Structure of adsorbed \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside layers on hematite

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Received 16 December 2003; accepted 26 February 2004
Available online 15 April 2004

Abstract
The composition, structure, and thickness of \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside self-assembled layers on hematite have been evaluated using infrared external reflection spectroscopy and spectral simulation techniques. From the qualitative and quantitative analysis of the reflection spectra of the same sample recorded at different specific angles of incidence and two polarizations, the orientation of the sugar ring and hydrocarbon chain were obtained. Both of these molecular groups are positioned parallel to hematite surface, the adsorbed molecules being at low (2.2-nm-thick layer) as well as higher (11-nm) coverages. The maltoside is adsorbed through interaction of sugar ring OH groups with hematite surface hydroxyl groups. The adsorption of maltoside is not very strong and desorption takes place easily from acidic and low-basic solutions but with more difficulty from strong-basic solution.

Keywords: Adsorption; \(n\)-Dodecyl-\(\beta\)-\(D\)-maltoside; Self-assembled layers; Infrared spectroscopy; External reflection

1. Introduction
Sugar-based surfactants are biodegradable, nontoxic, and synthesized from renewable materials and could potentially be substitutes for other harsh surfactants in various processes [1–4]. Sugar-based surfactants also exhibit some unusual properties. For example, it has been found that \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside adsorbs onto alumina, hematite, and titania, but very little on silica [5]. This behavior is clearly different from that of nonionic ethoxylated surfactants, which adsorb strongly on silica but weakly on alumina and hematite [6,7]. Investigation of adsorption mechanism of sugar-based \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside on alumina suggests no strong interactions between them with hydrogen bonds between hydroxyl groups on the surfactants and alumina surface hydroxyl species proposed to be the driving force for the adsorption on alumina [8].

In many processes, properties such as wettability and dispersion are very much dependent on the formation of surfactant aggregates and the structure of these aggregates in terms of conformation and orientation of species. In our previous work, it was suggested that \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside forms a bilayer when the surface is saturated [5]. A polarized infrared reflection technique is used in this investigation to quantitatively explore the nanostructure of the surface species. By correlating the simulated data with experimental data, the orientation angles of the transition moments of the major molecular groups in the adsorbed \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside molecules and the thickness of the adsorption layers were evaluated quantitatively. Application of this method makes it possible to gain a insight into the structure of the adsorbed layers and to understand the mechanisms of maltoside interaction with hematite surface.

2. Experimental
2.1. Materials
The hematite slab sample of 15 \(\times\) 30 mm size was a pure natural mineral obtained from Ward’s. X-ray diffraction confirmed the polycrystalline structure of hematite, \(\alpha\)-\(Fe_2O_3\). The >95% pure \(n\)-dodecyl-\(\beta\)-\(D\)-maltoside used was from Calbiochem. The molecular structure of the reagent is presented, for example, in Ref. [5]. Other reagents used were all of analytical grade. Distilled water from a Milli-Q plus system was used for all the experiments.
2.2. Preparation of the adsorption layers

The hematite sample was polished with emery paper and alumina powder. The final polishing was done with 0.03-µm alumina and the polished sample was washed with alcohol in an ultrasonic bath. The sample was then immersed in 50 ml of desired solution at pH 2, 8, and 10.0 ± 0.2 for a time period of 2 to 16 h. The solution concentration was from $1 \times 10^{-4}$ to $4 \times 10^{-2}$ M. Directly after contact with maltoside solution the surface of the hematite sample was quickly blotted to remove residual aqueous solution and then the reflection spectra were recorded immediately. Desorption was studied by immersing the sample, after adsorption and spectroscopic studies, in water at the same pH at which adsorption was carried out.

2.3. Infrared analysis

The infrared reflection spectra were recorded on a Bruker IFS88 FTIR spectrometer equipped with an MCT detector and a reflection attachment (Seagull). A wire-grid polarizer was placed before the sample and p- or s-polarized light provided. These accessories were from Harrick Scientific Co. The reflection spectra of the adsorption layers were obtained by the use of polarized light at different angles of incidence. The spectrometer was purged with dry air (Balston filter) to minimize the contribution of water vapor and carbon dioxide to the recorded spectra. The unit of intensity was defined as $-\log(R/R_0)$, where $R_0$ and $R$ are the reletivities of the systems without and with the investigated adsorption layer, respectively. Both the sample spectra and the reference spectra recorded at different angles of the incident beam are the average of 200 to 3000 scans, depending on energy throughput. All the spectra were obtained with 4 cm$^{-1}$ resolution (zero-filled = 2) with Blackman–Harris, three-term apodization. The reflection spectra of hematite and n-dodecyl-β-D-maltoside (compact pellet) were taken with a DTGS detector. In the latter case, the reference spectrum was recorded for an aluminum mirror.

3. Results and discussion

3.1. Optical considerations

The position and shape of the absorbance bands, which can be positive or negative for adsorbed layers, are very sensitive to the polarization and angle of the incident beam. The changes in the bands are dramatic and are caused by optical effects. As reported recently [9–12], the interpretation of the spectroscopic data requires spectral simulation and optical theoretical consideration of the system under investigation to distinguish optical effects from the chemical and structural effects of the adsorbed layer. An additional advantage of the theoretical treatment is the possibility of optimizing experimental conditions [9,10] to obtain reliable results in the shortest experimental time.

The optical properties of hematite were determined from the reflection spectra of the same hematite sample, used in the adsorption experiments applying the recently reported method [13]. In this method the optical properties are determined from several infrared reflection spectra of hematite recorded at different angles of incidence and two polarizations. The reflection spectra of hematite show that the sample is isotropic. This was supported by the X-ray diffraction results showing a polycrystalline structure for the sample. Hematite shows strong adsorption bands between 300 and 700 cm$^{-1}$ due to complex vibrations of the Fe–O bonds [14]. The optical data obtained for hematite are presented in Fig. 1.

The optical constants for maltoside (Fig. 1) were determined in a way similar to that reported recently [13] based on the reflection spectrum for maltoside. As a first approximation it was assumed that adsorbed maltoside has optical constants very similar to those of pure maltoside. Any difference between the recorded experimental spectrum and the simulated spectrum for the assumed composition and structure will indicate surface modification of the adsorbed maltoside species.

The spectral simulations were made with the exact equations based on Hansen’s formulas [15] for a multilayer system of isotropic and homogeneous phases with parallel interface boundaries. Details of the calculation can be found in previous works [9,10,16]. The calculations were performed using a three-phase model: Phase 1, air with a refractive index $n_1 = 1.0$ and an absorption coefficient of $k_1 = 0$; Phase 2, the adsorption layer; and Phase 3, the hematite sample, with optical constants as shown in Fig. 1.

Since reflection spectra are very sensitive to the conditions at which they are recorded, it is useful to know how the absorbance components for different polarizations vary with incident angles for a particular wavenumber. These calculations were performed with exact and approximate equations [10,16]. The latter allow the calculation of the two ab—
sorbance components, $A_{1\perp}$ and $A_{2\parallel}$, for p-polarized spectra, separately. The results obtained for the asymmetric stretching vibration ($v_{as}$) of the CH$_2$ groups at about 2920 cm$^{-1}$ are shown in Fig. 2. For a hypothetical isotropic 1.5-nm layer and p-polarization, the negative absorbance band with almost the same intensity can be observed at all angles below the Brewster angle. The Brewster angle, $\theta_B$, is 62° at this wavenumber. Because of the sharp decrease of the absorbance component with the increase of the incident angle above $\theta_B$ the positive band could be recorded with high difficulty (very low absorbance). At close vicinity of the $\theta_B$ the sharp decrease or increase of absorbance does not allow reliable recording of experimental spectra on a commercial spectrophotometer (for more explanation see Ref. [10]).

In the case of specifically oriented molecules in the adsorption layer, strong absorbance bands could be observed below and above the $\theta_B$ (Fig. 2), and the recorded bands will have reverse absorbance intensities when the angle of incidence passes $\theta_B$. Similar results were obtained for other major absorbance bands. More detailed description of optical considerations could be found in our previous reports [9,10].

On the basis of this discussion and the practical limitations in optical geometry and angular dispersion of the incident beam in commercial spectrometers, the following experimental conditions are proposed for spectroscopic investigation of self-assembled layers on hematite: (i) for s-polarization, a 20° angle of incidence, (ii) for p-polarization, angles of 20°, 50°, and 70°.

A spectral simulation of a hypothetical monolayer of maltoside on hematite was performed under the chosen optical conditions (Fig. 3). The spectrum simulated at 20° and s-polarization is not shown because absorbance intensities are very low and therefore it has only limited importance. Since these spectra are calculated for an isotropic layer all the observed variations between them are due to optical effects. As mentioned above, differences between simulated spectra and the experimental one indicate orientation or composition changes with regard to the assumed structure of the adsorbed layer.

3.2. Quantitative evaluation of the adsorbed maltoside layer

The orientation of the transition moment of a particular molecular group of the adsorbed molecules at an angle $\phi$ from the surface normal, assuming uniaxial symmetry, were determined by the procedure described recently [10] using the spectroscopic data recorded at p-polarization at different incident angles. The reflection spectra of the adsorbed layers recorded for s- and p-polarizations at 20° are almost exactly the same (not shown) indicating uniaxial symmetry of the produced surface layers.

The maltoside self-assembled layers were produced by holding hematite samples in maltoside solutions for 2 h at pH 2, 8, or 12. The amount adsorbed does not increase after 2 h. The recorded good quality spectra allow us to observe all the characteristic absorbance features in the high (aliphatic chain)- and low (sugar part)-frequency regions (Fig. 4). The band assignments and the peak positions of the major absorbance bands are listed in Table 1. The observed absorbance bands can be separated into three groups, which are discussed in the following sections.

3.2.1. Aliphatic stretching vibrations

In the higher frequency region, where the hydrocarbon stretching vibrations of the CH$_2$ groups take place, the simulated spectra are different from those recorded experimentally (Fig. 4). The experimental reflection spectrum at 50° shows the positions of the bands at 2921 and 2852 cm$^{-1}$.
Table 1

<table>
<thead>
<tr>
<th>Band position (cm(^{-1}))</th>
<th>Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3400, 3200</td>
<td>O–H stretching, intramolecular hydrogen bonding, physisorbed water present in sample</td>
</tr>
<tr>
<td>2924</td>
<td>CH(_2), asymmetric stretching</td>
</tr>
<tr>
<td>2853</td>
<td>CH(_2), symmetric stretching</td>
</tr>
<tr>
<td>1468</td>
<td>CH(_2), deformation</td>
</tr>
<tr>
<td>1379</td>
<td>CH(_3), deformation</td>
</tr>
<tr>
<td>1150</td>
<td>C–O stretching coupled with O–H, mainly in C–O–H groups</td>
</tr>
<tr>
<td>1080</td>
<td>C–O stretching coupled with C–C stretching, in C–O–H groups</td>
</tr>
<tr>
<td>1020</td>
<td>C–O stretching coupled with C–C stretching, mainly in C–O–C groups</td>
</tr>
<tr>
<td>912</td>
<td>Ring vibration</td>
</tr>
</tbody>
</table>

They are shifted to a lower frequency by 3 and 2 cm\(^{-1}\) compared to the expected positions (Fig. 3). These shifts indicate a stronger lateral interaction between the aliphatic chains of the adsorbed molecules [17,18] and an increase in packing density in the adsorbed layer versus that in the original surfactant sample. The recorded spectrum at 70° shows negative absorbance bands, while the predicted spectrum has strong positive absorbance bands, and the positions of the negative bands at 2923 and 2854 cm\(^{-1}\) are higher than anticipated. These differences indicate the specific orientation of the aliphatic chain in the adsorbed layer. The average tilt angle of the hydrocarbon chain axis from the surface normal was calculated using the procedure described recently [10] and then quantitative evaluation of the adsorbed amount were carried out based on spectroscopic data from the spectral regions of the asymmetric (band at 2921 cm\(^{-1}\)) and symmetric (band at 2852 cm\(^{-1}\)) stretching vibrations of the CH\(_2\) groups. For the adsorption layer produced at pH 12 the tilt angle is 79°, which indicates almost a parallel position of aliphatic chain versus hematite surface. The adsorbed layer produced from 4 × 10\(^{-2}\) M solution has an average thickness of 11 nm. The adsorption layers obtained at pH 2 and 8 (Figs. 5 and 6) show a very similar orientation of the aliphatic chain, with a tilt angle of about 80° (Table 2). The average adsorbed layer thicknesses are 4.4 and 5.0 nm, respectively.

It was found that desorption of maltoside from hematite is very quick at pH 2 and 8, while at pH 12 it is much slower. This probably results from positive charge of hematite below pH 9. The recorded reflection spectrum after desorption shows that the structure of the adsorbed layer remained...
the same while the adsorbed amount decreased to 2.3 nm (Fig. 7).

If the adsorption was performed at pH 12 from lower concentration of about $5 \times 10^{-3} \text{ M}$, the recorded spectra are very similar to that presented in Fig. 7. The orientation of the hydrocarbon chain is almost parallel to the substrate surface and the amount adsorbed is equal to 2.2 nm. Very similar results are observed at pH 8 (Table 2).

### 3.2.2. Sugar rings vibrations

In the lower frequency region between 1200 and 900 cm$^{-1}$ the second group of absorbance bands are clearly visible in the experimental spectra (Fig. 4). They could be assigned to complex vibration of the C–O, C–C, and OH groups. A comparison of the experimental and simulated results shows again very large differences between them. The experimental spectra show three major absorbance bands at around 1155, 1085, and 1020 cm$^{-1}$. The first two are positive at 50$^\circ$ and negative at 70$^\circ$ whereas the band at 1020 cm$^{-1}$ shows reverse behavior. The simulated spectrum (Fig. 3) at 50$^\circ$ does not predict any positive bands in this frequency region. The calculated spectrum at 70$^\circ$ shows three negative bands at 1154, 1110, and 1086 cm$^{-1}$ but with very low intensities while the most intensive band at 70$^\circ$ in simulated spectrum is positive at 1024 cm$^{-1}$. All these observations and a comparison of the experimental spectra with Fig. 2 where variation of the absorbance components in $x$ and $z$ directions versus angle of incidence are reported indicate that the absorbance bands at about 1155 and 1085 cm$^{-1}$ are characteristic for vibration of molecular groups with the dipole moment oriented vertically to hematite surface. It is based on the finding (Fig. 2) that only dipole moment in the $z$ direction can show positive value at 50$^\circ$ and negative at 70$^\circ$. At the same time the absorbance band at about 1020 cm$^{-1}$ is characteristic for vibration of the molecular groups with the dipole moment oriented parallel to the interface. These findings are conclusive, while it is more difficult to detect molecular groups of the sugar ring responsible for these three major bands. The band assignments proposed up to now are rather controversial. There is only agreement that the observed vibrations in the region 1150–900 cm$^{-1}$ are complex, but it is not possible to assign any band to a single stretching vibration [19–23]. The most detailed assignment of the bands in the region is proposed for $\beta$-D-glucopyranose on the basis of the potential-energy distributions [19]. It is proposed that all the observed experimentally bands are due to the combination of the C–O and C–C stretching with a stronger participation of the C–O groups in the observed absorbance. The complexity of the molecular group vibrations in this spectral region are the reason that it is not possible at present to use the spectral data characteristic for sugar ring vibrations in order to perform quantitative evaluation similar to that carried out for the stretching vibration of hydrocarbon chains.

Our experimental data show clearly that the major components of the bands at 1155 and 1085 cm$^{-1}$ have dipole moment vertical to interface and perpendicular to that producing the absorbance band at 1020 cm$^{-1}$. Taking under account all the available observations, we propose the following most probable assignments: the bands at 1151 and 1085 cm$^{-1}$ are mainly due to the stretching of the C–O groups as a part of the C–OH groups, and the band at 1020 cm$^{-1}$ is assigned to the stretching of the C–O groups in the two pyroside rings and between the rings. With this assignment, parallel positions of both maltoside rings on hematite surface and strong participation of the maltoside OH groups in surface bonding could be concluded.

### 3.2.3. OH group vibration

The simulated spectrum of adsorbed hypothetical layer of maltoside at 50$^\circ$ shows a strong broad band at about 3380 cm$^{-1}$ (Fig. 3). This band is due to the O–H vibrations of the sugar ring of maltoside. It can also be caused, at least partly, by the presence of the adsorbed water in the pure sample of maltoside. On the contrary, this broad band
(or more accurately a group of bands) is not visible in the related reflection spectra of the adsorbed layer (Figs. 5 and 6). Lack of a band in the experimental spectra indicates that the sugar OH group participates in the bonding of the surfactant to hematite surface through formation of a complex with hematite surface sites or more precisely with hydrated surface sites. Different hydration or in other words surface speciation of hematite surface at different pH could also have an influence on the adsorbed amount and desorption process.

3.2.4. Hematite surface speciation

All the experimental spectra presented are versus the same background, the spectrum of hematite immediately after polishing. It is expected that hematite contacted with aqueous solution will undergo hydration and different densities of surface hydrated groups are produced depending on pH. The changes in the surface groups of hematite after adsorption are well visible after comparison of the results obtained at different pH (Figs. 4 and 5). For example, a positive band at about 3200 cm$^{-1}$ is observed at pH 12 in the reflection spectra recorded at 50° and 70° (Fig. 4), while it is not present in the spectra obtained from the acidic solution at pH 2 (Fig. 5). This indicates changes in the surface OH groups of hematite.

The results obtained indicate that the composition and structure of the adsorbed layers are almost independent of solution pH and very similar for a wide range of solution concentrations. These observations agree with our previous findings [5]. However, the proposed structure of the adsorbed layer determined in this work is very different from that previously proposed [5]. Based on the adsorption and hydrophobicity experiments it has been proposed that maltoside molecules assume a vertical position on the hematite surface with the aliphatic chain toward the bulk solution at lower solution concentrations (hydrophilic coverage) and bilayer formation with chain–chain lateral interaction at higher solution concentrations (hydrophobic coverage). It has to be kept in mind that the results presented here describe samples, which were taken out of the solution in semidry or dry conditions. It is possible that in the absence of bulk aqueous solution, the original surface structure produced could be altered, and this new structure was in fact determined in this work. Usually when the organized structure collapses, random organization occurs, but that is not the case observed here. The structures determined for semidry or dry surface layers are very well organized. The vertical position of maltoside molecules in the adsorbed structure was proposed based on an increase or decrease in the observed hydrophobicity. It is possible that similar changes in hydrophobicity could be produced by parallel oriented maltoside molecules with specific orientation of hydrophilic hydroxyl groups toward the surface of hematite as was deduced from molecular level spectroscopic studies presented here.

4. Conclusions

$n$-Dodecyl-$\beta$-$D$-maltoside is adsorbed onto hematite surfaces through the OH sugar groups. Infrared spectra do not show a significant shift in the C–O band positions compared to pure samples of maltoside, which suggests its weak adsorption. This observation is supported by desorption studies that showed very easy removal of the adsorbed molecules at acidic and low basic pHs and difficult removal in strong alkaline solutions. Both the aliphatic-chain and two-sugar-ringing parts of the adsorbed molecules are oriented parallel to hematite surface. This orientation was found to be characteristic of all adsorbed layers produced at different pHs. The parallel position of sugar molecules for thicker and thinner adsorption layers indicates very specific adsorption. It is noted that the solution concentration at which sugar molecules are observed at hematite surface are above cmc (critical micelle concentration) of this surfactant. Below cmc the adsorption was below detection limit, which is around 0.4 nm. It cannot be excluded that the organized structure determined for the adsorbed layer performed in semidry or dry conditions is different from that originally produced in aqueous solutions. However, the observed organization of the adsorbed layer is striking and can explain all our previous surface induced observations.

Acknowledgments

The authors gratefully acknowledge the support of this work by the CNRS-NSF cooperation program (Project 4606), the National Science Foundation (INT-9603430, CTS-9622781, EEC-9804618), and the Department of Energy (DE-AC26-01BC15312).

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