

## THE ROLE OF WATER IN THE ANTIFOULING PROPERTIES OF ULTRATHIN ORGANIC ADLAYERS: EXPERIMENTAL AND COMPUTATIONAL EVIDENCE

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Water is essential to Life, mediating a wide variety of biological and other processes due to its many unique dissolving, dissociating, and solvating properties. Not surprisingly, this ubiquitous fluid is widely hypothesized to also play a key role in the antifouling of surfaces, although the precise underlying mechanism is still a matter of debate. 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 disturbance. Another school of thought rather favours the notion of ‘interfacial energy matching’, according to 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. In both cases, water in contact with surfaces may form a phase physically distinct from ordinary bulk water, as supported by experimental work. The nature and extent of this special zone of hydration are, also, debated. For instance, while some describe physically-distinct water interphases to project up to several hundred microns into the contiguous aqueous medium, others – in contrast – report the effect to be much more limited in range, to a few layers of water. Understandably, the contentious question of surface hydration – and its connection to antifouling – has been and continues to be relentlessly researched by many.

We used electromagnetic piezoelectric acoustic sensor (EMPAS) technology to investigate the antifouling properties of ultrathin organosilane coatings against full serum. A key result was the observation that, among a series of unimolecular adlayers with systematically-varied chemical structure, only the monoethylene glycol (MEG) variety incorporating a single, internal ether atom of oxygen in the chains was able to dramatically alter serum adsorption, the synergy being strongest for the MEG-OH system possessing distal hydroxyls. 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. The water absorptivity and structuring properties hypothesized for the MEG-OH system – and the key participation of the internal ether oxygen atom in the MEG chains – were confirmed using neutron reflectometry, which collectively with acoustic wave sensing provided convincing empirical evidence that these oxygen atoms would play a determining role in (the state of) surface hydration, hence antifouling. This experimental probing of surface hydration was next complemented by a series of molecular dynamics simulations that allowed for a better understanding of antifouling with respect to surface hydration to emerge; and a molecular-level mechanism – well in line with that generally invoked in the literature – to be rationalized in terms of a set of basic requirements (hydrophilicity, kosmotropicity, hydration strength, and water dynamicity). A ‘substrate effect’ to surface hydration was also proposed to explain the hydrogel-like characteristics of the antifouling MEG-OH ‘nanogel’ coating.