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On the hydration of subnanometric antifouling organosilane adlayers: A molecular dynamics simulation

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ABSTRACT

The connection between antifouling and surface hydration is a fascinating but daunting question to answer. Herein, we use molecular dynamics (MD) computer simulations to gain further insight into the role of surface functionalities in the molecular-level structuration of water (surface kosmotropicity) – within and atop subnanometric organosilane adlayers that were shown in previous experimental work to display varied antifouling behavior. Our simulations support the hypothesized intimate link between surface hydration and antifouling, in particular the importance of both internal and interfacial hydrophilicity and kosmotropicity. The antifouling mechanism is also discussed in terms of surface dehydration energy and water dynamicity (lability and mobility), notably the crucial requirement for clustered water molecules to remain tightly bound for extensive periods of time – *i.e.* exhibit slow exchange dynamics. A substrate effect on surface hydration, which would also participate in endowing antifouling adlayers with hydrogel-like characteristics, is also proposed. In contrast, the role of adlayer flexibility, if any, is assigned a secondary role in these ultrathin structures made of short building blocks. The conclusions from this work are well in line with those previously drawn in the literature.

1. Introduction

Water is essential for Life, mediating a wide variety of biological and other processes [1,2]. The reason lies in its many unique dissolving, dissociating/lysing, solvating, lubricating, etc properties [1,2]. Not surprisingly, water, through surface hydration, is hypothesized to also play a key role in the antifouling of surfaces [3–16] – a topic of great current interest in both fundamental and applied physical chemistry [14,17]. However, the precise underlying mechanism is a matter of debate, owing to the sheer number of influential parameters both on surface and foulant ends [4,8–15]. For example, one argument puts forth the ‘water barrier’ concept, wherein embedded and interfacial water molecules are tightly bound and organized into permeated structures that have an energy cost in terms of perturbation [3]. Another school of thought favors rather the notion of ‘interfacial energy matching’, in which there is no net energy gain for biological solutes – that are fully solvated in the bulk aqueous medium where they reside – to adsorb on hydrated surfaces [4,8,18]. In both cases, water in contact with surfaces may form a phase physically distinct from ordinary bulk water [4,5,8,16], as supported by experimental evidence [19–21]. The nature and extent of this special zone of hydration are, also, debated [4,8,21–23]. For instance, while some describe physically-distinct water interphases to project up to several hundred microns into the contiguous aqueous medium [21], others – in stark contrast – report surface kosmotropicity [24] (the ability of a surface to structure water at the molecular level) to be much more limited in range, to a few layers of water or less [4,8,19,20]. Understandably, the contentious question of surface hydration – with respect to its connection to antifouling – has been and continues to be relentlessly researched by many [3,4].

In recent contributions using acoustic wave physics, we reported on the critical role of surface hydration on the adsorption dynamics of serum interacting with monoethylene glycol (MEG)

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adlayers prepared on quartz [25] or gold [24] substrates. Another key feature was the observation that the internal ether oxygen in the MEG chains is necessary to impart coatings with pronounced antifouling behavior, the synergy being strongest for MEG-OH films possessing distal hydroxyl moieties (Fig. 1) [25]. We proposed the effect to be deeply rooted in a special intrafilm zone of hydration, from which a physically-distinct interfacial phase of water would stem [24,25]. The water absorptivity and structuring properties hypothesized for the MEG-OH coating – and the key participation of the internal ether atoms of oxygen [24,25] – were later confirmed using neutron reflectometry [26].

In the present article, we further elaborate on the surface hydration of the MEG-OH coating (on SiO_2) by supplementing our previous empirical results with those reported herein from MD simulations [6,8–10,15,27–29]. For comparison purposes, simulations are also performed with other, structurally-related organosilane adlayers derived from MEG-OH in a systematic manner (Fig. 1). Using the radial distribution function, we investigate whether and, if so, how water organizes within and atop these various adlayers. Analysis is also complemented with the calculation of adlayer energy and flexibility, as well as with the assessment of water lability and mobility. We finally conclude this original simulation study with a molecular-level rationalization of the role of water through surface hydration in the mechanism of antifouling. In the particular case of MEG-OH adlayer, this computational study of surface hydration constitutes a theoretical complement to previous experimental work, wherein the remarkable hydrogel-like [26], antifouling [25], and antithrombogenic [30] properties of such surface chemistry were reported.

2. Methods

2.1. MD simulations

2.1.1. Model details and simulation protocol

α-Quartz is the most stable polymorph of silica (SiO_2) at ambient conditions and the (001) surface is the most stable type [31]. A SiO_2 (001) surface slab of approximately 3.9 nm^2 in area and 0.9 nm deep was cut from bulk α-quartz (Fig. SI1) and 25 molecular residues were placed on one face, one bound to each Si atom. The bottom face of the surface slab is unfunctionalized. Models were constructed for molecular films of OTS, OTS-OH, O-OTS, MEG-OMe, and MEG-OH. Each coating was then encased in a tetragonal box of water with dimensions 5 × 5 × 10 nm, to give a total cell size of ~23,000 atoms (Fig. SI2). Each adlayer was allowed to equilibrate to a stable room temperature structure over 2.5 ns of molecular dynamics, and then subjected to a further 30+ ns of dynamics. Simulation input files and calculated film structures are available on request from the corresponding authors.

Molecular Langevin dynamics were performed using the NAMD program [32]. Periodic boundary conditions were applied, and Ewald summation was used to calculate the electrostatic interactions. A 1 fs time-step was used for dynamics by constraining covalent bonds to hydrogen. The substrate silicon and oxygen atoms were restrained to their crystallographic positions throughout the simulations. All hydroxyl and molecule atoms were unrestrained throughout the simulations.

Each model was first relaxed using 2000 steps of steepest descent minimization with respect to the CHARMM force field [33,34] and then brought to room temperature by gradually raising the temperature from 0 to 295 K over 2.5 ns of dynamics while simultaneously loosening positional constraints on the non-hydrogen atoms of the adlayer. Residue-quartz bond geometry and polarity were determined using periodic electronic structure calculations (see Supporting Information for details). The TIP3P model was used for water [35].

To model films obtained empirically, each molecular residue was not subjected to any further positional constraints (other than its binding to an Si atom), hence providing an adlayer model featuring a mixed population of upright and more horizontal chain conformations. Time- and structure-averaged values for residue conformations, dynamics, adlayer packing and surface hydration energetics were calculated using the central residue in the adlayer and its nearest neighbors. Unless otherwise noted, statistics for each model were generated for over 30 ns of dynamics, sampling every 20 ps to provide over 1500 statistically independent structures for each adlayer. Hence, all data points and error bars reported were calculated over 1500 residue conformations for each adlayer. Control simulations of adlayer packing were performed in a non-aqueous, vacuum environment. Image generation and Tcl script-based trajectory analysis was performed using the VMD program [36].

3. Results and discussion

3.1. Systematic MD simulations

As was the case for our original experimental work [25], we set out herein to perform the computational analysis of surface hydration in a methodical fashion, by modifying step-by-step the adlayer chains' chemical nature – from fully alkylated OTS to MEG-OH and MEG-OMe monoethylene glycols through the partly 'oxygenated' OTS-OH and O-OTS chains (Fig. 1). This systematic approach is intended to single out the influence each functional modification may have but also to unravel any collaborative or antagonistic effects. Full-coverage coatings are modeled on α-quartz substrates with (001) orientation and encompass 5 × 5 residues [37] with a chain separation of 4.9 Å and a lateral packing density of ~4.2 residue/nm^2 (or ~6.9×10^{-10} mol/cm^2) [38,39], leaving reasonable room for chain motion and water embedment (the van der Waals diameter of water is ~0.3 nm) [40,41]. Unless otherwise noted, MD simulations (or 'trajectories') lasted >30 ns and the presented data are those computed for the inner core of 3 × 3 residues.

3.2. Water distribution

In the present work, the radial distribution function (RDF) is used to describe the probability of finding water molecules organized at a certain distance from a reference taken herein on the adlayers. On a RDF *vs.* distance graph, this materializes as a distinct peak with proportional magnitude. In Fig. 2, it is therefore immediately visible that only the fully alkylated OTS adlayer would be unable to organize water [9,29]. In stark contrast, the MEG-OH adlayer would possess the highest likelihood to do so among the other coatings – in a multi-layered manner moreover (*vide infra*) [9,29]. Water density profiles for the two extremes of surface hydrophobicity and hydrophilicity, the OTS and MEG-OH adlayers, can be found in the Supporting Information. Additionally, we note that the OTS and MEG-OH adlayers, incidentally, displayed complete opposite antifouling behavior when exposed to full serum (MEG-OH being vastly superior) [25].

Determining the actual distribution of water within/atop an adlayer requires however localized RDFs to be generated. For example, Fig. 3, which overlaps 'innermost' RDFs where the reference is taken at the base of the coatings (see caption), reveals that adlayers lacking internal atoms of oxygen (*i.e.* OTS and OTS-OH) do not present peaks for water at ~2.5 and ~3.5 Å [9]. In other words, water would not be able to penetrate into these alkylated adlayers. This was demonstrated empirically for the OTS-OH system using neutron reflectometry (NR) [26]. Conversely, O-OTS, MEG-OMe and MEG-OH adlayers would be able to absorb and organize water