Interaction of alcohols with the calcite surface

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A clearer understanding of calcite interactions with organic molecules would contribute to a range of fields including harnessing the secrets of biomineralisation where organisms produce hard parts, increasing oil production from spent reservoirs, remediating contaminated soils and drinking water aquifers and improving manufacturing methods for such industrial products as pigment, soft abrasives, building materials and optical devices. Biomineralisation by some species of blue green algae produces beautifully elaborate platelets of calcite where the individual crystals are nanometer scale. Controlling their growth requires complex polysaccharides. Polysaccharide activity depends on the functionality of OH groups so to simplify the system in order to get closer to a molecular level understanding, we investigated the interaction of OH from a suite of alcohols with clean, freshly cleaved calcite surfaces. X-ray photoelectron spectroscopy (XPS) provided binding energies and revealed the extent of surface coverage. Molecular dynamics (MD) simulations supplemented with information about molecule ordering, orientation and packing density. The results show that all alcohols studied bond with the calcite surface through the OH group, with their carbon chains sticking away in a standing up orientation. Alcohol molecules are close-packed and form a well-ordered monolayer on the surface.

1. Introduction

Attention to organic and inorganic molecule interactions with calcite has increased in the recent past because a better understanding of the solid-fluid interactions that control inorganic and biogenic growth and dissolution of calcite will provide benefits in a range of fields. Biomineralisation, the production of hard parts by organisms such as oyster and egg shells, is a mystery that when cracked will provide insight into diseases such as osteoporosis and arthritis. Limestone and chalk provide a substantial portion of the world's hydrocarbon reservoirs so fuller appreciation of calcite surface interactions with oil and water will result in increased oil recovery. Calcite is a major component in aquifers so drinking water quality often depends on the fate of contaminants such as pesticides, heavy metals, petroleum products and organic solvents. Industrial materials such as pigments, soft abrasives, building materials and optical devices rely on efficient ways to produce calcite in various forms. The importance of carbonate speciation in Ca bearing solutions puts the $CaCO_3$-CO_2-H_2O system in the centre of global carbon cycling and controls the behaviour of CO_2 in the atmosphere.[1]

Although researchers have been studying calcite-fluid interactions for at least five decades, it is only recently that analytical instrumentation has become available that allows us to begin to probe the fundamental mechanisms that control calcite behaviour in complex systems, such as might take place inside a cell or deep within a hydrocarbon reservoir. Calcite is a simple, inorganic salt that is easy to nucleate, grow and dissolve in the laboratory. Ca serves as the cation and CO_3 as the anion. However, the Ca and O in the calcite crystalline structure give the compound some properties that make it attractive to organic molecules. Previous studies have shown some effect of organic molecules on dissolution, precipitation or recrystallisation of calcite, in natural systems or on laboratory grown calcite.[2-10]

Coccolithophores, a group of blue-green algae that cover their one cell with calcite shields called coccoliths, produce complex polysaccharides to control the growth of nanometer scale single calcite crystals.[11] Previous research in our group investigated the behaviour of coccolith associated polysaccharides that were extracted from cultured species and found that the adsorption activity of the macromolecules was largely a result of their OH functional groups.[12-16] The simplest inorganic molecule with an OH group is water and the simplest organic chain molecule is ethanol, where one end is OH and the other, CH_3. Investigation of systems containing calcite-water-ethanol provided new insight into the strength of bonding of simple OH compounds.[17-21]

In this paper, we now demonstrate the direct interaction between a mineral surface that is completely free of adventitious contamination with molecules that adsorb from a pure gas phase. Experimental evidence from X-ray photoelectron spectroscopy (XPS) is supplemented with a theoretical approach using molecular dynamics (MD) simulations to illustrate how the simplest model molecules adsorb through their OH functional group and to define the nature of those interactions, surface coverage, orientation and structure. The results reveal the mechanism by which complex organic molecules very likely interact with the calcite surface, significantly altering its properties.

2. Experimental methods

X-ray photoelectron spectroscopy (XPS) is a semiquantitative, surface sensitive technique that probes only the top 10 nm of a surface.[22] Experiments were carried out in a Kratos Axis Ultra^{DLD} chamber, using a monochromatised Al *Kα* (hν = 1486.6 eV) X-ray source at a power of 150 W. The typical pressure inside the ultra-high vacuum (UHV) chamber was 5 $\times10^{-10}$ mbar and never exceeded 5 $\times10^{-9}$ mbar during a scan. The vacuum chamber was designed with only dry pumps, i.e. turbomolecular and scroll pumps, so hydrocarbon contamination is kept extremely low. Calcite is particularly attractive to adventitious hydrocarbons (Adv C). Samples fractured in vacuum typically remain without an Adv C peak for few hours whereas in air, calcite usually attracts about 3 equivalent monolayers of Adv C in the 2 minutes that is needed to cleave, mount and insert a fresh calcite sample into the vacuum chamber.[23] The analyser pass energy used for high resolution scans was 10 eV. The instrument is fitted with an in vacuum fracturing device that permits cleavage of calcite crystals in situ, under UHV, thus avoiding atmospheric contamination.

The data were analysed using commercial software, CasaXPS,[24] and a Shirley background fit. A charge neutralizer minimized the effects of charging from the insulating calcite surface. The spectra were energy calibrated using the carbon peak associated with carbonate, at 290.1 eV.[23] No changes in peak position, width or intensity were observed during the experiments, implying that beam damage was negligible.[25]

The samples were cooled in flowing liquid nitrogen, condensed from dry N_2 gas that travelled through stainless steel capillary tubing to the sample holder. Radiative heating from a filament behind a plate close to the sample holder warmed the sample during the experiments.

Gas was injected into the reaction chamber through a gas line, back filling at a pressure between 5 x 10^{-8} and 1 x 10^{-7} mbar. To be consistent with previously published adsorption literature, the dosing unit used in this paper is the Langmuir (L) with the conversion: 1 L = 1.33 $\times10^{-6}$ mbar.s^{-1}. All gases were verified during dosing by means of a mass spectrometer attached to the chamber to ensure that the dosed gas was free of contamination. Ethane gas, 99.9% pure, came from a pressurized 20 L cylinder directly attached to the gas line. Methanol, ethanol and pentanol, which are liquid at room temperature, were injected from a glass vessel attached to the gas line. Several freeze-pump-thaw cycles were performed for each liquid until the mass spectrometer showed clean spectra that matched the reference spectra available in the NIST database.[26] In the case of t-butanol, which has a liquefaction temperature of 298 K, the liquid was gently warmed to 323 K so it would have sufficient vapor pressure in the gas line. The same freeze-pump-thaw treatment was used for t-butanol as for the other gases.

We used single crystals of optical quality, Iceland spar calcite from Ward's Scientific (USA). The calcite crystals were cleaved to produce rods by gentle scoring with a scalpel so they would fit in a sample holder with a hole in the middle. A part of the crystal that protruded from the stub was inserted into the in situ fracturing device, a clean sharp blade pressed the crystal against a copper block and gentle pressure easily cleaved the rod, exposing a fresh, clean surface of calcite that was free of adventitious carbon. Calcite cleaves perfectly along the {10.4} plane, producing surfaces that are very flat.[23] The surfaces produced this way were about 5 mm x 5 mm.

None of the gases studied in this paper adsorbed at room temperature, 300 K. Cooling the sample increases the sticking probability, offsetting the effects of vacuum, so to observe binding relationships between alcohol and calcite during physisorption, the weak adsorption process, we cooled the samples to 130 K.

We used classical molecular dynamics (MD) simulations to investigate the calcite surface in contact with the alcohols. Calcite has a rhombohedral crystal structure, space group $R\overline{3c}$, with *a*=*b*= 4.988 Å, *c*= 17.061 Å, α=β= 90° and γ= 120°. A calcite {10.4} surface was built using Materials Studio 5.0[27] and alcohol models (methanol, ethanol, t-butanol and pentanol) were built with the program antechamber in AMBER 10.0.[28] The surface had an area of 59.88 Å x 56.671 Å and was covered by a layer of alcohol molecules with thickness more than 20 Å. For each type of alcohol, the starting configuration was generated with a tool called genbox in the Gromacs program. The alcohol molecules were randomly packed into a rectangular box so as to avoid overlapping atoms or unrealistic configurations of high potential energy. The length of the box along the x and y axis was set to match the calcite surface. The alcohol box was relaxed with a short MD simulation of ~500 ps while its temperature was increased gradually from 0 to 300 K. The final configuration from the relaxing step was used to build the alcohol-calcite system by putting the alcohol box above the calcite surface at a distance of ~2.5 Å from the surface. This distance was chosen as optimal because it is not too far where it would take too long for the alcohol to adsorb on the surface and not too close, where the molecules could be trapped in a local minimum unable to move to more energetically favorable positions. A three dimensional periodic boundary condition was applied in the simulations and in each model, there was a vacuum of about 150 Å to avoid interactions between the system and its images. For each alcohol, an MD simulation was carried out using the Gromacs program[29] (Version 4.5.3) with a set of potentials designed for use at bioinorganic interfaces.[30] The total time for each MD simulation was 12 ns with a time step of 1 fs. For each simulation, the first 6 ns were used for equilibration and the last 6 ns trajectory was used for data analysis. The temperature in all of the simulations was set to 300 K using the Nose-Hoover thermostat method. The desorption temperature for the alcohols tested in this manuscript is 273 K, below the temperature set for the simulation. This could be the result of an overestimation of the binding energy at the calcite surface. One explanation could be the difference in time scale between MD simulation time (nanoseconds) compared to the XPS experiments (10s of minutes or hours). Another possibility could be that the potentials used in the simulation are slightly over predicting the binding energy values.

3. Results and discussions

The calcite crystals were cleaved in vacuum just prior the experiment, ensuring as clean a surface as possible. The XPS spectra from such surfaces revealed the characteristic peaks expected for calcite: Ca $2p_{3/2}$ at 347.6 eV, O 1s at 532.0 eV and C 1s at 290.1 eV, which is in excellent agreement with values from the literature for calcite cleaved in vacuum,[23] or exposed to air after cleavage.[31] No other elements were detected.

Figure 1 shows the C 1s spectra for a calcite crystal cleaved in vacuum and one cleaved in air and then introduced to the vacuum chamber. For the in vacuum cleaved sample, there is only one peak at 290.1 eV and it is attributed to the carbon in the carbonate group. In contrast, the spectrum from calcite cleaved in air has an extra peak around 285 eV which represents hydrocarbons, with a minor shoulder towards higher binding energy attributed to C-O bond. This is typical of adventitious carbon, contamination from air. The use of the in situ fracturing unit, thus creating clean surfaces, allows the direct study of gas interaction without possible interferences from contamination.

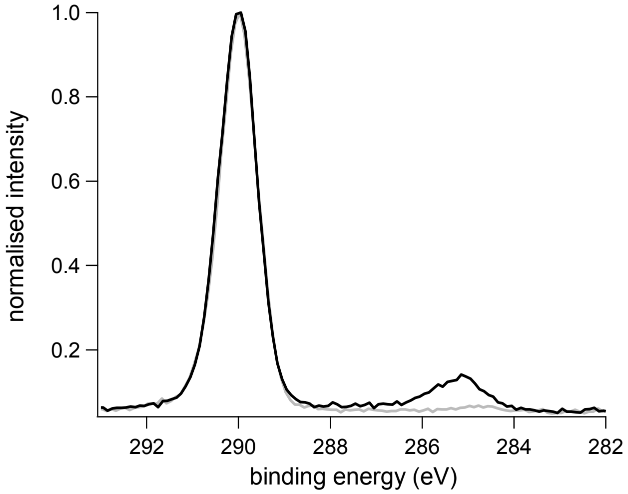


Figure 1: XPS carbon 1s spectra for calcite samples cleaved in vacuum (grey) and in air (black). Peaks at 290.1 eV are from carbonate and the peak at 285 eV results from adventitious carbon. No carbon contamination is present on calcite cleaved in vacuum.

3.1. Comparison between ethanol and ethane adsorption

Ethane does not adsorb on a fresh calcite surface at 130 K. Figure 2 shows carbon 1s spectra from experiments where 20 L of ethanol were dosed on fresh calcite surfaces at 130 K. Contrary to ethane, it is clear that ethanol adsorbs at the surface. At first, a multilayer of ethanol adsorbs on the chilled sample, which desorbs with slight heating to 155 K.

Examples in the literature for ethanol desorption on various substrates show a comparable temperature of desorption for a condensed multilayer, for example at 162 K for ethanol on $Mo_2C/Mo(100)$[32] and above 150 K on Pt(111).[33] In our work, the monolayer that remains adsorbed is bonded directly to the surface (Figure 2, grey line). The intensity and position of the peak representing this monolayer remain constant as the sample is heated further but at 273 K, it desorbs, returning the calcite surface to its initially completely clean state (Figure 2, black line). This reversibility of molecular adsorption on calcite contrasts with the dissociative desorption that has been observed on reactive metals, where new species have been detected by energy and mass spectrometry.[32,33]

The only composition difference between ethanol and ethane is the C-OH group, implying that ethanol binds to the calcite surface through OH. The two peaks that appear at 285.7 eV and 287.1 eV correspond to the CH_3 and the CH_2OH ends of the ethanol molecule (Figure 2, inset). The area ratio for these two peaks is 1:1, as expected for the stochiometric ethanol formula. This is in agreement with previous calculations showing a strong interaction of the -OH group with the calcite surface, forming two bonds, hydrogen from the alcohol attached to an oxygen from a carbonate group and oxygen from ethanol bonded to a surface calcium atom.[19]

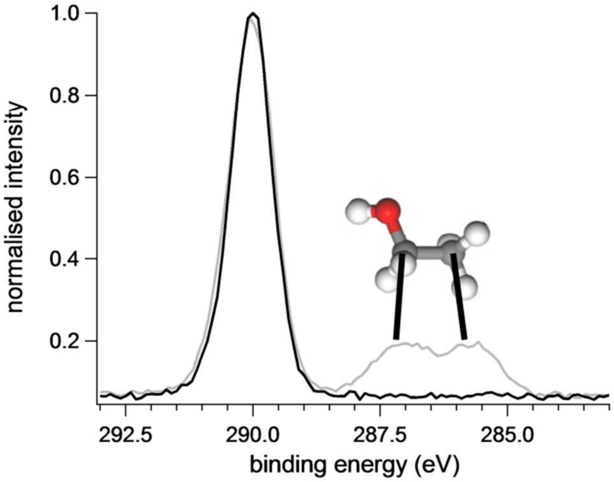


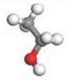
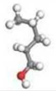
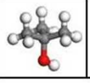
Figure 2: XPS carbon 1s spectra from calcite after dosing with ethanol (grey) on a surface prepared in vacuum at 130 K and heated to 155 K. The peak at 290.1 eV is attributed to carbonate, peaks at 285.7 eV and 287.1 eV represent CH_3 and CH_2OH from one monolayer of ethanol. After heating to 300 K, the surface returns to its initial clean state (black).

The fact that ethane does not sorb on calcite suggest that the adventitious carbon observed on calcite cleaved in air (such as Figure 1) is composed of more complex alkane molecules, or functional groups (like C-OH group) containing molecules that can anchor the surface.

3.2. Adsorption of methanol, pentanol and t-butanol

To get a better understanding of the interaction with the calcite surface, other types of alcohol were investigated, namely methanol (CH_3OH), pentanol ($CH_3(CH_2)_3CH_2OH$) and t-butanol ($(CH_3)_3COH$). The molecules are depicted in Table 1 together with binding energies derived from the XPS spectra shown in Figure 3. Methanol is the shortest, with only one carbon atom, pentanol has a longer straight carbon chain than ethanol and t-butanol is bulkier because the CH_3 groups protrude laterally. These alcohols were chosen to provide information about how the length and the geometry of the molecule affect adsorption.

Table 1: Alcohols used in this study. Molecule length[25] *and binding energies (BE) for the carbon atom attached to hydroxyl (C-OH) and the rest of the carbon chain (C-C or C-H) are listed. White balls represent hydrogen, grey, carbon and red, oxygen atoms.*

	Molecule	BE (eV) C-OH group	BE (eV) C-C and C-H	molecule length (Å) without (or with) hydrogen
methanol		287.4	-	2.84 (5.25)
ethanol		287.1	285.7	4.11 (6.51)
pentanol		286.9	285.7	7.94 (10.34)
t-butanol		287.3	285.5	4.11 (6.51)

The adsorption process for all of the alcohols that we tested was the same as for ethanol. After a dose of 20 L of gas, multilayers sorbed when temperature was 130 K. The weakly bound molecules from the multilayer desorbed with slight heating to 155 K. The monolayer left on the surface desorb as a result of further heating to 273 K, returning the calcite to its original, clean state. Figure 3 shows the XPS spectra and associated fits for a monolayer of methanol, pentanol and t-butanol after the desorption of the multilayer. The ethanol spectrum is included for direct comparison. All of the spectra display the peak around 287 eV that corresponds to the C-OH group. For pentanol and t-butanol, the peak around 285.6 eV represents the carbon atom(s) that form the alcohol chain. For methanol, this peak is missing as expected and for the other alcohols, the C-C/C-H peak area is proportional to the number of carbon atoms in the chain: 0 for methanol, 1 for ethanol, 3 for t-butanol and 4 for pentanol. The slight shift in the binding energy for the C-OH group in each alcohol is caused by the different chemical environment that the C bound to OH feels in each molecule, namely, shielding of the core level electrons decreases as chain length increases.

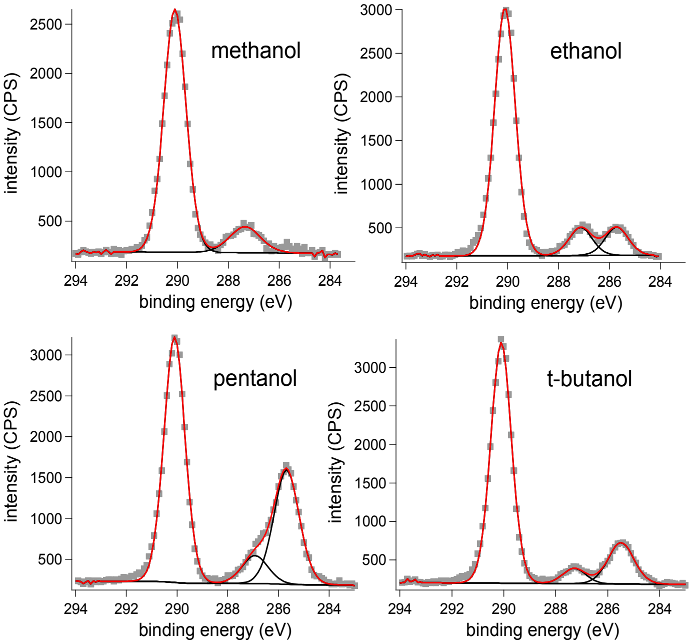


Figure 3: XPS carbon 1s spectra for methanol, ethanol, pentanol and t-butanol monolayer on calcite. Photoelectrons arising from C bonded in carbonate cause the peak at 290.1 eV. The peak at 287 eV, arises from C-OH group and at 285.5 eV, from carbon atom(s) in the alcohol chain.

3.3. Coverage and geometry at the surface

For a molecule to interact with a surface, the nature of the interaction is important, i.e. type of bonding, but characterisation of the degree of surface coverage and the orientation of the adsorbed molecules is pivotal for deriving a complete understanding of the surface properties. This section reports on investigations of the extent of surface coverage and its relationship with the geometry of the alcohol molecules.

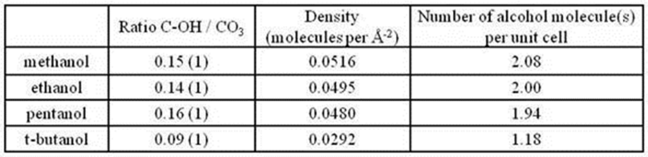
From the fits made for the XPS spectra shown in Fig. 3, the ratio of carbon bound as C-OH and the carbon of the carbonate have been estimated for the four alcohols tested (Table 2). This ratio is directly related to the actual coverage of the surface by alcohol molecules, because at these experimental conditions, only one monolayer exists on the calcite surface.

To supplement the experimental data, theoretical calculations were made to estimate the expected surface coverage of the four alcohols. A surface composed of 168 Ca-CO_3 units was exposed to ~600 molecules of each alcohol, which would represent a multilayer with thickness of more than 20 Å, certainly in excess of a monolayer. After the simulation reached equilibrium, top view snap shots from the four systems were compared (Fig. 4), the interfacial structures were examined by calculating density profiles out from the calcite surface (Fig. 5) and ordering in the first layers was explored (Fig. 6).

The surface unit cell on calcite {10.4} is rectangular, 8.10 Å x 4.99 Å.[23,27] It contains two Ca atoms and two carbonate groups. Table 2 lists the estimated coverage of alcohols, presented as a density of molecules per Å^{-2} or, if one multiplies by the unit cell area, as the number of molecules per unit cell.

Table 2: Density of electrons from MD, number of alcohol molecules per calcite surface unit cell and ratio for C-OH : CO_3 derived from XPS from experiments with methanol, ethanol, pentanol and t-butanol. The surface unit cell for the

calcite {10.4} face contains 2 Ca atoms and 2 carbonate groups.



	Ratio C-OH / CO_3	Density (molecules per $Å^{-2}$)	Number of alcohol molecule(s) per unit cell
methanol	0.15 (1)	0.0516	2.08
ethanol	0.14 (1)	0.0495	2.00
pentanol	0.16 (1)	0.0480	1.94
t-butanol	0.09 (1)	0.0292	1.18

There is good agreement between the C-OH : CO_3 ratio and the coverage estimated from the molecular dynamics simulations. The coverage is the same for methanol, ethanol and pentanol, i.e. the straight chain alcohols, so the distribution on the surface is similar, with one alcohol molecule for each calcium-carbonate pair, meaning 2 molecules per surface unit cell. We can conclude that the molecules extend out from the surface as a brush, anchored by their OH groups; they are too long to fit lying parallel to the surface (Table 1). On the other hand, the t-butanol coverage is lower. We can explain this as steric effects. T-butanol, with its CH_3 groups protruding laterally, simply takes more space. This steric effect would not have a long range effect so the alcohol molecules are close packed on the surface. The molecular dynamics snap shots show this nicely.

Fig. 4 shows top view snap shots for a calcite surface covered with methanol and t-butanol, after the simulations have reached equilibrium. The surface equilibrated with methanol, ethanol and pentanol have the same coverage and therefore only the methanol snap shot is presented. For the same area of calcite, the number of t-butanol molecules is lower than for methanol. It is clear that the width of t-butanol prevents higher coverage but regardless, the t-butanol layer is compact. The difference is only the number of molecules involved. The calcite surface accommodates as many alcohol molecules as it can, forming a compact, well ordered monolayer.

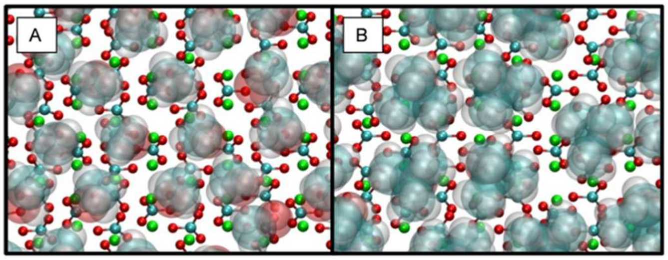


Fig. 4. Top view snap shots from simulations that have reached equilibrium for a calcite surface covered with methanol (A) and t-butanol (B). The surface area depicted is the same but coverage of t-butanol is lower because of steric effects. The adsorbed molecules are shown with their Van der Waals radius. Oxygen atoms are red; carbon, blue; calcium, green and hydrogen, white.

Fig. 5 shows side view snap shots of a monolayer of methanol, ethanol, pentanol and t-butanol on calcite after equilibrium was reached. All simulations have the same features: the alcohols are adsorbed to the crystalline surface through hydroxyl, with their carbon chain pointing away, to make a uniform and highly ordered layer. The carbonate groups in the top layers of the calcite crystal are reoriented because of reaction with the alcohol.

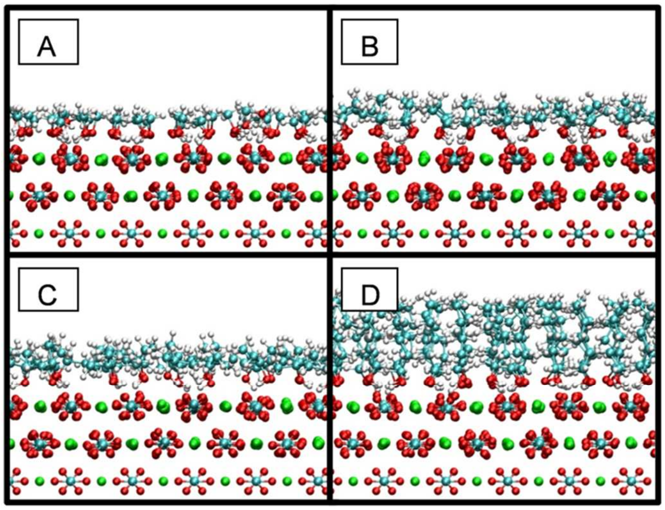


Fig. 5. Side view snap shots from the simulations of calcite with one adsorbed monolayer of methanol (A), ethanol (B), t-butanol (C) and pentanol (D). The alcohols form a well structured layer with the –OH group interacting with the surface. The molecules stand up, with their fatty end away from the calcite. The orientation of the carbonate groups in the top layers of the calcite crystal is modified by the adsorption. Oxygen atoms are coloured red; carbon, blue; calcium, green and hydrogen, white.

The mass density profiles from the simulations are depicted in Fig. 6. There is no mass directly above the calcite surface. At about 1.1 Å, a first peak corresponds to the O atom for each of the alcohols. Then there is one peak for the carbon in methanol, 2 peaks for the carbons in ethanol and 5 peaks for the carbon atoms in pentanol. The position(s) of the carbon peak(s) for these straight molecules is(are) clearly defined and correspond precisely to the number of carbon atoms in each of the simple chain alcohols, thus confirming the high degree of ordering and the upright configuration. The t-butanol has only one peak and it is high and broad. This is as expected for a molecule with 4 carbon atoms that are involved in the same sort of bonds and about the same height above the surface.

An important feature of Fig. 6 is the gap in mass density between the first, highly structured alcohol layer (denoted by the vertical thin black line) and the rest of the alcohol (to the right of the line), which is much less ordered but still feels the ordering of the monolayer through a few Å, as shown by the waves observed after the gap. The position of this gap is directly related to the length of the molecules: 3.8 Å for methanol (length = 2.80 Å), 4.8 Å for ethanol (length = 4.11 Å), 4.9 Å for t-butanol (length is 4.11 Å) and 8.6 Å for pentanol (length = 7.94 Å).

Because the molecules attach through the OH end, protrusion of the fatty ends produces a hydrophobic layer a few Ånströms away from the calcite surface. This layer changes the properties of the calcite, converting it from hydrophilic when freshly cleaved, to hydrophobic, after the adsorption of the alcohols. This layer formed on the calcite surface is consistent with the observations of previous studies, that investigated calcite behaviour during contact with both ethanol and water.[18-20] Water, that normally hydrates the calcite surface, is excluded by the alcohol. Such an alcohol layer, that renders the calcite surface hydrophobic, could protect the calcite surface from dissolution or precipitation, thus offering a possibility for an organism to alter the processes of crystal growth.

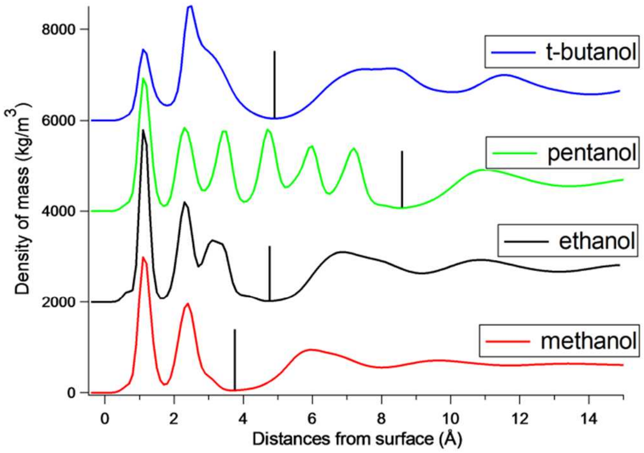


Fig. 6. Density profiles for methanol, ethanol, t-butanol and pentanol adsorbed on calcite. Thickness of the monolayer depends directly on the alcohol length. The vertical, black line marks the gap between the monolayer and the less structured, alcohol, that marks the beginning of the transition to the bulk. The first peak at 1.1 Å is caused by the O atom of the OH group. The following peak(s), at increasing distances from the surface, correspond to carbon atoms. The successive arrangement of these peaks indicates that the monolayer is well ordered and the chains protrude from the surface.

The radial distribution function (RDF) for O and H obtained from the calculations gives the same result for all four alcohols. Fig. 7 shows the atomic distances that were estimated. The oxygen atom of the alcohol is at equilibrium at a distance of 2.4 Å from a surface calcium atom and the alcohol hydrogen atom settles at 1.4 Å from an oxygen atom of a proximal carbonate group. These distances are similar to those reported for ethanol adsorbed on calcite by Sand *et al.*.[20] Our results demonstrate that the extent of alcohol binding on calcite does not depend on the chain length or the steric nature of the alcohol.

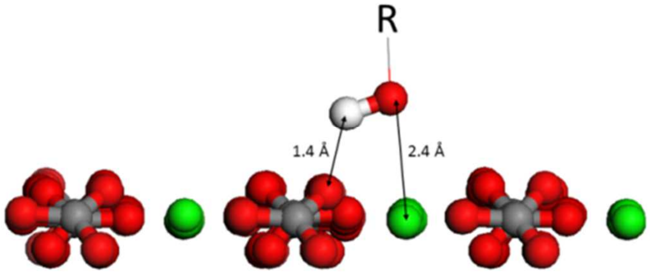


Fig. 7. Atomic distances derived from the MD simulations. Only the OH group is shown, the chain of the alcohol is represented by R. Oxygen atoms are coloured red; calcium, green; carbon, grey and hydrogen, white.

4. Conclusions

Both XPS and MD results demonstrate that ethane does not bind to calcite but ethanol does, through the activity of the hydroxyl group. Methanol, ethanol, pentanol and t-butanol all bind in the same way, forming a well ordered, compact monolayer. The alcohols are oriented with their hydrophobic portion pointing away from the surface. Molecule length does not influence surface coverage or structure of the monolayer but coverage decreases when the alcohol is bulky.

The first adsorbed layer is highly ordered, forming a hydrophobic layer over the hydrophilic calcite surface. Beyond the first layer is a gap in mass density, which distance from the surface is proportional to the length of the molecule, and beyond this, the bulk alcohol is less ordered.

The binding energies for the C-OH carbon atom recorded for alcohol on calcite are: 287.4 eV for methanol, 287.1 eV for ethanol, 287.3 eV for t-butanol and 286.9 eV for pentanol. MD simulations show that the oxygen atom of the alcohol molecules comes to equilibrium at 2.4 Å away from a calcium atom from the first calcite layer while the hydrogen atom sits 1.4 Å from an oxygen atom from a carbonate.

The straight chain alcohols adsorb at a density of 2 molecules per calcite unit cell, giving a ratio of 1 to 1 between the OH group and the Ca-CO_3 entity. The calcite surface accommodates as much adsorption of OH as is physically possible. This produces a tight, hydrophobic layer on calcite that would protect against dissolution and recrystallisation on flat surfaces. Steps would interrupt the hydrophobic layer continuity. The implication of this behaviour is important. By producing specific organic molecules, an organism can control precipitation and dissolution with extremely small quantities of material - only enough to cover a surface - by shifting the equilibrium state defined by thermodynamics in the simple system, thus allowing the organism to control growth and design crystals to fit its needs.

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