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

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S *Supporting Information*

ABSTRACT: Demonstrating how surface chemistry and self-assembled monolayers (SAMs) control the macroscopic properties of materials is challenging as it often necessitates the use of specialized instrumentation. In this hands-on experiment, students directly measure a macroscopic property, the floatation of glass coverslips on water as a function of modifying the terminal surface groups of the glass. The glass surface is chemically modified by the self-assembly of monomolecular layers formed by two organosilanes, 3-aminopropyltriethoxysilane and 1-octadecyltrimethoxysilane, which change the water contact angles. These SAMs alter the ability of the modified glass to support a mass, thus demonstrating that the bulk material property can be directly controlled by molecular surface chemistry.

KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Upper-Division Undergraduate, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Materials Science, Qualitative Analysis, Surface Science*
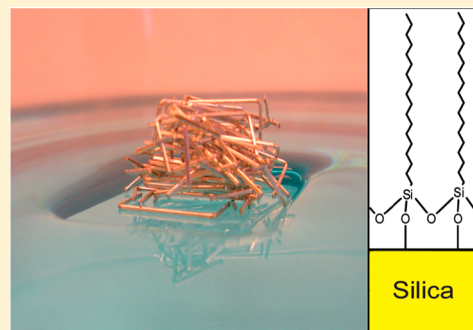
Surface chemistry plays a role in many important areas from catalysis to biodiagnostics.[1−4] In contrast to the extensive number of graduate and advanced programs that incorporate aspects of surface and materials chemistry, there has been limited development of hands-on laboratory exercises that illustrate the macroscopic effects of surface chemistry for the high school and undergraduate curricula. The majority of undergraduate physical chemistry textbooks include chapters or sections dedicated to colloidal and surface chemistry,[5] but the corresponding physical chemistry laboratory manuals include little material that can be implemented without dedicated instrumentation.[6−8] Thus, the molecular principles of surface chemistry, self-assembled monolayers (SAMs) are described in detail, but their associated macroscopic properties are rarely demonstrated in an introductory chemistry laboratory setting and especially in the context of a hands-on experiment.[9−11] This is generally attributed to the lack of specialized instrumentation in undergraduate laboratories that is able to characterize a single layer of molecules. For example, grazing angle ATR−FTIR spectroscopy, ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy instrumentation are not typically found in an undergraduate lab.[7,12]

Herein, a straightforward and facile experiment that allows students to generate monomolecular layers on glass substrates and to observe their effect on the macroscopic floatation of a glass coverslip is described. The phenomenon of floatation is commonly observed in water striders where the chemical and physical properties of their legs allow these insects to live on the surface of water.[13] This phenomenon is also commonly demonstrated with the floating needle experiment where a metal paper clip or needle will float on the surface of water.[14] The ability to visualize floatation makes surface tension a tangible concept for students and a well-suited method of characterizing the effects of surface modification.[15,16] In this laboratory experiment, glass coverslips float on water because the force of gravity is at equilibrium with counteracting buoyancy and surface tension (capillary force) of the water and interfacial tension. Because the mass of the glass coverslips remains the same in all experiments, the SAM modification directly alters the surface chemistry and consequently the floatation of the substrates. When a sufficient external mass is added to the substrate exceeding the magnitude of the counteracting forces, the glass coverslip sinks; thus, a maximum sustainable mass can be determined for each type of molecular modification to the glass surface. The difference in the maximum sustained mass is directly attributed to molecular modification to the surface of each type of substrate.

Organosilane SAMs are employed in this experiment because these can be prepared in a rapid and straightforward manner on conventional glass substrates.[3] SAMs of alkanethiol on Au films may also be used to perform this experiment (results not shown); however, glass was found to be more widely available to perform this experiment and precludes the use of a metal deposition chamber. The terminal functional groups of the SAMs alter the surface-wetting properties of glass substrates and consequently the maximum sustainable load. The effect of the monolayer is dramatic and highlights how a single layer of molecules, or a "molecular boat," can exert macroscopic (bulk) effects on an object. Note that the term molecular boat is not meant to imply buoyancy associated with the monolayer surface modification, rather this term ascribes the floatation of a glass

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substrate to the surface wetting properties of the self-assembled monolayer.

EXPERIMENTAL OVERVIEW

Organosilanes react with the terminal hydroxyl (−OH) groups on the surface of the silica (glass slide) in a condensation reaction to form a self-assembled monolayer (Figure 1). The
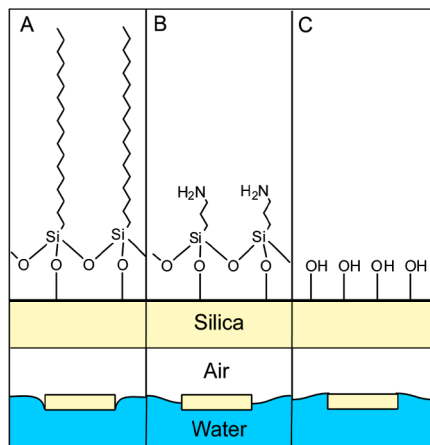

Figure 1. Schematic depicting the various surface modifications of a silica surface and the corresponding side-view of the water−substrate contact interface: SAM formed from (A) ODTS and (B) APTMS, and (C) hydroxy-terminated bare glass.

monolayer is further stabilized via condensation reactions between adjacent organosilanes, thus forming a network of siloxanes.[17] The wetting behavior and the surface free energy of the glass surface are controlled by the terminal functional groups presented by the SAMs.[18] In this experiment, two organosilanes are used, 1-octadecyltriethoxysilane (ODTS) and 3-aminopropyltrimethoxysilane (APTMS), which display a hydrophobic alkyl chain and a more hydrophilic amino group, respectively (Figure 1). Note that these are two representative reagents of hundreds of commericially available silanes. These monolayer modifications are directly compared to that of the terminal hydroxyl groups that are displayed on base-etched glass substrates. The effect on the surface tension and wetting behavior of the glass are measured by determining the force required to overcome the counteracting forces of surface tension and buoyancy to completely immerse the substrate. Hydrophobic interfaces such as the ODTS monolayers have large contact angles (for ODTS, $\theta \sim 110°$), which allow the formation of an indentation or "dimple" in the

water, thus requiring a larger sinking force.[19] Highly wetting surfaces such as the bare silica or amine-terminated monolayers display lower contact angles (for APTMS, $\theta \sim 50°$).[20]

MATERIALS

NaOH, hexanes, APTMS, ethanol, and acetone were all ACS grade reagents and acquired from Sigma Aldrich Corporation (St. Louis, MA). ODTS was acquired from Alfa Aesar (Ward Hill, MA). The glass coverslips were acquired from VWR, (West Chester, PA).

HAZARDS

The procedure calls for the use of volatile, flammable solvents (ethanol, hexane, and acetone), irritants (ODTS and APTMS) and a strong base (NaOH). The surface preparation should be conducted in a fumehood whenever possible, whereas the final demonstration can be conducted in a conventional classroom setting. Gloves and goggles should be worn when handling the glass coverslips and the chemical reagents.

EXPERIMENTAL PROCEDURE

Three sets of rectangular glass coverslips (22 mm × 30 mm, 25 mm × 25 mm, and 18 mm × 18 mm sizes) are etched in 1 M NaOH for 30 min. Two sets of coverslips are removed from the alkaline solution, washed with deionized water, ethanol, and acetone, and dried under a stream of N_2. Each set of coverslips is allowed to incubate in a 10 mM solution of ODTS or APTMS in hexanes for 1 h. The coverslips are flipped after 30 min to ensure complete exposure to the alkylsilane solution. Once the SAMs are formed, the coverslips are sonicated, washed with acetone, dried under a stream of N_2, and gently placed on top of a bath of deionized water. The altered surface properties of the glass can be investigated by determining the force the coverslip can support before sinking. The coverslips that remained in the NaOH solution (hydroxyl terminated) serve as a control and are washed with deionized water and ethanol and dried under a stream of nitrogen gas before being placed on the water. Any suitable small weight, such as conventional staples, can be used, but the weight must be easily placed on top of the substrate without touching the water. The glass coverslips were allowed to equilibrate for five seconds before the addition of each new mass. The experiment takes approximately 2−2.5 h (additional details are available in the Supporting Information).

RESULTS AND DISCUSSION

At equilibrium, the glass coverslips float on the surface of water, and the force of gravity, surface tension, interfacial tension, and
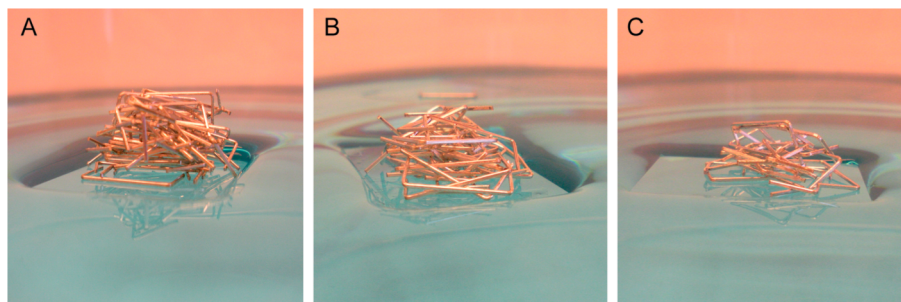

Figure 2. The indentations formed at the water−substrate interface for 2 mm ×30 mm glass coverslips varied according to terminal surface functional groups: SAM formed from (A) ODTS and (B) APTMS, and (C) hydroxy-terminated bare glass.

buoyancy are in balance. Glass is denser than water, which indicates that buoyancy alone is not sufficient to allow for floatation of the glass coverslips and that surface tension and interfacial tension forces play a significant role. The addition of a mass load upsets the equilibrium until gravity overcomes the forces of surface and interfacial tension and buoyancy, thereby causing the substrate to sink. Changes in the contact angle between water and the water−substrate interface alters the maximum load the substrate can carry before sinking. A quantitative description of the relationship between contact angle, surface geometry, and floatation has been previously detailed, and in summary, this analysis shows that maximum load is related to the perimeter of the object and the three-phase contact angle.[14,21,22]

To test the effect of SAM functionalization on floatation, three sets of ODTS, APTMS, and based-etched glass substrates were placed on the surface of water and external masses (staples) were added every 5 s until the substrates sank (Figure 2). The maximum force sustained by each substrate was calculated by summing the mass of the coverslip with the mass of the external load and determining the corresponding force of gravity. The maximum external load that was sustained by each type of surface functionalization is shown in Figure 3. The
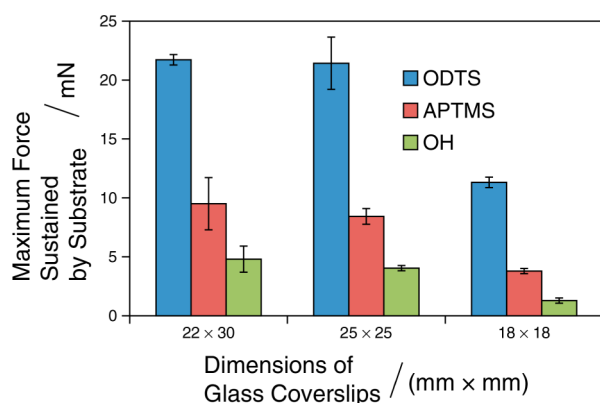

Figure 3. Plot of the maximum force of gravity required to completely immerse the different monolayer-functionalized glass substrates. This reported mass includes the mass of the coverslip as well as the external mass that was added to the substrate. Each error bar represents one standard deviation of two independent experiments.

ODTS-functionalized glass coverslips are reported to display a 110° contact angle (θ) at the air−water interface.[19] These substrates are extremely hydrophobic and consequently the ODTS substrates carried the largest mass loads before finally sinking (Figures 2A and 3). APTMS-functionalized substrates show intermediate contact angles (50°) and correspondingly sustain intermediate values of maximum load (Figures 2B and 3).[20] A similar trend is observed for the hydroxyl-terminated base-etched substrates (~0°). Importantly, the force of the surface tension is related to the perimeter of the substrate, and to test the role of this variable on floatation, three different sizes of glass coverslips were tested (Figure 3). Larger size coverslips were found to display larger values for maximum load across the various surface chemistries. For example, the 22 mm × 30 mm and the 18 mm × 18 mm glass coverslips had maximum load to perimeter ratios of 0.209 and 0.157 N/m, respectively, when functionalized with ODTS SAMs and ratios of 0.046 and 0.018 N/m, respectively, when left hydroxyl-terminated.

When the substrate is afloat, the factors that need to be considered are the force of gravity, buoyancy, surface tension, and the SAM−water interfacial tension. At equilibrium, it is possible to directly calculate the force of gravity and the surface tension force (F_γ = (perimeter of substrate) × cos(θ) × 72 mN/m), however, the buoyancy force (see "dimple" formed on the water surface in Figure 2) or the interfacial tension cannot be easily determined within the scope of this lab.[14,16,22] Nonetheless, molecular functionalization of the substrate provides for a facile method to alter the contact angle of the water−substrate interface, thereby changing the buoyancy force and surface and interfacial tensions while keeping the mass effectively constant. In fact, if the water−SAM interfacial tension was assumed to be zero, then the magnitude of the buoyancy force can be experimentally determined from the literature values of F_γ and the measured mass of the substrate. For example, the volumes of the indentation of the 22 mm × 30 mm substrate functionalized with OTDS-formed SAM and APTMS-formed SAM are calculated to be 1.5 and 0.59 mL, respectively, which is in agreement (within an order of magnitude) with qualitative estimates from the photographs of the dimples in the water (Figure 2).

■ STUDENT EXPERIENCE

Because of the simple setup and the visual nature of the results, this experiment is appropriate for both a first-year under-graduate general chemistry laboratory class and an upper-level undergraduate physical chemistry laboratory setting. A first-year laboratory class would focus on the effects of monolayer surface modification on the macroscopic properties, whereas a physical chemistry laboratory class would relate the concepts behind the experiment to the alteration of wetting behavior, surface free energy, and chemical potential. To gauge the student response to this experiment, 8 first- and second- year college students were asked to run the experiment and were then given a survey; in general, most students were supportive of this experiment being incorporated into their chemistry classes and said that they gained new knowledge about self-assembled monolayers and their effects. More details of this survey can be found in the Supporting Information.

■ POSSIBLE EXPERIMENTAL EXTENSIONS

This experiment can be further expanded to highlight certain aspects of molecular self-assembly. For example, mixed monolayers consisting of a binary mixture of adsorbates can be used to generate a range of water contact angles and maximum loads.[3,18] This highlights the ability to tune the molecular composition of the monolayers and their macro-scopic properties. The value of water surface tension can be modified by altering the surface pK_a[23] or by altering the solution pH, ionic strength, or by addition of surfactant and these variables may be introduced as additional challenge problems in discussing this demonstration within the class-room.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Student information; instructor notes; concept questions for students; results from a sample experiment; student response. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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