The Molecular Boat: A Hands-On Experiment to Demonstrate the Forces Applied to Self-assembled Monolayers at Interfaces

Introduction

Molecular structures can have profound effects on macroscopic properties. In this experiment, the floatation of glass coverslips is altered by modifying the terminal chemical groups on glass surfaces with two different organosilanes, 1-octadecyltriethoxysilane (ODTS) and 3-aminopropyltrimethoxysilane (APTMS). The organosilanes react with the terminal hydroxyl (-OH) groups on the surface of the silica in a condensation reaction to form self-assembled monolayers (SAMs) (**Fig. 1S**). The alterations to the wetting behavior and the floatation are quantified by determining the force of gravity when the forces of gravity, surface tension and buoyancy are in equilibrium.

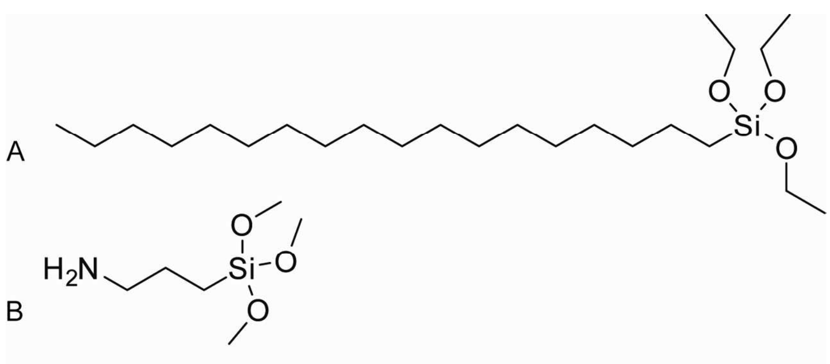

Figure 1S: Chemical structures of the organosilanes used in the experiment: (A) ODTS, and (B) APTMS

Safety

The procedure calls for the use of volatile, flammable solvents (ethanol, hexane, and acetone), irritants (the organosilanes) and a strong base (NaOH). To ensure safety, conduct the experiment in a fumehood whenever possible and always wear gloves and goggles when handling glass coverslips and the chemicals. Dispose of the chemicals in the appropriate organic waste container and place all used glass substrates in the broken glass container.

Procedure

Use tweezers to handle the glass coverslips to prevent contamination and injury. Place three sets of rectangular glass coverslips (22 × 30 mm, 25 × 25 mm, and 18 × 18 mm sizes) onto a Teflon rack and carefully lower it into a small beaker. Fill the beaker with enough 1M NaOH to completely cover the glass coverslips. Allow the glass to etch for 30 minutes. Remove two sets of the coverslips from the basic solution and wash with deionized water, ethanol, and acetone. Dry the glass under a stream of N_2. Incubate each set of coverslips at room temperature in about 20 mL of a 10 mM solution of ODTS in hexane or in a 10 mM solution of APTMS in hexane in a crystallization dish and cover for one hour. Flip the coverslips after 30 minutes to ensure complete exposure to the organosilane solution. When the SAMs are formed, sonicate the glass, wash with acetone and dry under a stream of N_2. Place the glass coverslips on top of a bath of deionized water. Wash the coverslips that remained in the NaOH solution with deionized water and ethanol and dry under a stream of N_2. To investigate the force the coverslip can support before sinking, place the staples one at a time on top of the coverslips. Ensure the staples do not touch the water.

Instructor Notes

Students can expect to spend approximately 2 to 2.5 hours on this experiment. To prepare the glass coverslips, the substrates must be etched in NaOH for 30 minutes and incubated in the organosilane solutions for 1 hour. During the waiting period, students can answer concept questions and determine the mass of the weigh out the staples and the glass coverslips. The time needed for the experiment depends on the number of different surface modifications and sizes of glass coverslips, as well as the number of trials. This could take 15 to 30 minutes. In order to conserve time, the glass coverslips can be prepared and etched in NaOH prior to the laboratory meeting.

Students can work in groups to form the self-assembled monolayers on the glass substrates and then individually to determine the maximum forces sustained by a set of substrates. The students can then share the data to obtain statistically relevant results.

Depending on laboratory's temperature, it may be necessary to gently warm the ODTS in a water bath to ensure the organosilanes are not polymerized, prior to functionalizing the glass coverslips. Note that the rectangular glass coverslips used in this experiment can be substituted with circular coverslips and coverslips with different dimensions. Likewise, ODTS and APTMS can be replaced with an array of other commercially available silanes to probe a wider parameter space of surface energies.

Concept questions for students

To help highlight how monolayer surface modification can greatly influence the macroscopic properties of a substrate, we include a few thinking questions for the students.

1. Draw a free-body diagram for a glass coverslip floating on the water's surface. What forces are pulling down? What forces are keeping the coverslip afloat? How do these forces change when the glass is functionalized with ODTS SAM? With APTMS SAM?
2. For the glass coverslips modified with APTMS (terminal amine group), how will the supported mass change as a function of pH of the water bath? Draw a hypothetical plot of pH vs. maximum sustained mass for the APTMS substrate.
3. How will surfactants affect the maximum load that can be carried by the substrate?
4. How would incomplete SAM formation or binary mixtures of monolayer (ODTS and APTMS, for example) affect the ability of the glass coverslips to support different masses?

Answers to concept questions

1. Draw a free-body diagram for a glass coverslip floating on the water's surface. What forces are pulling down? What forces are keeping the coverslip afloat? How do these forces change when the glass is functionalized with ODTS SAM? With APTMS SAM?

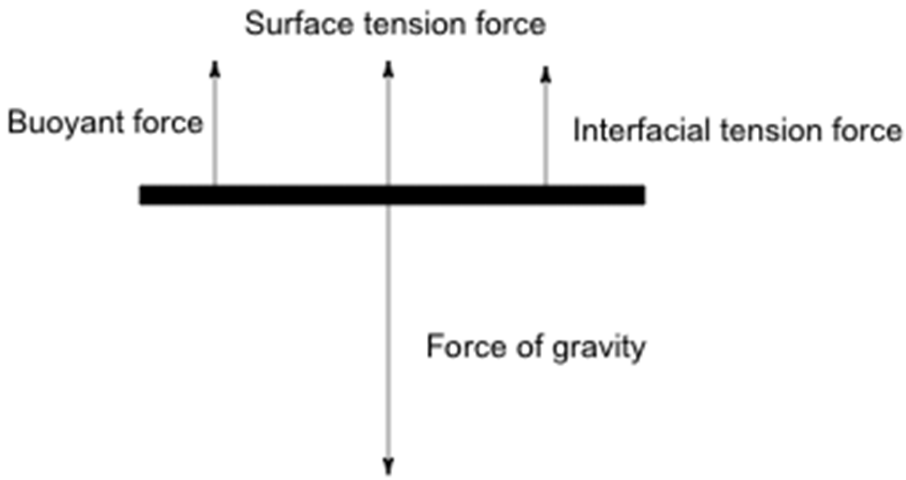

Figure S2: Z-force component of free body diagram for a glass coverslip floating on water

The forces related to buoyancy, surface tension and interfacial tension keep the coverslip afloat. The surface tension force is proportional to the size of the perimeter of the glass substrate.

2. For the glass coverslips modified with APTMS (terminal amine group), how will the supported mass change as a function of pH of the water bath? Draw a hypothetical plot of pH vs. maximum sustained mass for the APTMS substrate.

The effect of the pH depends on the pKa of the terminal amine group. When the pH of the water bath is significantly lower than the pKa, the amine groups are mostly protonated, charged and hydrophilic; the substrate will not support large masses. When the pH of the water is significantly larger than the pKa, the amine groups are neutral and more hydrophobic, thereby allowing the substrate to support a greater maximum load.

3. How will surfactants affect the maximum load that can be carried by the substrate?

Surfactants would decrease the maximum load that can be carried by the substrate. They decrease the effect of the SAM on the flotation of the substrate by interacting with both the water and the hydrophobic substrate.

4. How would incomplete SAM formation or binary mixtures of monolayer (ODTS and APTMS, for example) affect the ability of the glass coverslips to support different masses?

Surfaces that are incompletely functionalized with a SAM would be less effective in their ability to support masses and would support less mass compared to their completely functionalized counterparts. The "holes" where the monolayer was not formed would be hydrophilic. Substrates functionalized with a binary mixture of monolayer would probably support an intermediate maximum load compared to surfaces with SAMs composed of the pure components.

Additional Information

Table S1: CAS registry numbers for chemicals

Chemical Name	CAS Registry Number
Acetone	67-64-1
3-aminopropyltrimethoxysilane	13822-56-5
Ethanol	64-17-5
Hexanes	110-54-3
NaOH	1310-73-2
Octadecyltriethoxysilane	7399-00-0

Table S2: Masses of staples and glass coverslips

	Mass (g)*
staple	0.0320 ± 0.0002
22 × 30 mm glass coverslip	0.2344 ± 0.0031
25 × 25 mm glass coverslip	0.2364 ± 0.0036
18 × 18 mm glass coverslip	0.1152 ± 0.0013

* the uncertainity of the masses represent the standard deviation from measurements of ten independent samples

Results from Sample Experiment

The maximum force of gravity required to completely immerse the different monolayer-functionalized substrates was determined over two trials.

Table S3: Maximum load of staples for glass coverslips functionalized with ODTS

Dimension of glass coverslip (mm × mm)	Maximum number of staples	Mass of maximum load of staples (g)	Total mass of maximum load (g)	Maximum force sustained (mN)
22 × 30	62	1.9821	2.2165	21.72
25 × 25	61	1.9502	2.1865	21.43
18 × 18	32.5	1.0390	1.1542	11.31

Table S4: Maximum load of staples for glass coverslips functionalized with APTMS

Dimension of glass coverslip (mm × mm)	Maximum number of staples	Mass of maximum load of staples (g)	Total mass of maximum load (g)	Maximum force sustained (mN)
22 × 30	23	0.7353	0.9697	9.50
25 × 25	19.5	0.6234	0.8598	8.43
18 × 18	8.5	0.2717	0.3870	3.79

Table S5: Maximum load of staples for hydroxy-terminated bare silica

Dimension of glass coverslip (mm × mm)	Maximum number of staples	Mass of maximum load of staples (g)	Total mass of maximum load (g)	Maximum force sustained (mN)
22 × 30	8	0.2558	0.4901	4.80
25 × 25	5.5	0.1758	0.4122	4.04
18 × 18	0.5	0.0160	0.1312	1.29

Table S6: Relationship between maximum load and coverslip perimeter

	Maximum load to coverslip perimeter ratio (N/m)		
	22 × 30 mm	25 × 25 mm	18 × 18 mm
ODTS	0.209	0.214	0.157
APTMS	0.091	0.084	0.053
OH	0.046	0.040	0.018

Student Experience

In order to gauge response, students were given a survey and asked to rank as to how much they agreed or disagreed with the two statements shown below. They were asked to mark each response with a value that ranged from 0, absolutely disagree, to 5, absolutely agree. They were given also given space to provide additional comments.

Statement 1: I learned something about self-assembled monolayers and their effects (blue bars in Figure 1).
Statement 2: I would like to see this experiment as part of a chemistry course (red bars in Figure 1).

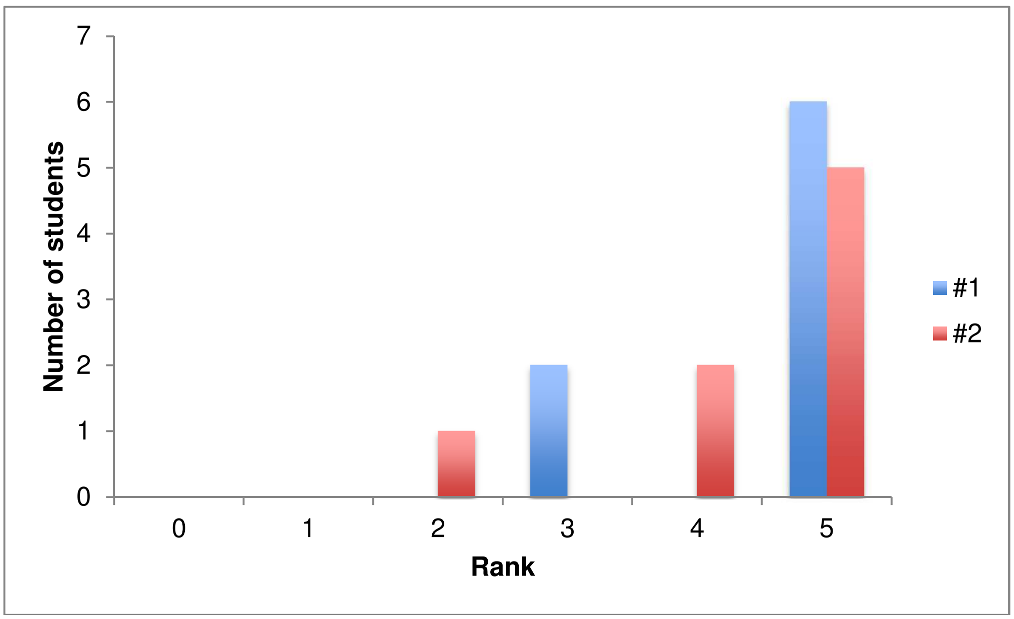

Figure S3: Histogram of responses from participating students (*n* = 8)

Comments:

"Cool!"

"This was a most educational demo. I gained a much better understanding of hydrophobic/ hydrophilic molecules."