliquot of the stock goethite suspension to a 15 mL polypropylene centrifuge tube, adjusting the pH to a target value between 4 and 10 using acid or base and adding a volume of stock glucose solution. All samples were diluted so that the total glucose concentration was 1.0 mM, corresponding to 0.95 $\mu mol/m^2$ of goethite, and the goethite concentration was 10 g/L. During batch sample preparation, the centrifuge tubes were continuously purged with $N_2(g)$ to avoid carbonate contamination. The samples were protected from light by wrapping the centrifuge tubes in aluminum foil. After equilibrating at 25 °C on an end-over-end rotator for 24 h, the pH of each batch sample was measured with a combination electrode from Mettler Toledo (InLab 422) that was calibrated with commercial buffers (Baker), at pH = 3, 7 and 9. Prior to quantitative measurements, the samples were centrifuged at 5000 rpm for 10 min and the supernatant was filtered through a 0.2 μm Sarstedt filter (Filtropur S 0.2). The supernatant was kept in a freezer before being analyzed to determine the glucose concentration.

A glucose recovery experiment was carried out in order to determine the extent of microbial degradation. A volume of glucose stock solution was transferred to a 15 mL polypropylene centrifuge tube. After dilution with ionic medium and pH adjustments, the glucose concentration was 1.0 mM. The samples were protected from light by wrapping the centrifuge tubes in aluminum foil, and after equilibrating at 25 °C on an end-over-end rotator for 24 h, the pH of each sample was measured. The samples were sterilized by filtration through a 0.2 μm filter, and kept in a freezer before being analyzed to determine the glucose concentration. The average glucose recovery was 103% after 24 h with a relative standard deviation of 3.3%. This indicates that the microbial degradation of glucose is insignificant under the experimental conditions studied herein.

2.3. Ion chromatography

Glucose amounts in solution were determined by ion chromatography (IC), on a Dionex system (ICS-3000) with a CarboPac PA 20 guard column followed by a CarboPac PA 20 column, and a 20 mM NaOH eluent.

2.4. Infrared spectroscopy

This set-up and method is thoroughly described in Loring et al. [14]. Titrations were performed in the absence of light to avoid photo induced reactions. A goethite suspension (10 g/L) was blanketed with a nitrogen atmosphere in a titration vessel thermostated at 25.00 ± 0.05 °C. It was pumped peristaltically in a closed loop through fluoroelastomer (Chemsure, Gore Industries) and PTFE tubing from the titration vessel to a flow-through ATR cell inside an evacuated infrared spectrometer (Bruker IFS-66v/s with a DTGS detector in a thermostated ±0.15 °C room). The flow-through attachment was custom built of inert materials (e.g. Pyrex glass, PEEK, PTFE) and was mounted on a single-reflection 45° ATR accessory (FastIR, Harrick Scientific) equipped with a ZnSe internal reflection element (IRE). The volume of the flow-through cell was approximately 1.5 cm^3, and mixing was facilitated within the cell by a propeller stirrer that was fixed above the IRE. Prior to the titration, a mineral overlayer was deposited onto the IRE by evaporating 0.7 mL of an approximately 2 g/L goethite suspension onto the crystal at 75 °C for 2.5 h under nitrogen. The purpose of the overlayer was to concentrate goethite particles close to the IRE/suspension interface. The infrared radiation, in the form of an exponentially-decaying evanescent wave, is most intense at this interface. Therefore, by using an overlayer, the infrared signal due to adsorbed organic ligand on the goethite surface is greatly enhanced. The purpose of the goethite suspension was to provide buffer capacity so that reasonable ligand concentrations can be employed, the ligand-to-surface-area ratio can be known (the surface area from the overlayer is negligible), and the pH can be properly controlled. This is not possible if only a dilute solution of the ligand in ionic medium is employed in the titration.